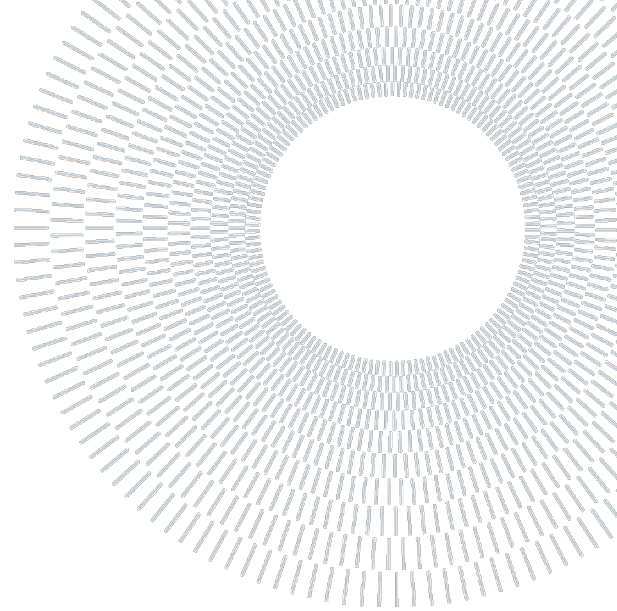




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EXECUTIVE SUMMARY OF THE THESIS

Electrodeposition of Zn-Cr alloy coatings for corrosion protection

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY

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ACADEMIC YEAR: 2022 - 2023

1. Introduction

Electrodeposited Zn-Cr alloy coatings have been researched as they could represent an improved alternative to pure zinc coatings. Pure zinc coatings are one of the most widespread treatments for corrosion protection, since they provide both sacrificial protection to steel substrate, being less noble than iron ($-0,76$ V SHE vs. $-0,44$ V SHE) [1], and barrier protection, as zinc has a corrosion rate that is 10-30 times lower than iron [2]. Chromium coatings, on the other hand, are also a popular finishing treatment for steel substrates, because they combine a high corrosion resistance with exceptional hardness and wear and abrasion resistance [1]. Unlike zinc coatings, which can be deposited through many other techniques such as hot-dip galvanizing [3] and sherardizing [4], chromium coatings are mainly electrodeposited from plating baths based either on hexavalent chromium or trivalent chromium, although trivalent chromium baths are now the standard electrolytes for such depositions due to the high toxicity of hexavalent chromium [1]. One of the main perks of electrodeposition is also its ability to allow for the deposition of alloys, which in turn

make for extremely useful coatings as they display heightened properties with respect to the parent metals [5]. Indeed, Zn-Cr alloy coatings have been reported to show increased corrosion resistance at lower thicknesses with respect to pure zinc coatings [6]. The properties of these deposits depend on their composition, which can vary as a consequence of both operational parameters and bath composition [6]: the corrosion resistance of such coatings has been reported to increase with increasing chromium contents, but the optimal value is considered to be 4-6 wt.%, above which deposits appear to be too powdery [7]. This study focuses on the effect that the bath composition, specifically factors such as Zn:Cr ratio, overall ionic concentration, pH and additives, and the operational parameters, namely the current density, have on the resulting deposits. After deciding on the final composition of the electrolyte and recovering several samples at different current densities, X-ray fluorescence spectroscopy (XRF) was employed to recover the composition and thickness of the coatings; X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) were used to further inspect the composition of the deposits and to rule out the presence of oxides, while Scanning electron microscopy (SEM) was employed to inspect the morphology of the

coatings. Tafel polarization curves were then used to analyze the corrosion behavior of deposits containing different chromium contents. Cyclic voltammeteries were performed to study the electrochemical behavior of the plating bath in terms of reactions and reduction potentials. Due to an encountered instability of the plating bath, most likely due to trivalent chromium, as reported in literature [8], UV-vis spectra for several trivalent chromium plating baths were recovered.

2. Experimental

2.1. Materials and methods

The final Zn-Cr alloy coatings were electrodeposited from an electrolyte with the following formulation:

| Compound | Molarity |
|---------------------------------------|----------|
| ZnSO ₄ · 7H ₂ O | 0,2 M |
| Trisurfin | 0,1 M |
| Na ₂ SO ₄ | 1 M |

Table 1: Formulation of final electrolyte.

