Hydrogen evolution reaction on electrodeposited Zn-Cr alloy coatings

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A B S T R A C T
The hydrogen evolution reaction (HER) on electrodeposited Zn-Cr alloy coatings with different thickness and Cr content was investigated in a 0.5 M Na2SO4 solution by electrochemical methods. The hydrogen evolution on the alloys starts at less negative potentials in comparison to that on Zn. Subsequently, with the potential shift in negative direction the rate of the HER on the alloy increases significantly faster. At low polarizing currents the hydrogen overvoltage on the alloys is closer to that on Zn, whereas at high polarizing currents it is closer to that on Cr. In the latter case the hydrogen overvoltage on the alloys is more than 200 mV lower than that on Zn. The lowering of the hydrogen overvoltage is related to the Cr content in the alloy. Almost similar values of the exchange current density for the HER on the alloys (Cr content in the range of 3 to 10 mass %) are determined. Based on the derived Tafel slopes Volmer reaction mechanism for the hydrogen evolution reaction on the alloys within the 0.25–10 mA cm−2 range current density range could be proposed. At higher polarizing currents the effect of Cr becomes more pronounced and presumably the electrochemical desorption appears to be the likely rate determining step.

1. Introduction

The alloying of Zn with the so-called iron-block metals (Fe, Co, Ni) or with Al, Ti, Mg has the advantage of an increased corrosion protection of the coatings at a reduced layer thickness, being important for a subsequent mechanical treatment and welding, and moreover for saving energy and raw materials [1,2].

The development of Zn-Cr alloy coatings for corrosion protection of steel substrates is motivated by the high protective potential and corrosion resistance of these layers, improving the endurance of steel substrates is motivated by the high protective potential and corrosion resistance of steel substrates. Prior to electrochemical investigations the electrodes were electrochemically degreased and pickled in dilute H2SO4 solution.

2. Experimental

Zn-Cr alloy coatings with a Cr content of 3, 5 and 10 mass % (±0.5 mass %) were electrodeposited from an electrolyte, containing 40 g l−1 Zn, 15 g l−1 Cr (added as sulphates) and PEG 6000 (1 g l−1), pH 2.0, adjusted with sulphuric acid, in a 20 l flow cell, flow rate 4 m s−1, current density within the 80–120 A dm−2 range, electrolyte temperature 40 °C onto mild steel substrates, in mass %: C-0.12, Mn-0.6, P-0.045, S-0.045 (Metall-Folien GmbH, Main, Germany) with dimensions 115 × 85 mm. The Zn-Cr coatings are having a thickness of 2.5 and 5 μm. Zn coatings with a thickness of 2.5, 5 and 7 μm were electrodeposited at the same conditions from an electrolyte without Cr(III) and PEG. Cr coatings were electrodeposited from a conventional Cr(VI) electrolyte. Metallic Zn and Cr metals were used for comparison, as well. Prior to electrochemical investigations the electrodes were electrochemically degreased and pickled in dilute H2SO4 solution.

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The HER studies were performed in a model corrosion medium of aerated 0.5 M Na₂SO₄, pH 5.9 at a temperature of 25 °C. All chemicals used were of analytical grade.

The HER on steel, Zn, Cr and Zn-Cr alloy coatings was investigated by using cyclic voltammetry in a three-electrode setup in a 50 ml cell, including a Hg/Hg₂SO₄ reference electrode (E = +645 V vs. NHE), the working electrode with a surface area of 0.2 cm² and a Pt counter electrode. All potentials are recalculated vs. NHE. The scan rate was 25 mV s⁻¹. The initial and end potential was the open circuit potential (OCP), the polarization was first in negative direction. Potential-time curves were recorded during galvanostatic polarization at different current densities. By using the potential values determined from these curves the hydrogen overvoltage (η) was calculated:

\[ \eta = E - E_{\text{eq}} \]

where

\[ E_{\text{eq}} = \frac{RT}{F \ln a_{\text{H}_2}} = -0.059pH \]

Thereafter, the corresponding Tafel plots were built. All experiments were carried out by using a potentiostat/galvanostat model 263A (EG&G Princeton Applied Research, USA) and software SoftCorr II.

