Electrolyte design and characterization of REACh-compliant Zn-W and Zn-W-Cu electrodeposits

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Abstract. Within this work, an entirely new electrolyte system for the electrochemical deposition of REACh-compliant Zn-W and Zn-W-Cu alloy layers was developed based on thermodynamic calculations. The required constants of complex formation were determined using potentiometric titrations. The layers were analyzed with regard to the layer microstructure (including coating thickness, chemical and phase composition), the optical properties (including gloss and color) and the passivation and corrosion behaviors. The Zn, Zn-W, and Zn-W-Cu layers are characterized by a decorative appearance, high uniformity, a nanocrystalline structure and natural passivation during the exposure in the climate chamber. Due to their particularly favorable optical properties and their pronounced natural passivation, the Zn-W alloy layers exhibit a great potential for industrial applications.

1. Introduction

Regarding the risk of a possible restriction in the use of Zn-Ni alloy layers as a result of the REACh regulation, there is a need to establish REACh-compliant alternatives. At the present time, Zn-Fe alloy layers are primarily used as a substitute for Zn-Ni, although these are inferior to Zn-Ni layers in terms of corrosion resistance (according to DIN 50962) and layer hardness [1]. In the scientific literature, there is also some information available on Zn-Mn [2, 3], Zn-Cr [4] and Zn-Fe-Cr [5]. However, those alloys have not been marketable so far. Alloy deposits of Cu and Zn have a long tradition. In recent years, research focused on the development of cyanide-free Cu-Zn electrolytes. Alternative complexing agents were investigated in order to align the strongly different potentials for the reduction of Cu and Zn ions and to enable the deposition of alloys with a high Zn content from aqueous solutions. Citrate is used as a complexing agent both in strong alkaline [6] and in neutral to weak acidic electrolytes [7]. In similar systems, ternary Cu-Zn-Sn [8] and Cu-Zn-Mo [9] alloy deposits were obtained. Pyrophosphate was used as a complexing agent at approximately neutral pH values [10, 11]. Furthermore, the deposition of Cu-Zn alloys was investigated in glconenate [12] and EDTA [13] electrolytes at neutral to moderately acidic pH values. All of these studies on the Cu-Zn deposition from cyanide-free baths have in common that maximum Zn contents of 30 to 40 % were targeted and Zn contents of more than 50 % were rarely achieved. The deposition of the so called “white brass” with a Zn content of up to 90 % was only performed in cyanide electrolytes [14]. To our knowledge, Zn alloys with a Cu content of less than 5 % were not reported in the literature so far.

Theoretically, in the alloy systems mentioned above, all elemental compositions could be achieved under the appropriate conditions, ranging from 100 % of Zn to 100 % of the alloying elements. However,
in case of the so called “induced co-deposition” [15], ignoble elements such as W can be co-deposited as alloying elements, although they cannot be deposited as a monometallic layer. In particular, Ni-W alloy deposits with up to about 25 % W have gained interest as potential alternatives to hard-chromium layers due to their high hardness [16]. In case of Fe-W-Zn, less than 10 % Zn were incorporated in order to improve the passivation behavior and the corrosion resistance of the Fe-W alloy deposit [17]. It was stated that the co-deposition of tungsten was related to the iron deposition and that the Zn incorporation took place independently [17]. Also, in case of an alkaline Zn-Ni-W electrolyte, the co-deposition of 4 % W could have been related to the deposition of 18 % Ni [18]. Nakano et al. observed no W co-deposition in case of an acidic electrolyte that contained only Zn and W ions [19]. Thus, no evidence was found that W ions can be co-deposited with Zn ions.

It can be concluded from the literature research that both Zn-Cu alloys from cyanide-free electrolytes with a low Cu content and binary Zn-W are potential alternatives to Zn-Ni coatings, but their properties have not been investigated yet. This article demonstrates the development of an electrochemical process for the deposition of Zn-rich Zn-Cu alloys from a cyanide-free bath using thermodynamic calculations. Furthermore, tungsten ions are added to the electrolyte in order to generate Zn-W and Zn-W-Cu alloys. As these alloys are entirely new, the microstructural and optical properties as well as the passivation behavior are described for the first time.