Trisurfin is a commercial chemical containing 67% chromium(III) sulfate, 25,8% sodium sulfate, and moisture: the electrolyte thus contained 0,067 M Cr₂(SO₄)₃, resulting in a 3:1 ratio between zinc sulfate and chromium (III) sulfate. The deposition employed titanium meshes coated with ruthenium and iridium oxides (Ti-MMO) as inert anodes, and carbon steel S235 substrates with an exposed area of 1,5 cm × 1,5 cm. Substrates were sanded with 240 grit and 400 grit sandpaper, rinsed and placed in ethanol in an ultrasonic sonicator for 10 minutes; substrates were then degreased with acetone, etched in 10 wt.% HCl, rinsed with deionized water and dried with nitrogen gas. After the deposition, substrates were rinsed and dried with nitrogen gas. The plating bath was maintained at 25°C and pH 2; agitation of 250 rpm was provided via magnetic stirrer. Several sets of samples were obtained; each set contained five samples deposited at respectively:

- 60 mA/cm² for 5 minutes
- 90 mA/cm² for 3 minutes and 20 seconds
- 120 mA/cm² for 2 minutes and 30 seconds
- 150 mA/cm² for 2 minutes
- 180 mA/cm² for 1 minute and 40 seconds

The electroplating bath was heated at 80°C for 1 hour and cooled down to the operating temperature of 25°C, to at least ensure the complete dissolution of all reagents.

Since the formulation of the electrolyte was obtained through trial and error, it allowed to study the effects of several variations.

2.2. pH variations

Several electrolytes with pH values varying from 2 and 4 with 0,5 increments were allowed to rest for three days, after which their pH had significantly dropped, signaling their instability. Solutions at pH 4 were particularly unstable since trying to increase the pH back to 4 caused clouding and precipitation; the Pourbaix diagram for Zn-Cr systems does indicate the presence of chromium as a hydroxides for pH values higher than 4 (fig. 1). Depositions were performed from solutions with different pH values: lower pH levels lead to higher amounts of chromium in the coatings (fig.2). The final plating bath was therefore maintained at a pH of 2, which was coherent with the sources [7].

2.3. Zn:Cr ratio

Depositions were performed from solutions containing different Zn:Cr ratios; all trials confirmed the general trend according to which higher ratios lead to higher amounts of chromium but to lower thicknesses (fig.3). Coatings obtained from both chloride-based electrolyte and sulfate-based electrolytes lead to the same conclusions.

To balance the two different trends, the final electrolyte contained 0,2 M ZnSO₄ · 7H₂O and 0,067 M Cr₂(SO₄)₃, meaning a 3:2 Zn:Cr ratio.

2.4. Ionic concentration

Despite higher Zn:Cr ratios leading to higher chromium amounts in the resulting coating, a higher overall ionic concentration was found to lead not only to lower chromium contents, but also to lower amounts of overall deposited mass. Concentrated solutions were found to lead to much thinner deposits compared to those obtained from diluted solutions at the same current densities (fig. 4). This phenomenon is likely related to the deposition mechanism of the alloy and the limiting current densities of the ionic species. According to the Zn-Cr Pourbaix diagram (fig.1), at pH 2, when the substrate is cathodically polarized, the following reactions occur in order:

- Hydrogen evolution

- Reduction of Cr^{3+} to Cr^{2+}
- Reduction of Zn^{2+} to metallic zinc
- Reduction of Cr^{2+} to metallic chromium.

When the substrate is cathodically polarized up to a given potential, the corresponding current density depends on several factors, such as the concentration. This is due to the fact that, according to the Butler-Volmer equation, at high overpotentials the deposition is limited by the diffusion of the metallic species in the bath. When the limiting current density is reached, it does not increase even at higher overpotentials. Therefore, it is very likely that concentrated solutions struggle to deposit thick coatings with high amounts of chromium because a higher ionic concentration yields a higher limiting current density for the reduction of Cr^{3+} to Cr^{2+} : in concentrated solutions, a higher current density is therefore needed to reach the same potential. To obtain coatings with the same composition, concentrated solutions require much higher current densities, which is a significant.

A more diluted formulation was thus chosen for the final electrolyte, which allowed to deposit coatings containing over 20 at.% chromium at much lower current density values, ranging from 60 to 180 mA/cm^2 against the 300-800 mA/cm^2 range more commonly found in literature [9].

2.5. Types of anions

Sulfates and chlorides are usually the most common choices for Zn-Cr electrolytes. Samples obtained from a chloride-based electrolyte containing 0,2 M $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, 0,067 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 2 M KCl at, respectively, 50 and 100 mA/cm^2 , were confronted with the samples obtained from the final sulfate-based solution, which have a similar ionic concentration and Zn:Cr ratio and were deposited at similar current density values, namely 60, 90 and 120 mA/cm^2 . XRD spectra (fig.5) allowed to point out that chloride-based plating baths lead to the deposition of oxides, as opposed to the deposition of metallic zinc and chromium that is obtained from sulfate-based baths. The presence of oxides may be the reason why coatings with chromium contents exceeding 1-2% chloride-based electrolytes appear pitch black or iridescent, while deposits from sulfate-based electrolytes appeared, at most, to be a dull, dark grey.

