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Etude du comportement d'un revêtement Fe-Cr-Ni-Si dans le zinc liquide

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STUDY OF THE BEHAVIOR OF A Fe-Cr-Ni-Si COATING IN LIQUID ZINC

Batch hot-dip galvanizing serves as a surface treatment for safeguarding steel against atmospheric corrosion. This process involves immersing metal components in a liquid zinc alloy bath to apply a protective coating. However, the repeated treatment of steel hangers that transport the parts between multiple galvanizing baths results in molten zinc corrosion. Furthermore, the zinc layer on these hangers not only wastes zinc but also requires an extra stripping step in HCl, adding to economic and environmental costs. The objective of this thesis is to develop materials that can prevent liquid zinc deposition and to understand the mechanisms of their damage.

A slurry process is utilized to produce a complex Fe-Cr-Ni-Si-P coating that can be used and produced industrially. Cyclic galvanizing tests prove that this coating reduces liquid zinc corrosion by 80% and zinc intake by 85% after 20 galvanizing cycles, in comparison to low-carbon DD13 steel. The preoxidation process is explored to enhance its performance further. Finally, a surface analysis using SEM-EDX at various stages of the galvanizing process provides insights into surface interaction mechanisms, examining the SiO₂ formation hypothesis and the role of different coating phases.

An atomic-scale DFT-AIMD simulation is employed to study the SiO₂-liquid Zn interface and calculate its interface energy. The Fe-Si model surfaces were also produced with SLM method. Both studies were managed in order to improve understanding of interactions in simplified systems compared to slurry coatings.

Keywords: batch hot-dip galvanizing, liquid zinc, coating, wetting, surface analysis, atomic simulation

ETUDE DU COMPORTEMENT D'UN REVÊTEMENT Fe-Cr-Ni-Si DANS LE ZINC LIQUIDE

La galvanisation à façon est utilisée comme traitement de surface pour protéger l'acier contre la corrosion atmosphérique. Ce processus implique d'immerger les composants métalliques dans un bain de zinc liquide afin d'appliquer un revêtement protecteur. Cependant, le traitement répété des structures d'accroche en acier assurant le transport des pièces entraîne leur corrosion par le zinc liquide. De plus, la couche de zinc déposée sur ces crochets non seulement gaspille du zinc, mais nécessite une étape supplémentaire de décapage à HCl, augmentant les coûts économiques et environnementaux. Cette thèse se concentre sur le développement et la compréhension des mécanismes à la surface des matériaux visant à réduire la déposition du zinc liquide.

Un procédé slurry est utilisé pour produire un revêtement complexe Fe-Cr-Ni-Si-P pouvant être utilisé et fabriqué industriellement. Des tests de galvanisation cyclique démontrent que ce revêtement réduit la corrosion par le zinc liquide de 80 % et la prise du zinc de 85 % après 20 cycles de galvanisation, en comparaison avec l'acier bas carbone DD13. Le processus de préoxydation est exploré pour améliorer davantage ses performances. Enfin, une analyse de surface à l'aide de la technique SEM-EDX à différentes étapes du processus de galvanisation offre des perspectives sur les mécanismes d'interaction de surface, examinant l'hypothèse de formation de SiO₂ et le rôle des différentes phases de revêtement.

Une simulation DFT-AIMD à l'échelle atomique est mise en oeuvre pour étudier l'interface SiO₂-liquide Zn et calculer son énergie d'interface. En plus, les surfaces modèles Fe-Si ont été produites par fusion laser. Ces deux études ont été menées pour élargir la compréhension des interactions dans les systèmes simplifiés par rapport aux revêtements slurry.

Mots clés : galvanisation à façon, zinc liquide, revêtement, mouillage, analyse de surface, simulation atomique

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Introduction

Zinc is an abundant element present in the earth's crust, with global reserves mainly concentrated in Australia, followed by China and Russia [1]. The predictions on available, extractable resources indicate that access to zinc is assured for decades to come, even with the growing demand for zinc [2]. Nonetheless, a worldwide effort is made to increase the recycling of this metal in order to advance the goal of developing a circular economy [2, 3]. The principal use of zinc is galvanizing [3].

Hot-dip galvanizing is a widely recognized surface treatment for steels that improves their atmospheric corrosion resistance through the formation of protective zinc coatings. In this process, steel parts are submerged in a molten zinc-base alloy at around 450°C for several minutes in order to form a protective zinc coating.

The process of batch hot-dip galvanizing is used to coat ready-to-use steel parts. Here, the dipping in zinc is preceded by immersion in different surface preparation baths, such as pickling in acid. Those steel parts are transported from one bath to another with the use of different types of hangers made out of regular steel. Consequently, the hooks receive the same surface treatment as the galvanized components. However, because they are reused multiple times, they go through it in a cyclical manner, with an additional step of dezincification in acid between each cycle.

The problem of hydrochloric acid and zinc waste emerges in galvanizing plants when steel hangers get wetted with liquid zinc. FeZn intermetallics are thus produced, which need to be removed with acid in order for the hooks to be used again. After a few cycles, this procedure consumes zinc, corrodes hangers, and creates chemical waste that needs to be recycled, adding to the financial and environmental costs. A better steel hanger material that is resistant to liquid zinc wetting needs to be developed in order to enhance the efficiency of galvanizing sites and reduce their losses.

This study aims to develop and comprehend the protective properties of a material that corresponds to batch hot-dip galvanizing limitations, an area that has not received much attention in the literature to date. The fundamental

premise of the study is that SiO_2 may increase the material's wetting resistance and, as a result, reduce zinc overconsumption.

Problems with those industrial materials are caused by complex physico-chemical interactions between atoms. Because of this, materials suitable for batch hot-dip galvanizing hangers and the difficulties they encounter are characterized at multiple scales. This work's multidisciplinary nature connects atomic-level simulation, nano- and micrometric surface analysis, as well as semi-industrial galvanizing treatments.

Investigation strategy

This multidisciplinary study was predicted to run following three axes. The examination of Fe-Cr-Ni-Si-P coatings under small-scale cyclic galvanizing treatment under circumstances akin to those found in industrial facilities formed the core of the research. Their performance was analyzed in terms of liquid zinc corrosion resistance and the deposition of zinc at the surface of coated samples. Those coatings were conceived in cooperation between the teams of the Université de Lille and the Ecole Européenne d'Ingénieurs en Génie des Matériaux in Nancy. The EEIGM team was also responsible for the production of coatings, thanks to their expertise in the slurry method. Furthermore, it was intended to test the evolution of coating wetting by liquid zinc using the Wilhelmy plate method and analyze those coatings under microscopic observation at various stages of the galvanizing cycle in order to comprehend the mechanisms of those coatings' degradation by galvanizing treatment.

Since the chemistry and microstructure of slurry coatings are extremely complex, the investigation was to be completed through the analysis of simplified systems. The core of the atomic-scale simulation was to develop a simple solid-liquid system of silicon oxide in liquid zinc, which was verified by an experimental measurement. Then, the system may be further complexified with additional elements present in the coating in order to better understand the impact of the coating composition on zinc deposition on the surface.

The simulation results were to be compared with sessile drop test results for liquid zinc wetting angle on Fe-Si model surfaces created by selective laser melting. The study that led to the proper formation conditions was carried out in collaboration with the Belgian Ceramic Research Centre in Mons. Unfortunately, the results that would tie various sections of this research together were not available due to technical problems with both wetting measurement methods.

This manuscript is structured into four chapters. The first chapter's bibliographic examination centers on the galvanizing process. It includes descriptions of different galvanizing methods, an in-depth analysis of every step in the batch galvanizing process, and an overview of the chemical interactions that occur. After that, a review of the literature on various solutions for liquid zinc corrosion developed for the continuous galvanizing process is presented and discussed.

The methods for surface analysis are presented in the second chapter. At first, a theoretical introduction to the wettability. This chapter's second section introduces the first-principles atomic scale simulation, including Density Functional Theory and *Ab Initio* Molecular Dynamics. It is followed by a literature study on the simulation of wetting. The description of the numerous experimental surface analysis techniques used later in this work takes up the third section of this chapter.

The third chapter of this document is dedicated to the analysis of wetting behavior at the SiO₂-liquid Zn interface. The first principal section centers on the development of an atomic-scale model of that interface through first-principles simulation. The objective of this work is to obtain the interface energy of this system and calculate its theoretical wetting angle. The creation of experimental FeSi model surfaces is discussed later in this chapter, and extreme surface analysis techniques are used to characterize those surfaces that are susceptible to the SiO₂ formation.

Following an examination at the atomic level and an initial development of the system through the creation of FeSi coatings, the material under study is enhanced with a complex Fe-Cr-Ni-Si coating that might potentially be adapted for industrial application. This coating is described and subjected to a cyclic galvanizing process in the fourth chapter of this study to assess its performance in terms of liquid zinc deposition at the surface and liquid zinc corrosion. Finally, the investigation of surface interaction mechanisms that take place in Fe-Cr-Ni-Si coating during batch hot-dip galvanizing is presented in this chapter. This study is conducted principally with a thorough microscopic analysis of samples at different stages of galvanizing treatment.

Chapter 1

State of art

1.1 Hot-dip galvanizing

According to the ISO 8044 standard, corrosion is a process in which metal properties deteriorate as a result of a physico-chemical interaction with the environment [4, 5]. Steel is a commonly used material in infrastructure, buildings, manufacture of means of transportation, and tools because of its high strength and low cost of production. However, it is also a metal that is easily corroded if not properly protected. The cost of corrosion in developed countries can be estimated at 3-4% of national gross national product (GDP) [6]. Many methods exist to protect the steel from corrosion, and most of them involve the use of zinc. Among those zinc protective methods, the most common one is galvanizing, but steel can also be coated with a protective layer via electroplating, Zn-rich paints, and vapor phase deposition [7].

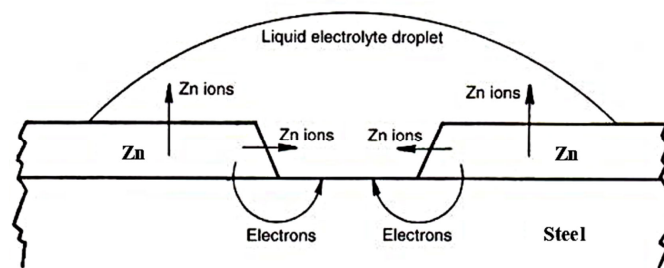


Figure 1.1: The mechanism of cathodic sacrificial protection [8]

Galvanizing is a surface treatment procedure that leads to the deposition of a zinc layer on the steel's surface in order to protect it from atmospheric corrosion. First, a French chemist, Paul-Jacques Malouin, discovered and documented the

steel-protective properties of zinc in 1742 [9]. However, it took almost a century before the first industrialization of the process. In 1836, the pickling process for cleaning iron and the role of flux salts in the procedure were discovered by a French inventor Stanislas Sorel [9]. Therefore, he succeeded in creating a zinc-covered steel sheet, as it is known today. He called this process "galvanization" in tribute to Luigi Galvani, who is well-known for his research on electricity [7, 9]. When steel parts are dipped in molten zinc, multiple intermetallics are created as a result of the metallurgical reaction between Fe and Zn, leading to the formation of a protective layer on the surface. Due to this technique, steel parts are protected by two different mechanisms: first, the zinc layer provides barrier protection, which isolates the steel from the environment, and second, cathodic protection (Figure 1.1. Also known as sacrificial protection, this type of protection sees zinc dissolve in place of iron in the event of a coating discontinuity due to the electropotential difference between Fe (-0,44 V/NHE with NHE, Normal Hydrogen Electrode [10]) and Zn (-0,76 V/NHE [10]). So, depending on the reaction's kinetics, this protection is guaranteed for a while.

Two types of hot-dip galvanizing processes can be distinguished: batch and continuous hot-dip galvanizing.

1.1.1 Batch hot-dip galvanizing

Batch hot-dip galvanizing is one of the industrial processes that is commonly used for the corrosion protection of a variety of ready-to-use steel parts, including guardrails, metallic frames, fasteners, or even bridge girders [11, 12]. The dipping in liquid zinc is preceded by several surface treatment steps (Figure 1.2).

The steel component is initially mounted onto a fixture and introduced in the first degreasing step. Since the subsequent treatments are carried out in aqueous solutions, the steel surface must be free of any impurities, such as natural and synthetic greases, oils, or even dust, that could decrease the quality of pickling and contaminate other surface treatment solutions. The most typical method of degreasing and cleaning uses an alkaline solution with a pH value of 11-14, at 60-80 °C. Chemical substances used are mainly sodium hydrate or sodium carbonate, which are able to saponify oils and disperse other contaminants. Alkaline degreasing requires a stage of thorough rinsing in order to prevent the formation of an oily layer on the surface of the pickling bath, which can lead to the pollution of the following fluxing step [7, 12].

Otherwise, a pickle (acid) degreaser can be used, mainly in phosphoric acid with degreasing additives, that can remove both hydrophobic and hydrophilic contaminants. This process is done at room temperature but may be less efficient than alkaline solutions [14]. Alternative methods, such as solvent and

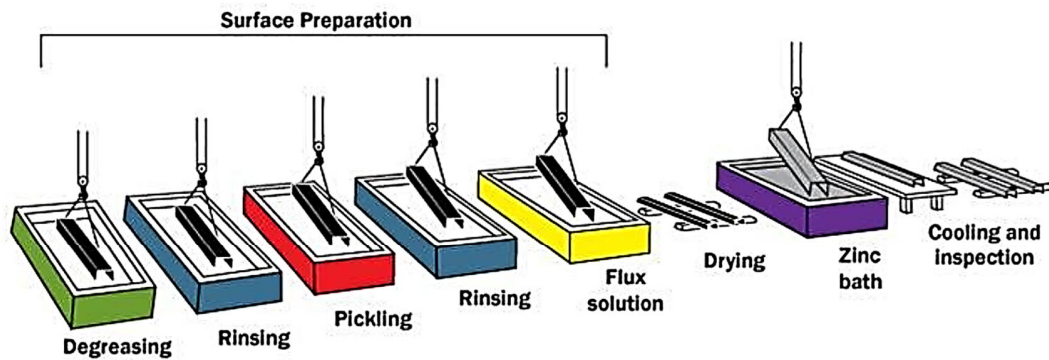


Figure 1.2: Schematic process of batch galvanizing [13]

biological cleaning, may be used, but they are more expensive or have negative environmental effects [7, 12].

Steel products are left to drip for a couple of seconds after each step in order to avoid carryover and pollution from the previous solution into the next. After being rinsed in water, parts are transferred into the acid solution for the step called pickling.

The purpose of the pickling process is to remove all oxides at the surface, and to achieve that, 30-33 wt.% hydrochloric acid at room temperature is almost exclusively used [7, 12]. Additionally, a little amount of corrosion inhibitor is also added to ensure that only iron oxides and not the steel itself dissolve. Furthermore, the pickling time must be as short as possible to limit the attack of steel. It may occasionally be preceded by the mechanical shot peening stage [12]. In order to maintain a steady pickling rate, the bath must be regularly regenerated with HCl and adjusted in concentration. The rinsing is done again after the pickling process. This time, multistage rinsing is applied to prevent the iron and hydrochloric acid enrichment of the flux solution.

Fluxing enables a smooth reaction between pickled steel and zinc by protecting the surface from oxidizing prior to submerging it in the molten zinc. It also ensures good wetting of the surface by the zinc. Throughout the history of galvanizing, flux was based on a mixture of ZnCl_2 and NH_4Cl salts. Two main proportions of those salts are used: double salt $\text{ZnCl}_2, 2\text{NH}_4\text{Cl}$ or triple salt $\text{ZnCl}_2, 3\text{NH}_4\text{Cl}$ [12, 15]. In Europe, the double salt is preferred [16], and it is composed of 56 wt. % ZnCl_2 and 44 wt. % NH_4Cl . In aqueous solution, a concentration of this flux salt must fall between 100 and 450 g/L [7]. In batch galvanizing, the fluxing is mainly accomplished through the process called

"dry galvanizing", in which the fluxed component is dried at temperatures over 100°C until all superfluous water has evaporated before being immersed in the zinc bath. Incompletely dried products could develop coating flaws, including porosity and uneven thickness [7]. The temperature should not rise above 140°C to avoid the decomposition of ZnCl_2 hydrates that take part in the fluxing mechanism [15].

In a wet galvanizing process, flux is added at the surface of the zinc bath, and the sample enters the molten metal in a wet state. This method is suitable for hollow bodies or tubes. [17]. An advantage of this method is that no drying is required. However, the content of aluminum must not exceed 0.002% to avoid defects in the coating [7].

Finally, well-prepared parts can be introduced into the zinc bath at 440-460°C. It is composed of at least 98% of pure zinc [18]. The bath's iron content will increase through the dissolution of components up to saturation at 0.03 wt. % at 450°C [19]. Despite being effective in reducing the amount of zinc ash that forms at the surface, the addition of aluminum is limited to 0.01 wt. % due to its reactivity with flux [20]. Nickel may be added to reduce the reactivity of Si-containing steel with liquid zinc (see 1.2.3.1), with the Ni content going up to 0.06 wt. %. A higher Ni content results in an increase in the thickness of the coating [19]. The addition of lead, bismuth, and tin improves the quality of the top layer of the zinc coating by reducing the surface tension, increasing the castability of zinc, and improving the appearance of the coating [19].

Before immersion and after removal from the bath, the surface of the liquid zinc must be thoroughly cleaned of zinc ash and compounds that result from flux decomposition. Immersion rate must be high enough so that the flux can be not decomposed before the metallurgical reaction takes place. Typically, an immersion rate of 2-3 m/min is used [12]. Removal should be conducted at a constant rate of at least 5 m/min to get the correct aspect of the coating and give time to operators to remove any excess zinc before its solidification [7, 12]. The thickness of the coating depends on the time spent in the zinc bath. At the end of the galvanizing process, parts are cooled in air or submerged in water to accelerate the cooling, and small components can be centrifuged in order to remove excess zinc [7].

An additional step of dezincification is applied to fixtures and defective parts after cooling. The zinc layer is removed in diluted hydrochloric acid, and cleaned parts can either be treated once again or used as fixtures for a subsequent galvanizing cycle [7].

1.1.2 Continuous hot-dip galvanizing

The invention of continuous hot-dip galvanizing is attributed to the Polish engineer Tadeusz Sendzimir, who developed the process in the 1920s in Shanghai [9]. With this method of hot-dip galvanizing, steel sheets, strips, and wires are treated [11, 12]. These low-thickness, high-length products are inserted into the continuous galvanizing line, as shown in figure 1.3.

Surface preparation is conducted differently from batch hot-dip galvanizing. In this procedure, steel sheet or other products are heat treated through annealing, which removes internal stresses, softens the material, ultimately obtaining the desired mechanical properties. On the other hand, the atmosphere in the furnace is controlled and composed mainly of a mixture of hydrogen and nitrogen, so that iron oxides are reduced at the surface [11, 21, 22]. However, the atmosphere can still contain a small partial pressure of H_2O and O_2 that, at high temperatures, can induce selective internal and/or external oxidation of certain alloying elements of steel such as silicon or manganese. These surface-located oxides decrease the wetting by zinc and therefore the quality of the coating [21, 23]. Hence, the atmosphere and the temperature in the furnace must be precisely controlled.

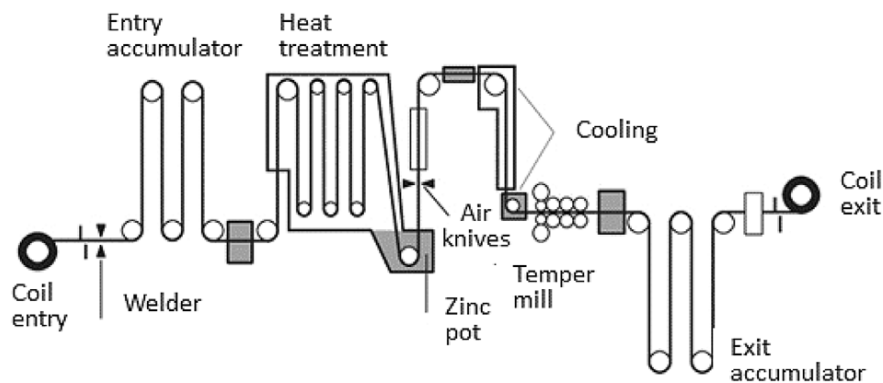


Figure 1.3: Schematic process of continuous galvanizing line [22]

After a surface preparation, preheated steel sheet enters on the sink roll the zinc alloy bath at 460-510°C for a very short time. The composition of the bath is characteristic for continuous galvanizing with a higher aluminum content. It may vary from 0.2 wt. % for microalloyed, 5 wt. % for low-alloyed, and 55 wt. % for high-alloyed zinc bath [7, 24]. After the withdrawal, excess zinc is removed with high-pressure air or nitrogen, and the sheet is allowed to cool down before being coiled again [11, 12]. Aluminum is added to avoid the formation of Fe-Zn intermetallics, which may cause defects during bending and stamping [21].

Short passage times in the molten zinc result in low opportunities for Fe-Zn intermetallics formation and therefore a very thin layer of the coating. The EN 10346:2015 standard specifies that it should be between 7 and 40 μm . [7, 12, 25](Figure 1.4). Meanwhile, in batch hot-dip galvanizing, coatings are thicker, with the EN ISO 1461 standard requiring coating thicknesses of at least 45 μm for steel thicknesses between 1.5-3 mm and at least 70 μm for steel with a thickness greater than 6 mm [18].

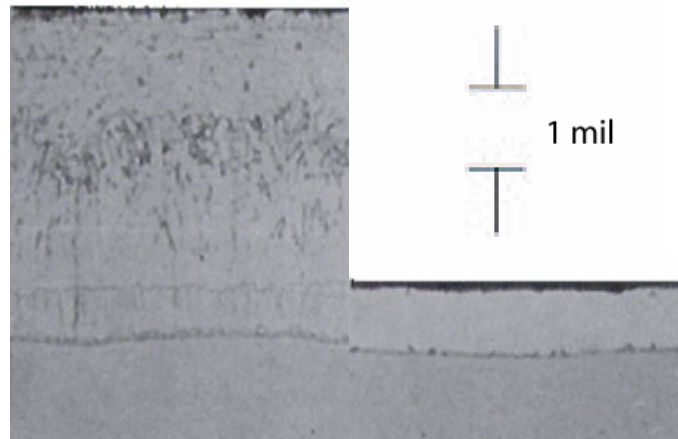
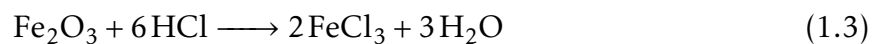


Figure 1.4: Comparison of a coating's thickness between batch and continuous hot-dip galvanizing [11] (1 mil = 25.4 μm)

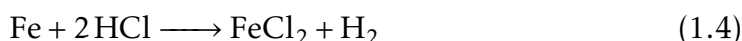
1.2 Steel reactivity in batch galvanizing process

1.2.1 Pickling

Steel rust is composed of three types of iron oxides: wüstite FeO , magnetite $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and hematite Fe_2O_3 [26], which are all solvable in hydrochloric acid, Cl^- ions adding an advantage to their solubility rate in comparison to other acids such as H_2SO_4 [27–29] and wüstite having the best solvability [7, 14, 30]. This dissolution of scale happens through reactions 1.1-1.3.



However, the reactivity of acid does not end at oxides; it attacks steel too. The mechanism of pickling is represented in the figure 1.5. The phenomenon of steel consumption is called "over-pickling", leading to the waste of the matter (0.3-0.4 wt. % of pickled steel [31]) and overuse of acid through the creation of H_2 gas bubbles as in reaction (1.4). Those bubbles can burst and mechanically detach the scale from the steel surface. Also, a part of the thus formed hydrogen can lead to the reduction of Fe^{3+} ions into Fe^{2+} ions (reaction (1.5)).



Pickling time in HCl is primarily influenced by acid concentration and tempera-

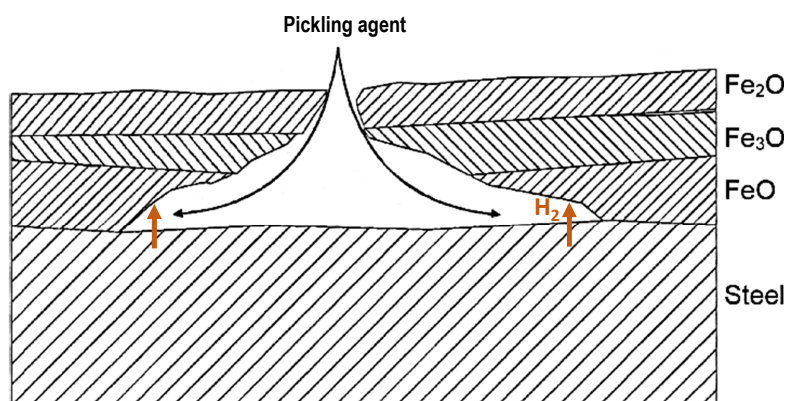


Figure 1.5: The mechanism of pickling. Figure adapted from [32].

ture, with time decreasing as each of those parameters rises. On the other hand, leaching of Fe ions into the HCl bath may slightly increase the pickling time [33].

Alloying elements of steel can also influence the picklability of steel. An increase in the Ni content of the alloy extends the pickling time [7] and also raises the corrosion resistance of steel in contact with hydrochloric acid [34, 35]. In low contents, Cr does not influence the pickling rate [7]. However, chloride ions from hydrochloric acid have the potential to attack the passivation layer formed by chromium and lead to corrosion by pickling [36–38]. The high content of silicon inhibits the pickling rate. As states Chattopadhyay et al. [39], for steels with Si content above 0.35%, oxide morphology at the surface of steel is mainly composed out of fayalite phase $Fe_{2.44}Si_{0.55}O_4$ which is harder to pickle than iron oxides and in consequence decreases pickling kinetics. If SiO_2 is formed at the surface of the steel, it will not react with hydrochloric acid [40].

The dissolution of iron by HCl and then the creation of Fe^{2+} ions may result in the formation of atomic hydrogen that can diffuse into the iron through its interstitial sites [7, 41–43].



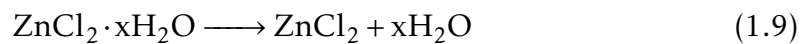
The pressure in the iron lattice rises due to the collected hydrogen, which is further confined by galvanizing intermetallic coatings. If the hydrogen concentration in the fracture tip is high enough, once a microcrack has been formed, for example, by overload or fatigue, the crack may propagate and lead to an early failure due to hydrogen embrittlement [7, 44–46].

Hydrogen embrittlement and overpickling of steel can be reduced with the use of corrosion inhibitors. Those are organic-based substances, such as colloids or organic bases [7, 47]. Amino compounds, such as hexamethylene tetra-amine, are deemed effective in HCl [46], but a mixture can be employed for synergistic effect. Their role is to limit the absorption of hydrogen in steel [12]. Once iron oxides are removed from the steel surface, positively charged organic inhibitors are adsorbed on the negatively charged cathode areas of iron, preventing H^+ ions from discharging on iron. Thus, the dissolution of iron is prevented [47].

1.2.2 Fluxing

Fluxing treatment provides good wettability and reactivity between steel and zinc during galvanizing through a complex mechanism of various potential reactions. After drying, the flux residue on the surface is composed of NH_4Cl and $\text{ZnCl} \cdot x\text{H}_2\text{O}$ as ZnCl is highly hygroscopic and capable of forming four distinct hydrates [48]. This thin layer protects steel from oxidizing during the transfer to the molten zinc.

When an object enters the zinc bath, it drags inside the zinc oxide ZnO that is formed at its surface, thus preventing the reaction with zinc, as represented in figure 1.6. One role of the flux is to dissolve this oxide to ensure better contact between the steel and the bath. When the object is lowered to come into contact with the zinc bath, it gets heated, salts decompose, and HCl is produced from NH_4Cl , while ZnCl_2 hydrate structures release water molecules (reactions (1.8), (1.9)).



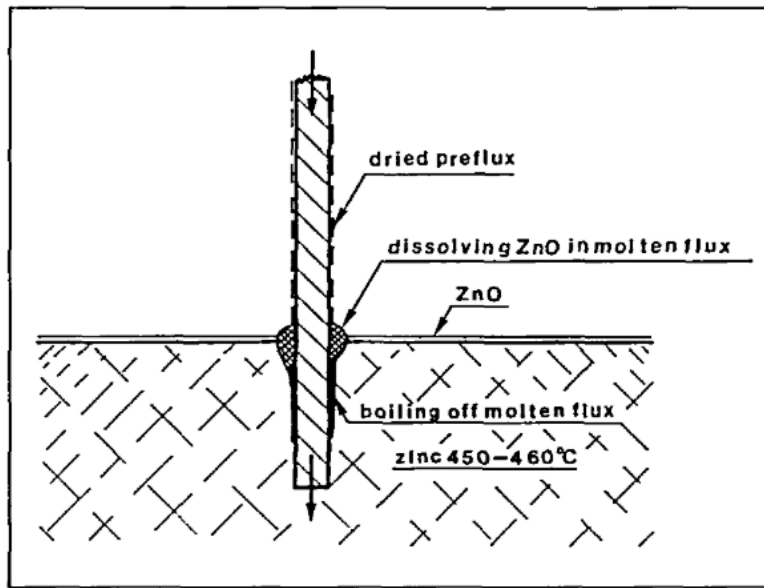


Figure 1.6: Dried preflux on the surface of an article dipped in molten zinc [15]

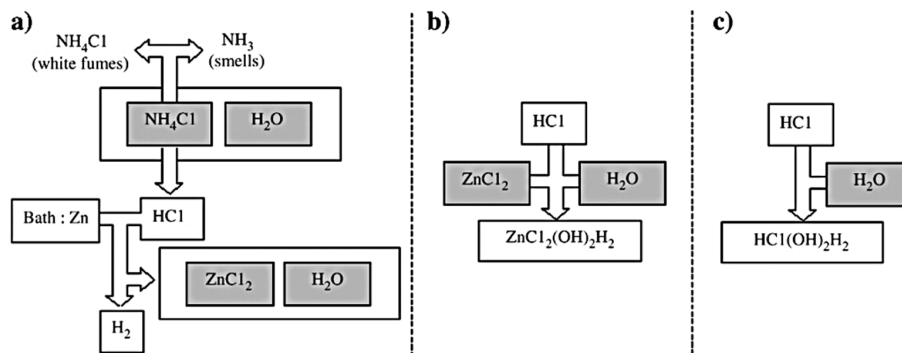
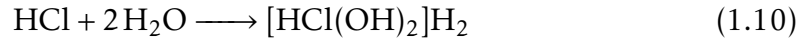


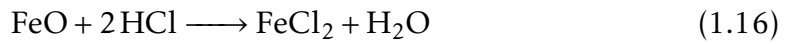
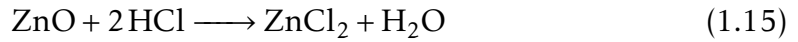
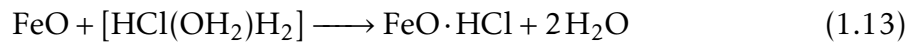
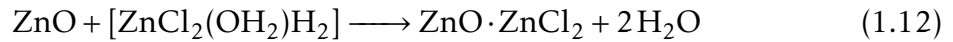
Figure 1.7: Diagrams of the chloride flux decomposition on the zinc bath [49]

Additionally, this hydrochloric acid and water of crystallization lead to the formation of very strong hydroxyacids that pickle the steel's surface and thus enable the iron-zinc reaction (reactions (1.10), (1.11)) [7, 15, 49]. This molten flux is then dragged on the steel surface into the bath and, after a brief moment, is boiled off so that zinc can react with iron (figure 1.6). The temperature of drying must therefore be kept below 150°C to prevent the hydrates from drying out. At the same time, the immersion rate must also be quick enough so that this

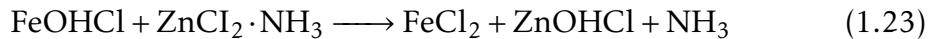
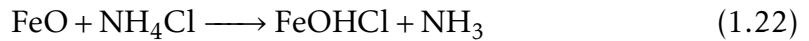
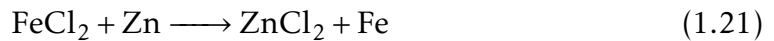
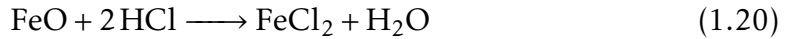
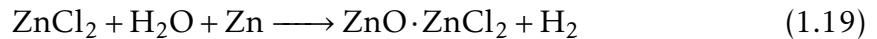
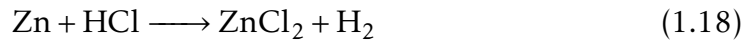
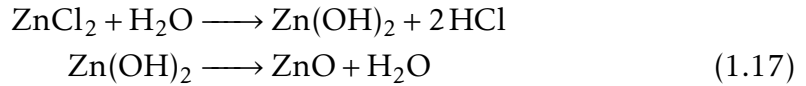
water is not evaporated and allows the formation of the active acids [15].



Those acids then attack zinc and iron oxide to create a clean iron-zinc interface (reactions (1.12)-(1.13)). Thus created Zn- and Fe-oxychlorides are insoluble in molten zinc and form skimmings [15, 45]. Other possible reactions were proposed in the literature, either with the NH_4Cl that has not yet decomposed or with the HCl formed on-the-spot (reactions (1.14)-(1.16))[12, 15]:



Finally, additional reactions can happen in the bath, resulting in the development of zinc ashes that float on the surface of the bath and must be skimmed off before the part is retrieved to ensure that no impurities are left on galvanized articles (reactions (1.17)-(1.23)). These ashes are formed through the reaction of molten zinc with flux components and consist of zinc oxides, various chlorides, or iron compounds [7, 50].



1.2.3 Reactivity of steel in molten zinc

Galvanizing coating is not simply a layer of zinc on the steel surface, as in the case of zinc paints. At galvanizing temperatures, intimate metallurgical reactions take place between iron and zinc, and Fe-Zn intermetallics form as a result. Galvanizing interface reactions can be divided into two principal elements with dissolution of iron in zinc, followed by nucleation and growth of intermetallic phases [51, 52].

Iron solubility in zinc melt was evaluated by Urednicek et al. [53] to be at 0.029 wt. % at 450°C. For Tang [54], the solubility limit is 0.030 wt. %. It is also not dependent on the Al content in the range used in batch hot dip galvanizing and increases with the bath temperature [55]. Guttman [52] defines the dissolution law of iron with the following mathematical description:

$$dC/dt = k_1(C_s - C) + k_0 \quad (1.24)$$

where C is the concentration of Fe dissolved in the bath and C_s its saturation concentration. On top of the first-order reaction law, a zero-order reaction component k_0 is added as the entire system is not in equilibrium, *i.e.* steel is not saturated with zinc. The reaction only slows down at the C_s point, and it continues further on. Dissolution of the iron over the saturation threshold causes the formation of ζ particles, called "hard zinc", that fall to the bottom of the zinc bath due to their specific gravity being higher than that of liquid zinc. This waste causes additional zinc consumption [19]. The Fe-Zn binary system has been vastly studied and adjusted since 1938 [56], with its most known version being that of Kubaschewski [57]. As can be observed on figure 1.8, on its zinc-rich side, the following phases can be found: zinc solid solution η , ζ , δ , Γ_1 and Γ_2 that is in contact with steel [51, 58]. A typical batch galvanizing coating with its intermetallic layers is represented on figure 1.9). η phase found on top of the coating comes from the solidification of melted zinc. It has a typical hexagonal close-packed (HCP) crystal structure with some iron substituting zinc in solid solution. Below, ζ phase is observed and defined as FeZn_{13} compound. It crystallizes in a C2/m centered monoclinic system [51, 60]. As can be observed on the phase diagram, the zeta phase is formed in a peritectic reaction at 530°C that takes place between δ phase and liquid zinc:



As can be observed on the figure 1.9, this phase has in one part a layer with columnar morphology, with some prolonged crystals formed above, surrounded by a solidified η phase. Marder [51] explains the morphology of *zeta* phase by the growth of initial crystals and, additionally, the nucleation of small crystals from

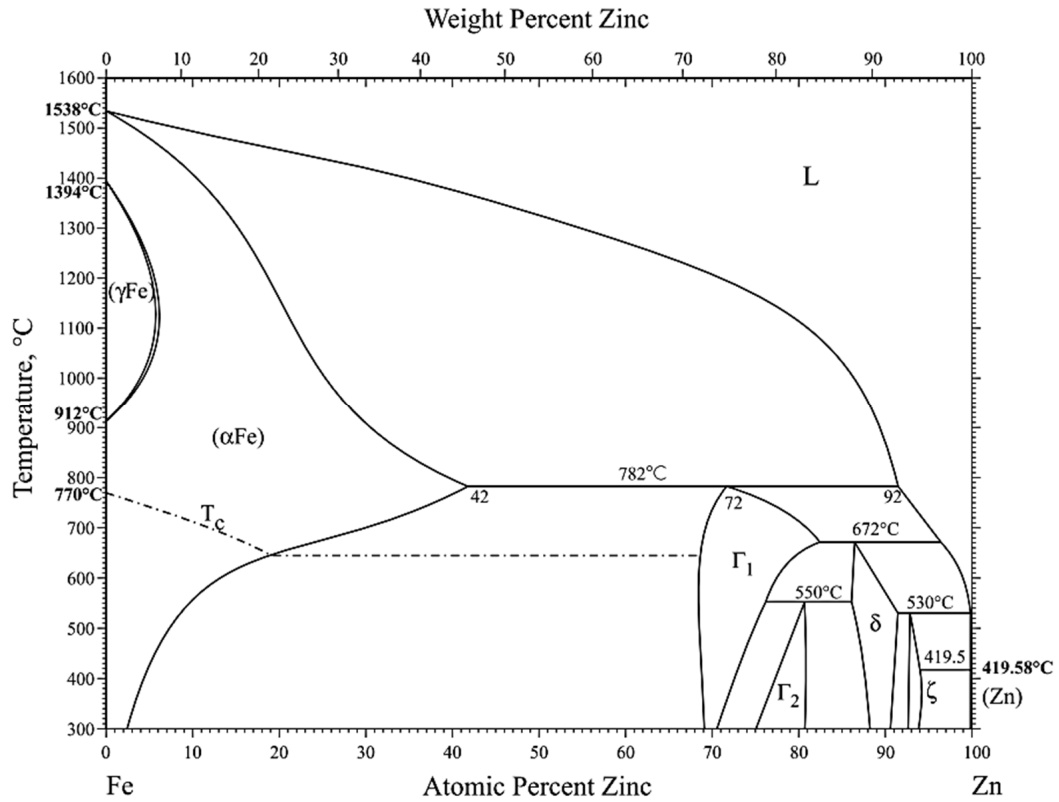


Figure 1.8: Fe-Zn phase diagram [59]

Fe-supersaturated zinc melt, separated by η phase. The characterization of the δ phase raises discussions. The existence of two crystallin structures named δ_{1k} or δ (FeZn_7) and δ_{1p} or δ_1 (FeZn_{10}) is debated. Okamoto et al. describe in their works [61, 62] the structure of two different structures, in contrast to some older works [63, 64] that mention only one δ phase forming in batch galvanizing conditions of temperature and immersion time. In either case, both delta phases have the same $P6_3/mmc$ hexagonal crystal structure [51, 60]. δ_{1k} is found on the iron-rich side and has a compact morphology, while δ_{1p} is closer to the zeta layer and has palisade morphology [51]. δ phase is created in a peritectic reaction between Γ phase and liquid:



The last intermetallic layer is Γ . Optically, this layer is so thin that it seems uniform, but it is composed of two phases - Γ_1 and Γ_2 . Γ_2 is the hardest phase in the coating (table 1.1) and has a face-centered cubic lattice (FCC). It is formed

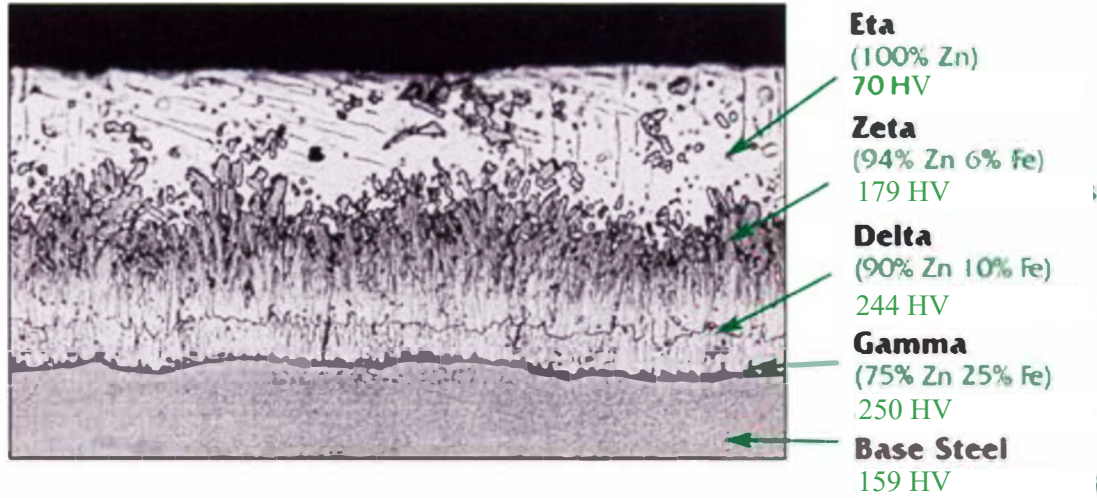


Figure 1.9: Micrograph of batch galvanized coating with composition in wt. % and HV, the unit of Vickers hardness [11]

by the peritectoid reaction between δ and Γ_1 phases at 550°C:



Finally, Γ_1 is the closest in composition and structure to the steel substrate, as it has a body-centered cubic lattice (BCC) and can contain up to 28 wt. % of iron. It is formed in the peritectic reaction between α -ferrite and liquid at 782°C:



Details concerning the properties of different layers of the galvanizing coating are detailed in table 1.1.

Phase	Compound	Fe content (wt.%)	Lattice	HV, 25 mg [65]
Eta η	Zn(Fe)	≤ 0.03	HCP	52
Zeta ζ	FeZn ₁₃	5-6	Monoclinic	208
Delta δ	FeZn ₁₀	7-12	Hexagonal	358
Gamma ₂ Γ_2	Fe ₅ Zn ₂₁	17-21	FCC	505
Gamma ₁ Γ_1	Fe ₃ Zn ₁₀	23-28	BCC	326

Table 1.1: Phases of galvanizing coating and its properties [51]

The reactions described above are correct for intermetallic formation if they form while cooling down. However, during galvanizing, the formation of intermetallic compounds takes place already in high-temperature molten zinc through diffusion. In that case, it is better to represent the 450 °C isotherm cut out of the Fe-Zn binary graph (Figure 1.10). It suggests that a specific formation order of intermetallic layers is thermodynamically preferred. The first phase that should form on top of the steel should be Γ_1 , followed by Γ_2 , δ , and finally ζ . However, as shown in the figure 1.9, the ζ phase is the most prominent, while the Γ phase is barely observable. It shows that not only thermodynamics but also kinetics must be taken into account to explain the mechanism of galvanizing coating formation.

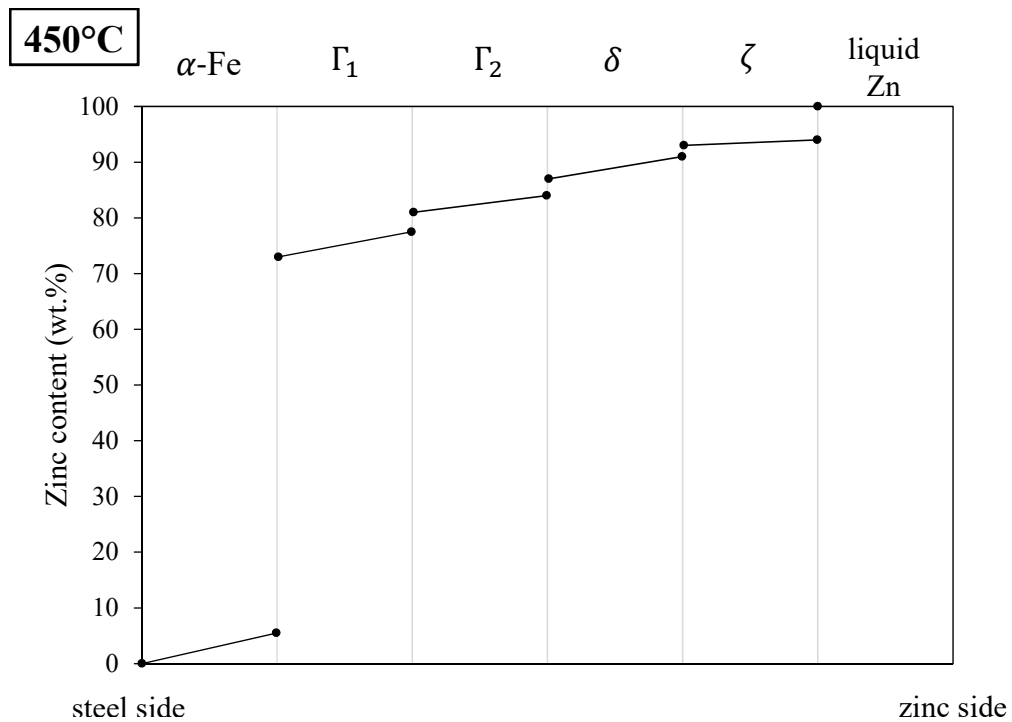


Figure 1.10: Thermodynamical diffusion profile for the steel-liquid zinc interface at 450 °C isotherm

The kinetics of growth of the galvanizing layer were profoundly studied by Jordan and Marder [51, 64] and summarized schematically on a figure 1.11. After an observation of the composition of the coating after different reaction times in a zinc bath, authors concluded that first the ζ phase nucleates and immediately after the delta phase appears. Actually, after only 5 s of immersion of steel in the zinc bath, both layers were observable, although the ζ layer was far thicker. δ phase grows in columns perpendicular to the interface, and ($\Gamma_1 + \Gamma_2$) appears after

30 s of immersion in the bath. Finally, an additional layer of separate crystals of ζ appears when zinc is supersaturated in iron. The following power-law growth

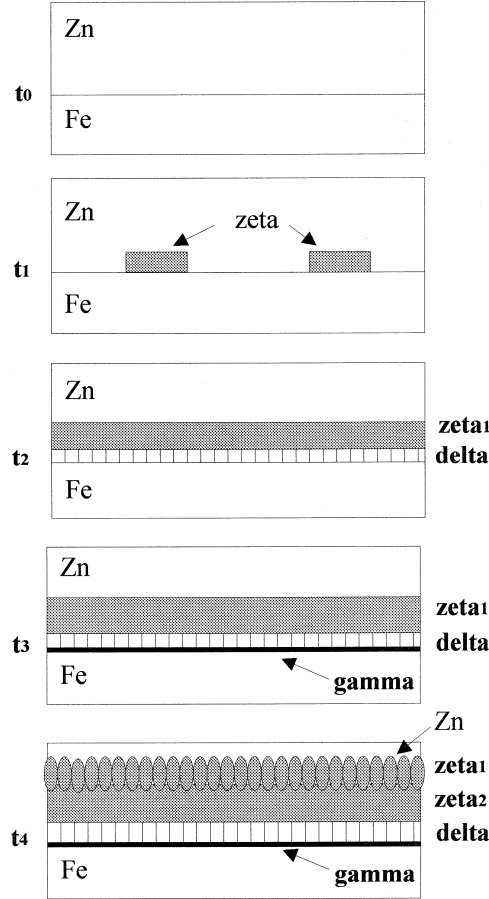


Figure 1.11: Schematic representation of Fe-Zn phase layer formation in time [64]

equation is applied to follow the growth of the layer thickness as a function of immersion time:

$$Y = Kt^n \quad (1.29)$$

with Y - growth layer thickness, K - growth rate constant, t - reaction time and n - growth rate time constant [64]. By combining their study with the results combined by Mackowiak and Short [66], Jordan and Marder concluded that for δ phase, the n value of 0.5 indicates bulk diffusion. n value ζ is 0.33, which may be related to the interfacial solid-liquid reaction. Finally, the average growth rate time constant for Γ equals 0.25 which indicates that the growth is controlled by grain boundaries. In their study, Jordan and Marder worked on alloys with

an average grain size between 10 and 20 μm . Value of n for a complete coating reflect the dominant phase in that coating, so for short-time immersions is closer to that of a ζ phase, while for longer times ($\geq 300\text{ s}$) its closer to 0.5, as δ is predominant [51, 64]. As can be observed at figure 1.12, zeta phase increases quickly at the beginning of the immersion and slows down later, while for delta the effect is inverse. Onishi et al. [67] have observed that the growth of phases happens with Zn- ζ and ζ - δ interfaces moving towards the zinc rich side, while Γ -Fe interface proceed towards the steel. In the short time of galvanizing, iron concentration in different phases is not at equilibrium, with interdiffusion taking place between coating layers. Several hours are needed before the constant iron concentration is attained [68].

