HOT DIP GALVANIZING OF Zn-Al-WO$_3$ COATING ON MILD STEEL: EFFECT OF SURFACE TREATMENT

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled '**Hot Dip Galvanizing of Zn-Al-WO₃ Coating on Mild Steel: Effect of Surface Treatment**'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

%   Percentage

wt.%   Weight Percentage

η   Eta phase

ζ   Zeta phase

δ   Delta phase

Γ   Gamma

Ɵ   Theta angle

°   Degree

°C   Degree Celsius

mm   Millimetre

nm   Nanometre

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
Al	Aluminium
Al_2O_3	Aluminium Oxide
EDX	Energy Dispersive X-Ray
FCC	Face Centered Cubic
Fe	Iron
FESEM	Field Emission Scanning Electron Microscope
HCl	Hydrochloric acid
HV	Hardness Vickers
ICDD	International Centre for Diffraction Data
MMC	Metal Matrix Composite
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NH4Cl	Ammonium Chloride
OM	Optical Microscope
STA	Stearic acid
SiO_2	Silicon dioxide
SiC	Silicon Carbide
TiO_2	Titanium Oxide
WO_3	Tungsten Oxide
WCA	Water Contact Angle
XRD	X-ray Diffraction

Zn   Zinc

ZrO_2 Zirconium Oxide

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CELUPAN PANAS GALVANIK SALUTAN Zn-Al-WO$_3$ PADA KELULI LEMBUT: KESAN RAWATAN PERMUKAAN

ABSTRAK

Kaedah galvanik digunakan untuk melindungi keluli daripada kakisan sejak dahulu. Walaupun lapisan galvanik dapat melindungi substrat keluli daripada kakisan amosfera, ia mungkin tidak dapat memberikan perlindungan kakisan jangka panjang dalam persekitaran yang sangat agresif. Tujuan projek ini adalah untuk membangunkan permukaan hidrofobik pada keluli lembut melalui proses tindak balas pada permukaan keluli tergalvani untuk meningkatkan rintangan kakisan. Zn-Al-WO$_3$ disalut pada keluli lembut melalui kaedah galvanik, diikuti dengan rawatan permukaan yang mengandungi asid stearik (STA) dan silikon dioksida (SiO$_2$). Molariti STA (0.002,0.005,0.008,0.01,0.02,0.05 M), jenis pelarut (etanol, aseton), masa rendaman (2,3,5 jam) dan komposisi salutan dipelbagaikan semasa rawatan permukaan. Beberapa pencirian seperti ketebalan, fasa salutan, morfologi, sudut sentuhan, kekasaran permukaan serta ujian kakisan telah dijalankan. Salutan Zn-Al-WO$_3$ mempunyai ketebalan purata 107 µm dan terdiri daripada lapisan perencatan dan lapisan luar. Kadar kakisan terendah 0.70727 mm/thn dan sudut hubung hidrofobik 122.29° direkodkan dengan 0.008M STA dalam larutan etanol selama 2 jam. 0.008M STA dalam rawatan permukaan selama 2 jam menunjukkan taburan zink stearate yang lebih baik. Penggumpalan berlaku lebih cepat dengan peningkatan molariti aseton dan masa rendaman, hasilnya kekasaran permukaan yang tidak rata dan mengurangkan hidrofobisiti. STA lebih larut dalam etanol berbanding aseton, oleh itu terbentuk dalam zink stearate yang lebih seragam and meningkatkan hidrofobisiti. Permukaan hidrofobik yang dihasilkan pada keluli tergalvani menunjukkan hasil baik dan berpotensi untuk menyediakan penyelesaian perlindungan kakisan yang kos efektik dan hijau.

HOT DIP GALVANIZING OF ZN-AL-WO$_3$ COATING ON MILD STEEL: EFFECT OF SURFACE TREATMENT

ABSTRACT

Traditionally, galvanizing has been used to protect steel from corrosion. Although galvanized layers may be able to protect steel substrate from atmospheric corrosion, they may not be able to provide a long-term corrosion protection in highly aggressive environments. The aim of this project is to develop hydrophobic surface on the mild steel by reaction process on the surface of galvanized steel to increase the corrosion resistance. Zn-Al-WO$_3$ was coated to the mild steel via hot dip galvanizing, followed by surface treatment containing stearic acid (STA) and silicon dioxide (SiO$_2$). Molarity of STA (0.002,0.005,0.008,0.01,0.02,0.05 M), solvent type (ethanol, acetone), immersion time (2,3,5 hours) and coating compositions were varied during surface treatment. Several characterizations such as thickness, phases of coating, morphology, contact angle, surface roughness as well as corrosion test were conducted. The Zn-Al-WO$_3$ coating has an average thickness of 107 μm and is made up of an inhibition layer and an outer layer. The lowest corrosion rate of 0.7073 mm/years and hydrophobic water contact angle of 122.29° were recorded with 0.008M of STA in ethanol solution for 2 hours. The 0.008M of STA in 2 hours surface treatment shows better distribution of feather-like lamellar structure of zinc stearate. Agglomeration occurs more quickly with increasing molarity and immersion time, leading to non-uniform surface roughness and reduced hydrophobicity. The STA more soluble in ethanol than acetone, thus formation of homogenous zinc stearate, increasing its hydrophobicity and anti-corrosion property. The obtained hydrophobic surface on galvanized steel yield a promising result and has potential to provide a cost effective and green solution for corrosion protection.

