

The Influence of tin ions on the electrodeposition of zinc

Dedicated to Professor Dr. Martin Stratmann on the occasion of his 60th birthday

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Tin has a strong influence on the electrodeposition of zinc already in concentrations of less than 1 ppm. Tin changes the mechanism, the deposition rate and the morphology of the resulting surface of zinc deposited from an acidic sulfate electrolyte. These severe changes are not obvious since both elements have similar overpotentials for hydrogen evolution as the dominant side reaction. The influence on the electrodeposition of zinc was studied using cyclic voltammetry on a rotating disc electrode, chemical analysis of the zinc layers, chronopotentiometric measurements, and investigations into the microstructure by SEM. It is shown that tin co-deposits with zinc starting at concentrations of about 1 ppm and therefore changes the structure of the zinc layer. A mechanism is presented that explains the significant drop in current efficiency in a pulsed deposition program, in which the codepositing tin acts as cathode during the off cycle leading to drastic anodic redissolution of the zinc.

1 Introduction

Zinc electrodeposition is a well-studied field due to its importance in electrowinning, as process for the production of high purity zinc and electroplating as corrosion protection for steel [1]. Impurities in the zinc electrolyte may have a large influence on the morphology and the properties of the resulting zinc layer. They also influence the current efficiency of the electroplating process. This is in particular true since zinc does not show a region of thermodynamic coexistence with water, i.e., it is not stable in the so-called electrochemical window in the *Pourbaix* diagram [2]. This means that zinc deposition from aqueous solutions under standard conditions is thermodynamically not possible [3,4]. However, high purity zinc shows a surprisingly high stability in aqueous solutions. The dissolution hindrance is

mainly due to the high overpotential for the hydrogen evolution which is the counter reaction for its anodic dissolution, a property that zinc shares with the elements from the same group cadmium and mercury. This situation changes dramatically when traces of more noble metals such as copper or tin are alloyed to the zinc or simply brought in contact to pure zinc, leading to a violent hydrogen evolution along with the dissolution of the zinc.

From a technical point of view, the electrodeposition of zinc from acidic sulfate solutions is of large importance. The main application is the electrodeposition on steel for the corrosion protection of steel [5,6]. Various aspects like the influence of the pH value, temperature and current density, the current efficiencies and the morphology of the zinc layer have been studied so far [7–9]. It has been reported that even an external magnetic field changes crystal growth due to a micro-magneto-hydrodynamic-effect [10].

The influence of the addition of organic additives on various aspects of zinc electrodeposition has been investigated thoroughly [11–13]. Despite their broad application in other fields they play a minor role in the electroplating process of steel. Therefore impurity effects have to be fully understood, so that properties of the deposited zinc layer might be controlled.

Also the effects of various inorganic impurities have been investigated in depth. Some of the impurities studied so far show strong effects on the current efficiency and/or morphology. It was reported that Ge has no influence on the morphology but addition of more than 0.1 mg/L leads to a depolarization of the electrode and a significant decrease in current efficiency of the electrodeposition of Zn [14]. Pb on the other hand polarizes the electrode

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and is incorporated into the deposited zinc layer [15]. It has also been reported that Pb deposits on the corners of the hexagonal crystal plane and leads to the formation of anti-hexagonal prisms thus causing a change in the morphology of the zinc layer [16]. Fe on the other hand has no significant influence up to concentrations of 5 g/L [17]. The same behavior is reported for Ni as impurity. Cu leads to the formation of powdery zinc layers [18]. Antimony is one of the most often investigated impurities due to its apparent effect starting at concentrations of 20 ppb [18–20]. Sn was reported to cause the formation of pinholes in heavy Zn coated sheets [16].

The goal of this work is to investigate the influence of Sn^{2+} on the electrodeposition of zinc to gain a better understanding on its influence on the electrogalvanizing process of steel sheets. Therefore cyclic voltammetry was performed on a platinum rotating disc electrode (RDE). The dependence of current efficiency, roughness, a main property for plated steel sheets used in automotive industry, of the resulting layer on the Sn^{2+} concentration was investigated on temper rolled low carbon steel sheets. This effect depends on the surface morphology of the zinc layer [21]. Finally scanning electron microscopy was used to study the influence of tin ions on the morphology of the deposited zinc layer.