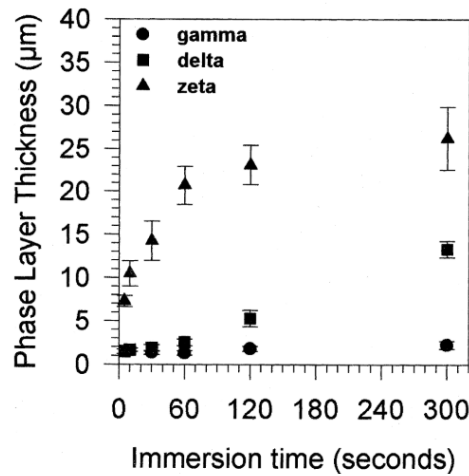


Figure 1.12: Individual Fe-Zn gamma, delta and zeta phase layer growth for a ULC steel substrate hot dipped at 450°C in a Zn bath [64]

1.2.3.1 Sandelin effect

The most famous effect of alloying elements on the reactivity of steel is that of silicon, called the Sandelin effect [69]. Phosphorous has a similar impact, and both effects are cumulative [70]. Steel is divided into four categories based on their Si content: low-silicon steels ($\leq 0.035\text{ wt. \% Si}$), steels from the Sandelin range ($0.035\text{--}0.12\text{ wt. \% Si}$), steels from the Sebisty range ($0.12\text{--}0.22\text{ wt. \% Si}$), and high-silicon steels ($\geq 0.22\text{ wt. \% Si}$) [7]. The three highest content groups of steel produce very thick coatings in hot dip galvanizing. This effect is considered negative for the quality of the coating and for the overconsumption of zinc. The relationship between the thickness of the coating and the silicon content is represented on the Sandelin curve (figure 1.13). As phosphorus contributes to

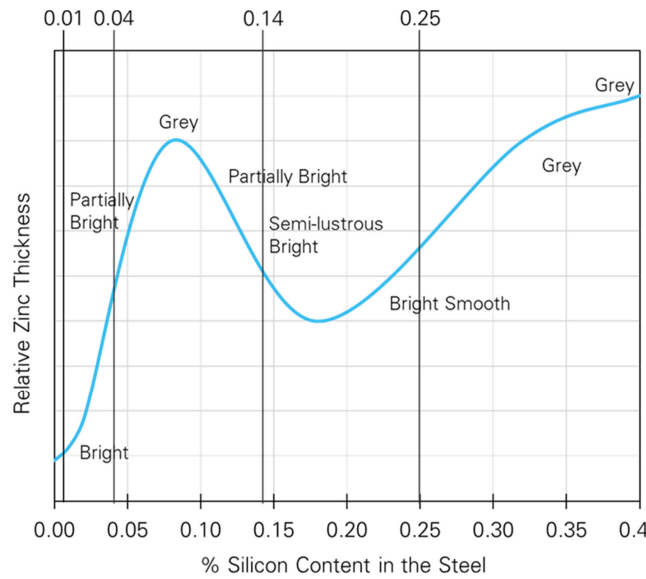


Figure 1.13: Sandelin curve showing the relationship between silicon and galvanizing coating thickness [71]

the high reactivity of steel with molten zinc, an Si equivalent can be calculated with the inclusion of P content (equation (1.30)). For hot-rolled steels and cold-rolled steels, the Si equivalent should be less than 0.09 % and 0.04 %, respectively. [10, 71, 73].

$$\text{Si equivalent} = \text{wt. \% Si} + 2.5 \times (\text{wt. \% P}) \quad (1.30)$$

As can be observed in the figure 1.14, coatings are not only thicker for non-low-silicon steels, but also their layer structure is disturbed. Kozdras et al. [74] proposed the mechanism of this higher layer growth. Solubility of Si in Γ_2 is much lower than in Γ_1 so this element accumulates in Γ_1 which plays a role as a barrier from δ phase and further reactivity.

In the Sandelin range, the coating has a significant ζ diffusion layer, the δ phase is reduced, and the η phase is almost inexistent. As Kozdras describes, Γ_1 layer is destabilized and forms small grains in the Γ_2 phase. The transfer of silicon to the δ phase is therefore facilitated. Zinc can then react with *delta* to transform it into *zeta*. However, a monoclinic ζ structure cannot accept as much Si as δ , and it retains it on its boundaries. Then, those boundaries become susceptible to penetration by the liquid, which again can transform δ into ζ , and the accelerated layer growth continues.

Another, more recent study by Reumont et al. [75] proposes a different model of reactivity (Figure 1.15). Here, homogeneous ζ phase nucleation in the liquid at a small distance from the substrate predominates over nucleation at the steel's

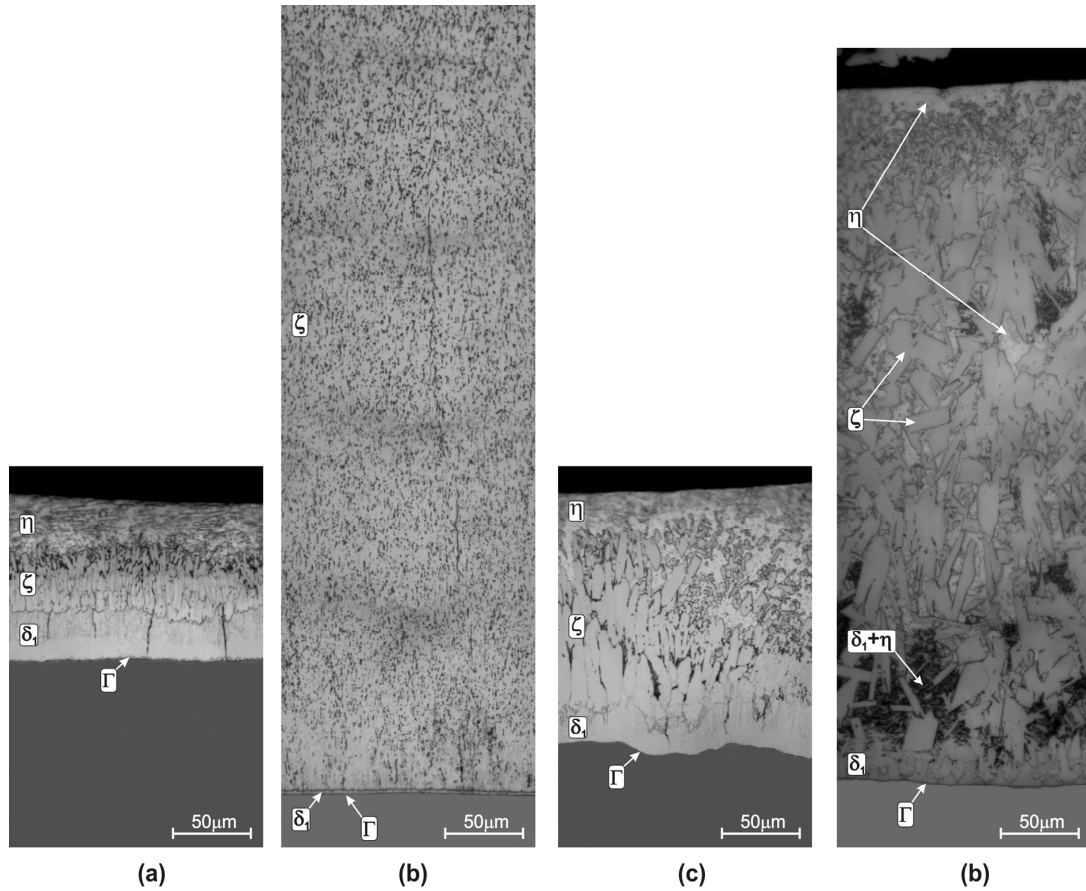


Figure 1.14: Structure of coatings obtained in the zinc bath on steels with different silicon content: low-silicon steel (a), Sandelin's steel (b), Sebisty's steel (c) and (d) high-silicon steel; temperature: 450 °C; immersion time: 3 min [72]

surface. It is caused by the presence of Si that is transferred from steel to the liquid and affects the Fe-Zn equilibrium. As a consequence, a thin film of liquid is trapped between steel and ζ crystals. Iron can readily diffuse across the film, promoting the growth of crystals until a unique ζ layer is formed. Besides, Si has low solubility in Fe-Zn intermetallics, with the exception of δ , which can accommodate some Si atoms. Also, the Fe-Zn-Si ternary system contains a weakly soluble in liquid zinc FeSi compound is present that is present at 450°C. Therefore, once the ζ layer is formed, the excess Si in the liquid zinc can lead either to the formation of FeSi particles or to the nucleation and growth of the δ phase. The high thickness of the coating is a result of this reaction being controlled by the high diffusion of iron in liquid Zn instead of in the ζ phase. Concerning the phosphorus, Chen et al. [76] describe it as being more soluble in

zinc than in intermetallics. In the case of those phosphorus rich steels, the mixed ζ -liquid Zn layer is formed, and channels of liquid zinc allow the connection of δ with outside liquid zinc that can erode the δ phase and promote the formation of ζ . The thickness of the coating increases with increasing P content.

Galvanizing coatings on Sebisty range alloys are similar to those of low-silicon steels, although the ζ phase is less compact and layers are less distinguishable. Zinc can more easily penetrate through the ζ phase, which leads to the growth of the δ phase and an increased thickness of the coating. Those steels can be used to find a compromise between galvanic coating thickness and the hardness of the steel promoted by the Si content. For high-silicon steels, the coating again gains in thickness, layers are not so well defined, but the ζ phase is composed of large crystals, not like in the case of Sandelin's steels. The coating's size depends on the temperature and decreases with a hotter bath [77].

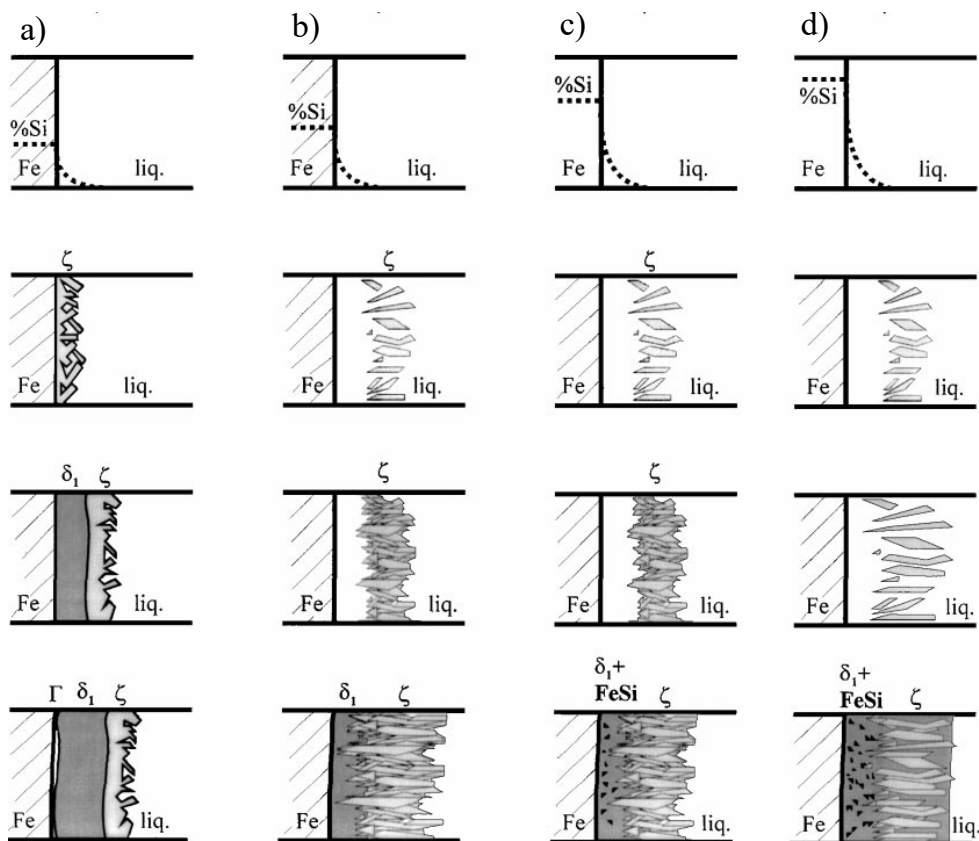


Figure 1.15: Modelling the steel-zinc reaction in a pure zinc bath at 450°C for a) low-silicon steels, b) steels from the Sandelin range, c) steels from the Sebisty range, and d) high-silicon steels [75]

1.2.3.2 Effect of other alloying elements on the reactivity with molten zinc

As was shown with the Sandelin effect, alloying elements can have an important influence on the thickness and composition of the galvanizing coating. In this section, the role of other common elements added to steel is to be discussed.

Carbon Low quantities of carbon do not influence the reactivity with liquid zinc. However, higher carbon content (≥ 0.3 wt. %) accelerates the dissolution of iron and consequently promotes the formation of a ζ layer, making the coating very brittle [73]. Interestingly, cementite (Fe_3C) is resistant to zinc attack, but increasing the content of C in pearlitic steels increases the reactivity of that steel. Differences between the behavior of lamellar and globular perlites in liquid zinc are observed [66].

Manganese Manganese is considered not to have a negative effect on the kinetics of the reaction Fe-Zn, but it can limit some local growth irregularities in the coating observed with plain carbon steels [66]. However, its higher content (≥ 1.25 wt. %) can improve the quality of the coating formed on steels from the Sandelin range by creating a more compact ζ phase [7, 73].

Nickel and chromium Both elements do not particularly change the kinetics of zinc-steel in galvanizing conditions [66]. However, iron has a temperature range of enhanced reactivity (495-530°C) that is extended in the presence of those elements, with 465-515°C for 11.6 wt. % Cr and 440-550°C for 5 wt. % Ni [78]. It is also to be noted, that the solubility of both elements in zinc at 450°C is far higher than that of iron, with the solubility of nickel equal to 0.42 wt. % and chromium equal to 0.73 wt. % [79] (figure 1.17). Nonetheless, Tang et al. [80] alert that the chromium solubility was overestimated, and in their study its value was 0.45 wt. % at 450°C. In the same study on Zn-Fe-Cr ternary, they state that in the Zn-rich corner at 450°C, the liquid is in equilibrium with ζ - FeZn_{13} and/or θ - CrZn_{17} phases. Tang also calculated Zn-Fe-Ni ternary [81] in which it is stated that in equilibrium, for wt. % Ni > 0.06 , the ζ phase is replaced by a ternary, Zn-Fe-Ni phase called *T*. As a result, the addition of Ni can limit the reactivity of silicon as the formation of ζ crystallites by formation of NiSi instead of FeSi [82], and the coating thickness goes back to normal [83].

The presence of the *T* ternary phase at the zinc-rich corner of the ternary phase diagram at 450°C and above was represented by different researchers [84, 85] and shown below on the figure 1.16. In the zinc-rich region, notably three phases can be distinguished: δ , that is well known as a FeZn intermetallic; Γ , that is present both in Fe-Zn (earlier noted as Γ_1) and Ni-Zn binary systems and in which atoms of iron and nickel are interchangeable [84]; and finally, a *T*

phase, that is a ternary Fe-Ni-Zn phase, whose structure is considered by Peng et al. [84] different from the Γ_2 phase from the Fe-Zn binary.

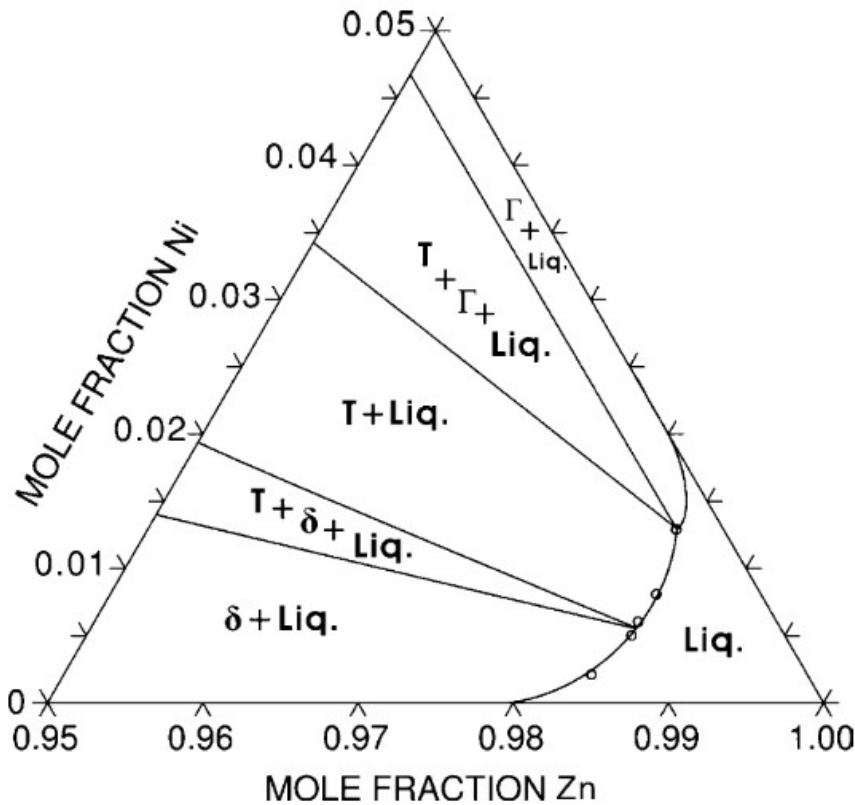


Figure 1.16: Fe-Ni-Zn phase diagram: the enlarged Zn-rich corner of the 560°C isotherm [84]

Others additions Ti, Nb, and V have no effect on the reactivity of steel in hot-dip galvanizing [66]. Molybdenum increases the reactivity at low content (≤ 5 wt. %) but at higher concentrations the reactivity is smaller compared to a Mo-free steel [66]. Increased content of sulfur (≥ 0.15 wt. %) leads to higher solubility of Fe in molten zinc and thick, brittle coatings [73].

1.2.4 Dezincification

At the end of the galvanizing cycle, the galvanizing coating is removed from conveying equipment like hooks or jigs with diluted HCl with the addition of a corrosion inhibitor. The goal is to remove only Zn and Zn-Fe intermetallics

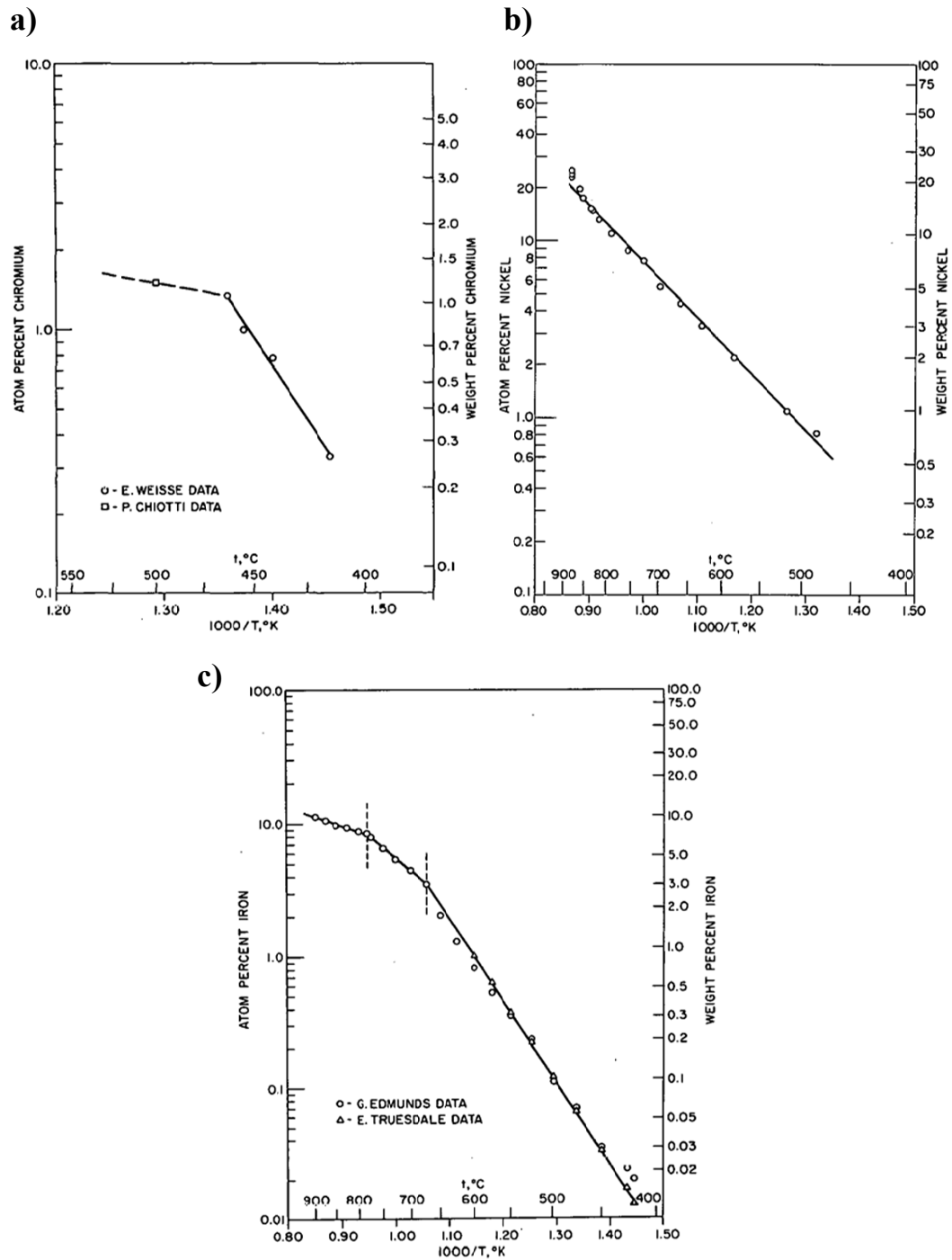
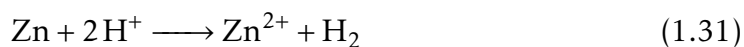


Figure 1.17: Solubility of a) chromium b) nickel and c) iron in zinc [79]

without the attack of steel [7]. As shown in reaction (1.31)[86], dissolution of zinc coating produces a high amount of hydrogen gas.



According to measures by Dou et al. [86], in the galvanizing coating, the dissolution of the zinc layer and then the dissolution of the steel substrate are not taking place simultaneously, with steel being attacked only when all protective layers are gone. Biryukov also shows the Zn-selective nature of the Fe-Zn δ phase in HCl [87]. To avoid the attack of iron, parts that have been dipped in acid must be removed once the operator observes the end of the effervescence in the bath [88].

1.3 Protection from the liquid zinc damage

In batch galvanizing, conveying systems must adapt to the different types and geometries of products to be galvanized. To transport those articles, crossbeams, hooks, chains, and other devices can be used. Those structures are also made of steel and are exposed to contact with liquid zinc, followed by dezincification after each galvanizing cycle. This cyclic galvanizing treatment leads to the phenomenon of corrosion by liquid zinc.

Corrosion by liquid zinc is a complex process linked to several chemical interactions and mechanical aspects. One of the mechanisms of liquid metal corrosion is the dissolution of one or several elements of alloy in molten metal [89]. The dissolution of iron in liquid zinc is controlled by the diffusion of the former into the latter, with the following the diffusion coefficient [90]:

$$D_{Fe}^{Zn(L)} = (9.8 \pm 0.1) \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$$

The second mechanism of corrosion by liquid metal is the formation of inter-metallic compounds between solid alloy and liquid metal [89]. As mentioned in 1.2.3, iron and zinc can form several intermetallics, and if, generally, in galvanizing, this reactivity between steel and zinc is considered advantageous for the formation of protective coating. However, when equipment from the galvanizing plant is affected by zinc, it can lead to weight loss and failure. Another element causing liquid metal corrosion can be pollution dissolved in the melt, mainly oxygen or carbon, that can lead to the oxydation (or carburation) of steel. The last main mechanism of corrosion in liquid metal is corrosion-erosion. For instance, in continuous galvanizing, the surface of sink rolls can also be eroded mechanically through the scouring of liquid metals [91].

Additionally, galvanizing plants are meeting additional zinc losses through a drag-out, caused by the good wettability of steel in the bath. Continuous galvanizing meets a similar problem with liquid zinc corrosion as sink rolls, stabilizing rolls, and the kettle containing the liquid zinc alloy are in constant contact with molten metal. The issues met by sink rolls with molten zinc are the pitting and formation of Fe-Zn intermetallics, leaching of Fe into the melt, and zinc slag adhering to their surface that affect their lifespan and quality of the coating [91]. Several studies [91–115] have already been conducted on the subject of the limitation of liquid zinc corrosion in continuous hot-dip galvanizing, and in this section, those solutions will be examined.

1.3.1 Stainless steel

316L stainless steel is commonly used for sink rolls and pot equipment for its good combination of resistance to Zn-Al melt, mechanical properties, and reasonable cost [92]. Xu et al. [116] conducted a comparative static corrosion test of 1015 low-carbon steel and two stainless steels (410 and 316L) in pure Zn melt. 316L stainless steel resisted the best to liquid zinc corrosion (figure 1.18). The authors attribute that to its high Ni and Cr content and fcc lattice, which showed better performance than the bcc or body-centered-tetragonal structure (martensite) because of its compact structure. Stainless steel has a high content

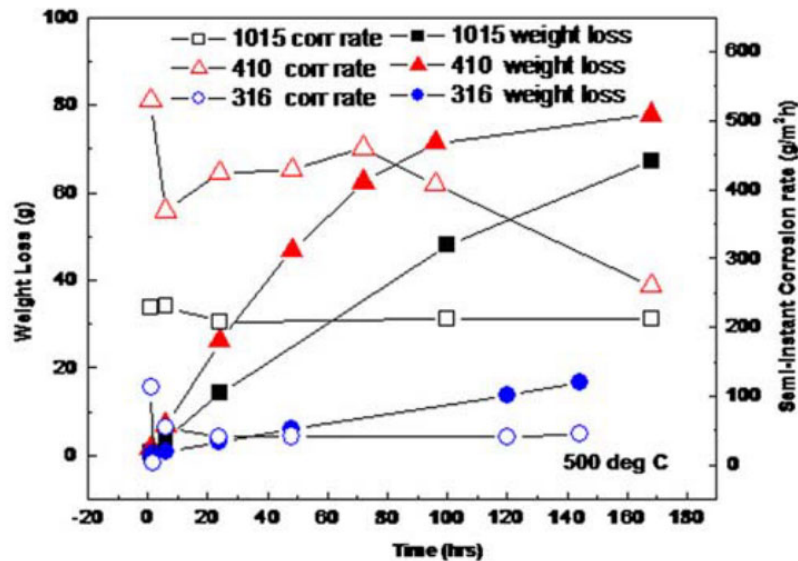


Figure 1.18: Weight loss and semi-instant corrosion speed of 1015, 410, and 316L steels exposed to pure zinc at 500 °C [116]

of Cr which naturally passivates to form a protective chrome oxide layer at the

surface. Zhao et al. [117] tested the influence of said oxide on the formation of intermetallics in a liquid zinc bath. The passivation was done either in air for different periods of time or in nitric acid. However, during the zinc treatment, oxides became unstable and only slightly decreased the growth of intermetallics in comparison to freshly ground steel. Those intermetallics were composed of ζ -(Fe, Cr)Zn₁₃ and δ -(Fe, Cr)Zn₁₀.

The addition of Al to the Zn melt inhibits Fe-Zn intermetallic formation as iron reacts preferentially with aluminum over zinc. Gay et al. [94] tested different stainless steels in baths with two Al contents (0.25 and 0.10 wt. %) and followed the increase in Cr and Ni content in the bath. Results across different types of steel showed that a higher content of Al in the bath caused higher dissolution. In their study, Co/Cr steels showed good performance in liquid zinc because of the formation of a protective FeAlCoCrZn layer. In bath with a lower content of Al, the dissolving rate was multiplied by 4. It was proposed that the formation of a "FeAlCrZn" inhibition layer in a high Al-content bath was the reason for the difference in performance. The article also described that stainless steels are not, in general, prone to intergranular corrosion in liquid zinc, contrary to carbon steel.

As is detailed in the article of Zhang et al. [92], the corrosive reaction on stainless steel equipment in a Zn-Al bath starts with the formation of a Fe₂Al₅Zn_x layer with a small content of Cr and Mo. In the early stages, this layer grows until it attains a steady thickness. Dross particles (Fe₂Al₅ type) present in the bath attach easily to this layer because of the similar crystallographic structure. Therefore, the Fe₂Al₅Zn_x layer plays the role of a precursor to the buildup. Once the aluminum supply from the bath becomes limited, δ -ZnFe phase areas form. The dissolution of the arriving strip to be galvanized is an important factor in the formation of a dross buildup on the stainless steel, and this buildup is observed to not be evenly distributed on all stainless steel equipment. This layer must then be regularly removed in order to maintain the good quality of the coating [94].

In continuous galvanizing, sink rolls are not only influenced by liquid zinc but also by friction. Yu et al. [95] studied the tribo-corrosion of 316L at 460°C and observed that the formed Fe-Al-Zn intermetallics are brittle enough to accelerate the wear. Additionally, wear sweeps all nuclei of Fe₂Al₅Zn_x, thus promoting the formation of δ -FeZn₁₀, which is less protective. Therefore, corrosion is also accelerated. In this manner, a synergic effect is created.

1.3.2 Protective coatings

Even though 316L stainless steel is better adapted to limit liquid zinc corrosion than other types of steel [116], several coatings were studied in order to further

improve the performance of galvanizing line equipment [95, 96, 99–104, 118]. As Co-based alloys like Stellite 6 have been shown to have good resistance to wear [98], but poor resistance to corrosion [96, 97] improved cobalt-based coatings were developed. The most common one is the WC–(10–15 wt·%)Co coating obtained by thermal spray coating (high velocity oxygen fuel (HVOF) spraying). Resistance to corrosion is based on reactions between WC and Co during preparation and thermal spraying that lead to the formation of Co–W–C phases: $\text{Co}_3\text{W}_3\text{C}$ and $\text{Co}_6\text{W}_6\text{C}$ phases [91, 96]. However, problems may arise from different coefficients of thermal expansion between the coating and substrate steel that lead to cracking of the material and, therefore, the attack of steel by liquid zinc [99]. Also, incorrect preparation of coatings can lead to the concentration of residual stresses and, thus, cracking [96]. Spallation and cracking can be limited by the correct thickness of the coating [96]. Cracks in WC–Co coatings can aid the penetration of zinc but also reactions of Al with Co that lead to the formation of CoAl , which can act as abrasive particles. In the study of Aboutalebi et al. [101] on the properties of WC–Co coatings with various Co contents, WC–17Co coatings had the best resistance to liquid zinc corrosion. The WC–Co corrosion mechanism is based on the dissolution of cobalt followed by the detachment of carbides [104].

The properties of WC–12Co on 316L steel were compared with another thermal spray coating, MoB–CoCr, by Zhang et al. [100]. In their test, MoB–CoCr showed better resistance to thermal shock with no obvious cracks after 300 cycles of quenching from 500°C to 25°C. WC–12Co had visible cracks and was peeling off at the same time. It was also observed that MoB–CoCr is wetted worse by zinc than the other coating, which results in higher resistance to molten zinc after 360 h of immersion. Chen et al. [102] tested different compositions of HVOF coatings and found that TiB–CoCr and, especially, MoB–NiCr coatings had even smaller weight losses than MoB–CoCr.

Xie et al. [118] measured the corrosion rate of 316L steel at 460°C to be 115.44 $\mu\text{m}/\text{day}$. They also tested 3 thermal spray coatings at 450°C: WC–12Co (6.82 $\mu\text{m}/\text{day}$), Mo–CoCr (5.77 $\mu\text{m}/\text{day}$) and a novel cermet coating: FeB–12 wt·%Al0.25FeNiCoCr with a corrosion rate of 16.17 $\mu\text{m}/\text{day}$. Even though the protection is lower than for WC–12Co and Mo–CoCr, the authors outline the advantage of the lower cost of the coating in comparison to other ones.

Plasma spraying oxide coatings such as Al_2O_3 or $\text{ZrO}_2\text{--Y}_2\text{O}_3$ present are interesting for their wear resistance, high-temperature properties, and especially their non-wettability by molten zinc that limits reactions between steel and bath [91, 96, 103, 104]. However, their lifetime is limited because they are very susceptible to crack formation and spallation [91]. They are, however, shown

to be more useful than classic WC-Co coatings in high temperature conditions and high-Al content baths [96, 104]. Liberski et al. [103] treated Al_2O_3 and ZrO_2 plasma spray coatings in molten zinc at 600°C , dipped for 24h, retrieved, and dipped again. Steel coated with Al_2O_3 was severely damaged after only 4 days, while ZrO_2 coating lasted 7 days. The authors attributed the loss of their protective properties to the porosity and thermal shocks occurring during immersion and to the difference in thermal expansion coefficients between the coatings and base steel. Meanwhile, later Nag et al. [104] report that Al_2O_3 and $\text{Al}_2\text{O}_3\text{--TiO}_2$ showed no weight loss during a 30-day static corrosion test in Zn-Al(0.14 wt. %) at 455°C . They were taken out of the bath every ten days, not every day and tests were done at lower temperatures than those of Liberski, which may impact the resistance of oxide coatings.

To counteract the tribo-corrosion, Yu et al. [95], suggest covering 316L steel with an enamel coating, made primarily of SiO_2 but also B_2O_3 , Li_2O , Al_2O_3 , Na_2O , CaO and CaF_2 . The amorphous $[\text{SiO}_4]$ network thus obtained at the surface is chemically inert in the Zn-0.2wt%Al alloy and is so compact that molten zinc cannot penetrate in it. In comparison to uncoated 316L steel and WC-12Co coating, this enamel coating experienced the least amount of material deterioration as a result of the test's cyclic friction loading.

1.3.3 Boride alloys and coatings

Another solution for protection against liquid zinc corrosion in continuous galvanizing is boride alloys and coatings. They are interesting as they are not wetted by liquid zinc [103, 108, 111] Boride alloys were largely studied by the team from Xi'an Jiaotong University in China [105–109]. They found that the Fe-B ratio of Fe-3.5 wt.%B cast steel was the most interesting in terms of its resistance to molten zinc, with its corrosion rate at 460°C being equal to $1.35\text{ }\mu\text{m/h}$ [105]. This resistance to corrosion is attributed by the authors to the presence of the Fe_2B phase in a netlike structure, which serves as the diffusion barrier to zinc penetration in iron. The corrosion mechanism is depicted in figure 1.19a. It starts with the dissolution of $\alpha\text{-Fe}$, which leads to the formation of intermetallics (ζ and δ phases). Next, internal stresses brought on by Fe/Zn reactions cause the formation of cracks and the spallation of Fe_2B . According to the findings of a study [106], FeB alloys enriched with Cr and Ni can further improve corrosion resistance through preferential leaching of Cr and Ni instead of Fe into molten zinc. In corrosion-wear experiments at 460°C in pure zinc [107], it was observed that the corrosion-wear rate of Fe-3.5 wt.%B steel with a netlike structure was almost 4.5 times lower than that of liquid zinc. [119] details that further augmentation of Ni content from 4 wt.% (as in [106]) to 10 wt.% can increase the resistance to corrosion through the transformation of the

from α - to γ -(FeCrNi) phase.

To take things one step further, directional alloys were prepared with alternating layers of α -Fe and Fe₂B [108]. They were tested in flowing zinc in two configurations facing molten zinc (figure 1.19). The test was conducted to study erosion-corrosion. The parallel configuration of the solid (Figure 1.19 b) showed a higher erosion-corrosion rate than the vertical configuration, regardless of the test temperature. Zinc diffusion into the solid is slowed down in vertical samples due to the pinning effect, which also lessens columnar boride spalling. However, a parallel sample is subjected to higher spalling and layer-by-layer material degradation. Corrosion products and spalled Fe₂B are removed with zinc, freeing the subsequent layers to be damaged. In contrast, in a vertical sample, corrosion products act as a barrier since they are difficult to wash off. In another study on oriented Fe-3.5 wt.%B steel, the authors looked at the effects of adding 0.30 wt.% Al to liquid zinc. It was shown that erosion-corrosion resistance was improved for both orientations by more than 85 %, with the vertical orientation once again performing better in flowing zinc [109].

Shen et al. [110] proposed another improvement of the Fe-B alloy, not only by adding chromium, but also aluminum, which was later preoxidized at 850°C in order to form protective Cr₂O₃, Al₂O₃, and FeCr₂O₄ oxides on the surface of the alloy. Moreover, Al₂O₃ was found to oxidize internally on the α -Fe. After 20 h at the oxygen partial pressure $p_{O_2} = 10^{-20.5}$ atm, a compact, continuous oxide layer was obtained at the surface. It was composed of M₂O₃ with M: Al, Cr, B. After 72 h of treatment in Zn-55 wt% Al at 600°C, a few small cracks were seen in the coating, but the oxide layer was unchanged and no visible damage was observed on the alloy. In comparison, corrosion was observed after treatment of a non-preoxidized alloy in the same conditions. This material is very promising for use in a molten-zinc environment. However, it can be seen on micrographs from the study that a thick layer of Zn-Al melt adhered to the surface of the coating, so potential zinc economy could not be attained if employed for batch hot-dip galvanizing equipment.

Liberski [103] investigated FeB and (FeCr)B in the form of a coating created via pack cementation. He measured high wetting angles through the sessile drop projection method for both compositions of coatings, thus proving their poor wettability with liquid zinc. Additionally, he put them in the corrosion resistance test in liquid zinc at 600°C in 24-hour cycles. FeB coating resisted for 41 days, while (FeCr)B coating extended the steel's protection up to 71 days. It was observed that the corrosion is initiated by small cracks that are penetrated by zinc. Once they produce Fe-Zn intermetallics, the increased volume of those phases widens the cracks and promotes contact between Fe and Zn.

Other borides can also be used as coatings on stainless steel, as mentioned

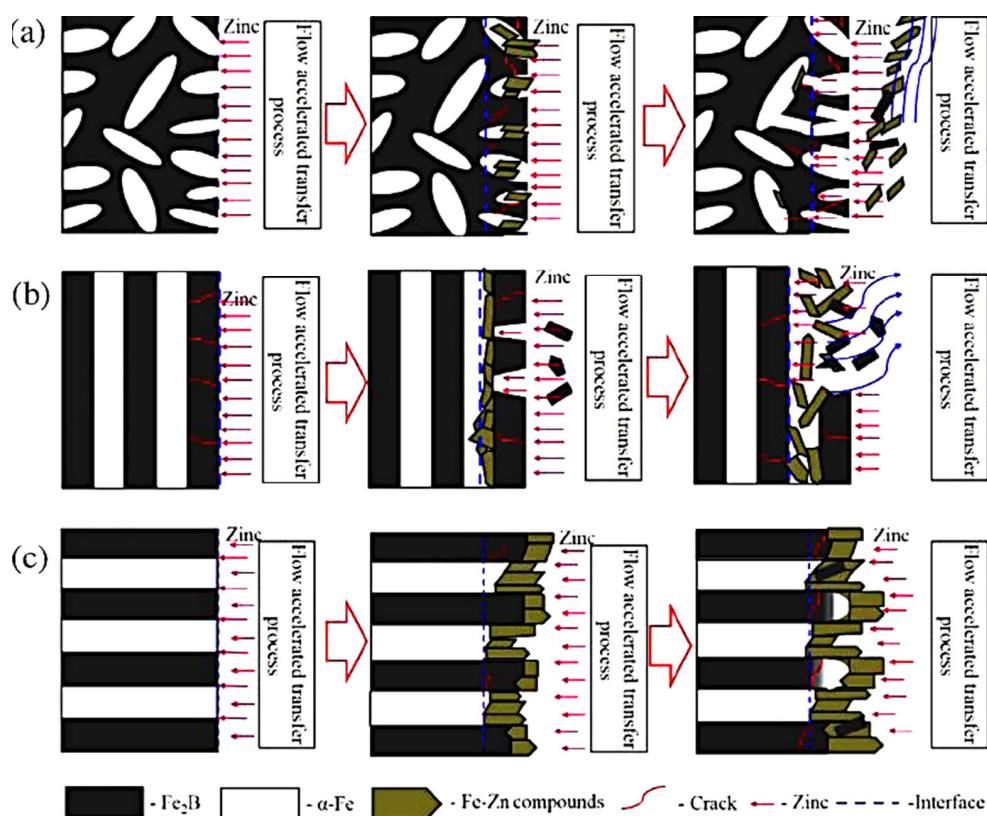


Figure 1.19: Erosion-corrosion mechanism of Fe-3.5 wt.%B alloy with non-oriented and oriented Fe_2B boride in flowing liquid zinc: (a) non-oriented sample (Crack-induced and flow-accelerated spalling manner); (b) parallel sample (layer-by-layer spalling manner); (c) vertical sample (corrosion and less spallation) [120]

in section 1.3.2 with an example of MoB-CoCr coating. Wang et al. [111] studied static corrosion ZrB_2 coating on 201 stainless steel formed by molten salt electrodeposition. In their tests at 550°C , the coating rested unchanged for 72 h. Cracks, however, began to appear in zones with high stress concentration after 96 h. Zinc thus started to penetrate and react with steel under the coating, leading nearby zones to detach from the substrate and facilitate additional corrosion.

1.3.4 Other materials

Some more materials were suggested for use in continuous galvanizing. Molybdenum is one among them [113, 114]. Wang et al. [113] investigated the influence of ZrO_2 doping on the liquid zinc corrosion at 460°C . For pure Mo, a corrosion

rate of $0.699 \mu\text{m/h}$ was obtained. With the addition of 2 wt% of ZrO it was reduced to $0.383 \mu\text{m/h}$. In a different study, Wang [114] doped Mo with Al_2O_3 . 2 wt.% of this oxide gave a corrosion rate of $0.364 \mu\text{m/h}$, which is comparable to doping with ZrO. For all three materials, those results are still worse than for Mo-CoCr coating with $0.240 \mu\text{m/h}$ [118].

The effects of oxidizing and nitriding-oxidizing on the zinc corrosion of Fe-21-9Mn steel were investigated by Fang et al. [115]. Interestingly, this material's natural zinc resistance was poorer than that of 316L stainless steel, and its rate of corrosion was twice as high. Yet, after oxidizing, no corrosion was observed for the first ten days in molten Zn-0.8 wt% Al at 460°C . For the nitridized-oxidized alloy, this incubation period took even 25 days. Throughout the test period, the corrosion rate for both the non-treated alloy and the 316L steel remained largely unchanged. In contrast, for the oxidized sample, the corrosion rate increased rapidly after 10 days and may potentially regain its original rate later. For the nitridized-oxidized sample, the corrosion rate rose slower, and after 40 days, it still did not attain that of 316L steel. Therefore, this surface treatment could be promising for use in hot-dip galvanizing.

1.3.5 Use of silicon for batch hot-dip galvanizing

UMET laboratory members studied bulk iron-silicon alloys with varying Si content, produced from commercial FeSi powders by casting in air [121]. Through analysis of potentiodynamic polarization curves, they observed that with higher Si content, the corrosion potential shifts to more anodic values, thus making the alloy more noble. They suggested that this effect may be caused by the formation of a SiO_2 layer at the surface of the material.

The formulation of the hypothesis of oxide layer formation at the surface of FeSi alloys resulted in the development of cyclic galvanizing tests to assess the materials' resistance to liquid zinc corrosion. Samples with Si content ranging from 0 to 25 wt.% underwent a treatment that included surface preparation typical of batch hot-dip galvanizing, followed by immersion in molten zinc at 450°C and dezincification. This cycle was repeated 19 times. As represented in the figure 1.20, it has been shown that a high content of silicon can improve the resistance of a material to liquid zinc corrosion. The weight loss during galvanizing cycles is fully minimized for alloys containing more than 20 wt.% Si.

However, as evidenced by the literature [121–124], Fe-Si alloys are brittle, which renders them unsuitable for use as hangers in batch hot-dip galvanizing facilities. Instead of being used as a bulk material, Fe-Si may be applied as a coating. The Fe-Si prealloy might be melted on the surface of a resistant part and then cooled to generate a homogenous layer of Fe-Si coating. However, as can be

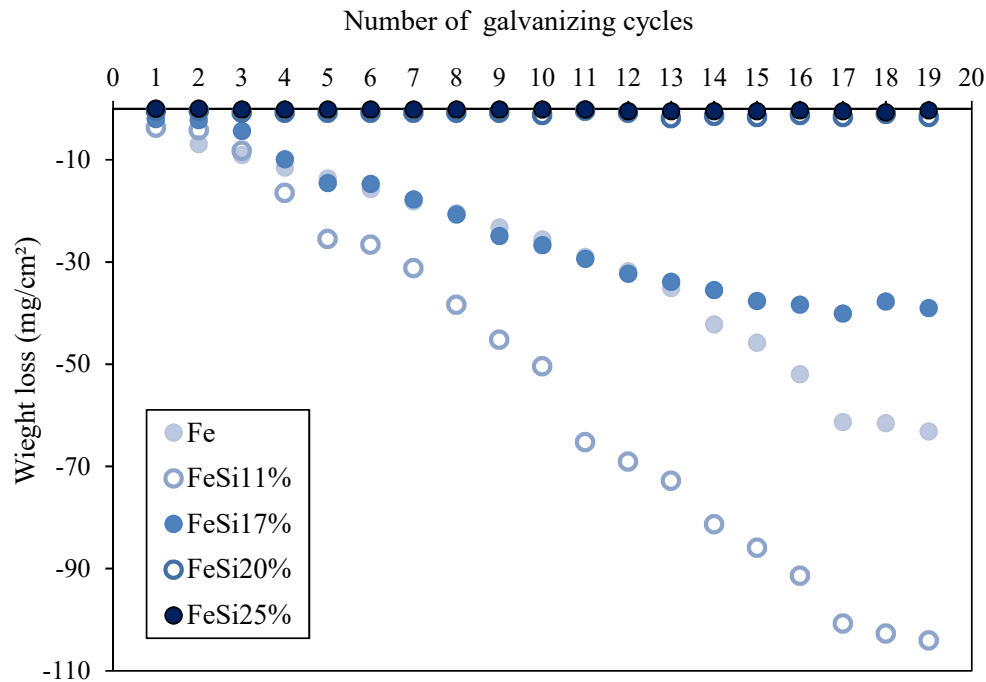


Figure 1.20: Total weight loss of FeSi alloys with different Si contents (wt.%) during 19 galvanizing cycles in liquid zinc at 450°C

observed on the Fe-Si phase diagram (fig. 1.21), melted silicon kept at constant temperature in contact with steel will tend to diffuse up to the point on the iron liquidus, which is always below 20 wt.% Si. Therefore, a fast enough coating formation method is necessary in order to trap the higher content of silicon at the surface.

1.3.6 Conclusion

A lot of studies have been done in terms of the protection of zinc pot equipment from liquid zinc corrosion in the domain of continuous galvanizing. However, the constraints laying on those parts are very different from those that lay on transfer elements present in batch hot dip galvanizing, as different surface treatments and galvanizing baths are used. In this branch of galvanizing, almost none substantial research has been done up to this moment. The main problem with batch galvanizing equipment lies in the cyclic galvanizing and dezincification of parts, which leads to high consumption of zinc and hydrochloric acid. This limits the use of all materials that are wetted and that react with molten zinc bath with extremely low Al content, like 316L stainless steel [125]. Non-wettable

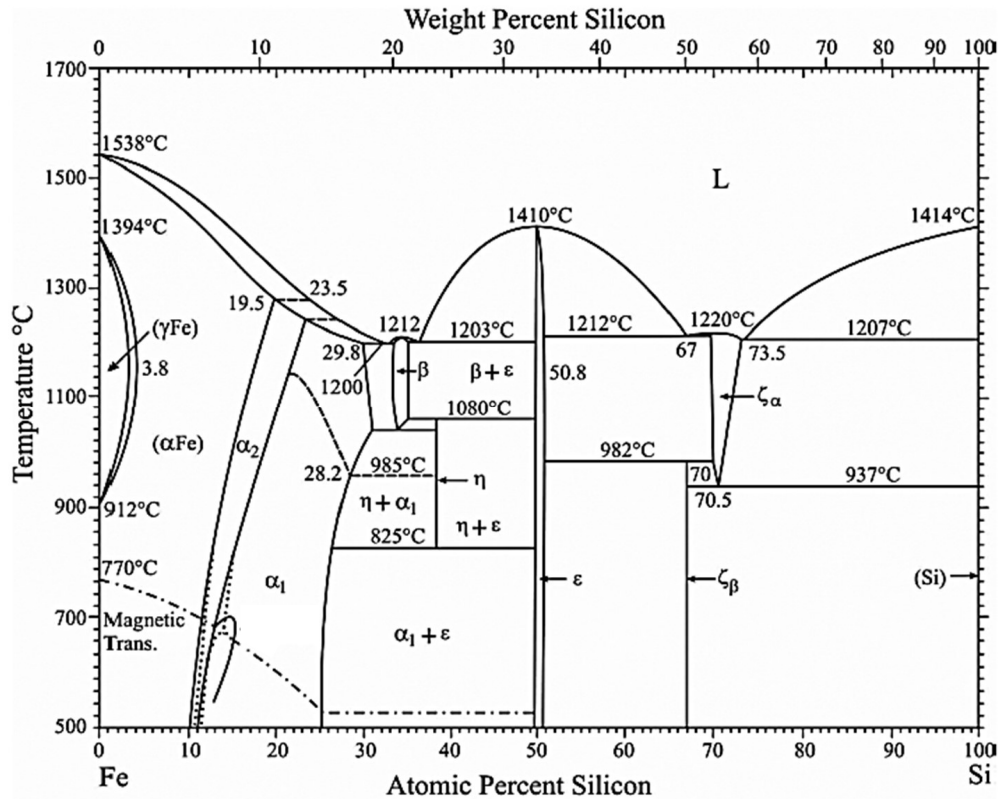


Figure 1.21: Fe-Si phase diagram [57]

oxide coatings are studied for use in continuous galvanizing, but they cannot withstand the thermal shock and mechanical stress of mounted pieces treated in batch hot-dip galvanizing [103]. Many of the non-wetting solutions discussed above were also noted to be degraded through cracking as a result of mechanical and thermal interactions.

Additionally, the cost of materials prevents the use of many continuous galvanizing solutions. Even more expensive methods in continuous galvanizing may be interesting if they reduce the necessity of pausing production for maintenance. However, because 316L stainless steel is five times more expensive than standard steel [126], industrial sites' revenue is insufficient to justify its use in order to reduce the loss of steel from liquid zinc corrosion. Coatings, instead of bulk materials, could be more interesting, but those used in continuous galvanizing are also too expensive, with cobalt, as an example, costing 33 000 USD/t [127].

Finally, usage of materials or coatings capable of oxidation could be interesting for application in batch hot-dip galvanizing, either through formation of natural non-wetting oxides or through preoxidation.

This thesis offers a batch hot-dip galvanizing solution that is more adapted to the limitations of this particular industrial procedure.

Chapter 2

Methods: surface analysis, *ab initio* simulation, and material production techniques

2.1 Introduction

This study uses a variety of techniques to examine interactions at the interface between liquid zinc and studied solid materials. One of the most important aspects of protecting steel galvanizing equipment from liquid zinc is to reduce its wettability and reactivity with this molten metal. This is why theoretical aspects of wetting are presented in the first part of this chapter. Next, the theory of *ab initio* simulation is described. It is a type of simulation done at the atomic scale that gives access to interface and surface energies of the system. Using those values and the Young equation (described in 2.2.1), a contact angle θ can be computed and compared to the experimental one. The outcomes of this simulation will be discussed in chapter 3. Next, various experimental analysis techniques are presented in this chapter. They involve extreme surface analysis methods, such as ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) or XPS (X-Ray Photoelectron Spectroscopy), that give access to the material's composition at the first couple of nanometers. Other methods that were used in this study to understand mechanisms of interface interactions, for instance, Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray spectrometry (EDX), will have their principles and applications detailed in this section. This chapter will conclude with a presentation of two methods used to manufacture coatings studied in this thesis.

2.2 Wetting

Wettability is the ability of a liquid to maintain contact with a solid surface. It results from the equilibrium between adhesive forces between solid and liquid and cohesive forces within the liquid.

2.2.1 Wetting of an ideal surface

For ideal solid, flat, smooth, chemically homogeneous surfaces in equilibrium, wetting can be represented by a numerical value of the contact angle θ , which is defined by the equation of Young (1805) [128]:

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

with γ_{LV} , γ_{SV} standing for the surface energy of liquid and solid, respectively (in a given atmosphere or vacuum), and γ_{SL} standing for the interface energy between solid and liquid (as shown in figure 2.1). θ_Y is a contact angle at equilibrium. Molecules in the liquid are held together through cohesive interactions.