The Cr content in the alloy coatings and the coatings thickness were determined by X-ray fluorescence analysis (XRFA) (Fischerscope XDL-B, Software WinFTM 6.09). The elemental composition was also measured by Energy Dispersive X-ray (EDX) spectrometer supported with Genesis software (USA).

The surface roughness of Zn and Zn-Cr coatings was measured by means of MicroProf® (FRT, Fries Research and Technology GmbH, Germany) using a non-contact CHR 150 N optical sensor. The surface morphology was also analyzed by XL 30 environmental scanning electron microscope (ESEM) with field emission gun FEI Co., Netherlands. The profile and roughness measurements, as well as three-dimensional (3D) area analyses, directly from the stereoscopic images of the specimen surface were carried out using MeX software from Alicona A.

3. Results and discussion

3.1. Cyclic voltammetry

In 0.5 M Na₂SO₄ solution the HER proceeds with the highest rate on steel and it is most hindered on Zn (Fig. 1). The alloying of Zn with Cr rises the catalytic activity of the coatings towards the HER, since Cr has lower hydrogen overvoltage than Zn. The rate of the HER on the Zn-Cr alloy increases fast with the shift of the potential in negative direction and the rate values stay intermediate between those for steel and Zn (Fig. 1).

In a practical aspect, a good corrosion protection from a minimum thickness of the coating is required. However, possible hydrogen embrittlement of the steel substrate should also be considered, which can be influenced by the effect of the coating thickness on the kinetics of the HER. Due to its specific, rough structure (large hexagonal crystallites, Fig. 2) the thin Zn coating (2.5 μm) does not densely cover the substrate and a depolarizing effect from the steel on the cathode process is evident (Fig. 3). In contrast, no definite effect of the thickness of the Zn-Cr coatings on the cathode reactions is established. In fact, the Cr content in the alloy has stronger influence on the electrochemical performance.

The cathode branch of the Zn voltammogram shows clearly pronounced maximum at about −1.13 V. In a solution of Na₂SO₄ the Zn surface is commonly covered by a film consisting of Zn oxide as a main corrosion product and Zn hydroxide, present in different amounts [6]; accordingly the observed maximum can be related to reduction of Zn oxide and hydroxide:

\[ \text{ZnO} + 2\text{H}^+ + 2e^- \rightarrow \text{Zn} + \text{H}_2\text{O} \]

\[ \text{Zn(OH)}_2 + 2e^- \rightarrow \text{Zn} + 2\text{OH}^- \]

At the second scan the maximum is considerably smaller, shifted in less negative direction (Fig. 3, inset). The reproducibility of the maximum after the second scan is related to the controlled process of surface oxidation of the coating in the anode part of the voltammogram. Subsequently, the increase of the cathode current at more negative potentials corresponds to the HER from water (2H₂O → 2e⁻ → H₂↑ + 2OH⁻), a reaction proceeding with a high overvoltage on Zn. No visible hydrogen (gas bubbles) evolution occurs during the complete cathode polarization scan.

The Zn-Cr alloy surface after deposition and contact with air contains mainly Zn oxides/hydroxides (see Appendix Surface state). On the cathode branch of the voltammogram for the alloy coating just a shoulder at −1.13 V is recorded (Fig. 4). This suggests a smaller amount and/or a different property of the oxide layer on the Zn-Cr alloy surface. The latter is suggested also by the Auger parameter of 2010 eV, characteristic for Zn²⁺ oxidation state, which is considerably smaller than that typical
for the surface of pure Zn (2014 eV, Appendix Surface state). In addition, an influence of the surface morphology should be considered (see also Section 3.4. Surface area). After the reduction of the oxide layer the profile of the voltammogram is determined by the HER on the alloy, i.e. the hydrogen evolution on the alloys starts at less negative potentials in comparison to that on Zn. At potentials below $-1.35$ V enhanced hydrogen evolution is observed.

The anode branch of the voltammograms exhibits maxima resulting from oxidation of the corresponding layers. The anode maximum for the Zn coating forms on the reverse scan after polarization to a vertex potential of $-1.17$ V, i.e. straight after the cathode reduction of the oxide layer and before the offset of the HER (Fig. 4, inset). The anode maximum, at a potential of about $-1.05$ V could be related to formation of insoluble Zn oxy-hydroxide film.