2 Experimental

2.1 Chemicals

Three different electrolytes were used during the experiments. The p.A.-Zn-electrolyte was an analytical grade sulfate electrolyte with 90 g/L Zn^{2+} ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ p.A. Roth GmbH) and 20 g/L Na^+ (Na_2SO_4 p.A. Baker), the pH value was 1.55 (H_2SO_4 p.A., Merck). The p.A.- Na_2SO_4 -Electrolyte was the same without Zn and the industrial-Zn-electrolyte was taken from an industrial electrogalvanizing line (voestalpine Stahl GmbH, Linz, Austria). A comparison of impurity-concentrations of the electrolyte is shown in Table 1. SnSO_4 (p.A. from Sigma) was used as additive to the electrolytes to simulate the impurity.

2.2 Cyclic voltammetry

Cyclic voltammetry (CV) was done using a platinum disc rotating disc electrode (Tacussel, France) Pt-RDE and a SimPot potentiostat (M. Schramm, HHU-Düsseldorf, Germany). The electrolytes

Table 1. Concentrations of main impurity elements in the used electrolytes

Impurity (mg/L)	p.A.-Zn-electrolyte	Industrial electrolyte
Cu	1.0	1.1
Fe	1.5	3 200
Ge	<0.1	<0.1
Ni	0.6	7.6
Pb	0.9	0.7
Sb	<0.1	<0.1
Sn	<0.1	<0.1

studied were the p.A.-Zn-electrolyte and the p.A.- Na_2SO_4 -electrolyte. Temperature was kept at 40 °C using a thermostat and a double walled glass cell. Cyclic voltammetry was carried out between -1.0 and 1.5 V *versus* SHE with a potential scan rate of 10 mV/s and a rotation speed of $\omega = 600$. The reference in use was a μ -mercury-sulfate reference electrode described by Lill and Hassel [22] and kept at a constant distance of 10 mm from the RDE. To study the influence of Sn^{2+} , SnSO_4 was added to the electrolytes just before measurements to minimize oxidation effects.

2.3 Electroplating

Electroplating for the determination of the changes of the zinc morphology due to addition of Sn^{2+} was done in a flow cell at an electrolyte velocity of 4 m/s and a current density of 800 mA/cm² using an EA-PS9036-240 galvanostat (Elektro-Automatik GmbH & Co. KG, Viersen, Germany). In order to simulate an industrial vertical plating process, the current was interrupted with 24 pulses (duty cycle: 0.8 s on, 1.0 s off). The temperature was kept at 55 °C using a Lauda PROLine RP855 thermostat. A DSA (dimensionally stable anode) made from titanium coated with iridium doped titanium oxide from De Nora (Milan, Italy) was used as anode. The final thickness of the zinc layer was about 7.5 μm for roughness measurements and for determination of the morphology. The steel substrate in use was a temper rolled low carbon steel sheet from voestalpine Stahl GmbH.

2.4 Determination of the current efficiency and layer thickness

The current efficiency was calculated from measurements of the Zn-layer-thickness with a Fischerscope[®] X-ray System XLD[®]-B spectrometer using the WinFTM[®] software and the charge measured during deposition.

2.5 Dissolution measurements

Dissolution measurements of the zinc layers were performed at room temperature in an EG & G PARC flat cell using an IM6e potentiostat from Zahner[®] electric connected to a NPROBE CorrElNoise[™]-technology device from Zahner Messtechnik. The electrolyte in use was the standard p.A.-Electrolyte and an Ag|AgCl|KCl (3 M) was used as reference electrode. Zinc-layer thickness of all samples was about 7.0 μm (measured thickness is shown in Table 2) to ensure comparability.

Table 2. Measured Zn-layer thickness of samples used for dissolution measurements

Sample name	Zn-layer thickness (μm)
Analytical grade	7.05 ± 0.11
Analytical grade + Sn	6.97 ± 0.12
Industrial	6.93 ± 0.11
Industrial + Sn	6.88 ± 0.06

2.6 Surface characterization

A Zeiss Supra 35 FEG-SEM was used to obtain the SEM images.

Roughness measurements were performed according to ISO 16610 using a Hommel T1000 (Hommel Werke, Germany). The roughness was calculated as the mean value of 5 separate measurements on each sample. The Δ -values are always the difference between the measurement results of the surface of the cold rolled steel sheet and the results of the zinc-layer deposited on the same sheet.

3 Results and discussion

3.1 Cyclic voltammetry

In the cyclic voltammograms, shown in Fig. 1, severe changes in the electrochemical behavior of the electrolytes due to the addition of small amounts of Sn^{2+} can be seen. Without Sn^{2+} the cathodic scan of the cyclic voltammogram shows the typical *upd*-regime from -0.1 to -0.85 V versus SHE where bulk electrodeposition of zinc starts. With addition of Sn^{2+} the *upd* region of the CV disappears completely. The hydrogen evolution in this region is therefore suppressed. Tin also leads to a depolarization of the cathode by 90 mV and a steeper increase of the current in Zn-bulk-deposition. In the cathodic scan no dependency on the Sn^{2+} concentration was observed.