CHAPTER 1

INTRODUCTION

1.1   Introduction

Steel is widely utilized in engineering applications because of its reasonable cost, broad availability, flexibility of manufacturing, and better mechanical strength. However, the drawback of the steel which has poor corrosion resistance severely affects its performance and service time in their application such as automotive, construction, marine as well as oil and gas industries. The steel corroded because a chemical or electrochemical reaction between the steel surface and oxygen. Thus, many approaches are used to improve steel corrosion resistance, such as cathodic protection, anodic protection, the addition of inhibitors, and metallic coatings (Shibli et al., 2015). Zinc coatings are frequently used to protect steel. Zinc coatings can be applied in a variety of ways, including hot dip galvanizing, electroplating, spraying, mechanical plating, and painting. Hot dip galvanizing is the most efficient method because it provides good mechanical properties, ductility, low density, corrosion resistance, low cost, and recyclability (Polyakov et al., 2021).

However, most of the galvanized steel may undergo corrosion due to highly exposed to the humidity and the corrosive atmosphere. The water vapor creates a thin film corrosive electrolyte on the surface of galvanized steel which accelerating the corrosion and producing white rust (Liu et al., 2020). For example, the aggressive ions attacked the galvanized steel in marine industries and cause it to rapidly corrode. Several metal oxides or mixed oxides are added into the galvanic bath to improve the performance of the zinc coating and enhance the alloying characteristics of Zn–Fe alloy phases. According to Deepa et al., (2020), the addition of a very small amount of metal oxides such as TiO_2, Al_2O_3,

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ZrO$_2$, ZnO, and CeO$_2$ in hot-dip zinc coatings can improve galvanic performance and corrosion resistance. Arunima et al., (2020) found that the addition of 0.2 wt.% of tungsten oxide WO$_3$ nanoparticles-incorporated in hot-dip zinc aluminium (Zn-0.1wt% Al) are able to form hydrophobic surface with contact angle of 112.3° and obtained low corrosion rate of 6.54 $\times$ 10^{-6} mmpy. The coating on the surface turning to hydrophobic or superhydrophobic which prevent the water molecules adhering on the surface.

In addition, Cao et al., (2021) proposed a simple method for fabricate a super-hydrophobic coating on hot-dipped galvanized steel by modified the surface treatment using stearic acid to achieve super hydrophobicity property. The STA is an organic compound consists of long alkyl chain fatty amides and fatty acid which employed with low surface energy and have good potential to react with metal ions such as forming into zinc stearate "flowerlike" structure. The authors such as Hu et al., (2019), Polyakov et al., (2021), Zang et al., (2014),Li et al., (2018), Wei et al., (2020), and Feng et al., (2011) created superhydrophobic surface using surface treatment of STA in ethanol solution. Meanwhile, Jafari and Farzaneh (2012) used STA and acetone for surface treatment to obtain superhydrophobic surface. Thus, a proper study is required to understand the surface modification treatment. Knowledge gain in this study might benefit the galvanizing industry.

1.2   Problem Statement

Zinc was used as coating layer for steel due to its high reactivity than steel causing it to serve as sacrificial anode. However, the galvanized steel still undergoes corrosion due to more surface contact with the corrosive medium especially in marine, construction and

oil and gas industries. The aggressive ions from corrosive medium severely deteriorate the zinc passive layer as it reaches the steel surface. Improving surface wettability should be the best option to reduce the contact with solid surface and the corrosive medium. In recent years, there are some researchers proposes the new method as incorporating with nanoparticles such as tungsten trioxide, WO_3 (Arunima et al., 2020) and zinc oxide, ZnO (Gurav et al., 2014) to improve the hydrophobic properties on the surface of galvanized steel. The hydrophobic properties help to repels the water molecules stick on the surface as it reduces the contact between the substrate and corrosive medium. The hydrophobic property can be achieved by surface modification using low surface energy or micro–nano structure material by forming into rough surface. In addition, due to its low surface energy and potential reactivity with metal cations, STA has been used in many studies for surface modification to achieve hydrophobic properties (Hu et al., 2020; Polyakov et al., 2021; Li et al., 2018; Wei et al., 2020). The distribution of zinc stearate on the galvanized coating may be affected by the molarity of the STA. Despite the fact that Gurav et al., (2014) conducted a study on the use of different molarity of STA using ZnO coated on glass substrate, no work has been done on the different molarity of STA on galvanized steel. As a result, research on molarity and solvent is required, focusing on the effect of different molarities of STA in different solvent and immersion times during surface treatment of galvanized mild steel.

1.3   Research Objectives

a) To evaluate the hydrophobic property using different molarities of STA in different solvent and immersion times.

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b) To determine the corrosion resistance of galvanized steel after surface treatment.

1.4   Thesis Outline

This thesis is divided into five chapters. The first chapter includes the research background, problem statement, objective and thesis outline. The second chapter is a review of the literature. In this section, all of the processes and methods used, such as hot galvanizing and surface modification, are briefly explained. The third chapter explains the methodology, which includes the materials and chemicals used, the procedure of the experiment, and the characterization methods. All of the findings are clearly discussed and analyzed in Chapter 4. The discussion of raw material characterization, phases, and coating thickness, as well as the effect of surface treatment influences by STA molarities, solvent, and immersion times was detailed out. The final chapter concludes and summarizes the overall findings.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Steel is most essential component of all industries, especially in the building and construction industries, due to excellent strength, durability, versatility, availability, and affordability (Arunima et al., 2022). Despite the development of numerous new and improved materials for design purpose, steel remains the primary building material for vehicles, appliances, and industrial equipment. Mild steel is one of the most extensively used materials in a variety of industrial applications, including automotive, oil and gas, and marine due to its compatibility with a variety of industrial purposes (Shibli et al., 2015). Steel corrosion is the irreversible degradation and loss of quality of steel are caused by the electrochemical or chemical reactions of the steels surface and oxygen. Steel corrosion is influenced by various of factors, including ambient air temperature, the presence of chemical vapours, and humidity (Ran et al., 2019).