Anode maximum for the alloy coatings is not registered until the cathode scan enters the potential range of hydrogen evolution. The maximum appears at about $-1.10$ V. The area of this maximum becomes larger with the shift of the vertex potential to more negative values, down to about $-1.45$ V, and respectively higher current densities are reached (Fig. 5). Since a non-buffered solution is used, due to intensive hydrogen evolution a pronounced alkalization at the electrode surface takes place. Referring to the Pourbaix potential-pH equilibrium diagram for the Zn-H$_2$O system in an alkaline environment at a potential of about $-1.15$ V soluble HZnO$_2$$^-$ ions are formed: $\text{Zn} + \text{H}_2\text{O} = \text{HZnO}_2^- + \text{3H}^+ + 2e^-$. EDX analysis of Zn-Cr electrode surfaces after 100 cyclic voltammograms with start and end potential of OCP and a vertex potential of $-1.55$ V, showed enrichment of the surface in Cr, indicating depletion in Zn. Consequently, the maximum for the alloy coatings could be associated with formation of soluble HZnO$_2$$^-$ ions diffusing from the electrode surface. With the further potential shift to less negative potentials (and at a lower OH$^-$ concentration) formation of solid Zn oxide-hydroxide film is also to be considered.

3.2. Galvanostatic measurements

The investigations under galvanostatic conditions confirmed a lower hydrogen overvoltage on the Zn-Cr alloys in comparison to that on Zn coatings. For Zn-10%Cr alloy at a current density of 10 mA cm$^{-2}$ the hydrogen overvoltage is about 200 mV lower than that on Zn (Fig. 6). The potential-time curve for the thinnest Zn coating once again reflects the influence of the steel substrate (Fig. 7).
3.3. Kinetics of the hydrogen evolution

Fig. 8 shows characteristic polarization curves for the example of Zn, Cr and Zn-3%Cr coatings. The Tafel plots for the reduction of hydrogen on Zn, Cr, Zn-3%Cr, Zn-5%Cr and Zn-10%Cr coatings are built by using the data from the corresponding polarization curves and are presented in Fig. 9. A clear linear relation between $\log j$ and overvoltage is observed within the 0.25–10 mA cm$^{-2}$ current density range. At low polarizing currents, resp. current densities the hydrogen overvoltage on the alloys is closer to that on Zn and at higher polarizing currents it is closer to that on Cr. It has been reported that the hydrogen overpotential on electrolytic Zn alloys, containing about 15 mass % of a component with a lower hydrogen overpotential (Ni, Cu, Fe) is similar to that on the pure alloying metals, as for the Zn-Co alloy it is even lower than that on pure Co [7]. The electrochemical performance of the Zn-Cr alloy coatings could be related to differences in the surface state of the coatings (see Fig. 4, the cathode branch of the Zn-Cr and Zn voltammograms related to reduction of surface oxide) and could also be an indication about a different reaction mechanisms of the HER (similar to that on pure Zn or pure Cr) depending on the current density range. Further increase of the current density leads to steep rise of the overvoltage for all the systems as well as to stronger potential oscillations in the curves due to intensive hydrogen evolution (Fig. 10).

Kinetic parameters of the HER for the examined electrodes were derived from the Tafel plots, a graphical representation of the Tafel equation:

$$\eta = a + b \log j$$

where $\eta$ is the overpotential and $j$ is the current density [8]. The Tafel parameters are defined as: $b = \frac{2.303RT}{\alpha nF}$ and $a = b \log j_0$, where $j_0$ is the exchange current density and $\alpha$ is the transfer coefficient (or symmetry coefficient), $n$ is the number of transferred electrons.