In the anodic scan of the pure zinc electrolyte the dissolution of zinc can be observed between -0.75 and -0.49 V versus SHE. Addition of Sn^{2+} leads to a second dissolution peak starting at -0.22 V versus SHE. The peak area shows a dependence on the concentration of Sn^{2+} but not the potential of the rising edge and can be therefore associated with the dissolution of Sn. Most likely tin co-deposits with zinc even for concentrations lower than 10 ppm. This is proven by the analysis of the zinc layer electrodeposited in the flow cell, which shows a content of about 180 ppm of Sn in the Zn-layer. Tin is known to have an overpotential for the hydrogen evolution reaction that is quite similar with that of zinc, so the suppression of hydrogen-

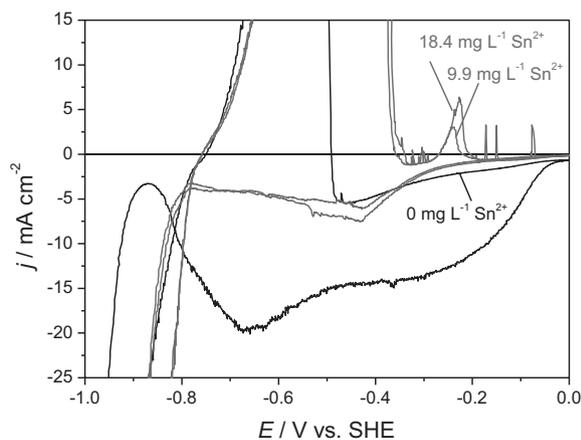


Figure 1. Cyclic voltammetry on a Pt-RDE in a ZnSO_4 electrolyte at pH 1.55 with addition of Sn^{2+}

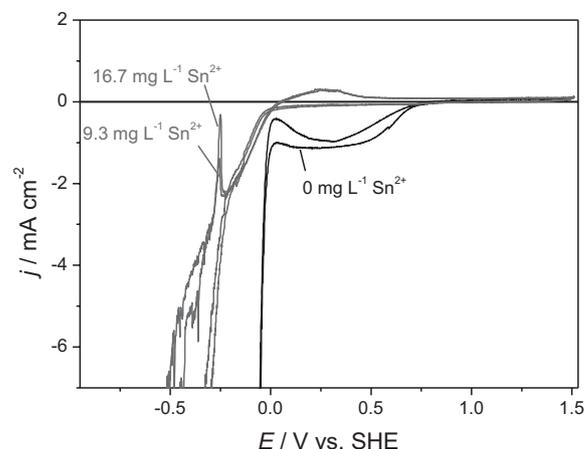


Figure 2. Cyclic voltammetry on a Pt-RDE in a Na_2SO_4 electrolyte at pH 1.55 with addition of Sn^{2+}

evolution in the *upd* region is not in disagreement with these findings.

CVs in the p.A.- Na_2SO_4 -electrolyte show similar effects as the CVs in zinc electrolytes (Fig. 2). With addition of a small amount of Sn^{2+} hydrogen-evolution is suppressed to some extent although the effect is not as dominant as in the p.A.-Zn-electrolyte. Tafel-plots show, that the dependency of the current on the potential decreases from a factor of 16 to 6.5 after addition of Sn^{2+} . This means α , the charge transfer coefficient, is changing due to Sn^{2+} addition. This could be explained by the deposition of tin and therefore a change in surface activity. Looking at the anodic sweep the dissolution of tin is observed again and confirms this assumption.

3.2 Influence of Sn^{2+} on the current efficiency

Addition of Sn^{2+} leads to a decrease in current efficiency for the zinc deposition. Two aspects have to be considered here. The hydrogen evolution as a result of the tin inclusion in the zinc layer is probably negligible since both elements have quite similar overpotentials for the hydrogen evolution. However, a synergistic effect that causes some lowering of the overpotential cannot be excluded. In this case hydrogen evolution as a side reaction could take place at a higher rate.

The second aspect is a possible dissolution of zinc during pauses. The investigated process for electroplating is, as usual in the industry, a pulse plating process with times where no potential is applied. Figure 3 shows the dissolution of zinc-layers in ZnSO_4 -electrolyte deposited with an electrolyte containing Sn^{2+} compared to deposits from electrolytes without Sn^{2+} .