Steel has the limitation and shorter service time due to poor corrosion resistance. Developing a passivation layer on a metal substrate is one of the most efficient steps to prevent metals from corrosion, and chromate passive layer has long been a popular corrosion inhibitor in the steel industry due to its exceptional corrosion resistance and self-healing capabilities. Unfortunately, because of the chromate's high toxicity and severe effects to the environment, the pollution authority law is becoming more rigorous as public awareness of environmental protection rises, the use of the chromate is being phased out (Zhan-Fang et al., 2017).

Zinc coatings are commonly used to protect steel against corrosion because they have high mechanical strength and give cathodic electrochemical protection. Zinc is the most extensively used protective metal coating due to its lower cost and large reserve, as well as its non-toxicity and recyclability (Polyakov et al., 2021). Among many methods of zinc coating, hot dip galvanizing techniques are commonly used to coat zinc on the steel surface due to its reliable, cheap cost and reusable. The hot dip galvanized steels have been used in various industries such as automotive, electrical appliances, construction, aerospace and marine. The addition of additives to the galvanic zinc bath, such as metal oxides and mixed oxides, is critical for improving the alloying characteristics of Zn–Fe alloy phases (Maniam & Paul, 2021). This can enhance inner alloy structures while also lowering zinc consumption, making the process more cost-effective. However, the galvanized steel has high wettability which further reduce by tuning into superhydrophobic properties through surface treatment. Surface wettability is determined by the chemical composition of the surface layer as well as the microstructure of the topography (Brassard et al., 2014).

2.2 Steel

Steel is an alloy that is mostly made up of iron and carbon. Steel's attractiveness arises from its inexpensive cost of production, forming, and processing, as well as the availability of its two basic resources and its unbeatable variety of mechanical capabilities. Steels may be divided into a few primary classes based on their chemical compositions.

Steels are classified into three groups based on their chemical composition: carbon steels, low-alloy steels, and high-alloy steels. High-carbon steels have a carbon content of more than 0.5 percent; medium-carbon steels have a carbon content of 0.3 to 0.49%; mild-

carbon steel have a 0.15-0.29%; low-carbon steels have a carbon content of 0.05 to 0.14 %; extra-low-carbon steels have a carbon content of 0.015 to 0.04%; and ultralow-carbon steels have a carbon content of less than 0.014%. Carbon steels are also classified as having a manganese content of less than 1.64%, a silicon content of 0.6%, and a copper content of 0.6%, with sum of additional components of less than 2%. Low-alloy steels include up to 8% alloying elements; high-alloy steels contain more than 8% alloying elements. Apart from carbon, there are many alloying elements commonly added into steel based on the desired properties. The application of steel chosen based on its chemical composition which influences its mechanical and physical properties. For example, low carbon steel used for car bodies and wires, mild carbon steel used for building or bridge construction and piping, medium carbon steel used for machinery, high carbon steel used for railroad rails.

2.3   Corrosion Mechanism of Steel

Corrosion is the unexpected event which occurs gradually, and irreversible deterioration of metals induced by environmental physical-chemical or chemical reaction. Corrosion of steel is the result of an electrochemical or chemical reaction between the metal and a corrosive environment (Wang et al., 2011).The reaction of chemical corrosion of metals takes place in non-conductive environments, usually gaseous conditions. When the gas in contact with metal, it dissociates into ions which adsorb on the metal surface and leading to the corrosion on top of the substrate. Typically, chemical corrosion occurs on the steels where the steel oxidizes and undergoes reduction spontaneously. For corrosion by electrochemical reaction occurs in the presence of electrolyte where the transfers of ions occur due to the redox reaction. In this redox reaction, the metal is oxidized in anodic reaction while the oxygen undergoes reduction at the cathodic reaction. In steel

composition, the major percentage of element present is iron, Fe which are contributing to the corrosion of steel. Firstly, the iron, Fe undergoes oxidation while the oxygen, O_2 undergoes reduction as forming into iron(II)hydroxide, $Fe(OH)_2$ as the combination reaction. Then, this iron(II)hydroxide react with oxygen and forming into hydrate iron(III)oxide, $2Fe_2O_3^{.}H_2O$ (Kreysa et al., 2004). The equation of formation of iron oxide is shown below. Figure 2.1 shows overall corrosion mechanism of steel.

Cathodic Reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Anodic Reaction: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

Combine equation: $2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$ [Iron(II) hydroxide]

Final equation: $4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O$ [hydrated Iron (III) oxide]
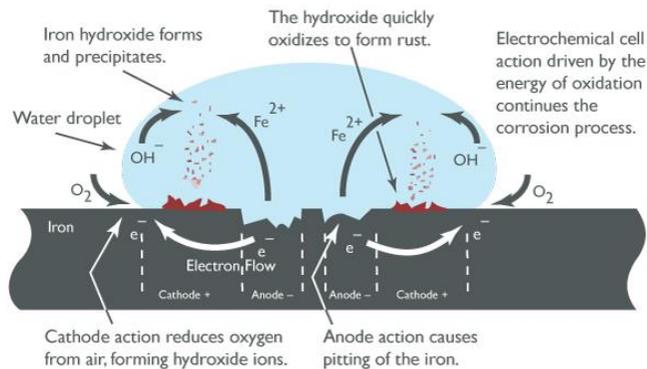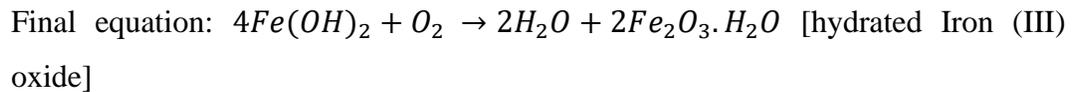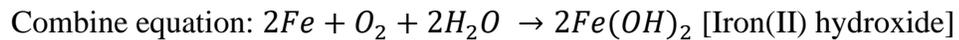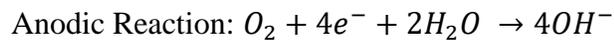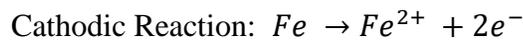
Figure 2.1   Overall corrosion mechanism of Steel (Huyett., 2020)

