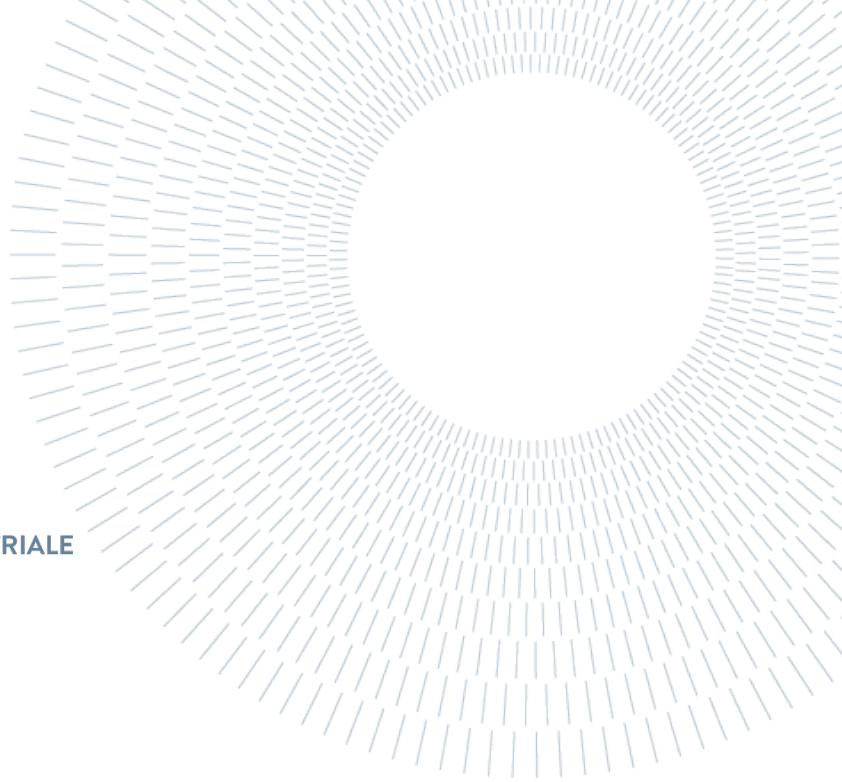




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Electrodeposition of Zn-Cr alloy coatings for corrosion protection

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ABSTRACT

This dissertation focuses on the electrodeposition process of zinc-chromium alloy coatings and investigates the electrochemical properties of the plating bath and the composition, appearance and corrosion resistance of the resulting coatings. The state of the art offers a broad overview of electroplating as a whole and of the electrodeposition of alloys, and later focuses on the electrodeposition of zinc coatings and chromium coatings. Zinc coatings are a staple finishing treatment for carbon steel components, acting as sacrificial barriers to increase the corrosion protection of the substrate while also increasing its lifetime due to their slower corrosion rate; after describing various deposition techniques, the advantages and the specifics of zinc electroplating are highlighted. The discussion then focuses on electroplated chromium coatings, which are able to provide a high corrosion resistance while also being exceptionally hard, wear resistant and abrasion resistant: the distinction between the early plating baths based on toxic hexavalent chromium and the more modern trivalent chromium electrolytes is explored. Zinc-chromium alloy coatings are finally discussed: literature highlights their higher corrosion resistance with respect to pure zinc at lower thicknesses and suggests applications in the automotive field. In the experimental portion of this dissertation, several plating baths are produced to test the effects of several variables on the resulting coatings: the consequences of changes in parameters such as pH, anions, bath concentration, Zn:Cr ratio and current density are discussed. Buffers and complexing agents such as boric acid and glycine are tested, but are ultimately deemed unsuitable. Several analyses are carried out on final samples: SEM images show progressive dendritic growth, XRD and EDS rule out the presence of oxides and XRF is employed to establish the composition and thickness of the coatings; Tafel polarization tests show increasing corrosion resistance for higher chromium contents. Final considerations highlight underlying problems in the electrolyte relating to its stability.

ABSTRACT ITALIANO

Questo progetto di tesi riguarda l'elettrodeposizione di rivestimenti di leghe zinco-cromo e studia le proprietà elettrochimiche dell'elettrolita e la composizione, l'aspetto e la resistenza a corrosione dei relativi rivestimenti. Lo stato dell'arte offre un quadro generale riguardo le basi dell'elettrodeposizione e riguardo l'elettrodeposizione di leghe, e successivamente si concentra sui rivestimenti rispettivamente di zinco e di cromo. I rivestimenti di zinco sono uno dei trattamenti principali per manufatti in acciaio al carbonio, dato che aumentano la resistenza a corrosione del substrato come rivestimenti sacrificali e di barriera, grazie anche alla loro più modesta velocità di corrosione; dopo aver descritto varie tecniche di deposizione, si evidenziano i vantaggi e i dettagli della loro elettrodeposizione. La discussione si sposta poi sull'elettrodeposizione di cromo, i cui rivestimenti conferiscono un'alta resistenza a corrosione insieme ad un'eccellente durezza e resistenza all'usura e all'abrasione: si esplora dunque la differenza tra i primi elettroliti a base di cromo esavalente, composto altamente tossico, e i più moderni elettroliti a base di cromo trivalente. Infine, la discussione tratta di rivestimenti di leghe zinco-cromo: la letteratura evidenzia la loro maggiore resistenza a corrosione a spessori minori rispetto allo zinco puro e suggerisce l'applicazione nell'ambito dell'automotive. Durante la parte sperimentale, vengono prodotti numerosi elettroliti per testare gli effetti di diverse variabili sui relativi rivestimenti: si discutono gli effetti di cambi in parametri quali il pH, gli anioni di base, la concentrazione del bagno, il rapporto Zn:Cr e la densità di corrente. Vengono testati buffer e complessanti come l'acido borico e la glicina, che vengono infine esclusi in quanto non idonei. I rivestimenti finali vengono sottoposti a numerose analisi: immagini al SEM mostrano una progressiva crescita dendritica, XRD e EDS escludono la presenza di ossidi e l'XRF viene utilizzato per stabilire composizione e spessore dei rivestimenti; le curve di polarizzazione potenziodinamiche mostrano infine un aumento della resistenza a corrosione per maggiori percentuali di cromo. Le considerazioni finali evidenziano problemi persistenti nell'elettrolita relativi alla sua stabilità.

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INTRODUCTION

Electrodeposition is a very valuable surface treatment that allows to easily deposit micrometric metallic coatings on top of conductive surfaces, thus improving the aesthetic characteristics and modifying and enhancing the properties of the underlying substrate, in order to better protect it against the environment and increase its lifespan.

The vast popularity of this technique speaks volumes about its advantages. First off, its rather simple setup makes it extremely cost effective compared to other treatments. It only consists of an electrochemical cell with a two-electrode configuration: the electrodes are externally connected to a power generator, and they are placed in a tank containing the electrolyte. Such setup, especially at the industrial scale, may vary and slightly increase in complexity, with its size being the most obvious variable. The number and the distribution of the anodes can also be altered in order to optimize the uniformity of the coating on the substrate, and another commonly employed component is a source of electrolyte agitation, which further contributes to the conformality of the deposit. All things considered, the main cost that has to be factored in is related to the electric current that is employed, which can be considerable in the case of large-scale industrial processes as what remains constant is the current density, not the current itself.

The other very important perk of this type of deposition is the possibility it grants to also deposit alloys and even composite coatings. The deposition of alloy coatings is often desirable as they can display better and enhanced properties with respect to the parent metals, which further increases those of the substrate. Electrodeposition is a very valid option for the deposition of alloys which can sometimes be hard to obtain with other, more traditional, treatments, such as thermal techniques in the case of two metals with very different melting points. This deposition process allows to deposit a wide range of alloys, and it can, in most cases, grant a precise control in terms of the relative amount of the metallic species, as it is strictly related to the applied voltage: this feature is very important since having a very precise composition is sometimes critical in order to maximize the desired property of a given coating, as in the case of Zn-Ni alloys which provide the best corrosion resistance when they contain 14% Ni. In terms of composition control, the few exceptions are related to thermodynamic issues where the deposition potentials of the two elements are too far apart, or

separated by hydrogen evolution; however, additives can usually be employed to, at least partially, fix this type of issue.

Besides these key features, there are several other reasons why electrodeposition is considered to be more advantageous compared to other deposition techniques. Considering, for example, the case of hot dipping, going the electrochemical route enables to deposit a much more uniform coating while simultaneously avoiding any thermal modifications of the underlying substrate that may alter or compromise its original mechanical properties. Moreover, the wide variety of additives that can be included in the formulation of the electrolyte, from brighteners to leveling agents, allows to significantly improve and control the properties of the final coating.

One of the only real limitations of electrodeposition is related to the geometry of the substrate, which should not be excessively complex. In fact, while employing multiple strategically positioned anodes and appropriately stirring the electrolyte undoubtedly help increasing the conformality of the deposit, this treatment is still heavily reliant on the direction of the applied current lines, and a substrate with too complex of a shape may not be the ideal candidate. Finally, due to the very nature of the process, electrodeposition is limited to conductive substrates only, although with an appropriate pretreatment it is possible to also coat polymeric materials and silicon wafers.

Nevertheless, electrodeposition is still widely considered to be the most convenient and efficient way to obtain a metallic coating on a metallic component, making it a pillar in terms of surface engineering processes. Although this status means there already are many electrodeposited coatings that are considered standard, consolidated procedures for either corrosion protection, wear resistance, and other purposes, there is always room for improvement, and research has not stopped: the electrodeposition of zinc-chromium alloy coatings, the focus of this dissertation, is a rising topic of interest in terms of electrochemical applications, as studies have shown that the mix of these two metals, both staple treatments by themselves, can cause a significant increase in corrosion protection.

1 FUNDAMENTALS OF ELECTRODEPOSITION

As the name suggests, the nature of this surface treatment is electrochemical, meaning that it is based on redox reactions occurring at a given interface: the reduction reaction occurring at the cathode, which in this case is also the substrate, is what effectively allows to obtain a coating.

1.1. Main reactions

Redox reactions are the fundamental staple of electrochemistry: these reactions, reduction and oxidation, which are always paired and occurring together, involve a variation in the oxidation state of the chemical species at hand, and, in order for this to occur, electrons are exchanged. Reduction, occurring on the cathodic area, entails a decrease in the oxidation number of the involved species and consumes electrons, whereas oxidation, occurring on the anodic area, causes an increase in the oxidation number and releases electrons. In the case of electrodeposition, these reactions are not spontaneous: the necessary driving force for any reaction to take place is supplied by the means of an external power supply, which allows the circulation of the electrons involved in the redox processes.

However, unlike traditional redox reactions such as metal corrosion, in order for a coating to be effectively electrodeposited the reduction and the oxidation must occur on two separate conductive surfaces: the designed substrate is the cathode, and the other electrode, which may be either inert or sacrificial, is the anode.

Undoubtedly, the most relevant reaction taking place in the electrolyte is the metallic reduction occurring on the cathodic surface, which relies on the presence of metallic cations in the electrolytic bath. When an external bias is applied, the cations in the solution migrate towards the cathode, as do the electrons in the external circuit: the cathode thus becomes the interface at which the recombination of the ions and the electrons takes place, hence reducing the metallic cations into solid metal, which is deposited on the surface of the electrode. This entails that the coating is originated from the metallic species that were present in the electrolytic bath. Longer application times and higher current densities will generally result in thicker metallic coatings.

As stated, there can be no reduction without a balancing oxidation: while the metallic coating is being deposited on top of the cathodic surface, other chemical species are oxidized at the anodic interface. Depending on the nature of the anode, the two most common oxidation reactions are either oxygen evolution for inert anodes or metal dissolution for sacrificial anodes.

Reduction at the cathode: $Me^{z+} + ze^{-} \rightarrow Me(s)$

Oxidation at the anode: $2H_2O \rightarrow O_2 + 4e^{-} + 4H^{+}$ (inert anode)

$Me(s) \rightarrow Me^{z+} + ze^{-}$ (soluble anode)

It is important to note that unwanted side reactions can also take place alongside the reactions of interest, with hydrogen evolution being the most undesirable, albeit the most common. Like all side reactions, of course, it represents lost power: hydrogen is generated at the cathode through the reduction of protons or by the splitting of water, meaning that part of the electrons that are externally provided are wasted and cannot partake in the reduction of the metallic species, thus reducing the efficiency of the process. Moreover, since this reaction occurs at the cathode, other significant complications can arise, which can effectively damage the substrate and the coating. For example, since hydrogen is a gas, its evolution entails the creation of bubbles which can compromise the homogeneity of the coating that is being deposited, by either leaving strokes as the bubbles rise to the top or even forming craters; hydrogen evolution can also pose a threat to the integrity of the substrate, which can be affected by hydrogen embrittlement. Finally, as this reaction also consumes hydrogen ions, it causes the alkalization of the cathodic area: a higher pH can lead to undesired effects such as the precipitation of metal oxides rather than the deposition of a metallic coating, meaning that an efficient buffer is required [1 – 5].

1.2. The setup

As seen so far, the electrodes are clearly one of the key elements in the deposition process, and an external power supply providing the electric current is needed. Besides these components, in order to close the circuit two separate types of conductors are needed:

- An electric conductor, a wire connecting the electrodes externally which accounts for the passage of the electrons;
- An ionic conductor, the ion-containing solution in which the electrodes are immersed that allows the ions to flow from the anode to the cathode, or vice-versa, and has to display a series of given characteristics.

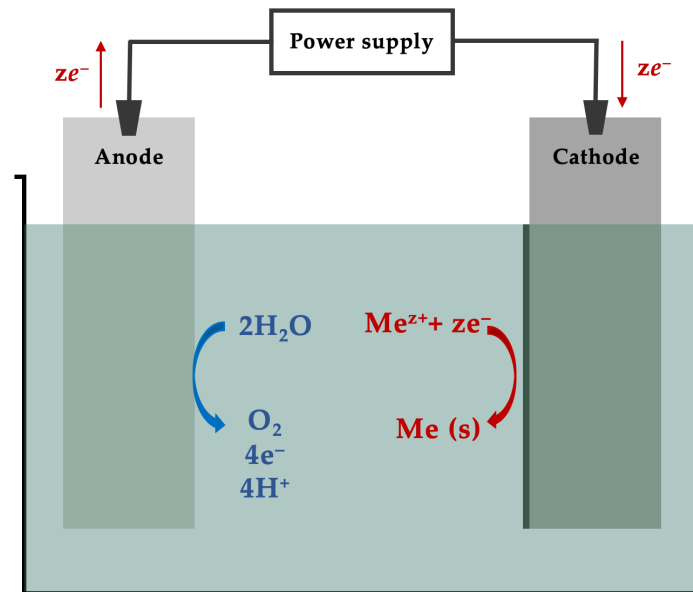


Fig. 1: Standard setup of a galvanic cell

As mentioned earlier, the main feature that can vary about this standard setup is the size: for a given deposition process, the employed electric current or voltage will have to be adjusted accordingly as the current density needs to remain constant. Besides that, the cell will likely also contain a source of agitation, which generally increases the conformality of the coating leading to a higher quality. This is related to the fact that, while the coating is being deposited, the metallic cations are being consumed at the cathodic surface, meaning that the ionic concentration at the interface is lower than the nominal concentration in the bulk; therefore, an external source of agitation is able to promote the replenishment of the ions from the bulk towards the substrate, making the process more efficient. The agitation of the bath can be achieved in several ways: for small scales applications and research purposes, it is common to use a magnetic stirrer; in other cases, to obtain an even higher degree of stirring, it is possible to use external pumps, gas bubbling or ultrasonic devices [1].

It is also possible to modify the setup by changing the characteristics of the anode: for example, an easy way to improve the conformality of the deposit on a cathode with more of a complex shape is to employ multiple anodes and place them strategically in the electrolytic bath in order to modify the direction of the field lines and optimize the deposition process. In a simpler case, the shape and size of the anode can also be modified to achieve the same purpose: for instance, it is possible to employ a curved electrode to better surround a cathode that would require more than just straight field lines to be properly coated. Finally, it is also necessary to make an important distinction between the types of anode that can be used:

- Sacrificial anodes are actively consumed during the deposition process. The zero-valent metal constituting the anode dissolves freeing metallic ions in the electrolyte and electrons in the external circuit. Sacrificial anodes made of the same metal that is being deposited are thus very useful in maintaining the concentration of the metallic species in the bath, contrasting their consumption due to the cathodic reaction. It is therefore very common for sacrificial anodes to be employed, especially at the industrial scale. This is obviously the easiest route to choose especially for single metal depositions with high cathodic efficiencies. Sacrificial anodes also represent a valuable option in the case of the deposition of alloy coatings, although it requires careful consideration as this represents a more complex scenario. Of course, it is possible to employ a single-metal soluble anode if the alloy contains only a very low percentage of a second metal; otherwise, it is necessary to use separate anodes of the two parent metals connected to two separate circuits and alternate their dissolution, each lasting a different amount of time, to maintain the desired bath composition, or to place them in the solution intermittently. Using a soluble anode made of the exact alloy that needs to be deposited is uncommon, as most alloys are heterogeneous and would not dissolve evenly [6].
- Insoluble anodes are inert, and are usually made of platinum or titanium coated with mixed oxides of ruthenium and iridium (Ti-MMO). Their main advantage is that they retain their shape and size and they do not need to be replaced as often as sacrificial anodes; however, they do not aid in maintaining the concentration of the metallic ions in the bath, which needs to be regenerated periodically. Additionally, they cause a gradual decrease in the pH of the electrolyte, because the oxygen evolution reaction produces hydrogen ions as a

byproduct. The presence of a good buffer in the electrolyte is therefore essential [6]. This dissertation will exclusively feature the use of insoluble anodes, as the modest volumes of electrolyte that are required for these small-scale depositions are easily replaceable.

1.3. The electrolyte

In electroplating, the electrolyte plays the most prominent role as it is the source of the metallic precursors and the vessel through which the ions flow towards their respective electrodes. A plating bath usually contains:

- The metallic ions of the species that is deposited during the process, which are usually introduced as salts;
- Other salts are added to the electrolyte in order to increase its ionic conductivity, which greatly impacts the deposition process as the ohmic losses associated to the resistivity of the electrolyte are a primary source of energy waste. However, it is necessary to factor in the solubility limit of the salt, because only the species that dissociate contribute to the increase in the conductivity of the bath. Moreover, higher concentrations also cause a slight viscosity increase in the electrolyte which is not beneficial to the mobility of the ions, and thus increases electrolyte losses due to drag out. These limits can be partly overcome by increasing the temperature, which increases the solubility of the species while simultaneously decreasing the viscosity of the bath [5].
- Buffering agents are often required in order to maintain a stable pH in the electrolyte, which is crucial as most metals can only be deposited in certain pH ranges, according to their Pourbaix diagram. It is common for the pH to vary locally at both electrodes: the oxidation reaction usually acidifies the area, as seen in the case of insoluble anodes, while the pH in cathodic area usually becomes more alkaline, especially when hydrogen evolution occurs as a side reaction. However, if these reactions do not balance each other, the local pH variation starts to spread to the bulk, which decreases the efficiency of the process: a higher pH can promote the deposition of metal hydroxides, while a lower pH can kickstart unwanted side reactions [5].

- Other additives can also be employed to target specific issues. Levelling agents can be used to improve the coating conformality on rough substrates, as they cause a preferential deposition in the valleys rather than on the asperities of the surface; brighteners can be added to improve the appearance of the coating; complexing agents are commonly added to stabilize the electrolyte by shifting the reduction potential of the metallic species [5].