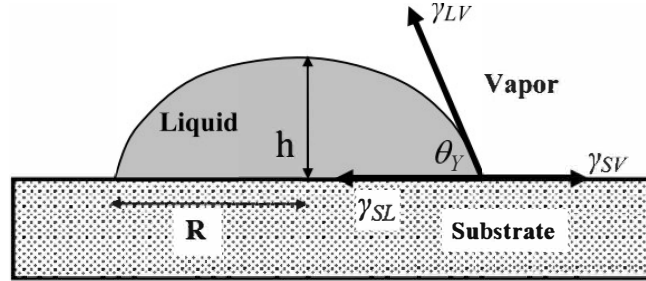


Figure 2.1: Interfacial tensions at the three-phase contact line with R , the radius of the drop base, and h , the height of the droplet. The drop is small enough to neglect the action of gravity [129]

Surface molecules cannot completely interact with other ones; therefore, they have surplus energy γ_{LV} , also known as surface tension. The molecule will try to minimize this energy by reducing the surface area, which leads to a spherical form of droplets. To increase the surface area A of a liquid, work must be provided, such as:

$$\partial W = \gamma_{LV} dA \quad (2.2)$$

The coefficient between surface change and work change is then surface tension γ_{LV} . This value can also be defined as [128]:

$$\gamma_{LV} = \left(\frac{\partial F}{\partial A} \right)_{T,V,n_i} \quad (2.3)$$

with F , free energy of Helmholtz. This variation of energy is for a constant temperature, volume, and amount of substance. It is measured in J/m^2 .

As shown in figure 2.2, for a contact angle θ below 90° , the surface is wetted by the liquid with perfect wetting at $\theta=0$. For a θ value above 90° , the solid is considered non-wettable by the liquid in question. If the surface energy of the solid is higher than that of the liquid, the liquid will tend to spread and wet the surface. Conversely, if the surface energy of the solid is lower, the liquid will tend to form a drop. This relation is determined by the spreading parameter S , for which a negative value describes partial wetting, and for $S > 0$, the surface is wetted completely by the liquid, and it spreads entirely to form a thin film on the top of the surface [130]. S is defined as follows:

$$\begin{aligned} S &= \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \\ &= \gamma_{LV}(\cos \theta - 1) \end{aligned} \quad (2.4)$$

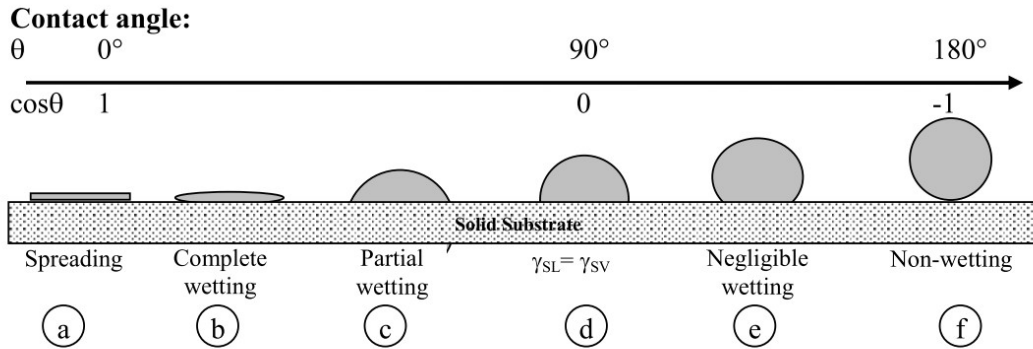


Figure 2.2: Liquid drop on a solid surface. The condition $\theta < 90^\circ$ indicates that the solid is wetted by the liquid, and $\theta > 90^\circ$ indicates non-wetting. Limits of $\theta = 0$ and $\theta = 180^\circ$ define complete wetting and complete non-wetting, respectively [129]

2.2.2 Wetting of non-ideal systems

Wetting in non-ideal systems involves more complex behaviors, often due to the interplay of various factors such as surface roughness, chemical interactions, and heterogeneities [128, 131, 132].

In ideal systems, the Young equation gives only one contact angle at equilibrium, which depends only on surface and interface energies on the contact line. However, in real systems, contact angle exists in a range defined by contact angle hysteresis (CAH). This changing contact angle can be observed in the case of a droplet on a vertical or tilted surface with gravity pulling the drop in one direction, thus creating two different contact angles (Figure 2.3a) or when the liquid is pumped in or out of a droplet (Figure 2.3b) [133]. CAH is defined as a difference between the advancing contact angle θ_A and the minimum contact angle θ_R , called receding contact angle [131]:

$$\Delta\theta = \theta_A - \theta_R \quad (2.5)$$

θ_A and θ_R are, accordingly, the maximum and minimum contact angles possible so that the contact line is not in motion.

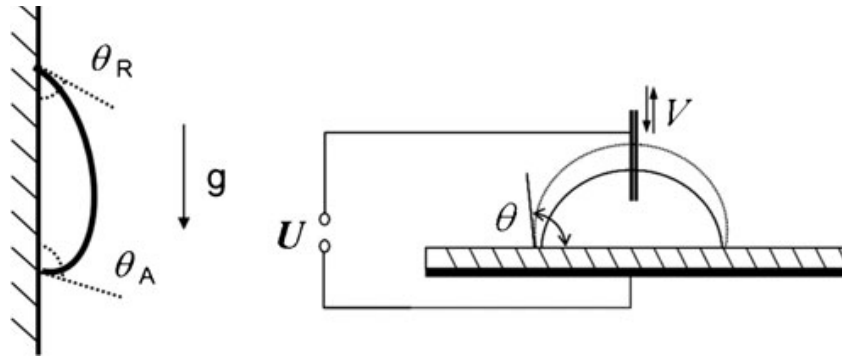


Figure 2.3: a) A drop on a vertical surface, stuck at the critical advancing angle θ_A and the critical receding angle θ_B , b) both the advancing and receding angle can be measured by slowly pumping liquid into or out of a sessile drop [133]

In practice, a surface has some level of roughness that can significantly impact wetting behavior. When a liquid comes into contact with a rough surface, it can penetrate into the surface irregularities, leading to the observation of an apparent contact angle θ_{app} , which is an angle observed at thermodynamic equilibrium (Figure 2.4). Wenzel [134] proposes an equation that shows the relation between the Young contact angle and the apparent contact angle on a rough surface:

$$\theta_W = r \cos \theta_Y \quad (2.6)$$

with r , roughness factor, being a ratio between an actual, rough surface and a geometrical, perfectly smooth surface. The apparent angle θ_W is called the Wenzel angle. With increasing roughness, θ_W decreases for wetting systems and increases for non-wetting systems [132].

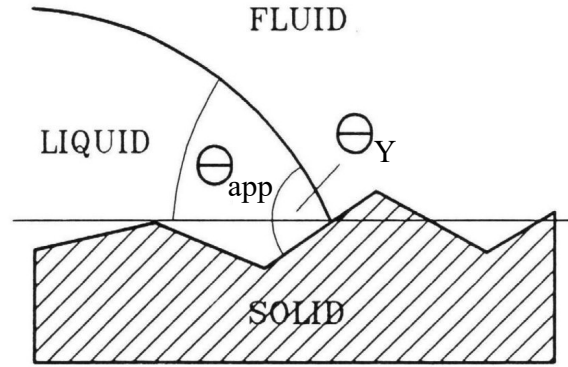


Figure 2.4: The intrinsic contact angle, θ_Y , and the apparent contact angle, θ_{app} , on a model rough surface [135]

Another factor influencing the wetting of non-ideal systems is chemical surface heterogeneity, meaning it has different chemical compositions across different regions that can have different wetting properties (Figure 2.5). Cassie and Baxter equation [136] describes the effect of this heterogeneity on the resulting contact angle at equilibrium:

$$\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.7)$$

with f_1 , f_2 , fraction of according chemical phases at the surface and θ_1 , θ_2 , contact angles at equilibrium obtained between the liquid and corresponding surface. θ_C apparent angle is also called Cassie angle. This model is adapted for surfaces where different phases are small in comparison to the drop size.

In the case of specific textures such as pins with sharp corners on non-wettable surfaces ($\theta > 90^\circ$), liquid cannot easily penetrate the irregularities, and thus the air is trapped under the liquid (Figure 2.6). As a result of this texture, the apparent angle does not follow the Wenzel law but the Cassie-Baxter law for composite material solid/air [130, 137].

2.2.3 Reactive wetting

Reactive wetting takes place in a system where a reaction occurs at the solid-liquid interface during the spreading of a droplet. Notably, this is the case of steel wetted by liquid in hot-dip galvanizing [138, 139]. At the interface, a

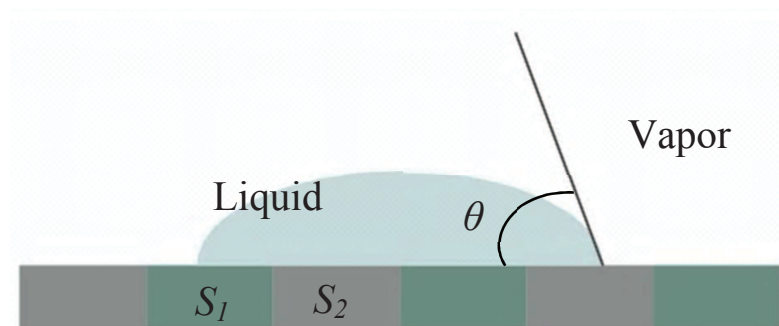


Figure 2.5: Liquid drop on a heterogeneous surface [132]

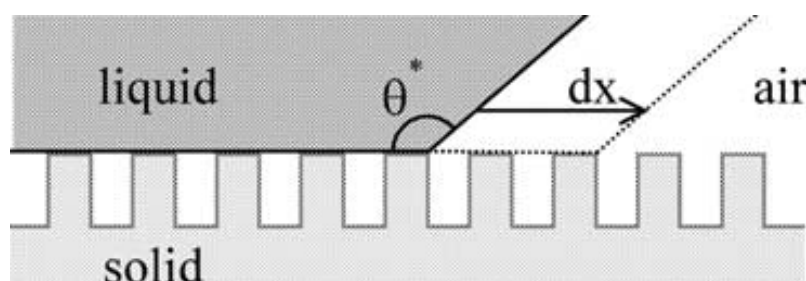


Figure 2.6: Liquid deposited on a model surface with holes and spikes: for contact angles larger than 90° , air is trapped in the liquid, inducing a composite interface between the air and the drop [137]

diffusion of solid atoms into the liquid, or inversely, dissolution of the solid, and the formation of a new intermetallic can take place in a reactive system [130, 140, 141], thus creating two main categories [128]. On one hand, wetting with dissolution only causes a change in solid composition that induces a change in surface energy. The other type is wetting with the creation of an intermetallic that can be more or, contrarily, less wettable than the surface. Reactive wetting happens in five stages. It starts with an initial rapid spreading, similar to non-reactive wetting, followed by an initial quasi-equilibrium stage. Next, an interfacial front advances until it stops, and then the drop height decreases. Once all the movement ceases, final wetting equilibrium is attained [140, 141].

In the case of dissolutive wetting, the Young law for a wetting equilibrium cannot be applied, as the triple line is not plane anymore (Figure 2.7). In this

new configuration, equilibrium is expressed by the following rule [142]:

$$\frac{\gamma_{SL}}{\sin \theta_1} = \frac{\gamma_{SV}}{\sin \theta_2} = \frac{\gamma_{LV}}{\sin \theta_3} \quad (2.8)$$

Experimentally, only an apparent wetting angle of $180^\circ - \theta_1$ is measured.

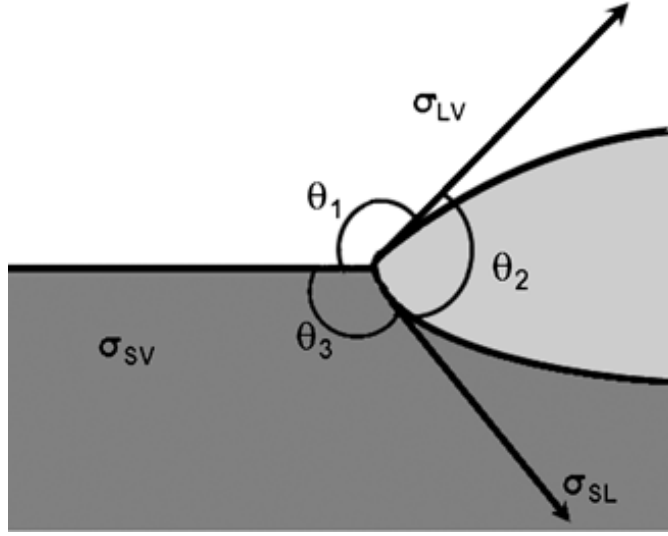


Figure 2.7: Equilibrium configuration in the presence of dissolution of the solid [142]

When a new product forms at the solid-liquid interface, it can be limited to the area covered by the drop or extend beyond into the free solid surface [143], as represented on the figure 2.8. In the first configuration (Figure 2.8a), the final Young's contact angle is similar to the one of non-reactive wetting, with γ_{SL} being replaced by the interaction between the product and the liquid instead of the original substrate, γ_{PL} . In the configuration from fig.2.8b, also γ_{SV} must be corrected by the interaction of the product, γ_{PV} [143].

2.3 *Ab initio* simulation

In chapter 3, a solid SiO_2 -liquid Zn interface system will be studied through computational simulation in order to evaluate its interface energy, γ_{SL} . For this investigation, the *ab initio* simulation approach was selected. With the help of physical constants alone, the family of *ab initio* (first principles) methods permits the prediction of material properties for unknown systems without any experimental input. The density functional theory (DFT) used in this study is

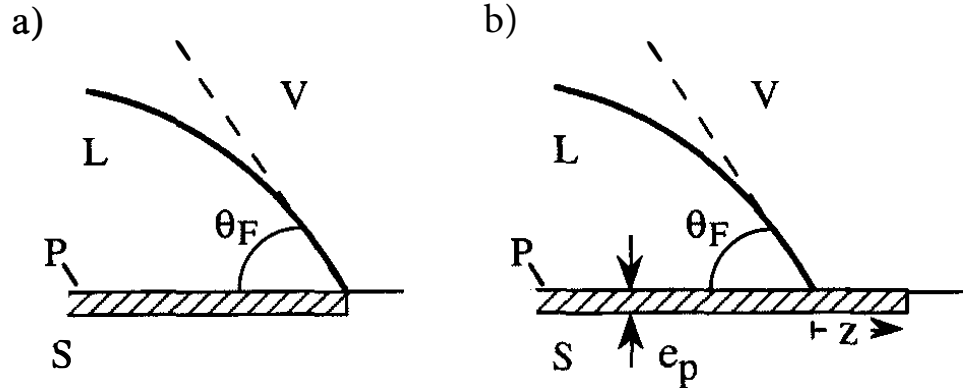


Figure 2.8: Possible configuration of the triple line in reactive wetting [143]

one of those methods, and its principles will be introduced in the following section.

2.3.1 DFT calculations

Atomic interactions are very complex to simulate because they are, in fact, interactions between each electron of each atom in contact. In the case of zinc, which has 30 electrons in movement around its core, $\approx 3 \times 10^{32}$ electron-electron interactions are to be considered. A fundamental equation that describes the electronic structure of a system with many atoms and electrons is known as the Schrödinger equation:

$$H\Psi = E\Psi \quad (2.9)$$

with H , molecular Hamiltonian, E , total energy of the system, and Ψ , wave function. The wave function $\Psi(x_1, x_2, \dots, x_N)$ describes in its entirety a quantic system with N electrons, with $x_i = (r_i, s_i)$, r_i representing 3 coordinates of space, and s_i , a spin of an electron. Further, a simplified notation r is used, with $r = (r_1, \dots, r_N)$. For a system with N electrons, the Ψ function depends therefore on $4N$ parameters. The complexity of the problem increases significantly with the addition of new atoms added to the system.

The molecular Hamiltonian is defined as:

$$H = T_N + T_e + V_{NN} + V_{eN} + V_{ee} \quad (2.10)$$

with T_N , T_e , kinetic energy operators of nuclei and electrons, respectively, and V_{NN} , V_{ee} , V_{eN} , potential energy operators representing interactions between nuclei, between electrons, and between nuclei and electrons, respectively.

The Born-Oppenheimer approximation [144] is proposed to simplify the

problem. A proton's mass is 1836 times greater than that of an electron. According to this approximation, nuclei move far more slowly than electrons because of this significant mass difference, and as a result, they can be thought of as static points with electrons circulating around them. The kinetic energy of nuclei is therefore null and becomes a constant, E_{NN} . Thus, the equation (2.10) becomes:

$$H_{elec} = T_e + V_{eN} + V_{ee} + E_{NN} \quad (2.11)$$

Density Functional Theory (DFT) is a quantum-mechanical atomistic method that facilitates the study of the electronic structure of many-body systems, even though it involves certain simplifications. DFT is framed by two theorems proposed by Hohenberg and Kohn [145]. The first theorem states that for each system of interacting particles in an external potential $V(r)$, this potential is uniquely determined by the *electronic density* $\rho(r)$ of the system of particles in its ground state. The second theorem defines an energy functional, $E[\rho]$, for the system and proves that the ground-state electronic density minimizes this energy functional. This approach replaces a N -body problem with a single variable, electronic density. If the functional is known, determining the ground energy of the system at a given $V(r)$ is relatively straightforward.

Kohn and Sham [146] developed a method to describe this functional, in which an interacting system of electrons is replaced by a fictional non-interacting system of electrons that is subjected to the mean field generated by other electrons. Thus, the energy functional in the Kohn and Sham systems is:

$$E_{KS} = T_s[\rho] + V_s[\rho] \quad (2.12)$$

with $T_s[\rho]$, the kinetic energy equal to that of a gas of non-interacting electrons, and $V_s[\rho]$, the external potential in which electrons are in movement. It is described as:

$$V_s[\rho] = \int V_{ext}(r)\rho(r)dr + E_{Hartree}[\rho] + E_{N-N} + E_{xc}[\rho] \quad (2.13)$$

with $\int V_{ext}(r)\rho(r)dr$ representing interaction between the electronic density and the external potential of nuclei. Corrective terms are included in the exchange-correlation term E_{xc} , and $E_{Hartree}$ specifies a repulsion between the electrons:

$$E_{Hartree}[\rho] = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' \quad (2.14)$$

Given Kohn and Sham's modifications, a new Hamiltonian, called mono-electronic Hamiltonian H_{KS} , that can be solved analytically can be defined as:

$$H_{KS}\Psi_i(r) = \epsilon_i\Psi_i(r) \quad (2.15)$$

$$\left[-\frac{1}{2}\nabla^2 + V_s(r)\right]\Psi_i(r) = \epsilon_i\Psi_i(r) \quad (2.16)$$

with ϵ_i , the eigenvalue of energy corresponding to the state Ψ_i .

The solution of Kohn-Sham equations yields orbitals $\Psi_i(r)$ that replicate the initial electronic density of a multielectronic system.

$$\rho(r) = \sum_i^N |\Psi_i(r)|^2 \quad (2.17)$$

The only unknown term is an exchange-correlation potential V_{xc} . From this potential, a functional of energy of exchange and correlation E_{xc} is derived. The *exchange* part is responsible for the repulsion between the electrons of the same spin, while *correlation* corresponds to the fact that the electrons are not independent in reality. Different approaches and approximations can be chosen in order to estimate the E_{xc} , such as Local Density Approximation (LDA) or General Gradient Approximation (GGA).

2.3.2 *Ab Initio* Molecular Dynamics

Molecular Dynamics (MD) is a simulation technique that models the evolution of a system of particles over time. The movement of particles in a given environment of temperature and pressure is calculated based on Newton's equation of motion, solved at each time step. Through atoms' attraction, repulsion, and collisions with one another, one may track the paths and behaviors of individual atoms in this kind of simulation [147].

In classical MD, all interaction forces are calculated based on the empirical interatomic potentials. This type of simulation can be applied to systems containing even millions of particles. However, selecting the appropriate empirical potential can be a challenging task. Since those empirical potentials use predetermined bonding arrangements, a classical MD is unable to simulate the formation or breaking of chemical bonds.

On the contrary, in *Ab Initio* Molecular Dynamics (AIMD), calculations are more accurate, and a calculation of forces is based on quantum mechanics theoretical calculations obtained through the DFT approach instead of using an experimental fitting [148]. Therefore, to achieve this better precision, a larger

computation time will be required, and the number of particles in the system will need to be constrained. Additionally, AIMD can provide more details on the various electronic characteristics of the system than classical MD can.

2.3.3 Simulation software

The *Vienna Ab Initio Simulation Package* (VASP) is software used for DFT and AIMD calculations during this project. This software is based on the plane-wave method, in which every eigenfunction of a monoelectronic Kohn-Sham equation is expressed on the plane-wave basis sets [149].

VASP is based on the use of pseudo-potentials, which means that only valence electrons are treated independently, while core electrons are treated together as a mean field. The interactions between the electrons and ions are described using the *Projector Augmented Wave* (PAW) method [150]. The PAW pseudo-potentials noticeably reduce high-frequency wavefunctions close to the nucleus by setting up a linearized approximation. Those pseudo-potentials are adapted to the exchange and correlation energy of a functional PBE, developed by Perdew, Burke, and Ernzerhof [151].

Two arbitrary parameters are introduced in code VASP to discretize continuous spaces. To reduce the discretization error, a convergence calculation must then be implemented as a function of those parameters.

A problem involving N electrons is solved in a reciprocal space called *k-space*. This space needs to be discretized using *k-points* in three spatial directions in order to solve various integrals. In general, the meshing of the reciprocal space is finer, and there are fewer errors when there are a greater number of k -points.

Moreover, the decomposition of wave functions into a sum of plane waves is done following Bloch's theory [152]. Since such sums are infinite, the number of contributions to the plane wave representation must be limited by setting an energy cutoff, E_{cut} .

Four primary files must be filled out with the proper parameters in order to launch a VASP computation for a given system [149]:

- INCAR file: Contains all the parameters for the calculation. It sets the type of calculation (relaxation or molecular dynamics). Depending on the system under study and the kind of results desired, parameters in this file can be optimized.
- POSCAR file: The examined cell properties, namely its size in three dimensions, are included in this file together with details regarding the nature, number, and initial positions of the atoms in the cell.

- KPOINTS file: It specifies the Bloch vectors (k-points) used to sample the k-space. Additionally, one can manually set up a mesh or select between two forms of automatically created meshing (Gamma-centered and Monkhorst-Pack).
- POTCAR file: Contains computed data about the chemical elements present inside the system and their PAW-PBE pseudo-potentials, that are used for each element in this study. This file should not be modified and is the intellectual property of VASP.

Additionally, VESTA software was used for the visualization of POSCAR files and the creation of the supercells. BASH and Python scripts were used to automate the data post-treatment process.

2.3.4 Simulation of wetting at atomic scale

Mechanisms of wetting of a solid by a liquid are often simulated through large-scale classical Molecular Dynamics [153–157]. In systems composed of even 10^6 liquid atoms, surface tension, viscosity, and contact angles can be measured. Those systems may represent spontaneous or forced spreading on flat surfaces or fibers, or material imbibition over time [153]. Webb et al. [154] also used MD to model reactive wetting in a liquid Al/Cu system (fig. 2.9).

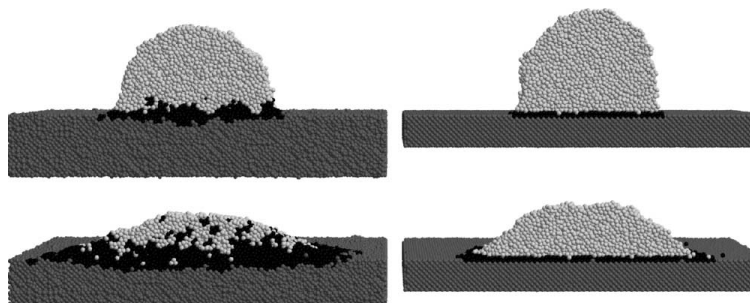


Figure 2.9: Cross-section snapshots of the simulations at $T = 1200$ K for (left) reactive and (right) non-reactive systems. Images are shown for (top) $t = 100$ ps and (bottom) $t = 400$ ps. Ag atoms with only Ag nearest neighbors are light gray, Cu atoms with only Cu nearest neighbors are dark grey, and all other atoms are black [154]

AIMD simulation was also used to model some solid-liquid systems for many applications. Ding et al. [158] used it to study interactions between alloy elements in steel and oxygen dissolved in lead bismuth eutectic (LBE) molten alloy. An iron(110)–liquid LBE interface model (with 72 Fe, 21 Pb, and 26 Bi

atoms) was created first. Then, an atom of oxygen and/or one of the alloying elements of steel ($X = \text{Fe, Cr, Ni, Al, Si}$) were placed either at the surface of the steel or in liquid LBE. Simulations were led under 500°C . This study led to a better understanding of the dissolution and formation of metallic oxides in this solid-liquid system.

Colombeau [159] in his PhD thesis used AIMD simulation to investigate liquid metal embrittlement in the liquid Hg/solid Cu system that is characterized by full spreading of the liquid. In the works of Zhang et al. [160], electronic structures were calculated in a liquid Al/TiB₂ system. The additional difficulty of this solid-liquid couple is that the TiB₂ surface could be composed of either B or Ti terminations. As a result, multiple configurations had to be investigated.

Shi et al. [161] endeavored to create metals that are resistant to corrosion for the purpose of hot-dip galvanizing. They used first-principles simulations in an effort to determine the system's wetting angle in order to do so. The strategy was to use the Young relation ((2.2.1)) to determine the wetting angle by individually calculating the surface energies of Zn and, in this case, TiAl, as well as the interface energy of the Zn/TiAl system. Their method provided a wetting angle that closely agrees with experimental results.

Shi used a value of liquid zinc surface energy calculated by Qiao et al. [162]. Their work was done using VASP and PAW-PBE pseudo-potential. A cutoff energy of 227 eV and a single k-point were used in this study. Temperature control for all dynamical simulations was achieved in the canonical ensemble (NVT) using a Nosé thermostat [163]. In this simulation system, 216 atoms were arranged in a cubic box with random positions and periodic boundary conditions. The pair correlation function $g(r)$, which illustrates how density changes as a function of distance from a reference particle, was calculated by the authors to verify that the structure under study is liquid. These test findings are represented in figure 2.10, along with a comparison to other researches. The allure of $g(r)$ curves is typical for a liquid, even when compared to experimental measurement (fig. 2.10a). It suggests that, using the parameters selected for this investigation, AIMD is an appropriate method for calculating zinc's liquid structure.

The bulk molten zinc supercell was used by the authors to obtain the viscosity of the liquid. Further, through a relationship between viscosity and surface tension proposed by Egry [166], the former was calculated. The linear relationship between the temperature (in $^\circ\text{C}$) and surface tension of zinc (in N/m) is represented in equations (2.18) and (2.19).

$$\text{Experiment: } \gamma = -0.00264T + 1.94316 \quad (2.18)$$

$$\text{Calculation: } \gamma = -0.00111T + 1.17912 \quad (2.19)$$

The experimental equation was based on the results of the study of liquid zinc

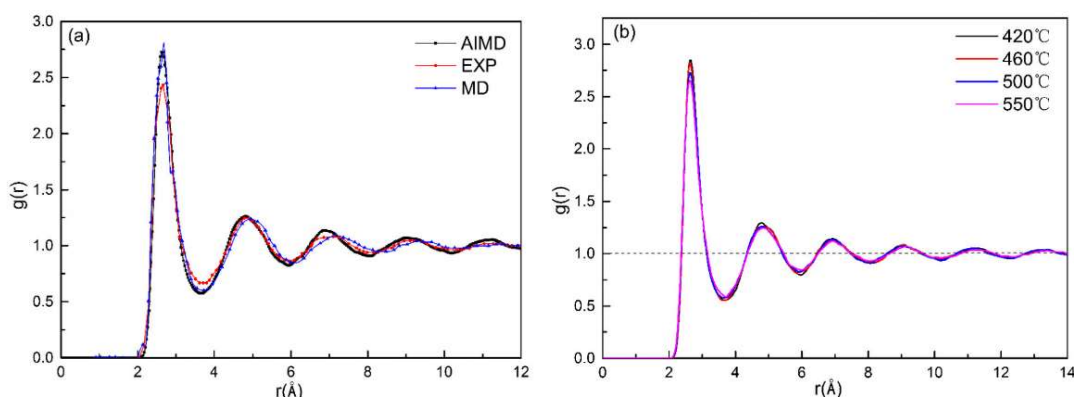


Figure 2.10: Pair-correlation functions of liquid zinc at different temperatures [162]. a) Comparison of pair-correlation calculation for liquid zinc at 500°C with the experimental result by Waseda [164] and MD calculations by Lin [165] b) Temperature dependence of the pair distribution functions calculated by Qiao [162]

in air by M.Y. He [167]. For the galvanizing temperature of 450 °C, it equals 0.75516 N/m. The surface tension calculated with the AIMD method equals 0.67962 N/m. In the study of Qiao et al., AIMD simulation results in 11% of relative error.

2.3.4.1 Simulation of an amorphous solid

Silicon oxide will be an important compound studied in chapter 3. When Si is exposed to the atmosphere, it will grow a native layer of SiO_2 that may be amorphous [168]. This section's goal is to examine how first-principles simulation might be used to create an amorphous structure, even though only a crystalline SiO_2 will be later simulated.

In DFT, the supercell is considered to be repeated periodically on its boundaries. Thus, not many atoms are needed to represent a perfect crystal, as its one unit cell represents the entirety of the material. The issue arrives for amorphous materials, such as glass, as their structure lacks a long-range order. This property dictates the use of a higher number of atoms and a bigger cell size, which is linked to the longer computational time [169]. Sarnthein et al. [170] obtained their amorphous structure of SiO_2 by starting with a liquid at 3500 K, then quenching the liquid to 300 K, thus obtaining an amorphous network. They used a Car-Parinello first-principles simulation and a local density approximation (LDA) for the description of the electronic structure. The liquid SiO_2 was modeled with 72 atoms. The initial configuration of atoms was generated by Monte Carlo using the empirical potential, then allowed to diffuse at high

temperatures in order to lose memory of this initial configuration. The configuration obtained after quenching was judged amorphous, as the Si-O-Si bond angle distribution was broad, extending from 110 to 180°, while in α -quartz it is 144° [171].

Van Ginhoven et al. [169] proposed a different approach. They generated multiple independent configurations of amorphous SiO₂ through classical MD to save computation time. Each of them was composed of 72 atoms. The samples were generated using various initial configurations, and the same cooling process was applied to quench them. The resulting glass structures were optimized and annealed with AIMD. Multiple samples were used in order to represent different medium-range structures of atoms existing in a long-range amorphous material. Those small samples, on average, resulted in a good agreement with the results obtained for a larger system made with 1479 atoms in terms of structural characteristics such as a ring size distribution.

A different approach was chosen by Le et al. [172] that justified working with a β -cristoballite polymorph of SiO₂ instead of an amorphous one because it forms at high temperatures and its atomic density is very close to that of amorphous silica.

2.4 Surface analysis experimental techniques

The objective of the following analyses is to determine experimentally what the chemical composition of different studied samples is at different scales in terms of the depth of the measurement. Moreover, methods for characterization of the cristallographic composition and surface texture of the coating will be introduced in this section.

2.4.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is an analytic method used for a wide range of materials. Unlike traditional optical microscopy, which is based on light, this microscopic study relies on the emission of electrons. When an electron beam is sent on the surface of a sample, its internal electronic structure is disturbed, and two types of electrons are emitted, as represented in figure 2.11. Secondary electrons (SE) are those emitted from the upper layers of the coating, giving access to the study of the topography of the sample. Backscattered electrons (BSE) come from a deeper portion of the sample and give the possibility of observing a chemical contrast, *i.e.*, the ability to discriminate heavier elements from lighter ones through the intensity of their shade of gray. Another signal emitted from the material are photons that can be used for a more detailed

chemical analysis through X-ray spectroscopy methods, as described in section 2.4.1.1 [173].

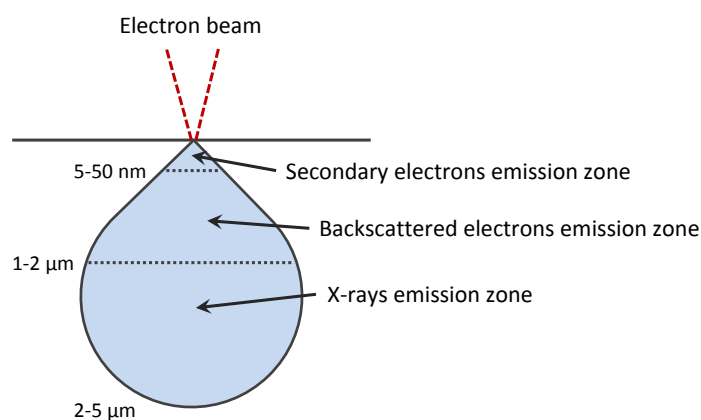


Figure 2.11: Interaction volume, showing the depth of penetration of the electron beam [174]

In this study, samples were analyzed with a Jeol JSM-7800F LV with a Field Emission Gun (FEG). FEG produces a smaller electron beam that leads to a better resolution of the analysis than other types of emission guns. It can provide a magnification up to $\times 1\,000\,000$ and a spatial resolution of 0.8 nm at 15 kV and 1.5 nm at 1 kV. The tension of 15 or 20 kV is used in this work.

2.4.1.1 X-Ray Spectroscopy

Energy-Dispersive X-ray spectroscopy (EDX) EDX is the most common analytical technique that is coupled with SEM observations. Photons emitted by the material and detected with EDX can be distinguished based on their energy, which is characteristic of different chemical elements. Consequently, EDX enables both qualitative and quantitative descriptions of the punctual composition; chemical composition cartographies can also be produced using this technique. With this method, elements with a concentration greater than 0.1 wt.% and an atomic number above 5 can be detected [175]. As photons can come from a volume of 1 μm and more, it has to be taken into consideration that their spatial resolution is less precise than that of images obtained with SEM.

Samples were analyzed with an 80 mm³ SDD EDX spectrometer by Oxford Instruments attached to the Jeol SEM. Data treatment was done with the AZtec 6.0 software.

Electron probe micro-analyzer (EPMA) The approach used by EPMA analysis and the SEM-EDX investigation is similar. The sample is subjected to an electron

beam that ejects the X-ray photons analyzed by the equipment. Contrary to the EDX analysis, EPMA is based on the principle of Wavelength X-Ray Dispersion Spectroscopy (WDX), which separates the data based on X-ray diffraction into distinct wavelengths rather than energy. Compared to EDX, WDX has superior spectral resolution, is able to identify elements with atomic numbers higher than 3, and has a detection limit of 100 ppm or less for the majority of elements [176]. The background noise is also lower than for EDX, which leads to a better quantitative analysis. However, the time of analysis is longer.

The EPMA analysis was conducted using Cameca SX100 instrument. All the elements were calibrated with pure metals.

2.4.2 Extreme surface analysis

The EDX analysis, as previously mentioned, provides information on the composition of material originating from electrons at a depth greater than 1 μm below the surface. This approach cannot detect the presence of a protective, non-wettable oxide at the surface whose layer is thinner than this value, as is hypothesized. More subtle analysis techniques are therefore needed to observe the composition at the extreme surface of the material, and those used in this study are explained in the following sections.

2.4.2.1 X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) is a spectroscopic technique based on the photoemission principle. The term *photoemission* refers to the emission of electrons, or *photoelectrons*, by a substance resulting from the absorption of an electromagnetic wave such as light and its photons. That photoelectron can be ejected from an atom if the energy absorbed from the photon surpasses its binding energy [177]. Figure 2.12 illustrates the photoemission principle. Given that the spectrometer is limited to measuring the kinetic energy of expelled electrons, E_b , the binding energy, can be calculated from (2.20).

$$E_k = h\nu - E_b - W_f \quad (2.20)$$

with E_k , the ejected photoelectron's kinetic energy, $h\nu$, the energy of the incident photon, and W_f , a work function of a spectrometer [177].

The spectrum then shows this energy, and each element produces distinct XPS peaks that represent the electron configurations within atoms (e.g., 1s, 2s, 2p, etc.). Furthermore, binding energy is dependent on an electron's chemical environment. As a result, a slight shift in a peak's position can be seen when measuring the same element in different settings. Thus, XPS can be used to

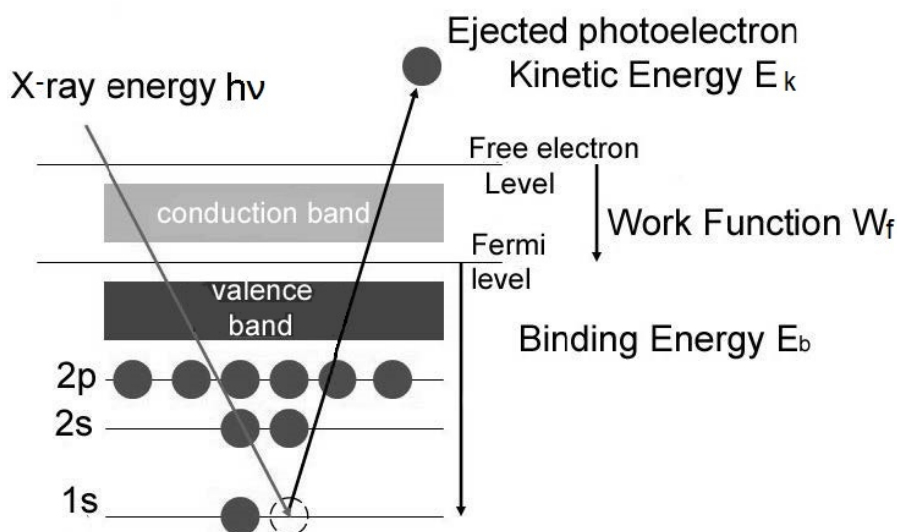


Figure 2.12: Photoemission principle [178]

identify the chemical state (*e.g.*, oxidation state) of an atom.

All chemical elements, with the exception of hydrogen and helium, can be identified with this technique. The mean depth of the analysis is approximately 5 nm, but if grazing incidence is used, it can be lowered even to the atomic monolayer. The limit of detection for an element is around 10^{20} atoms. cm^{-3} , 10^{12} atoms. cm^{-2} for a surfacial monolayer [179]. The material studied with this method is preferred to have homogeneous phase composition and low surface roughness.

The analysis in section 3.3 was performed on the Kratos Axis UltraDLD (2009) X-ray photoelectron spectroscope at the Institut Chevreul in Villeneuve-d'Ascq by the Unité de Catalyse et Chimie du Solide staff.

2.4.2.2 Time-of-Flight Secondary Ion Mass Spectroscopy

Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) is a very sensitive analytical technique based on bombarding the sample with a primary beam of ions and then analyzing the secondary ions that are ejected from the surface. After that, the elemental, isotopic, or molecular composition of the sample's surface is determined with a mass spectrometer. This mass measure is obtained by studying the time of flight needed to reach the detector. This method can detect trace amounts of elements, down to the ppb level, in favorable conditions. This method is, however, not well adapted to the quantitative analysis of elements in high concentration in the material [180].

ToF-SIMS can be used in several ways. First, in a selected region, highly sensitive mass spectroscopy can be achieved. The other possibility is to realize a depth profile in which a sputter beam of ions of Cs or O₂ is used to dig a crater while a second analysis beam is ejecting the secondary ions along the path (Figure 2.13). Ultimately, 2D chemical mapping can be prepared, and 3D images can be reconstructed if combined with depth profile analysis. This method's application is limited, as reliable results necessitate low surface roughness and chemical homogeneity in the surface plane as well as in the depth. For this reason, it can only be applied to a specific subset of the study's samples.

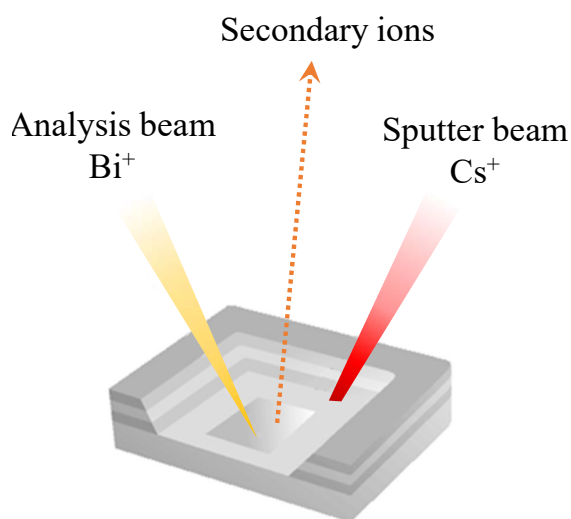


Figure 2.13: Schematic representation of elemental depth distribution analysis with ToF-SIMS

The analysis in section 3.3 was done on the IONTOF ToF-SIMS 5 instrument in Institut Chevreul in Villeneuve-d'Ascq by the Unité de Catalyse et Chimie du Solide staff. The depth profile of elemental composition was realized with the Cs⁺ beam sputtering a crater and the Bi⁺ beam progressively analyzing the crater bottom.

2.4.3 Additional methods of analysis

2.4.3.1 X-Ray Diffraction

A method for analyzing a material's crystallographic structure is called X-Ray Diffraction (XRD). It works by subjecting the material to X-ray radiation at various incoming angles. According to Bragg's law (equation (2.21)), if the sample is crystallized, it will diffract the X-ray in particular directions toward

the detector.

$$2d \sin \theta = n\lambda \quad (2.21)$$

with d , the spacing between the diffracting planes, θ , the incident angle, n any integer, and λ , the wavelength of the X-ray beam.

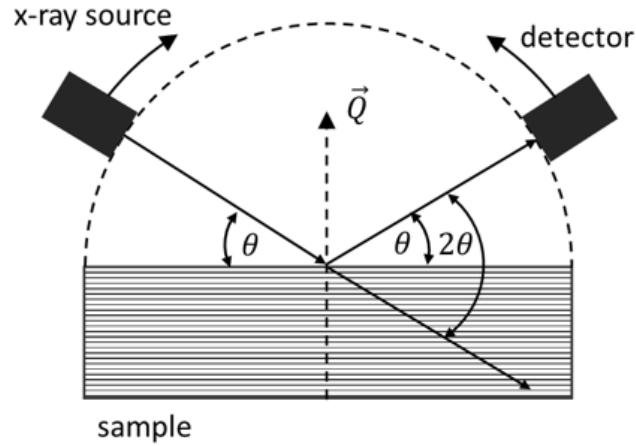


Figure 2.14: X-ray diffraction measurement in Bragg-Brentano geometry [181]

Different crystallographic phases will produce different peaks at the diffractogram that are identified by the comparison with the database. This method is complementary to X-ray spectroscopy methods in improving the understanding of the crystallographic phase composition of the different materials studied in this project. Moreover, the existence of the surfacial oxide could potentially be detected under the condition that it is crystallized. XRD cannot analyze the structure of amorphous phases. In this study, massive, metallic samples are analyzed and cannot be ground. Its surface roughness and eventual preferential orientations of crystallographic phases make a quantitative analysis impossible, only qualitative analysis is possible.

The crystal structure of the samples was characterized with a Rigaku Smartlab X-ray diffractometer in Bragg-Brentano geometry (Figure 2.14), with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The data is analyzed with the DIFFRAC.EVA software by Bruker.

2.4.3.2 Profilometry

A profilometer is a piece of equipment used to measure a surface's profile and quantify its roughness. In this project, measurements were done with a no-contact optical interferometrical profilometer. Interference microscopy involves

measuring the difference in the path between two beams of light, which leads to the determination of surface characteristics such as topography.

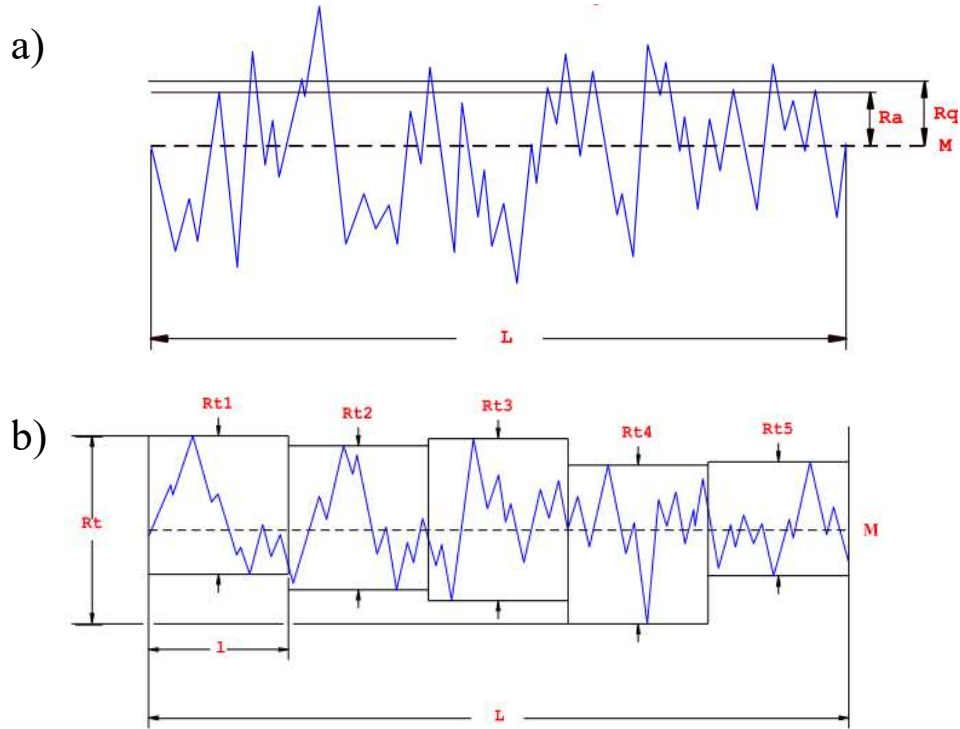


Figure 2.15: Definition of Ra , Rq , and Rz with M , the mean line, l , sampling length, and L , evaluation length [182]

Rugosity is an indicator of small-scale fluctuations of amplitude in the height of a surface. In this study, three values are followed: Ra , Rq and Rz . The figure 2.15 represents the definition of those values. They are measured against the mean line M , which serves as the reference line from which the profile deviations are calculated. Afterwards, the length across which the surface parameters are assessed is known as the evaluation length L . It should be composed of multiple sampling lengths l , which stand for the nominal wavelength separating waviness from roughness.

The arithmetic average of the absolute values of the profile heights over the length L is called the roughness average, or Ra , while Rq is the root mean square average of the profile heights over the same length (fig. 2.15a).

Finally, the Average Maximum Height of the Profile, Rz , is the average of the successive values Rti , which represent the vertical distance between the profile's highest and lowest points over a sampling length l (Figure 2.15b). This average

is found within the evaluation length L .

Bruker's ContourGT-K 3D Optical Microscope was used for the analyses. Its lateral resolution goes up to 300 nm, and the resolution on the z-axis is lower than 1 nm.

2.5 Material production methods

This section explains the procedures and specific manufacturing conditions that were employed to form the coatings that are covered in chapters 3 and 4 of this thesis.

2.5.1 Selective Laser Melting

Selective Laser Melting (SLM) is a layer-by-layer manufacturing method that was chosen for the preparation of model surfaces described in the later part of the chapter 3. It consists of heating a powder bed up to the melting temperature with a laser source [183]. A partnership was formed to produce those coatings with the Belgian Ceramic Research Centre in Mons, Belgium, which possesses the equipment and expertise needed to work with the SLM technique.

The coating is created with a Fe-Si powder containing 30 wt.% of silicon. The grain size is restricted to 50 μm . In a propeller agitator, a mixture of 75 wt.% Fe-Si powder in butan-1-ol (an alcohol solvent) in which 1 wt.% of ethylcellulose is dissolved is formed. Ethylcellulose serves as a binder. Spray-coating is used to put two layers of this mixture on the substrate. In this study, DD13 steel plays a role as a substrate (Table 4.1). The final deposition is about 80 μm thick.

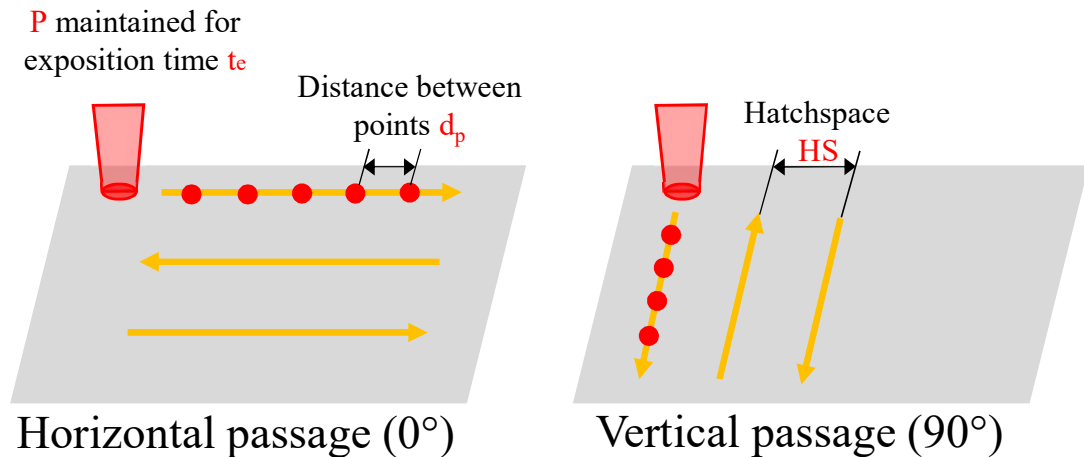


Figure 2.16: Schematic representation of a SLM treatment

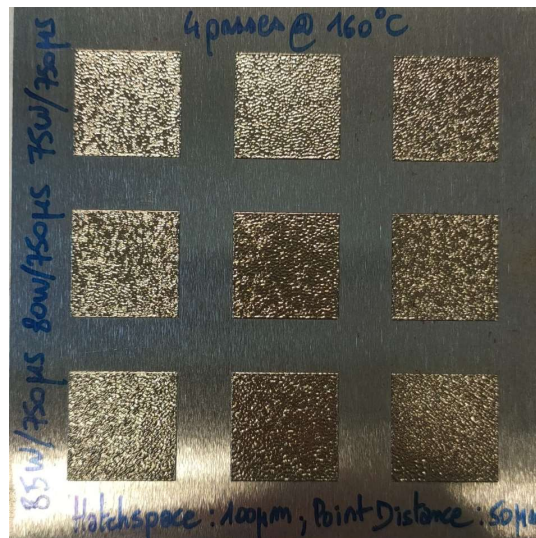


Figure 2.17: Example of a plate covered with coatings prepared under different conditions of laser power

This deposition is then treated with SLM. The Renishaw-AM125 SLM machine employed in the present study uses a fiber laser ($\lambda = 1070 \text{ nm}$), and the building chamber is maintained in an inert gas environment. This method is schematically represented in figure 2.16. The substrate is heated at 160°C . The laser makes four passes over the selected area. Laser tracks are first directed horizontally, then turned by 90° , followed again by 0° and 90° . The point distance between two consecutively irradiated laser spot areas was adjusted to $50 \mu\text{m}$, while the hatchspace, which is the distance between two successive parallel laser tracks, was set to $100 \mu\text{m}$. The laser power was 75, 80, 85, 90, 95, or 115 W in various trials. The exposure time for each point was established at 600, 750, 800, 1000, or 1250 μs . Different combinations of laser power and exposure time were tested in order to obtain the correct Si content at the surface of the sample (Figure 2.17).