There are several factors which affects the corrosion rate of the steel. Air humidity is the primary cause of corrosion of steel when exposed to the atmosphere. The corrosivity of atmosphere is determined by the type and concentration of particles as well as pollutants (Kreysa et al., 2004). Sulphides and chlorides are playing the vital role in the air pollution. In industrial areas, the ambient corrosivity increases due to the high

concentration of sulphur dioxide by the combustion of fossil fuel. In seashore areas, the number of chlorides is very high and the chances to get the steel corroded is higher. Corrosion of steel occurs quickly in acidic solutions. In diluted alkaline solutions, on the other hand, it is relatively corrosion resistant (Yu et al., 2020).

2.4   Corrosion Protection on Steel

Corrosion protection refers to all approaches, tactics, and procedures that are used to prevent corrosion damage. There are two type of corrosion protection procedure such as active and passive which shown in Figure 2.2. Active corrosion protection means minimized or prevent occurrence of corrosion by modifying the corrosion process, material-selection, application, structure, and production. Nevertheless, this procedure requires an efficient of passive corrosion-protection methods. Passive corrosion protection is achieved by isolating the metal surface from the corrosive agent through the protecting coating layers. There are some requirements need to be fulfilled by the protection layer. For example, the protective layer must free from pores, bond tightly to the base material, able to withstand to mechanical forces, have sufficient elasticity, and have corrosion resistant properties. In recent years, steels products use various method for corrosion protection. For instance, coatings using paints on steel parts, metallic plating methods such as hot-dip plating or thermal-spray coatings and by creating duplex system such as hot-dip galvanizing (Kreysa et al., 2004).
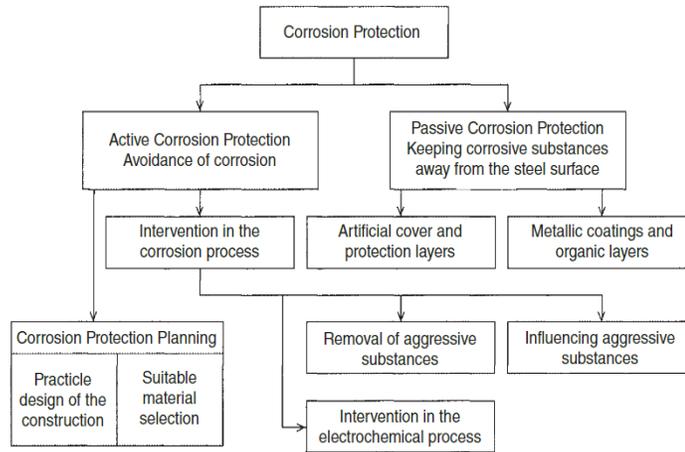
Figure 2.2   Procedure of corrosion protection (Kreysa et al., 2004).

2.5   Zinc Coating on Steel

Zinc has good alloying properties, allowing it to combine well with other metals. Zinc coatings provide steel buildings and components with highly effective and long-lasting corrosion protection. Because of its highly sacrificial behaviour and lower electrochemical potential than ferrous metals such as mild steel or carbon steel, zinc is the most typically selected metal for corrosion production when considering the objective use and costs (Wang et al., 2013). Zn is often used to coat mild steel to reduce corrosion by minimum of 50%. It is also the fourth most used metal, with global manufacturing just below iron, aluminium, and copper. Furthermore, zinc and its corrosion products are less hazardous than cadmium and have been shown to be the best choice for corrosion-resistant coatings (Maniam & Paul, 2021). The high amount of zinc produced is used to protect iron and steel from corrosion (Marder., 2000). The more active zinc metal tends to corrodes over steel substrate by a cathodic reaction and preventing steel from anodic corrosion. Zinc coating on steel provide exceptional corrosion resistance in a variety of environments, including corrosive seawater and contact with a variety of natural and artificial compounds.

The application of zinc coating is wider in various industries, for instance, automotive, aerospace, building and construction, oil and gas, marine and etc.

Zinc coatings are commonly used to protect steel against water corrosion in two ways: barrier protection and galvanic protection. The zinc coating that isolates the steel from the corrosion environment, in barrier protection, will degrade before the corrosive environment reaches the steel. At ambient temperatures, zinc is less noble than iron and will sacrificially corrode to protect the substrate steel, even if some of the steel is exposed as scratches in the coating. There are several principal methods for zinc coating as shown in Table 2.1.

Table 2.1   Principal method for zinc coating(Kreysa et al., 2004)

Methods	Common thickness coating (μm)	Process Technology
Batch hot dip galvanizing	Less than 20	Immersion in liquid zinc bath
Continuous hot dip galvanizing	12 to 25	Passing through liquid zinc bath
Thermal spraying	80-200	Spraying of molten zinc
Electroplating	Less than 50	By electric current in aqueous electrolytes
Sherardizing	15-25	Diffusion steel at below melting temperature of zinc
Mechanical plating	10-20	By means of crystal balls
Zinc - powder coating	10-120	Through coating, rolling, spraying, immersing

2.6   Hot Dip Galvanizing

When the French chemist Malouin discovered the capability of coating iron and steel pieces with liquid zinc in 1741, he introduced hot-dip galvanizing technique. He detailed the technique in the same way as it is still done in wet galvanizing today. However, because there was no low-cost procedure for cleaning iron or steel surfaces at the time, it was not practical to use it on an industrial scale. After discovering the pickling technique for cleaning iron and steel surfaces, an engineer working in Paris named Stanislaus Sorel was the first to succeed in the practical use of hot dip galvanizing in 1836. On May 10, 1837, he received a patent for a method of preventing ferrous and steel parts against corrosion by cleaning them and immersing them in molten zinc (Kreysa et al., 2004).