2.6. Current density

While the necessary current density to achieve a certain cathodic polarization varies based on the bath concentration, once the concentration has been fixed, it is possible to state that higher current densities lead to overall higher chromium contents in the deposits; however, higher current densities also lead to higher amounts of evolved oxygen gas at the cathode, which decreases the quality of the coatings, and they also lead to dendritic growth, resulting in a very porous or even powdery deposit. Hull cell samples are generally quite useful as they allow to display how the deposit changes as a function of the current density both in terms of composition and appearance. Hull cell samples were used, for example, to test the effect of different current densities for electrolytes with different Zn:Cr ratios (fig.6). However, Hull cell samples can sometimes be too rough of an approximation to quantitatively establish the relationship between the current density and the composition of the deposits, especially if the variation is steep and the Hull cell samples are small. As a matter of fact, the Tenori Hull cell from Yamamoto-MS that was used in this dissertation was only fit to contain 33 mL of electrolyte and, when the composition variation was sudden, it proved to be more useful to perform single depositions with small progressive current density step increases (fig.7).

2.7. Tested additives and complexing agents

It was unclear why boric acid seemed to be such a popular buffering agent in literature, since its buffering ability is shown at much higher pH values [7, 10]. Nevertheless, its effect was tested and did not prove to have any buffering ability when the solutions were left to rest (table 2) nor during prolonged 10-minute depositions during which the pH was periodically measured. Boric acid was therefore discarded. Succinic acid was also tested and discarded as it led to similar results. Glycine, on the other hand, initially seemed to work really well as a buffering agent (fig.8); however, it led to confusing results. While the initial 10-minute deposition was performed right after the addition and dissolution of glycine, other trials, with different amounts of glycine, were conducted after the solution had been heated at 80°C for 1 hour [11] and cooled down to the working temperature of 25°C. Regardless of the

concentration, all solutions proved to have a much lower buffering ability with respect to the first trial (fig. 9). It is therefore theorized that glycine only works as a buffering agent when it is not acting as a complexing agent for trivalent chromium, since heating the solution is supposed to accelerate the complexation reaction. Moreover, solutions containing glycine that had been heated showed a decrease in chromium content (fig. 10), which proved the complexing behavior of glycine, since complexing agents tend to decrease the reduction potential of the involved species. Cyclic voltammeteries performed on trivalent chromium electrolytes and zinc electrolytes, each with and without glycine, not only showed that glycine hinders the deposition of chromium (fig. 11), but also facilitates the deposition of zinc, since it increases its reduction potential (fig. 12). Ultimately, glycine was excluded from the final formulation of the electrolyte, as it did not favor the codeposition of the alloy nor did it display any buffering effect.

Moreover, glycine-containing electrolytes proved to be rather instable and to lead to inconsistent, sometimes non-reproducible results. Even heated electrolytes which had rested for different amounts of time appeared to behave differently and lead to different deposits; sometimes, even if the solutions had been prepared the very same way, they appeared to lead to different results, be it in terms of composition or in terms of appearance of the coating.

Finally, the effects of PEG 3000 were tested, as it seemed to lead to good results according to the literature [12]; however, this addition actually lead to very poor results, especially in terms of appearance.

3. Results and discussion

Three sets of samples were deposited; the results were generally reproducible. Coatings obtained at lower current densities appeared dull and light gray; deposits with higher amounts of chromium became darker, visibly more dendritic, more porous and brittle, and manifested a lower adhesion to the substrate. The use of an ultrasonic sonicator greatly helped in improving the adhesion. The deposits appear relatively homogeneous with an average thickness ranging from 3,5 to 4,5 μm (table 2). Chromium content

varies relatively smoothly with the current density (fig. 13).

The average efficiency was evaluated considering the deposited mass of each coating, their composition, and the total charge density Q , with reported values of:

- 78% at 60 mA/cm² (DS = 2,3452)
- 82% at 90 mA/cm² (DS = 5,5416)
- 96% at 120 mA/cm² (DS = 26,6658)
- 84% at 150 mA/cm² (DS = 21,1215)
- 81% at 180 mA/cm² (DS = 15,2329)

XRD and EDS analyses proved samples to only contain metallic zinc and metallic chromium (fig.14).