2.5.2 Slurry method

The method used for elaboration of coatings studied in chapter 4 is called the fused slurry method, developed by Priceman et al. [184]. It consists of creating a coating from a liquid precursor suspension treated at high temperature in a controlled atmosphere. Because of its versatility, this suspension, also known as slurry, can be applied to pieces of complex geometry and size that are frequently employed in batch hot dip galvanizing. It is applied to the steel part by immersion, spraying, or brushing. The surface tension and viscosity of the

slurry can be improved with the addition of various products [185]. Because of the high wetting ability of molten metallic elements, the resulting coating has a fairly uniform thickness (standard deviation within a few microns). This technique produces extremely adherent coatings because, unlike oxide coatings covered in 1.3.2, at high temperatures, fused elements of the precursor and iron diffusing from the steel form an intimate metallic bond, preventing the issue of thermal shock.

Slurry coatings were synthesized by the technology transfert and development platform from EEIGM (Ecole Européenne d'Ingénieurs en Génie des Matériaux), the "Halle des Matériaux", in Nancy, France.

To create fused slurry coatings, pure and prealloyed elements of final composition as given in table 2.1 were homogenized in the Turbula T2-F shaker-mixer for 2 h. All particle sizes were inferior to 100 μm . After that, those powders were dispersed in a binder solution containing 12 wt% polyvinyl alcohol (PVA) in distilled water. This suspension was then stirred once more for an hour. Before being covered with the slurry suspension, DD13 steel plates were ground with using P240 and P600 SiC papers and ultrasonically cleaned in acetone at room temperature. Subsequently, suspension was applied to the steel surface by immersion at a constant withdrawal rate of 5 cm/min. Then, it was left to dry in the air for a few hours. The thus prepared plates were heated in an industrial TAV THF 80/80/250 vacuum furnace. The thermal cycle started with a debinding step at 350°C and a high temperature 10 min step at 1040°C with a heating rate of 10°C/min. This thermal treatment was followed by the slow cooling of the plates in the furnace. Operating vacuum was close to 10^{-5} mbar.

Element	Ni	Cr	Si	P
%wt	57.0	28.5	8.8	5.7

Table 2.1: Global composition of the slurry

Chapter 3

Wetting of model surfaces

3.1 Introduction

As shown in the study described in section 1.3.5, silicon is an important element to include in order to protect steel equipment from zinc in batch hot-dip galvanizing plants, as it can limit any weight loss of material during cyclic batch hot-dip galvanizing treatment. Silicon, when exposed to the atmosphere, forms a native silicon oxide, SiO_2 [186]. Moreover, SiO_2 does not react and is not wetted by liquid zinc [187, 188]. FeSi alloys can therefore serve as a foundation for the creation of effective protective materials. The main focus of this chapter will be the examination of the SiO_2 surface.

The first part of this chapter will be dedicated to the first-principles simulation of a solid SiO_2 -liquid Zn interface. The development of an atomic-scale model was chosen in order to verify if the presence of SiO_2 influences the wetting by liquid zinc and to better understand the mechanisms that affect materials' wetting behavior, since DFT-AIMD simulation is able to provide some thermodynamic values that are extremely challenging to measure experimentally, such as interface energy. The role of this section is to develop a model of a simple interface that may be complexified in the future. Those simulations lead to the calculation of the theoretical wetting angle of the system through the calculation of different interface energies, *i.e.*, between solid and liquid, liquid and gas, and solid and gas.

The second part of this chapter is dedicated to the experimental model surfaces of FeSi alloy coatings. As mentioned in 1.3.5, bulk FeSi alloys are fragile and therefore not adapted to use in transfer structures for batch galvanizing. This is why the idea of the formation of FeSi coatings is researched. The manufacturing conditions of those surfaces are thus studied, and in order to confirm the formation of SiO_2 at their surface, those materials are further characterized

using ToF-SIMS and XPS analysis methods.

3.2 *Ab initio* simulation of wetting of quartz by liquid zinc

This section is focused to the simulation of the $\text{SiO}_2\text{-Zn}_{(l)}$ interface with DFT and AIMD first-principles methods. The crystalline α -quartz form of SiO_2 is the polymorph selected for the present study. As discussed in section 2.3.4.1, simulating an amorphous body is complex and requires a lot of atoms to represent it. In order to simplify the model and save some time of calculation at the beginning, a simple crystal form was preferred. That structure was chosen since DFT measurements are led in 0 K and α -quartz is stable at low temperatures. Additionally, this structure presents corner-sharing oxygen tetrahedra around Si atoms and therefore can be compared to siloxane rings in the amorphous SiO_2 structure [172].

In order to simulate and evaluate the wetting properties of zinc on quartz, three supercells were created: a SiO_2 surface in vacuum, a liquid zinc surface in vacuum, and a $\text{SiO}_2\text{-Zn}_{(l)}$ interface. In this study, no gaseous phase was taken into account. For each supercell, surface energies are γ_{SV} , γ_{LV} , and γ_{SL} , respectively. Those values inserted into Young's relation (equation (2.2.1)) lead to the calculation of wetting angle θ , which can be compared with experimental values to verify the model. The schematic representation of the system is represented in figure 3.1.

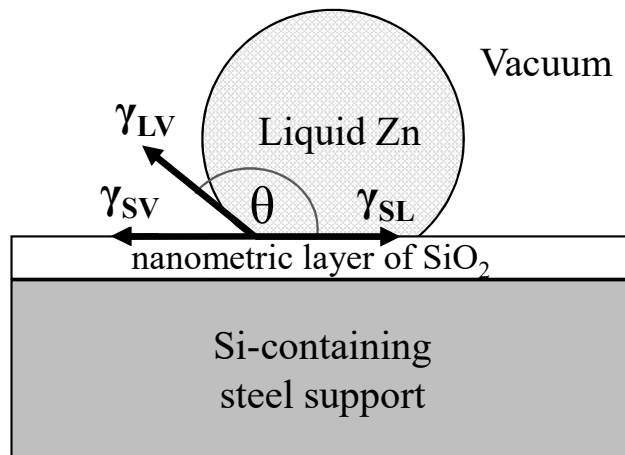


Figure 3.1: A schematic representation of the wetting system to simulate

3.2.1 Interface energy calculation

Surface energy is a measurement of the excess energy present at the material's surface that results from the breaking of interatomic bonds and is not balanced in contrast to the bulk of the substance.

The Gibbs free energy, G , is defined as [189]:

$$G = E + PV - TS \quad (3.1)$$

with E , the total internal energy, P , pressure, V , volume, T , temperature, and S , the entropy of the system.

The variation of this free energy is thus defined as follows:

$$dG = -SdT + VdP + \sum_{i=1}^C \mu_i dN_i + \gamma dA \quad (3.2)$$

with μ_i and N_i , the chemical potential and the amount of component i , C , the number of components, and A , the area of the planar interface. Finally, the surface energy γ can be calculated using this equation.

In further work, the dP factor is regarded null, and the DFT calculations are performed at 0 K, thus the SdT factor is also null. γ can be described by the following formula:

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,P,N_i} \quad (3.3)$$

with G , Gibbs free energy, and A , area of the surface.

The entropy term should be carefully considered in high-temperature AIMD simulations. However, for the sake of simplicity, it is assumed that this term for bulk and surface compensate for each other and thus are neglected in this study. Furthermore, it appears that this issue is not addressed in other liquid simulation research [160, 162, 190].

In conclusion, the γ can be calculated with the following equation:

$$\gamma = \frac{1}{A} \left[G - \sum_{i=1}^C \mu_i dN_i \right] \quad (3.4)$$

This section provides the equations required to determine γ_{SV} of SiO_2 in vacuum, γ_{LV} of liquid zinc in vacuum, and γ_{SL} of SiO_2 - $\text{Zn}_{(l)}$ interface. The parameters that need to be obtained via DFT-AIMD simulation are going to be indicated.

3.2.1.1 SiO₂ surface energy

According to the equation (3.4), the surface energy of the crystal SiO₂ in this investigation can be expressed as follows:

$$\gamma_{SV} = \frac{1}{2A} [E_{SV} - N_{Si}\mu_{Si}^{SiO_2} - N_O\mu_O^{SiO_2}] \quad (3.5)$$

with E_{SV} , ground-state energy of the SiO₂-vacuum supercell; N_{Si} , N_O , number of Si and O atoms in the supercell; $\mu_{Si}^{SiO_2}$, $\mu_O^{SiO_2}$, chemical potential of Si and O in SiO₂. The area A is doubled, as in this type of simulation, a supercell is composed of a block of atoms with a surface on each end.

The chemical potentials of Si and O in SiO₂ cannot be directly calculated via DFT simulation, and they are interdependent at given temperature and pressure. Hence, the equation (3.5) can be simplified. The Gibbs free energy of SiO₂ in its bulk state, which can be approximated by the ground-state energy of the SiO₂ unit cell, can be represented as:

$$G^{SiO_2} = \mu_{Si}^{SiO_2} + 2\mu_O^{SiO_2} \quad (3.6)$$

By combining equations (3.5) and (3.6), the final formula of surface energy in function of one variable becomes:

$$\gamma_{SV} = \frac{1}{2A} [E_{SV} - N_{Si}G^{SiO_2} + (2N_{Si} - N_O)\mu_O^{SiO_2}] \quad (3.7)$$

Although the precise value of $\mu_O^{SiO_2}$ is unknown, it can be expressed as a range of values under specific conditions. In fact, the existence domain of a biphased system Zn(l) + SiO₂ can be specified without the appearance of a third phase, such as Si(s), ZnO or O₂(g).

To assure that SiO₂ is thermodynamically stable and no Si and O₂ form as a third phase through the equilibrium $SiO_2 \rightleftharpoons Si + O_2$, the chemical potential of elements in SiO₂ should be lower than that of a corresponding pure substance chemical potential:

$$\mu_{Si}^{SiO_2} \leq \mu_{Si}^{Si(s)} \quad (3.8)$$

$$\mu_O^{SiO_2} \leq 2\mu_O^{O(g)} \quad (3.9)$$

These boundaries can be established through the use of SiO₂'s formation enthalpy:

$$\Delta H_f^0(\text{SiO}_2) = G^{\text{SiO}_2} - \mu_{\text{Si}}^{\text{Si(s)}} - 2\mu_{\text{O}}^{\text{O(g)}} \quad (3.10)$$

The lower boundary of that range results from combining the equation 3.10 with the inequality (3.8):

$$\Delta H_f^0(\text{SiO}_2) \leq 2\mu_{\text{O}}^{\text{SiO}_2} - 2\mu_{\text{O}}^{\text{O(g)}} \quad (3.11)$$

The upper limit is obtained with the second inequality (3.9):

$$\mu_{\text{O}}^{\text{SiO}_2} - 2\mu_{\text{O}}^{\text{O(g)}} \leq 0 \quad (3.12)$$

In order to further narrow the value range of $\mu_{\text{O}}^{\text{SiO}_2}$, a second condition can be proposed, *i.e.*, that zinc oxide ZnO cannot be formed, as in equilibrium $\text{Zn} + \text{O}_2 \rightleftharpoons 2\text{ZnO}$. Similarly to the first condition, two inequalities are given to avoid ZnO formation:

$$\mu_{\text{Zn}}^{\text{Zn(s)}} \leq \mu_{\text{Zn}}^{\text{ZnO}} \quad (3.13)$$

$$\mu_{\text{O}}^{\text{O(g)}} \leq \mu_{\text{O}}^{\text{ZnO}} \quad (3.14)$$

Likewise, $\Delta H_f^0(\text{ZnO})$ and G^{ZnO} are defined as follows:

$$\Delta H_f^0(\text{ZnO}) = G^{\text{ZnO}} - \mu_{\text{Zn}}^{\text{Zn(s)}} - \mu_{\text{O}}^{\text{O(g)}} \quad (3.15)$$

$$G^{\text{ZnO}} = \mu_{\text{Zn}}^{\text{ZnO}} + \mu_{\text{O}}^{\text{ZnO}} \quad (3.16)$$

Finally, a new limit is obtained by combining the inequality (3.13) with (3.16):

$$\mu_{\text{O}}^{\text{SiO}_2} \leq G^{\text{ZnO}} - \mu_{\text{Zn}}^{\text{Zn(s)}} \quad (3.17)$$

To obtain the surface energy γ_{SV} and to determine the value range of $\mu_{\text{O}}^{\text{SiO}_2}$, E_{SV} , G^{SiO_2} , $\mu_{\text{Si}}^{\text{Si(s)}}$, $\mu_{\text{O}}^{\text{O(g)}}$, G^{ZnO} , and $\mu_{\text{Zn}}^{\text{Zn(s)}}$ must be calculated with DFT simulation.

3.2.1.2 Liquid zinc surface energy

AIMD simulations are run at temperatures exceeding 723 K in order to generate molten zinc. Because this thermodynamic parameter is temperature-dependent, a new chemical potential must be determined at each calculation temperature. With E_0 representing the potential energy, E_k representing the supercell's kinetic energy, and N_{Zn} denoting the amount of zinc atoms in the supercell, the chemical

potential at a particular temperature is defined as:

$$\mu_{Zn}^{Zn(l)}(T, P = 0) = \frac{E_0 + E_k}{N_{Zn}} \quad (3.18)$$

The liquid zinc surface energy can then be calculated based on the determined chemical potential of liquid zinc. The surface energy γ_{SV} at a particular temperature can be found using the equation (3.20), which is obtained from the equation of the total energy of the liquid zinc supercell with a free surface.

$$E_{LV} = E_0 + E_k = \mu_{Zn}^{Zn(l)} N_{Zn} + 2A\gamma_{LV} \quad (3.19)$$

$$\gamma_{LV} = \frac{E_{LV} - \mu_{Zn}^{Zn(l)} N_{Zn}}{2A} \quad (3.20)$$

As a result, AIMD simulations must provide E_{LV} and $\mu_{Zn}^{Zn(l)}$ at different temperatures.

3.2.1.3 SiO₂-Zn_(l) interface energy

Equation (3.21) can be used to calculate interface energy from the last set of simulations on SiO₂-Zn_(l) interface.

$$\gamma_{SL} = \frac{E_{SL} - N_{Zn}\mu_{Zn}^{Zn(l)} - N_{Si}\mu_{Si}^{SiO_2} - N_O\mu_O^{SiO_2}}{2A} \quad (3.21)$$

with E_{SL} , the total energy of SiO₂-Zn_(l) supercell; N_{Zn} , N_{Si} , and N_O , the number of Zn, Si, and O atoms in the supercell; and $\mu_{Zn}^{Zn(l)}$, $\mu_{Si}^{SiO_2}$, and $\mu_O^{SiO_2}$, the chemical potentials of zinc, silicon, and oxygen. Both the chemical potential of zinc and E_{SL} are temperature-dependent.

This equation can then be further simplified using equation (3.6) to obtain a single variable, $\mu_O^{SiO_2}$.

$$\gamma_{SL} = \frac{E_{SL} - N_{Zn}\mu_{Zn}^{Zn(l)} - N_{Si}G^{SiO_2} + \mu_O^{SiO_2}(2N_{Si} - N_O)}{2A} \quad (3.22)$$

$\mu_O^{SiO_2}$ boundaries are the same as in the case of SiO₂ surface, but this time simulations are conducted at high temperatures, and the condition of preventing ZnO formation must be adapted to the new chemical potential.

3.2.2 SiO₂ surface energy γ_{SV}

This section describes all of the supercells used in the search for γ_{SV} of quartz, as well as the optimization of the simulation parameters, such as k-points. In addition, the chemical potentials of various components are estimated at 0 K using DFT simulation. Next, the results of the simulation of SiO₂ (0001) surface energy in function of $\mu_O^{SiO_2}$ are represented and discussed.

3.2.2.1 Preliminary DFT simulations

In order to calculate $\mu_{Si}^{Si(s)}$, a cubic unit cell of diamond structure (Fd-3m), which is the most common Si crystallographic form, composed of 8 atoms per cell, was used (figure 3.2a). The cutoff energy and k-points used are listed in table 3.1. Ground-state energy obtained for this cell is of $(-43.398\,45 \pm 0.000\,04)$ eV. The precision of the result is therefore better than 1 meV (Figure 3.3a). The resulting chemical potential of silicon, obtained by dividing the ground-state energy of the unit cell by the number of atoms it is composed of, is $\mu_{Si}^{Si(s)} = -5.425$ eV/atom.

As oxygen's standard reference state is gaseous, it is problematic to choose its correct unit cell at 0 K, hence to calculate the ground-state energy and the chemical potential of oxygen. Therefore, a referenced value of oxygen's chemical potential $\mu_O^{O(g)}$, which equals -4.485 eV/atom, was used in further calculations [191].

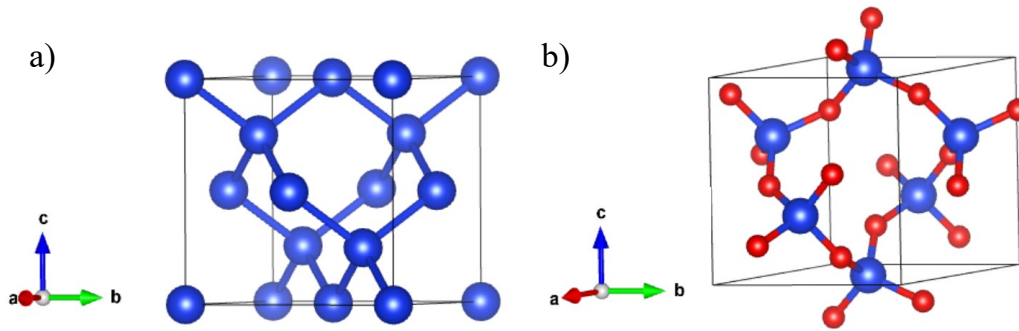


Figure 3.2: Unit cell visualization of a) Si ($a=b=c=5.43070$ Å, $\alpha=\beta=\gamma=90^\circ$) and b) α -quartz SiO₂ ($a=b=5.028$ Å, $c=5.519$ Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$)

Next, a bulk quartz SiO₂ cell was examined. The trigonal (P3₂21 space group) stoichiometric unit cell of quartz is composed of nine atoms (Figure 3.2b). The calculation parameters are given in table 3.1. The results of the k-point convergence test lead to the ground-state energy of the quartz unit cell of $(-71.132\,06 \pm 0.000\,02)$ eV (figure 3.3b). The free energy of one SiO₂ molecule

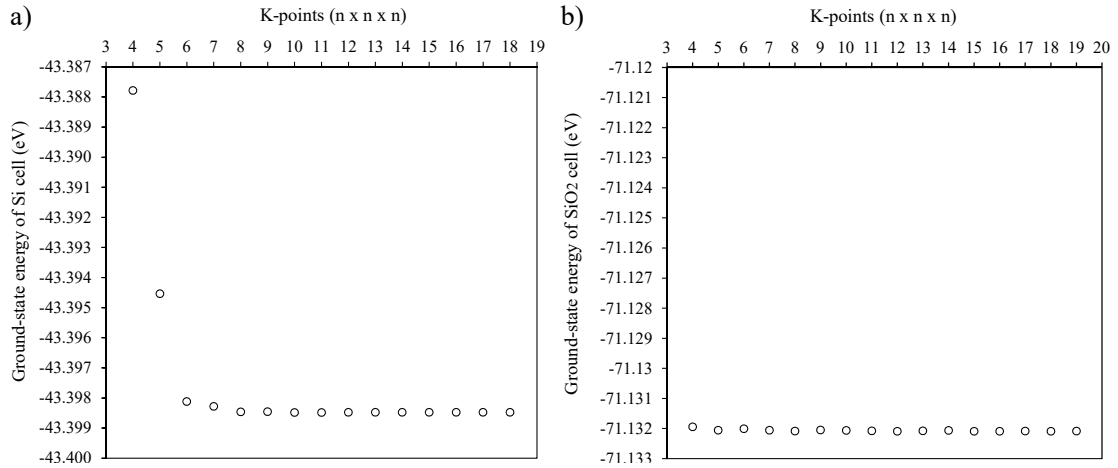


Figure 3.3: Convergence of the ground-state energy of a) Si and b) SiO₂ in function of increasing k-points (k-points are equal in every direction)

is calculated by dividing the ground-state energy of the unit cell by the number of molecules in the cell. Therefore, $G^{SiO_2} = -23.7107$ eV/SiO₂ formula unit.

The hexagonal unit cell (P63/mmc space group) with two atoms per unit was chosen to determine the $\mu_{Zn}^{Zn(s)}$ in order to identify a $\mu_O^{SiO_2}$ boundary (Figure 3.4). Table 3.1 contains the calculation conditions, and figure 3.5a depicts the k-point convergence test. The resulting chemical potential of solid zinc is $\mu_{Zn}^{Zn(s)} = -1.26592$ eV/atom.

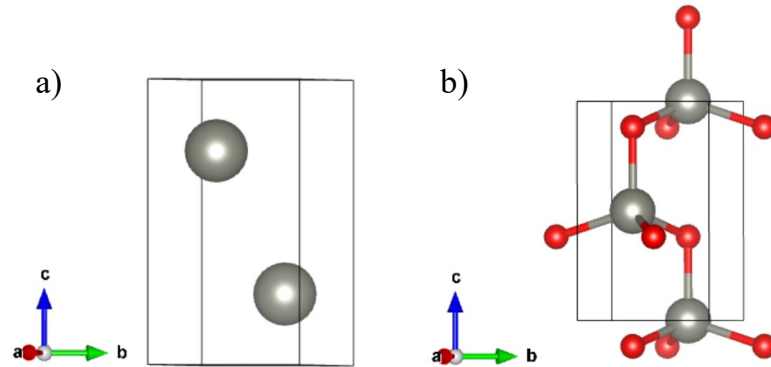


Figure 3.4: Unit cell visualization of a) Zn ($a = b = 2.6640$ Å, $c = 4.94670$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and b) ZnO ($a = b = 3.24940$ Å, $c = 5.20380$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$)

Finally, G^{ZnO} is calculated from the hexagonal unit cell of ZnO (P63mc space group). The resulting free energy of ZnO, again obtained by dividing ground-

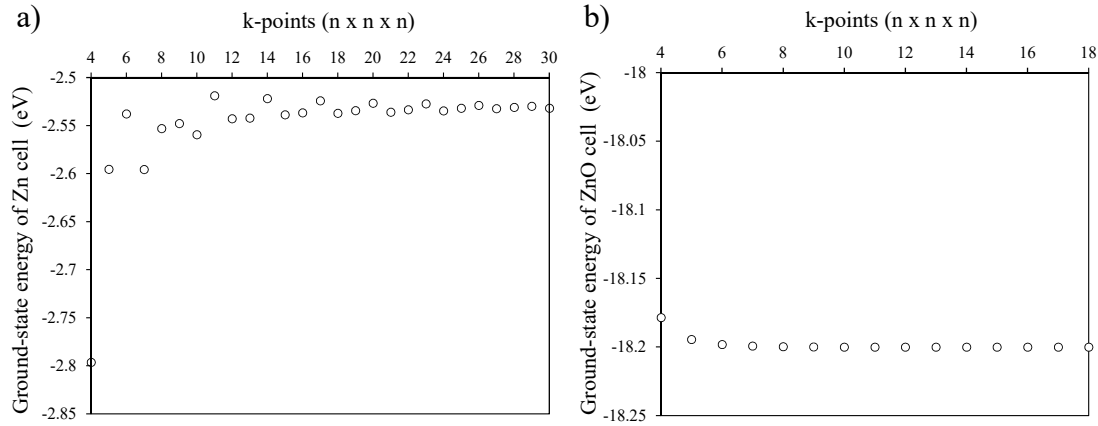


Figure 3.5: Convergence of the ground-state energy of a) solid hcp-Zn and b) ZnO in function of increasing k-points (k-points are equal in every direction)

state energy (fig. 3.5b) by the number of ZnO formula units in the unit cell, is $G^{ZnO} = -9.100$ eV/ZnO formula unit.

Supercell	Cut-off energy (eV)	K-points	Ground-state energy (eV/atom)	Chemical potential (eV/atom)	Free energy (eV/formula unit)
Si _(s)	400	4 × 4 × 4	-43.39845(4)	5.425	
SiO ₂	600	9 × 9 × 9	-71.13206(2)		23.7107
Zn _(s)	416	25 × 25 × 25	-2.532(1)	-1.26592	
ZnO	600	9 × 9 × 9	-18.1999(2)		-9.100

Table 3.1: Simulation conditions and results for bulk Si, SiO₂, Zn, and ZnO supercells

3.2.2.2 SiO₂ (0001) surface supercell and its surface energy

At last, the supercell of the SiO₂ surface was created. It was decided to work with the surface made of a (0001) crystallographic plane of α -quartz. (0001) surface was chosen because of its simplicity and because it was studied in literature [172, 192], thus providing the results for comparison. It was necessary to respect two aspects when constructing this surface. The first one was to construct symmetrical surfaces with a plane mirror at the center of the model to prevent the formation of an electrostatic dipole inside the cell, which would cause the

surface energy estimates to be distorted. The second feature was to create a void area above and below the model with a thickness of about 10 Å in order to obtain no interaction with the layer that is above or below by periodicity. Also, in order to avoid spurious interactions between the two surfaces, a surface energy convergence test was realized to find the correct number of layers by calculating the ground-state energy of the system with different-sized supercells (Figure 3.6). As in presence of surface, the supercell size in the c-axis direction increased considerably, the k-point was modified to $9 \times 9 \times 1$. Other parameters were the same as in the case of the SiO_2 unit cell study.

Another aspect to take into account are the different possible terminations of the slabs, with two oxygen, one oxygen, or free silicon atoms at the surface (Figure 3.7). A preliminary study of surface energy convergence (Equation 3.7) indicates that for the three surface terminations, especially the -O termination, a 10-layered SiO_2 slab is appropriate to represent the bulk-like behavior of the oxide (Figure 3.8).

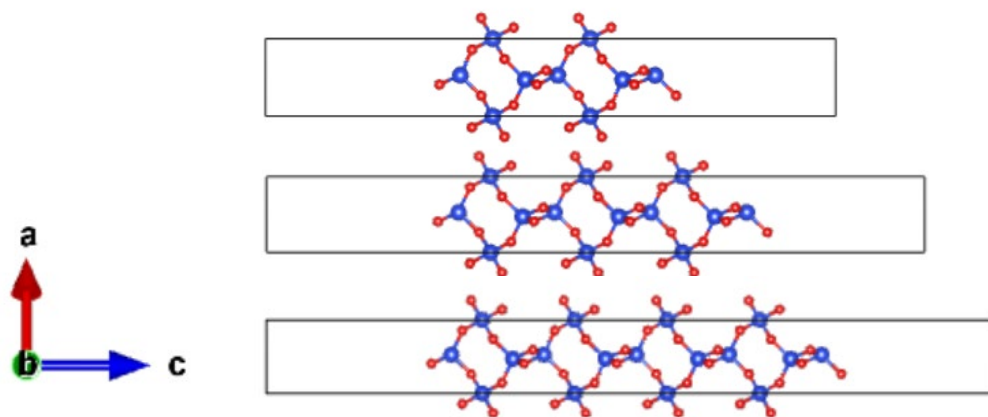


Figure 3.6: Visualization of SiO_2 supercells containing 7, 10, and 13 Si layers

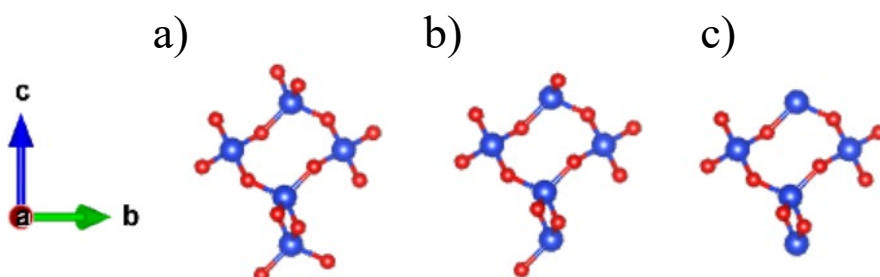


Figure 3.7: Possible surface terminations of an α -quartz cell: a) -OO termination, b) -O termination and c) -Si termination

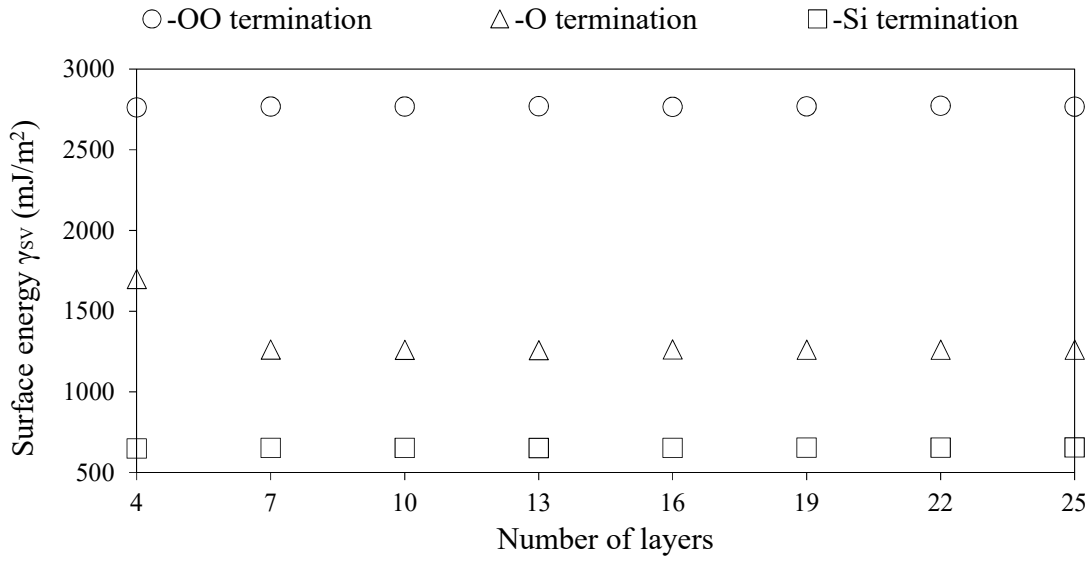


Figure 3.8: SiO_2 surface energy convergence in function of different numbers of Si layers in the supercell for the three terminations of the (0001) surface. A variable $\mu_{\text{O}}^{\text{SiO}_2}$ was fixed here at -9.146 eV/atom

Using the chemical potentials that were previously calculated, the $\Delta H_f^0(\text{SiO}_2)$ equals -9.3221 eV and the $\mu_{\text{O}}^{\text{SiO}_2}$ limits are:

$$-9.1461 \text{ eV} \leq \mu_{\text{O}}^{\text{SiO}_2} \leq -4.4850 \text{ eV} \quad (3.23)$$

The value of the γ_{SV} in function of the $\mu_{\text{O}}^{\text{SiO}_2}$ in the defined range of existence of SiO_2 is represented in figure 3.9. The single oxygen termination is never the most thermodynamically stable in this range; therefore, it is unlikely that this type of surface is present. The -Si and -OO terminations are the most stable in different value ranges. -Si termination is preferred in the Si-rich zone for lower chemical potential values, and -OO termination is more stable on the other side of the range.

Finally, a new upper limit is obtained by forbidding ZnO formation. The equation (3.17) gives the following value:

$$\mu_{\text{O}}^{\text{SiO}_2} \leq -7.8341 \text{ eV} \quad (3.24)$$

The new limit is represented in figure 3.9. In these boundaries, the curve of -Si terminations is the lowest; therefore, Si atoms at the free surface are the most stable form. This surface type is kept for further interface modeling in order to

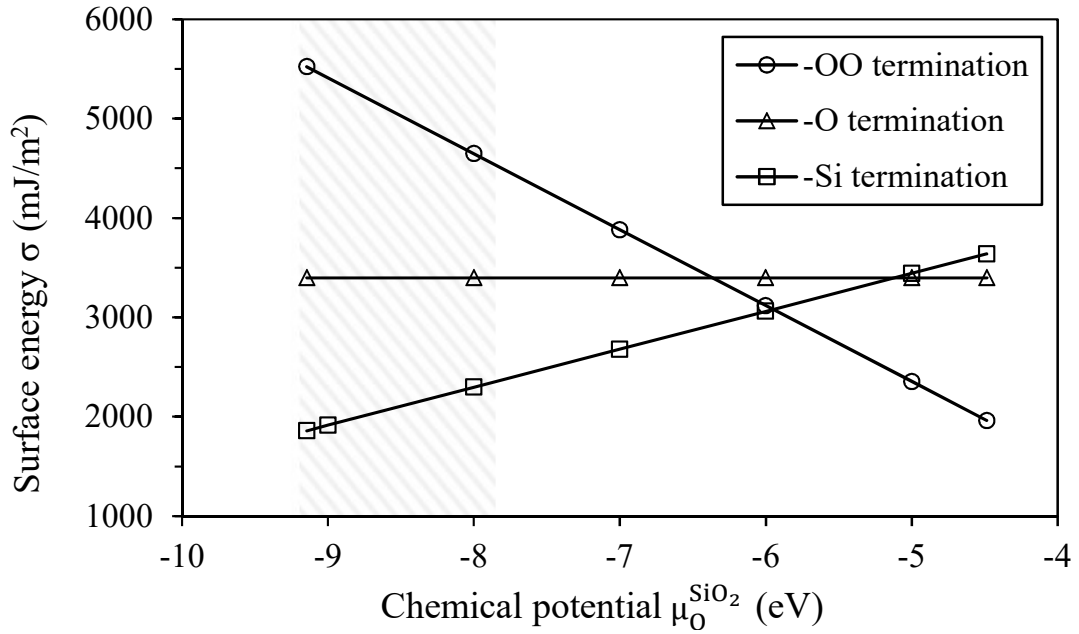


Figure 3.9: Surface energy of SiO_2 (α -quartz) in function of 3 terminations: -Si, -O, and -OO. The gray zone defines the potential range that excludes both the formation of ZnO and the decomposition of SiO_2 .

reduce the number of simulations. Yet, all three surface types could be examined because interactions with Zn atoms may differ from those at the free surface.

3.2.2.3 Discussion

The choice of -Si terminations on the $\text{SiO}_2\text{-Zn}_{(l)}$ interface was confronted with the bibliography.

The study of the free $\alpha\text{-SiO}_2$ surface can be found in the article written by Zhang et al. on the SiO_2/Al solid-solid system [192]. They realized their calculation in the CASTEP code, using the GGA-PBE and LDA functionals. Those different methods could be the source of the bulk chemical potentials of constituents being two orders of magnitude bigger than in this study. Their calculation of chemical potentials is not detailed enough to deduce where this important difference comes from. However, at the end, the heat of formation $\Delta H_f(\text{SiO}_2)$ is only 5% bigger than with this VASP simulation. Similar to this work, the (0001) surface is chosen by Zhang [192], motivated by its stability and probability of forming in reality. The size of the SiO_2 supercell is identical in both studies, with symmetric surfaces on both ends as well as the same formula for surface energy. However, the discrepancies in the form of the curves in the

domain of existence are observed in figure 3.10a.

Comparing with figure 3.10 shows that the tendencies of the -2O and -Si curves are similar in function of $\mu_O^{SiO_2}$, and the resultant surface energy is fairly identical for -Si terminations. In the case of -2O terminations, the surface energy is similar on the Si-rich side, but the slope is more steep in this PhD study, and the energy on the O-rich side is lower than for Zhang et al. Additionally, more important differences between this earlier study and the present one are noticed for -O termination. With -O terminations, the cell is stoichiometric; therefore, $N_{Si} = \frac{1}{2}N_O$. By replacing N_{Si} in equation 3.7, the following equation is obtained:

$$\gamma_{SiO_2} = \frac{1}{2}A \left[E_{int} - \frac{1}{2}N_O G^{SiO_2} \right] \quad (3.25)$$

which proves that the curve is independent of $\mu_O^{SiO_2}$ and should be constant. This can be seen clearly in figures 3.9 and 3.10b, which cast doubt on the findings of Zhang et al. (fig. 3.10a) and justify the results of this section of the study on the SiO₂ surface.

For the formation of the SiO₂/Al surface, the authors decided to use the O-terminated surface, as in a natural setting the atmosphere would be oxygen rich and therefore promote the formation of oxygen terminations, whereas in this PhD study the role of the oxygen atmosphere was not taken into account and the termination was chosen solely on the basis of their stability in the given $\mu_O^{SiO_2}$ range. Single oxygen was chosen over double oxygen in order to simplify the system and by following the work of Tea et al. [193]. They analyzed in their article the influence of oxygen defects at the SiO₂/Al interface on electron tunneling in electronic devices. They did it by studying electronic states in systems with one or two oxygen atoms removed from the silicon at the surface. No surface terminations were indicated as preferential in their work. Therefore, the choice of -O terminations by Zhang et al. gives the impression of being unjustified.

The study of Le et al. [172] was based on the β -cristobalite. They also worked in VASP and used a GGA functional. As can be observed in figure 3.10b, the tendencies of -Si termination (called by authors "SiO") and -2O ("SiO₃") curves are similar to those of this thesis. Their -O termination curve ("SiO₂") is also constant. The surface energy that they calculated is in the same order of magnitude but systematically lower by circa 1.5 J/m² for -Si and -O terminations. However, one must keep in mind that a different crystallographic structure was examined in this instance.

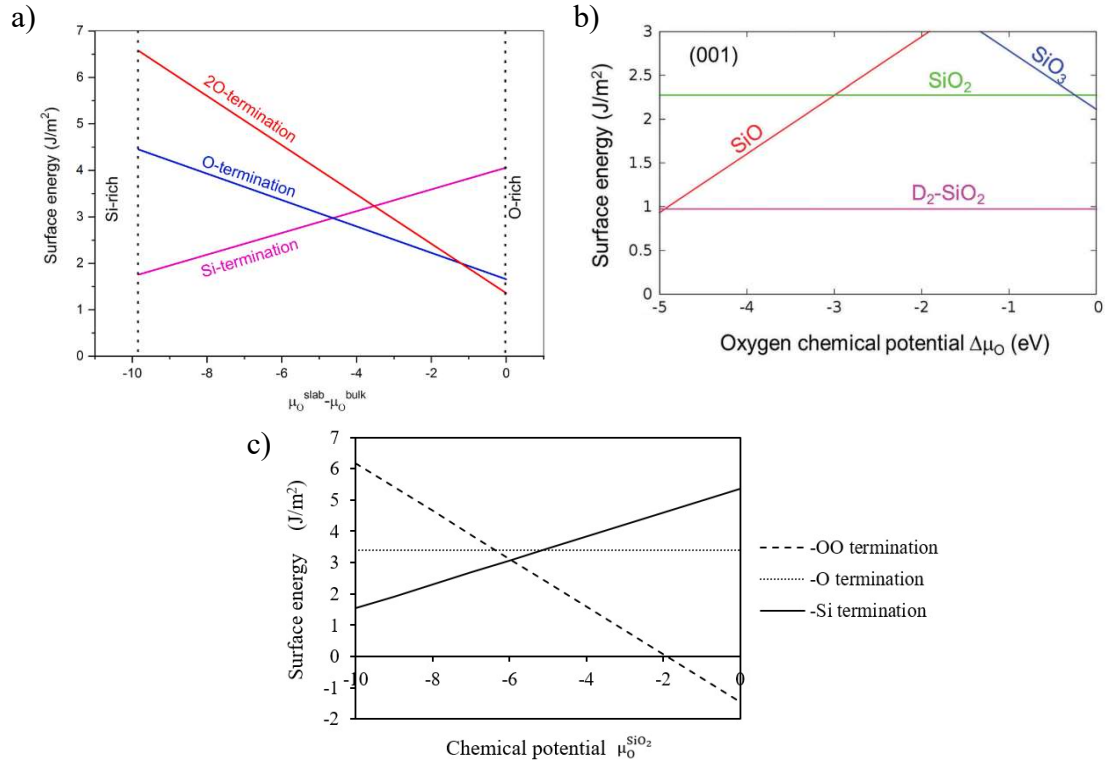


Figure 3.10: a) Surface free energies of Si-, O-, and 2O-terminated α -SiO₂ (0001) [192]; b) Calculated surface energies of the various terminations of the β -cristobalite (001) surface as a function of the oxygen chemical potential $\Delta\mu_{\text{O}}$ [172]; c) Figure 3.9 of this work adapted to the ranges of other studies for comparison

3.2.3 Liquid zinc surface energy γ_{LV}

This section is dedicated to the AIMD simulation of liquid zinc in order to obtain its γ_{LV} .

3.2.3.1 Chemical potential of liquid zinc at high temperatures

AIMD simulation was performed in the NVT system with a Nosé-Hoover thermostat. The initial zinc configuration used for AIMD simulation of bulk molten zinc was one hpc unit cell doubled in all three directions. The supercell size needs to be adjusted to ensure that the zinc behaves consistently and that the internal pressure in the supercell does not rise with temperature in order for high-temperature simulations to be accurate and results to not be overestimated. Therefore, the volume needed for each atom to be at zero pressure is adapted by adjusting the height of the supercell on the c-axis.

Since zinc was hard to melt directly at 723 K (450°C), preliminary calculations were performed at this point for a linear decrease in temperature from 1000 at the beginning to 723 K at the end. $4 \times 4 \times 4$ k-point gamma grids were used for a first preliminary sweep in volumes, which aimed to target the accurate zone for the volume and accelerate the calculation. In parallel, an investigation on the impact of the thermostat parameter "SMASS" was conducted; however, since it had no significance on pressure computations, it was reported in Appendix A. The results of the study on the pressure were shown in figure 3.11.

As it can be observed, a volume of the supercell exists for which the internal pressure is null. Further investigations were done at constant, higher temperatures. The volume per atom required for the cell to be at null pressure at these temperatures is shown in the table 3.2. The final pressure profile is represented in appendix B (fig. B.2).

Temperature (K)	800	1000	1200	1500
Volume per atom ($\text{\AA}^3$)	16.8578	18.0046	18.5824	19.4663

Table 3.2: Volume per atom of zinc for which the pressure in the supercell is null at different temperatures

Once the correct supercell size was found, the chemical potential of liquid zinc at high temperatures could be researched. Four simulations were run at 800, 1000, 1200, and 1500 K. 4000 steps were simulated for bulk samples. 10 000 steps with a total simulation time of 20 ps for each temperature were applied for samples with the free surface. This simulation length lets the equilibrium be attained for the calculation of the mean $E_0 + E_k$ (Appendix B).

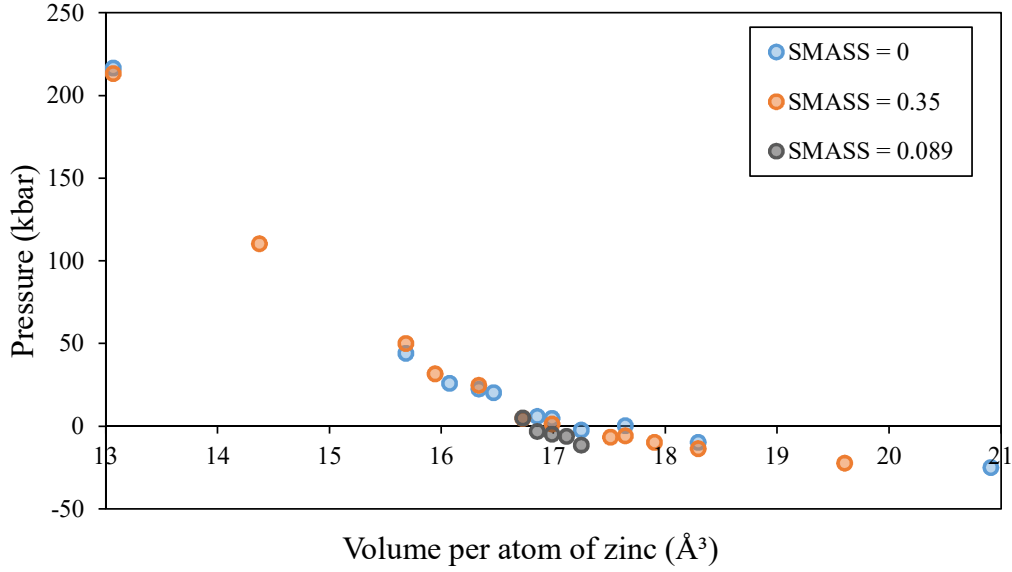


Figure 3.11: An example of an evolution of total pressure with the volume per Zn atom at 723 K for a $4 \times 4 \times 4$ k-point grid. Cell parameter a_{Zn} was kept constant and equals 4.94 Å.

The atomic layer density in function of the relative position z , as indicated by equation (3.26), can be tracked to verify that the supercell is well melted.

$$\rho(z) = \frac{\langle N_{at} \rangle_z}{2A\Delta z} \quad (3.26)$$

with $\langle N_{at} \rangle_z$, the time-averaged number of atoms in the layer between $z - dz$ and $z + dz$ planes [190]. The time-averaged value is obtained by collecting all the positions ever occupied by each atom and then dividing them by the number of simulation steps.

After observation of different atomic density functions in figure 3.12, the cells can be considered melted at temperatures above 1000 K. However, the extremely noticeable peaks that correspond to the basal planes of solid hexagonal zinc (fig. 3.12a) demonstrate that it is not melted at 800 K. Consequently, the value for $\mu_{Zn}^{Zn(l)}(T = 800K)$ will not be exploited but rather extrapolated from the values at a higher temperature. Furthermore, the results at the industrial galvanizing temperature of 723 K (450°C), which is considerably lower, can only be extrapolated.

Figure 3.13 shows the determined values of $\mu_{Zn}^{Zn(l)}$ for simulations conducted at 1000, 1200, and 1500 K. These findings thus made it possible to derive a linear law, which was then applied to extrapolate the μ values at 800, 723, and 0

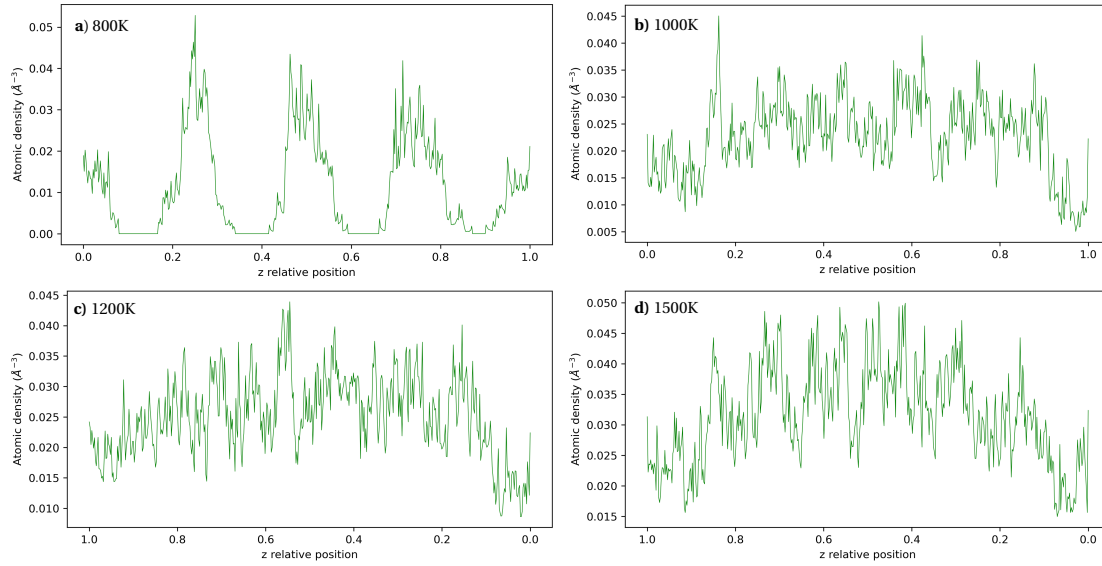


Figure 3.12: Evolution with temperature of the atomic density along z in a bulk liquid zinc supercell: a) 800 K, b) 1000 K, c) 1200 K, d) 1500 K.

K. The result obtained in section 3.2.2.1 at 0 K using ordinary DFT calculation (-1.2659 eV/at) and the value for μ_{Zn}^{Zn} at 0 K extrapolated from AIMD results (-1.2090 eV/at) are fairly consistent. The relative error between those results is of 4.5%. At 450°C , the resulting $\mu_{Zn}^{Zn(l)}$ equals -1.0035 eV/at. All $\mu_{Zn}^{Zn(l)}$ obtained in this study are represented in table 3.3.

T (K)	1500	1200	1000	800	723	0
$\mu_{Zn}^{Zn(l)}$ (eV/at)	-0.7831	-0.8667	-0.9255	-0.9816*	-1.0035*	-1.2090*

Table 3.3: Values $\mu_{Zn}^{Zn(l)}$ obtained at different temperatures with AIMD simulation. (*) signifies values that were extrapolated from the linear regression of other results.

3.2.3.2 Surface energy of liquid zinc in vacuum in high temperatures

The study of molten zinc surface was initiated by a k-points convergence test on a solid hcp-Zn supercell build with four $2 \times 2 \times 2$ Zn cells stacked on top of each other in the c -axis and with $20 \text{ \AA}$ vacuum on the top. The existence of a vacuum relieves pressure. As a result, unlike bulk Zn supercells, no investigation for null pressure is required for Zn surface ones because it should have no effect

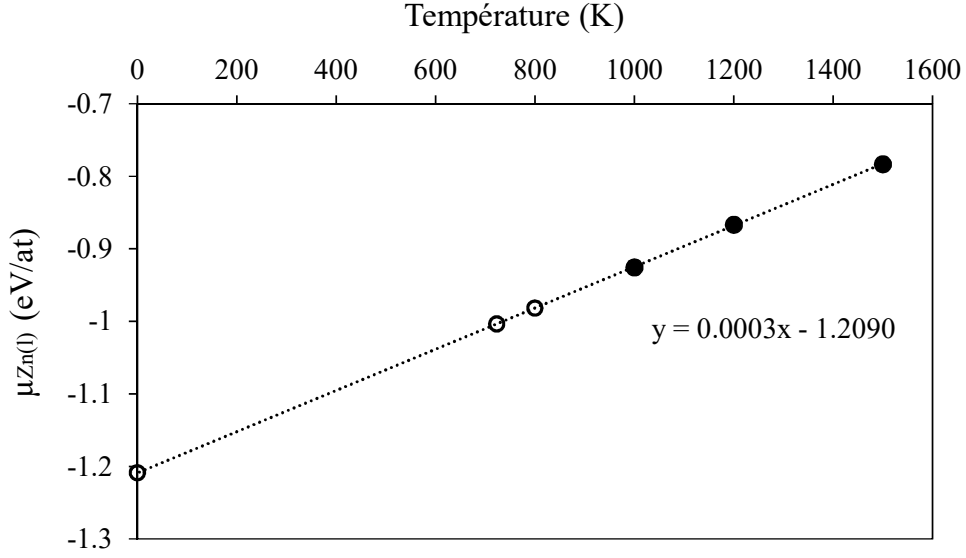


Figure 3.13: Chemical potential of liquid zinc in function of temperature at null pressure (3.2). The results for 800, 723, and 0 K (open circles) come from an extrapolation with the linear law y .

on the supercell's final energy. Parameter a is constrained to that of SiO_2 , a_{SiO_2} being around twice as big as a_{Zn} . As represented on figure 3.14, convergence is attained for $15 \times 15 \times 1$, and the supercell's ground-state energy in this condition is $(1.2382 \pm 0.0003) \text{ eV/atom}$.