The hot dip galvanization method is used to provides a combination of good qualities such as high mechanical strength, processability, lighter weight, resistance to corrosion and low cost. It is a useful corrosion-prevention technique since corrosion reduction not only prevents the loss of steel as a material, but also helps to resource conservation and waste avoidance. Material recycling contributes significantly to environmental conservation. Owing to its excellent corrosion resistance, hot dip galvanized steels have been widely employed in industrial industries such as vehicles, electrical home appliances, and construction (Shibli et al., 2015). Some researchers have improved the steel properties using hot dip galvanizing methods. For example, Yu et al., (2020) and Shibli et al., (2015) have developed the hot dip galvanizing process by controlling process parameter such as composition of bath, pre-treatment, dipping, annealing process to tune the structural characteristics. The development of desired hot dip coating properties may be achieved by tuning intermetallic and multiphase interdentrices.

There are three main stages in hot dip galvanizing process which is surface cleaning or treatment process (degreasing, pickling, fluxing), galvanizing and inspection process. The process flow chart of galvanizing is shown in Figure 2.3.
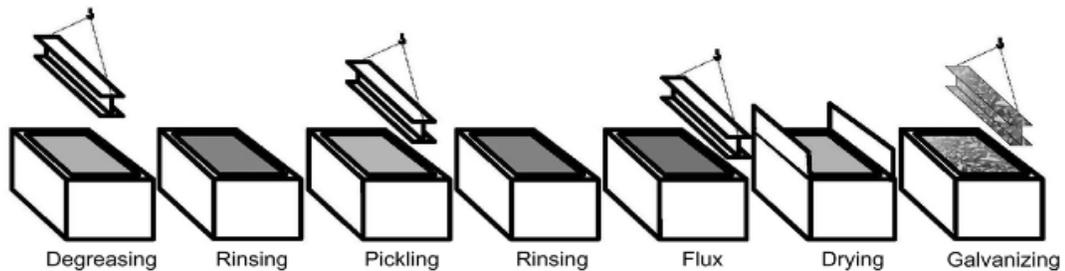
Figure 2.3   Process flow of galvanizing operation (Kuklík & Kudláček, 2016b)

Surface treatment is mandatory steps for the substrate before undergoing galvanizing process. The surface treatment process involves degreasing, pickling, and fluxing. After each time degreasing and pickling, the substrate needs to rinse thoroughly with distilled water before proceeding with other process. At the end of surface treatment or fluxing, the substrate required to completely dried followed by dipping into galvanizing bath.

Prior to galvanizing, the steel substrate must be cleaned of any pollutants and a rough surface must be created to ensure adequate adhesion of the galvanized layer. Synthetic greases, oils, residues of welding, and organic pollutants are among the contaminants that may be removed with a wet chemical technique. Caustic cleaning is almost like a wet surface preparation that is done using an alkali solution. For example, for washing or caustic cleaning, an 8% NaOH aqueous solution heated to $65°C$ for 10 minutes

is applied. Other forms of degreasing chemicals, depending on the type of pollution, might also be utilized.

The pickling treatment is used to remove surface scales that occur because of high-temperature operations like as rolling or welding. A dilute solution of heated sulphuric acid or hydrochloric acid is used as pickling agents. The use of 8% HCl as a pickling agent for steel substrate was discussed by the author Shibli et al., (2015). Notably, steel coupons could also be prepared by being pickled in 14% HCl at room temperature for 20 minutes. Picking inhibitors prevent steel from being attacked by mineral acid by reducing the formation of atomic hydrogen and decreasing the risk of hydrogen embrittlement failure (Shreyas et al., 2021).

The substrate is rinsed with distilled water after pickling. Finally, fluxing is done to remove oxides from the surface, prevent additional oxidation, and provide a smooth surface for uniform reaction. There should be specific requirements for the fluxing agent: to clean the sample surface and the molten zinc to cause the reaction to occur between zinc and steel; to prevent splattering when wet samples are dipped; producing thinner coatings; to reduce ash formation by reducing oxidation of the surface; to prevent overheating when dipping large sample or during "double dipping" and to minimize defects by preheating thin samples (Marder., 2000). In Arunima et al., (2020) study the steel samples were fluxed into 30 wt.% NH_4Cl solution to improve adhesion of molten zinc on steel surface.

Finally, the steel component is galvanized by immersing it in 98% pure molten zinc at $450^{\circ}C$. Zn-Fe intermetallic are formed when molten zinc combines with iron. Zinc is then progressively withdrawn from the bath and drained away using vibrating or centrifuging.

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Then it was cooled in air or quenched in water. The immersion period can be adjusted to control the thickness of the coating, which is made up of Fe-Zn alloy phases at the interface and a pure zinc top coating. Good cooling control is also required since the zinc might continue to react with the substrate, causing more alloying and reducing the coating quality. Once all done, the galvanized sample was carefully checked to ensure the zinc coating adhere perfectly on the steel.

