
Sustainable Approaches for the Synthesis of Coatings on AZ31 Magnesium Alloy

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STATEMENT OF ORIGINALITY

I, **Chandra Sekhar Rauta**, registered on **July 6th, 2020** do hereby declare that this thesis entitled "**Sustainable Approaches for the Synthesis of Coatings on AZ31 Magnesium Alloy**" contains literature survey and original research work done by the undersigned candidate as part of Doctoral studies.

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ABSTRACT

Magnesium (Mg) alloys are attractive lightweight structural materials due to their low density, high specific stiffness, and good impact resistance. Their high chemical reactivity, however, results in poor corrosion performance and limits long-term use in aggressive environments. Electroless surface coatings have been widely reported as an effective route for enhancing the corrosion resistance of Mg alloys.

In the first major phase of this work, a quaternary electroless Ni-Zn-Cu-P coating was synthesized on Mg AZ31 alloy. The study focused on optimizing the coating parameters, specifically the concentrations of Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$), Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$), and Sodium hypophosphite ($\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$), using the Taguchi Design of Experiment (DOE) (L27 orthogonal array). The resulting coatings exhibited substantial improvements in microhardness, increasing from 87 $\text{HV}_{0.01}$ for the substrate to values as high as 650 $\text{HV}_{0.01}$ with a plating time of 10 min. To accurately predict microhardness based on input parameters, Artificial neural network (ANN) with feed-forward backpropagation algorithms were employed. The best-performing model (ANN 3-7-1) yielded a high regression coefficient ($R^2 = 0.982$), validating the effectiveness of machine learning in surface property prediction. Microstructural analysis confirmed the formation of amorphous, nodular coatings with fine elemental distribution and good adhesion to the substrate. It is identified that the coating fails beyond 10 min of plating time.

The second phase of this research investigated the underlying causes of coating failure and aimed to mitigate the environmental and safety concerns associated with conventional pretreatment methods that uses hazardous chemicals such as Hydrofluoric acid (HF) and Chromic anhydride (CrO_3). To achieve this, an eco-friendly, single-step pretreatment route based on aqueous Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) was employed to enable the deposition of Ni-W-P coatings. It was identified that the coating fails because of rapid evolution of hydrogen during plating as a result of high rate of deposition. The addition of Ammonia (NH_3) in the plating bath (T1) promoted higher deposition kinetics, whereas the NH_3 -free bath (T2) produced thicker, crack-free coatings. The defect-free T2 coatings exhibited superior mechanical performance and significantly improved corrosion resistance compared to both the substrate and T1

coatings. Nanoindentation tests revealed that the T2 coatings achieved a hardness of 7.73 GPa, with better elastic recovery and a higher H/Er ratio, indicating superior wear resistance. Electrochemical impedance spectroscopy and Tafel analysis further confirmed the enhanced corrosion protection offered by the T2 coatings, supported by greater charge transfer resistance and lower corrosion current density.

Since conventional electroless coatings do not inherently exhibit superhydrophobicity, their applicability remains limited for functional surface technologies such as self-cleaning, anti-icing, and anti-fogging. To address this limitation, in the third part of this work, a Superhydrophobic surface (SHS) is developed on AZ31 magnesium alloy using environmentally benign chemical method. The fabricated surfaces display a Cassie–Baxter wetting state with an apparent static contact angle (CA) of approximately 155° .

While droplet impact dynamics on SHS have been widely investigated at low-to-moderate Weber numbers, the low- We regime remains comparatively less understood. Here, we examine the impact behavior of water droplets on SHS in the low Weber number range ($We < 17$). Existing theoretical descriptions for the maximum spreading factor ($\beta_{\max}$) typically rely on scaling arguments and empirical correlations. In this study, an improved theoretical formulation for $\beta_{\max}$ is proposed by incorporating a geometric approximation of the droplet profile at maximum spread. The developed model shows good agreement with the present experiments and with existing models reported in the literature.

Detailed analysis of droplet morphology reveals the formation of short-lived toroidal configurations and the presence of two distinct minima in the height evolution, highlighting previously unreported features of inertial–capillary coupling at low impact energies. Additionally, a holding time (t_h) is introduced, defined as the duration for which the droplet remains at its maximum spread. The holding time is observed to decrease with increasing Weber number and is empirically described by $t_h = 5.2 - 2.84 We^{0.2}$. These results provide improved physical understanding of droplet spreading and recoil in the low- We regime and offer useful design guidelines for superhydrophobic coatings intended for low-energy liquid–surface interactions, including self-cleaning interfaces and microfluidic applications.