Samples also underwent SEM imaging, which shows an increasingly more dendritic morphology for higher current density values (fig. 15 – 19).

Tafel polarization curves (fig. 20) were recovered to assess the corrosion resistance of the alloy; tests were performed in 0,1 M Na₂SO₄, using an Ag/AgCl reference electrode and a platinum mesh as a counter electrode. The curves show that the that coated samples exhibit a lower corrosion potential than the substrate, which is to be expected due to the sacrificial nature of the coating. Increasing amounts of chromium tend to make the coatings nobler than pure zinc, as their corrosion potential increases, while still preserving their sacrificial barrier function. The second set of anodic peaks at higher potentials is associated with the dissolution of the zinc coating; coatings with higher amounts of chromium display a significantly less pronounced dissolution peak, likely related to the beneficial effect of chromium. Cyclic voltammeteries performed on the Zn-Cr electrolyte and on a pure zinc electrolyte (fig. 21) confirm the beneficial effect of chromium, which strongly hinders the dissolution of the coating.

However, the Tafel polarization curves also show that the coatings still behave as active metal, meaning that the presence of chromium is not high enough to promote its passivation.

3.1. Issues and instability of the electrolyte

Despite the decent results, there are many still-standing issues in the electrodeposition of Zn-Cr alloys: besides the need of additives to improve the morphology of the coating and limit the issues associated with the dendritic growth of most deposits, the main problem with these plating baths is their stability. It is clear that some unknown reactions must be taking place in the

bath and affecting its electrochemical behavior. This unpredictable behavior is likely due to the presence of trivalent chromium, which can undergo a large number of possible reactions, like hydrolysis, olation, oxolation and polymerization [1]. There is also a serious lack of general knowledge regarding their electrochemical behavior [1]. The composition of the samples seems to vary based on the time at which the depositions take place; samples deposited on the same day of the preparation of the solution had a much higher chromium content with respect to those deposited 6-26 days later, which were mostly reproducible (fig. 22). This discrepancy is likely due to the instability and unknown reactions occurring in the solution.

UV-vis spectra (fig. 23) were acquired to highlight possible changes in trivalent chromium electrolytes. The passage of time caused a significant difference both for heated solutions and for non-heated solutions, signaling that the electrolyte undergoes some changes during time. Nevertheless, it remains unclear whether temperature and time lead to the same changes in solution.

4. Figures and tables

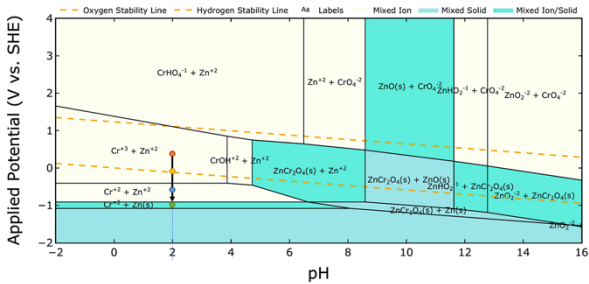


Fig. 1. Pourbaix diagram for the Zn-Cr system

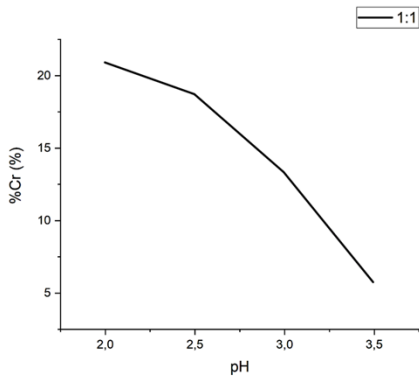


Fig. 2. Dependence of the content of chromium in the deposits on the pH of the electroplating bath

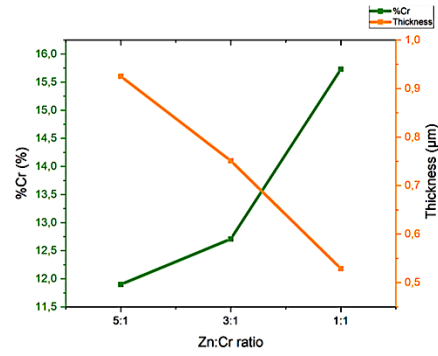


Fig. 3. Dependence of the content of chromium in the deposit (green) and the thickness of the deposit (orange) on the Zn:Cr ratio