The composition of the plating bath is therefore a key factor in electroplating: even small changes in the concentration of the species, their ratios, and their overall presence can greatly impact the final coating, both in terms of appearance and in terms of properties, morphology, and chemical composition. Water-based electrolytic solutions are the most widely employed type of bath since they are cheaper, more conductive and water can easily dissolve most salts and other additives. However, the main downside is the high chance of developing hydrogen and oxygen evolution as secondary reactions due to water reacting and participating in the reactions. It is therefore possible to opt for different ionic conductors, mainly molten salts: the resulting electrolyte has a very high conductivity and is a lot less likely to develop secondary reactions, but the required temperatures at which it is obtained and must be maintained are generally very high, making this option a lot less feasible [1]. Another valuable type of non-aqueous electrolyte is based on organic solvents, such as ethylene glycol. The main perk of an organic electrolyte is that the bath requires a much lower maintenance with respect to molten salts, while still preventing the side reactions related to water splitting that usually lower the efficiency of the process in aqueous electrolytes. Despite these advantages, it is necessary to point out that the solubility of the metallic species in organic electrolytes is considerably lower than in their aqueous counterparts, and that the higher viscosity of an organic medium results in ohmic losses and a much higher energy consumption, although this issue can be limited by heating up the solution [7].

2 ZINC-CHROMIUM ALLOY COATINGS

Alloy coatings are a very popular choice when it comes to protective layers for steel components: the combination of two different metals allows to combine their properties and provide very specific characteristics to the underlying substrate. Zinc-chromium alloys are not yet of commercial use as a surface treatment, as their electrochemical behavior and their properties as a coating are still under investigation. Nevertheless, when researching such a subject, it is clearly very important to have a broad overview of the electrochemistry and characteristics of the two main components of the alloy of interest.

2.1. Zinc coatings

Coating a steel substrate with zinc is a very widespread treatment that is often employed for corrosion protection: this procedure is so popular that zinc-coated steel has its own name, galvanized steel. Besides providing barrier protection, zinc coatings also provide sacrificial protection to the substrate, because zinc has a standard reduction potential that is lower than that of steel ($-0,76$ V SHE vs. $-0,44$ V SHE), meaning that this contact creates galvanic coupling [3, 8, 9, 10]. Therefore, when the steel component is exposed to a corrosive environment, the corrosion process preferentially affects the zinc coating, which is dissolved, while the steel substrate is unaffected as it is in cathodic protection conditions. As these coatings are easy to produce and also quite cheap, especially when compared to other treatments which may opt for nobler metals to provide corrosion resistance, they are such a popular option that they represent around half of the global consumption of zinc [3]. Moreover, although these coatings are corroded over time to protect the substrate, their corrosion rate is around 10-30 times lower than that of mild steel, granting the substrate an even longer service life [11]. This, however, does not mean that they can be employed universally in any environment. Since the protection they provide is sacrificial and dependent on their thickness, they should not be used in conditions where their corrosion rate would skyrocket, such as in very acidic conditions. Moreover, zinc coatings should not be employed in environments where the temperature exceeds 40-60°C: above this temperature range, a phenomenon called polarity reversal causes zinc

to become nobler than steel, meaning that the galvanic coupling would work against the substrate, which would be likely to develop pitting or crevice corrosion if the coating is scratched or porous [11]. Nevertheless, zinc coatings are a very valuable treatment for steel substrates, with their ideal working conditions being indoor or outdoor applications against atmospheric corrosion in neutral environments, or even against water corrosion for hard waters with a pH in the range 7-12 [11].

One of the advantages of zinc coatings is the variety of the deposition methods that can be chosen. Pretreatment of the substrate is always necessary, and usually includes degreasing either in alkaline solutions or organic solvents and pickling in acidic solutions to remove superficial oxides: other techniques, such as shot-blasting, can also sometimes be employed [8, 10, 12].

2.1.1. Hot-dip galvanizing

With its first development dating back to the mid 1700s, hot-dip galvanizing is to date the most ancient and long-standing zinc deposition technique [9]. In this process, the steel substrate is dipped in a tank of molten zinc in order to obtain a coating that ranges from a few tens to a few hundred microns in thickness, which can be advantageous since a thicker coating provides a longer-lasting barrier protection against corrosion [10, 13]. However, since this method involves molten zinc, the temperatures it reaches are quite high, exceeding the melting point of zinc at 420°C: this can cause several problems, mostly regarding the effects it has on the substrate. Especially in the case of large steel components, it is necessary to lower them in the molten zinc very slowly, to avoid any splashes; however, as a large portion of the substrate is initially left out of the bath, the hot steam surrounding it can easily cause its oxidation, making it a less-than-ideal substrate [10]. Moreover, even if the substrate manages to avoid oxidation, its mechanical properties can still be affected, as the high temperatures can modify its microstructure and cause unwanted phase changes that may alter its behavior, which is especially undesirable in the case of high-strength steels [14, 15]. Nevertheless, the coatings that can be obtained with this technique are characterized by a quite high service life, lasting up to 50 years [15], and are usually able to properly cover edges and joints, assuring the corrosion protection of these critical points. The zinc deposit

resulting from this process is also characterized by a layered structure as the high temperatures of the bath, usually around 450°C, promote the interdiffusion and the reaction between iron and zinc, causing the creation of intermetallic phases, which can be advantageous as they increase the superficial hardness of the component [9, 10, 15]. In order to better control the growth and behavior of these intermetallic phases, very low amounts of alloying elements can be added to the molten zinc bath, which is therefore usually not made of pure zinc: for example, different amounts of aluminum can inhibit the formation of the Zn-Fe phases, bismuth can increase the fluidity of the bath, while a low percentage of tin is responsible for the characteristic “spangle” crystallization pattern of the final coating [15].

2.1.2. Sherardizing

Discovered in the early 1900s, sherardizing is a diffusive heat treatment taking place at temperatures below the melting point of zinc, usually around 300°C, which is a considerable advantage as the mechanical properties and the microstructure of the substrate will be significantly less likely to be affected by the procedure [12, 16]. This technique was initially also known as “dry galvanizing” since it was not based on a liquid zinc bath of any kind [12]. In sherardizing, the steel component is placed in a rotating container along with zinc powder, which must be rather pure and contain at least 95% zinc, and other inert fillers. Fillers are usually precise grades of sand which must not react with either the component or the zinc powder and their purpose is mainly to separate the zinc particles to prevent sintering and to avoid harsh collisions between the component and the container [12, 16]. The sherardizing process results in a diffusion coating with a layered structure: the amount of zinc in the coating decreases towards the substrate, as the processing temperatures not only promotes the diffusion of the zinc particles towards the component, but also the solid-state interdiffusion of the coating and the substrate, resulting in a very hard and uniform coating. This technique gives the component a matte gray finish, and is usually followed by passivation or paint layers to better protect the coating, both to improve its appearance and to further increase the corrosion protection it gives the substrate. Sherardized zinc coatings are usually less thick than the ones obtained from hot-dip galvanizing, averaging at 10-60 µm, depending on the processing time. The treatment time is, in fact, one of the main

disadvantages of this technique, as it often requires many hours for the results to be satisfactory; however, it is particularly useful to coat small components with complex shapes as it is able to lead to extremely uniform coatings [12, 16].

2.1.3. Zinc electroplating

Electroplating is a very common and convenient way to deposit a rather thin zinc layer on steel components: unlike hot-dip galvanizing and sherardizing, electroplating does not involve particularly high temperatures, meaning that there is a net distinction between the steel substrate and the zinc coating, no layered structure, and no risk of unwanted changes in the mechanical properties of the component. It is also a fairly simple and straightforward technique and it allows to coat substrates of any size with no limitations related to the heat source. With electrodeposition as a process dating back to the 1800s, zinc electroplating has significantly evolved in time, especially in terms of composition of the electrolyte [9]. Before the 1980s, the electrolytes that were employed for this process were alkaline, and mainly based on cyanides [3, 14]. They mostly contained zinc cyanide, sodium cyanide and sodium hydroxide: the presence of the latter compounds was necessary to make zinc cyanide soluble and release zincate ions in the bath [3, 17]. Cyanide zinc baths worked at operating temperatures ranging from 20-60°C and famously lead to very bright deposits [3, 17]. They represented a standard conventional procedure in the 70s, but due to their toxicity and high environmental impact they were gradually modified into low-cyanide baths and microcyanide baths and, eventually, fell into disuse [3]. To replace them, non-cyanide alkaline electrolytes were developed. The main problem with the absence of cyanide ions was that the lack of their complexing effect initially lead to very poor results and powdery deposits, but they were successfully replaced by organic additives, mainly carriers and brighteners, such as polyvinyl alcohol or polyaliphatic amines [3].

Nevertheless, nowadays acid electrolytes are by far the most popular type of zinc electroplating bath, making up over 50% of all zinc baths [17], and mainly use either chlorides or sulfates as zinc precursors. Chloride baths are based on zinc chloride and usually also contain either potassium chloride, sodium chloride or

ammonium chloride to increase the conductivity of the bath, while sulfate baths are based on zinc sulfate and contain sodium sulfate or even chloride salts, which have a much higher solubility and thus confer a much higher conductivity, for the same purpose [9]. Acid baths also have a very high efficiency, usually between 95% to 98% [3, 17], over the whole range of operable current densities, while alkaline electrolytes usually have a really high efficiency only at higher current densities, which is not ideal since depositions carried out at high current densities lead to dendritic growth; however, it is also necessary to point out that acid electrolytes produce duller-looking coatings with respect to cyanide baths and thus need many additives and a more complex formulation to lead to bright deposits [17]. In general, it is also common for the coating to undergo finishing treatments, especially if better aesthetic properties are also required for decorative reasons, since the electroplated deposits easily become matte and duller due to air exposure: it is common to opt for a chromate conversion treatment or to apply a coat of paint, or to combine the two treatments [3].

Acid baths usually operate at pH values between 3 and 5 and often require a buffer, such as boric acid, to avoid pH variations [17]. In fact, one of the main drawbacks of zinc electrodeposition is that, at any pH value, the reduction potential of zinc is always lower than that of hydrogen, meaning that hydrogen evolution at the cathode is always present as a side reaction. Besides lowering the efficiency of the deposition, potentially damaging the coating and putting the substrate at risk of developing hydrogen embrittlement, hydrogen evolution also causes local alkalization, which could entail the deposition of zinc hydroxide instead of metallic zinc, making the presence of a buffer fundamental [3, 17].

While being an extremely popular procedure per se, zinc electrodeposition holds even more weight considering that it was the starting point of the development of many zinc-based alloy coatings, which are able to provide a higher corrosion resistance and a higher-quality finish [3, 18, 19]. Zn-Ni alloys are the most prominent example: nickel is more noble than zinc and thus increases its corrosion resistance, and when it is present in quantities higher than 10% it makes the coating more passive. However, to avoid altering the sacrificial nature of the zinc coating, the nickel content must be lower than 15%, making the Zn-Ni alloy coatings containing 14% Ni the best performing ones [3, 17]. Zn-Fe alloy coatings are a cheaper alternative which have the same working principle as iron is more noble

than zinc and still increases its durability and corrosion protection since it slows down the corrosion of the deposit. Alloying zinc with elements from the iron group (Fe, Co, Ni) became especially popular to replace cadmium, which used to be widely employed as an alloying element but was banned due to its high toxicity [18].

2.2. Chromium coatings

Chromium coatings are one of the most common surface treatments performed on metallic components. Their popularity is related to the wide variety of properties they possess: not only do they provide very high corrosion resistance, but their high hardness and low friction coefficient also make them extremely resistant to wear and abrasion [3, 20 – 23]. Since chromium has a much more limited variety of deposition techniques with respect to zinc, electroplating is the standard procedure that is adopted: the only other option is physical vapor deposition, which is only used for very specific high-temperature applications, since chromate conversion coatings, despite being a popular treatment, entail the modification of the superficial layer of the substrate rather than the deposition of an external coating [21]. Electroplated chromium deposits are usually divided into two categories:

- Functional coatings, which are often referred to as “hard chromium” deposits, are characterized by a thickness greater than 0,80-1 μm [3, 20], and are the ones that best display the aforementioned properties [3, 20 – 22]. It is important, however, that they be deposited on top of a suitable substrate: while being very hard, these deposits are also quite brittle, which means that they can be easily crushed if the substrate is too soft. Because of this, they are usually deposited onto hardened steel or on top of other coatings, such as nickel [3].
- Decorative coatings are much thinner and are mainly applied for aesthetic purposes [3, 20 – 22].

While generally the basics of electrodeposition are quite simple and straightforward, the case of chromium electroplating is an exception as it is based on more complex mechanisms, some of which are still unclear, especially since chromium can be found

in nine different oxidation states ($-2, -1, 0, +1, +2, +3, +4, +5, +6$), which can be present in different forms and complexes and be involved in different reactions. As a matter of facts, coordination chemistry plays a very prominent role in chromium electroplating since the complexes formed by the different chromium anions are at the center of the deposition process; however, the knowledge regarding chromium coordination chemistry is still too superficial to explain many of the mechanisms that are involved [3, 20].

2.2.1. Hexavalent chromium plating baths

Plating baths based on hexavalent chromium were originally the most widely employed electrolytes for chromium electrodeposition, and only started being slowly replaced during the 1970s due to the very serious hazard that hexavalent chromium represents [3]: as a matter of facts, Cr(VI) is highly toxic and poses great health risks since it is carcinogenic and can also easily cause shorter-term issues such as irritation, inflammation and ulcers of the skin and airways [20]. Nevertheless, hexavalent chromium plating baths were extremely popular and difficult to replace. The electrolyte is based on chromium trioxide, CrO_3 , which is commonly referred to as chromic acid, although chromium trioxide is really the anhydride form of chromic acid, H_2CrO_4 , which is actually formed in the solution. This compound is the primary source of hexavalent chromium in the deposition process, which then forms a large variety of ions by bonding with oxygen: chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions are the most important species in the solution, although many other ionic species are also formed. The main peculiarity of this deposition process is that chromium cannot be deposited by itself, and the presence of a catalyst is always required [3, 20, 21]. The most commonly employed catalyst are sulfate anions, which are usually added as sulfuric acid: the presence of sulfates is fundamental since they prevent a series of reactions leading to the formation of unwanted trivalent chromium complexes, which would greatly hinder the deposition [3]. It is also important for the sulfate anions to be present in a specific amount, since too low or too high a concentration will lead to no deposit: the ideal chromic acid to sulfate ratio is about 100 : 1 [3, 20, 21]. It is, however, very common to find double-catalyzed systems, which also employ fluoride-based species along with the sulfates, usually fluosilicate or

fluoborate, greatly improving the deposition rate and the efficiency of the process. Nevertheless, the cathodic efficiency of hexavalent chromium baths is still quite low, ranging from 10-12% for standard solutions and reaching around 20% when fluoride catalysts are added. These chromium deposits are usually achieved at high current density values, ranging anywhere from 30-80 A/dm², and the plating bath usually operates at temperatures of about 55-60°C [3, 20, 21]. Moreover, due to the composition of the plating bath, these solutions are extremely acidic, with pH values that are off the normal scale and are even slightly negative [3]. Since titanium and steel and other types of insoluble anodes dissolve in this kind of electrolyte, insoluble lead alloy anodes are usually employed [3]: these lead alloys generally contain either 6-8% antimony or 4-6% tin, since lead by itself would be too susceptible to corrosion in electrolytes containing fluoride species [20]. Lead is also very useful because it is capable of reoxidizing trivalent chromium to hexavalent chromium, thus hindering the depletion of hexavalent chromium in the solution [3]. Insoluble anodes are employed because soluble chromium anodes, besides being a lot more expensive than chromic acid, have a nearly 100% anodic dissolution efficiency and, due to the extremely low cathodic efficiency that characterizes these electrolytes, they are unsuitable because the chromium content in the bath would drastically increase in time [3, 20].

Electrodeposited chromium coatings are characterized by a microcracked structure: since this deposit is very hard and brittle and characterized by high tensile stresses, when it surpasses a certain thickness (0,5-0,75 μm) it cracks, because the internal stresses exceed its cohesive strength [3, 20], although another theory suggests that the cracks could also be due to the formation of unstable chromium hydrides during plating [21]. Nevertheless, this structure is not necessarily a disadvantage, as it can be beneficial for some applications since the microcracks can store lubricant and provide a "self-lubricant" behavior on top of the very high hardness and low friction coefficient that are inherent to the coating [3, 20, 21]. Electroplated chromium is also very popular since it generally does not require any finishing treatment because the deposit is able to spontaneously passivate, which also means that the thin Cr₂O₃ layer that is formed on top of the coating has a self-healing behavior. In fact, chromium coatings are commonly electrodeposited as a finishing treatment themselves, not only when they are deposited as decorative coatings, but also on top of other protective coatings to

increase their physical properties while providing a pleasing finish, with the most prominent example being nickel-chromium systems, in which chromium is deposited on top of a nickel coating [3, 20, 21]. Nickel undercoats are especially employed when corrosion resistance is particularly important: despite the corrosion resistance of chromium being extremely high, its microcracked structure and brittleness may represent a disadvantage for this purpose [3], so nickel is applied as a protective undercoat, while hard chromium coatings are usually applied by themselves if their main purpose is wear resistance [21]. For the same reason, chromium duplex coatings could also be applied to provide better corrosion protection. This process entails the deposition of a base chromium layer which is very thin and uncracked and another thicker microcracked layer on top of it, which also assures its characteristic hardness [3, 20, 21].

2.2.2. Trivalent chromium plating baths

Despite the many perks of the coatings obtained from the hexavalent chromium baths, during the 1970s a lot of research went into the development of trivalent chromium electrolytes, since hexavalent chromium baths proved to be far too toxic and hazardous to be a sustainable practice. However, the development of trivalent plating baths is by no means an easy task [3, 20, 21].

The main issue with the deposition of trivalent chromium is with its coordination chemistry: Cr(III), which is the most stable valence state of chromium, has a very strong tendency to form polynuclear complexes, most of which are hexacoordinate and characterized by a certain degree of kinetic inertness [3]. In aqueous solutions, the main complex that most trivalent chromium salts form is called the hexaaquachromium(III) complex, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ [3, 22, 24]: the main issue with this complex is that, despite its thermodynamic stability being relatively low, its kinetic stability is extremely high, which greatly hinders the deposition process [22]. Moreover, what complicates the deposition process from trivalent plating baths is the very large amount of mechanisms and reactions that trivalent chromium can undergo: besides aquation, from which the hexaaquachromium(III) complex is formed, several other reactions can take place, such as hydrolysis, olation, oxolation and polymerization [3]. In particular, olation deriving from the

hydrolysis of the trivalent aqua complexes can cause further problems in the deposition since it entails the formation of hydroxochromium(III) groups which greatly hinder the deposition of metallic chromium. Indeed, since this reaction is catalyzed by the Cr(II) ions [3, 21, 22] produced during electrolysis, the presence of species in the solution which are able to complex divalent chromium, such as formic acid, is also required [21].

As mentioned previously, the main issue with the hexaaquachromium(III) complex is its great kinetic inertness, which prevents the transport and the subsequent reduction of chromium on the cathodic surface: therefore, while hexavalent chromium could not be reduced without catalysts, trivalent chromium plating baths require complexing agents. These ligands, which are usually organic, such as glycine or formic acid, are thus able to substitute the coordinated water molecules around the trivalent chromium ion and the resulting complexes are able to migrate towards the cathodic surface much more easily, because they do not possess the same kinetic inertia as the hexaaquachromium(III) complex [21, 22, 24 – 26]. Similarly to hexavalent chromium and its catalysts, the complexing ligands must be present in specific ratios with respect to the trivalent chromium content [26].