Next, a preliminary test was conducted in order to attain the bulk-like behavior of a liquid zinc supercell with a surface and to eliminate the influence of two free surfaces interacting with each other. As in the case of SiO_2 , the ground-state energy of zinc supercells of different numbers of $2 \times 2 \times 2$ Zn cells added on top of each other in the c-axis was calculated until convergence (Figure 3.15). All those calculations were done for $15 \times 15 \times 1$ k-points. Eight zinc units seem to give a converging result, with an energy of -1.2223 eV/atom . The comparison with the $\mu_{Zn}^{Zn(l)}$ obtained for a unit cell without a surface and without the constrained of a_{SiO_2} shows a difference in energy of 3% that can be attributed to elastic deformation.

With reference to figure 3.16, the atomic density function was used to characterize the melting of the zinc in presence of a surface. It's interesting to note that, at all temperatures, the bulk of the zinc appears to have completely melted, but some distinct peaks can be seen near the surface. This highlights the fact that the melt seems to happen from the inside of the cell to the outside. This simulation behavior is surprising, since the melting is expected to start at the

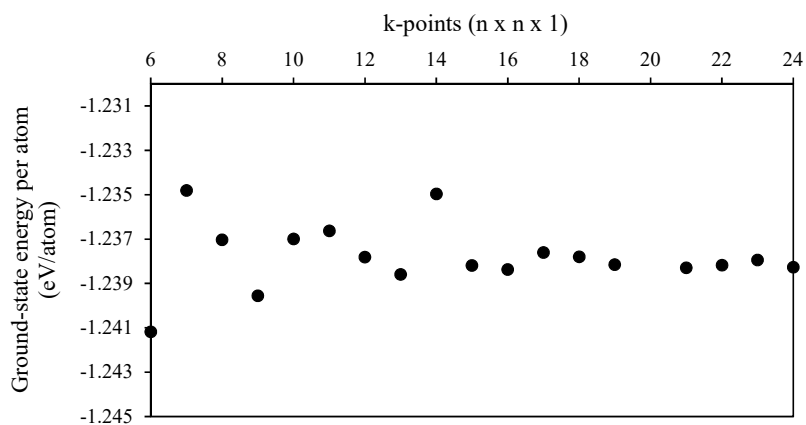


Figure 3.14: Convergence of the ground-state energy of Zn supercell with a free surface in function of k-points

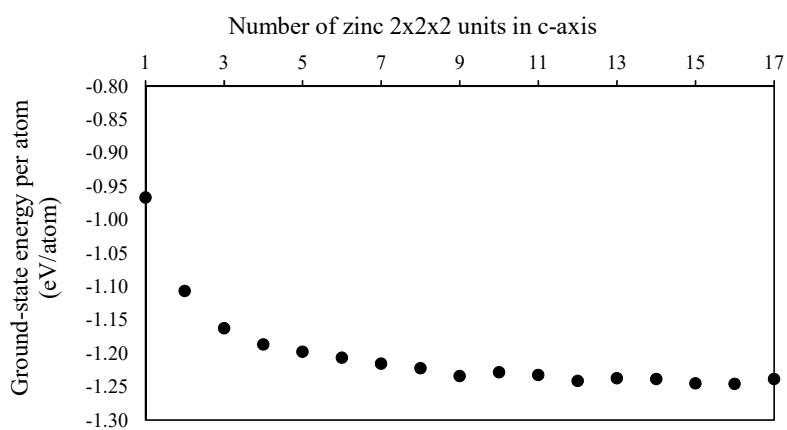


Figure 3.15: Convergence of the ground-state energy of Zn as a function of the number of zinc layers

surface since it is less stable than the bulk material. This could be related to the way that VASP initiates the velocities of atoms to give them kinetic energy. Because a surface supercell has a large vacuum zone, no additional supercell size adaptation is required to obtain a null pressure in this supercell. As can be seen from the pressure profiles in appendix B, the pressure in surface zinc supercells is lower on average than that of bulk liquid zinc supercell.

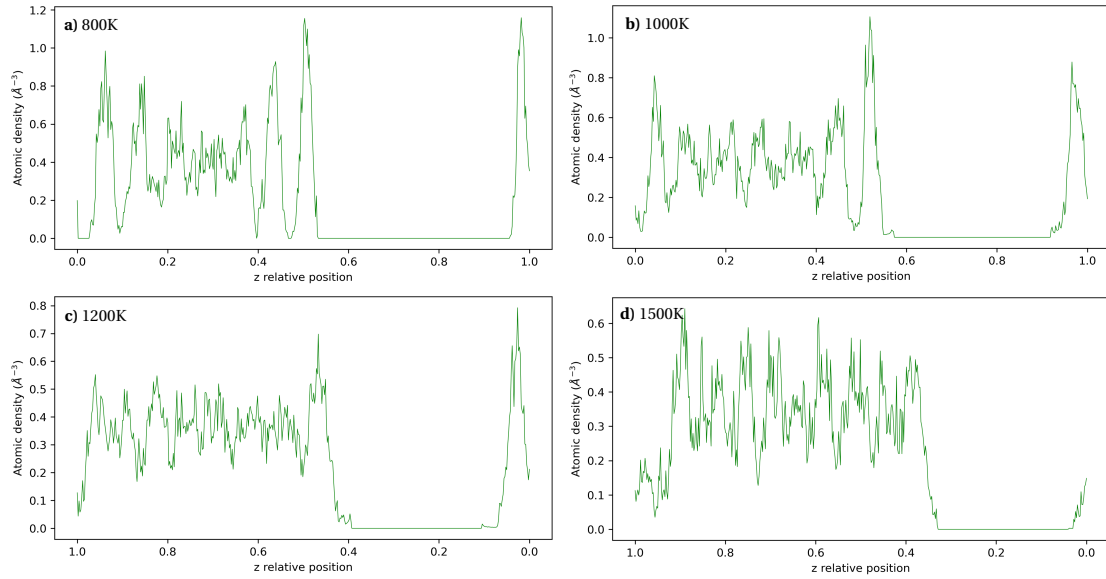


Figure 3.16: Evolution with temperature of the atomic density along z in a bulk liquid zinc supercell at a) 800 K, b) 1000 K, c) 1200 K, d) 1500 K.

Using equation (3.20), previously acquired chemical potentials, and the supercell energy of the liquid zinc surface in vacuum generated from AIMD simulation, it is possible to finally determine the surface tension γ_{LV} of liquid zinc. Figure 3.17 illustrates these findings. The value for 723 K had to be deduced once more through extrapolation and equals 426 mJ/m^2 .

3.2.3.3 Discussion

The surface tension of liquid zinc calculated in this work (426 mJ/m^2 at 450°C) must be compared to other experimental and computational data. To begin with, the value has the correct order of magnitude when compared to other research [162, 167, 194–196] and declines as temperature rises, as expected [195]. Some of the calculated results based on semi-empirical predictions at zinc’s melting point (419.53°C) are close to the surface tension of this study and equal 466 mJ/m^2 [194, 195]. Qiao et al. [162] computed it with the AIMD method on a

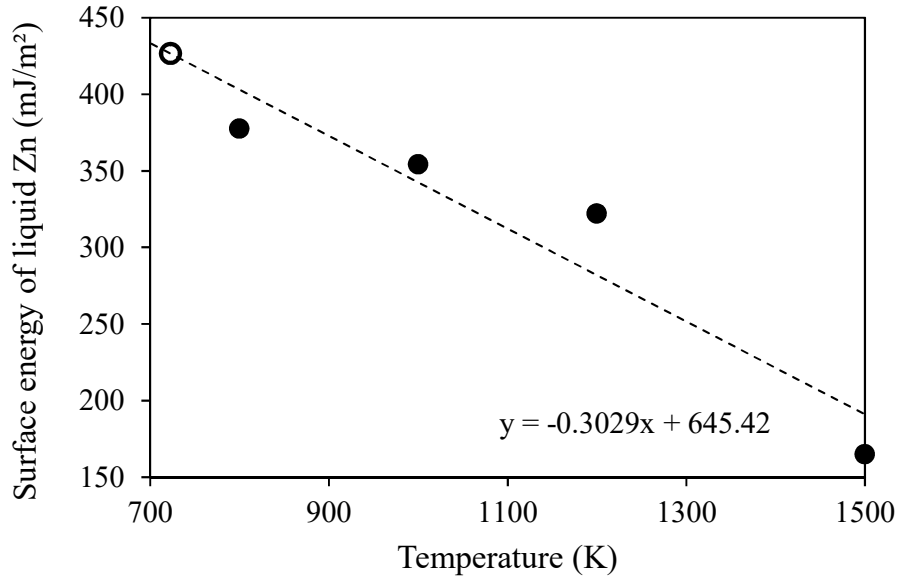


Figure 3.17: Evolution with temperature of surface tension on liquid zinc in vacuum. γ_{LV} at 723 K (open circle) was extrapolated with the linear law y .

significantly larger zinc supercell (218 Zn atoms) and found 679.62 mJ/m². This result is closer to the experimental data, such as 755.16 mJ/m² [167], 745 mJ/m² [197] and 767 mJ/m² [196] at 450°C, or 789-815 mJ/m² at melting point [195]. Consequently, the value generated in this PhD study is nearly twice as low as the experimental result. This discrepancy could be attributed to the insufficient size of the zinc supercell, either in the number of layers on the c-axis or the small size of the cell in the a-b plan. Additionally, the AIMD calculations were performed in a $4 \times 4 \times 4$ k-point mesh, which is not an optimal parameter for computation of this system but was chosen in the initial approach given the shorter simulation time. Further, it was not improved because of time constraints. Also, this study is conducted in a vacuum, so the γ_{LV} is not influenced by the presence of gas in the atmosphere, unlike experimental results.

3.2.4 SiO₂-Zn_(l) interface energy γ_{SL}

This last component of the simulation study focuses on the AIMD simulation findings on an SiO₂-Zn_(l) interface system. These results include calculating the interface energy γ_{SL} and then estimating the wetting angle created by molten zinc on the α -SiO₂ (0001) surface. The discussion of the findings and potential directions for further research may be found at the end of this section.

3.2.4.1 Model of $\text{SiO}_2\text{-Zn}_{(l)}$ interface

The constructed interface is done between (0001) $\alpha\text{-SiO}_2$ and the basal plane (0001) of hexagonal zinc. Since the zinc unit cell parameter is nearly half of a_{SiO_2} , the zinc unit cell in the interface plane needs to be doubled. It results in a mismatch of around 6% between the cells. The interface supercell's a and b parameters are constrained to a_{SiO_2} , because the zinc will further melt and its SiO_2 that shall impose the interface surface dimensions. As explained in section 3.2.2.2 on the results of surface energy of SiO_2 , a surface with free Si atoms is chosen for interface studies.

The initial superposition of Si and Zn atoms is the next component in the interface formation that is considered. Figure 3.18 shows three configurations that were examined. A situation where a Zn atom is positioned directly on top of the Si atom is described by arrangement a (3.18a). Consequently, Si/Zn has a coordination number of 1. The Si/Zn coordination number in arrangement b (3.18b) is three because the Si atom is equally spaced from three Zn atoms. Finally, the configuration c (3.18c) exhibits two Zn atoms at an equal distance from Si atoms, resulting in a coordination number of two.

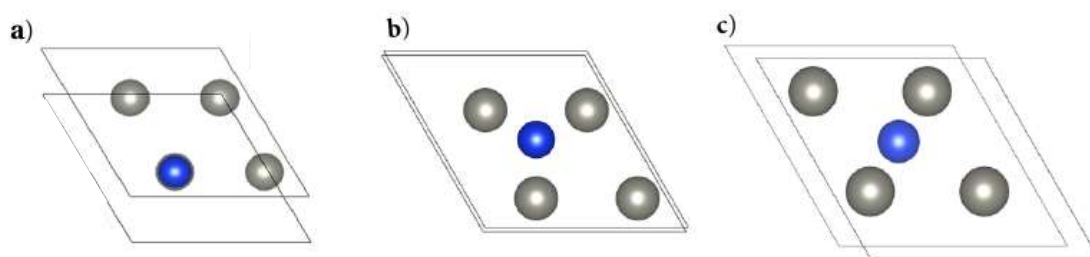


Figure 3.18: Visualization of three different arrangements possible at the $\text{SiO}_2\text{-Zn}_{(s)}$ interface for free-Si terminations of the SiO_2 surface

Energy convergence was examined in three supercells with different configurations at the interface. Next, as shown in figure 3.19, this investigation was carried out by relaxing the supercell for k-point meshes matching $n \times n \times 1$. A convergence of the energy is obtained for $n > 13$, but for arrangement c, the curve starts diverging for $n > 18$. $14 \times 14 \times 1$ k-point mesh is good to be used for precise calculations on those supercells, but to initially cut on the time of computation, all following AIMD studies are done with $4 \times 4 \times 1$. The ground-state energy of the cell is the lowest for arrangement b; this combination is then used for later studies. However, this initial arrangement should disappear with zinc melting, so it should not influence the final result of γ_{SL} . The final supercell is represented in figure 3.20.

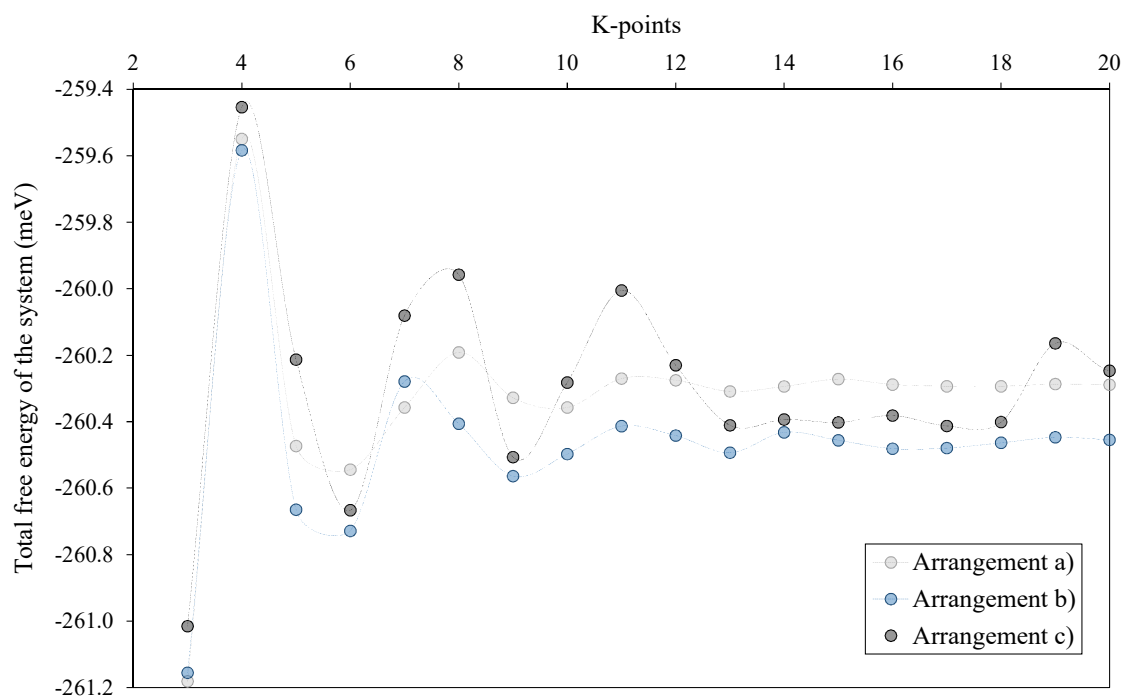


Figure 3.19: Ground-state energy of the $\text{SiO}_2\text{-Zn}_{(s)}$ interface as a function of k-points for the three interfaces defined in fig. 3.18

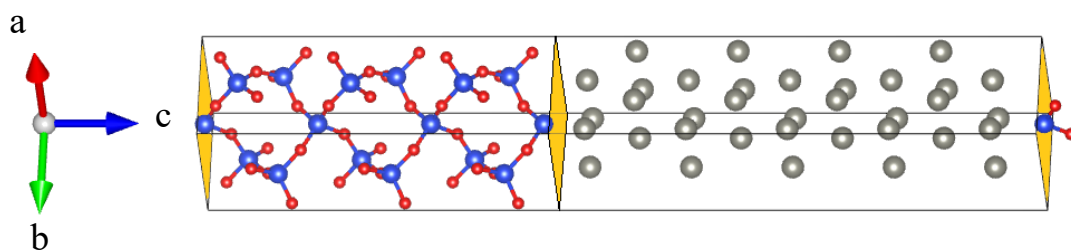


Figure 3.20: Visualization of the supercell used to simulate the (0001) $\text{SiO}_2\text{-Zn}_{(l)}$ interface (10 Si, 18 O, and 32 Zn atoms)

3.2.4.2 Results of atomic-scale *ab initio* simulations of interfaces

Considering an increase in the number of atoms in the interface supercell, further investigation was realized only at 1000 and 1500 K. 2500 steps were simulated for interface supercells due to time limitations (Appendix B). The quartz should remain solid at those temperatures, whereas the zinc end should melt. As can be seen in figure 3.21, the atomic density along the z-axis was again used to characterize the melting. Though the three simulations in these graphs have the same number of steps, there is a discernible difference in the zinc state. At 1500 K, it is evidently melted, yet at 1000 K, certain atomic planes are still clearly visible. Figure 3.21a shows an interesting observation: melting appears to begin at one interface, despite the assumption that the two interfaces are equivalent. The interface energies will still be determined using those simulations.

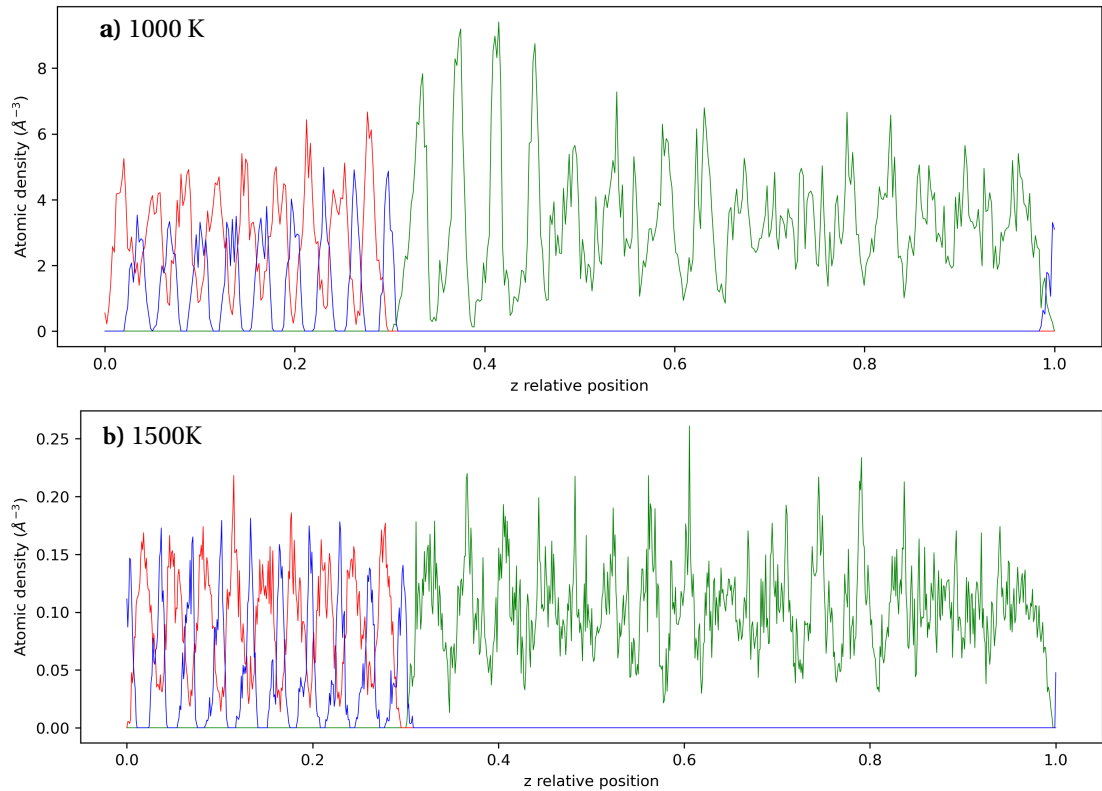


Figure 3.21: Evolution with temperature of the atomic density along z-axis in a bulk liquid zinc supercell. Zinc atoms are in green, oxygen atoms in red, and silicon atoms in blue.

Next, the interface energy was calculated for each temperature and is represented in figure 3.22. The upper limit for $\mu_O^{SiO_2}$ was adapted, as the $\mu_{Zn}^{Zn(l)}$ depending on temperature was used in equation (3.17). The interface energy is much larger than the surface energy of SiO_2 or liquid Zn. The extrapolated value at 450°C is in the range [2557;3356] mJ/m². With γ_{SL} calculated for only two temperatures, it is difficult to say whether it rises or falls with temperature. However, thermodynamically, γ_{SL} in this system should be positive, and with $S = \frac{-dG}{dT}$, it should decrease with rising temperature. As can be observed in appendix B (fig. B.6), the pressure in the supercell is high because, erroneously, the size of the supercell in the c-axis was not correctly adapted as in the case of the liquid zinc, which may result in an excess of surface energy due to the pressure perpendicular to the interface.

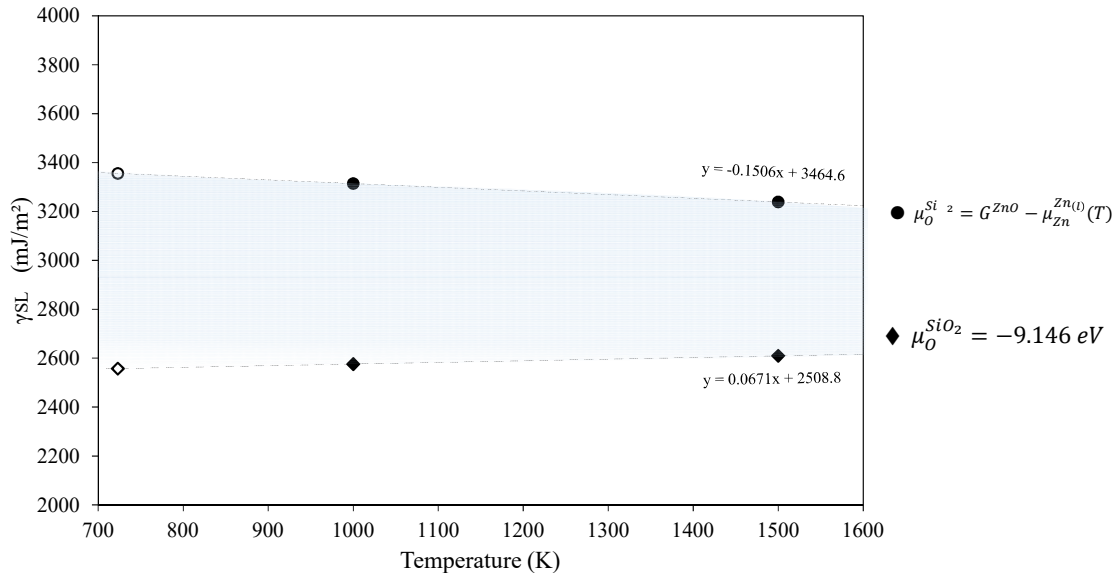


Figure 3.22: Interface energy of a SiO_2 - $Zn_{(l)}$ system in function of temperature and $\mu_O^{SiO_2}$. Values for 723 K (open circles) were extrapolated from linear laws γ .

3.2.4.3 SiO_2 - $Zn_{(l)}$ wetting angle

The wetting angle of the SiO_2 - $Zn_{(l)}$ system can be estimated using the obtained range of interface energy and the predicted prior surface energies of a SiO_2 and liquid zinc in vacuum. This angle can be calculated using the Young law (equation (2.2.1)):

$$\theta = \arccos\left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}\right) \quad (3.27)$$

At calculated temperatures, $\cos \theta$ values at all temperatures are not within the $[-1,1]$ range. Therefore, the equation (3.27) has no solution. However, the wetting angle at 723 K can be estimated by extrapolating the ratio of interface energies inside the cosinus, as shown in figure 3.23. It can be observed that the ratio is less than 0 for the given $\mu_O^{SiO_2}$ range, and it enters the $[-1,1]$ range at the limit $\mu_O^{SiO_2}$ of -9.146 eV. This value yielded a wetting angle of 124° . This result indicates that the surface is essentially non-wetted by liquid zinc, as the wetting angle is over 90° .

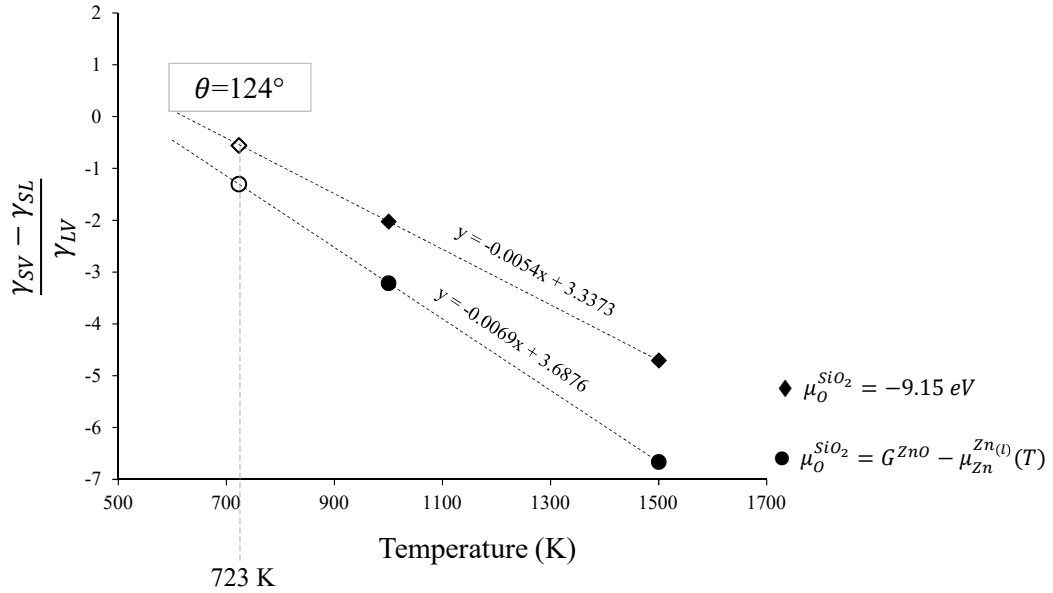


Figure 3.23: Interface energy of a SiO_2 - $Zn_{(l)}$ system in function of temperature and $\mu_O^{SiO_2}$. Values for 723 K (open circles) were extrapolated from linear laws y .

3.2.4.4 Discussion

Experimental results show that SiO_2 is hardly wetted. It was reported to be 163° in the dry atmosphere at 723 K [198], or else to vary from 133 to 112° between 773 and 973 K [188]. The simulated value of the wetting angle of 124° is lower than the experimental ones, but it also suggests the non-wetting of the SiO_2 surface by liquid zinc. The atmosphere present in experimental research may cause slight differences in results with this simulation, which was conducted in a vacuum.

In this study, the entropic effects on the system were neglected, similar to other AIMD research, in which they did not seem to be taken into account [162, 190]. Also, other studies [172, 192, 193] preferred to use the oxygen terminations for the formation of their interfaces. In this study, the investigation of the most stable terminations suggested the use of -Si terminations due to their stability, but it would be interesting to repeat the study in order to observe if it plays a role in the final result. In the study of Le et al. [172], a formation of bonds between Zn and O can be observed when oxygen is at the surface. In this PhD investigation, the oxygen from SiO_2 does not seem to diffuse into zinc. Otherwise, it might react with molten zinc and form ZnO , which would induce a small reactivity and a slight decrease in the wetting angle.

3.3 Experimental model surfaces

Si-rich alloys, as shown in figure 1.20, are an interesting answer in the search for zincophobic materials since they can produce non-wettable silicon oxide SiO_2 . However, since the Fe-Si alloys are brittle [122–124], they are unsuitable for use as galvanizing hangers in their bulk state and may be replaced by coatings. The thermodynamical difficulty of manufacture of FeSi coatings, as described in 1.3.5, may be solved with a laser fusion process, detailed in section 2.5.1, that is utilized in this section to create model coatings with a silicon concentration of 20 wt.% or more. The best coatings are then evaluated using the extreme-surface analysis methods of XPS and ToF-SIMS.

3.3.1 Coating's composition

Model surface structures differ depending on the parameters of the laser beam's power and exposure time. Figure 3.24 depicts the combinations investigated in this study, particularly those that resulted in the development of ≥ 20 wt.% Si at the sample's surface. The composition of the samples was explored by SEM-EDX analysis of the sample's cross-section.

		Exposure time (μs)				
		600	750	800	1000	1250
Power (W)	75					
	80					
	85					
	90					
	95					
	115					

Figure 3.24: Diagram of SLM parameter combinations done during this study. In green, parameters that led to the formation of ≥ 20 wt.% of Si at the surface; in red, those that did not.

At first, a series of samples made with 90 W were evaluated. The exposure time ranged between 750 and 1250 μs . The thickness of the coating grows substantially with increasing exposure time, as shown in figure 3.25, since there is more time for iron from the base material to diffuse into the coating. It is observable that the coating has a uniform structure. At longer exposure times, 1000 and 1250 μs , the Si content at the surface is very low, with roughly 7.5

wt.% Si in average, with the rest of it being iron. There is substantially more silicon at the surface at 750 μs , with 18-20 wt.% Si. The Si content is, however, not consistently above 20 wt.% Si. This is why further research for optimal formation conditions was conducted.

A sample made at 115 W-800 μs has about 15 wt.% Si at the surface, while at 95 W-600 μs , this content is above 19 wt.%.

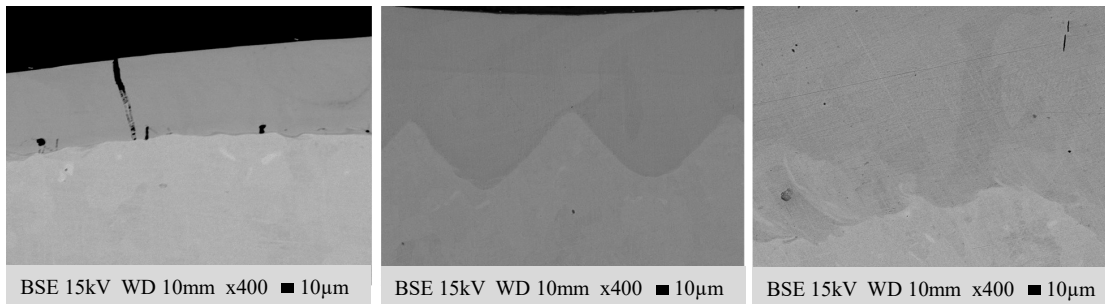


Figure 3.25: SEM images of model surfaces prepared with 90 W laser beam and a) 750 μs , b) 1000 μs , c) 1250 μs exposure time

It was decided to prepare samples at $t_e = 750 \mu\text{s}$ and with lower laser beam powers of 75, 80, and 85 W. The thickness of the coating does not appear to alter considerably with the power of the laser beam, as seen in figure 3.26, with the thickness ranging from roughly 75 to 85 μm . All coatings exhibit significant cracking. At the surface, all of those samples have a non-homogeneous, two-phase structure, with a homogeneous phase near the coating-steel interface. The thickness of the homogeneous phase increases with the laser beam power. It has 19 wt.% Si at 75 W, up to only 13 wt.% Si at 85 W.

In the two-phase region, the density of solutes in the matrix appears to decrease with increasing power. At 75 W, the solute is composed of 31 wt.% Si on average, falling to 27 wt.% at 85 W. The matrix has 23 wt.% of Si at the lowest power and 20 wt.% Si at the highest. When measuring an area near the surface with both phases included, the Si concentration is always greater than 20 wt.%, and the overall composition is best for a sample made at 75 W with 26 wt.% Si. It is thus preferable to operate under reduced exposure time and laser beam power circumstances in order to get the coating with the best composition in terms of resistance to liquid zinc corrosion, which is above 20 wt.% Si, as stated at the beginning of this chapter. While comparing with the Fe-Si phase diagram (fig. 1.21), the solute of the two-phase region would correspond to the ϵ -FeSi compound, while the solute would correspond to the η -Fe₅Si₃ compound. With longer diffusion time, if no laser melting is involved, an α phase with a lower Si content would be predominant.

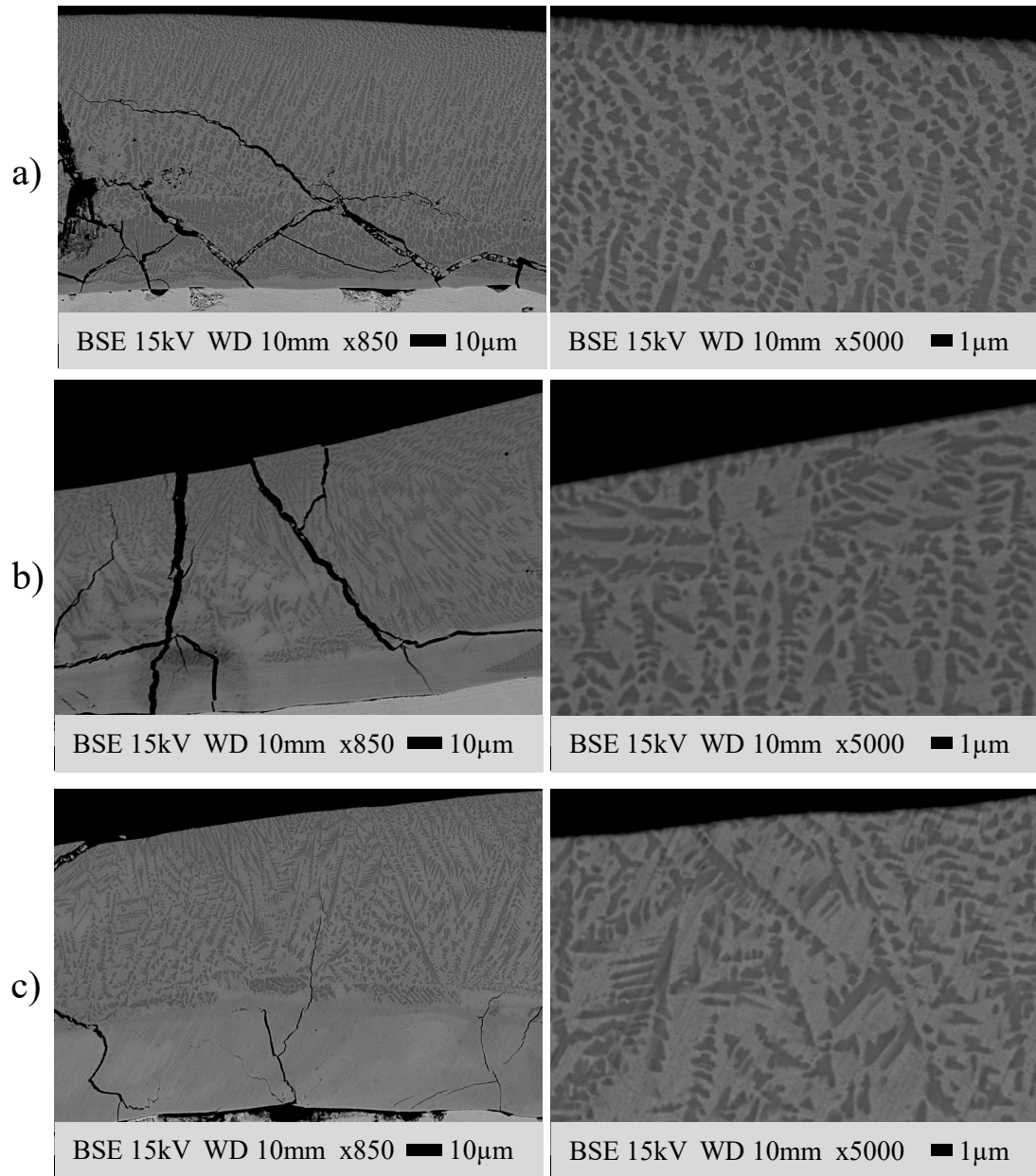


Figure 3.26: SEM images of model surfaces prepared with 750 μ s and a) 75 W, b) 80 W, c) 85 W laser beam.

3.3.2 Extreme surface characterization

The extreme surface study was performed on three model surfaces formed at 750 μs and 75, 80, and 85 W, since those samples had the highest Si concentration at the surface and were expected to develop the most protective oxide layer, which can be too thin to be detected with SEM-EDX analysis.

Initially, the samples were studied using a ToF-SIMS technique in order to know their composition according to their depth profile just beneath their surface. A cesium ion beam (2kV, 195 nA) was used to create a crater of $200 \times 200 \mu\text{m}$. The results of this analysis are represented in figure 3.27. The depth that was studied is estimated to be about 600 nm after 500 s, *i.e.*, the erosion rate was roughly 1.2 nm/s.

There is a high amount of oxygen within the first 200 nm, as can be seen in figure 3.27. The quantity of OH ions observed at the surface grows in conjunction with increased power. In comparison to other ions, there are few SiO_2 ions identified on the surface under any conditions, but the ToF-SIMS analysis are not qualitative. Silicon is rather detected mainly in the form of SiO ions.

As the 75 W-750 μm sample presents the highest content of Si and SiO_x at the surface, it was chosen for a detailed study of the first seconds of the depth profile analysis and next, the XPS analysis. The zoomed-in ToF-SIMS results for this sample are represented in figure 3.28. At the beginning of the measurement, SiO ions, as well as OH and Fe ions, are detected. Additionally, SiO_2 , O, Si, and three different forms of carbon ions are detected. The carbon and SiO_2 content then rapidly decreases. The surface appears to be dominated by understoichiometric silicon oxide, some carbon pollution, and adsorbed water.

A sample cleaned with acetone and ethanol was studied through the XPS analysis. A $700 \times 300 \mu\text{m}$ area was investigated. C, Fe, Si, O, N, and a trace of Ca, Na, and K, as well as maybe some Al, have been discovered at the surface. The quantitative analysis of the key elements can be found in table 3.4 and concerns the first 5-10 nm from the surface.

Even though the sample was properly cleaned, contamination was found at the estimated first 2 nm. There is contamination of organic hydroxydes C–OH and other organic compounds, but no adsorbed water (fig. 3.29e). There is around 47 at.% carbon at the surface, with 20% of that appearing to be carbon bonded to silicon (Si–C).

About 10 at.% of Si is detected at the surface. The Si peak appears to have two main contributions (fig. 3.29b). The first majority peak (80% of Si) corresponds to SiO_2 . It does seem to be amorphous or imperfectly crystallized, as a well-crystalline quartz peak should be at 102.2 eV. The second peak (20% of total Si) is further subdivided into two components: Si–C and metallic Si.

Finally, iron represents about 2.3 at.% of the surface composition, and it

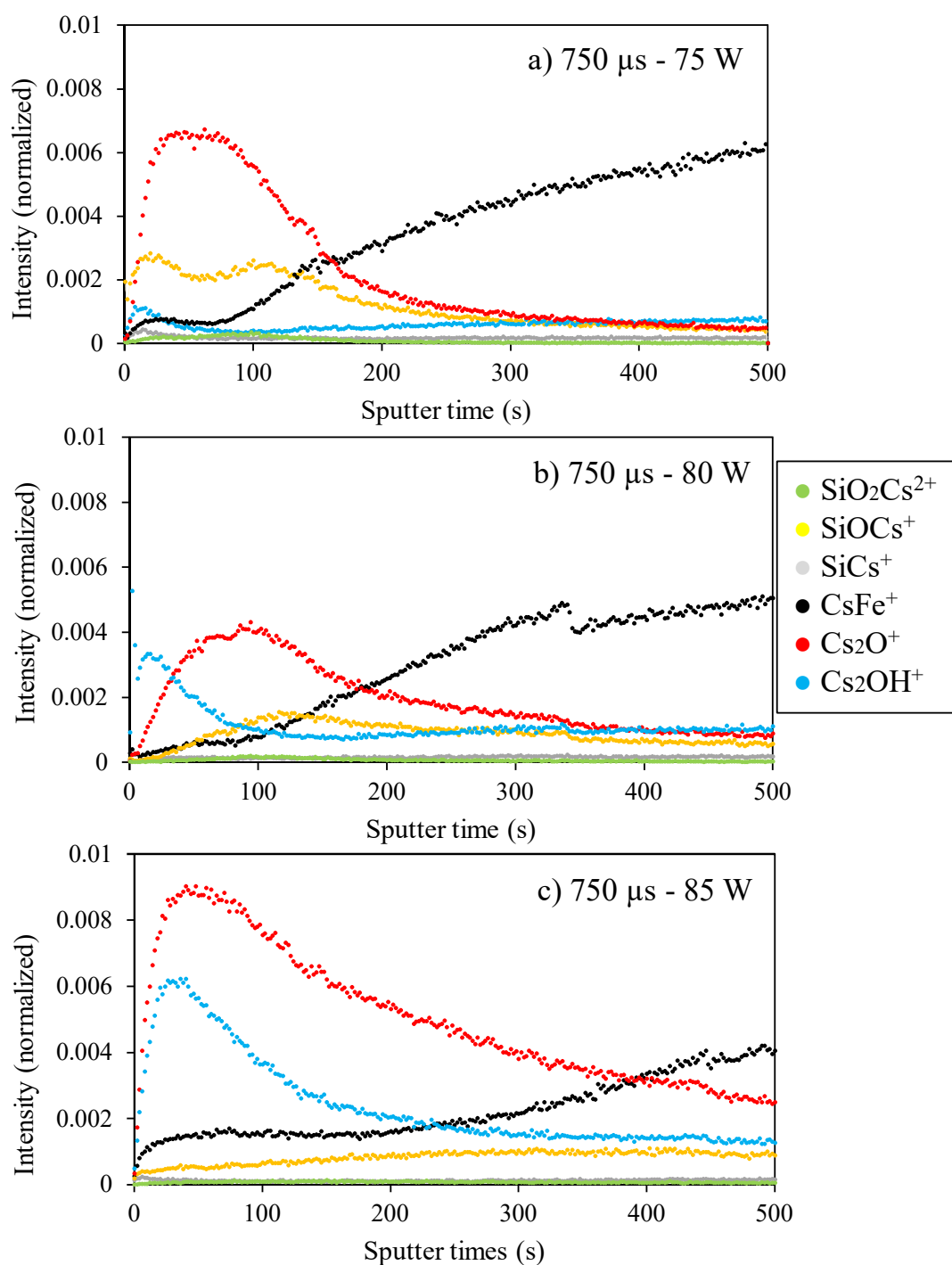


Figure 3.27: General overview of the results of the ToF-SIMS depth profile analysis for three model surfaces. The intensity was normalized by comparing it to the total intensity.

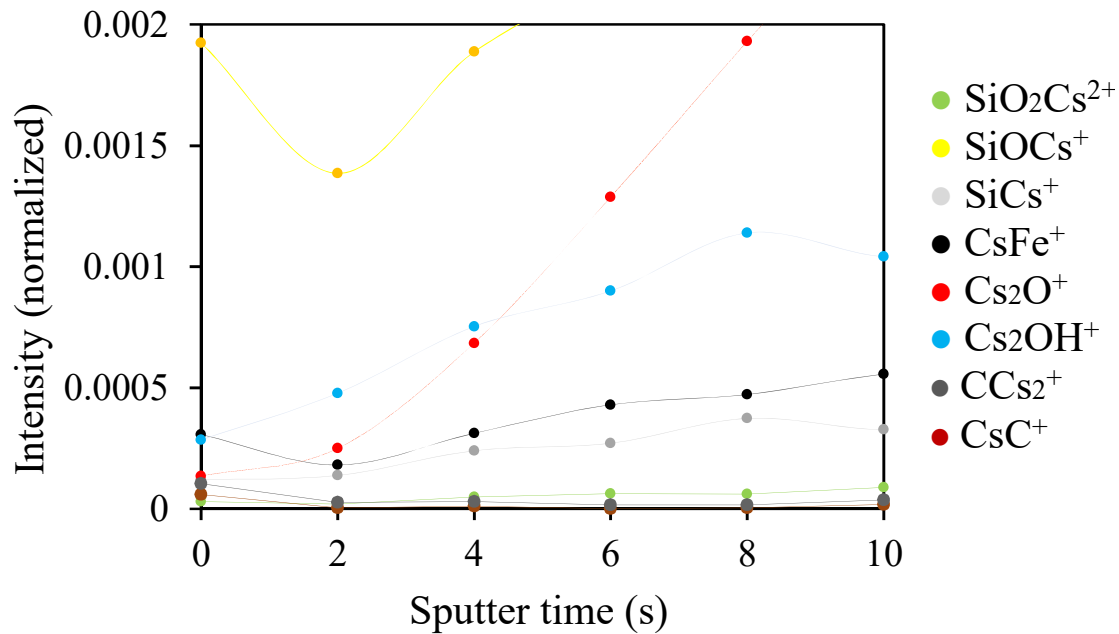


Figure 3.28: The beginning ToF-SIMS depth profile analysis for a 75 W-750 μ s model surface. The intensity was normalized by comparing it to the total intensity.

can be divided into two contributions: metallic iron and iron oxyde Fe_2O_3 (fig. 3.29f).

Both analyses show that an understoichiometric silicon oxide exists at the surface. ToF-SIMS detects little carbon, and SiO_x seems to be predominant, while XPS shows a high content of organic pollution, surpassing the silicon content. In general, all samples stored in the air will contain carbon pollution at the surface. However, in this case, it seems fairly high and can be linked to the SLM coating fabrication procedure. Actually, the ethylcellulose, which is a binder in the powder mixture, is combusted during the laser treatment. Some of this carbon may form bonds with silicon and be detected as SiC with XPS. Hydrogenated oxygen could be derived from organic pollutants rather than adsorbed water, as it was not discovered using XPS.

Because XPS detects more carbon contamination than silicon, it is possible that the carbon layer is above the silicon one. Carbon drops rapidly in ToF-SIMS, while SiO ions are important from the beginning for the next couple of hundred seconds. Therefore, it may be on the surface of the sample alongside SiO_x , forming a heterogeneous surface rather than a layer-by-layer structure. Because carbon is utilized in crucibles for zinc melting and hence cannot react with this molten metal [199], it may contribute to the eventual nonwetting behavior.

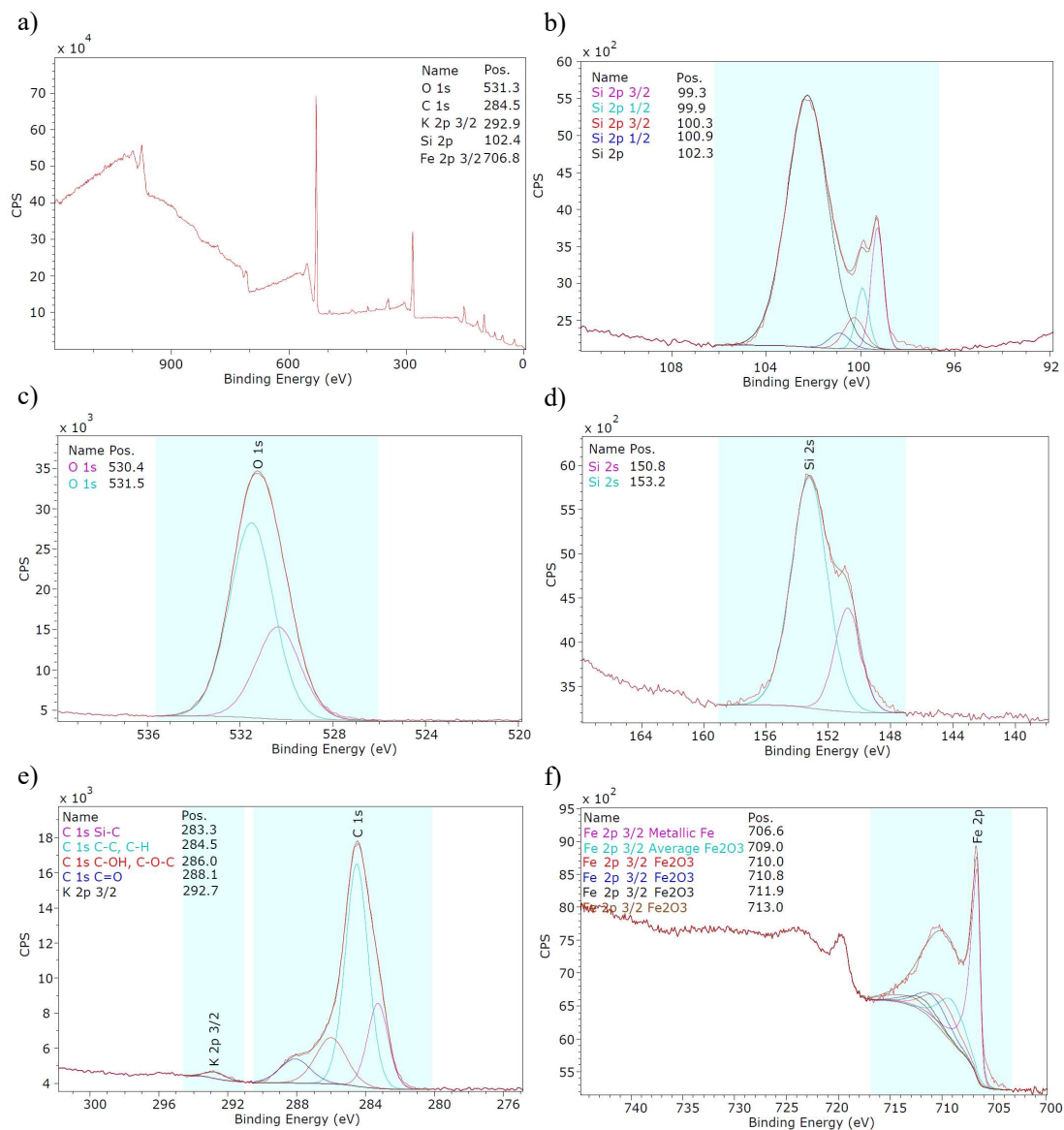


Figure 3.29: XPS results on model surface sample 750 μm -75 W. All peaks were calibrated with the metallic Fe peak at 706.6 eV

Element	Core level	Position (eV)	Concentration (at.%)	Attribution
O	1s	530.4	13.1	
	1s	531.5	27.7	
C	1s	283.3	9.2	Si–C
	1s	284.5	26.6	C–C, C–H
	1s	286	7.4	C–OH, C–O–C
	1s	288.1	3.9	C=O
Si	2p _{3/2}	99.3	1.1	metallic Si
	2p _{1/2}	99.9	0.6	
	2p _{3/2}	100.3	0.5	Si–C
	2p _{1/2}	100.9	0.2	
	2p	102.3	7.6	Si oxide
Fe	2p _{3/2}	706.6	0.9	metallic Fe
	2p _{3/2}	709	0.4	
	2p _{3/2}	710	0.4	
	2p _{3/2}	710.8	0.3	Fe ₂ O ₃
	2p _{3/2}	711.9	0.2	
	2p _{3/2}	713	0.2	

Table 3.4: Quantitative XPS analysis of 750 μm –750 W model surface

3.4 Conclusion

The objective of the DFT-AIMD simulation in this research was to develop a method of evaluation of the interface energy γ_{SL} between solid SiO_2 and liquid zinc that cannot be obtained directly through experimental methods but must rather be calculated from the separate evaluation of the surface energy of the solid γ_{SV} and the liquid γ_{LV} and a measurement of the wetting angle between the two substances. The AIMD method was applied to study the interface interactions between a solid and a liquid [190, 200], but not necessarily to calculate the interface energy. The further calculation of the wetting angle is useful to compare the numerical results with experimental tests but may be obtained through other numerical methods, such as Molecular Dynamics [153],

that cannot furnish γ_{SL} .