2.7   Intermetallic phases form during hot dip galvanizing

When a ferrite substrate is dipped in molten zinc, metallurgical interactions between iron and zinc produce a heterogeneous composition of distinct phases, which is known as a hot dip galvanized coating. The phase diagram of Fe-Zn is shown in Figure 2.4. The coating is made up of an exterior layer of η-eta layer and interior layers of intermetallic iron and zinc phases such as zeta (ζ)) layer, delta (δ) layer and gamma (Γ) layer as shown in the Figure 2.5. These intermetallic layers are tougher than the underlying steel, therefore they offer a lot of protection against coating degradation (Shibli et al., 2015: Marder., 2000)
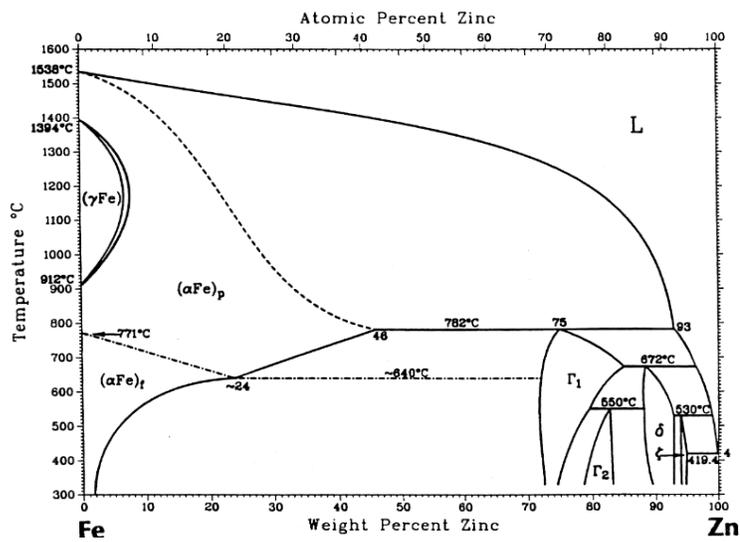
Figure 2.4   Phase diagram of Fe-Zn (Marder., 2000)

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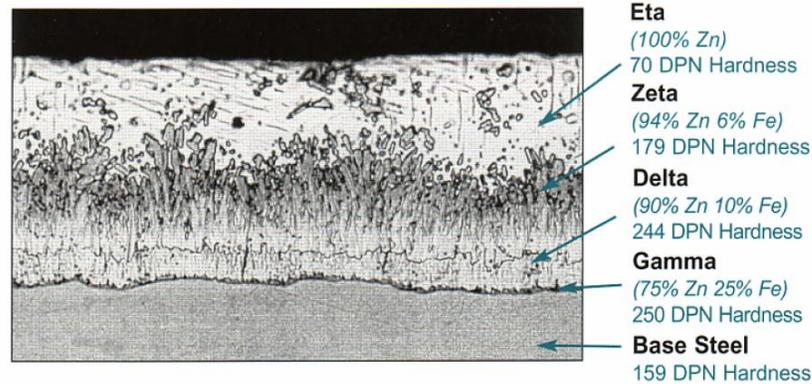
Figure 2.5   Intermetallic layers present in a conventional hot dip galvanized coating
(Yeomans, 2004)

The iron concentration of the zeta (ζ) phase, FeZn$_{13}$, is about 5-6% by weight. It is generated via a peritectic interaction between the delta (δ) phase and liquid zinc at approximately 530°C. The zeta (ζ) phase was discovered to occur between the free zinc eta (η) phase and the delta (δ) phase during controlled diffusion investigations in the absence of aluminium. The zeta (ζ) phase features a monoclinic unit cell and an atomic structure with an iron atom and a zinc atom at the vertices of a slightly deformed icosahedron surrounded by 12 zinc atoms. Icosahedra connect to create chains, which pack together in a hexagonal array.

FeZn$_{10}$, the delta (δ) phase, has a hexagonal unit cell and an iron content range of 7.0 to 11.5% by weight. At 665°C, it is made from another peritectic reaction, gamma (Γ) and liquid. The delta (δ) phase was previously divided into two morphologies: delta$_{1P}$, a palisade morphology obtained on the zinc-rich side, and delta$_{1K}$, a compact morphology obtained on the iron-rich side, both of which were discovered during long-term (4h) and high-temperature (553°C) immersions. Both morphologies are now known as delta (δ) phase since they share the same crystallographic structure. Only one delta (δ) phase

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morphology was documented for the short-term immersions encountered in galvanising (Marder, 2000).

Fe_5Zn_{21}, the gamma$_1$(Γ_1) phase, has a FCC lattice structure with a range from 17 to 19.5 wt.% iron content at 450°C. At approximately 550°C, it is formed through a peritectoid interaction between the gamma (Γ) and delta (δ) phases. The gamma$_1$(Γ_1) phase appears as a continuous layer between the gamma (Γ) and delta (δ) layers and may be created by heating at low temperatures for extended periods of time (Kuklík & Kudláček, 2016a). The Gamma$_1$ phase has the greatest microhardness values. At 450°C, the gamma (Γ) phase, Fe_3Zn_{10}, is BCC structure with an iron content ranging from 23.5 to 28.0 wt.%. It is formed through a peritectic reaction between a liquid iron and liquid zinc at 782°C and has a maximum solubility of Fe in Zn at 665°C at the delta (δ) phase peritectic temperature. The summary of intermetallic characteristics of Fe-Zn intermetallic phase of hot dip coating is shown in Table 2.2.