Trivalent chromium plating baths are usually based on chromium salts such as sulfates, perchlorates or chlorides, with chlorides being the most common choice since they lead to more homogeneous deposits as they are more likely to form complexes [26]. More salts, chlorides or sulfates, are used to improve the conductivity and boric acid is usually added as a buffer, along with the complexing ligands and wetting agents [20 – 22]. The pH of these baths is a lot less acidic than chromic acid solutions, ranging between 2-4 [20, 25, 26]. The working temperature can range from 25-55°C, though it is usually closer to room temperature since higher temperatures promote olation and oxolation reactions which are counterproductive [3]. Although many of the deposition mechanisms are still unclear, it is very likely that the reduction mechanism leading to a zerovalent chromium coating is actually a two-step process: trivalent chromium is first reduced to divalent chromium, and then divalent chromium is reduced to metallic chromium [20, 23, 24].

Moreover, one aspect that characterizes both the trivalent and the hexavalent chromium plating baths is the main side reaction occurring at the cathode:

hydrogen evolution, which always occurs due to the fact that the reduction potentials of both plating baths are lower than that of hydrogen, wastes a lot of power. In fact, this reaction occurs in large amounts, which is attested by the very low cathodic efficiencies of these processes [20].

Coatings obtained from trivalent chromium plating baths are slightly different than the ones obtained from chromic acid baths: their color is closer to gray than to the bluish hue that characterizes the latter deposits [3, 21] and they have a slightly lower hardness, especially since they lose a lot of adherence when their thickness exceeds 3 μm , making it difficult to achieve “hard chromium” coatings [20]. However, the process is characterized by a much higher efficiency, around 30-40% [20, 21], while the deposits are also much more uniform and homogeneous [20]. Trivalent chromium is also able to be used as a precursor for the electrodeposition of many alloys, which could not be achieved with hexavalent chromium as it is not suitable for alloy plating [3]. On top of that, trivalent chromium is much different than its hexavalent counterpart since it is not toxic nor hazardous to health and to the environment, which is obviously a great advantage. However, a challenging aspect of the trivalent chromium plating baths is their stability: since so many reactions can take place, these electrolytes tend to greatly change and evolve over time, making the end results quite unpredictable [20].

2.3. Electrodeposition of alloys

One of the main advantages of electroplating as a technique is its ability to deposit a wide array of alloys of several different metals, which quickly gained popularity after its first introduction in the mid 1800s [6]. As a matter of fact, the electrodeposition of alloys nowadays has met a huge commercial success because it allows to obtain coatings which display a wider range of different properties with respect to single metal deposits [2]: the alloy coatings usually offer a higher performance, as they may present a higher corrosion or wear resistance, a higher density, hardness, toughness, or are generally superior in other different ways [4].

Electroplated alloy coatings display different characteristics than thermally obtained alloy coatings, as they may differ in phase structure [4] or in properties due to the different crystallization process [1]; electroplating as a technique also differs from

metallurgical procedures, such as hot-dipping, as it does not impact the microstructure and properties of the substrate. Moreover, electroplated alloy coatings can also be subjected to thermal post-treatments which cause precipitation hardening [4] and which can also be useful to remove incorporated hydrogen if severe hydrogen evolution occurred as a side reaction [1].

2.3.1. Principles of alloy electroplating

The electrodeposition of alloys is not as easy to describe as that of single metals because of the many electrochemical processes occurring, which are rarely independent of each other [2]. The main requisite for the electrodeposition of an alloy is that the reduction potentials of the two metals that need to be codeposited have to be fairly close together [1, 2, 4, 6], although no generalization can be made regarding their precise proximity [6].

It is possible to classify all alloy electrodeposition processes into the following five main groups. The first three processes are generally referred to as “normal codeposition”, since they entail the preferential deposition of the more noble metal, while the last two are referred to as “abnormal codeposition”, since the less noble metal is deposited preferentially [1, 6].

- Equilibrium codeposition: in this process, the deposited alloy is in equilibrium with the solution, thus the ratio of the metals in the coating is equal to that in the solution. This plating system, however, is very rare [1, 6].
- Regular codeposition: in this system, the deposition is under diffusion control. The deposition potentials of the two metals are usually quite far apart; the more noble metal is deposited preferentially and its content increases with a higher ionic concentration in the solution, temperature and stirring, and with lower current densities [1, 6]. This is likely the case of zinc-chromium alloys.
- Irregular codeposition: this deposition is not controlled by diffusion, but by the irregularities in the potentials of the metals in the solution; this usually occurs when the potentials are close together and with metals which form solid solutions, and the more noble metal is still deposited preferentially [1, 6].
- Anomalous codeposition: in this process, the less noble metal is deposited preferentially and it is present in the alloy in a higher amount. Due to this

anomaly, the deposition can only occur under certain conditions and it is quite rare, as it seems to only affect the codeposition of some of the alloys of the iron group (Fe, Co, Ni) [1, 6].

- Induced codeposition: this technique is adopted for some metals which cannot be electroplated by themselves, such as molybdenum and tungsten, but can be codeposited. The metals from the iron group are therefore used as “inducing metals” as they allow for the deposition of the ones that, by contrast, are called “reluctant metals” [1, 6].

2.3.2. Partial polarization curves

Polarization curves are graphs that represent the relationship between the applied potential and the current density circulating in the system when electrodepositing a coating. In particular, partial polarization curves represent the two separate parent metals during the deposition of the alloy, and allow to study the type of deposit that can be obtained at different values of potential and current density: as a matter of fact, by controlling these parameters, it is possible to determine the composition of the alloy, since, at a given potential, the two metals are codeposited in the same ratio as their partial current densities, i_A/i_B [1, 4].

During the codeposition, the polarization curves, which have a similar trend, can either overlap, intersect or be separated:

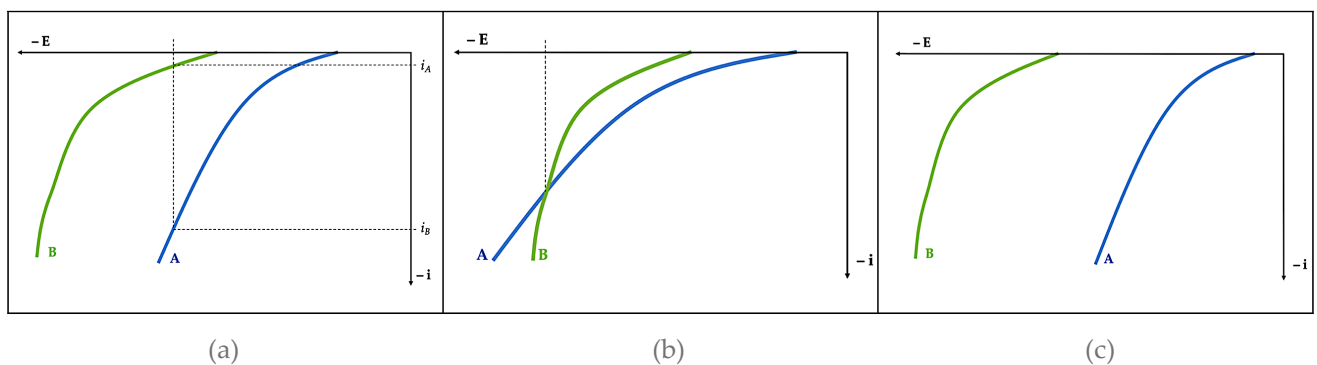


Fig. 2: (a) overlapping, (b) intersecting and (c) separated polarization curves

In general, it is necessary to have overlapping polarization curves (a) to achieve the simultaneous deposition of the two metals [2], which means that they should be similar and close enough to each other [4]. Otherwise, if the two curves are too far

apart, the substrate will need to be cathodically polarized to an excessive amount before the deposition of the less noble metal (in this case, metal B) starts, meaning that there will be either no proper control of the composition of the alloy or that there will be no alloy at all, especially in the presence of pervasive side reactions such as hydrogen evolution. Moreover, in case (b), intersection of the two curves represents the conditions under which metal A and B can be codeposited in the same amount. In general, it is clear that deposition occurring at low polarization will produce a coating primarily made of the more noble metal, while a higher polarization will enrich the alloy with the less noble metal, despite the fact that higher amounts of hydrogen will be evolved, resulting in poorer efficiency and quality of the coating [4]. Although these partial polarization curves display the operating conditions to obtain an alloy of a given composition, the curves themselves can be modified by changing the formulation of the electrolyte [1, 2, 4, 6].

2.3.3. Facilitating the deposition of alloys

As mentioned previously, the main requisite to codeposit two metals is for their deposition potentials to be fairly close together. However, since the reduction potential of a metal is not only a function of the standard potential but also a function of other variables, such as the temperature, the activity of the metal ions and their cathodic overpotential, which in turn depend on other variables, such as the concentration of the metallic ions, the pH of the solution, etc., it is possible to modify the polarization curves and bring the deposition potentials of the metals closer together, to facilitate their codeposition [1, 4]. The main changes that can be made for this purpose are the following:

- Using complexing agents: complexing agents are species, either organic or inorganic, which coordinate around the metallic cations in the solution forming a complex, which changes both the activity of the metal ions and their deposition mechanisms [1]. The complexes are usually characterized by a lower, less noble deposition potential with respect to the simple ions, which means that, if the nobler metal is present as a complex, the deposition potentials of the two metals will be brought closer together, facilitating the codeposition

[1, 2, 6]. As a matter of fact, to be effective, the complexing agents must be chosen appropriately as to reduce the potential of the nobler metal to a greater extent than that of the less noble metal [1]. Many species can serve as complexing agents, such as ammonia, citrates, tartars, fluorides, amino acids such as glycine, etc., but the most important complexing agents are cyanides [1,6]: they are so important that alloy electroplating (mainly of brass and bronze) started taking place around the same time cyanides were introduced in electrodeposition, in the mid 1800s [6]. The plating baths that contain complex ions for alloy deposition can be divided into "single" complex baths, if both metals form complex ions from the same complexing agent, and "mixed" plating baths, if only one metal forms complex ions or if a different complexing agent is employed for each metal [6]. However, complexing agents also have their downsides. First of all, since they lower the deposition potential of the metals in the solution, alloys of metals which have a deposition potential that is already quite low, such as chromium and manganese, will deposit with very low cathodic efficiencies, if at all. Moreover, complexing agents can display such strong adsorption to the deposit that it can start representing a weakness rather than an advantage, since they can produce very brittle, cracked or exfoliated coatings if their absorption is too strong [6].

- Lowering the concentration of the more noble metal can sometimes help in favoring the deposition of the alloy, but this approach is rarely considered since it causes only a very small shift of the reduction potential [6]. As a matter of fact, lowering the potential of just 0,1 V requires a dilution of over two orders of magnitude [2, 6], which is rather inefficient. Furthermore, employing solutions which are too dilute of the more noble metal would mean obtaining an electrolyte whose concentration changes quite fast, meaning that it would be difficult to obtain alloys with a reproducible composition [6]. However, if the alloy can be deposited, changing the concentration and ratio of the two metals does have an effect, as it allows to obtain different compositions of the alloy. In particular, it is possible to deposit the alloy in its entire composition range (at least, in the compositions that can be deposited) by just varying the ratio of the two metals; it is also possible to change the composition by keeping the same ratio and change the overall concentration, but it is less effective as the composition of the deposit only varies over a limited range [6].

- Depositing the nobler metal at its limiting current density: if the nobler metal is under limiting current density conditions, a further polarization will not increase the amount of deposited metal, while the less noble metal will start being deposited when its deposition potential is reached. The partial polarization curves will thus appear to have the following trend [2]:

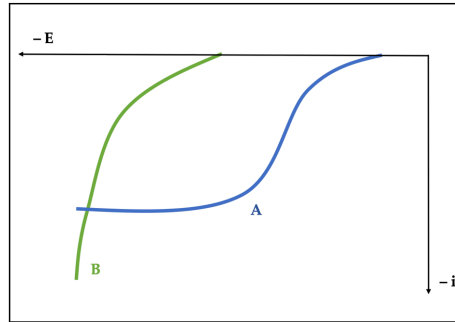


Fig. 3: Partial polarization curves; metal A under limiting current density conditions

The deposit may be unsatisfactory since depositing at the limiting current density usually leads to dendritic growth or powdery deposits; however, it is possible to limit this problem by employing surface-active substances that are capable of inhibiting dendritic growth [2].

- Adding specific surface-active species can also favor the deposition of alloys: such compounds must be able to selectively inhibit the deposition of the more noble metal, thus shifting the polarization curve of a few hundred mV [1, 2].

2.4. Electrodeposited Zn-Cr alloy coatings

The focus on zinc-chromium alloy coatings is mainly related to their enhanced corrosion resistance with respect to pure zinc coatings, while their protection remains of barrier and sacrificial nature [27 – 29, 31 – 33]. It has been reported that their corrosion resistance increases slightly for chromium contents higher than 4-6 mass%, while showing a sharp increase above 10 mass% [28]. Moreover, Zn-Cr coatings also display a higher corrosion resistance at a lower thickness compared to pure zinc, which decreases from 7,5-10 μm to 3,5-5 μm [29, 32]. These coatings therefore find many applications in the automotive industry [27 – 29]: this treatment allows to overcome construction limitations since Zn-Cr alloy coatings have a better formability

and weldability due to their reduced thickness, on top of displaying a higher corrosion resistance [32].

The properties of these deposits largely depend on their composition, which is highly reliant on factors such as the zinc to chromium ratio, the concentration of the metallic species in the electrolyte, the operating current density and the temperature and pH of the bath [32]. Electroplating allows to deposit coatings with a chromium content that reaches up to 40 mass% [27, 28], and although, as previously mentioned, the corrosion resistance increases sharply for chromium contents exceeding 10 mass%, sources report that the optimal chromium amount to achieve the best performance is around 3-7 mass% [32, 35], or more narrowly 4-6% [34]. Above this range, the deposit tends to become powdery and, despite the higher corrosion resistance, it is hard to obtain satisfactory deposits [32]. The poorer quality of the deposits containing higher amounts of chromium is likely a consequence of several factors: first of all, such coatings require current densities which are much higher than what is considered the norm, ranging anywhere from 5 to 120 A/dm² (average values from 30 to 80 A/dm²) [28, 29] with no codeposition of the two metals being reported for values below 5 A/dm² [27]. This codeposition is also likely to occur under limiting current density conditions for zinc, and such a condition easily leads to powdery coatings [27]; moreover, the high current densities and high polarization that are required for this process to occur, along with the low pH of the electrolyte, mean that hydrogen evolution, which always occurs, is increasingly severe for higher current densities and deposited amounts of chromium. One disadvantage of the Zn-Cr deposit, compared to pure zinc, is that the growing surface is also a better catalyst for hydrogen evolution, which is therefore even more severe than during the deposition of zinc from acid baths [33].

2.4.1. Issues in the electrodeposition process

Besides the aforementioned complications related to the depositions of coatings with higher amounts of chromium, this process presents some inherent difficulties concerning the codeposition of the two metals [27]. The first category of difficulties is related to the presence of trivalent chromium, whose electrodeposition is already a complicated process per se, due to the high kinetic stability of the

hexaaquachromium(III) complex that is formed in aqueous solutions and the many reactions it can undergo [31], not to mention the lack of general knowledge that characterizes this treatment and the fact that the trivalent chromium electrolytes can change during time with little predictability [20]. Moreover, despite the reduction potential of the two species not being extremely far apart, the deposition process is complicated by the fact that said potentials are very negative, meaning that the codeposition requires the substrate to be highly cathodically polarized. Indeed, the problem lies in the fact that the reduction of chromium is not a direct reaction from trivalent to metallic, $Cr^{3+} + 3e^- \rightarrow Cr(s)$, which would occur at $-0,74$ V SHE, a value very close to the reduction potential of zinc, $-0,76$ V SHE. Instead, the reduction of chromium is a two-step process, with the first reaction, $Cr^{3+} + e^- \rightarrow Cr^{2+}$, occurring at $-0,41$ V SHE, and the second reaction, $Cr^{2+} + 2e^- \rightarrow Cr(s)$, occurring at $-0,91$ V SHE. [31, 37] Since this process requires such a high polarization, the deposits easily result to be powdery, especially if zinc is being deposited at its limiting current density [27, 32]. Moreover, hydrogen evolution not only decreases the efficiency of the process and possibly damages both the coating and the substrate, but it can increase the pH at the cathode to such a high amount that it can cause the deposition of chromium hydroxides and oxides [31]. However, as previously explained, the reduction potentials of the metallic species and their deposition behavior can be partly modified through the use of additives and complexing agents to favor the codeposition.

2.4.2. Complexing agents and additives

Several compounds have been studied as possible complexing agents for this process.

- Polyethylene glycol (PEG) is a popular organic additive, whose effects are greatly influenced by its molecular weight. Its main working mechanism is the polarization of the zinc and hydrogen reduction reactions, which is likely due to the compound being adsorbed on the active sites of the growing layer, thus inhibiting said reactions [30, 31]. The optimal concentration of this species is usually between 0,5-1,0 g/L, since higher concentrations do not yield different results. The molecular weight of PEG should ideally range from 1500-6000

g/mol, since too high or too low a molecular weight leads to an insufficient polarization and actually causes a more irregular distribution of the final deposit. Moreover, studies on PEG stability during electrodeposition, especially at high temperatures and high current densities, show that for prolonged use the polymer starts to decompose into molecules with lower molecular weight, which is an unwanted effect [31].

- Polypropylene glycol (PPG) has also been used alternatively to PEG, since its working mechanism is similar, as it is based on the inhibition of the zinc reduction, bringing the deposition potentials of zinc and chromium closer together. However, with respect to PEG, PPG leads to slightly less negative deposition potentials (a difference of about 100 mV) [30].
- Glycine is a popular complexing agent for trivalent chromium baths: however, as an additive it does not facilitate the codeposition of zinc and chromium, because, as a complexing agent for chromium, it actually shifts the reduction potential of chromium towards lower values, increasing the distance between the deposition potentials of the two metals. However, as previously discussed, it is useful in contrasting the creation of the hexaaquachromium(III) complex and kinetically aiding the deposition of chromium; moreover, unlike boric acid, it does work as a good buffering agent in the Zn-Cr electrolyte, and when added along other additives, such as PPG, it can actually improve the appearance, density and adherence of the coatings [30].
- Boric acid is the most common addition to the standard Zn-Cr electrolyte, although in this situation it technically should work very poorly as a buffering agent, since this compound only shows its buffering ability at much higher values of pH; some sources, however, believe boric acid may serve a role as a possible catalyst for the deposition process [30, 34].

2.4.3. Standard formulations and operational parameters

Zn-Cr electroplating baths are usually based on sulfates, using zinc sulfate (ZnSO_4) and trivalent chromium sulfate ($\text{Cr}_2(\text{SO}_4)_3$) as precursors, with various amounts of hydration: heptahydrate zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and hexahydrate chromium (III) sulfate ($\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$) are the most commonly employed reagents. The presence of other salts, generally sulfates as well, is necessary to increase the

conductivity of the bath, with the most common choices being sodium sulfate (Na_2SO_4) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) [28 – 31, 33 – 35]. The most common concentration of zinc sulfate is around 0,6 M, while that of chromium (III) sulfate is generally between 0,2-0,3 M, although sometimes lower amounts of zinc sulfate and chromium(III) sulfate are employed, 0,2 M and 0,05 M respectively [27]. Despite the electrolyte being most often based on sulfates, sometimes chromium can be introduced as a chloride (CrCl_3), with the additions of salts such as ammonium chloride (NH_4Cl) and sodium chloride (NaCl) for conductivity [34].