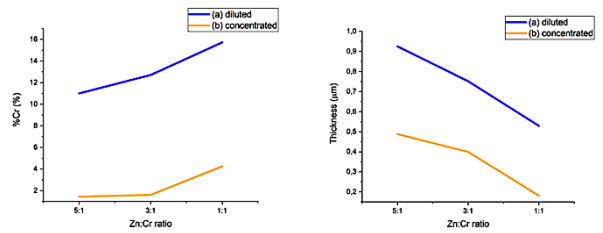


Fig. 4. Dependence of the content of chromium and the thickness of deposits obtained from diluted (blue) and concentrated (yellow) electrolytes

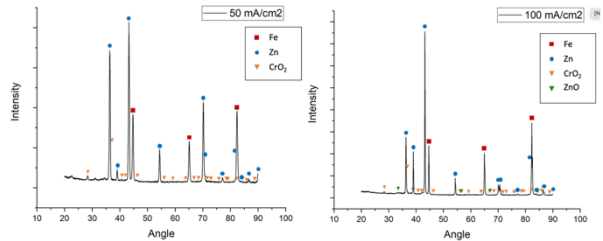


Fig. 5. XRD spectra of samples from chloride-based baths

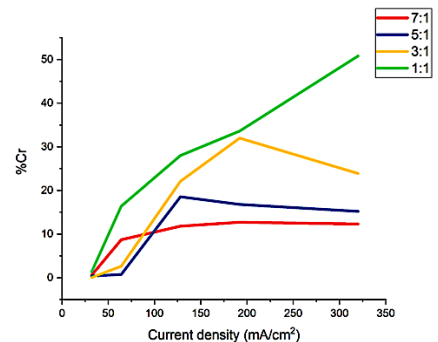


Fig. 6. Chromium content varying with the current density for different ZnSO₄:Cr₂(SO₄)₃ ratios, as retrieved from Hull cell samples

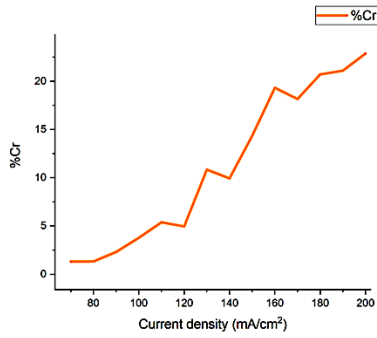


Fig. 7. Chromium content varying with the current density for the 3:1 ZnSO₄: Cr₂(SO₄)₃ electrolyte, as retrieved from 14 single-deposition samples

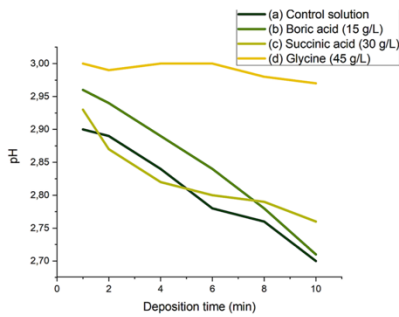


Fig. 8. Comparison of the buffering ability of (a) a control solution, (b) boric acid, (c) succinic acid and (d) glycine during a 10-minute long electrodeposition

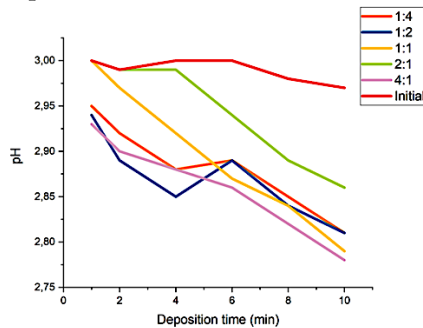


Fig. 9. Comparison of buffering ability of glycine when the solution has been heated vs. when it has not been heated (red line)

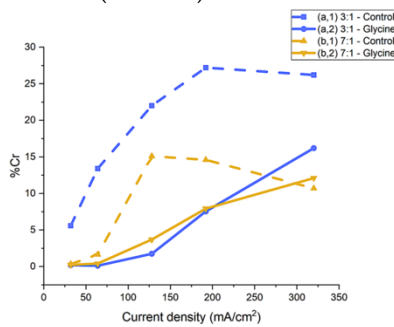


Fig. 10. Comparison of the chromium content of deposits obtained from electrolytes without (1) and with (2) glycine, for 3:1 (a) and 7:1 (b) zinc sulfate to chromium sulfate ratios

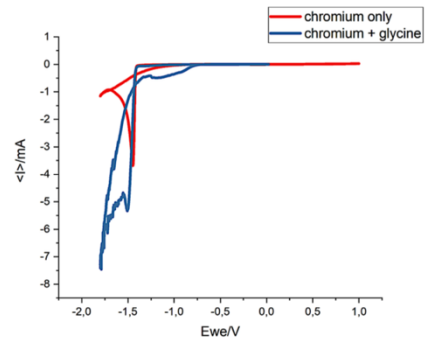


Fig. 11. Cyclic voltammeteries for chromium electrolytes without (red) and with (blue) glycine