Table 2.2   Characteristics of Fe-Zn intermetallic phase of hot dip coating (Marder., 2000.; Shibli et al., 2015)

Phase	η	ζ	δ	Γ_1	Γ
Stoichiometry	Zn	$FeZn_{13}$	$FeZn_{10}$	Fe_5Zn_{21}	Fe_3Zn_{10}
wt.% of iron	0	5-6	7-11.5	17-19.5	23.5-28
Crystal structure	HCP	Monoclinic	Hexagonal	FCC	BCC
Atoms/unit cell	6	28	555	408	52

The generation of each phase in relation of Zn-Fe is shown in Figure 2.6. The formation of phases is shown in sequence from t_0 to t_4 according to its time. At t_0, there are no interaction occurs as no phases are found in t_0. As the time increases from t_0 to t_1, a new phase is generated which is zeta phase in the boundary between iron and zinc. At the alpha Fe/zeta boundary, zeta layer nucleation is followed by delta-phase formation (t_2). At the shortest reaction times, after 5 s, both zeta and delta phases formed a continuous layer, revealing that there was no apparent delay in their development. After 30 seconds of incubation, the gamma phase (t_3) was discovered. At the $zeta_1$/delta boundary, a second zeta layer ($zeta_2$) forms between 30 and 60 seconds of response time, t_4 (Jordan & Marder, 1997).
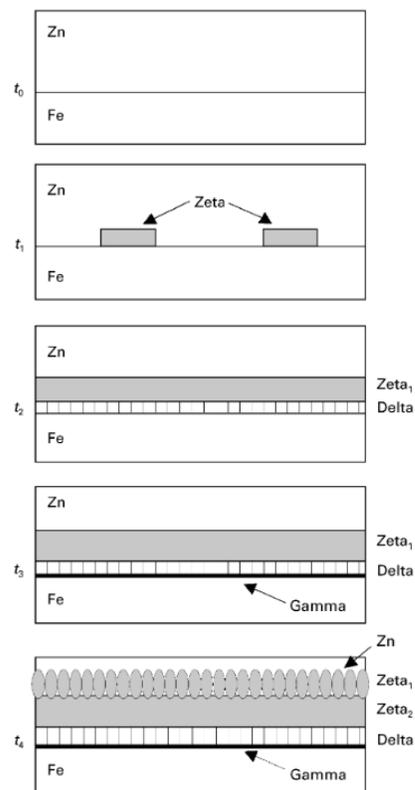
Figure 2.6   Schematic diagram of formation of Fe—Zn phase layer formation
corresponds to t_0 to t_4 (Jordan & Marder, 1997)

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2.8   Hot Dip Galvanizing parameter

Hot dip galvanizing method is most efficient coating method by controlling its parameter carefully. The most controlling parameters are composition of bath, withdrawal speed, immersion time and temperature. This parameter needs to be controlled is based on their desired properties.

2.8.1   Bath Composition

In general galvanizing, the steel is immersed into the zinc bath at high temperature causing chemical reaction between zinc and iron as forming into Zn-Fe intermetallic. This zinc coating acting as a sacrificial layer to prevent ferrous substrates from corrosion, they are prone to rapid corrosion in a short period of time, which has a significant impact on the overall performance and long-term durability of the coatings depending on the environment. Improvements in galvanizing processes are required to enhance the quality of coating and hence its longer the service life. To increase the performance of hot dip zinc coatings, many additives are added to the molten zinc bath. The addition of components like aluminium, magnesium, and nickel improves the galvanic performance of hot dip zinc coatings. The adding of lead and antimony in small amounts (0.004–0.200 %) might increase the coating uniformity and adhesion drastically. In molten zinc bath, aluminium is one of the most regularly utilized additions. Aluminium has the capacity to slow the rate of oxidation of molten zinc and so minimize the spangle size, improving the coating uniformity. The inclusion of aluminium in the molten zinc bath slows the development of the Fe-Zn intermetallic layer and lowers iron loss into the bath via the production of Fe_2Al_5 and $FeAl_3$ intermetallic layers during hot dip galvanization (Kuklík & Kudláček, 2016a).

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The addition of Al (0.15–0.2 wt.%) in molten zinc bath has been shown to suppress the formation of Fe-Zn intermetallic layer at the steel coating interface.

A study by Deepa et al., (2020) stated that the addition of 1 wt.% Al to the zinc bath increases the coating properties such as improving in galvanizing processes in terms of electrochemical and topographical characteristics hence it improves electrochemical performance of zinc coatings. The relation between the annealing environment and the microstructure of Zn-Al coated dual phase steel was investigated by Liu et al., 2009. As a function of the decrease in aluminothermic reaction during the hot-dip zinc process, they explored the coexistence of Fe-Al intermetallic compounds and needle-like Fe-Zn compounds. The growth of a continuous layer of the compound that is in equilibrium with the Zn bath may temporarily block the production of Fe-Zn compounds. This may result in the production of a zeta(ζ), delta(δ), or Fe_2Al_5 phase layer, depending on the Al concentration of the Zn bath. According to the Zn-Fe-Al ternary equilibrium phase diagram, the zeta(ζ) phase layer may develop epitaxially on the substrate at a very rapid pace, but it will be out of equilibrium with the substrate alpha (α) iron (Marder., 2000). Figure 2.7 shows ternary phase diagram for Zn-Fe-Al at 450°C.
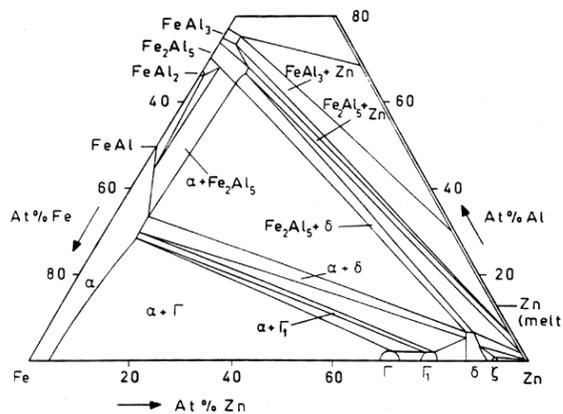
Figure 2.7   Phase diagram of Fe-Al-Zn at 450°C (Marder., 2000).