Most electrolytes seem to have been formulated following A. Brenner's considerations regarding the concentration of the metallic species: the electrolyte should, in fact, contain the nobler metal in a higher concentration, since doing the opposite would cause too fast a depletion of the bath as the nobler metal is present in a much higher amount in the alloy and is thus consumed much faster [6]. However, some sources report that, while too low a zinc concentration ($< 0,2$ M) leads to thin deposits with black streaks, too high a concentration ($> 0,5$ M) causes the amount of chromium in the alloy to be unacceptably low; simultaneously, the chromium concentration in the bath should be higher than that of zinc because zinc is deposited first. Chromium concentrations lower than 0,6 M would allegedly lead to low chromium content and poor quality, with the ideal concentration being 0,8 M [34].

The bath is usually maintained at a pH ranging from 1,6 – 2,5 [27 – 31, 34, 35], with the most common value being 2: working below pH 2 causes even more severe hydrogen evolution, while working at higher pH can cause the deposition of chromium hydroxides and oxides [34] or the precipitation of non-metallic zinc and chromium [32], compromising the final coating.

The working temperature ranges from room temperature to around 40°C [27 – 31, 34, 35]; however, higher temperatures are likely to cause enhanced hydrogen evolution at the cathode leading to lower efficiencies. Therefore, a temperature range of $20\text{-}25^\circ\text{C}$ is believed to be optimal to increase the quality of the coatings. Agitation of the bath is also important for quality as it promotes the detachment of the gas bubbles formed during hydrogen evolution [34].

During electroplating, the working current density is rather high as a consequence of the nature of the process itself, ranging anywhere from $5\text{-}120$ A/dm^2 , with an

average of 30-80 A/dm² [28, 29]; the consequences of depositing the coatings at such high current densities have already been discussed. The cathodic efficiency for this process is relatively low due to the pervasiveness of the side reactions, although different sources cite different efficiencies which range from 35-55% [30] to 50-70% [32], with some reaching even up to 80% [27].

3 EXPERIMENTAL PROCEDURES

The final part of this dissertation will concern the experimental procedures and the characterization methods that were employed.

3.1. Materials and methods

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

ZnSO ₄ · 7H ₂ O	0,2 M
Trisurfin	0,1 M
Na ₂ SO ₄	1 M

Trisurfin is a commercial chemical containing 67% chromium (III) sulfate, 25,8% sodium sulfate, and moisture. This means that adding 0,1 M Trisurfin entails adding 0,067 M Cr₂(SO₄)₃, resulting in a 3:1 ratio between zinc sulfate and chromium (III) sulfate, and an additional 0,0258 M of sodium sulfate.

The anodes used in the deposition were titanium meshes coated with ruthenium and iridium oxides (Ti-MMO). Substrates had a working area of 2,25 cm² (1,5 cm × 1,5 cm) and were made of carbon steel S235, containing 0,075% C, 0,460% Mn, 0,015% P, 0,010% S, 0,020% Si, 0,040% Al, 0,015% Ni, 0,015% Cr and 0,010% Cu. In order to prepare the substrates for the deposition, they were sanded with 240 grit and 400 grit sandpaper. They were then rinsed and placed in ethanol in an ultrasonic sonicator for 10 minutes. The cathodic area of interest was then delimited using Kapton tape. The substrates were then degreased with acetone and etched in a solution of 10 wt.% HCl. Finally, they were rinsed with deionized water and dried with nitrogen gas to avoid oxidation.

The electrolyte was maintained at a temperature of 25°C and a pH level of 2. The bath was provided with agitation via magnetic stirrer rotating at 250 rpm. The deposition process was carried out at current density values ranging from 50 to 300 mA/cm²,

corresponding to 5 to 30 A/dm². After the deposition, the samples were immediately extracted from the electrolytic cell, rinsed with deionized water and dried with nitrogen gas. The samples were weighed before and after the deposition to retrieve the weight of the deposit.

X-ray fluorescence spectroscopy (XRF) was employed in order to determine the thickness and atomic percentage composition of the final coatings. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were employed to further inspect the composition and morphology of the deposits. Hull cell samples were retrieved to study the behavior of the electroplating bath at different current densities, while cyclic voltammetry was used to investigate the electrochemical properties of the bath in terms of reactions and reduction potentials. Finally, to study the corrosion behavior of the deposits, Tafel polarization tests were carried out in a 0,1 M Na₂SO₄ solution using a three-electrode setup, using an Ag/AgCl reference electrode, a platinum grid electrode as a counter electrode, and glassy carbon as a working electrode.

The final formulation for the electrolyte was achieved through trial and error, which allowed to study the effect of chemical and operational changes on the resulting coatings. The effect of such changes will be discussed below.

3.2. Variations of formulation and operational parameters and their effects

3.2.1. Variations of the pH

One of the earliest changes that were made concerned the pH of the electrolyte. The pH was varied between 2 and 4 with 0,5 increments. The solutions rested for three days before the pH was tested again: in all cases, the pH had significantly dropped, signaling their instability. It was immediately clear that the solutions at pH 4 were particularly unstable: trying to increase it back to 4 turned the solution cloudy and caused precipitation. This is likely due fact that at pH 4 chromium can only be present in the solution as a hydroxide, as shown by the Zn-Cr Pourbaix diagram [38].

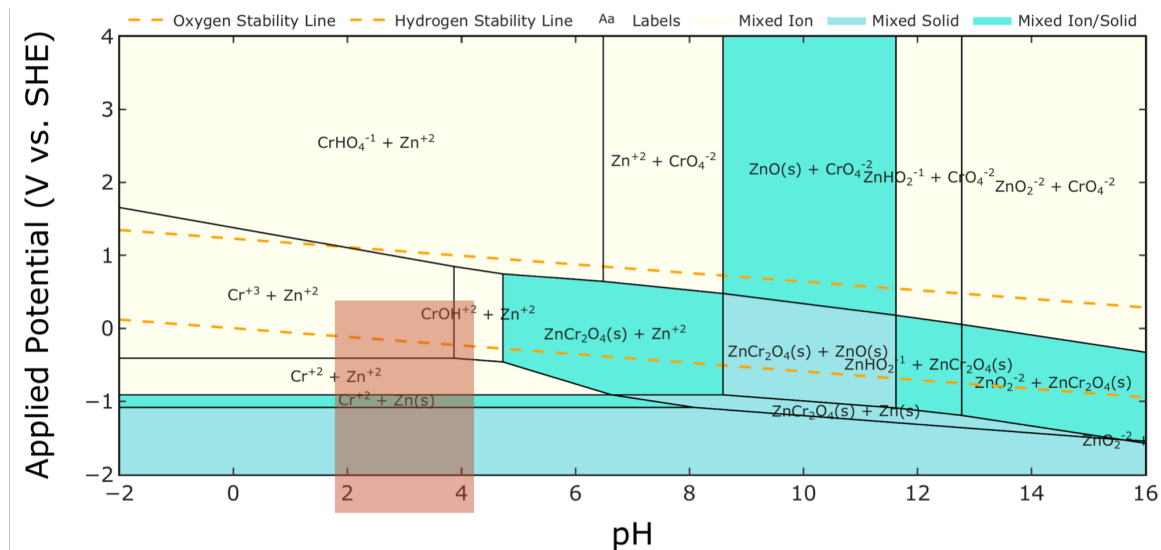


Fig. 4: Pourbaix diagram for the Zn-Cr system

Hull cell samples were obtained with current densities varying from 8 to 80 mA/cm² from chloride-based solutions containing 0,2 M ZnCl₂·2H₂O and 0,2 M CrCl₃·6H₂O. The results reported below only consider deposits obtained at 80 mA/cm², which was the only value out of the selected current densities that led to a significant chromium content in the coating.

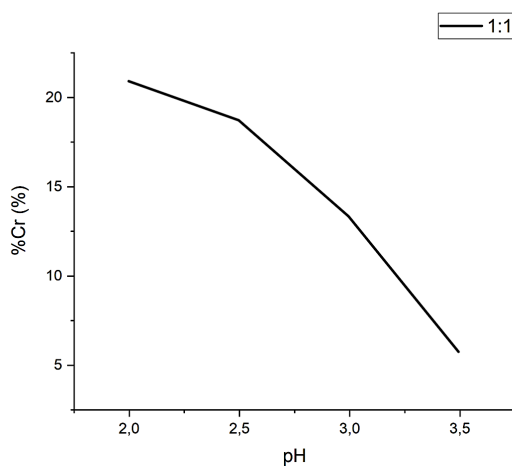


Fig. 5: Dependence of the content of chromium in the deposits on the pH of the electroplating bath

As the results show, the chromium content in the deposit significantly decreases at higher pH values. Moreover, due to the side reactions occurring at the cathode and causing local alkalization, it is more likely that the pH could locally exceed the value

of 4, which the Pourbaix diagram shows being the starting point for the deposition of chromium hydroxide.

It was therefore established to maintain the plating bath at a pH level of 2, both to facilitate the deposition of chromium and to avoid excessive local alkalization at the cathode; this pH value is also coherent with the literature regarding Zn-Cr codeposition [27 – 31, 34, 35].

3.2.2. Variations of the Zn:Cr ratios

One of the first changes that were monitored were those caused by a variation in the Zn:Cr ratio; in particular, three ratios were considered, 1:1, 3:1 and 5:1 respectively. Many trials confirmed the general trend according to which higher zinc to chromium ratios leads to a higher chromium content in the resulting coatings, but also leads to lower thicknesses.

The following plot considers deposits obtained at 80 mA/cm^2 from three separate chloride-based solutions at pH 2 containing $0,2 \text{ M ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 M KCl and respectively:

- $0,2 \text{ M CrCl}_3 \cdot 6\text{H}_2\text{O}$ for a 1:1 ratio
- $0,067 \text{ M CrCl}_3 \cdot 6\text{H}_2\text{O}$ for a 3:1 ratio
- $0,04 \text{ M CrCl}_3 \cdot 6\text{H}_2\text{O}$ for a 5:1 ratio

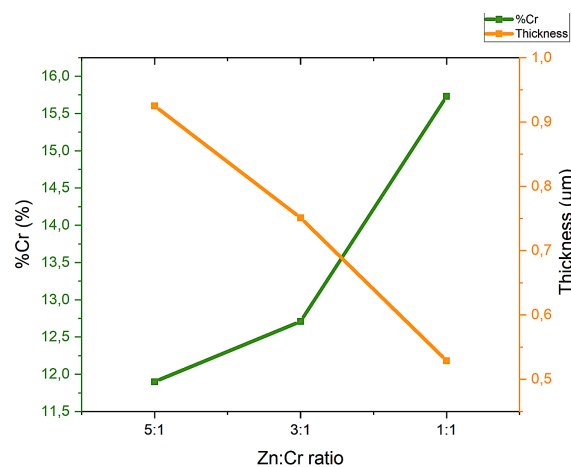


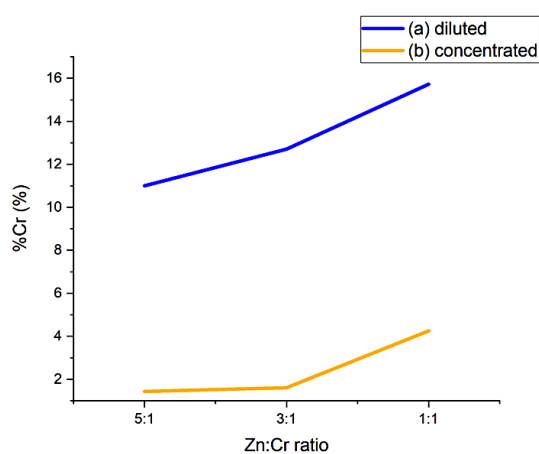
Fig. 6: Dependence of the content of chromium in the deposit (green) and the thickness of the deposit (orange) on the Zn:Cr ratio

Other trials, carried out with sulfate-based solutions, led to the same conclusions.

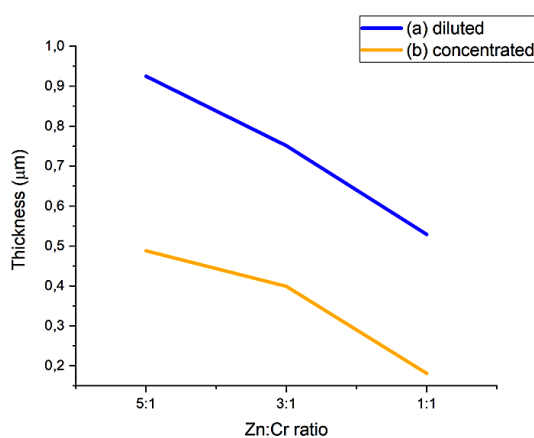
Eventually, it was determined that the final electrolyte would maintain a composition of 0,2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0,067 $\text{Cr}_2(\text{SO}_4)_3$, making for a zinc sulfate to chromium sulfate ratio of 3:1, meaning a 3:2 Zn:Cr ratio, which is a popular choice according to several sources [28 – 31, 33 – 35]. This ratio was chosen as it allowed to have a slightly higher chromium content in the final coating while still following Brenner's considerations [6] regarding the ratio of the nobler to the less noble metal. After this was settled, the major changes to control the chromium content were made regarding the overall concentration of the electrolyte and, finally, regarding the current density.

3.2.3. Variations of the overall concentration of the electrolyte

As it has been established, the chromium content in the deposits increases for higher chromium concentrations in the bath, meaning for higher Zn:Cr ratios. One could therefore expect to obtain higher amounts of deposited chromium when increasing the concentration of chromium in the bath while also increasing the overall concentration of the metallic species, zinc included. However, concentrated solutions not only led to lower amounts of deposited chromium, but to overall lower amounts of deposited mass. Coatings deposited from concentrated solutions proved to be much thinner than deposits obtained from a diluted solution with the same Zn:Cr ratio at the same current density.



(1)



(2)

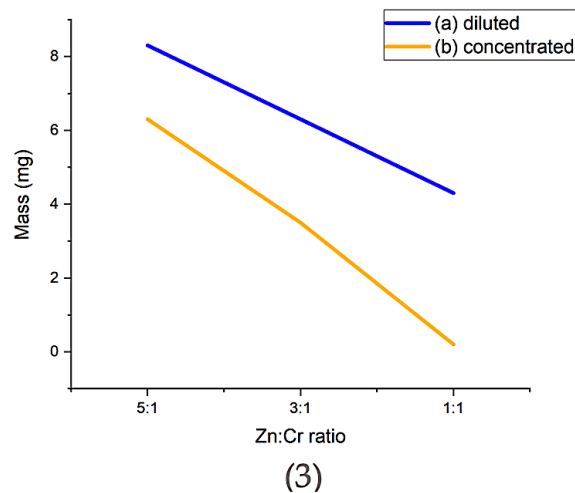


Fig. 7: Dependence of the content of chromium in the deposit (1), the thickness (2) and the mass (3) of the coating for a diluted (blue, a) and a concentrated (yellow, b) electrolyte, here represented for different Zn:Cr ratios

These data correspond to coatings obtained from three diluted chloride-based solutions at pH 2 containing 0,2 M $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, 2 M KCl and varying amounts of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, leading to Zn:Cr ratios of respectively 5:1, 3:1 and 1:1, and from three concentrated chloride-based solutions containing 0,6 M $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, 2 M KCl and varying amounts of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, leading to Zn:Cr ratios of respectively 5:1, 3:1 and 1:1. All deposits were obtained at 80 mA/cm^2 on carbon steel substrates.

The most likely explanation is related to the deposition mechanism of the alloy.

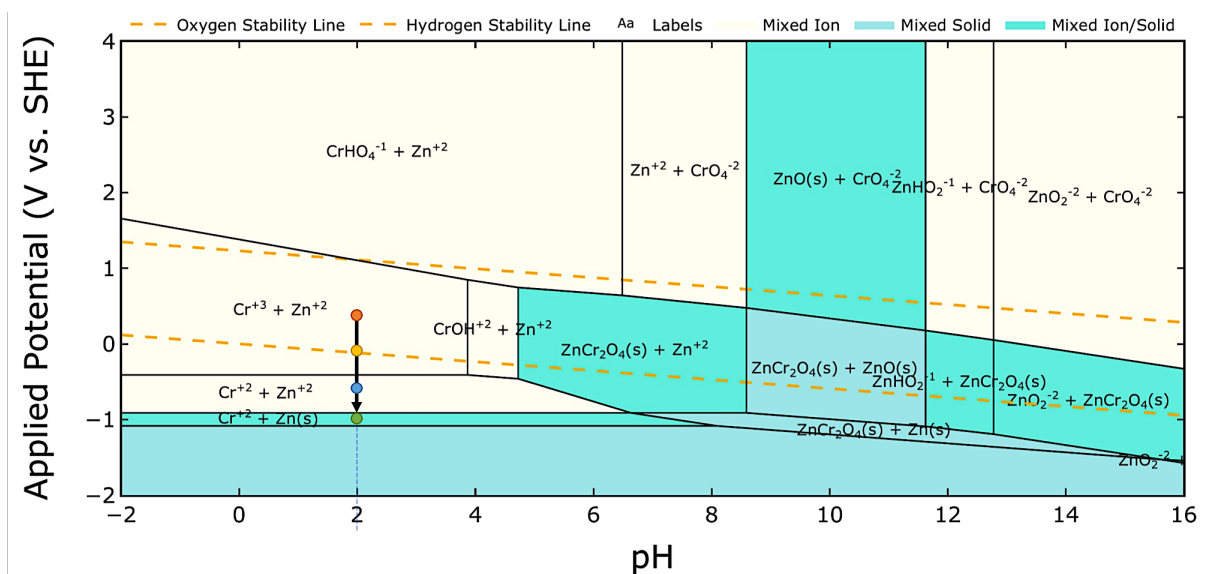


Fig. 8: Pourbaix diagram for the Zn-Cr system and reduction reactions occurring at pH 2

Referencing the Zn-Cr Pourbaix diagram [38] at pH 2, it is possible to see that when the substrate is cathodically polarized, the following reactions occur in order:

- Hydrogen evolution, which is inevitable, starts at the cathode;
- Trivalent chromium ions, Cr^{3+} , start to be reduced to divalent chromium ions, Cr^{2+} ;
- Zinc ions start being reduced into metallic zinc and deposited on the substrate;
- Finally, divalent chromium ions Cr^{2+} start being reduced into metallic chromium and deposited on the cathodic surface, creating the alloy.

This is the reason why the chromium content increases at increasing current densities, and the reason why below a certain current density there is no chromium in the alloy whatsoever. However, when the substrate is cathodically polarized up to a given potential, it does not correspond to a univocal value of current density: the corresponding current density depends on several factors.

As a matter of fact, at high overpotentials the deposition process is limited by the diffusion of the metallic species in the electrolyte, according to the Butler-Volmer equation. As the overpotential increases, the current density, instead of increasing, reaches a stagnant value, the limiting current density, which is linearly proportional to the concentration of the metallic ions in the bulk of the solution. This means that at higher concentrations, there are more trivalent chromium ions in the solution, and a lot more current is required in order to reduce them to divalent chromium ions before the reduction of zinc can begin. In other words, for more concentrated solutions, a higher current density is required to reach the same potential.