The obtained data are given in Table 1. The values of the exchange current densities for the HER on Zn are close to data found in the literature (10$^{-8.9}$ A cm$^{-2}$ [6]; N. Martyak et al. [9] reports 10$^{-10}$ A cm$^{-2}$ for hydrogen gas evolution on Zn); the values of the exchange current densities for the HER on Cr, are similar as well (within the range of 10$^{-6}$–10$^{-8}$ A cm$^{-2}$ [10], 5.0 $\times$ 10$^{-8}$ A cm$^{-2}$ [11]). The minor deviations of the present data from the literature data could be related to different chemistry of the solution and surface conditions. Note that the following kinetic analysis are applicable to surfaces spontaneously oxidized in air (uncontrolled way) in aerated sodium sulfate solution, i.e. under the specific conditions of these experiments.
If the electrochemical desorption is rate determining at low negative potentials the Tafel slope would yield a value of about 40 mV decade\(^{-1}\). At high overvoltages, generally the Heyrovsky mechanism takes place. Attempts for kinetic descriptions of the HER via two-step (Volmer-Heyrovsky, Volmer-Tafel or Heyrovsky-Tafel) and even three step (Tafel-Volmer-Heyrovsky) mechanisms depending on potential ranges have also been made [14].

In the present study, the values of the Tafel slope determined for the Zn-Cr alloys are somehow higher, but close to the characteristic value of 118 mV decade\(^{-1}\). It is possible that also at the high cathodic currents a certain amount of unreduced oxide remains on the electrode surface, affecting the slope of the Tafel plot. It is worth mentioning, that the theoretical value of 118 mV decade\(^{-1}\) is calculated for a clean, not oxidized surface. However, considering the obtained \(b\) values for the HER on the Zn-Cr alloy coatings and the peculiarities of the Zn-Cr system, a Volmer reaction mechanism as a dominant step in the 0.25–10 mA cm\(^{-2}\) current range could be suggested. It has been postulated in theoretical analysis on hydrogen overvoltage for different electrode materials that the kinetics of the electrode process, for overvoltages larger than approximately 0.1–0.15 V is essentially controlled by the rate of discharge of hydrogen ions [15]. Furthermore, at higher polarizing currents, where the oxide layer is probably less stable and a surface enriched in Cr is exposed, the effect of Cr becomes more pronounced (Ar\(^+\) ion sputtering also reveals higher surface concentration of Cr, see Appendix Surface state), Since Cr is a good catalyst for adsorbing hydrogen apparently the HER proceeds on a surface covered with hydrogen. Thus, in view of data for Cr [11,16] and theoretical considerations, Heyrovsky mechanism appears to be the likely rate determining step at high polarizing currents. Moreover, at high polarizing currents the susceptibility of the alloy to hydrogen and possible hydrogen ingress/release will influence the kinetics of the HER.

The Tafel slopes for hydrogen evolution on the Zn electrodes (Table 1) have considerably higher values than the theoretical value of 118 mV decade\(^{-1}\). Anomalously high Tafel slopes, \(b = 240\) mV exhibited on polarization curves of Zn at \(pH 5.8\) in Na\(_2\)SO\(_4\) have been previously determined for the alloys are similar and in two orders of magnitude lower than that obtained for electrolytic Zn. The exchange current density characterizes the electrocatalytic activity of the electrode at equilibrium conditions. However, a certain current density is required for the HER to proceed at a measurable rate. Therefore, in order to compare the electrocatalytic activity of electrodes, it has been suggested to compare rather the overvoltage at a certain current density \([12]\). That is why, the last column in Table 1 presents the values of the hydrogen overvoltage for the investigated systems at a current density of 0.01 A cm\(^{-2}\), allowing comparison.

Other kinetic parameters, which are proposed to be used for characterization of the electrocatalytic activity of electrodes towards the HER are the value of the Tafel slope \(b\) and the value of the transfer coefficient \(\alpha\) \([12,13]\). It is generally accepted that, if the Volmer reaction step is rate determining the resulting Tafel curve should yield a slope of 118 mV decade\(^{-1}\). The Volmer mechanism (the so called “slow discharge mechanism”) is valid for the HER on electrodes, including Zn that are unable to adsorb hydrogen atoms to any great extent \([8]\). The Tafel mechanism (the so called “catalytic mechanism”) is characteristic for the HER on the metals of the Pt group and the distinctive Tafel slope is 30 mV decade\(^{-1}\).

If the electrochemical desorption is rate determining at low negative potentials, the Tafel slope would yield a value of about 40 mV decade\(^{-1}\). At high overvoltages, generally the Heyrovsky mechanism takes place. Attempts for kinetic descriptions of the HER via two-step (Volmer-Heyrovsky, Volmer-Tafel or Heyrovsky-Tafel) and even three step (Tafel-Volmer-Heyrovsky) mechanisms depending on potential ranges have also been made [14].