2. Experimental and materials

The basic thermodynamic electrolyte design was conducted for Zn and Cu ions and different complexing agents. The equilibrium state of the electrolytes was described by the law of mass action. Furthermore, the optimal pH working range of the electrolyte was calculated by considering the protonation behavior. The simplified chemical equations are summed up in table 1. The complex equilibrium equations were mathematically solved using a non-linear equation system. A MatLab routine was created for this purpose.

| law of mass action | solubility behavior | protonation equilibrium |
|------------------|--------------------|-------------------------|
| [Me] + [KB] ⇋ [KBMe] | [Me]^{2+} + [OH]^{-} ⇋ [Me(OH)]_{n} \downarrow | [H]^{+} + [KB] ⇋ [HKB] |
| \[ K = \frac{[KBMe]}{[Me^{2+}] + [KB]} \] | \[ K = [Me^{2+}] \cdot [OH^{-}]^{n} \] | \[ K = \frac{[HKB]}{[H^{+}] + [KB]} \] |

The required thermodynamic equilibrium constants K were determined using the potentiometric titration, which was first described by Martell [20]. A modified iterative algorithm was used to determine the equilibrium constants of unknown systems:

1) Definition of default equilibrium constants and proton concentrations,
2) definition of the law of mass action,
3) solving the equation using the Newton’s method,
4) error optimization,
5) starting the next iteration step with the updated parameters or ending the process.

The experimental setup is shown in figure 1. The potentiometric acid-base-titrations were carried out in the pH range from 2 (adjusted by the addition of HCl or H_{2}SO_{4}) and 12 (incremental addition of NaOH). The experiments were carried out at a constant concentration of [KB] = 0.01 mol/l and different [KB]:[Me] ratios ranging from 1:0 to 1:5.

As a result of the electrolyte design, the basic Zn electrolyte consists of 27.26 g/l (0.2 mol/l) ZnCl_{2} and 67 g/l (0.5 mol/l) C_{4}H_{6}O_{6} (malic acid). The additives C_{6}H_{10}O_{6}, C_{10}H_{6}BrN and H_{2}BO_{3} were used in order to improve the coating quality and the process stability. The elements W and Cu were added as 2.94 g/l (0.01 mol/l) Na_{2}WO_{4} and 0.5 g/l (0.002 mol/l) CuSO_{4}·7H_{2}O. For further characterization, cold
rolled sheets of the unalloyed steel CR1 (according to ISO 3574) were electroplated at a current density of 1 A/dm² at 30 °C and pH 6 for 60 minutes. A soluble Zn anode was used as the counter electrode.

As a standard procedure, the thickness and the chemical composition of the coatings were determined using the X-ray fluorescence analysis (XRF, FISCHERSCOPE X-RAY XAN, Fischer, Sindelfingen, Germany). In favor of a higher precision, the chemical composition was also determined after chemical digestion using the inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300, Perkin Elmer, Waltham, USA). The microstructural analysis was performed at the metallographically prepared coating cross-section using optical microscopy (OM, GX51, OLYMPUS, Shinjuku, Japan) and scanning electron microscopy (SEM, LEO-1455VP, Zeiss, Oberkochen, Germany). Phase analyses and crystallite-size measurements were conducted utilizing X-ray diffraction (XRD, D8 DISCOVER, Bruker AXS, Karlsruhe, Germany). In order to quantitatively describe the optical appearance of the coatings, reflectometric gloss measurement (micro-TRI-gloss µ, BYK Gardner, Geretsried, Germany) was performed under an incidence angle of 20° as defined in DIN 67530 for high reflecting surfaces. The color of the coatings was measured using a spectrometer (spectro-guide, BYK Gardener, Geretsried, Germany) with the illuminant D65 and the 10° standard observation angle and visualized using the CIE Lab color space. Different commercial coatings were used as references in order to illustrate the gloss and color.

Prior to corrosion testing, the samples were exposed to artificial weathering in a climate chamber (KB 300, Liebisch, Bielefeld, Germany) for up to 21 days, which enabled the formation of a natural passive layer. Each climate cycle consisted of a humid phase (95 % relative humidity for 2 h at 28 °C) and a dry phase (60 % relative humidity for 4 h at 21 °C). The electrochemical corrosion measurements were performed by the Federal Institute for Materials Testing and Research (BAM) using a gel electrolyte based on agar, which does, in contrast to conventional aqueous electrolytes, not chemically dissolve the passive layer during the measurement. The testing conditions are described in more detail in [21]. For each coating, the open circuit potential (OCP) was recorded for 5 min before performing potentiodynamic polarization tests. As an indicator of the corrosion resistance of the passive layer, the polarization resistance was determined using electrochemical impedance spectroscopy (EIS).
3. Results and discussion