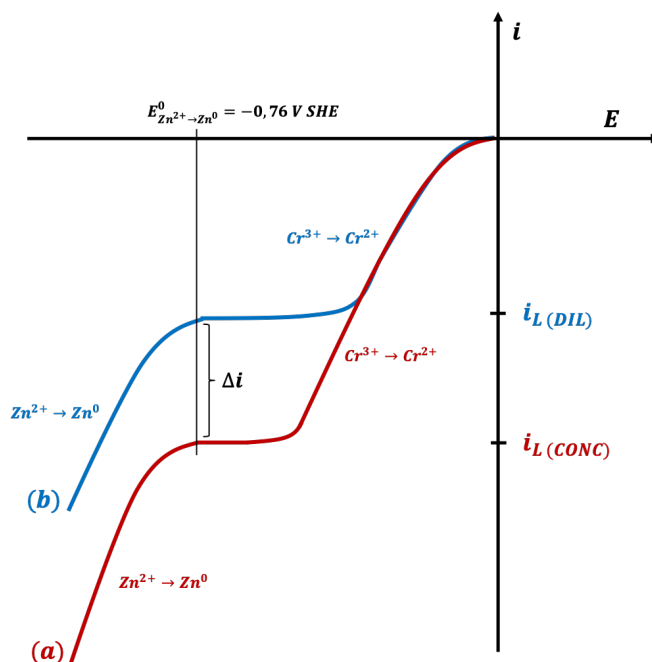


Fig. 9: Potential vs. current density dependence for Zn-Cr systems with different concentrations

Therefore, working with more concentrated solutions entails working at higher current densities to obtain the same results.

Due to these considerations, it was established to use lower concentrations for the formulation of the final electrolyte, landing on a formulation based on 0,2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0,067 $\text{Cr}_2(\text{SO}_4)_3$. This also explains why the current densities that were employed for the deposition of the coatings are considerably lower than the values cited in many sources, ranging from 60 to 180 mA/cm^2 against the 300-800 mA/cm^2 range more commonly found in literature [28, 29]. However, choosing to work at a lower concentration also implies that the depletion of metallic ions in the bath will occur much faster.

3.2.4. Change in the type of anion

Sulfates and chlorides are by far the most popular choices in terms of anions on which the plating bath is based. The differences between chloride-based baths and sulfate-based baths will be hereby discussed.

The chloride-based electrolyte contained:

ZnCl ₂ ·2H ₂ O	0,2 M
CrCl ₃ ·6H ₂ O	0,067 M
KCl	2M
H ₃ BO ₃	10 g/L

Two samples were obtained at current density values of (a) 50 and (b) 100 mA/cm² respectively, on carbon steel substrates with an exposed area of 1,5 cm², for 5 minutes each.

XRD analyses reported the presence in the resulting coatings of zinc and chromium oxides:

Sample (a)		Sample (b)	
Iron (substrate)		Iron (substrate)	
Zinc		Zinc	
Chromium dioxide	CrO ₂	Zinc oxide	ZnO
Hematite (substrate)		Chromium dioxide	CrO ₂

Table 1: XRD results for deposits obtained from chloride-based solutions

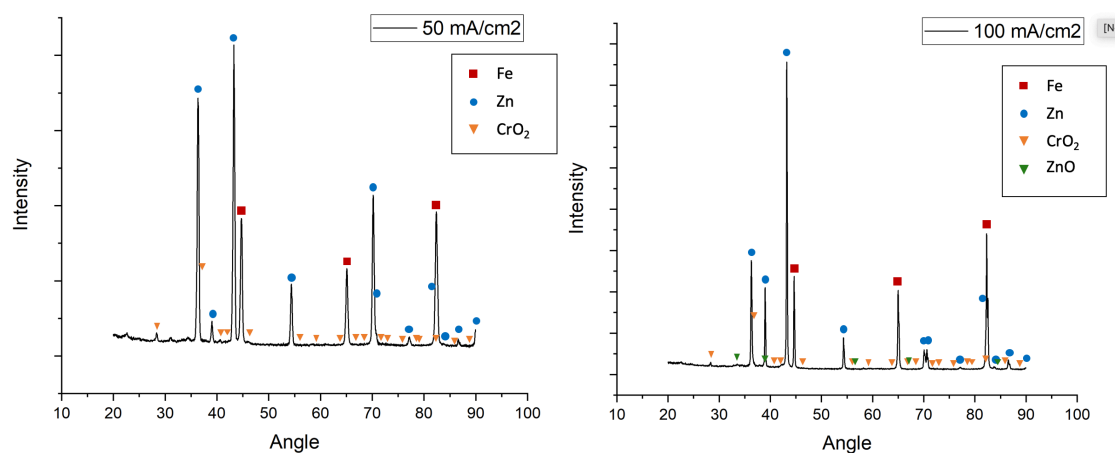


Fig. 10: XRD spectra for samples from chloride-based electrolytes

Instead, the aforementioned final sulfate-based electrolyte contains:

ZnSO₄ · 7H₂O 0,2 M

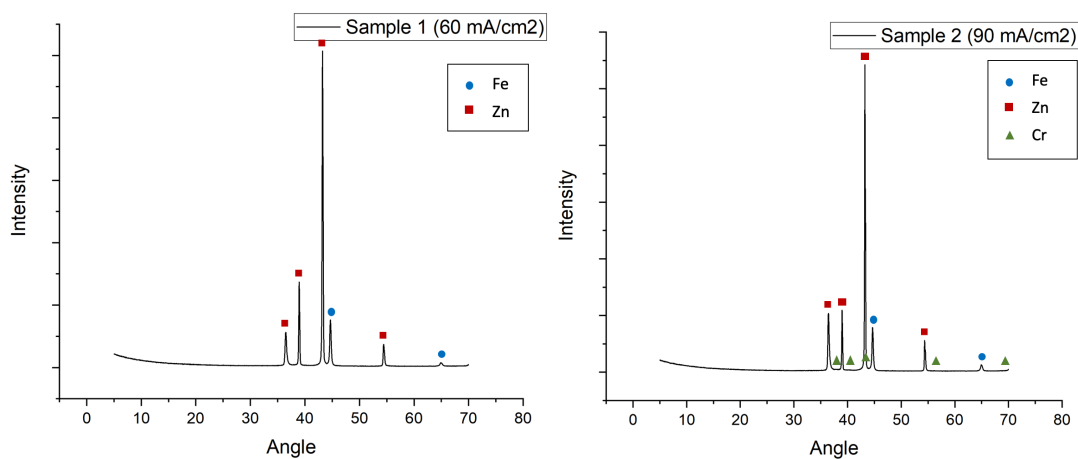
Trisurfín 0,1 M

Na₂SO₄ 1 M

The resulting coatings were deposited on carbon steel substrates with an exposed area of 2,25 cm² each respectively in the following conditions:

- 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 deposition time was adjusted so that the total charge density was kept constant at 1,8 C/cm². Despite having been deposited at much higher current density values, XRD analyses reported no presence of oxides of any kind in either coating. All coatings deposited from the sulfate-based solution only contained metallic zinc and metallic chromium.



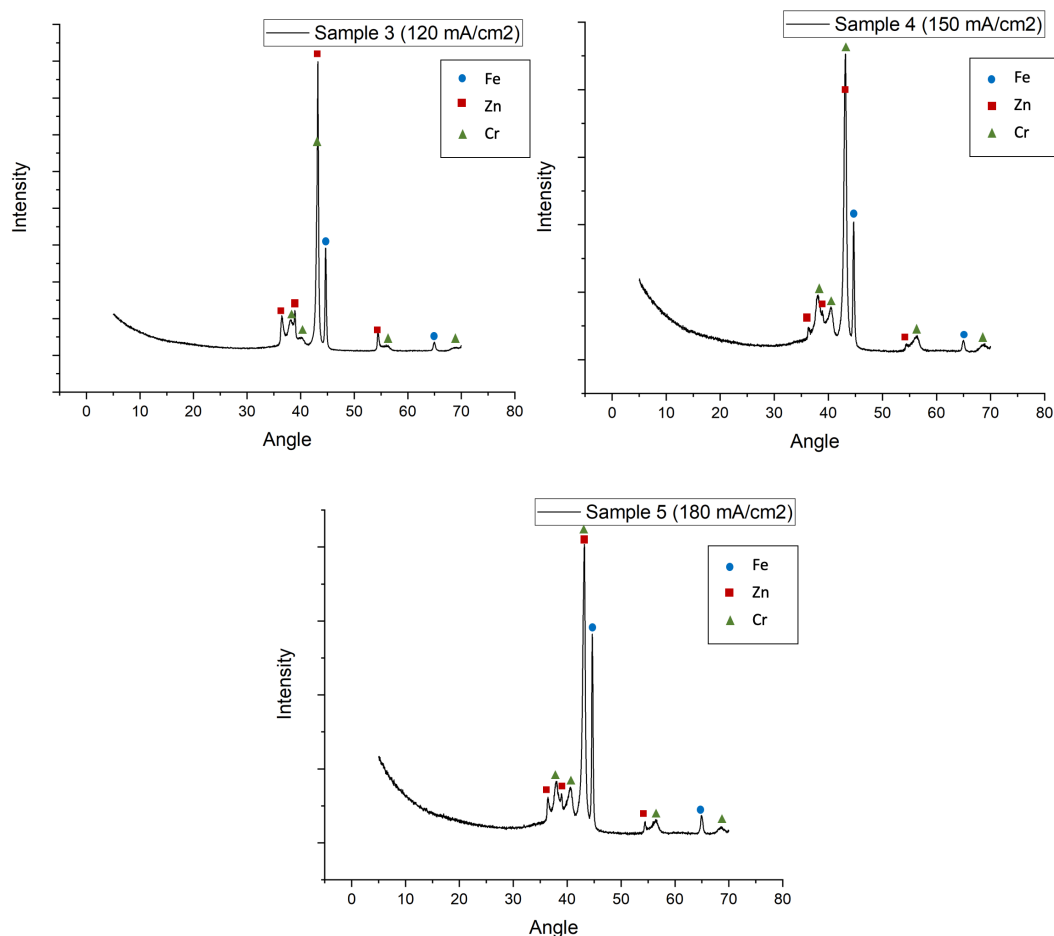


Fig. 11: XRD spectra for samples from sulfate-based electrolytes

The presence of oxides in the deposits obtained from the chloride-based bath may possibly be the reason why coatings containing an amount of chromium exceeding 1-2%, both in Hull cell samples and in single-deposition samples, appeared pitch black, burnt, or iridescent; conversely, deposits obtained from the sulfate-based bath, even at higher current densities appear dull, dark grey.

This final sulfate-based formulation is also coherent with a majority of the literature, as most sources mentioned using sulfate-based solutions with a zinc to chromium ratio varying between 1:3 and 1:4 [28 – 31, 33 – 35].

3.2.5. Variation of the current density

As previously explained, the necessary current density to achieve a certain cathodic polarization, and subsequently a certain composition of the deposit, strongly depends

on the concentration of the bath. However, once the concentration has been fixed, it is fair to say that an increase in the value of the current density leads to an overall higher chromium content in the coating. However, higher current densities also amplify the amount of hydrogen evolution occurring at the cathode as a side reaction, which in turn worsens the quality of the coating and risks to damage the substrate as well; moreover, higher current densities are also increasingly more likely to cause dendritic growth, which eventually turns into powdery deposits. Since the current densities that are required in the electrodeposition of zinc-chromium alloys are higher than average, most deposits tend to be rather porous, with samples deposited at the highest current densities displaying clear dendritic growth.

An easy and common way to study the relationship between the applied current density and the chromium content in the coating is using the Hull cell, an electrochemical cell in the shape of a right trapezoid with standardized dimensions. As the cathode is placed on the diagonal side, due to the geometry each portion of the surface will be subjected to a different current density, leading to a coating with a varying composition.

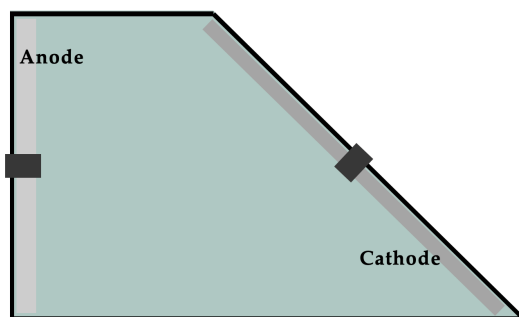


Fig. 12: Standard configuration of a Hull cell

Several Hull cell samples were retrieved for every formulation that was tested out; the table below represents four Hull cell samples obtained from different sulfate-based electrolytes with a standard content of zinc sulfate and sodium sulfate at:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0,2 M
Na_2SO_4	1 M

And, respectively, the following amounts of chromium sulfate from Trisurfin and their relative zinc sulfate to chromium sulfate ratios:

- 0,2 M $\text{Cr}_2(\text{SO}_4)_3$ for a 1:1 ratio
- 0,067 M $\text{Cr}_2(\text{SO}_4)_3$ for a 3:1 ratio
- 0,04 M $\text{Cr}_2(\text{SO}_4)_3$ for a 5:1 ratio
- 0,029 M $\text{Cr}_2(\text{SO}_4)_3$ for a 7:1 ratio

Each Hull cell was obtained from depositions with a current of 1600 mA lasting 1 minute and 15 seconds each. The composition and thickness of the deposits was retrieved with XRF tests. The following graph better represents the trend that can be retrieved from the Hull cell samples.

i (mA/cm ²)	7:1		5:1		3:1		1:1	
	%Cr	Thickness (μm)	%Cr	Thickness (μm)	%Cr	Thickness (μm)	%Cr	Thickness (μm)
32	0,570	1,16	0,393	1,15	0,040	1,00	1,34	0,870
64	8,70	2,02	0,737	1,96	2,62	1,80	16,4	1,48
128	11,8	0,352	18,54	3,75	22,1	3,40	28,0	2,72
192	12,7	0,567	16,8	0,537	32,0	0,469	33,6	1,13
320	12,3	0,477	15,2	0,609	23,9	0,706	50,8	0,933
Average	9,206	0,914	10,35	1,602	16,12	1,476	26,03	1,427

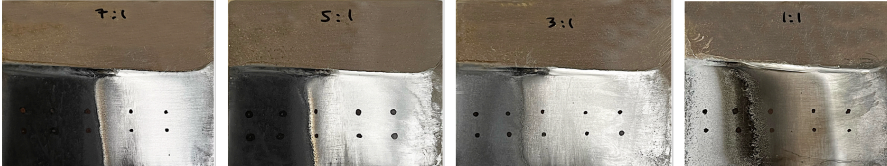


Table 2: Hull cell samples for sulfate-based electrolytes with varying ZnSO_4 : $\text{Cr}_2(\text{SO}_4)_3$ ratios

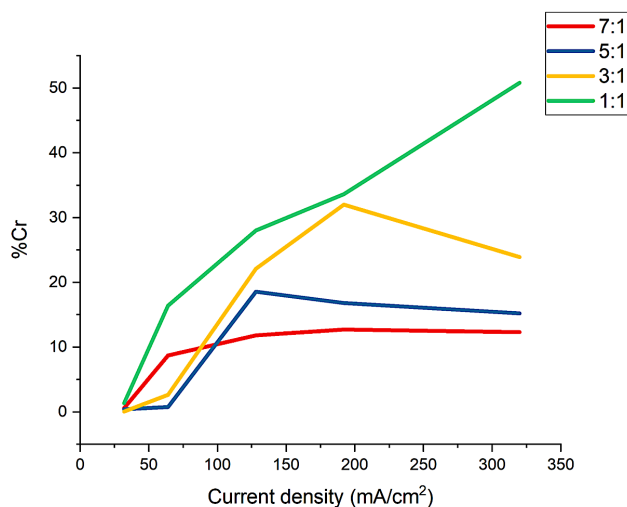


Fig. 13: Chromium content varying with the current density for different ZnSO_4 : $\text{Cr}_2(\text{SO}_4)_3$ ratios, as retrieved from Hull cell samples

However, as useful as Hull cell samples can be to have a broad overview on how the chromium content changes with the current density, it is not the most precise way to quantitatively display said relationship. This is especially true considering the small dimension of the resulting samples, which were obtained using a Tenori Hull cell from Yamamoto-MS fit to contain 33 mL of electrolyte.

As a matter of fact, what appeared to be a sudden plateau-like increase in the chromium content of the coating from Hull cell samples was likely just a steep linear increase. When 14 single-deposition samples were retrieved from the final electrolyte, each deposited at current density values separated by a progressive 10 mA/cm² step increase, it was possible to confirm the latter case.

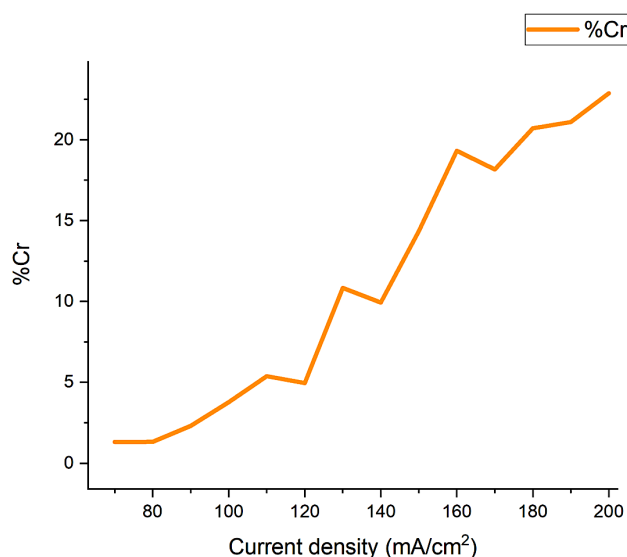


Fig. 14: Chromium content varying with the current density for the 3:1 ZnSO₄: Cr₂(SO₄)₃ electrolyte, as retrieved from 14 single-deposition samples

3.3. Tested additives

Many sources pointed out that, to aid the codeposition, some additives might be of help [30, 31, 34]. The first compound that was tested was boric acid, which is a commonly used buffer in electrodeposition in acidic mediums.

3.3.1. Buffers and complexing agents

Boric acid appeared to be so common in literature that all tested formulations included it at first, at a concentration of 10 g/L. However, it became rapidly clear that it actually had little to no effect as a buffer. Several samples of chloride-based electrolytes based on 0,2 M $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 M KCl with different Zn:Cr ratios and different initial pH levels were made, and their pH was tested again after three days:

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 3: Variation of the pH despite the use of boric acid

To test its buffering ability against variations related to electrochemical changes, a prolonged deposition lasting 10 minutes was performed, measuring the pH every two minutes, starting from pH 3. The electrolytes were sulfate-based, containing 0,2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 1 M Na_2SO_4 and 0,2 M $\text{Cr}_2(\text{SO}_4)_3$, added as Trisurfin. The depositions were carried out on carbon steel substrates with an exposed area of 2,25 cm^2 at a current density of 150 mA/cm^2 . However, the results were unsatisfactory, as boric acid only showed a marginal improvement, ending at a pH of 2,71 versus the final pH of 2,70 of the control solution.

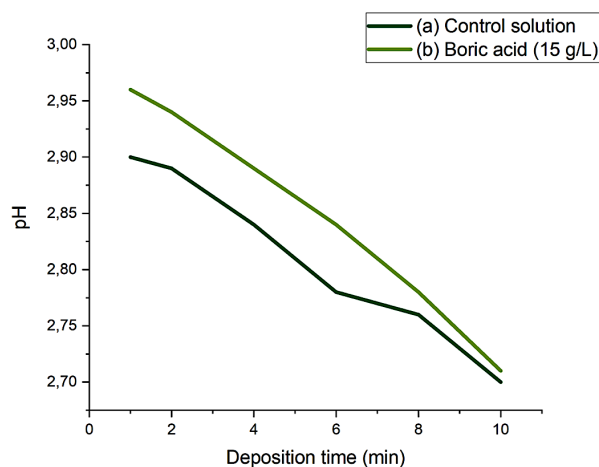


Fig. 15: pH variation during a 10-minute deposition for (a) an electrolyte without boric acid and (b) an electrolyte containing 15 g/L of boric acid

These results, however, were coherent with the literature, which stated that boric acid does not really work as a buffer at such low pH values, as its buffering ability is shown at much higher pH values [30, 34]. Boric acid was therefore excluded from the formulation of the final electrolyte, as it seemed to serve very little purpose.