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>(a), mV</th>
<th>(b), V</th>
<th>(j_0), A cm(^{-2})</th>
<th>(\alpha)</th>
<th>(\eta), V</th>
</tr>
</thead>
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<tr>
<td>Zn electrolytic</td>
<td>1.75</td>
<td>0.238</td>
<td>(4.5 \times 10^{-8})</td>
<td>0.25</td>
<td>–1.301</td>
</tr>
<tr>
<td>Zn metallic</td>
<td>1.77</td>
<td>0.217</td>
<td>(7.0 \times 10^{-9})</td>
<td>0.27</td>
<td>–1.338</td>
</tr>
<tr>
<td>Zn-Cr 3%</td>
<td>1.30</td>
<td>0.142</td>
<td>(6.9 \times 10^{-10})</td>
<td>0.42</td>
<td>–1.300</td>
</tr>
<tr>
<td>Zn-Cr 5%</td>
<td>1.35</td>
<td>0.140</td>
<td>(2.3 \times 10^{-10})</td>
<td>0.42</td>
<td>–1.074</td>
</tr>
<tr>
<td>Zn-Cr 10%</td>
<td>1.25</td>
<td>0.132</td>
<td>(3.4 \times 10^{-10})</td>
<td>0.45</td>
<td>–1.002</td>
</tr>
<tr>
<td>Cr electrolytic</td>
<td>1.65</td>
<td>0.307</td>
<td>(4.1 \times 10^{-6})</td>
<td>0.19</td>
<td>–1.052</td>
</tr>
<tr>
<td>Cr metallic</td>
<td>1.48</td>
<td>0.211</td>
<td>(1.1 \times 10^{-7})</td>
<td>0.28</td>
<td>–1.056</td>
</tr>
</tbody>
</table>

* Overpotential at 0.01 A cm\(^{-2}\) derived from the respective Tafel curves.

The \(j_0\) values for the alloys are similar and in two orders of magnitude lower than that obtained for electrolytic Zn. The exchange current density characterizes the electrocatalytic activity of the electrode at equilibrium conditions. However, a certain current density is required for the HER to proceed at a measurable rate. Therefore, in order to compare the electrocatalytic activity of electrodes, it has been suggested to compare rather the overvoltage at a certain current density \([12]\). That is why, the last column in Table 1 presents the values of the hydrogen overvoltage for the investigated systems at a current density of 0.01 A cm\(^{-2}\), allowing comparison.

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![Fig. 11. Morphology (SEM images) of: Zn (a), Zn-3%Cr (b) Zn-5%Cr (c) and Zn-10%Cr (d) coatings. Thickness of the deposits 5 μm.](image-url)
reported [17]. Anomalous Tafel slopes were also obtained in NaCl, pH 5.8: \( b = 415 \text{ mV} \) and \( b = 330 \text{ mV} \); in NaClO4 at pH 5.8, \( b = 330 \text{ mV} \). The poor reproducibility in the pH 5.8 solutions was assumed to be caused by the presence of an oxide film of variable morphology, compactness or thickness, despite the rigorously controlled experimental conditions. According to the authors the oxide film is non-passivating and therefore probably porous. Hydrogen evolution via water reduction can occur at the film-solution interface as a consequence of the semiconducting properties of the ZnO [17].

By combining electrode kinetic data with gas-phase hydrogen adsorption behaviour for the HER on Cr a radical-ion mechanism: \( \text{H}_3\text{O}^+ + e^- + M - H + M + H_2 + H_2O \) has been concluded [10]. The data for the HER (\( j_b = 5.0 \times 10^{-8} \text{ A cm}^{-2}; b = 129 \text{ mV} \)) obtained in the study were referred to a non-passivated Cr surface. High \( b \) values on Cr were also explained by the presence of a surface oxide. It has been noted that the oxide covered Cr surface is capable of supporting hydrogen ion reduction and it is likely that Cr passivates are due to the formation of semiconducting Cr deficient oxide film [16]. Subsequently, our \( b \) value data (Table 1) could be related to an oxidized Cr surface.