3.1. Process design

The equilibrium state of free metal ions and metal ions, which are bound in complexes, can be calculated using the thermodynamic law of mass action. It is generally assumed, that the metal deposition can only take place by the reduction of free metal ions. With increasing complex stability (high equilibrium constants $K$), the concentration of free metal ions decreases. Consequently, the Nernst potential for the metal deposition is shifted to more negative values. By the use of selective complexing agents, the Nernst potentials of the generally more noble metal Cu and the ignoble metal Zn can be aligned, which enables the simultaneous deposition of both metals. By considering the protonation equilibrium and the solubility of the complexes, optimal pH working ranges can be predicted, which are characterized by a high electrolyte stability and a low probability of precipitation and cementation.

As shown in figures 2 and 3, free metal ions are dominating at pH values below 2. Within a range of pH 4 to pH 9, malic acid forms stable complexes with both Zn and Cu ions and the precipitation of insoluble hydroxides can be suppressed. The free metal concentrations of both Zn and Cu are reduced due to complexation, which is generally related with an increasing throwing power of the electrolyte. The difference of the Nernst potentials of Cu and Zn is still higher than 1 V. The Cu concentration in the electrolyte is significantly lower than the Zn concentration. Hence, the deposition of Cu is limited due to the ion diffusion and Zn-rich alloy coatings can be achieved. Above pH 9, insoluble Zn and Cu hydroxides are formed. In order to ensure a high electrolyte stability and a sufficient complexation, the further experiments were conducted within the stability range of the malic acid complex at pH 6.

**Figure 2.** Zn species as a function of the pH value in 0.5 mol/l malic acid + 0.2 mol/l Zn.

**Figure 3.** Cu species as a function of the pH value in 0.5 mol/l malic acid + 0.002 mol/l Cu.
3.2. Microstructure
Both the Zn-W and the Zn-W-Cu coatings are characterized by a smooth surface and a high uniformity of the coating thickness, as can be seen from figure 4. At increased magnification, some pores can be recognized within the Zn-W-Cu coatings (figure 5) with the aid of the BSD detector (material contrast). This indicates that the side-reaction of hydrogen evolution took place. However, the current efficiency of the metal deposition was still about 85 % at a current density of 1 A/dm², which is comparable to a commercial alkaline Zn electrolyte.

The ICP-OES measurements revealed a W content of about 0.7 % for the Zn-W alloy coating. The Zn-W-Cu alloy coating contains about 0.1 % W and 0.5 % Cu. All Zn and Zn alloy coatings from malic acid electrolytes exhibited a crystalline structure. No other phases could be detected by XRD besides the hexagonal Zn phase, due to the low contents of the alloying elements below 1 %. Because of the strong texture of the Zn alloy coatings, the crystallite size was only quantifiable at the preferred crystal plane. Each of the new Zn and Zn alloy layers exhibits a crystallite size of about 50 nm, which is similar to the crystallite size of a commercial bright Zn layer. The nano-crystalline microstructure is achieved by the addition of brighteners, which inhibit the crystal growth in thickness direction and it is beneficial with respect to the mechanical properties such as hardness and ductility.

3.3. Optical appearance
The optical appearance is one of the most important properties of Zn layers as they are being used for the corrosion protection of steel parts. Although all Zn and Zn-alloy layers from the malic acid electrolyte and the commercial Zn layer are characterized by the same crystallite size, they exhibit strongly different gloss values. This can be ascribed to the different levelling ability. In the case of the commercial Zn layer, there is only some geometric leveling of the substrate roughness, which results in a slight increase of the surface reflectance (figure 6). In contrast to this, the Zn and Zn-alloy layers exhibit a significantly higher gloss. This indicates that metal deposition preferably took place in deepenings which leads to a strong leveling of the surface roughness. The highest gloss of more than 900 gloss units (GU) was observed for Zn-W. This gloss level is almost comparable to a mirror finish, which is typically characterized by a gloss level of more than 1000 GU.