After boric acid was discarded, other additives were analyzed. As glycine seemed to be a popular additive in Cr(III) and Zn-Cr plating baths, it was tested in sulfate-based electrolytes in various concentrations and at two different pH levels, 2 and 3. First off, glycine definitely proved to be a strong buffer, as some sources had pointed out [30]. The same aforementioned 10-minute deposition test was performed on glycine to test its buffering ability; the sulfate-based solution with the same basic composition was provided with 45 g/L of glycine. Meanwhile, succinic acid in a 15 g/L concentration was also tested as a buffer, but it led to similarly unsatisfactory results to those of boric acid.

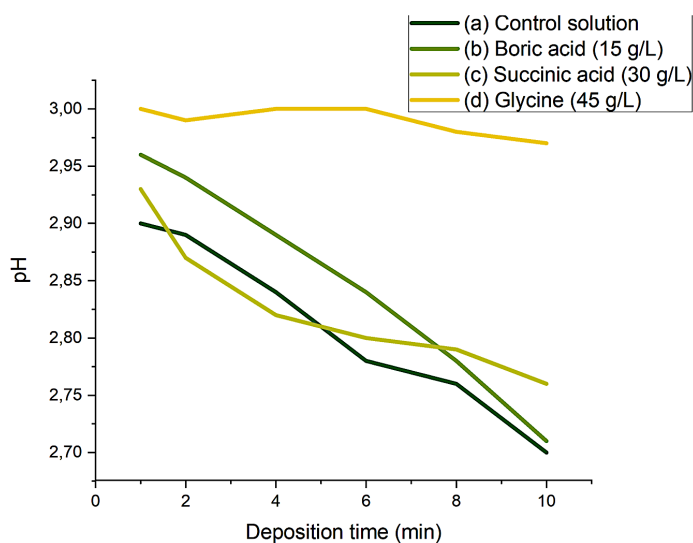


Fig. 16: Comparison of the buffering ability of (a) a control solution, (b) boric acid, (c) succinic acid and (d) glycine during a 10-minute long electrodeposition

Despite its buffering capability, the addition of glycine to the plating bath led to some confusing results.

Glycine proved its complexing ability towards chromium, which is likely responsible of the color change of the solution from green to deep blue, by effectively lowering the chromium content in the resulting deposits, as it was to be expected. Hull cells obtained from two sulfate-based electrolytes at pH 2 containing 40 g/L of glycine were

confronted with Hull cell samples obtained from their respective control solutions. The base solutions contained 0,2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 1 M Na_2SO_4 and two different amounts $\text{Cr}_2(\text{SO}_4)_3$, added as Trisurfin, to give respectively a 3:1 and a 7:1 zinc sulfate to chromium sulfate ratio. Solutions were heated for 1 hour at 80°C and cooled down to the working temperature of 25°C ; Hull cell samples were obtained from depositions with a current of 1600 mA for 1 minute and 15 seconds. Results, except for outlier values, show a decrease in chromium content in the deposit due to the presence of glycine.

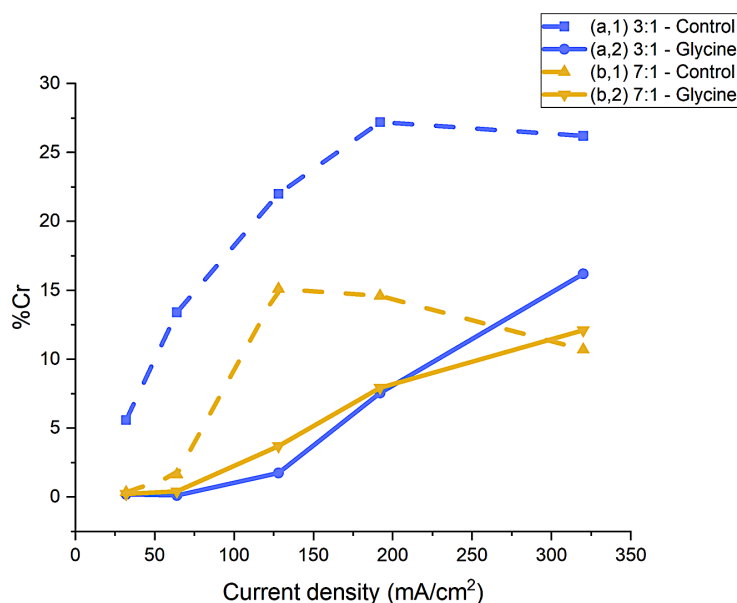


Fig. 17: Comparison of the chromium content of deposits obtained from electrolytes without (1) and with (2) glycine, for 3:1 (a) and 7:1 (b) zinc sulfate to chromium sulfate ratios

It is also possible that glycine cannot act as a buffer and as a complexing agent at the same time. Sources [30] that cite glycine as a good buffer for Zn-Cr plating baths do not report heating the solution before the deposition, while sources regarding the role of glycine as a complexing agent for trivalent chromium [25, 26] prepare the solution by heating at temperatures varying from $80\text{-}100^\circ\text{C}$ for around 1 hour and letting it cool down after the deposition. Performing the 10-minute deposition test to monitor the pH variations of electrolytes containing glycine which had been heated at 80°C for 1 hour show a much lower buffering ability. It is possible that heating accelerates the complexation of chromium which may have had only just begun in the electrolyte used in the previous 10-minute deposition. The following tests were performed from five different solutions containing varying amounts of glycine, to obtain five different

chromium(III) sulfate to glycine ratios, respectively 1:4, 1:2, 1:1, 2:1, 4:1. The base of each electrolyte contained 0,2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 1 M Na_2SO_4 and 0,029 M $\text{Cr}_2(\text{SO}_4)_3$ added as Trisurfing; by comparison, the electrolyte which was used for the first 10-minute deposition contained a chromium(III) sulfate to glycine ratio of around 3:1. However, all concentrations led to very similar pH variations, which did not hold up to the initial results.

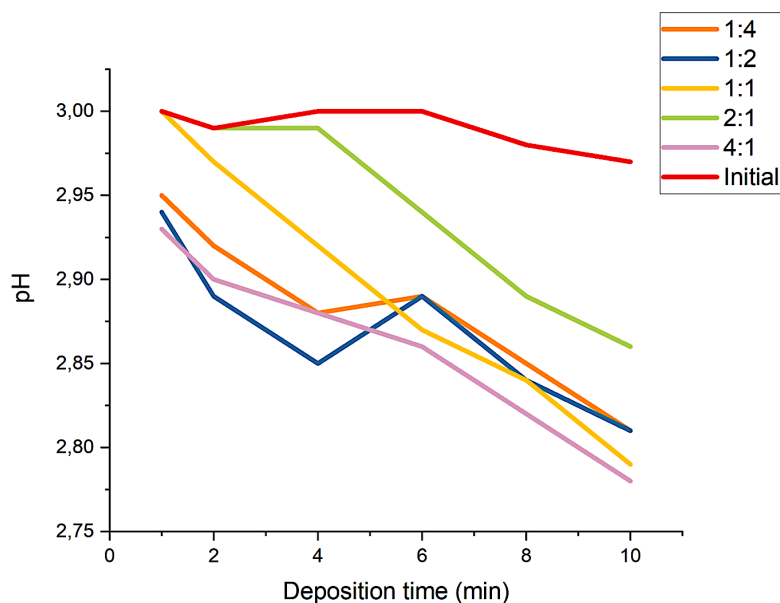


Fig. 18: Comparison of buffering ability of glycine when the solution has been heated vs. when it has not been heated (red line)

It is therefore plausible that at first, when glycine has probably only begun reacting with the chromium ions, the unreacted portion of glycine worked well as a buffer, while later on, after heating the solution and presumably completing the reaction, it only serves as a complexing agent, thus losing a lot of its buffering ability.

To further elucidate the role of glycine, cyclic voltammetries were performed on four separate electrolytes to separately test the effect of glycine on zinc and chromium. All four solutions contained 1 M Na_2SO_4 and they had the following compositions, respectively:

- 0,2 M ZnSO_4
- 0,2 M ZnSO_4 + 40 g/L glycine
- 0,029 M $\text{Cr}_2(\text{SO}_4)_3$
- 0,029 M $\text{Cr}_2(\text{SO}_4)_3$ + 40 g/L glycine

Additionally, all the solutions were adjusted to pH 2. The chromium(III) sulfate solutions were based on the addition of Trisurfur. Cyclic voltammeteries used an Ag/AgCl reference electrode, a platinum grid electrode as a counter electrode, and glassy carbon as a working electrode. Glassy carbon was chosen as the working electrode due to its high overpotential for hydrogen evolution. Between each test, the electrode was etched with H_2SO_4 and mechanically polished with an alumina powder suspension.

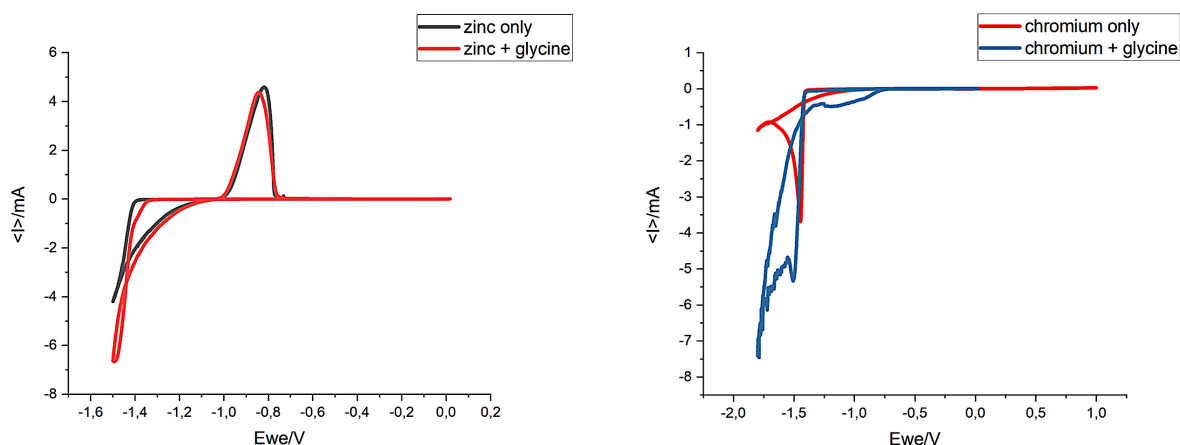


Fig. 19: Cyclic voltammeteries for electrolytes based on zinc, zinc and glycine, chromium, and chromium and glycine

The cyclic voltammeteries led to some interesting results.

- Despite the initial expectations that glycine would have no effect on the deposition of zinc, it seems that glycine actually facilitates its reduction, likely behaving as a complexing agent. It is, however, interesting to point out that glycine apparently facilitates the deposition by increasing the reduction potential of zinc, instead of decreasing it like most complexing agents. Nevertheless, it is clear that the deposition is promoted, considering both the nobler reduction potential and the increased value of the cathodic current.
- The cyclic voltammeteries also confirm the role of glycine as a complexing agent for chromium: it appears that its main effect is increasing the stability of divalent chromium, since glycine increases the reduction potential of the reduction from trivalent chromium to divalent chromium, while simultaneously decreasing the reduction potential of the reduction from divalent chromium to metallic chromium. Nevertheless, the ultimate result is

that higher overpotentials are needed to obtain the deposition of metallic chromium, as it was expected.

Ultimately, the combination of these two effects explains the decreased chromium content in samples obtained from electrolytes containing glycine, since glycine simultaneously favors the deposition of zinc while inhibiting the deposition of chromium.

Cyclic voltammeteries were also performed on the final electrolyte, which has the following formulation:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0,2 M	
$\text{Cr}_2(\text{SO}_4)_3$	0,067 M	(added as Trisurfin 0,1 M)
Na_2SO_4	1 M	

The results were compared to the cyclic voltammetry performed on the pure zinc electrolyte. Both solutions had been heated to 80°C for 1 hour and rested for a week before the cyclic voltammeteries were performed.

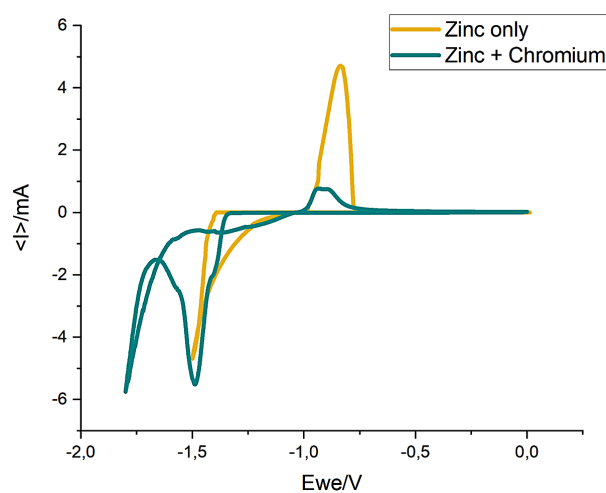


Fig. 20: Cyclic voltammeteries for the zinc-chromium electrolyte and for the pure zinc electrolyte

The most prominent feature of these results is the relative difference in the anodic peaks: it is very clear that the presence of chromium has a strong hindering effect with respect to the dissolution of the coating. Moreover, following the cathodic branch of the Zn-Cr cyclic voltammetry (blue), it is possible to see a significant current at

potentials higher than the reduction of zinc (yellow), possibly indicating the reduction from Cr(III) to Cr(II). Still, an inflection point signaling the start of the zinc reduction in the Zn-Cr electrolyte appears at the same potential of the reduction of zinc in the pure zinc electrolyte: this means that the deposition of zinc is virtually unaffected by the presence of chromium.

Nevertheless, the main problem with the addition of glycine was the instability of the solution and the inconsistency of many of the results that were recovered. The preparation process for the electrolyte, which entails heating at 80°C for 1 hour, certainly accelerates any reaction that is occurring, as attested by the color change of the solution, from pine green to a dark, purplish blue. Such color change occurs spontaneously overtime without heating the solution, but it is unclear how long this process would normally take. Moreover, the sources cite heating the solution as a step of the preparation process [25, 26], but do not state the reason behind it, nor does it appear to be certain whether it suffices in bringing to term any occurring reaction in the solution. It is therefore unclear whether the solution is considered to be stable. As a matter of fact, 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.

For example, samples were obtained at pH 2 from two different electrolytes with the same formulation containing:

ZnSO ₄	0,2 M	
Na ₂ SO ₄	1 M	
Cr ₂ (SO ₄) ₃	0,029 M	(added as 0,043 M Trisurfin)
Glycine	45 g/L	

The solution had been heated at 80°C for 1 hour and cooled down to a working temperature of 25°C; the depositions were carried out at 60 mA/cm² for 5 minutes and at 40 mA/cm² for 7 minutes and 30 seconds on carbon steel substrates with an exposed area of 2,25 cm². In both cases, the depositions occurred just after the solutions had reached the proper working temperature. However, the results turned out to be rather different:




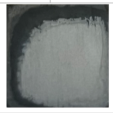
<i>i</i>	60 mA/cm ²		40 mA/cm ²		<i>i</i>	60 mA/cm ²		40 mA/cm ²	
	% Cr	Thickness (μm)	% Cr	Thickness (μm)		% Cr	Thickness (μm)	% Cr	Thickness (μm)
Pt 1	-0,006	3,79	-0,029	3,81	Pt 1	0,546	2,70	-0,008	4,07
Pt 2	0,058	4,08	0,020	4,69	Pt 2	0,929	3,18	0,165	4,40
Pt 3	-0,018	3,82	-0,035	4,61	Pt 3	1,78	1,93	0,032	6,43
Average	0,011	3,895	-0,015	4,369	Average	1,084	2,602	0,063	4,967
									

Table 4: Different samples obtained from electrolytes with the same composition, preparation and operational parameters

3.3.2. Polyethylene glycol (PEG) 3000

The addition of PEG with molecular weights ranging from 1500 to 6000 g/mol and in concentrations ranging from 0,1 to 1,0 g/L seemed to lead to good results according to the literature [31]. PEG 3000 was added to the following formulation in three different concentrations, respectively 0,1 g/L, 0,5 g/L and 1,0 g/L:

ZnSO ₄	0,2 M	
Na ₂ SO ₄	1 M	
Cr ₂ (SO ₄) ₃	0,029 M	(added as 0,043 M Trisurfin)
Glycine	45 g/L	

The solution did not undergo the heating portion of the bath preparation as it was not cited as part of the process, and neither was the control solution. The fact that the control solution was not heated therefore signifies that the glycine had likely not reacted with the chromium ions, and thus was not acting as a complexing agent. Depositions were conducted at pH 3 and 25°C with a current of 1600 mA for 1 minute and 15 seconds. However, the addition of PEG 3000 led to very poor results and only Hull cell samples were retrieved:

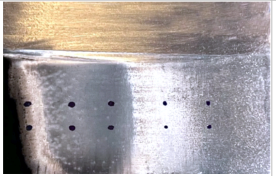
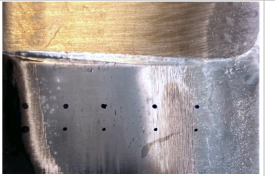
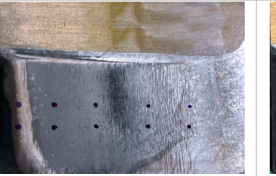
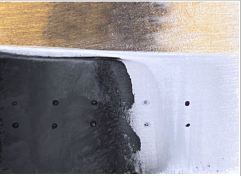
<i>i</i>	0,1 g/L PEG 3000		0,5 g/L PEG 3000		1,0 g/L PEG 3000		Control solution	
	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	%Cr	Thickness (μm)
32	3,06	0,210	4,89	0,571	6,11	0,208	0,025	1,22
64	10,5	0,931	9,01	1,80	10,2	0,976	2,32	2,01
128	10,8	2,07	9,54	2,32	10,5	2,07	10,1	1,50
192	11,6	2,74	11,7	2,69	11,4	2,70	10,1	1,08
320	5,84	2,72	5,59	2,24	5,81	2,77	10,6	1,12
								

Table 5: Effect of the addition of different concentrations of PEG 3000 to an unheated sulfate-based bath containing glycine

3.4. Final results and discussion

Due to the unsuccessful tests regarding the additives, the final electrolyte had the following formulation:

ZnSO₄ · 7H₂O 0,2 M

Cr₂(SO₄)₃ 0,067 M (added as Trisurfin 0,1 M)

Na₂SO₄ 1 M

Despite not containing glycine, the electroplating bath was still 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. The bath was maintained at pH 2.

As previously mentioned, carbon steel substrates were sanded with 240 and 400 grid sandpaper, rinsed, cleaned in ethanol in an ultrasonic sonicator for 10 minutes, masked with Kapton tape leaving an exposed area of 2,25 cm² (1,5 cm x 1,5 cm), degreased with acetone, etched in a 10 wt.% HCl solution, rinsed with deionized water, and dried with nitrogen. After the deposition, they were once again rinsed and dried.

Samples were deposited while maintaining a bath agitation of 250 rpm through the use of a magnetic stirrer; they were obtained with five different current densities:

- 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

Three sets of samples were deposited; the results were generally reproducible. The coatings deposited at lower current densities appeared dull and light gray, while deposits containing higher amounts of chromium became darker, visibly more dendritic and more porous. Samples deposited at high current densities manifested a lower adhesion to the substrate and appeared to be rather brittle as parts of them detached from the surface. Using an ultrasonic sonicator greatly helped in improving the adhesion of the coatings to the substrate, and ultimately it is likely that the detachment of the coatings at the edges of the exposed area was more due to the higher relative current density at the borders of the substrate rather than to the nature of the coating. The deposits appear relatively homogeneous; the average thickness ranges from 3,5 to 4,5 μm .