The calculation of the surface energy of SiO_2 could have been found already in the bibliography [172, 192]. However, the results found in this study seem to be viable in comparison to those studies and to be an improvement, especially on the study of Zhang et al. [192], which represented seldom ambiguity in their results. The one experimental result documented is that by Brunauer et al. (1956) [201], which estimates 259 mJ/m^2 for amorphous silica at 23°C . This is much lower than the values obtained in this study; however, it does not regard the same structure or temperature of the measurement.

It is complicated to find data in the literature that could serve to validate or refute the obtained values of the chemical potential of liquid zinc, $\mu_{\text{Zn}}^{\text{Zn}_{(l)}}$. The surface energy of liquid zinc obtained in this research is however twice as low as the experimental value found in the literature [167, 195, 196]. The numerical value calculated through the AIMD method by Qiao et al. [162] is also closer to the experience. The size of their supercell was however much higher, and the method of calculation of γ_{LV} did not consist in the search of $\mu_{\text{Zn}}^{\text{Zn}_{(l)}}$ and the surface energy calculation from the total energy of the supercell, but rather from the indirect calculation from the diffusion coefficient and the shear viscosity. Therefore, even though at this moment the result obtained in this PhD study is not correct, it may be ameliorated with a study on the larger supercell and represents a different method of calculation of this parameter.

Finally, no values of γ_{SL} of SiO_2 - $\text{Zn}_{(l)}$ interface are found at this moment in the literature. The calculation of the interface energy ratio present in the Young equation shows that the silicon oxide is not wetted by the liquid zinc at the galvanizing temperature, which is in agreement with the experimental results.

Also, the presence of oxygen in the atmosphere was not studied in this research, while a question may be asked about how it would influence the interface interactions. In batch hot-dip galvanizing, even though the dipping is done in air, the fluxes applied to the galvanized parts reduce the oxides that may form. Therefore, theoretically, the addition of oxygen to the simulation atmosphere may lead to the formation of ZnO at the surface of the drop if it is formed before SiO_2 and Zn come into contact, thus leading to the formation of $\text{ZnO}_{(s)}$ - $\text{SiO}_{2(s)}$ interface. The addition of oxygen might also help to fix the chemical potential of oxygen and thus decide finally which SiO_2 termination should be used.

It is challenging to evaluate whether the AIMD simulation is suitable for modeling and research on a practical zincophobic material. A system containing a solid and a liquid necessitates a large number of atoms, resulting in a lengthy calculation time. Further research might concern adding other metallic elements and oxides that may be found in galvanizing equipment, such as iron and its

oxides, but also chromium or nickel, could be investigated, either in bulk or as atomic inclusions in other systems. Not only crystallized bodies, but also amorphous bodies, may be studied. Because of all of these constraints, the AIMD simulation might require far too long to calculate in order to accurately represent mechanisms occurring at the interface between liquid zinc and potential protective materials.

The SLM coating formation technology allows for a high Si content at the steel surface. Nonetheless, it does not appear to be a suitable fabrication approach for batch galvanizing equipment protection. To begin with, the galvanizing parts are far too massive to be coated with SLM. Furthermore, because this is a layer-by-layer process, a flat substrate is required, which is not the case for hooks. Finally, the significant level of cracking of coatings shows that their mechanical resistance might be insufficient for industrial application. Furthermore, it was not possible to conclude in this study if the SiO_2 layer that is thus formed is sufficient to limit the wetting by liquid zinc due to the lack of results from wetting angle measurements.

SLM was shown to be interesting for the creation of FeSi alloys on the surface of steel. However, the fast diffusion of silicon in iron, represented by a Si content far lower than the initial 30 wt.% if the laser conditions chosen were too severe, makes selecting the optimal fabrication conditions extremely difficult, with a risk in terms of repeatability at a larger production scale. Thus, pure Fe-Si coating does not appear to be a viable solution for galvanizing coating protection, and an alternative production procedure for more complex alloys has to be developed.

Chapter 4

Slurry Fe-Cr-Ni-Si-P coatings

4.1 Introduction

As discussed in 3.3, Fe-Si alloys with high Si content do not undergo any liquid zinc corrosion. Additionally, SiO_2 is not wetted with liquid zinc. For this reason, silicon is an important element that can improve the galvanizing equipment's resistance to liquid zinc. Unfortunately, given thermodynamics, it is difficult to obtain a Fe-20wt%Si coating; so, a more complex alloy was created for this purpose. As in the case of stainless steel used in continuous hot-dip galvanizing, the addition of Ni and Cr to the combination may improve steel's resistance to corrosion in high temperature and corrosive solutions. They do not, however, restrict the wetting with liquid zinc. These components could be combined with silicon, which helps reduce wetting, to create a coating that is both mechanically more durable and resistant to corrosion and wetting. Furthermore, phosphorus is added to the mixture in the coatings examined in this study in order to lower the alloy's fusion temperature. This characteristic is important to the procedure that was selected to elaborate the coating.

While it has been established that a 20 wt.% Si is a good value to prevent corrosion caused by liquid zinc, the coating under investigation in this study has a lower mean Si content. A preliminary study [202, 203] examined the liquid zinc corrosion of various coating compositions under batch galvanizing conditions. The composition that exhibited the lowest corrosion rate, akin to that of 316L stainless steel, was retained for this investigation to enhance comprehension of the processes occurring at the coating-zinc interface. This thesis did not aim to investigate the optimal composition, or that with the maximum silicon content conceivable.

In this chapter, coatings were prepared using the slurry method. The principle and manufacturing conditions were detailed in section 2.5.2. Those coatings

underwent multiple galvanizing cycles in a laboratory setting, and their performance was compared to that of regular low-carbon steel. The weight change of samples at various phases of the galvanizing cycle was used to trace resistance to wetting by molten zinc and corrosion by liquid zinc. This chapter will cover the protocol of the galvanizing experiment as well as the numerical performance results of this study in terms of liquid zinc corrosion and the zinc deposition resistance of the hereby prepared coatings. In the later part of this chapter, the SEM-EDX analysis performed on different samples that underwent the cyclic galvanizing treatment is represented in order to better understand the interactions between the slurry coating and liquid zinc. In order to improve the parts' resistance and produce a non-wettable layer of SiO_2 at the surface, slurry coatings underwent a preoxidizing treatment. The final section of this chapter presents the performance and microscopic analysis results of this experiment.

4.2 Materials and experimental protocol

4.2.1 Base steel

The samples used for further batch hot dip galvanizing tests were prepared out of the DD13 hot-rolled low-carbon steel sheet. The 10×10 cm plates with the 5 mm diameter holes (Figure 4.1) were shear cut, and the thickness of the steel sheet was 3 mm. Table 4.1 provides information on the standard composition of DD13 steel. Optical observation of polished steel revealed its ferritic microstructure (Figure 4.2). Using a Mitutoyo AVK-C1 hardness tester, its Vickers hardness was determined to be 118 ± 8 HV, with an applied load of 10 kg.

Element	C	Mn	P	S
%wt	≤ 0.08	≤ 0.40	≤ 0.030	≤ 0.030

Table 4.1: Composition of the DD13 steel according to EN 10111 standard [204]

4.2.2 Coating characterization

The coating obtained by the slurry process is characterized in this section through different analysis methods. Its chemical composition was analyzed with SEM-EDX and with EPMA for more precision. Crystal structure was also characterized by X-ray diffractometry in Bragg-Brentano geometry.

The mean thickness of the coating obtained with the slurry method is 50 μm . The coarse microstructure of the coating is very complex with numerous phases,

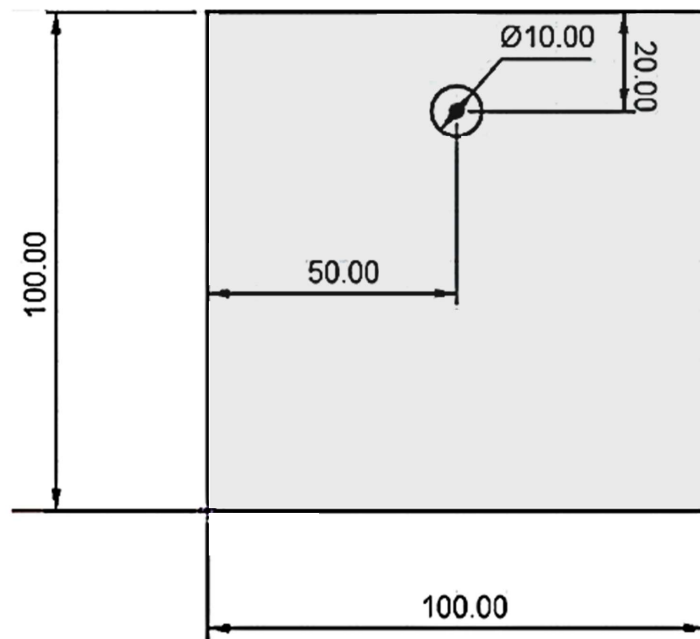


Figure 4.1: Plan of the steel sample in mm. The thickness of the plate is 3 mm

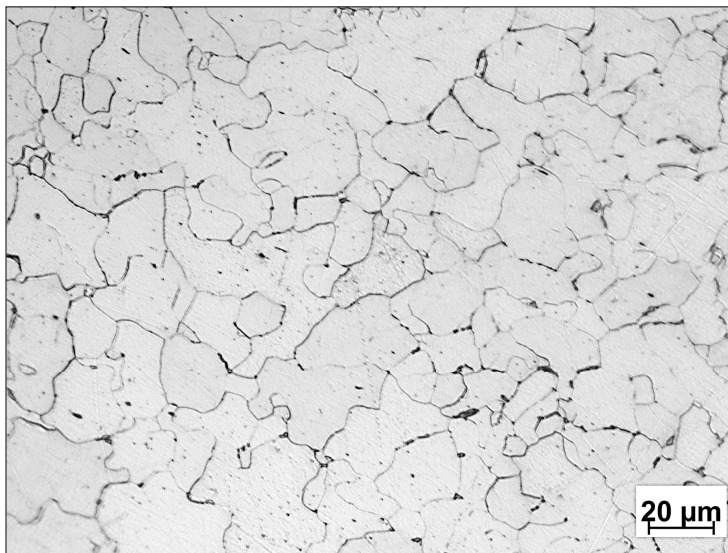


Figure 4.2: Image of the microstructure of a DD13 steel sample taken with an optical microscope (Olympus BX70)

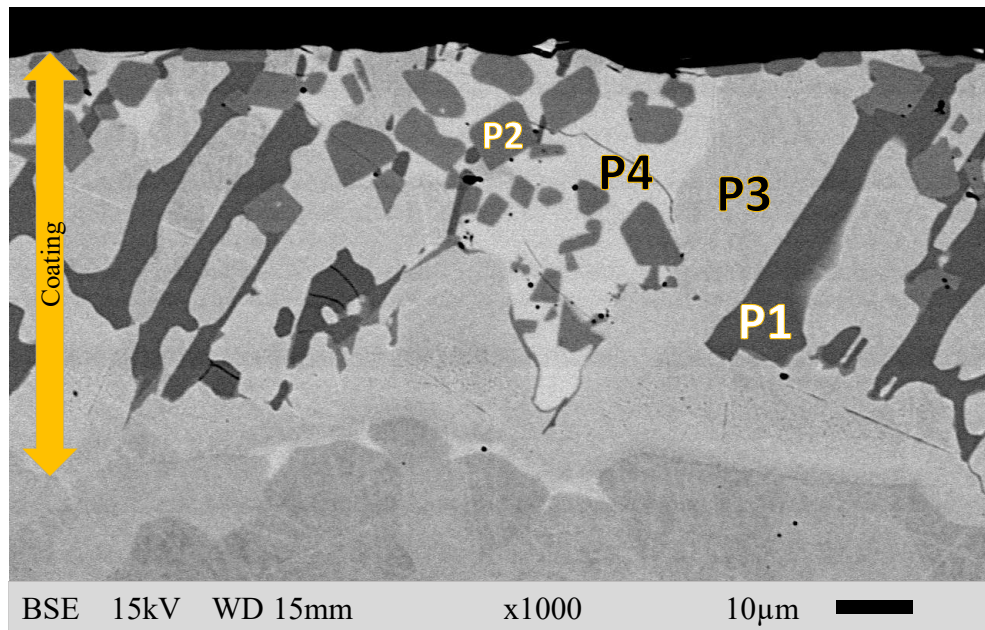


Figure 4.3: SEM-BSE image of a cross-section of the coated sample

as represented on figure 4.3. SEM-EDX analysis shows the presence of four main phases. Results are a mean value of five point analyses per phase. The very dark lamellar phase, P1, has a very high content of phosphorous (17.3 wt.%), Cr (36.5 wt.%), and Ni (25.5 wt.%), in addition to 18.1 wt.% Fe and 2.4 wt.% Si. The P1 phase presents a coarse, eutectic-like microstructure. The phase P2, mainly in rectangular shape and in dark gray, presents a very high content of Cr (49.9 wt.%), Ni (37.1 wt.%), and Si (7.4 wt.%), with a small presence of Fe (4.1 wt.%) and P (1.3 wt.%). P3 phase, in contact with the steel matrix, shows the highest content in Fe (35.7 wt.%) with a lot of Ni (44.9 wt.%) and a high content in Cr (13.5 wt.%) and Si (5.8 wt.%). The highest Fe content in the P3 phase, the most prevalent phase in the coating, indicates the high steel dissolution in the Cr-Ni-Si-P liquid alloy. The P4 phase, in light gray, shows the highest content in Si (9.9 wt.%) with P (3.7 wt.%), Cr (13.4 wt.%), Fe (12.5 wt.%), and a matrix of Ni (60.3 wt.%). The EPMA analysis of phases is given in table 4.2. The composition of the phases is close in terms of the order of abundance of each element per phase, but not identical regarding the numerical value of the EDX results. Further SEM-EDX analysis of the surface of the sample revealed additional, rare phase P5, very rich in chromium with on average 75.6 wt.% Cr, but also 10.0 wt.% P, 11.6 wt.% Fe, and a small amount of Ni and Si (2.4 and 0.5 wt.%, respectively). Coating's surface is represented in figure 4.4.

Furthermore, all of the peaks of the coating's diffractogram (Figure 4.5) were

%wt \ Phase	P1	P2	P3	P4
Si	2.6	8.4	6.3	10.9
P	19.1	1.2	0.2	4.2
Cr	34.9	48.4	12.7	12.2
Mn	0.1	0.1	0.1	0.3
Fe	17.4	3.6	34.4	11.4
Ni	25.9	38.4	46.4	60.9

Table 4.2: Elemental composition of different phases of slurry coating (as presented on figure 4.3) in wt.%, obtained with EPMA analysis. These results are the average values of two punctual analyses.

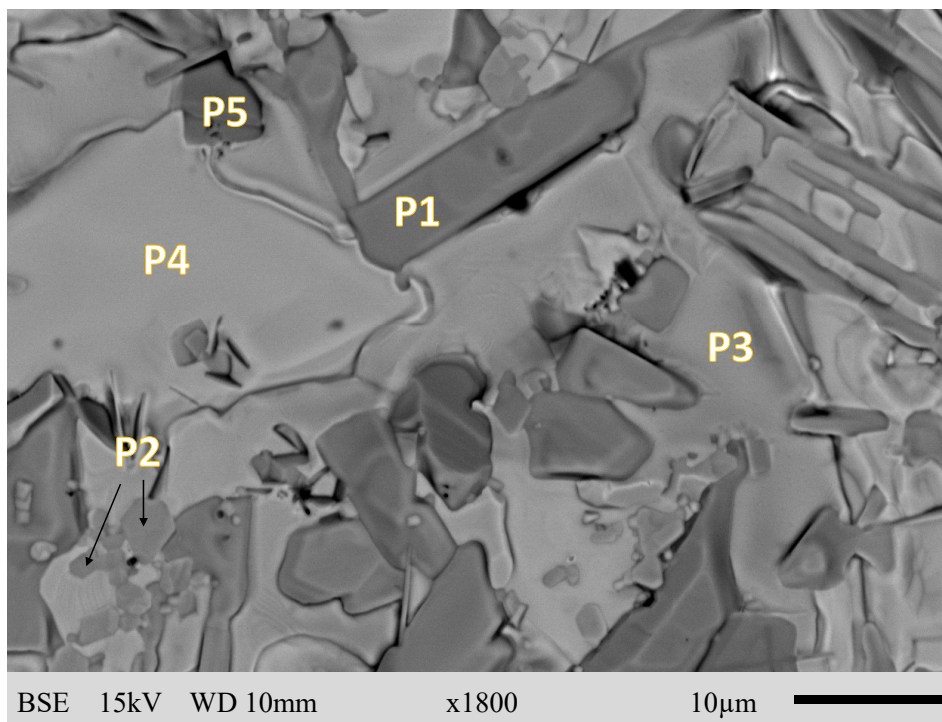


Figure 4.4: SEM-BSE image of the surface of the coated sample

attributed to one of four crystal phases. $\text{Cr}_{1.2}\text{Ni}_{0.8}\text{P}$ phase of Pnma space group ($a=5.89 \text{ \AA}$, $b=3.52 \text{ \AA}$ and $c=6.76 \text{ \AA}$) corresponds well with P-rich P1 phase, whereas P2 phase, which has a high Cr content, matches well with $\text{Cr}_3\text{Ni}_2\text{Si}$ (Fd-3ms, $a=10.62 \text{ \AA}$). The $\gamma\text{-(Fe,Ni)}$ and $\text{Ni}_{16}\text{Cr}_6\text{Si}_7$ have the same space group Fm-3m ($a=3.57 \text{ \AA}$ and $a=11.12 \text{ \AA}$ respectively). Regarding the EPMA results of P3 and P4 phases, P4 corresponds to $\text{Ni}_{16}\text{Cr}_6\text{Si}_7$ with its higher Si and Ni content. The proportion does not match perfectly; therefore, the lattice parameter was adjusted. Consequently, $\gamma\text{-(Fe,Ni)}$ suits the P3 phase.

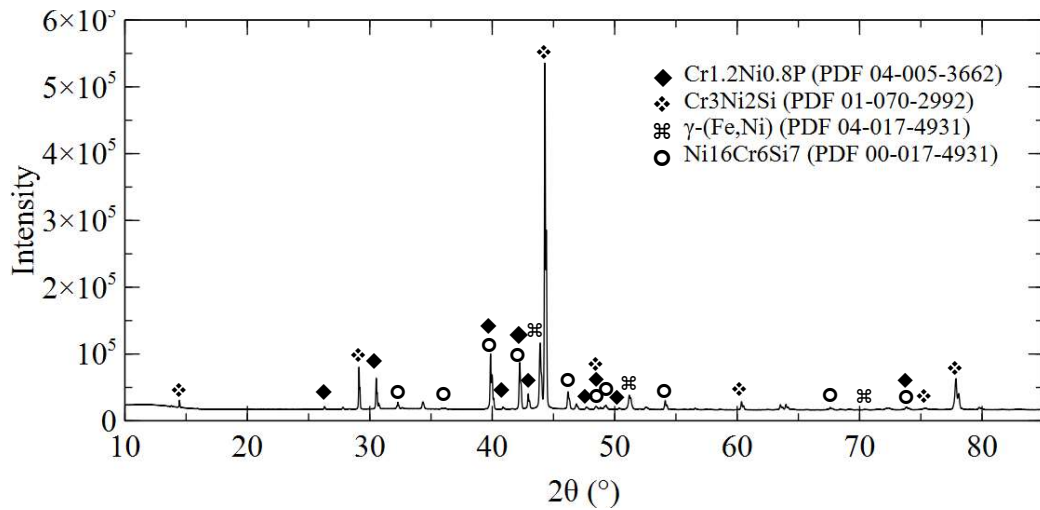


Figure 4.5: X-ray diffractogram of the slurry coating

Finally, the hardness of coated samples is slightly higher than for base steel, with $199 \pm 52 \text{ HV}$.

4.2.3 Galvanizing

In order to study liquid zinc corrosion and zinc deposition on the surface of plates, the following protocol was realized in order to best reproduce industrial parameters of the batch galvanizing process. Two types of samples were examined: those covered in the process outlined in 2.5.2 and those of uncoated DD13 steel. Uncoated samples were cleaned with ethanol before coating and after the slurry process, and afterwards they were kept free of grease; thus, no additional degreasing step was applied in this experimental procedure. At the beginning of each galvanizing cycle, samples were stripped for 20 min in 30 % hydrochloric acid at room temperature. Next, those samples were rinsed twice in distilled water for 30 s. Following that, a fluxing process in the industrial bath JTech Flux with Polytenisid 55 surfactant was applied for 4 min. Fluxing took place

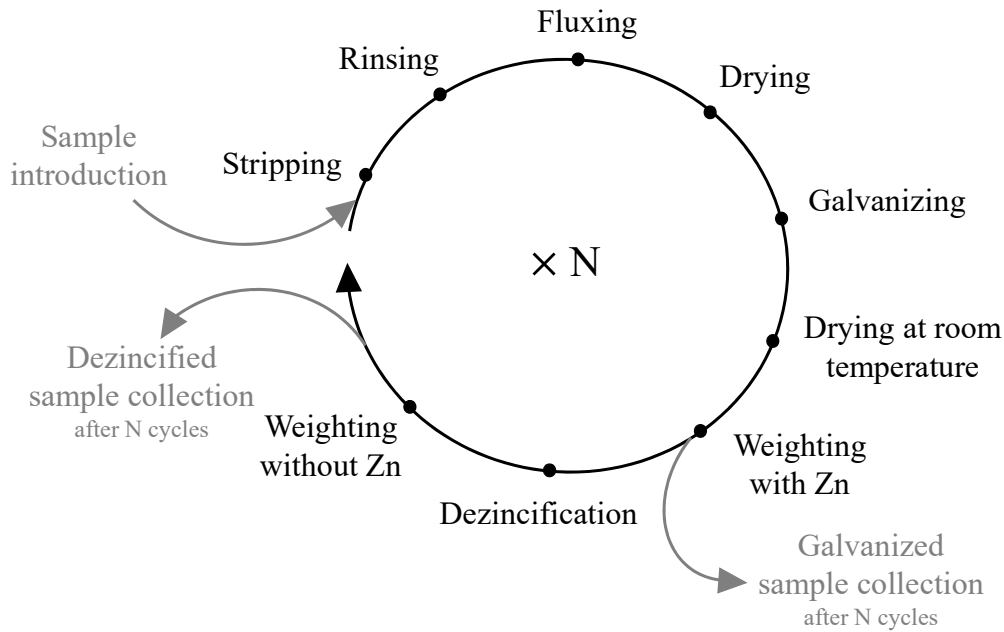


Figure 4.6: Experimental galvanizing cycle applied during this study on uncoated steel plates and plates coated with slurry coating, with $N \in \{1, 3, 5, 7, 9, 11, 15, 20\}$

Element	Zn	Al	Cd	Pb	Cu	Sn	Fe	Ni	Bi
%	98.7	0.098	0.012	0.79	0.049	0.23	0.018	0.016	0.0061

Table 4.3: Zinc bath composition measured by the ICP-AES technique

in a heated bath at 45-50 °C with a pH range of 3.5-4.5. Next, samples were transferred into a drying oven set at 110 °C for 10 min. Finally, samples were introduced into the zinc bath at $450 \pm 2^\circ\text{C}$ for 5 min. Immersion and removal of plates from the bath were done at a steady rate of 2 cm/s. The composition of the zinc bath is given in table 4.3. After a zinc treatment, samples were left to cool down in the air at room temperature. Next, those samples covered with zinc were weighted for the first time. After that, a dezincification step was applied in 10 % hydrochloric acid until the removal of all zinc, signaled by the cease of production of H_2 gas bubbles. Then, samples were rinsed in distilled water, dried, and weighted again. Thus completed cycle, samples were reintroduced into the stripping bath for the subsequent cycle.

For coated plates, many galvanizings were carried out, and after the 1st, 3rd, 5th, 7th, 9th, 11th, 15th, and 20th cycles, a pair of samples (one with a zinc

layer and the other stripped) were recovered for further examination. Thus, the standard deviation of results after each cycle was calculated with 16 samples for the first cycle, 14 until the third cycle, 12 until the fifth, and so forth. Additionally, DD13 steel plates that were left uncoated underwent five cycles of galvanization as a reference., with a standard deviation calculated for 6 samples at the first cycle, 4 until the third, and 2 until the fifth cycle. The experimental cycle is schematized in figure 4.6.

4.3 Experimental results

4.3.1 Corrosion resistance

The resistance of coatings to liquid zinc corrosion was evaluated by the weight loss of samples through galvanizing. The difference between the mass of the zinc-free plate at the N-cycle and the sample's initial weight before galvanizing was used to calculate the weight reduction. Then, this mass was normalized by the surface of the plates. Figure 4.7 illustrates these findings. Uncoated samples were tested as a reference as well, but only for five galvanizing cycles because of the lengthy dezincification process and considerable hydrochloric acid consumption during this treatment. Since the steel sample's composition is uniform, it is assumed that its rate of corrosion will remain constant over subsequent cycles. The curve was extrapolated up to 20 cycles because the trend was also strictly linear for the first 5 cycles.

By comparing the slopes of regression curves for uncoated and coated samples, it can be easily observed that weight loss is much more important for uncoated DD13 steel. In total, after 20 cycles, mass loss for coated samples was 81 % lower than for uncoated steel. As can be observed for points corresponding to coated samples, the corrosion rate doubled after about 10 first cycles. Chapter 4.5 will cover the cause of this behavior change. If the second slope is taken as the final corrosion rate for coated samples, the corrosion rate is almost nine times lower than for uncoated steel. Nonetheless, it is possible that this corrosion rate will alter after 20 cycles due to the coating's irregular phase distribution and chemical composition. Additionally, due to time constraints, galvanizing cycles were not continued until the complete dissolution of the coating and recuperation of the base steel corrosion state.

Finally, no mechanical degradation of the coating was observed, neither through detachment nor cracking due to the high temperature.

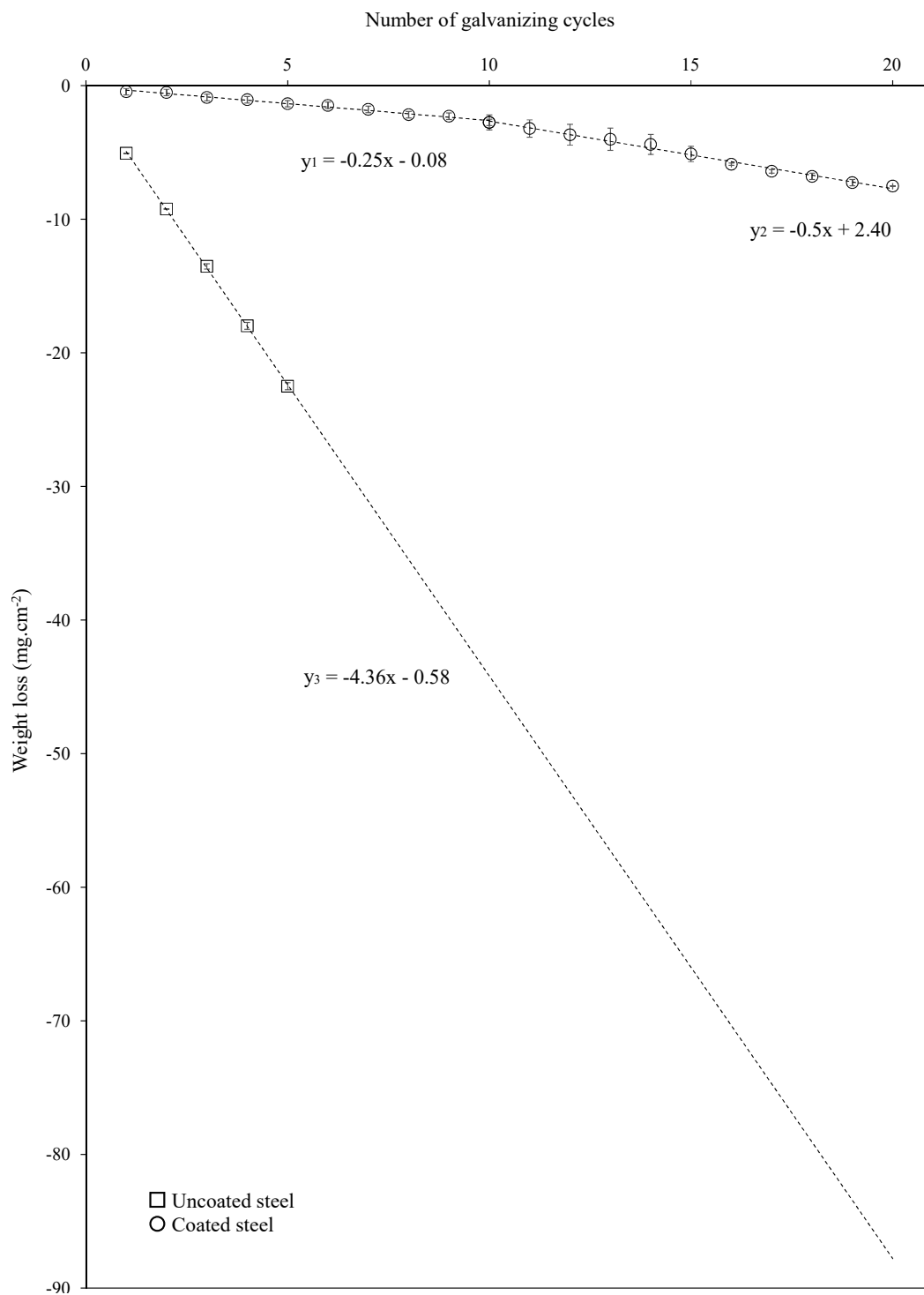


Figure 4.7: Weight loss of Si-Cr-Fe-Si-coated and uncoated steel plates in the course of galvanizing cycles.

4.3.2 Zinc deposition on slurry coatings

The weight of zinc that settled on surface samples during each galvanizing cycle was the second parameter determined during the galvanizing tests. This was done by tracing the weight difference between the sample with zinc after the galvanizing phase and the sample without zinc after dezincification. It provides an indication of the amount of zinc that reacted during galvanizing and/or was removed from the sample's surface upon removal from the zinc bath. It is not a precise measurement of wetting parameters, like wetting angle, but rather an indirect wetting evaluation. The measures' results are shown in figure 4.8.

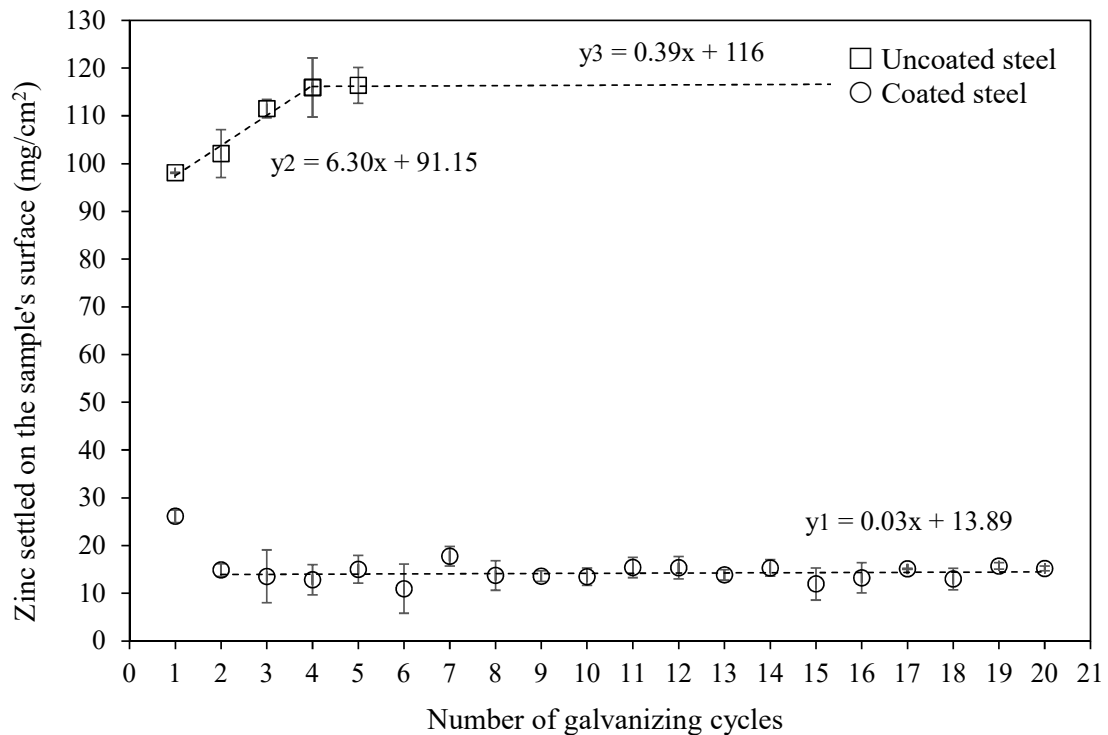


Figure 4.8: Mass of zinc deposited on the surface of coated and uncoated steel plates in course of galvanizing cycles

The amount of zinc that was deposited on the surface of pure steel plates was, on average, 98 mg/cm² during the first cycle, and it increased throughout the next four cycles. After that, it appeared that the zinc content had stabilized at 116 mg/cm² per cycle, and this value was extrapolated for further cycles. However, not enough cycles were realized to be sure if this zinc quantity would not grow for further cycles.

For coated samples, it can be easily observed that the quantity of zinc deposit

on the surface of plates is far lower than for uncoated plates. For the first cycle, 26 mg/cm^2 are measured, which is almost four times less than for uncoated steel. After the first cycle of conditioning, the behavior is further improved, and only around 14 mg/cm^2 of zinc have settled on the surface of the plate per galvanizing cycle. In total, after 20 galvanizing cycles, with extrapolation for uncoated samples taken into account, about 85% of zinc can be saved if slurry coatings are applied.

This difference can be easily observed visually, as represented in the figure 4.9. Figure 4.9c shows a surface of pure DD13 steel after galvanizing, with the characteristic galvanizing spangle motif. Additionally, the zinc coating is uniformly thick and smooth across the sample's surface. After the initial galvanizing cycle, the surface of samples coated with slurry material is fully coated with zinc, but it seems more dull and lacks any sparkle (fig. 4.9a). Samples' appearance changes after the second cycle, when zinc is deposited unevenly across the sample's surface, covering some regions completely and others to varying degrees of thickness (fig. 4.9b). This appearance remains this way for every subsequent cycle. It indicates that there is much less interaction between the liquid zinc and the slurry coating than there is between the molten zinc and bare steel.

4.3.2.1 Adhesion of zinc

As shown in figure 4.10, further steps were added to the experimental procedure carried out on two samples that underwent 20 galvanizing cycles in order to better investigate the interactions between coated materials and zinc. Once the zinc coating was depositioned and the samples were weighted, an additional step of mechanical removal of the zinc coating was performed by brushing with a soft brush for 2 minutes. It is interesting to test the adhesion of zinc, because if it were easy to remove mechanically, it could be recycled directly by fusion in a molten zinc bath. In order to quantify how much zinc is weakly adhering to the zinc, the mass of the plate was weighted after this mechanical treatment, before the next step of dezincification. Figure 4.11 shows the percentage of mass of zinc that was mechanically removed in relation to the total mass of zinc deposited on the plate following galvanizing. Since the sample's mass remained essentially constant in comparison to the mass before brushing, the mechanical removal of zinc from it was ineffective after the first galvanizing. Thus, for the initial galvanizing cycle, the zinc coating is strongly adherent to the sample's surface. The results change over the subsequent cycles, although not much. Beginning with the second cycle, samples collect less zinc, but when it settles, it sticks to the surface rather firmly. On average, only 10-11% of zinc can be removed mechanically, although the results are quite dispersed, as shown in figure 4.11.

Compared to low-alloyed steel, this slurry coating composition greatly reduces interactions with liquid zinc, though it does not completely eliminate them, as demonstrated by the difficulty of zinc's mechanical removal. Therefore, zinc still needs to be eliminated chemically before a part is reused.

4.4 Discussion and perspectives

Fe-Cr-Ni-Si-P coatings produced with the slurry method have proven to be an interesting improvement over the materials typically utilized for batch hot-dip galvanizing hooks and jigs. Cyclic galvanizing tests revealed that steel coated with those compounds exhibits noticeably less weight loss as compared to uncoated samples. After 20 cycles, the weight loss was up to 81% lower when coated samples were used. This results in a longer life cycle for batch galvanizing equipment. This benefit is, however, secondary, as the low cost of replacing corroded hooks does not outweigh the higher expenses associated with coating application.

The most important improvement is the significant decrease in wetting caused by liquid zinc if coated hangers are used. First off, there is a noticeable decrease in the intake of liquid zinc. The resulting economy of zinc was estimated at 85% after 20 galvanizing cycles. In this study, it was also shown that the little zinc that still settles on the surface is not easily removable with mechanical action, thus the adhesion of zinc is still strong locally. The corrosion rate is also non-null, contrary to what could have been seen with Fe-20 wt.%Si alloy (fig. 1.20). Those results show a great potential for slurry coatings for their use on batch hot-dip galvanizing hangers, although the composition might be improved with a higher Si content that could provide protection similar to that measured for FeSi alloys.

A study by Henckens et al. (2014) [205] estimated zinc as a scarce resource that will be depleted in less than a century. According to a more recent analysis published in 2023 by Rostek et al. [3], pure zinc primary resource amounts shouldn't pose any long-term problems. Nevertheless, short-term availability may be impacted by geopolitical or technological challenges in some parts of the world. Therefore, reducing the excessive consumption of zinc is crucial from both an economic and ecological perspective. This might be done in part by using slurry coatings on batch galvanizing equipment.

Moreover, less zinc taken out of the zinc bath on the surface of hooks leads to lower consumption of hydrochloric acid and a lower need for retreatment of those zinc-enriched acid baths. Furthermore, with less zinc needed to be removed, the time required for dezincification is much reduced, which enhances a galvanizing site's daily performance.

However, it is necessary to realize longer tests, ideally on an industrial scale, to determine the lifespan of coated equipment and, consequently, evaluate if the cost of saved zinc and acid exceeds the cost of applying coatings. First industrial trials done in cooperation with Aximum Produits de Sécurité show that the quantity of zinc settled on the surface of coated hooks is still visibly lower after 30 galvanizing cycles in comparison to uncoated hooks, as represented in figure 4.12. However, no numerical results were yet obtained for tests at the industrial scale.

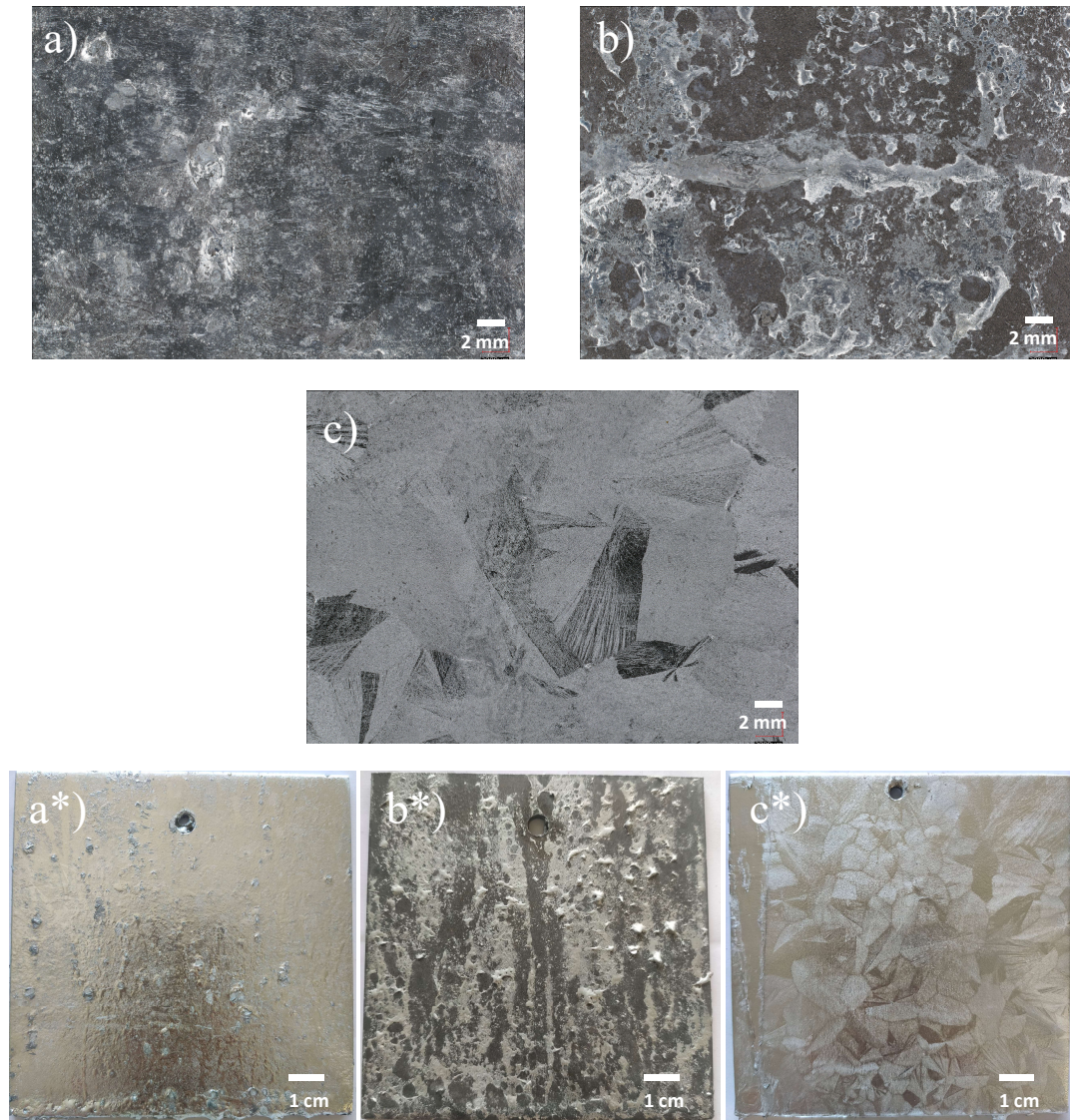


Figure 4.9: Image of surface of a) steel with slurry coating after 1 galvanizing cycle; b) steel with slurry coating after 3 galvanizing cycles; c) DD13 uncoated steel after 1 galvanizing cycle. Images were taken with a Keyence 3D optical microscope. Macroscopic photographs of the full samples are shown in a*), b*), and c*).

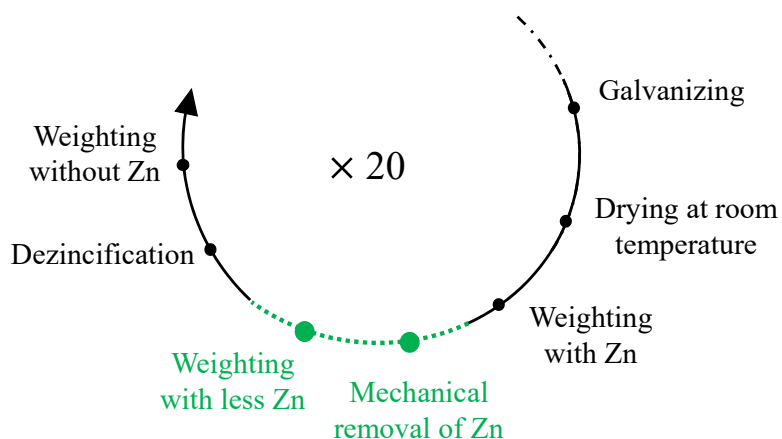


Figure 4.10: Simplified plan of the experimental process with additional steps of mechanical removal of the zinc layer

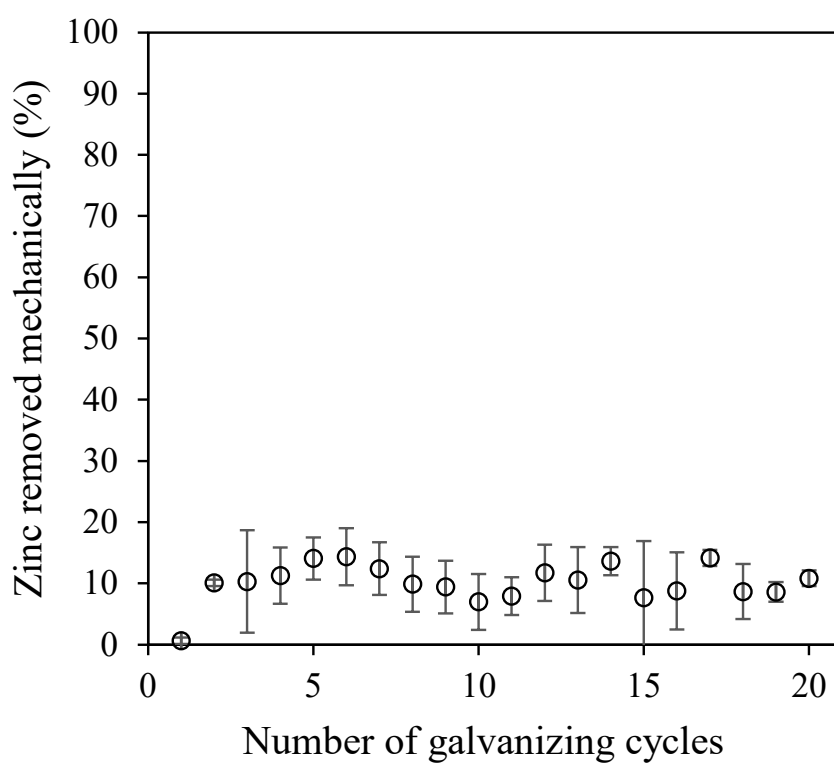


Figure 4.11: Percentage of the zinc mass removed mechanically from coated samples during galvanizing cycles

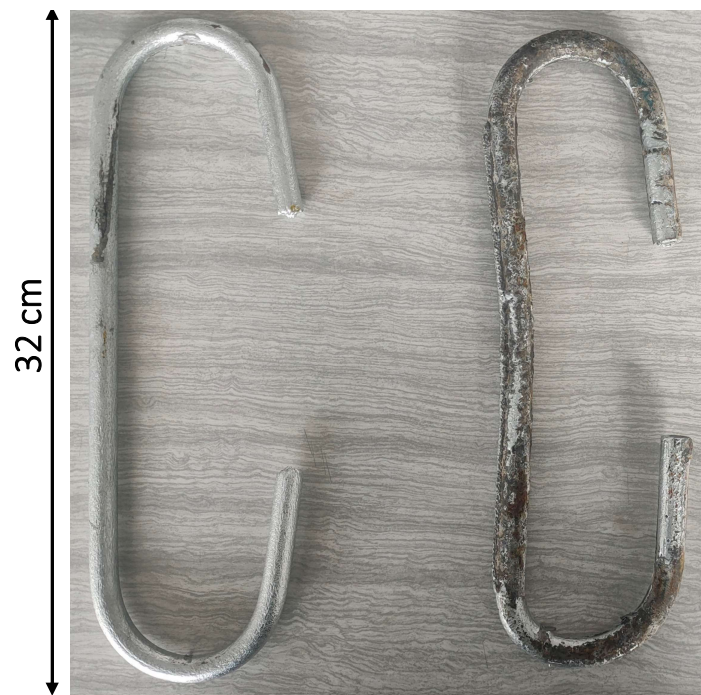


Figure 4.12: Photography of the hooks used in the batch galvanizing plant. On the left, an uncoated hook after 1 cycle; on the right, a hook coated with a slurry coating after 30 galvanizing cycles

4.5 Mechanisms at the slurry coating/liquid zinc interface

A complete SEM-EDX examination of samples was undertaken to investigate the change in behavior of the slurry coating vis-à-vis liquid zinc between the first and subsequent cycles, as well as the variation in liquid zinc corrosion rate. Those samples were galvanized multiple times; some were examined immediately after zinc deposition, while others were analyzed after a dezincification procedure. The mechanism at the coating-zinc interface was investigated by following the role of various elements present in different phases of the coating.

In order to improve the readability and distinction between different samples, they will be named according to the following rules: The first letter will describe if the sample was coated with the slurry coating (G) and then, eventually, preoxidized (Pr). The subsequent number represents the number of galvanizing cycles that a specific sample underwent. The following part will determine whether the sample was left with zinc on its surface (Z) or dezincified (NZ). For example, the sample *Pr15-NZ* represents a steel plate with a slurry coating that underwent preoxidizing treatment and 15 cycles of galvanizing. Prior to analysis, it was also dezincified in HCl. Other potential name changes will be addressed when applicable.

4.5.1 Profilometry

The roughness investigation was carried out to understand the reasons for how the coating's wetting behavior varied during galvanizing cycles. Measurements were taken on previously prepared degalvanized samples that had undergone 1, 3, 15, and 20 galvanizing cycles. Each sample was subjected to five analyses.