The interfaces will only approach equilibrium after all the Fe-Zn intermetallic have emerged. The delta (δ) phase, as well as a Fe_2Al_5 phase layer, will be in thermodynamic equilibrium with the alpha (α) iron sample. The formation of the potential inhibition intermetallic layer compound was determined by the Al concentration in the bath. Hence, the minimum Al content required for full inhibition by $Fe_2Al_5Zn_x$ (η) at 450°C is approximately 0.15 % Al, which is slightly higher than the concentration required for the transition from the delta (δ) phase to $Fe_2Al_5Zn_x$ (η), which is the thermodynamically stable phase (Marder., 2000). Figure 2.8 shows the possible formation of the inhibiting layers based on the composition of aluminium.
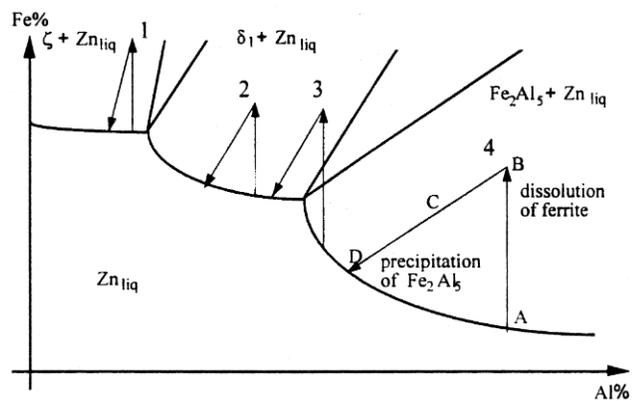
Figure 2.8   Mechanism of formation of the inhibiting layer (Marder., 2000)

The aluminium exists in two forms in the Zn bath which makes aluminium harder to control. The balance of the Al is present in the intermetallic particles and is dissolved in the liquid Zn phase. Aluminium in liquid solution, often known as "active" or "effective" aluminium, can block the Fe-Zn reaction during galvanizing. Because supersaturated Fe may mix with Zn and Al to generate Al-containing zeta (ζ), delta (δ), and $Fe_2Al_5Zn_x$ (η) particles, the quantity of Al in the liquid Zn is also substantially influenced by the amount of dissolved Fe in the bath.

2.8.2   Bath Temperature

The hot dipping bath is typically kept at a temperature of 440 to 460°C for pure molten zinc. When the temperature exceeds 480°C, most of the main chemical interactions between iron-zinc alloy coatings and molten zinc take place. Below 480°C, a compact Zn-Fe alloy forms on the steel surface, with alloying activity finally ending. Above this critical temperature, the alloy layer fragments, allowing zinc to pass into the metal, leading to the formation of high amount of slag. The bath temperature may be adjusted to modify the nature and thickness of the intermetallic layers to the application requirements. Mahdi et al., (2018) conducted study using hot dip galvanizing in the pure zinc bath using various temperature and time to compare the thickness of coating and the results of his studied is shown in the Table 2.3. From his studies, the temperature 550°C chosen as suitable temperature because it recorded the highest thickness of coating.

Table 2.3   The average thickness of coating with different immersion temperature
(Mahdi et al., 2018)

Temperature (°C)	Average thickness of coating (μm)
450	106
500	128
550	159
600	55
650	53

2.8.3 Immersion time

The alloying processes begin after the substrate has been immersed in the molten zinc bath for around 20 seconds. For optimal alloying processes, a length of 4-5 minutes is usually maintained. When heavier products are to be galvanized, they are submerged for extended periods of time to improve zinc penetration and total coating thickness. The dipping time may be adjusted to adjust the type and thickness of the intermittent layers as well as the coverage area. As zinc diffusion gets quicker with longer immersion time, the thickness of the generated zinc layer increases. When the time of immersion is very shorter approximately lesser than 30 seconds, the interaction between two metals changing phase from liquid-solid to solid-solid diffusion is lower. Hence, minimal thickness of zeta (ζ) phase is formed. As the immersion time increase as two minutes, the zeta (ζ) phase continuously grows thicker and new phase generated, delta (δ) phase. Thus, the overall thickness of coating will be increases. If the immersion time more than five minutes, its further increase the thickness of coating due to diffusion of returning into liquid-solid and phases which formed at faster rate. Therefore, the increasing immersion time results in continuous formation of diffusion in phases such as gamma, delta and zeta. Table 2.4 shows the relationship of immersion time and thickness of coating at various temperature by (Mahdi et al., 2018). From his studies, the longest time, 10 minutes immersion time recorded the highest thickness coating in bath temperature 500°C.

Table 2.4   The galvanizing thickness layer for different immersion time and temperature (Mahdi et al., 2018)

Bath Temperature (°C)	450	500	550	600	650
Time (min)	Thickness (µm)				
0.5	103.3	28.2	75.2	47.7	57.6
1	77.8	28.2	103.0	50.0	83.9
2	61.8	81.7	121.0	56.1	95.1
5	93.3	105.7	123.3	59.1	43.1
10	108.9	192.7	188.1	74.4	33.6

2.8.4   Withdrawal speed

When the interaction between iron and zinc is achieved, the steel substrate is removed from the bath. The thickness of hot dip galvanized coatings is determined by the rate of withdrawal. For the development of a clear shining zinc coating, an optimal withdrawal rate of 1.5m per minute is commonly maintained. A homogeneous unalloyed zinc layer is created if the withdrawal speed is too slow, while an uneven coating is formed if the withdrawal speed is too high. As a result, the withdrawal speed should be modified to adjust the type of coating, thickness, and surface texture (Shibli et al., 2015).

2.9   Creating of hydrophobic surface using hot dip galvanizing

Most of the galvanized steel may undergo corrosion due to highly exposed to the corrosive atmosphere. The corrosive ions such as chlorides are severely attacked and destroy the coated zinc layer until its expose to the steel surface. Therefore, many