In a general manner, if the electron transfer phenomena occur in a given system, the transfer coefficient \( \alpha \) is at least approximately equal to 0.5 [18]. In fact, the 0.5 value is theoretically and experimentally obtained from investigations of an elementary process in the case of a single reaction. The stronger deviations from this value for Zn and Cr observed in the present study indicate a complex reaction occurring at the electrodes (most probably oxidation along with the HER).

### 3.4. Surface area

The investigations showed, that the HER proceeds with lower over-voltage on the alloy in comparison to that on Zn. This is related to the effect of the alloying element, but the difference of the real surface areas of the Zn and Zn-Cr coatings (visible also to the naked eye) should be considered as well. Fig. 9 shows SEM images of Zn and Zn-Cr alloy coatings. The Zn coating is composed of densely packed large hexagonal crystallites with edge lengths of about 3–4 \( \mu \text{m} \). The normal to their basal planes is slightly tilted with respect to the substrate plane, which allows observation of growth steps on the prismatic faces (Fig. 11a). A more regular coverage, in respect to that observed in Fig. 2 is worth to mention. The occasionally observed globular formations on top of the polygonal polycrystals (Fig. 11b, c) are actually dendrites having a chemical composition close to that of the base coating. The Zn-10%Cr coating consists of densely packed polycrystalline particles whose size varies between 0.08 and 0.8 \( \mu \text{m} \) (Fig. 11d).

Profile and roughness measurements, as well as three-dimensional area analyses, directly from the stereoscopic images were performed in attempt to determine the degree of difference of the real surface area of the Zn and Zn-Cr coatings from the geometric one. The mean roughness values indicate about three times higher roughness of the Zn coating in comparison to that of the Zn-Cr alloy coating, containing 10 mass % Cr (Fig. 12). The difference in the real surface areas is also evident from the 3D-SEM images (Fig. 13).

No attempt for evaluation of the real surface areas of the layers by electrochemical methods [19] was done because of difficulties in selecting a range from the voltammograms were only charging of the double electrical layer takes place. On the other hand, on the cathode branch of the voltammogram for the alloy (see Fig. 4) the smaller peak compared to those of pure Zn also indicates less exposed surface area. However, the difference in the surface areas does not put doubts...
about the effect of alloying. On the contrary, the higher roughness of the Zn coatings in comparison to that of the Zn-Cr coatings implies a larger difference in the hydrogen overvoltage for these two systems. Regarding the exchange current density the difference would lead to closer values of this parameter.

4. Conclusions

The alloying of Zn with Cr facilitates the HER. At a current density of 10 mA cm\(^{-2}\) the hydrogen overvoltage on the Zn-10%Cr alloy is more than 200 mV lower than that on Zn. At low current densities the hydrogen overvoltage on the alloys is closer to that on Zn and at higher polarizing currents it is closer to that on Cr.

The values of the exchange current density for the HER on the alloys with different Cr content are similar. The obtained values are in about two orders of magnitude lower than the exchange current density for the HER on Zn. However, the higher roughness of the Zn coatings supposes larger differences in the hydrogen overvoltage and closer values for the exchange current density.

Based on the values of the Tafel slope derived for the Zn-Cr alloys, Volmer mechanism for the HER within the 0.25–10 mA cm\(^{-2}\) current density range is suggested, i.e. the reaction mechanism accepted for the HER on Zn. At higher polarizing currents the effect of Cr becomes more pronounced and presumably the electrochemical desorption appears to be the likely rate determining step.

The high values of the Tafel slope and the low values of the transfer coefficient (in respect to the theoretical ones) obtained for Zn and Cr suggest a complex reaction occurring at the electrodes.

The alloy coatings have finer and denser structure, which enables an efficient barrier isolation of the steel surface regarding hydrogen embrittlement of the steel substrate by using a thinner layer compared to electrodeposited Zn coatings.

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Appendix A. Surface state of Zn-Cr alloy

In order to complement the studies and obtain information about the surface chemical state of the alloy an investigation of Zn-10%Cr sample was performed by XPS. Data were taken on the “as is” surface and after 5 min of sputtering.