It can be seen that the pure Zn-layers deposited from the p.A.-Zn-electrolyte dissolve more slowly than the layers deposited from industrial electrolytes. The dissolution rate of the layers from a p.A.-Zn-electrolyte containing small amounts of tin is nearly the same than for layers from industrial electrolytes and about 1.3 times higher than the dissolution rate of the high purity zinc layers. Addition of Sn^{2+} to the industrial electrolyte leads to a two times higher dissolution rate of the deposited zinc layer compared to the industrial electrolyte.

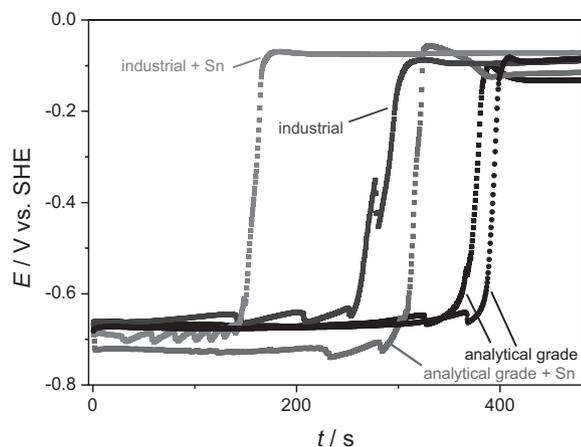


Figure 3. Dissolution transient in ZnSO_4 electrolyte of $7.5 \mu\text{m}$ thick zinc layers deposited from different electrolytes

Combining that information with the knowledge of the plating process shows that more zinc can be dissolved in the pauses where no potential is applied. This is most likely the reason for the decrease in current efficiency.

3.3 Influence of Sn^{2+} on the morphology of the zinc layer

SEM images of zinc deposited from the p.A.-Zn-electrolyte and the industrial electrolyte show zinc platelets with hexagonal shape. The hexagonal platelets of the industrial electrolyte are

smaller than the ones from the analytical grade electrolyte, indicating a higher nucleation tendency.

After addition of 5 mg/L Sn^{2+} a severe change of the layer morphology from platelets to nodular crystals with smooth crystal faces is found for both electrolytes (Fig. 4). The grain size increases in both electrolytes but the difference between industrial and p.A.-Zn-electrolyte survives.

Further increase of the concentration of Sn^{2+} in electrolyte shows no further changes in morphology. While this change in morphology is due to the codeposition with tin, in which tin may occupy prominent positions on the crystal surface it also has an influence on the current efficiency. This decrease in current efficiency with addition of Sn^{2+} may be a result of an increase in hydrogen evolution due to the increase in surface area for the smaller crystals. This effect might be more pronounced in comparison with the marginal difference in the overpotentials for the hydrogen evolution. The morphology could also lead to hydrogen evolution in which small bubbles are formed with a tendency to stick to the cathode surface.

3.4 Influence of Sn^{2+} on the roughness of the zinc layers

Due to the addition of small amounts of Sn^{2+} the roughness of the deposited zinc-layers increases instantly. Amounts of less than 1 mg/L lead to a dramatic increase in the Ra-value. Figure 5 shows the dependency of surface roughness of the Zn-layer on the Sn^{2+} concentration as a ΔRa -value. This value is defined as the difference between the surface roughness of the steel substrate