The chromium content in the coatings varies relatively smoothly with the current density.

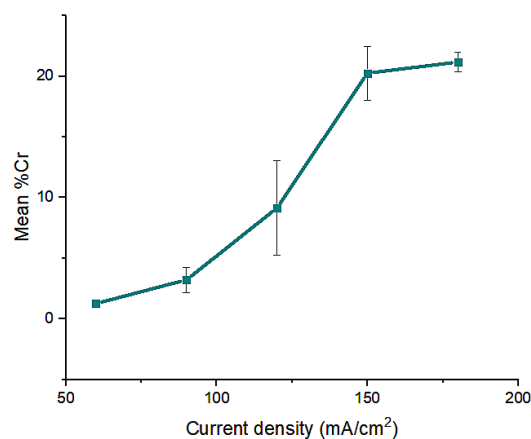


Fig. 21: Variation of chromium content with the current densities for different sets of samples

The following tables report the chromium content and the thickness of each coating for all three sets; results were retrieved via XRF.

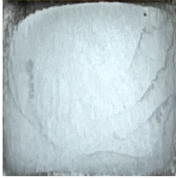

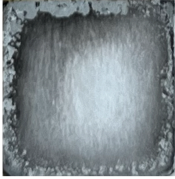
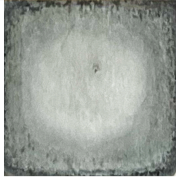
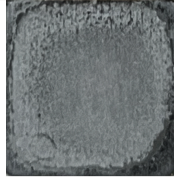
i (mA/cm ²)	60		90		120		150		180	
	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)
Pt 1	0,302	3,83	1,30	3,27	4,48	3,15	17,6	3,89	17,4	3,20
Pt 2	1,63	3,90	4,83	3,72	13,7	3,69	22,5	4,72	22,5	4,08
Pt 3	1,65	4,49	2,49	3,73	5,51	3,57	24,3	5,09	21,5	3,41
Average	1,194	4,075	2,872	3,575	7,904	3,469	21,45	4,568	20,45	3,563
										
Weight (mg)	10,6		10,4		18,0		(30,0)		7,6	

Table 6: First set of electrodeposited Zn-Cr alloy coatings

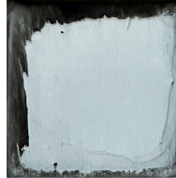
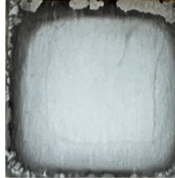
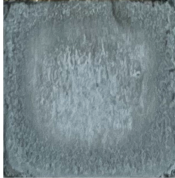
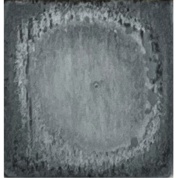
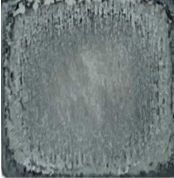
i (mA/cm ²)	60		90		120		150		180	
	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)
Pt 1	0,949	3,22	1,50	3,22	12,8	3,58	17,5	3,94	17,5	3,20
Pt 2	1,54	3,28	2,90	4,18	15,0	3,96	23,7	5,44	24,1	3,79
Pt 3	0,855	3,75	2,80	3,54	12,7	3,51	23,8	4,94	21,5	3,74
Average	1,114	3,416	2,399	3,679	13,50	3,683	21,63	4,776	20,99	3,574
										
Weight (mg)	10,3		(23,3)		9,4		11,4		9,5	

Table 7: Second set of electrodeposited Zn-Cr alloy coatings

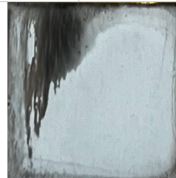
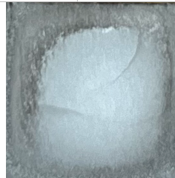
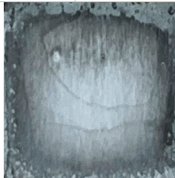
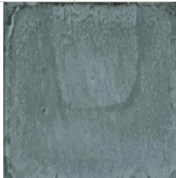
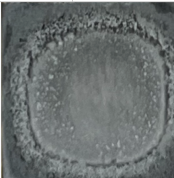
i (mA/cm ²)	60		90		120		150		180	
	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)	% Cr	Thickness (μm)
Pt 1	0,610	3,63	2,28	3,20	4,39	3,09	15,4	3,09	18,2	3,78
Pt 2	2,20	3,01	5,77	3,52	4,26	3,24	19,5	3,72	25,4	5,13
Pt 3	1,70	4,65	5,14	3,10	9,50	4,10	18,2	3,71	22,6	4,29
Average	1,503	3,764	4,395	3,273	6,052	3,477	17,70	3,505	22,07	4,398
										
Weight (mg)	10,9		11,3		14,9		8,2		11,0	

Table 8: Third set of electrodeposited Zn-Cr alloy coatings

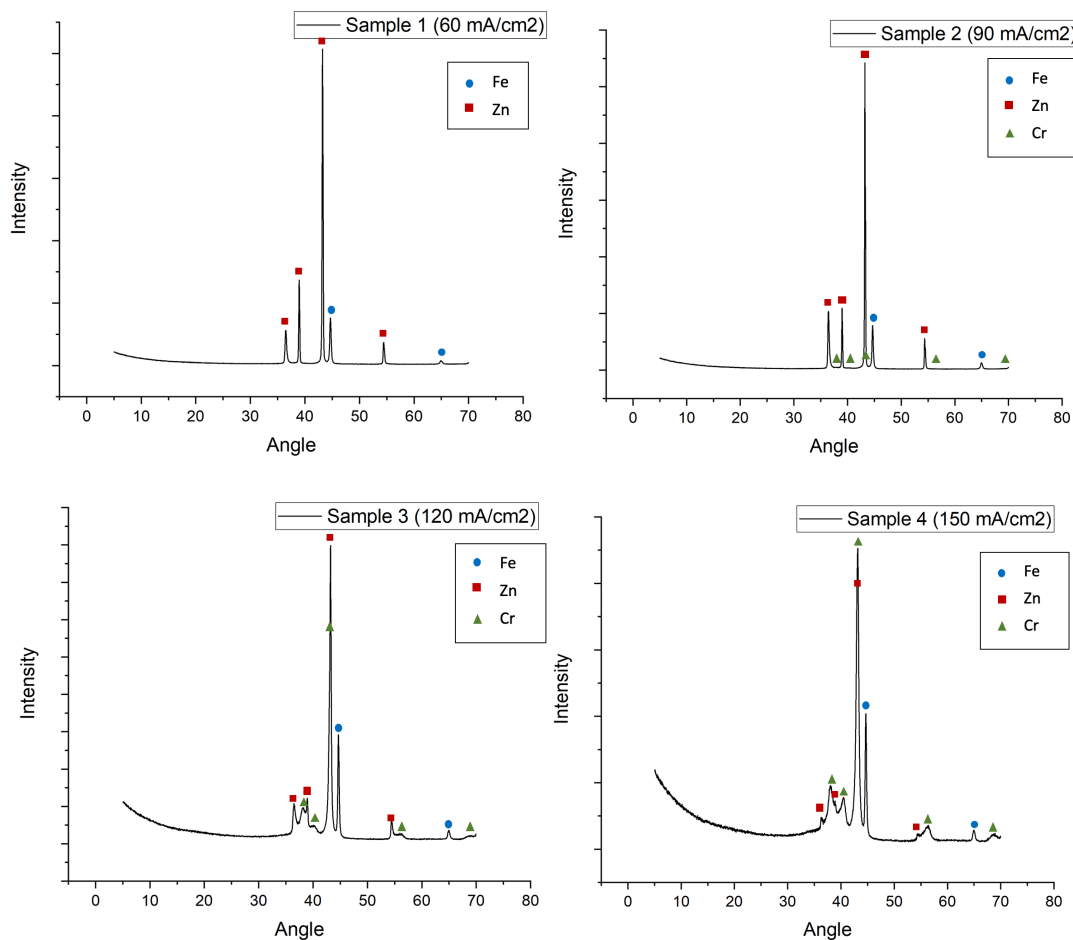
The cathodic efficiency of the deposition was evaluated considering the deposited mass of each coating, their composition, and the total charge density Q , following this relationship:

$$C.E. = \frac{(z_{Cr} \cdot n_{Cr} + z_{Zn} \cdot n_{Zn}) \cdot F}{Q} \cdot 100$$

Excluding outlier values (sample n.3 and n.4 of set n.1 and sample n.2 of set n.2), the average cathodic efficiency was reported to be:

- 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 tests were performed on the first set of samples: all coatings were reported to only contain metallic zinc and metallic chromium.



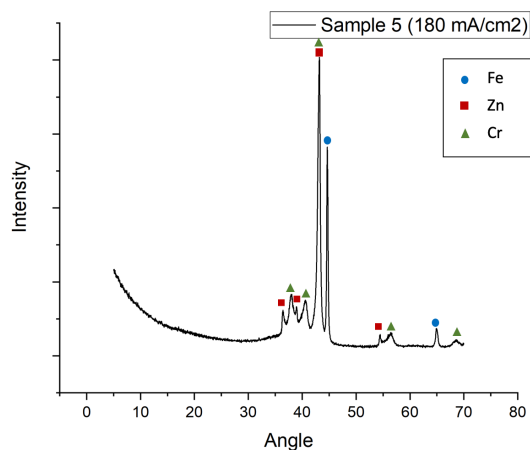


Fig. 22: XRD spectra for the first set of samples

The first set of samples also underwent SEM imaging: it is possible to see the morphology changes with increasing current densities, shifting from a more compact deposit to a highly dendritic coating.