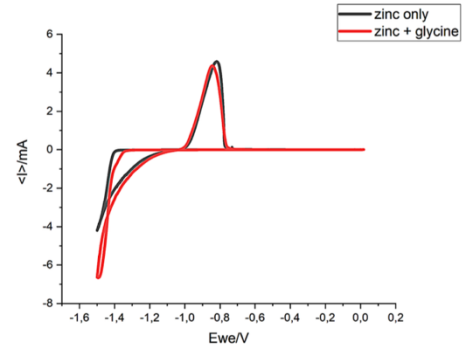


Fig. 12. Cyclic voltammeteries for zinc electrolytes without (blue) and with (red) glycine

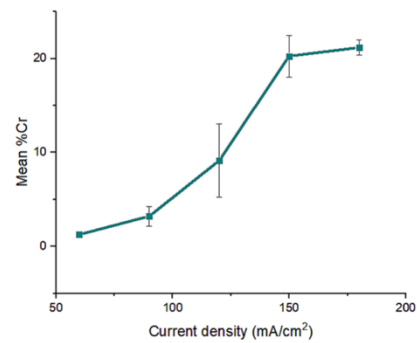
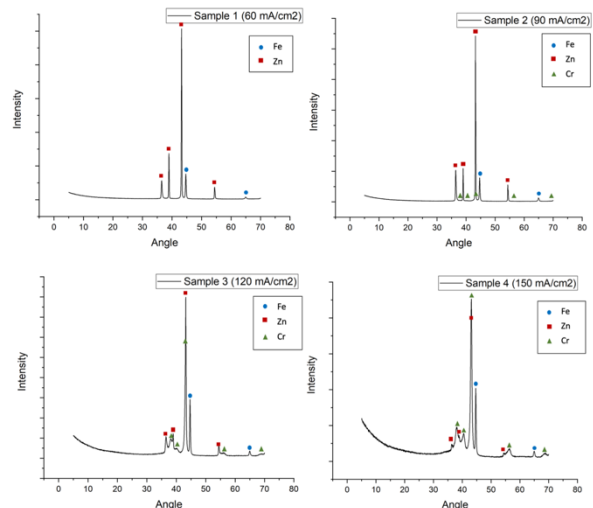


Fig. 13. Variation of chromium content with the current densities for different sets of samples