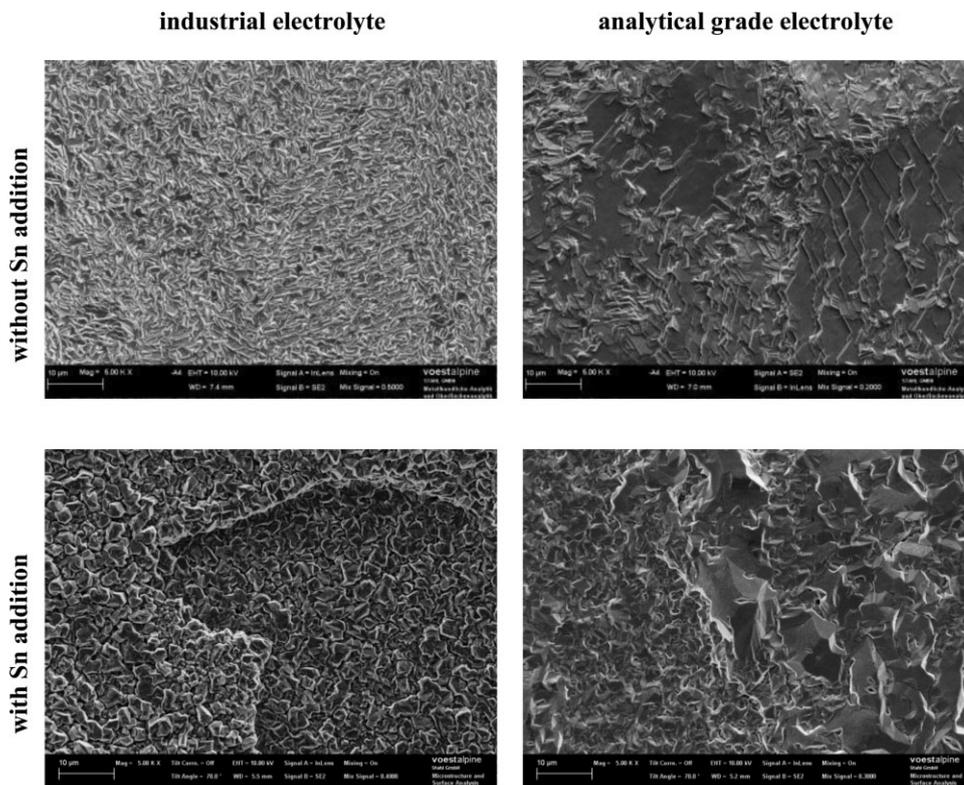


Figure 4. SEM images of zinc electrodeposited on cold rolled low carbon steel from an analytical grade electrolyte (right) or an industrial electrolyte (left) without and with addition of Sn^{2+}

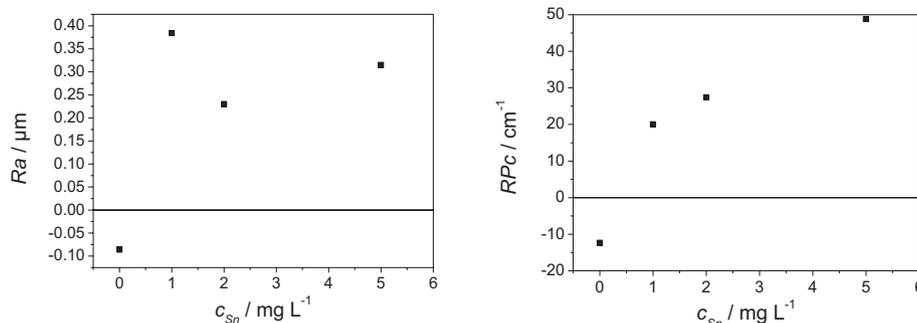


Figure 5. Influence of Sn^{2+} on the difference in roughness between the zinc layer and the steel substrate

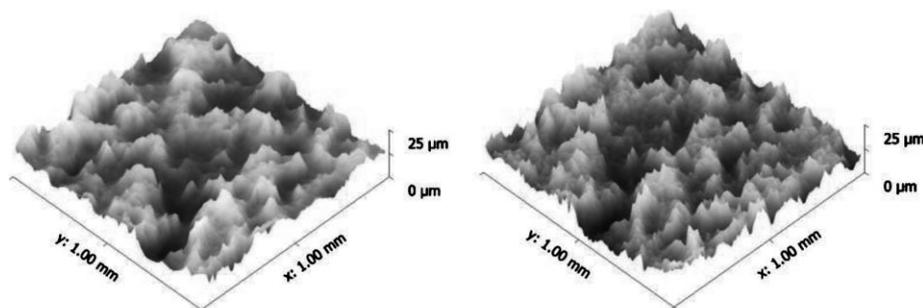


Figure 6. Topography of a steel sheet (left) and the corresponding zinc layer electrodeposited from an electrolyte containing 2 mg/L Sn^{2+} (right)

and the zinc layer on the same sample ($\Delta Ra = Ra_{\text{Zn}} - Ra_{\text{Steel}}$). In the investigated concentration range no significant dependency of ΔRa -value on the Sn^{2+} concentration has been found. The differences in the ΔRa values are within the error of measurement of the roughness probe.

An increase in the ΔRPc -value and the same concentration dependence was also detected. This can be explained by the morphology of the zinc layer from electrolytes with Sn^{2+} addition and their nodular grown crystals. Figure 6 shows the change of surface topography due to electroplating of zinc with electrolytes containing Sn^{2+} additions.

4 Conclusions

It has been shown that Sn^{2+} as impurity in the electrogalvanizing process of zinc has a major influence on the properties of the deposited zinc layer:

- Sn is incorporated into the zinc layer by electrochemical co-deposition.
- It leads to a decrease in current efficiency due to an accelerated dissolution of the zinc layer and possibly also hydrogen evolution in the electrolyte by galvanic microelements.
- The morphology of the zinc layer changes from hexagonal platelets to nodular grown crystals.
- Sn leads to an increase in surface roughness of electrogalvanized steel sheets.

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5 References

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