The X-ray photoelectron experiments were carried out on AXIS Supra electron spectrometer (Kratos Analytical Ltd., a Shimadzu Group Company) with base vacuum in the analysis chamber of \(-10^{-9}\) mbar. A monochromatic Al K\(_x\) excitation radiation with photon energy of 1486.6 eV was used. The photoemitted electrons are separated, according to their kinetic energy. The detection system is characterized by hybrid type (electrostatic and magnetic) lenses of the analyzer, charge neutralizer operating with low-energy electrons. The used spot size aperture in front of the lenses and the analyzer pass energy of 20 eV determine an instrumental resolution of 0.54 eV (FWHM of Ag 3d\(_{5/2}\) peak). The accuracy of the binding energy determination is within \(\pm 0.1\) eV. The energy scales of the XPS spectra were calibrated with respect to the C1s peak position of the adventitious hydrocarbons at 285 eV. The sample surface was cleaned by Ar\(^{+}\) ion sputtering (ion energy of 4 eV, ion current of \(-2\) μA), sputtering time of 5 min.

The “as is” surface showed the typical adventitious C at 285 eV which amount was reduced after the sputtering. An increase of the intensity of the Zn2p\(_{3/2}\), peak after the sputtering was detected, but no change of the binding energy (BE) for both surfaces (1022.2–1022.3 eV) was observed. The kinetic energy of the Auger peak L\(_{2}\)M\(_{4}\)M\(_{4}\) at 987.2–987.4 eV gives an Auger parameter close to 2010 eV which is characteristic for Zn\(^{2+}\) oxidation state. It has to be noted, that this parameter is considerably smaller than the one typical for the surface of pure Zn (about 2014 eV).

Analysis of the Cr 2p peaks indicated a significant contribution from overlapping with the Zn LMM Auger peaks. When comparing the most intensive peaks of Zn and Cr, the relative sensitivity factor (RSF) for the Zn2p\(_{3/2}\) and Cr2p\(_{3/2}\), i.e. 3.726 and 1.618, respectively has to be considered. The values show more than two times lower sensitivity of the XPS method to the detection of Cr than to the detection of Zn. The BE of the Cr2p\(_{3/2}\) peak at 577.3–577.5 eV indicates Cr\(^{3+}\) oxidation state.

A more appropriate approach for determination of the amounts of Zn and Cr is the use of the 3p-photoelectron peaks. In this case, also the difference in the kinetic energies is smaller (1486.6–44)–(1486.6–89) = 45 eV (whereas the difference in the energies of the 2p\(_{3/2}\) peaks of Zn and Cr is (1486.6–577)–(1486.6–1022) = 445 eV). The photo electrons with small difference in the kinetic energies are emitted from similar in thickness surface layers, i.e. the error in the determination of the surface atomic concentration of Zn and Cr is also smaller. Fig. 1 shows the 3p-photoelectron spectra of Zn and Cr before and after sputtering.

From the O1s scans, the surface O is identified as a mixture of metal oxides/hydroxides (531 eV), O\(_1\) and organic oxides (532 eV), O\(_3\) (Fig. 2a). After the sputtering, the O1s peak shifts to the lower BE's (530 eV) associated with Zn or Cr oxides (Fig. 2b).

From the analysis of the element’s regional scans and taking into account the RSF for the detected elements the surface chemical composition was calculated (Table 1).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Zn</th>
<th>Cr</th>
<th>O1</th>
<th>O2</th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>“As plated”</td>
<td>6.8</td>
<td>1.0</td>
<td>2.8</td>
<td>19.2</td>
<td>65.2</td>
<td>5.0</td>
</tr>
<tr>
<td>After 5 min sputtering</td>
<td>11.3</td>
<td>1.6</td>
<td>5.5</td>
<td>17.8</td>
<td>59.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

*RSF values and photoelectron peaks:

C 1s O 1s Cr 3p Zn 3p Si 2p

RSF 0.278 0.78 0.281 0.939 0.328

From the overall elemental composition it can be concluded that the alloy surface contains oxides/hydroxides of Zn and in a smaller amount of Cr, C in organic compounds and Si, related to contamination of the surface.

![Fig. 1. Cr 3p and Zn 3p spectra of Zn-Cr alloy coating before and after sputtering.](image-url)
References


Fig. 2. O 1s spectra of Zn-Cr alloy coating before (a) and after sputtering (b).