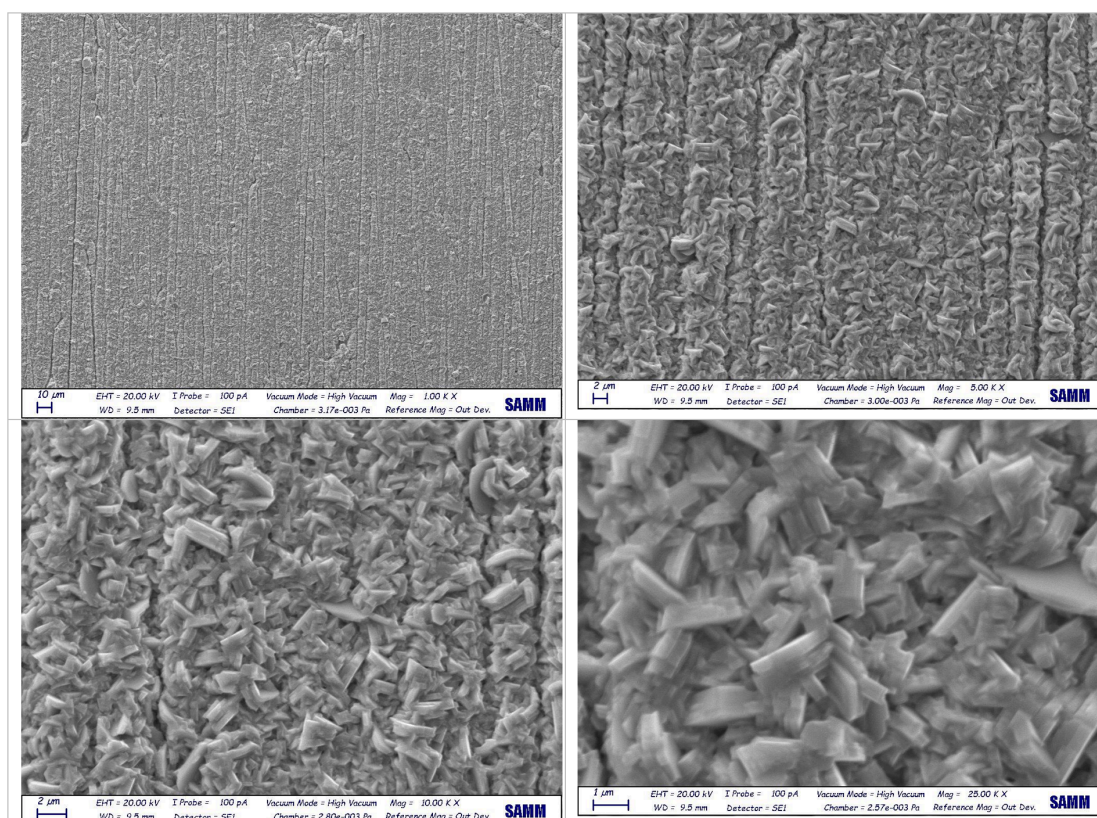


Table 9: SEM images for Zn-Cr coating deposited at 60 mA/cm²

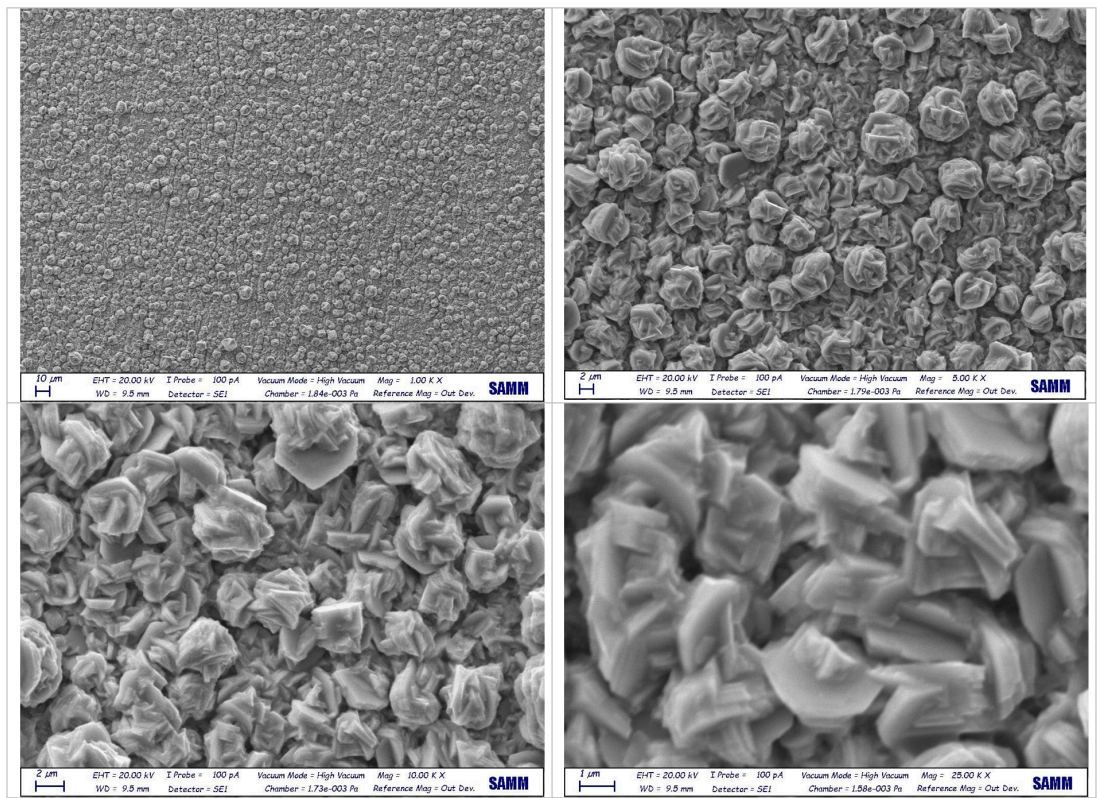


Table 10: SEM images for Zn-Cr coating deposited at 90 mA/cm^2

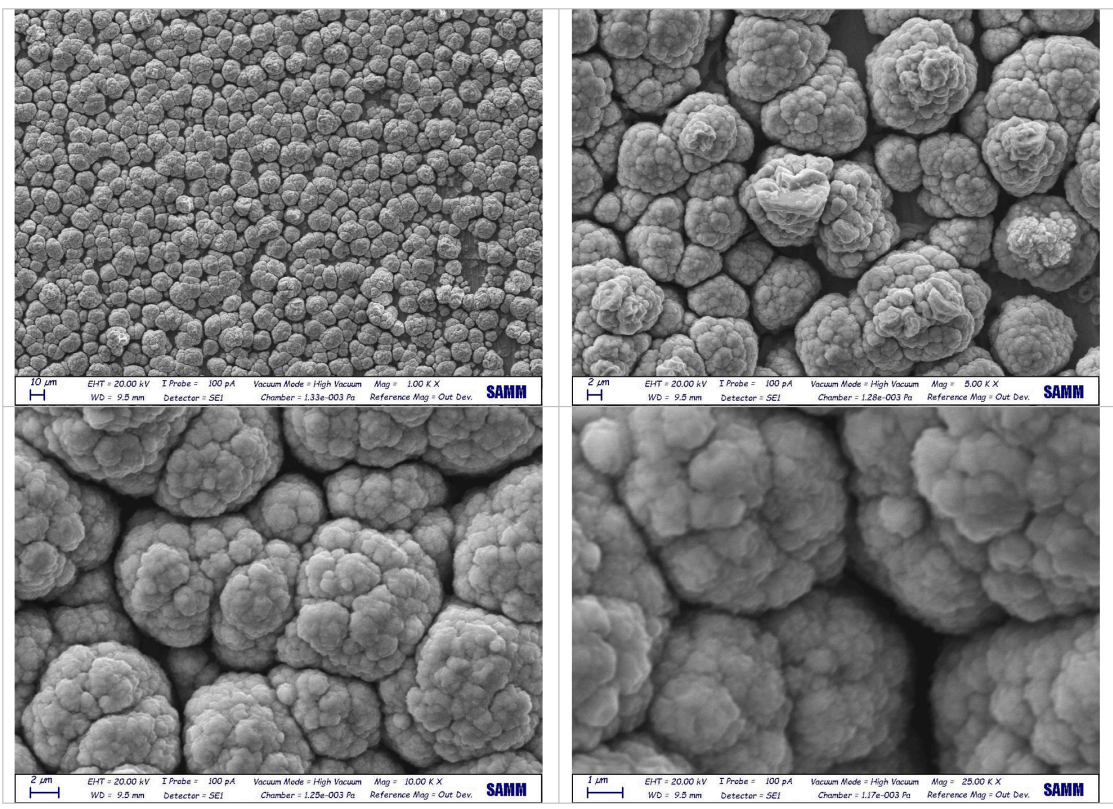


Table 11: SEM images for Zn-Cr coating deposited at 120 mA/cm^2

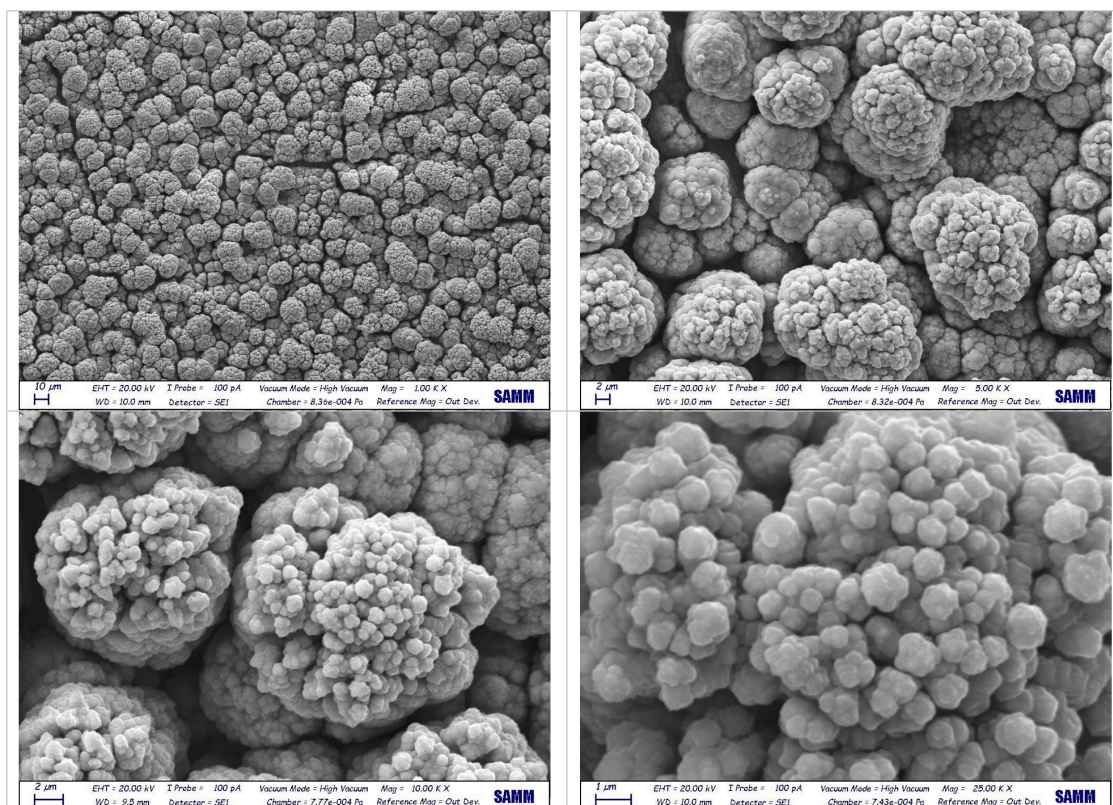


Table 12: SEM images for Zn-Cr coating deposited at 150 mA/cm^2

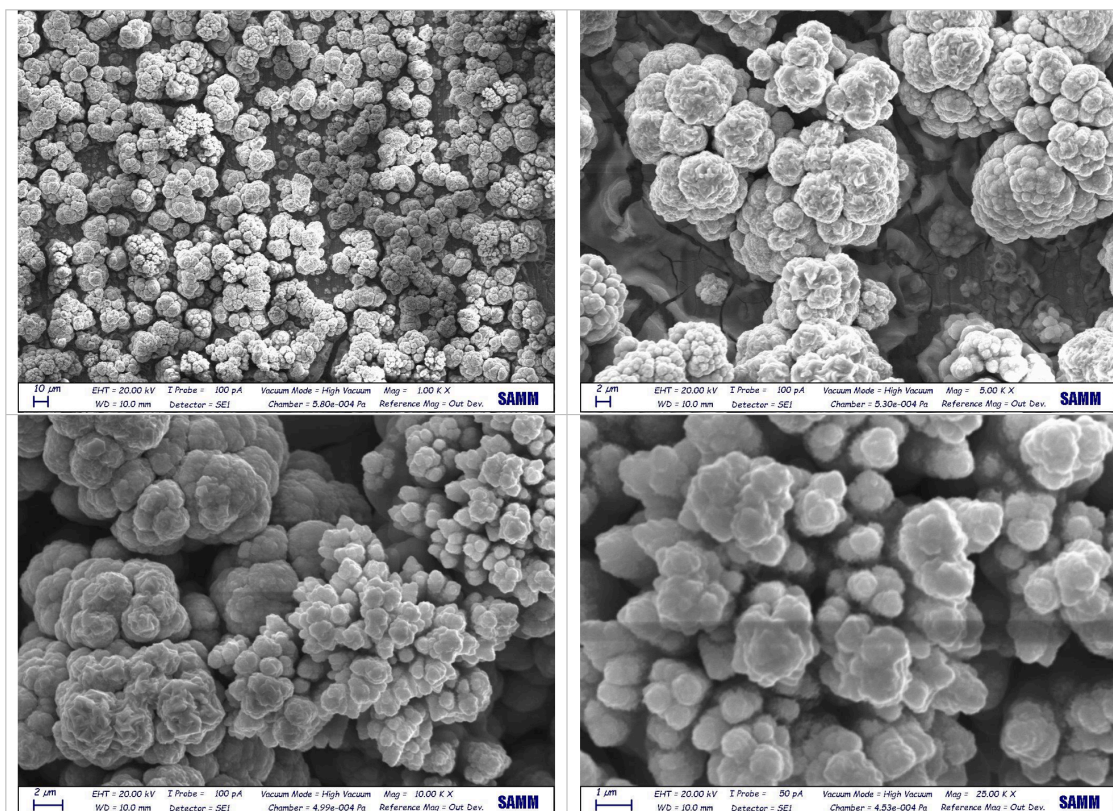


Table 13: SEM images for Zn-Cr coating deposited at 180 mA/cm^2

Finally, the second set of coatings underwent Tafel polarization tests in order to assess the corrosion resistance of the alloy; the first sample was approximately considered to represent a pure zinc coating as a reference. The tests were performed in 0,1 M Na₂SO₄, using an Ag/AgCl reference electrode and a platinum mesh as a counter electrode.

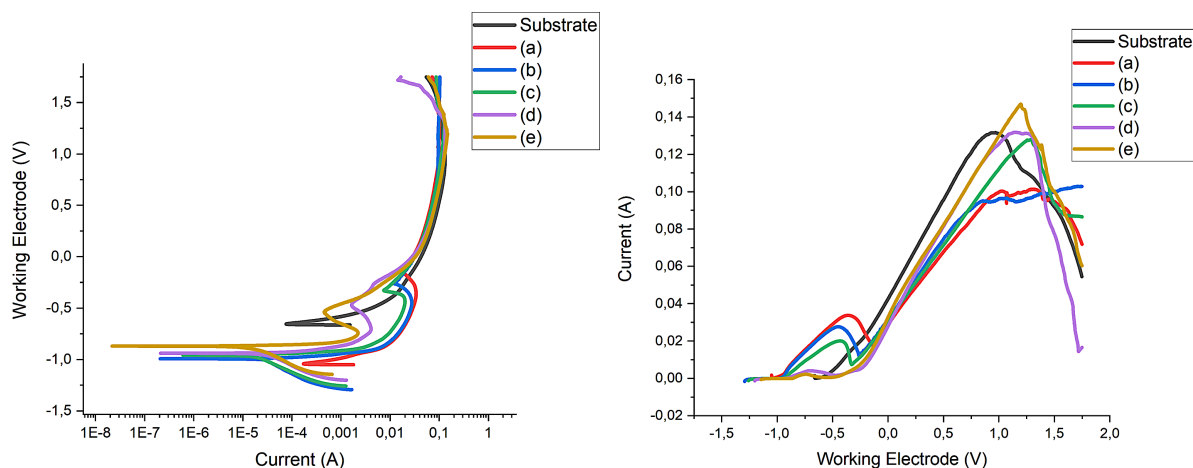


Fig. 23: (a) Tafel polarization curves recovered for all samples; (b) the same results plotted on a linear scale.

The Tafel polarization curves (a) show that coated samples exhibit a lower corrosion potential than the substrate. This shift is to be expected if the standard reduction potentials of zinc or iron (substrate) are taken into account; increasing amounts of chromium in the deposits tend to make the coatings more noble than pure zinc, as their corrosion potential increases, while still preserving their sacrificial barrier function. A set of anodic peaks at potentials higher than the corrosion potential is associated to the dissolution of the zinc coating; after its complete removal, the polarization curves tend to start following the polarization curve of the substrate. However, it is possible to see that coatings containing higher amounts of chromium display a significantly less pronounced dissolution peak, suggesting that the addition of Cr might have a beneficial effect on the zinc coating corrosion behavior, which is confirmed by the cyclic voltammeteries performed on the electrolyte. This effect is better represented in graph (b), which shows the gradual drop in the height of the dissolution peak of the coating. Despite this, the Tafel polarization curves show that components coated with Zn-Cr alloys still behave as active metals, meaning that the chromium content in the coating is not sufficient to promote the passivation of the deposit.

3.5. Remaining issues in the electrolyte

Despite the decent results that were obtained, there are many still-standing issues in the electrodeposition of zinc-chromium 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 electrolyte, thus affecting the electrochemical behavior of the solution: this peculiar unpredictable behavior is likely due to the presence of trivalent chromium, since, as many sources point out in literature, they can undergo a large number of possible reactions, such as hydrolysis, olation, oxolation and polymerization [3], and, moreover, there is a serious lack of general knowledge regarding their electrochemical behavior [3, 20, 31]. It has also been pointed out specifically that these electrolytes tend to change in time, and this type of instability has also been encountered during this dissertation.

Two electrolytes were made at different times, both at pH 2, both with the very same composition, and both had been heated at 80°C for 1 hour before they reached the working temperature of 25°C:

ZnSO ₄ · 7H ₂ O	0,2 M	
Cr ₂ (SO ₄) ₃	0,067 M	(added as Trisurfin 0,1 M)
Na ₂ SO ₄	1 M	

From the first electrolyte, some samples were obtained on the day that the solution was prepared and several others were deposited during the course of the following month. The first coatings that were recovered had a much different composition and appearance with respect to all other samples that were deposited later on. The latter samples were deposited in a time span of 6 to 26 days after the preparation of the solution, and they all showed similar, much more consistent results.

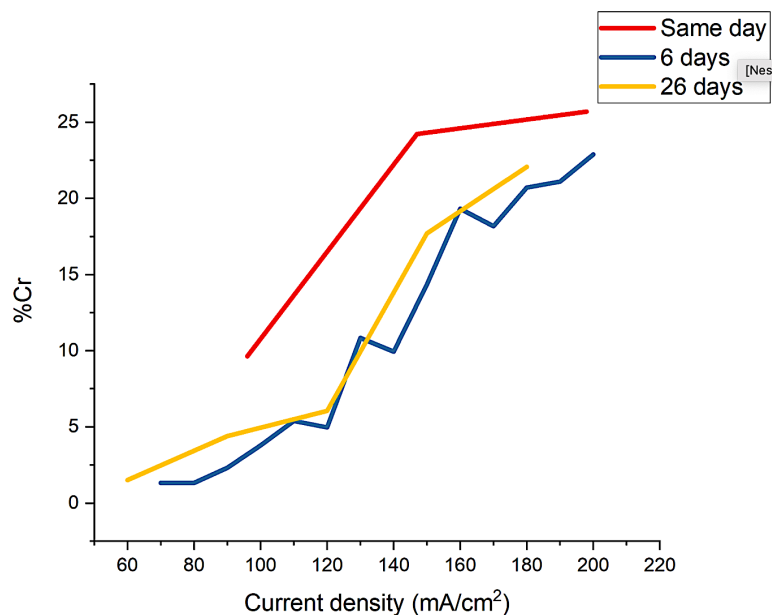


Fig. 24: Chromium contents of deposits obtained at different points in time (electrolyte n.1)

Therefore, the second electrolyte was prepared, and depositions were attempted on the same day of the making of the solution and 7 days later: a similar trend emerged, at least for the lower current densities; samples at higher current densities were not retrieved for the same-day deposition as the coatings were starting to flake off too much.

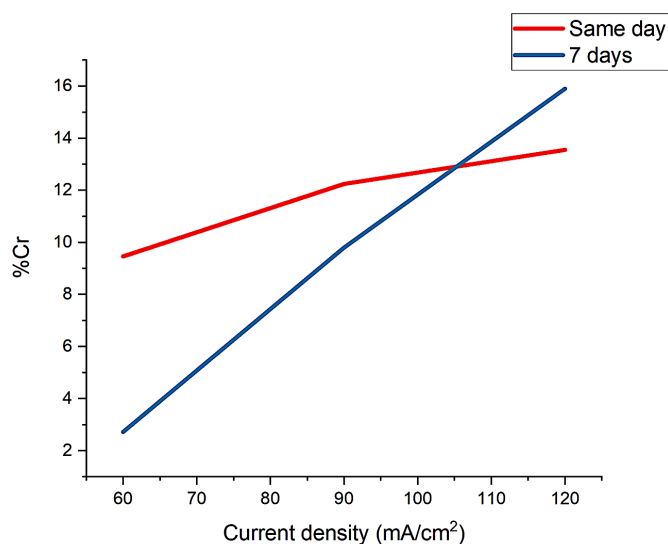


Fig. 25: Chromium contents of deposits obtained at different points in time (electrolyte n.2)

At this point, one could argue that this decrease in the chromium content of the electrolyte could possibly be related to the depletion of the metallic ions in the bath,

since the deposition process employed insoluble anodes. However, this is rather unlikely, for two main reasons:

- Concerning the first electrolyte, only five samples were obtained from the bath on the same day of its preparation, while during the following month a total of over 30 samples were prepared. If the change in the composition of the coating was related to ionic depletion, it would make more sense to notice a gradual change in composition, rather than a sudden change after only five depositions which remains stable for the over 30 following depositions.
- As it has been investigated, lower concentrations tend to lead to a higher chromium content at the same current density, due to a lower limiting current density; moreover, since zinc is the metal that is preferentially deposited in higher amounts, the ionic depletion of the bath would have probably resulted in a lower Zn:Cr ratio in the solution. Both events would have more likely led to an initial gradual increase in the chromium content rather than in a sudden drop that seems to remain constant.

However, samples obtained from the first electrolyte 42 days after its initial making started, once again, showing a slightly higher content in chromium. It is unclear whether this change is related to other unknown reactions or to ionic depletion, since over 40 depositions had occurred at this point:

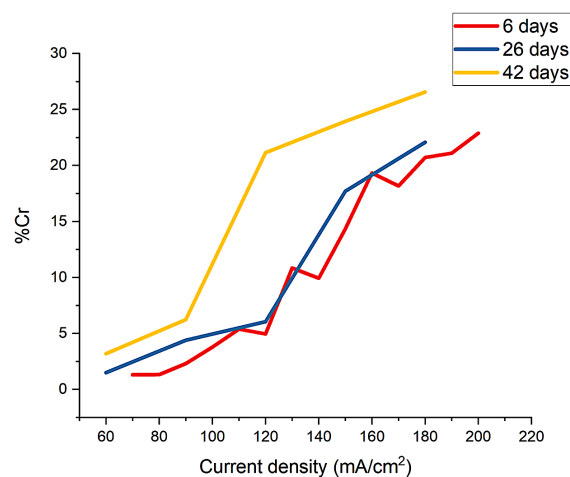


Fig. 26: Comparison of chromium content of deposits obtained 42 days after the preparation of the electrolyte

Nevertheless, it is clear to see that these electrolytes present a relatively high instability and can sometimes lead to inconsistent results, making it hard to predict the precise

behavior of the electrolyte and the deposition process: a deep analysis of the evolution of the electrochemical behavior of the bath is therefore necessary in order to assure a much higher consistency in terms of results.

UV-vis spectra were also acquired to highlight possible changes in trivalent chromium electrolytes. Four solutions were made, all with the following composition:

$\text{Cr}_2(\text{SO}_4)_3$ 0,067 M (added as Trisurfin 0,1 M)

Na_2SO_4 1 M

Two solutions were made one week before UV-vis spectra were acquired, and only one of them was heated at 80°C degrees for 1 hour; two other solutions were made on the same day of the recovery of the spectra, and only one of them was heated at 80°C for 1 hour before cooling down to room temperature. The UV-vis spectra highlighted some distinctions in all solutions: 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. Sources report that changes may be due to the oxidation of the hexaaquachromium(III) complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and or/ due to its conversion into $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ [39], which could also explain the significant change in behavior. Nevertheless, it remains unclear whether temperature and time lead to the same changes in solution.

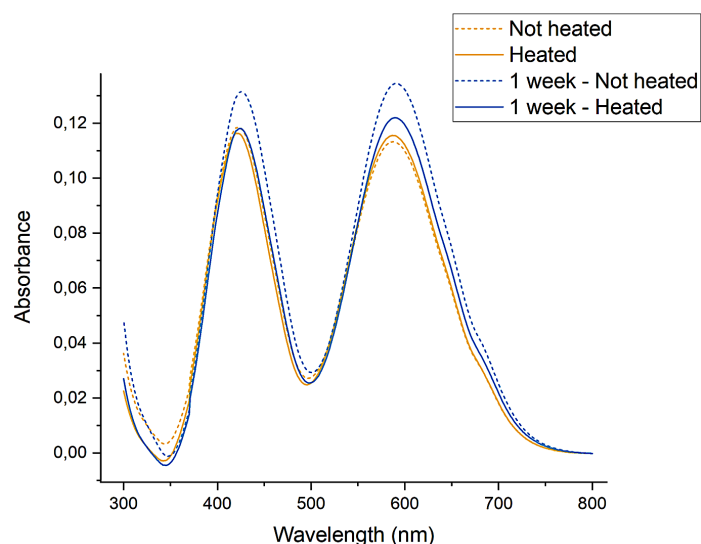


Fig. 27: UV-vis spectra of trivalent chromium electrolytes: comparison between heated (dashed line) and non-heated (solid line) solutions and between ready-made (yellow) and aged (blue) solutions

4 CONCLUSIONS, FUTURE DEVELOPMENTS AND APPLICATIONS

This dissertation aimed to study and analyze the electrochemical behavior of electrolytes based on zinc and trivalent chromium, and to determine the properties of the resulting the coatings. This intent proved to be challenging, as electrolytes containing trivalent chromium ions can undergo several changes that have not been thoroughly studied and reported, sometimes leading to unpredictable and non-reproducible results. It is therefore of the utmost importance in the future to closely monitor the changes occurring in the plating baths during time and as a function of other variables, such as the influence of heating during the preparation of the solutions.

Overall, the Zn-Cr alloy coatings that were deposited did prove to offer a higher corrosion protection with respect to their pure zinc counterparts: the 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. It is therefore possible to conclude that, while the presence of chromium in the deposits offers a higher corrosion protection with respect to pure zinc, the coatings still retain their sacrificial nature.

The deposits containing the highest amounts of chromium, however, also exhibit a highly dendritic morphology due to the high current densities at which they are obtained. They are therefore porous and rather brittle, and testing more additives to facilitate the codeposition of the alloy would certainly be of importance. Finding suitable complexing agents to favor the deposition of chromium at lower current densities would be crucial in order to enhance the morphology and physical properties of the deposits; alternatively, finding appropriate additives to promote a more homogeneous deposition would also provide great improvements. It is also important, in the future, to focus on the analysis of the physical properties of the coatings, on top of their corrosion behavior: testing their hardness and adherence-related properties, such as wear and abrasion resistance, are important aspects to include to fully characterize the coatings.

Zn-Cr alloys represent a valid future option for automotive applications. Besides their increased corrosion resistance at lower thicknesses with respect to pure zinc coatings, sources [32] report an increased weldability and formability, which would be especially beneficial for these applications. In particular, welding represents an issue for galvanized steel, since it causes the complete evaporation of the protective zinc layer while releasing toxic fumes; since an increased weldability is reported, it is likely that the presence of chromium in the deposit could also limit this problem.

Ultimately, the results that were obtained during this dissertation appear to be very promising: the more modest ionic concentration of the electrolyte allowed to deposit coatings containing a considerable amount of chromium at current densities that are much lower and more manageable than the average values found in literature, and all characterization tests proved their much higher corrosion resistance. 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. Further research regarding the electrochemical behavior of the bath and a more in-depth characterization of the physical properties of the deposits are certainly needed, but the recovered results were overall considered to be very positive.

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