As shown in figure 4.13, roughness parameters vary linearly, and no significant difference is observed between the 1-cycle and 3-cycle samples. As a result, roughness modification cannot account for the change in wettability after the first galvanizing cycle. However, error bars become more prominent over time, most notably in the *Rz* parameter, which refers to the deviation between the maximum height and depth of the roughness profile. This data suggests that some phases of the coating must be targeted more aggressively by liquid zinc than others. Further surface investigations were thus performed to better understand the causes of corrosion.

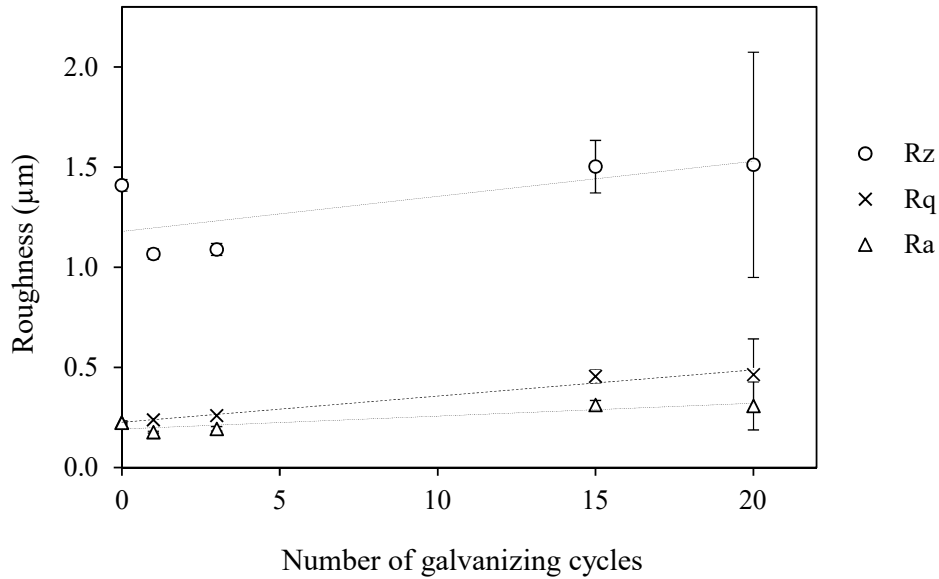


Figure 4.13: Evolution of roughness parameters Ra, Rz, and Rq over the course of galvanizing cycles

4.5.2 Zinc coating on bare steel plates

Figure 4.14 represents a cross section of a DD13 steel plate without the slurry coating after one immersion in molten zinc, as a reference to further results on Fe-Cr-Ni-Si-P coated samples. The thickness of the zinc layer that has settled on the plate is fairly uniform, at $143 \pm 3 \mu\text{m}$.

At the steel-zinc interface, a uniform layer is present. It is composed of $92.0 \pm 0.2 \text{ wt.}\%$ zinc, $7.2 \pm 0.1 \text{ wt.}\%$ iron, and trace amounts of oxygen ($0.7 \pm 0.4 \text{ wt.}\%$). This chemical composition corresponds well with the δ phase present in typical galvanizing coatings. Above, big, well-defined, angular crystals appear and are also dispersed up to the surface of the coating. Their iron content is a little bit lower than for the last layer, at $6.4 \pm 0.2 \text{ wt.}\%$ Fe and $92.4 \pm 0.5 \text{ Zn}$. Also, some Al ($0.4 \pm 0.2 \text{ wt.}\%$) and O ($0.9 \pm 0.4 \text{ wt.}\%$) are detected. This composition may be attributed to the ζ phase. Finally, the upper layer of the coating, in which some ζ crystals are embedded, is solidified zinc. White dots are Pb-rich impurities.

4.5.3 Formation of Fe-Zn intermetallics on slurry coating

Naked-eye observation of a sample covered with zinc after the first galvanizing cycle (figure 4.9a) suggests good wetting by liquid zinc and the possible formation of Fe-Zn intermetallics. However, an SEM analysis of a cross-section of such

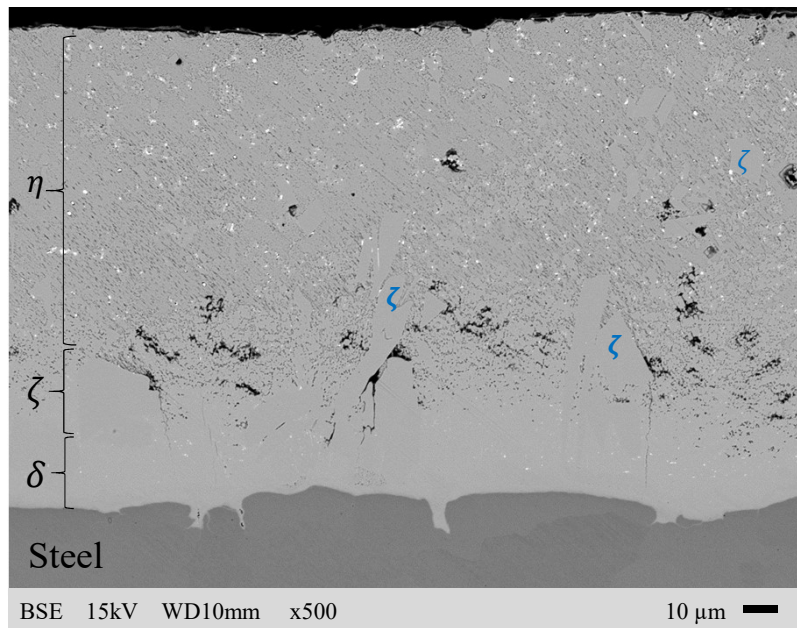


Figure 4.14: BSE-SEM image of a cross-section of an uncoated DD13 steel plate covered with zinc after one immersion in galvanizing bath

a sample (figure 4.15a) reveals that the intermetallic formation is quite limited, with only a few δ crystals observed in solidified zinc. The mean composition of such a delta phase is given in table 1.2.3. It is to be noted, that not only iron, but also nickel can be found in this phase. The Al content is considered to come from the galvanizing bath.

For the following cycles, the wetting visibly decreases (fig. 4.9b). The SEM cross-section images (figure 4.15b) are deceptive since they frequently show a zinc layer on top, which could be there due to a multiple anchorage of zinc throughout different phases. Rarely, some intermetallic phases are observed; either an intermetallic of composition given in table 4.4 or another δ phase with a composition akin to the first cycle is occasionally seen. The X phase has a little bit more Ni than Fe, and on occasion, an additional form of this compound, denoted as X_{Ni} , can be seen (fig. 4.15c). This phase contains much more nickel.

As previously stated, formed intermetallics are quite uncommon; however, when they are present, they are found above the coating's matrix, *i.e.*, phases P3 and P4 with a face-centered cubic structure, whose compositions are detailed in the previous chapter (table 4.2). The composition of intermetallics reflects the high iron and nickel levels found in those phases. In those phases, silicon and chrome concentrations are minimal, while phosphorus is missing. The liquid zinc corrosion of the coating may be driven by the intermetallics formed

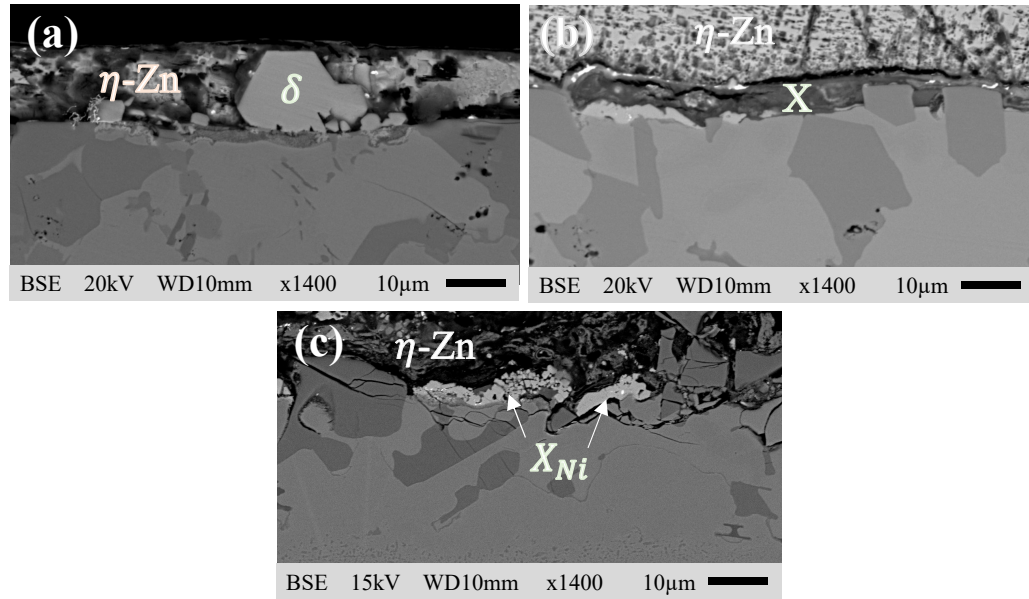


Figure 4.15: BSE-SEM images of intermetallics formed between zinc and the slurry coating in samples a) G1-Z b) G3-Z, and c) G9-Z

%wt	Phase	δ	X	X_{Ni}
O		1.4 ± 0.5	2.8 ± 2.3	0.5 ± 0.6
Si			0.2 ± 0.4	0.1 ± 0.1
Al		0.6 ± 0.5	0.3 ± 0.4	
Cr			0.9 ± 0.4	0.3 ± 0.4
Fe		6.4 ± 1.9	4.2 ± 0.8	1.7 ± 1.8
Ni		2.0 ± 1.7	6.6 ± 1.3	12.6 ± 0.9
Zn		89.6 ± 2.2	84.9 ± 4.1	84.7 ± 2.2

Table 4.4: Mean chemical composition of different intermetallics detected at the coating/zinc interface of galvanized samples

between the liquid zinc and the matrix and further dissolved in HCl prior to the subsequent galvanizing treatment.

Comparison of compositions of intermetallics noted X and X_{Ni} with Fe-Ni-Zn ternary phase diagram (fig. 1.2.3.2) lets the attribution of the phase X containing 4.2 wt.% Fe and 6.6 wt.% Ni to the true ternary phase T [84, 85], while the nickel-rich X_{Ni} phase to the Γ phase, similar to that of Ni-Zn binary [84].

Kong et al. [206] studied the dissolution of solid Ni in liquid Zn saturated with Fe in 450°C. In their study, they detected four different (Fe,Ni)-Zn intermetallics. None of them corresponded with the Ni-enriched hexagonal δ phase detected in this work. Two of them, however, correspond to the phases called X and X_{Ni} earlier in this study, with one phase (called by authors Γ_2), with 5 %at Fe, 6 % Ni, and 89 % Zn, and the other one (called by authors γ), with 11.5 % Ni and 88.5 % Zn. Those phases were attributed to compounds $Fe_5Ni_6Zn_{89}$ and $NiZn_8$, respectively. They come to the conclusion that, in the conditions of their study, the dissolution of nickel is governed by the diffusion of Ni atoms across a concentration boundary layer in the liquid. Moreover, in contrast to solid Ni in pure zinc, the " Γ_2 " phase in a Fe-saturated environment accelerates this dissolution. Yu et al. [207] also report an important dissolution of Ni and Fe in liquid zinc.

It can therefore be proposed that the liquid zinc corrosion mechanism for this coating consists in the formation of (Fe,Ni)-Zn intermetallics that are later dissolved in hydrochloric acid, as they are never observed in dezincified samples. The small number of intermetallics may raise the question, of whether this is the only mechanism that is to be taken into account. However, as seen in figure 4.7, the weight loss for coated samples is significantly lower than that of DD13 steel, which forms far more intermetallics with zinc. The small number of intermetallics in coated samples may well translate into a slow corrosion rate.

Eventually, the pickling process in concentrated HCl may be linked to further weight loss. The analysis of the concentration of elements of the coating dissolved in hydrochloric acid could not have been conducted. However, the nickel and its alloys are considered resistant to this acid [208], therefore the influence of this step might be minimal.

4.5.4 Role of the phosphorus-rich phase

The microscopic examination of the evolution of the coating, with a focus on alterations around the phosphorous-rich P1 phase, reveals an intriguing role for this phase in the liquid zinc corrosion mechanism. Figure 4.16 shows that the P1 phase is primarily located in the coating's upper part, near the surface. In Fig. 4.16b, zinc forms an intermediary phase (dark gray) with the coating

after three galvanizing cycles. It is clear that this intermetallic forms around the two grains of the P1 phase on the right and does not consume them, unlike the matrix. After nine cycles (fig. 4.16c), matrix degradation continues, but P1 remains resistant. Figure 4.16d) illustrates that the P1 phase is not dissolved by zinc or acid but rather eliminated from the coating through matrix dissolution and decohesion of the P-rich phase.

An interesting depiction of this preferential attack by zinc can be observed in figure 4.16e, which represents an eutectic area in the coating. It is formed with a dark-gray net of P1 phase with P3 grains inside. At the zinc-coating interface, it can be observed that the upper layers of the net are untouched while the grains inside disappear. Simultaneously, below the eutectic, a thin light-gray line corresponding to zinc is detected. It indicates that the zinc penetrates the matrix with greater ease and bypasses the eutectic area, which will eventually be completely removed by decohesion. It is unclear if the eutectic region appeared during the heat treatment of slurry coating formation, as it was not observed regularly in different samples but only in the G15-Z one.

An analysis of different cross-section images, such as 4.16b, suggests that there is no preferential dissolution at the matrix/P1 interface. Unlike in the case of grain boundaries in some steels [209, 210], matrix/P1 boundary does not seem to be affected by zinc diffusion. However, as seen in 4.16e, zinc can diffuse easily in fractures.

In chapter 4, it was observed that the corrosion rate accelerates after around the 10th cycle. Analogically, it can be observed in the micrographs that the P1 phase becomes way more scarce at the same time. The thickness of the coating seems to be significantly smaller for samples G14 and G20 than for those requiring a lower number of galvanizing cycles. It could then be postulated that the P1 phase is not reactive with liquid zinc, therefore diminishing the reactive contact area. Then, once the P1 phase is eliminated, the contact between less resistant phases and liquid zinc is improved, which would lead to accelerated corrosion.

The evacuation of the P1 phase might also be accelerated by its brittleness. In some samples, webs of cracks were observed in the P-rich phase (in dark gray in fig. 4.17). Philips et al. [211], in their work on braze alloys, also notice the brittleness of this CrNiP phase.

To investigate the liquid zinc corrosion inhibitory ability of the P1 phase, a specific sample depleted of phosphorus was analyzed (G20-NP). That sample was prepared in the same slurry method conditions and received the same galvanizing treatment as the G20 sample. After the last dezincification, both of those samples were subjected to XRD analysis. Those results are represented in figure 4.18.

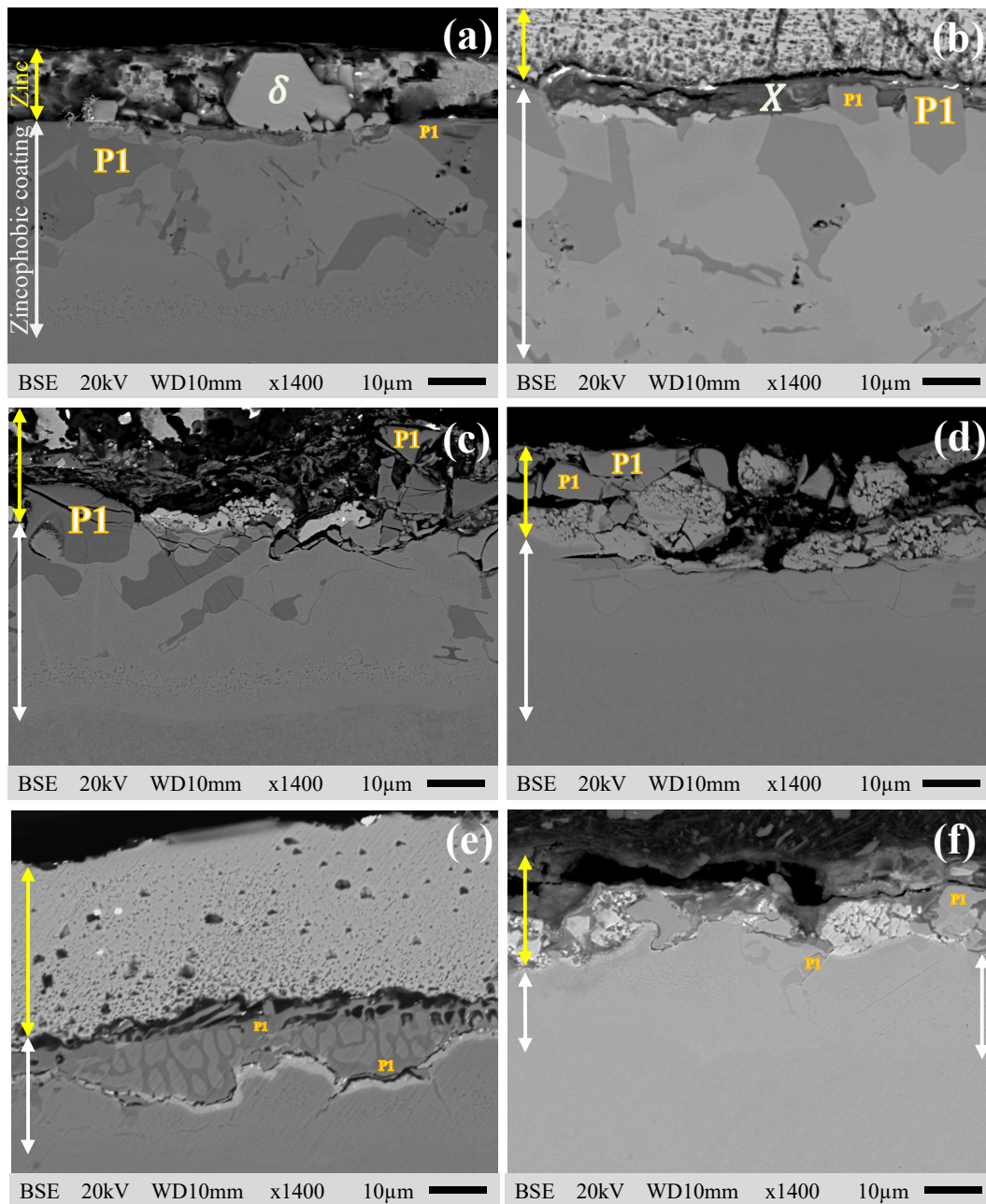


Figure 4.16: BSE-SEM images of cross-sections of samples a) G1-Z, b) G3-Z, c) G9-Z, d) G11-Z, e) G15-Z, f) G20-Z, with a special indication of the P1 phase throughout galvanizing cycles

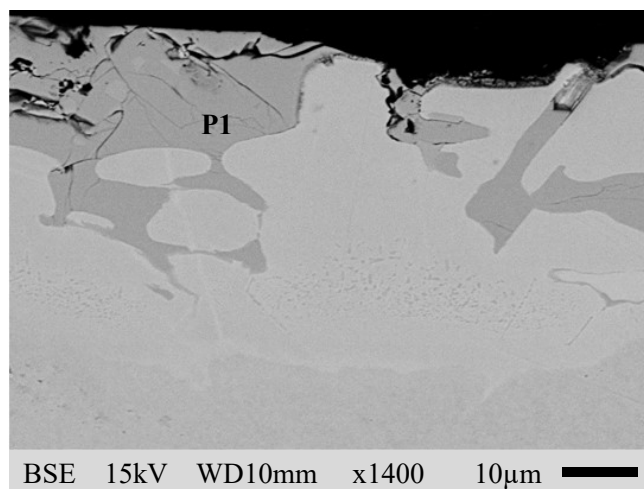


Figure 4.17: BSE-SEM image of a cross-section of a sample G7-NZ

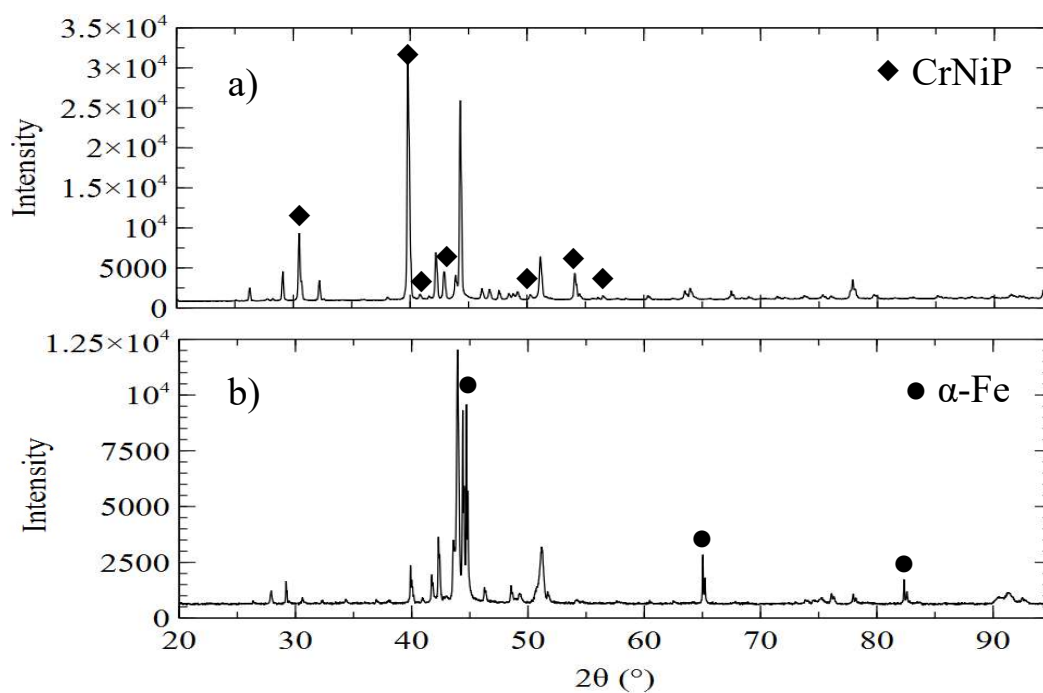


Figure 4.18: Diffractograms for samples a) G20-NZ and b) G20-NP-NZ. The differences resulting from the presence or absence of phases detailed in fig. 4.5 are not represented for legibility reasons.

The main difference between two diffractograms resides in the disappearance of the P1 phase peaks (cf. fig. 4.5). Another notable distinction is the presence of α -Fe in the G20-NZ-NP phase. It implies that if no P1 phase is present in the coating, the contact area between Ni-rich phases and liquid zinc is increased, resulting in their faster dissolution. The identification of α -Fe in the substrate steel shows that the coating became so thin that phases under the coating could be detected, unlike in the G20-NZ phase, which contained the P1 phase from the beginning.

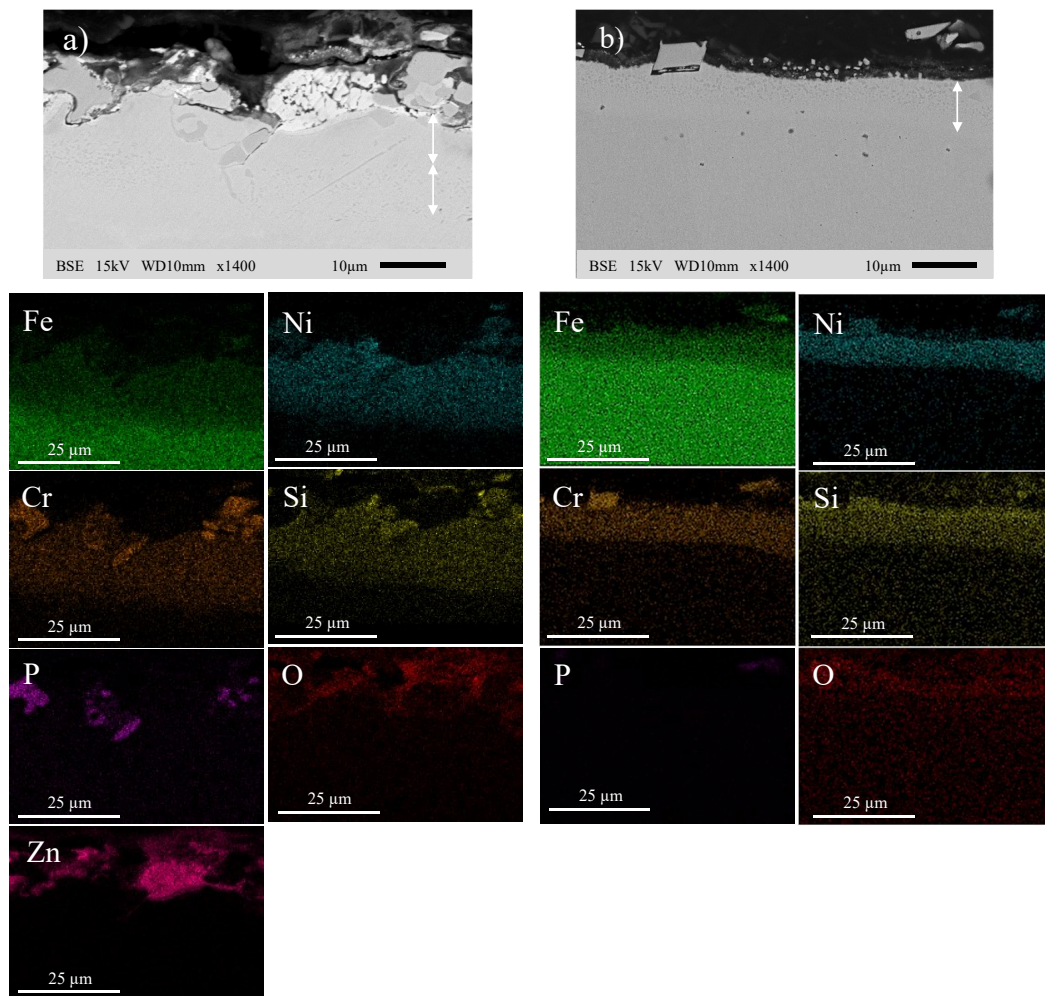


Figure 4.19: SEM-EDX cartographies for cross-sections of samples a) G20-Z and b) G20-NP-NZ

After 20 galvanizing cycles, the coating without phosphorus in the mix is almost half as thick as the coating with P1 phase, according to the EDX exam-

Cycle	0	1	3	11	15	20
Si(%at)	12.8 ± 0.7	14.0 ± 1.5	13.0 ± 1.5	12.8 ± 0.4	13.2 ± 1.0	12.2 ± 1.3
O/Si	0.2 ± 0.1	0.8 ± 0.3	1.3 ± 0.5	1.6 ± 0.2	2.3 ± 0.3	2.0 ± 0.6
Cr/Si	1.6 ± 0.2	1.9 ± 0.3	2.0 ± 0.4	1.8 ± 0.2	1.5 ± 0.2	1.5 ± 0.3
Ni/Si	2.8 ± 0.3	1.0 ± 0.2	1.3 ± 0.2	1.2 ± 0.1	1.1 ± 0.3	1.2 ± 0.4
Fe/Si	1.4 ± 0.3	1.2 ± 0.2	1.1 ± 0.2	1.3 ± 0.1	0.9 ± 0.1	0.7 ± 0.2
P/Si	0.9 ± 0.1	1.0 ± 0.3	0.9 ± 0.3	0.9 ± 0.1	0.7 ± 0.1	0.7 ± 0.2

Table 4.5: Mean proportions of elements at the coating's surface. EDX analysis was realized on samples G0, G1-NZ, G3-NZ, G11-NZ, G15-NZ, G20-NZ

ination of those two samples (white arrows in fig. 4.19). Therefore, it can be said that the metallic phosphide phase $Pnma$ orthorhombic crystal structure increases the coating's resistance to liquid zinc corrosion and, consequently, the product's lifetime.

4.5.5 Wetting behavior evolution

Although the impact of various phases on liquid zinc corrosion has already been covered, further investigation is required to comprehend how coatings' wetting behavior changes after the initial galvanizing cycle. In order to achieve this, an analysis of the samples' chemical composition as seen from the surface was undertaken. The findings are shown in table 4.5 as well as in figures 4.21 and 4.22.

Lower wetting may result from the formation of SiO_2 oxide, as suggested in chapter 3. Therefore, one should look for the appearance of oxygen in the same regions of the EDX map as silicon. It can be observed from figures 4.21 and 4.22 that the oxygen mostly occurs on top of the matrix, avoiding the P1 phase grains. The oxygen cartography is quite similar to that of silicon (fig. 4.20); nonetheless, it is not impossible to rule out the possibility that oxygen is associated with other matrix elements, such as iron, chromium, or nickel. Also, as can be seen in table 4.5, the oxygen content rises throughout galvanizing cycles. One hypothesis for the change in wetting behavior might be that between the first and second galvanizing cycles, the quantity of oxides is high enough to decrease the interaction with liquid zinc. Also, an important loss in intensity on Ni maps after the first galvanizing cycle correlates well with the data displayed in table 4.5. This loss in nickel may reveal the silicon on the surface, allowing the formation of protective oxide that limits wetting for further cycles.

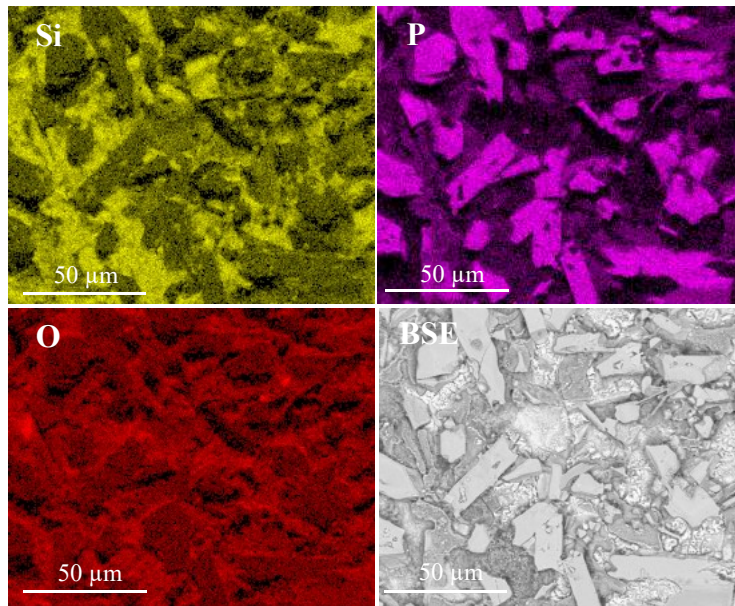


Figure 4.20: EDX cartographies of Si, O and P for sample G3-NZ, observed at the surface. The contrast on the oxygen cartography was increased in the image post-treatment.

The observation of phosphorus maps in figures 4.16 and 4.22 reveals that the size and form of the P1 phase grains vary with no clear correlation to galvanizing cycles. As each map represents a different sample, this difference may come from manufacturing. In fact, if a given sample were placed closer to the furnace walls or in the middle of the lot, they may have different cooling rates, leading to microstructures that are more or less coarse.

A point analysis of the evolution of different phases leads to a better understanding of their affiliation with oxygen. First of all, the P1 phase is never oxygenated through galvanizing cycles. The chrome-rich P2 phase does not gain oxygen content as well. For this reason, a more detailed presentation of their composition is omitted. Moreover, as mentioned in section 4.2.2 an observation from the top reveals the apparition of another Cr-rich phase, P5, not detectable in cross-section analysis (75 wt.%Cr, 11.5 %Fe, 10.0 %P, 2.5 %Ni, 0.5 %Si) (fig. 4.23). This phase does not gain oxygen for the first three cycles and was not found in samples that underwent more cycles.

Initially, the matrix is composed out of two phases: P3 and P4. However, once the coating is galvanized and dezincified, the distinction between those phases becomes more subtle. Especially, that, as can be seen in table 4.5, the mean Ni content at the surface declines radically after the first galvanizing cycle.

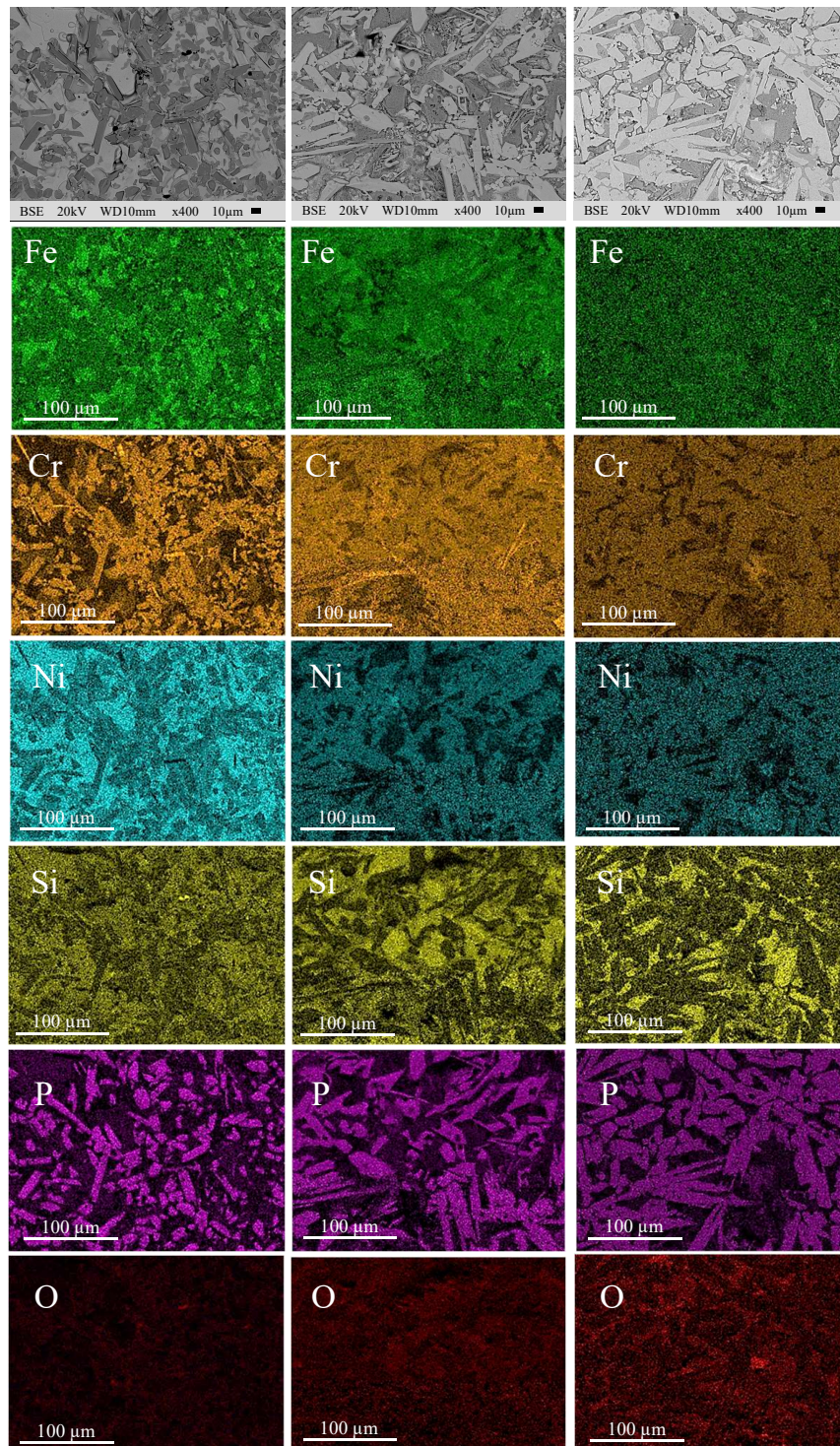


Figure 4.21: Elemental EDX maps of samples G0, G1-NZ, G3-NZ, observed at the surface

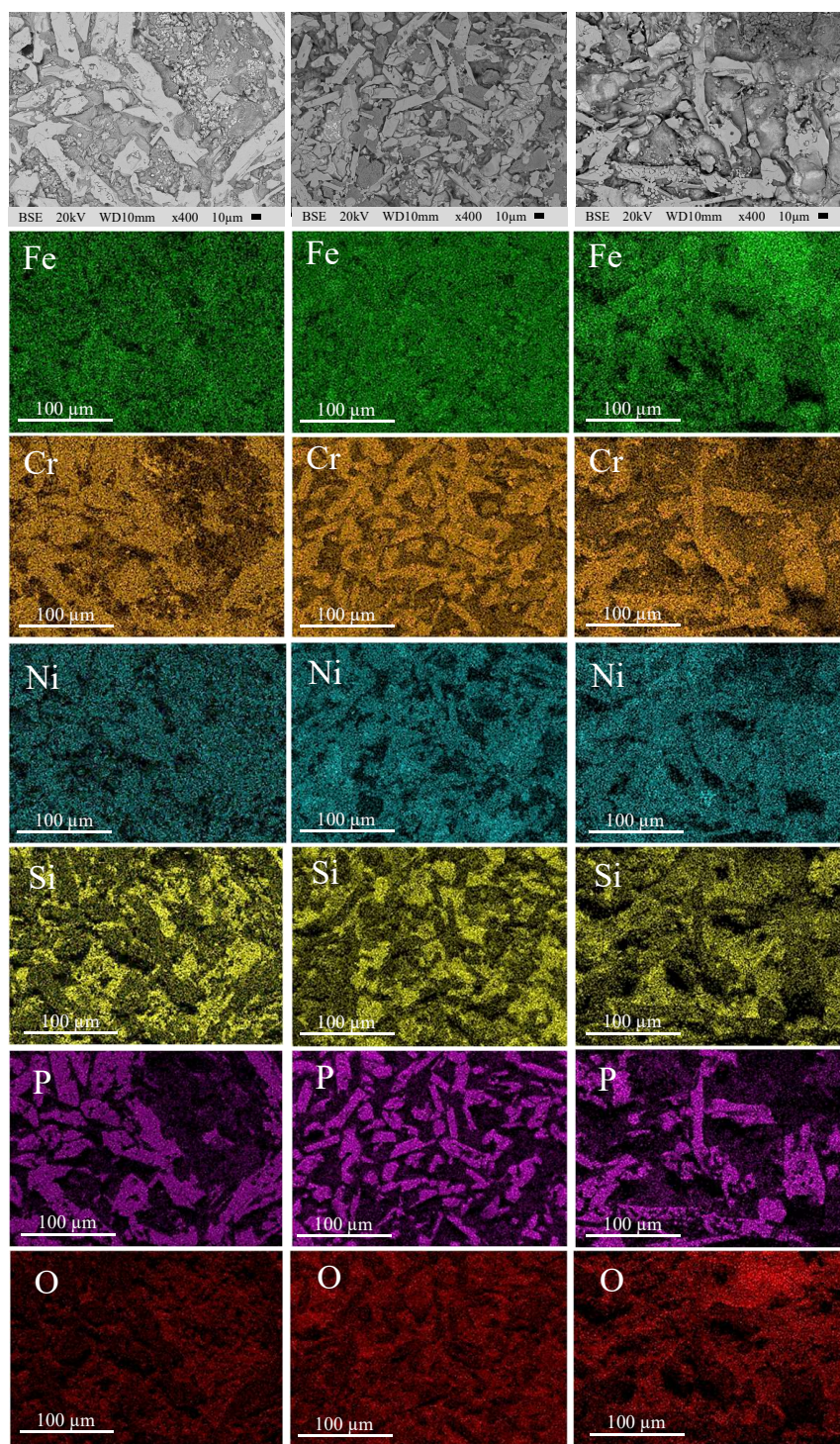


Figure 4.22: Elemental EDX maps of samples G11-NZ, G15-NZ, G20-NZ, observed at the surface

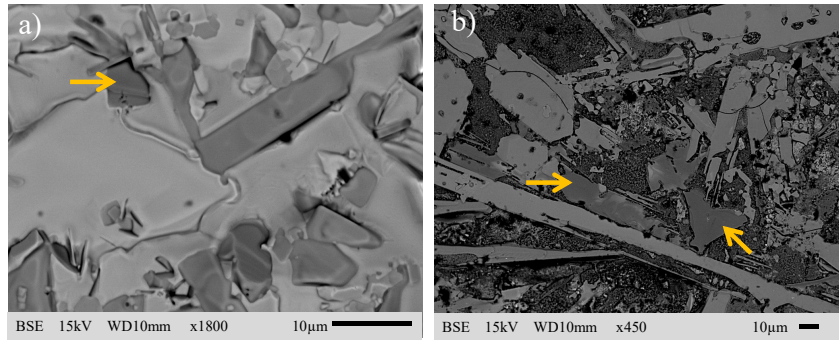


Figure 4.23: BSE-SEM images of samples a) G0-NZ and b) G1-NZ, with the P5 phase indicated with an arrow

	G0		G1		G3		G20	
	wt.%	σ	wt.%	σ	wt.%	σ	wt.%	σ
O			3.3	1.0	7.8	3.7	6.0	1.3
Si	5.8	0.9	10.5	1.8	7.9	4.9	10.1	3.0
P	0.1	0.2			0.3	0.2	0.5	0.3
Cr	11.7	0.4	15.4	1.2	13.5	1.3	12.7	0.6
Fe	38.5	0.7	35.6	1.4	34.4	4.1	34.2	1.5
Ni	44.0	0.5	35.2	2.5	36.2	10.5	36.5	4.7

Table 4.6: P3 phase evolution throughout galvanizing cycles

Thus, the P4 phase, originally rich in nickel, can be only distinguished by its phosphorus content. Tables 4.6 and 4.7 list compositions of different phases that may represent the evolution of the matrix throughout galvanizing cycles. The evolution of phases is not uniform, which is represented by, at times, very high standard deviations. In general, the content of oxygen seems to increase throughout cycles. Additionally, it may be said that after the first cycle, P4, with its high initial Ni concentration, loses nickel more drastically than P3. Furthermore, the P4 phase appears to generate two composition populations: one more lean in nickel (Table 4.7a,c,e) and a second with a higher nickel content (Table 4.7b,d,f). Since the proportional content of other elements changes with oxygen and nickel, it appears to be difficult to track their evolution.

Samples observed from the top are those that underwent dezincification to remove their zinc coating. The wetting of samples is good for the first cycle and decreases for the following ones. Therefore, a change must take place during the first dezincification. Observation of those surface samples reveals a sharp decline in the nickel content at the surface at that particular time. The initial wetting

G0			G1		G3		G20	
			a		c		e	
	wt.%	σ	wt.%	σ	wt.%	σ	wt.%	σ
O			5.5	2.1	7.8	5.4	10.9	2.8
Si	11.5	0.5	20.2	3.9	23.3	3.2	19.4	0.3
P	4.3	0.2	3.0	2.1	1.9	0.4	2.3	0.2
Cr	12.4	0.1	35.6	4.3	42.9	12.0	26.5	2.2
Fe	12.1	0.2	31.1	1.2	22.2	2.4	31.4	0.1
Ni	59.7	0.4	4.6	2.2	2.0	0.5	9.4	0.3
			b		d		f	
			wt.%	σ	wt.%	σ	wt.%	σ
O			8.4	3.9	9.5	3.5	15.0	3.2
Si			16.9	4.1	21.4	2.3	15.9	1.5
P			1.6	0.6	4.4	1.4	2.8	1.3
Cr			29.4	3.2	20.9	4.2	17.0	1.7
Fe			26.0	1.4	31.0	3.8	24.4	5.3
Ni			17.8	3.0	12.8	5.1	25.0	5.4

Table 4.7: P4 phase evolution throughout galvanizing cycles. Compositions a, d, and e show the evolution of population lean in Ni, while b, d, and f represent a population richer in Ni.

might be thus initiated by an interaction between the nickel and zinc, either by dissolution or by the formation of intermetallics. As previously mentioned, cross-section images did not show any significant intermetallic formations; however, it is possible that they are too thin to be detected with SEM-EDX.

As no point analysis indicated any pure oxide layer but only oxygenated phases, it is probably too thin to detect. As shown in section 3.3.2, the native SiO_2 thickness is a couple of nanometers. Therefore, to detect it, more sensible analysis methods need to be used. However, taking into account the heterogeneity of the coating as well as the surface plane and depth makes any rigorous study of this material with ToF-SIMS or XPS too complex.

However, the superposition of oxygen maps with those of silicon suggests that protective oxides are mostly formed by silicon. It is interesting to note that although there is less wetting after the second cycle, weight loss still occurs. As a result, liquid zinc can pass through a potential oxide layer to some extent. The significant silicon concentration in the material inhibits any weight loss caused by liquid zinc corrosion, as fig. 1.20 demonstrates. In the case of slurry coating, weight loss is only slowed down. Therefore, it is possible to hypothesize that the oxide may not completely cover the matrix's surface or may be mixed in composition, leaving it vulnerable to the action of zinc.

4.6 Improvement of slurry coating's performance

In the previous section, slurry coatings were proven to decrease the wetting of steel parts from zinc. The hypothesis formed for this behavior was the formation of a native, thin layer of SiO_2 on the surface of the coating that is not wettable by liquid zinc, as discussed in chapter 3. Moreover, it was observed that the protection increased after the first cycle, thus suggesting that this oxide may develop during the initial galvanizing treatment. In order to improve the performance of the zinc coating already for the first cycle, the idea of preoxidizing the samples was formulated.

The generation of silicon oxide on the surface of silicon by treating it at a high temperature in an oxygen-containing atmosphere is commonly used in the field of semi-conductors [212, 213]. In general, the growth of the oxide layer is realized at a temperature between 700 and 1100°C [214]. Furthermore, the Ellingham diagram shows that the partial pressure of oxygen in air is sufficient for silicon oxidation at those temperatures. In this part of the study, one high-temperature treatment was chosen to test the potential of preoxidation on the improvement of the coating's performance, but further optimization of those conditions should be conducted in future studies.

4.6.1 Preoxidizing process

Coated samples prepared by the same method as described in 2.5.2 underwent a heat treatment of 850°C for 1 h in air. After that time, samples were left to cool slowly in the furnace. Thus prepared samples underwent the same galvanizing treatment as described in 4.2.3. Three pairs of samples were treated for 1, 5, and 15 galvanizing cycles.

Afterwards, one sample that underwent 15 galvanizing cycles was once again heat treated at 850°C for 1 hour, to test if the initial performance of the preoxidized samples could be restored. That sample was galvanized five additional times. Further, this sample is represented in figures 4.24, 4.26, and 4.25 as "preoxidized-regenerated".

4.6.2 Preoxidizing influence on performance

4.6.2.1 Corrosion by liquid zinc

Figure 4.24 shows weight-loss results demonstrating the preoxidized coating's resistance to liquid zinc corrosion. For the first ten cycles, the corrosion rate is similar to that of non-preoxidized samples (slope of γ_1 on fig. 4.24), suggesting that the generated oxides either do not completely cover the coating's surface or are permeable to the coating's dissolution. The corrosion rate rises for cycles 10-15 (slope of γ_2 on fig. 4.24), but not as much as it does for samples that have not been preoxidized (slope of γ_2 on fig. 4.7). Thus, the resistance to liquid metal corrosion is slightly improved after the preoxidation.

The last five cycles were performed on a sample that underwent a second oxidation treatment. It seems that its weight loss is comparable to cycles 15-20 of a non-preoxidized sample. However, as only one regenerated sample was examined, the numerical value of the corrosion rate cannot be generalized. With the corrosion rate for those later cycles catching up to the corrosion rate of non-preoxidized samples, the influence of preoxidation can be considered very low or even negligible.

4.6.2.2 Wetting by liquid zinc

Figure 4.25 shows the mass of zinc deposited on preoxidized coatings in comparison to non-preoxidized ones. With 4 mg/cm² of zinc per plate in the first cycle, there is a noticeable improvement in terms of wetting protection. This effect is, however, not persistent, as the wetting slowly increases through the first ten cycles. Finally, zinc deposition stabilizes from the 10th cycle at around 9 mg/cm² per cycle, which is less than the stabilized mean value of 14 mg/cm² per cycle. Preoxidation results in an additional 46% zinc economy compared

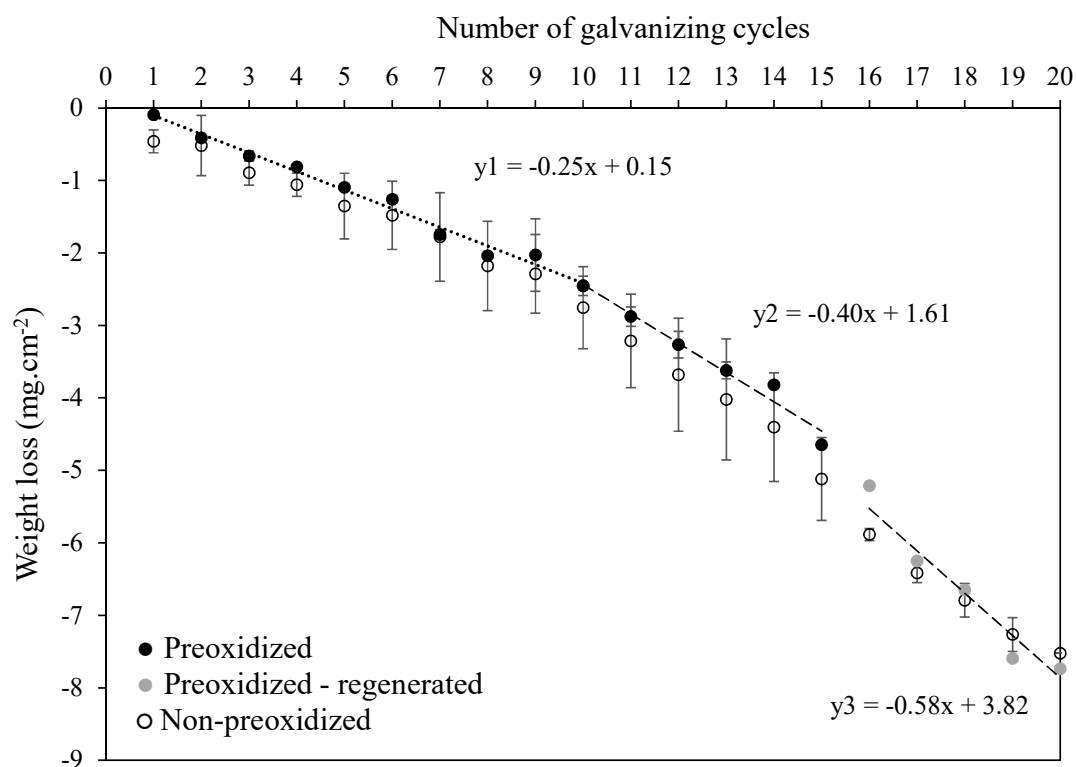


Figure 4.24: Weight loss of preoxidized coated samples in comparison to non-preoxidized coated samples in the course of galvanizing cycles. Also, the effect of regeneration of preoxidation is represented.

to non-preoxidized samples and a 93% zinc economy compared to uncoated samples, if this stabilization holds true for subsequent cycles.

Next, the effect of preoxidation regeneration was studied. For the first galvanizing cycle after the second heat treatment, the good performance of the coating was somewhat restored, with 5.8 mg/cm^2 of zinc. However, for cycles 2-5, the mean value of settled zinc was around 9 mg/cm^2 per cycle, as before regeneration.