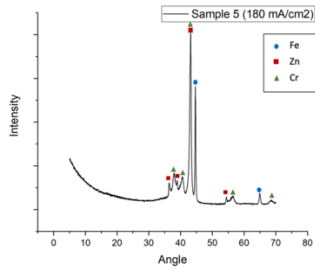


Fig. 14. XRD spectra for the first set of samples

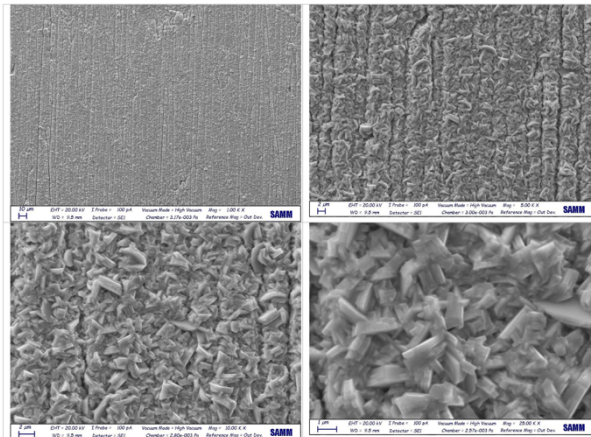


Fig. 15. SEM images for sample at 60 mA/cm²

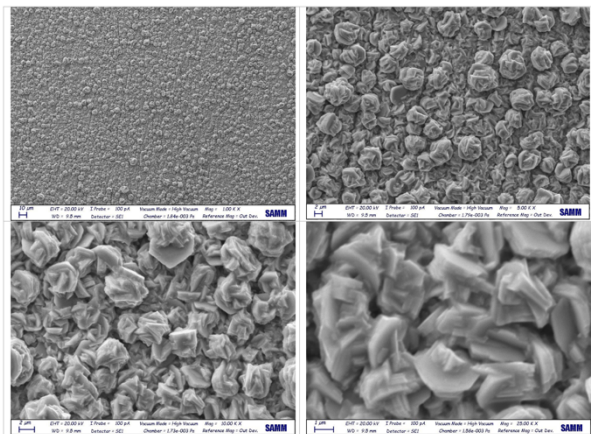


Fig. 16. SEM images for sample at 90 mA/cm²

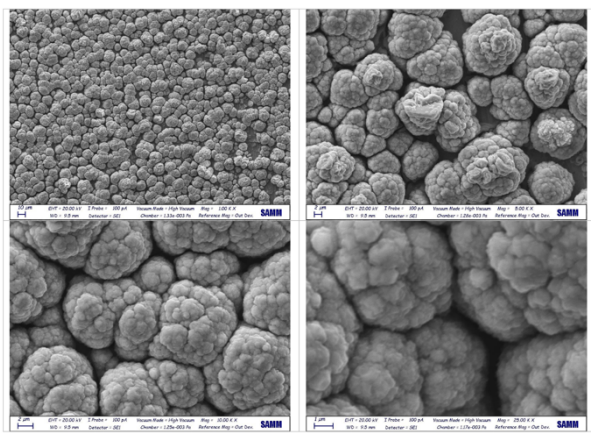


Fig. 17. SEM images for sample at 120 mA/cm²

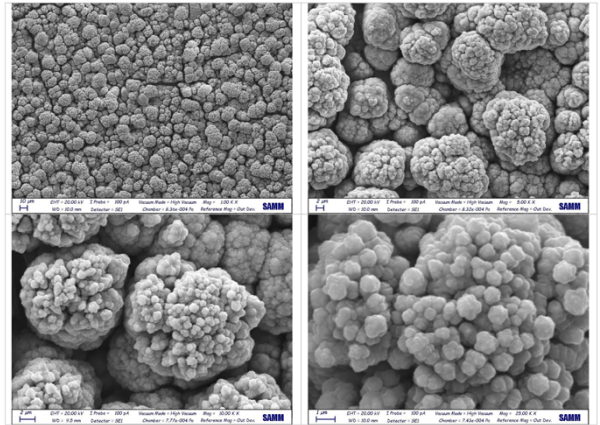


Fig. 18. SEM images for sample at 150 mA/cm²

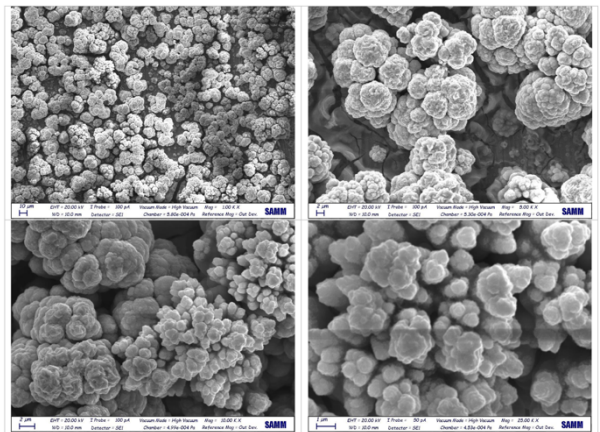


Fig. 19. SEM images for sample at 180 mA/cm²

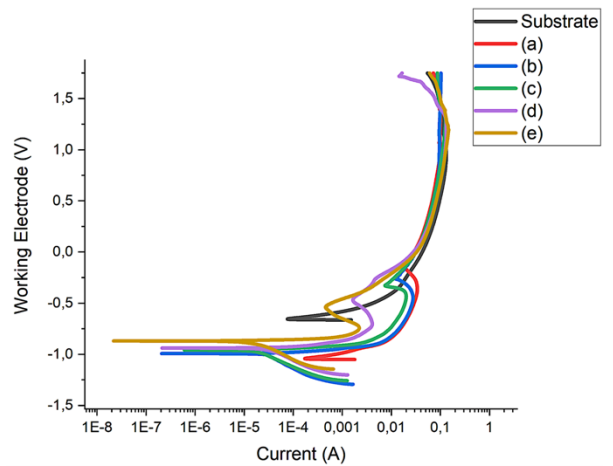


Fig. 20. Tafel polarization curves for each sample, (a-e) for increasing chromium content and current density