The CIE Lab color space is described by a cartesian coordinate system with the axis “a” ranging from -150 (green) to 100 (red), the axis “b” ranging from -100 (blue) to 150 (yellow) and the axis “L” ranging from 0 (black) to 100 (white). The standard illuminant D65 corresponds with a color temperature of 6504 K, which is comparable to the average daylight according to DIN 5033-7. As can be seen from figure 7, the brightness (L value) is similar for all Zn and Zn-alloy coatings. In comparison with the monometallic Zn reference coating from an alkaline electrolyte, the color of the Zn coating from the

![Figure 4. LM images of the cross-section of a) Zn-W and b) Zn-W-Cu layers.](image)

![Figure 5. SEM image (BSD) of the coating cross-section of Zn-W-Cu.](image)
malic-acid electrolyte is shifted towards yellow. When considering both color and gloss, the appearance of the new Zn coating is comparable to conventional bright nickel deposits. The color of the Zn-W-alloy coating is comparable with the color of a Zn-Fe reference layer, which was deposited from a commercial alkaline electrolyte. In this case, the b-value is similar to the color of bright nickel and the a-value indicates a slight green color portion, which is comparable to Cr coatings from Cr(VI) electrolytes. Compared with the color of Zn-W coatings, Zn-W-Cu coatings are characterized by a color shift towards yellow and red due to the addition of Cu. All Zn and Zn-alloy coatings are characterized by a decorative appearance, which might be further optimized by a subsequent passivation treatment.

**Figure 6.** Gloss values of different Zn and Zn alloy coatings under an incidence angle of 20°.

**Figure 7.** CIE Lab coordinate system showing the color of Zn, Zn alloy and reference coatings; illuminant D65, 10° standard observation angle.
3.4. Passivation behavior
The potentiodynamic polarization measurements, which were performed with the gel electrolyte, generally show a decrease of the corrosion current density with increasing exposition time in the climate chamber, as shown for the Zn-W alloy coating in figure 8. This already indicates that the corrosion rate, which is directly related to the corrosion current density by the Faraday’s law, decreases due to the growth of the natural passive layer. In theory, the corrosion rate of a system also decreases inversely proportional to the increasing polarization resistance, which is obtained from EIS measurements [22]. This correlation can be verified (figure 9). The polarization resistance increases over the exposition time for each of the Zn and Zn-alloy layers. The highest polarization resistance was measured for Zn-W coatings, while the polarization resistance of Zn-W-Cu is almost at the same level compared to a monometallic Zn layer which was obtained from the malic acid electrolyte. This observation indicates that the polarization resistance, and consequently the corrosion resistance, strongly depends on the chemical composition of the Zn alloy coating. Even a W-content of 0.7 % (compared to 0.1 % W for Zn-W-Cu) obviously enhances the polarization resistance of the natural passive layer significantly.

Figure 8. Potentiodynamic polarization curves of Zn-W layers after exposition in the climate chamber for up to 21 days.

Figure 9. Development of the polarization resistance of Zn and Zn alloy coatings after exposition in the climate chamber for up to 21 days.

4. Conclusions
As potential alternatives to Zn-Ni coatings, REACh-compliant Zn-W and Zn-W-Cu alloy coatings were successfully deposited and characterized for the first time. In addition to the existing scientific literature, it was shown that Zn-rich Zn-Cu alloy coatings can be deposited from a cyanide-free bath and that the induced co-deposition of tungsten is not only related to the deposition of iron-group elements or Cu, but can also take place in combination with the Zn deposition. Within the stage of the development of a new electrolyte, which is based on the complexing agent malic acid, the calculation of the thermodynamically stable Zn and Cu species as a function of the pH value proved to be a valuable instrument. In this way, extensive experimental depositions at different pH values were not required. A sufficient complexation of the metal ions was achieved within the stability range of the malic acid complexes at pH 6 without the formation of insoluble hydroxides. Due to the addition of further electrolyte components, such as a brightener, a wetting agent and a pH buffer, nanocrystalline coatings with a high homogeneity and compactness were achieved. All Zn and Zn alloy coatings from the new malic acid electrolyte are characterized by a high gloss and a slightly yellowish color. The Zn-W coating exhibits the highest gloss and a color, which is comparable to already established alkaline Zn-Fe coatings. By applying electrochemical characterization techniques using gel electrolytes, it was observed that for all Zn and Zn alloy layers, natural passivation takes place during exposition in a climate chamber. However, the corrosion resistance strongly depends on the chemical composition of the Zn alloy coating. It turned out
that even a small W content of 0.7 % is suitable in order to significantly raise the polarization resistance of the natural passive layer. From the perspective of both the decorative appearance and the pronounced natural passivation, the Zn-W layers have a high potential for the substitution of Zn-Ni-alloy coatings in industrial applications.

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