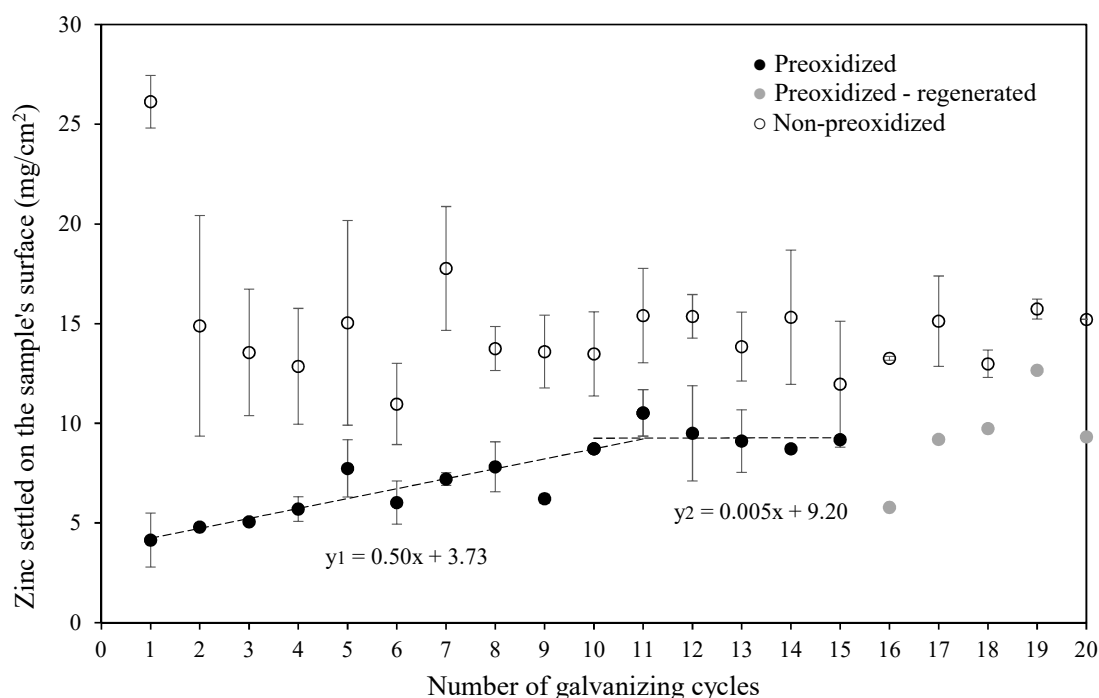


Figure 4.25: Mass of zinc deposited on the surface of a preoxidized coating in comparison to a non-preoxidized coating in the course of galvanizing cycles. Also, the effect of regeneration of preoxidation is represented.

The measure of zinc adhesion was carried out as described in section 4.3.2.1, and the results are represented in figure 4.26. A significant enhancement is noticeable in the preoxidized samples that experienced a single galvanizing cycle. Here, more than 80% of zinc was removed from the sample's surface with the slightest touch, indicating little to no interaction between the liquid zinc and the preoxidized sample. In contrast, it was impossible to mechanically remove zinc from non-preoxidized coatings after the first cycle. For subsequent cycles, the quantity of zinc removed mechanically from preoxidized samples decreased following a square root law until it reached the performance of non-preoxidized coatings.

The regeneration of the preoxidizing was again proven not effective, as already for the first cycle, the zinc removal was only half as good as for freshly preoxidized coating. Later on, the regenerated sample almost immediately attained the adhesion level of non-preoxidized coatings.

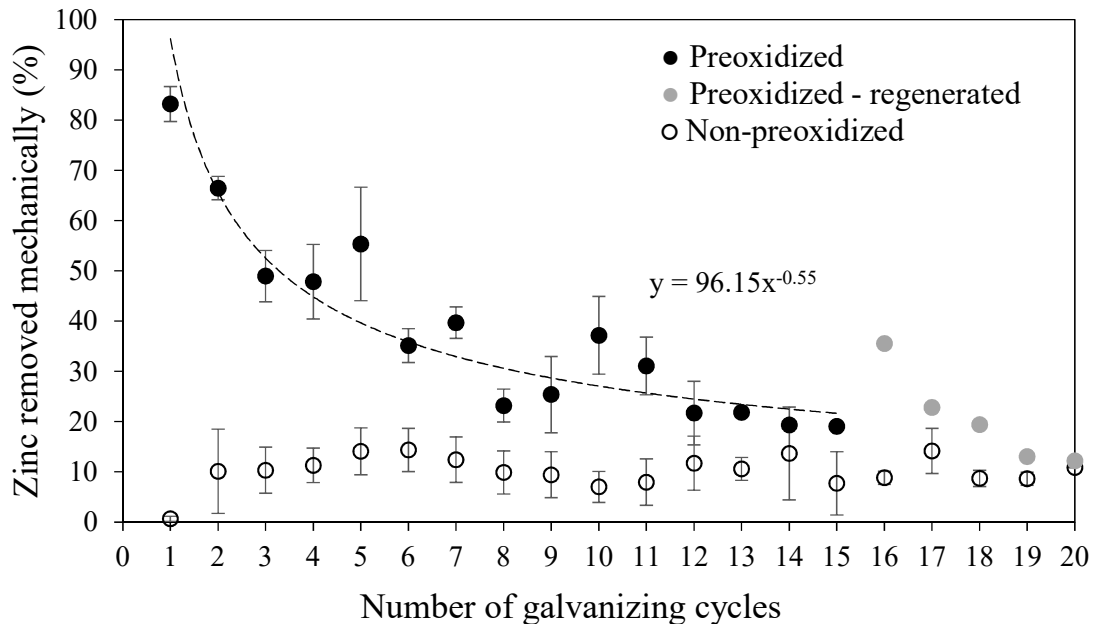


Figure 4.26: Proportion of mechanically removed zinc from preoxydized coating in comparison to non-preoxidizing coating in the course of galvanizing cycles. Also, the effect of regeneration of preoxidation is represented.

4.6.3 Microstructural evolution in preoxidized samples

Using SEM-EDX analysis, the evolution of microstructures as a result of the preoxidizing treatment and subsequent galvanizing cycles was also investigated. Figure 4.27 and table 4.8 represent how the composition was influenced by the heat treatment in air. The cartography of oxygen (fig. 4.27 shows that this element is no longer predominantly located in silicon-rich regions. In particular, the P4* phase seems to be poorer in oxygen compared to the rest of the coating. It is most prevalent above the P3* matrix phase.

The top analysis is not conclusive on the nature of the oxide formed at the surface, as all phases are similar to the original ones, only with 11–14 wt.% of oxygen in the mix (table 4.8). Certain oxides can be observed thanks to the cross-sectional investigation. It is important to interpret their composition, as shown in figure 4.28, cautiously because the interaction volume can exceed this

	P1*		P2*		P3*		P4*	
	wt. %	σ	wt. %	σ	wt. %	σ	wt. %	σ
O	13.4	8.1	14.2	5.2	11.7	3.0	11.5	2.5
Si	1.7	0.4	6.2	1.1	4.6	1.8	8.1	1.5
P	12.0	4.1	0.8	0.1	0.0	0.1	2.7	0.6
Cr	41.4	7.3	50.3	1.5	19.2	4.4	18.5	3.7
Fe	14.5	3.4	3.9	0.4	31.1	3.6	10.9	0.5
Ni	16.9	6.4	24.5	5.5	33.4	3.8	48.3	4.7

Table 4.8: Elemental composition of phases found at the surface of Pr0 sample

Cycle	0		15		15 (regenerated)	
	at. %	σ	at. %	σ	at. %	σ
O	33.2	4.9	30.6	7.0	43.4	2.0
Cr	24.1	0.7	19.2	2.3	24.9	1.7
Fe	14.5	0.7	11.0	2.1	7.9	4.4
Ni	13.7	2.1	17.6	4.6	9.6	3.2
P	8.8	1.1	10.7	1.7	9.5	1.2
Si	5.8	0.7	11.0	0.8	4.7	0.4

Table 4.9: Mean atomic composition of surface EDX cartographies of samples Pr0, Pr15-NZ, and Pr15-NZ-Reg

oxide's thickness. However, the point analysis suggests that possible oxides formed through preoxidizing are similar to Cr_2O_3 (B) and CrSiO_x (A).

Analysis of the evolution of preoxidated samples after fifteen cycles, represented in table 4.9, shows that along the galvanizing cycles, the content of chromium decreases while silicon rises. After the second, regenerative heat treatment of a sample that underwent fifteen cycles, the Cr/Si proportion returns to the initial one.

As dictated by the Ellingham diagram, SiO_2 is more thermodynamically stable than chromium oxides. Therefore, after the heat treatment, silicon should oxidize preferentially. However, from the kinetic standpoint, the Cr oxidation activation energy is lower [215, 216] than that of silicon [217–219], which is why CrO_x oxide seems to be predominant for freshly preoxidized surfaces. This high quantity of CrO_x content would contribute to the excellent wetting protection for the first galvanizing cycle. However, Zhao et al. [220] described how in passivated stainless steel, a (Fe,Cr,Ni)-Zn intermetallic forms, even though the oxide inhibits the reaction between zinc and steel. This may explain

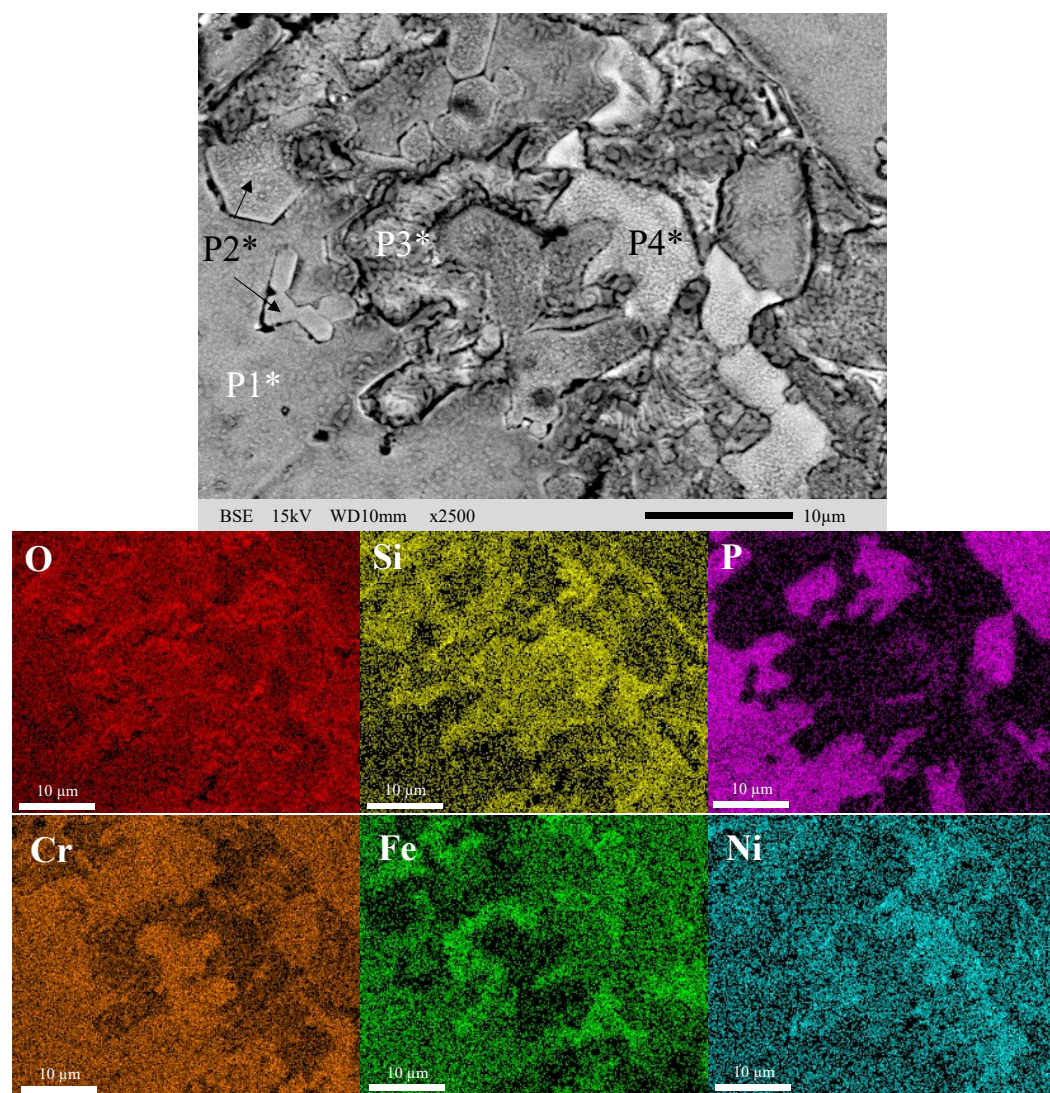


Figure 4.27: Elemental EDX cartographies and BSE-SEM image of the surface of the sample Pr0

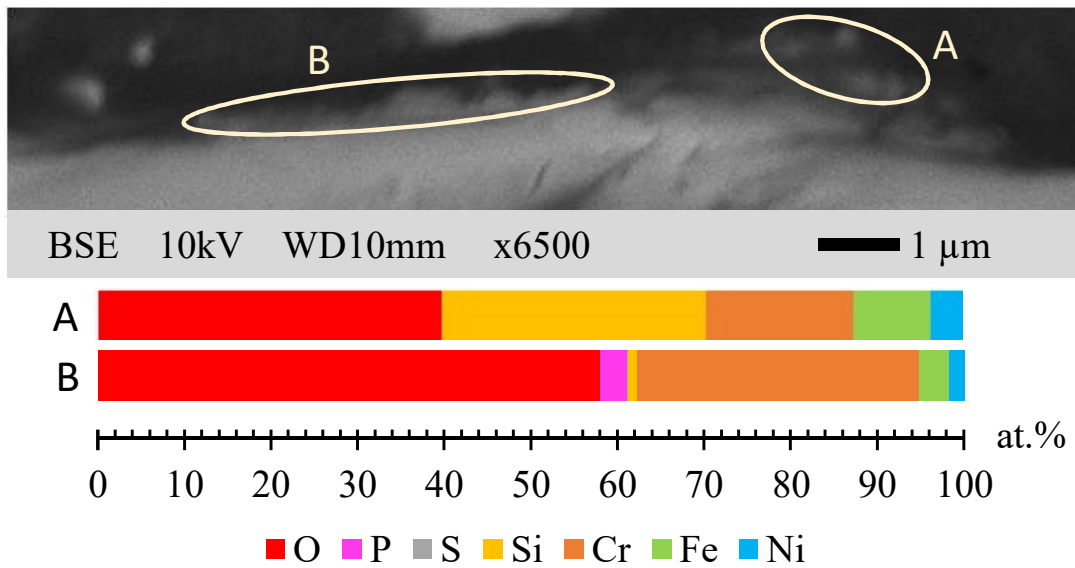


Figure 4.28: BSE-SEM cross-section image of oxides detected at the surface of the Pr0 sample. Below, the composition of oxide areas obtained via EDX analysis.

why, through galvanizing cycles, the Cr content at the surface decreases, thus increasing wetting. The following limited wetting might be attributed rather to SiO_2 , as for non-preoxidized samples.

This first preoxidation study is not entirely conclusive, as the interaction volume analyzed with the EDX method might be too important to correctly measure the chemical composition of oxides at the surface, and other spectroscopic methods might be used to determine the nature of existing bondings. It appears though that the preoxidizing conditions chosen for this experiment promote the chromium oxides formation, improving the zinc deposition resistance, which then wears out with galvanizing treatment. It is possible that those performance gains might not justify using additional energy for the heat treatment. Additionally, preoxidation regeneration appears to be inefficient for slurry coatings. Therefore, other preoxidizing conditions of atmosphere and temperature might be tested in order to foster the formation of SiO_2 and to verify if a more noticeable zinc resistance improvement could be obtained.

4.7 Conclusion on surface interactions mechanisms

Figure 4.29 illustrates the schematic representation of slurry coatings' wetting protection and liquid zinc corrosion mechanism during batch hot-dip galva-

nizing for samples that did not undergo any preoxidizing. Of the four coating phases, the P2 phase may be assimilated to the P1 phase, as it does not form intermetallics and is removed from the coating by decohesion. Given that, it is left out of the figure for simplicity reasons.

During the first passage of the coating in liquid zinc, a strong diffusion of Ni from the P4 phase can be observed. As P4 is placed only in the upper layer of the coating, it disappears from the coating earlier than in other phases. Additionally, P4 and P3 become fairly indistinguishable as P4's Ni content falls. The other matrix phase, P3, also loses its Ni and Fe content, but it is less important. After retrieval from the zinc bath, the surface is covered with a zinc layer, no matter the phase. However, this wetting does not result in a uniform intermetallic layer, but only a few scattered δ crystals that are composed of Fe and Ni. Following dezincification, the zinc layer is removed, and the surface is depleted of Ni. At this stage, more silicon atoms are revealed, which are capable of forming an oxide layer. Only matrix phases, P3 and P4, partake in the formation of oxides.

Thus formed oxide layer results in limited wetting in the following galvanizing cycles. Even though the wetting is significantly limited, the oxide phase might be either discontinuous or be a mixed oxide susceptible partially to reaction with zinc, as for later cycles other intermetallics, T and Γ , can form. Therefore, the matrix cannot be completely excluded from being partially wetted by zinc. Also, the P1 phase does not seem to contribute to the wetting protection, as it is strongly present at the surface from the beginning, but the wetting behavior changes after the first cycle. The P1 phase, however, contributes to the protection from liquid zinc corrosion. It plays a role as a barrier to intermetallic formation. The dezincification again removes zinc and newly formed intermetallics but does not influence the P1 phase.

Thus formed oxide layer results in limited wetting in the subsequent galvanizing cycles. Even though the wetting is significantly limited, the oxide phase may be discontinuous or a mixed oxide partially susceptible to reaction with zinc. This is because in subsequent cycles, new Fe-Ni-Zn intermetallics, T and Γ , may form. As a result, it is impossible to fully rule out that zinc will partially wet the matrix. Additionally, the P1 phase does not seem to contribute to the wetting protection, as it is strongly present at the surface before the first cycle, but the wetting still occurs. On the other hand, the P1 phase helps to prevent liquid zinc corrosion. It acts as a barrier to the production of intermetallic compounds.

For subsequent galvanizing cycles, the wetting behavior stays constant; therefore, the oxide presence is still postulated. However, the continuous formation of intermetallics and their dissolution eventually leads to the decohesion of P1 phase grains if the matrix around them is consequently consumed. Finally, the liquid zinc corrosion may accelerate once all P1 grains are removed.

It must be admitted that the evidence of SiO_2 appearance on the surface and its influence on the wetting behavior changed is rather presumptive than direct. Supposed oxides are very thin, and it is challenging to produce a meaningful elemental characterization at strong magnifications using the SEM-EDX approach. Unfortunately, ToF-SIMS and XPS analyses are not suitable for this type of coating because of the roughness. Also, as it is very complex in the plane of the surface as well as in its depth, one can never be certain which of the phases is clearly analyzed at the moment. Yet, numerous analyses of each sample at different stages of galvanizing would be expensive and might not yield a conclusive result. The use of higher-resolution microscopic techniques, such as Scanning Transmission Electron Microscopy (STEM), is interesting to consider in order to learn more about the nature of oxides. Also, a GDOES analysis may be interesting for this type of analysis, as it may show if there is any enrichment in a certain element, presumably silicon, that could migrate from the core to the surface of the coating [221].

The role of the stripping in 30% HCl during each galvanizing cycle on the weight loss of the coating was not identified. If the coating is attacked during this step, it would be at a comparable level or lower than that of ordinary steel, as both nickel and silicon extend the pickling time, as discussed in section 1.5. However, the leaching of coating elements into the stripping bath might be quantified with inductively coupled plasma mass spectrometry (ICP-MS).

In regard to the results of this research, it might be worthwhile to investigate other conditions of coating manufacturing. Firstly, it could be a good idea to suggest using an alternative heat treatment, particularly one that allows for quicker cooling. This could result in the development of a finer, less prone to cracking P1 phase. As molten zinc may be greatly slowed down in its consumption of matrix by a netlike P1 phase at the surface, eutectic microstructure formation may be the strategy.

Secondly, some modifications to the coating's composition might be taken into account. Given that the P1 phase is brittle in contrast to the austenitic matrix, a significant phosphorus addition does not appear to be the best course of action. On one hand, a decrease in the nickel content and an increase in chromium would result in the formation of phases less likely to react with zinc and capable of forming oxides. However, since silicon is found in Ni phases rather than chromium ones, an addition of Ni may facilitate the dissolution of Si and allow for a larger Si content in the coating. An optimal balance between the dissolution of nickel and the reduction of wetting by SiO_2 should be assessed in this situation.

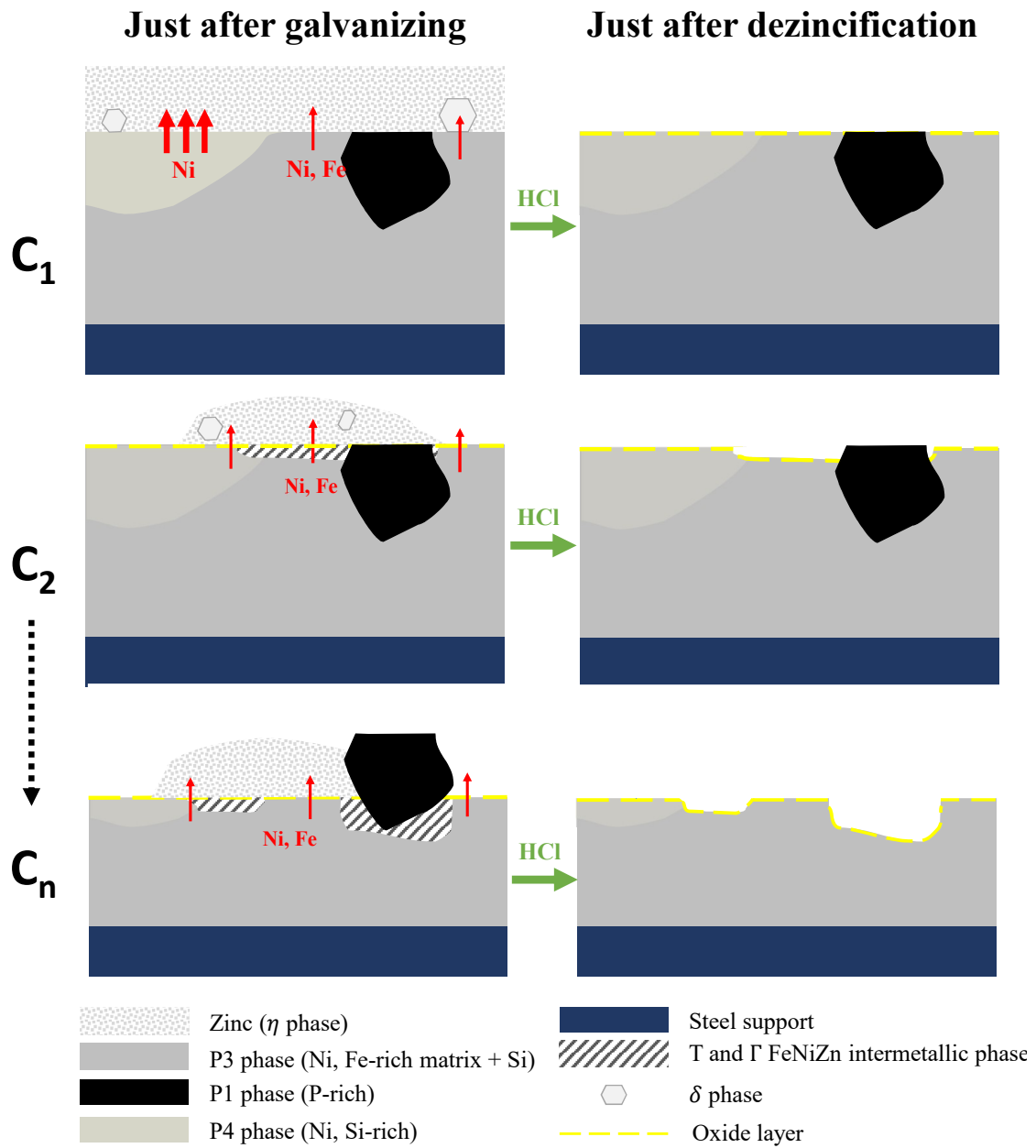


Figure 4.29: Schematic mechanism of interactions between slurry coating and liquid zinc along galvanizing cycles

Conclusion

The research of materials resistant to liquid zinc wetting and corrosion was not well developed in the domain of batch hot-dip galvanizing. The numerous solutions found for molten zinc corrosion protection in continuous galvanizing cannot be applied in its sister process because of different mechanical limitations. This thesis had the objective of developing the methods of study of zincophobic materials and learning their performance and mechanisms of protection.

This work provided an opportunity to collaborate with specialists from a variety of fields, including theoretical simulators, extreme surface researchers, as well as industrials in galvanizing.

The first large part of the study was a first-principles simulation of a wetting system. Following a hypothesis of SiO_2 not being wetted by liquid zinc, the initial simulated system of solid α -quartz - liquid Zn was established, with the premise, that it could be complexified in the future. With the calculated wetting angle validated by experimental values, the system can give access to thermodynamical information, such as SiO_2 -liquid zinc interface energy γ_{SL} .

The Density Functional Theory (DFT) analysis of α -quartz (0001) surface energy revealed that in vacuum, -Si terminations are the most stable form of this surface. The results could have been confronted with the literature [172, 192] and clarify the ambiguities that were previously reported, which represents a benefit of this section of the study.

The liquid's surface energy (γ_{LV}) was then investigated using *Ab Initio* Molecular Dynamics (AIMD) simulation. This energy was tested on a system with a much greater number of atoms in the literature [162], where the surface energy was calculated indirectly and the result was close to the experimental value for liquid zinc at 450°C. In contrast, the mean energy of the supercell was used to compute the surface energy of liquid zinc in this work for a small system. This method proved to be inefficient, as the final γ_{LV} , equal to 426 mJ/m² at 450°C, was nearly half as large as the one obtained through experiments. However, this weakness was not critical, as doubling the γ_{LV} value does not change the final interface result significantly.

The $\text{SiO}_2\text{-Zn}_{(l)}$ interface simulation was not yet addressed in the literature. Here, as a function of chemical potential of oxygen in SiO_2 ($\mu_{\text{O}}^{\text{SiO}_2}$), interface energy γ_{SL} at 450°C was found to be in the range $[2557;3356] \text{ mJ/m}^2$. Once surface energy of SiO_2 , of liquid and interface energy were determined, the $\cos \theta$ may have been computed using the Young equation. A result confirming non-wetting of SiO_2 by liquid zinc was achieved in all ranges of $\mu_{\text{O}}^{\text{SiO}_2}$ and temperatures. Finally, through extrapolation, a value of wetting angle between liquid zinc and solid quartz was calculated and equals 124° , which is a value coherent with experimental values and indicates non-wetting of a silicon oxide surface. Consequently, the interface simulation method used in this work indicates a proper tendency for interaction between those two substances.

This study also shows that atomic-scale simulation is a powerful tool that needs a very delicate adjustment. Therefore, its use for the creation of more complex solid-liquid interface systems, including amorphous bodies or the diffusion of alloying elements from solid to liquid and vice versa, necessitates high computation power and very meticulous preparation in order to obtain results that might present a truthful explanation of interactions and help in the research of new, protective materials.

Then, a model FeSi coating made with laser fusion was studied in order to evaluate if it is possible to obtain a high content of Si ($>20 \text{ wt.}\%$) at the surface in a highly thermodynamically disadvantageous system. After a study of laser parameters, good conditions were finally obtained with the laser exposure time of $750 \mu\text{s}$ and the laser power of 75 W . Those parameters lead to the formation of a biphasic coating, with both phases containing more than $20 \text{ wt.}\%$ of silicon. Also, an extreme surface analysis with XPS and ToF-SIMS methods revealed that such a coating is capable of forming a native oxide layer that, theoretically, would limit the wetting by liquid zinc. However, the final confirmation through wetting angle measurement could not have been conducted yet.

Although the correct manufacturing conditions for the FeSi coating formation were defined, this method seems impossible to industrialize when the brittleness of the coating and the cost and complexity of production are taken into account.

Afterwards, the slurry process was used to form complex coatings that may be used in the batch galvanizing industry. Those coatings were tested through a cyclic galvanizing test. The surface analysis of the samples revealed that they are resistant mechanically and to thermal shock. This resistance may be attributed to the presence of nickel, chrome, and diffused iron, which form an intimate bond between the substrate steel and the coating. The analysis suggests that limited zinc deposition at the surface of samples is linked with the

oxygen content increasing on top of the silicon-rich phases and, supposedly, an SiO_2 formation. Also, surprisingly, phosphorus, originally added to the mix to decrease the melting temperature of the slurry precursor, was proven to form phases limiting the liquid zinc corrosion of the coating, as it does not react with zinc to form intermetallic compounds.

However, the initial hypothesis of SiO_2 formation at the surface of the slurry coating could not have been fully confirmed as SEM-EDX, as the interaction volume of this analysis might exceed the thickness of the oxide layer. The coating also appeared far too complex to be analyzed through XPS and ToF-SIMS methods. The research for an adapted method of analysis of extremely fine layers of oxides at such materials should be made.

The reactivity of the coating lies in the matrix phases of the coating, which have a high content of Ni and Fe. Those two elements form zinc binary and ternary compounds during the immersion in the galvanizing bath that are later dissolved during the dezincing treatment, leading to the coating's weight loss in the course of the galvanizing cycles. The presence of nickel in the coating might seem negative for its resistance, but it provides the mechanical resistance of the coating, and Ni-rich phases can contain more beneficial silicon than others.

The preoxidation treatment was also applied to the coating in order to observe if the wetting protection could be improved with the generation of surface oxides before the galvanizing treatment. The conditions used here suggest the initial formation of chromium oxides that fade away during galvanizing cycles. Those chromium oxides seem to be responsible for a significant decrease in zinc deposition at the surface of samples during initial galvanizing cycles.

The composition of the coating studied in this research showed only partial protection from wetting. In order to further improve the wetting protection, it would be interesting to search for a continuous SiO_2 layer, either through a study of preoxidation conditions that would privilege SiO_2 formation instead of chromium oxides or through a play on the coating composition. Actually, the preliminary test on FeSi alloys showed that 20 wt.% Si can limit entirely any degradation due to interaction with liquid zinc, but this study showed that significant improvement in comparison to regular steel can be obtained for materials containing nearly half as much silicon.

The formation of slurry coatings with the slurry process seems promising for use in batch hot-dip galvanizing. This method can be used for various geometric forms of steel parts and is a process that can be industrialized. The performance demonstrated is also positive, with an 81% improvement in liquid zinc corrosion and a significant decrease in zinc settled on the surface of the material after each galvanizing cycle, with 85% zinc saved after 20 cycles in comparison to regular

low-carbon steel. The preoxidizing treatment showed a further, even though limited in time, improvement in liquid zinc wetting protection. A patent on slurry coatings for batch hot-dip galvanizing was deposited as a result of this study.

In order for the coatings to be industrialized, it is necessary to conduct an evaluation of the lifespan of the coating, which was not yet done during this research. For this moment, the industrial-scale tests show that the coating can stand at least 30 galvanizing cycles. A Life Cycle Assessment (LCA) and a cost analysis are the evaluations that should be done in order to verify if the energy costs of the heat treatment necessary for the formation of the coating, as well as the potential cost of preoxidizing, are balanced by the savings made by less zinc wasted and less hydrochloric acid bath used and treated. Also, a potential increase in the performance of the galvanizing caused by shortening the time of dezincification, or even the elimination of this stage, should be taken into account.

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Appendix A

Nosé mass optimization in AIMD

A thermostat regulates the temperature of the supercell in a standard NVT ensemble during AIMD. The Nosé-Hoover thermostat was utilized in this research. It relies on applying a hypothetical Nosé mass to regulate the simulation's temperature oscillations' frequency [163]. It is defined as:

$$Q = \frac{2gkT}{(\omega < s >)^2} \quad (\text{A.1})$$

with Q , the imaginary Nosé mass (defined in VASP as SMASS), ω , a typical phonon pulsation, $< s >$, an extra degree of freedom for heat bath, and g being the number of independent momentum degrees of freedom of the system ($3N_{\text{atoms}}$).

By default, $\text{SMASS} = 0$ establishes an oscillation frequency that results in 40 oscillations being completed over the course of the simulation (fig. A.1a). The allure of the temperature-step function is shaky and irregular.

Then, a theoretic calculation and simulation tests led to the $\text{SMASS} = 0.089$ (fig. A.1b), which is characterized by a smooth envelope of the temperature-step function.

The limitation of excessive temperature amplitude and low harmonicity with an almost sinusoidal curve for $\text{SMASS} = 0.089$ (fig. A.1d) in contrast to $\text{SMASS} = 2$, where the irregular peaks reveal the higher harmonicity (fig. A.1c), drove the choice of the former for AIMD simulations in this study. Actually, the SMASS describes the thermal inertia of the thermostat. In order to prevent the system under study from affecting the thermostat, the fictive mass SMASS must be sufficiently big. However, it must not match a frequency that is too high to prevent the system's frequency from acting as a carrier wave for the thermostat's frequencies and creating throbbing phenomena. However, this choice is system-

specific because SMASS is reliant not only on phonon dispersion value but also on temperature.

This study has shown that the calculation of SMASS was rather efficient in finding which value to enter into VASP. Finally, it has to be noticed that SMASS had no relevant effect on pressure calculations 3.11.

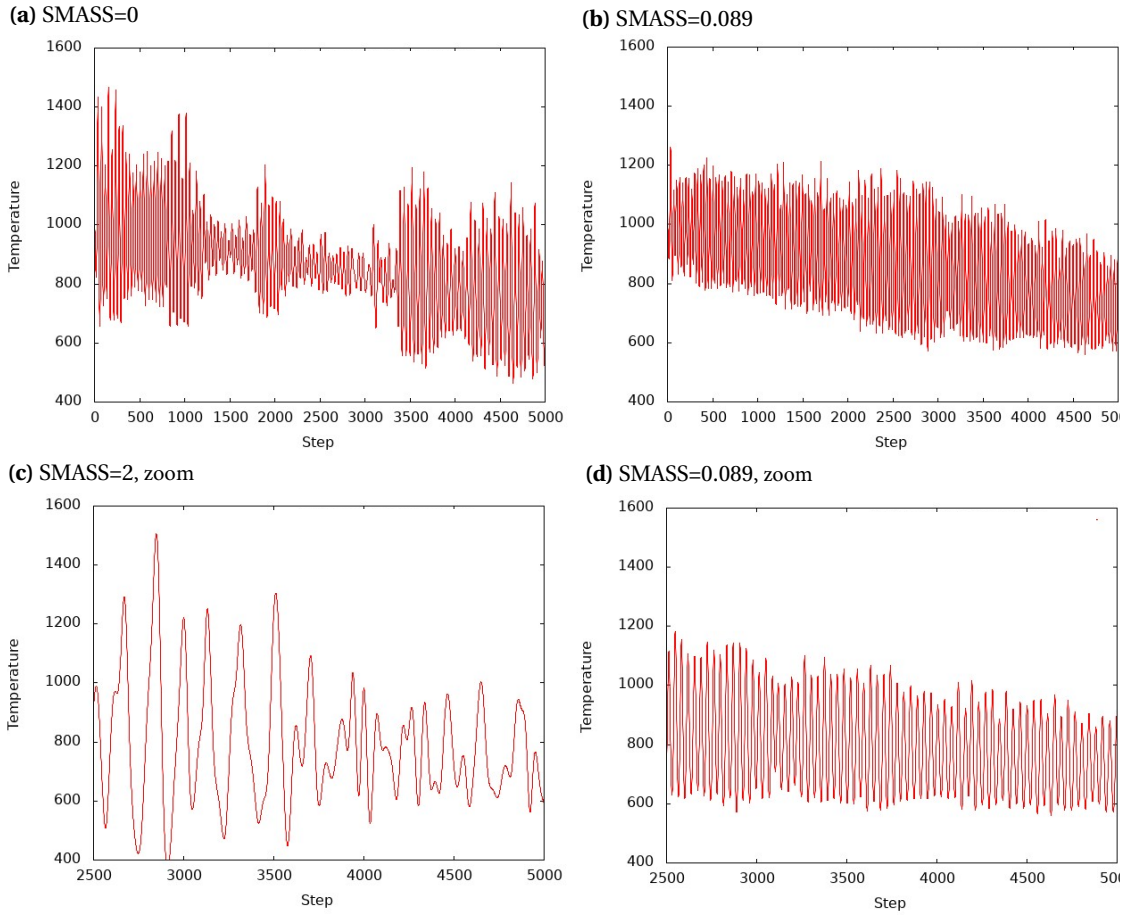


Figure A.1: Temperature in function of calculation step for $\text{SMASS} \in \{0, 0.089, 2\}$ between the initial temperature 1500 K and the final temperature of 723 K after 5000 steps. This calculation was done for the liquid zinc supercell.

For constant temperature studies of liquid zinc, the following Nosé masses were recalculated and applied: 0.2515 at 1500 K, 0.2 at 1200 K, and 0.1677 at 1000 K.

Appendix B

Energy and pressure variation in AIMD

B.1 Bulk liquid Zn

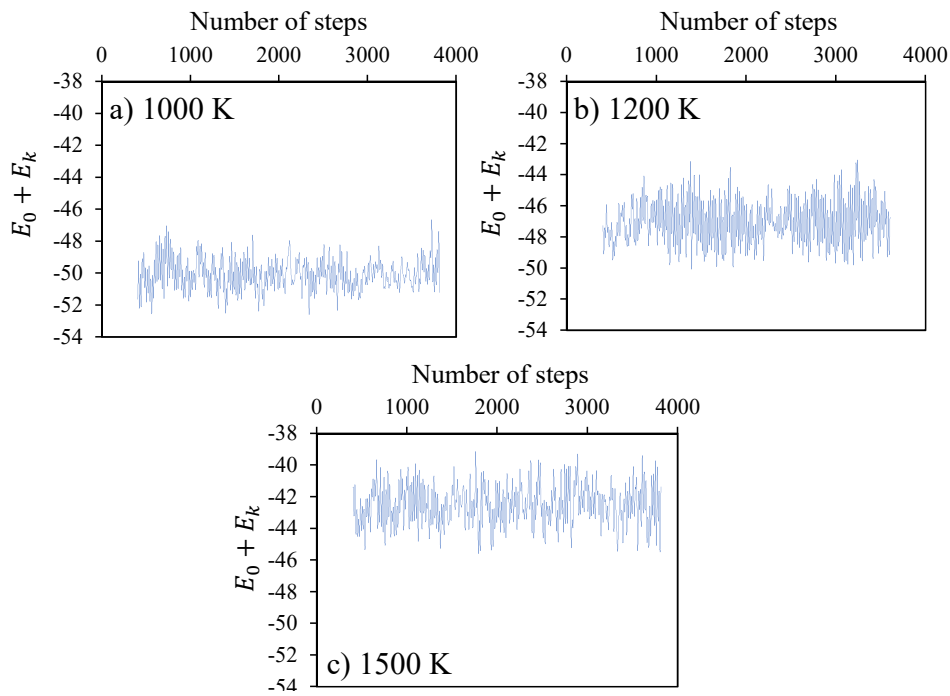


Figure B.1: $(E_0 + E_k)$ energy sum variation as a function of AIMD simulation steps for a bulk liquid zinc supercell

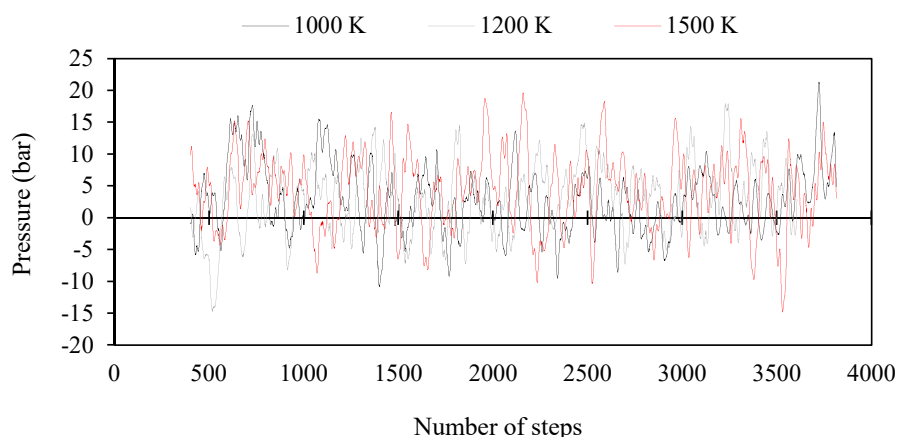


Figure B.2: Pressure in the bulk liquid zinc supercell during hot temperature simulation, with the mean pressure of 3 bar at all three temperatures

B.2 Liquid Zn surface in vacuum

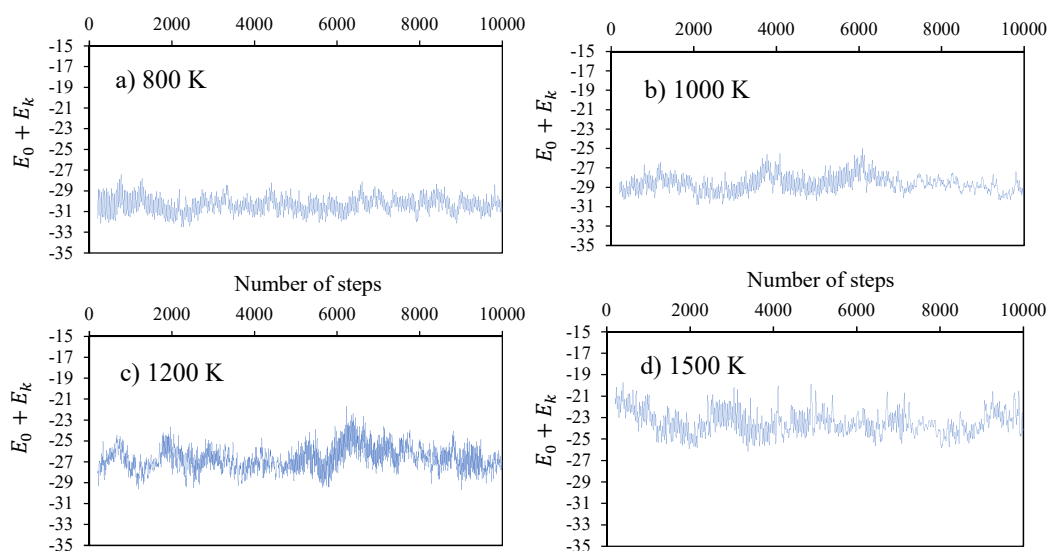


Figure B.3: $(E_0 + E_k)$ energy sum variation as a function of AIMD simulation steps for liquid zinc surface in vacuum supercell

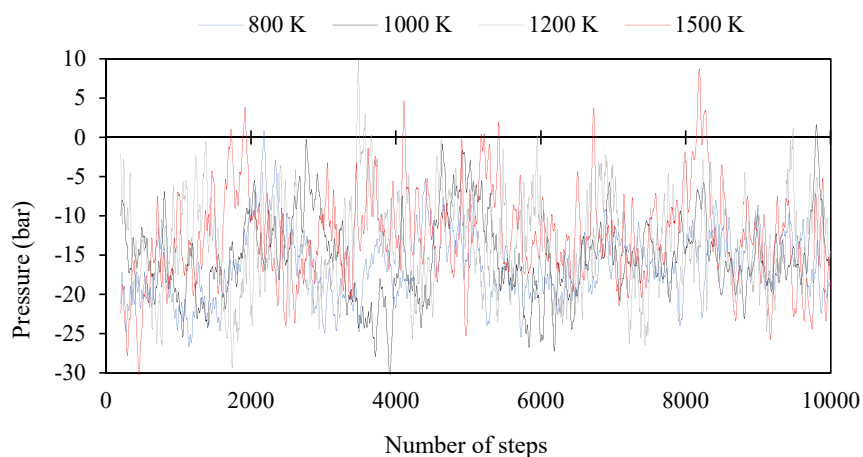


Figure B.4: Pressure in the liquid zinc surface in vacuum supercell during hot temperature simulation, with the mean pressure of -16 bar at 800 K, -15 bar at 1000 K, -14 bar at 1200 K and -13 bar at 1500 K.

B.3 SiO₂-Zn_(l) interface

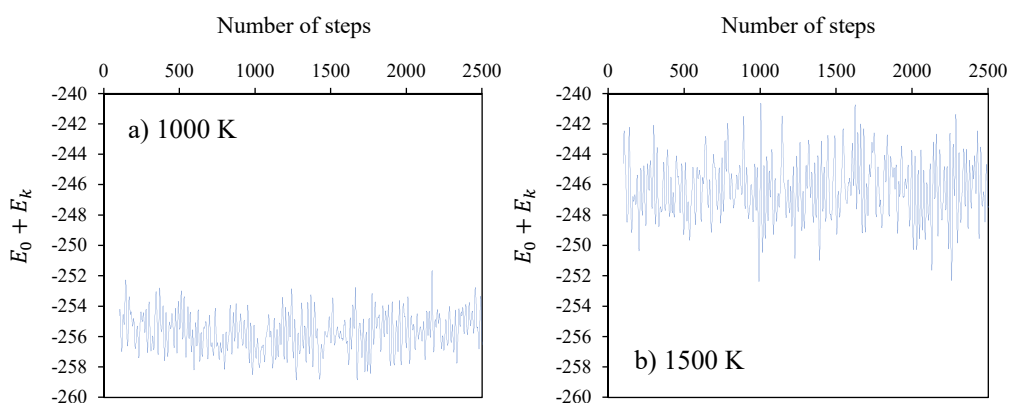


Figure B.5: $(E_0 + E_k)$ energy sum variation as a function of AIMD simulation steps for SiO₂-Zn_(l) interface supercell

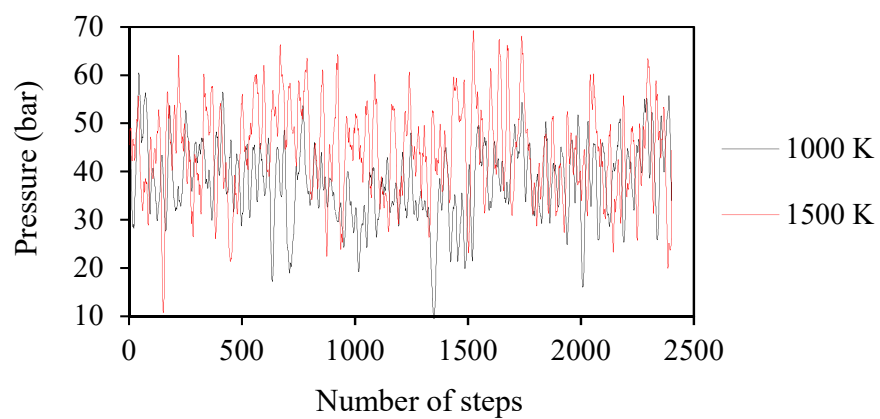


Figure B.6: Pressure in the $\text{SiO}_2\text{-Zn}_{(l)}$ interface supercell during hot temperature simulation, with the mean pressure of 38 bar at 1000 K and 44 bar at 1500 K.

STUDY OF THE BEHAVIOR OF A Fe-Cr-Ni-Si COATING IN LIQUID ZINC

Batch hot-dip galvanizing serves as a surface treatment for safeguarding steel against atmospheric corrosion. This process involves immersing metal components in a liquid zinc alloy bath to apply a protective coating. However, the repeated treatment of steel hangers that transport the parts between multiple galvanizing baths results in molten zinc corrosion. Furthermore, the zinc layer on these hangers not only wastes zinc but also requires an extra stripping step in HCl, adding to economic and environmental costs. The objective of this thesis is to develop materials that can prevent liquid zinc deposition and to understand the mechanisms of their damage.

A slurry process is utilized to produce a complex Fe-Cr-Ni-Si-P coating that can be used and produced industrially. Cyclic galvanizing tests prove that this coating reduces liquid zinc corrosion by 80% and zinc intake by 85% after 20 galvanizing cycles, in comparison to low-carbon DD13 steel. The preoxidation process is explored to enhance its performance further. Finally, a surface analysis using SEM-EDX at various stages of the galvanizing process provides insights into surface interaction mechanisms, examining the SiO_2 formation hypothesis and the role of different coating phases.

An atomic-scale DFT-AIMD simulation is employed to study the SiO_2 -liquid Zn interface and calculate its interface energy. The Fe-Si model surfaces were also produced with SLM method. Both studies were managed in order to improve understanding of interactions in simplified systems compared to slurry coatings.

Keywords: batch hot-dip galvanizing, liquid zinc, coating, wetting, surface analysis, atomic simulation

ETUDE DU COMPORTEMENT D'UN REVÊTEMENT Fe-Cr-Ni-Si DANS LE ZINC LIQUIDE

La galvanisation à façon est utilisée comme traitement de surface pour protéger l'acier contre la corrosion atmosphérique. Ce processus implique d'immerger les composants métalliques dans un bain de zinc liquide afin d'appliquer un revêtement protecteur. Cependant, le traitement répété des structures d'accroche en acier assurant le transport des pièces entraîne leur corrosion par le zinc liquide. De plus, la couche de zinc déposée sur ces crochets non seulement gaspille du zinc, mais nécessite une étape supplémentaire de décapage à HCl, augmentant les coûts économiques et environnementaux. Cette thèse se concentre sur le développement et la compréhension des mécanismes à la surface des matériaux visant à réduire la déposition du zinc liquide.

Un procédé slurry est utilisé pour produire un revêtement complexe Fe-Cr-Ni-Si-P pouvant être utilisé et fabriqué industriellement. Des tests de galvanisation cyclique démontrent que ce revêtement réduit la corrosion par le zinc liquide de 80 % et la prise du zinc de 85 % après 20 cycles de galvanisation, en comparaison avec l'acier bas carbone DD13. Le processus de préoxydation est exploré pour améliorer davantage ses performances. Enfin, une analyse de surface à l'aide de la technique SEM-EDX à différentes étapes du processus de galvanisation offre des perspectives sur les mécanismes d'interaction de surface, examinant l'hypothèse de formation de SiO_2 et le rôle des différentes phases de revêtement.

Une simulation DFT-AIMD à l'échelle atomique est mise en oeuvre pour étudier l'interface SiO_2 -liquide Zn et calculer son énergie d'interface. En plus, les surfaces modèles Fe-Si ont été produites par fusion laser. Ces deux études ont été menées pour élargir la compréhension des interactions dans les systèmes simplifiés par rapport aux revêtements slurry.

Mots clés : galvanisation à façon, zinc liquide, revêtement, mouillage, analyse de surface, simulation atomique