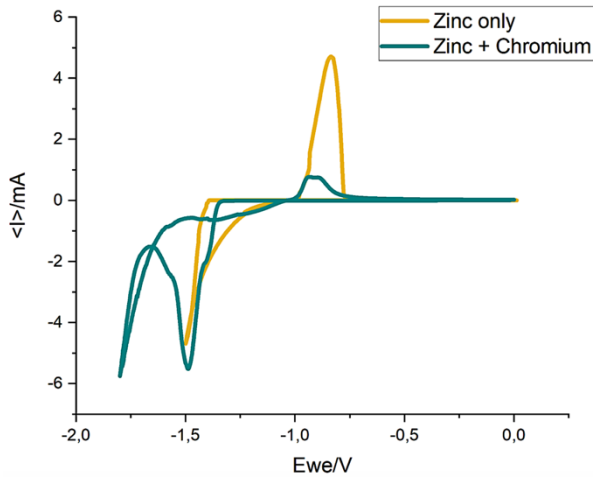


Fig. 21. Cyclic voltammeteries of Zn-Cr electrolyte (blue) and pure zinc electrolyte (yellow)

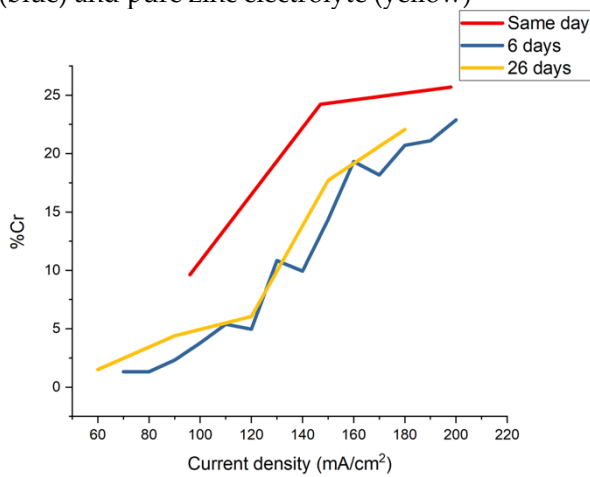


Fig. 22. Chromium contents of deposits obtained at different points in time

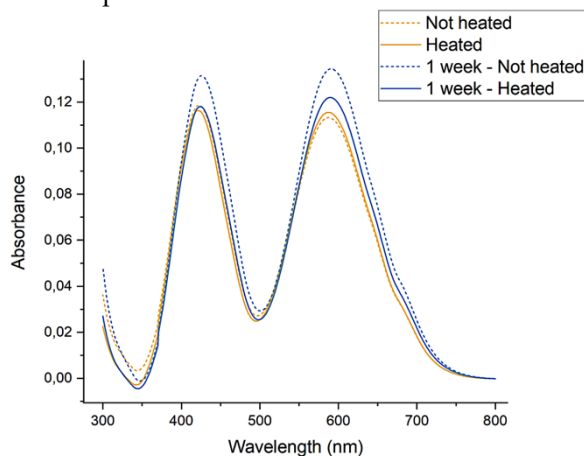


Fig. 23. UV-vis spectra of trivalent chromium electrolytes: comparison between heated (dashed line) and non-heated (solid line) solutions and between ready-made (yellow) and aged (blue) solutions

| Compound | Molarity |
|---------------------------------------|----------|
| ZnSO ₄ · 7H ₂ O | 0,2 M |

| | |
|---------------------------------|-------|
| Trisurfin | 0,1 M |
| Na ₂ SO ₄ | 1 M |

Table 2: Formulation of final electrolyte.

| pH/Zn:Cr | 4 | 3,5 | 3 | 2,5 | 2 |
|----------|------|------|------|------|------|
| 5:1 | 2,75 | 2,70 | 2,60 | 2,39 | 1,82 |
| 3:1 | / | 2,80 | 2,51 | 2,35 | 1,77 |
| 1:1 | 2,26 | 2,36 | 2,19 | 2,13 | 1,86 |

Table 2: Variation of the pH despite the use of boric acid

5. Conclusions

Overall, the Zn-Cr alloy coatings that were deposited did prove to offer a higher corrosion protection with respect to pure zinc: Tafel polarization curves and the cyclic voltammeteries display how higher chromium contents result in a progressively hindered dissolution and heightened corrosion resistance. However, the presence of chromium is not sufficient to passivate the deposit, and all samples still behave as active metals, and the coatings still retain their sacrificial nature. Deposits containing the highest amounts of chromium, however, also exhibit a highly dendritic morphology, and are therefore porous and rather brittle; testing more additives to facilitate the codeposition of the alloy is thus fundamental. Testing their physical properties, such as hardness and adherence-related properties, is also an important step to perform to fully characterize the coatings.

Moreover, the more modest ionic concentration of the electrolyte allowed to deposit coatings containing a considerable amount of chromium at much lower current densities than the average values found in literature. The instability of the electrolyte was the main true limitation for these depositions, which is especially challenging due to the lack of intrinsic knowledge regarding the changes that the plating bath undergoes.

6. References

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