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LIST OF ACRONYMS

LIST OF SYMBOLS

Symbol	Description
σ	surface tension
ρ	density of liquid
μ	viscosity of liquid
θ	contact angle
D	Outer diameter of droplet
D_0	Initial droplet diameter
β	Spreading factor ($\beta = D/D_0$)
β_{max}	Maximum spreading factor ($\beta = D_{max}/D_0$)
ε	Height factor ($\varepsilon = h/D_0$)
$\varepsilon_{min,1}$	First minimum height factor ($\varepsilon_{min,1} = h_{min,1}/D_0$)
ε_{min}	Minimum height factor (global minima) ($\varepsilon_{min} = h_{min}/D_0$)
ε_{max}	Maximum height factor ($\varepsilon_{max} = h_{max}/D_0$)
t_c	Total contact time of droplet
t_s	Spreading time (time to reach maximum spreading)
t_r	Retraction time (time from maximum spreading to separation)
U_0	Impact velocity of droplet
v_s	Velocity of spreading
v_r	Velocity of retraction
c_r	Coefficient of retraction
E_k	Kinetic energy, subscripts 0 and f refer to the states before impact and at maximum spreading
E_s	Surface energy, subscripts 0 and f refer to the states before impact and at maximum spreading
E_v	Viscous dissipation
We	Weber number
Re	Reynolds number
Oh	Ohnesorge number

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
ANN	Artificial neural network
CA	contact angle
CAH	contact angle hysteresis
DI water	de-ionised water
DOE	Design of Experiment
DOF	Degrees of Freedom
EDS	Energy Dispersive Spectroscopy
LM	Levenberg-Marquardt
MAE	mean absolute error
MAPE	mean absolute percentage error
Mg	Magnesium
MS	Mean square
MSE	mean squared error
RMSE	root mean squared error
OCP	open circuit potential
SEM	Scanning Electron Microscopy
S/N ratio	Signal to noise ratio
SHS	Superhydrophobic surface
SS	Sum of Squares
WCA	water contact angle
XRD	X-ray Diffraction

LIST OF CHEMICALS

CH₃(CH₂)₁₆COOH Stearic acid

C₄H₄O₄ Maleic acid

CrO₃ Chromic anhydride

CuSO₄ · 5 H₂O Copper sulphate pentahydrate

FeSO₄ · 7 H₂O Iron (II) sulfate heptahydrate

HF Hydrofluoric acid

HNO₃ Nitric acid

H₂SO₄ Sulfuric acid

NaC₂H₃O₂ Sodium acetate

Na₃C₆H₅O₇ · 2 H₂O Trisodium citrate

Na₂CO₃ Sodium carbonate anhydrous

NaH₂PO₂H₂O Sodium hypophosphite

Na₂WO₄ · 2 H₂O Sodium tungstate dihydrate

NH₃ Ammonia

NH₄HF₂ Ammonium bifluoride

NiSO₄ · 6 H₂O Nickel sulfate hexahydrate

PdCl₂ Palladium chloride

ZnCl₂ Zinc chloride

ZnSO₄ · 7 H₂O Zinc sulphate heptahydrate

Part I

Background

INTRODUCTION

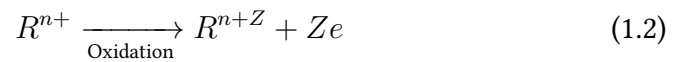
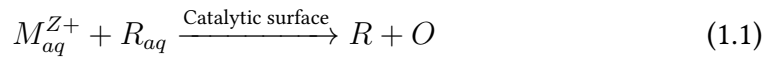
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This chapter introduces the basic ideas of surface engineering and explains why improving a material's surface is often essential for enhancing its overall performance. Since the surface is the part most exposed to wear, corrosion, and environmental damage, the chapter highlights how surface treatments can significantly extend the life of engineering components. It briefly reviews common surface-modification methods, with particular focus on electroless coating. The principles behind this technique, its chemical reduction process, uniform metal deposition, and advantages over conventional plating—are discussed in simple terms.

1.1 Background and Motivation

Surface engineering is a specialized area within materials science that aims to improve the performance of solid materials by modifying the characteristics of their surfaces. Although the internal bulk of a material provides its overall strength and structural support, it is the surface that directly confronts the environment and therefore experiences the highest degree of wear, corrosion, and mechanical stress. Because many forms of degradation—such as frictional wear, chemical corrosion, fatigue damage, and creep—originate at or near the surface, enhancing this region is often far more effective than altering the entire material. Surface engineering draws on a combination of chemical, mechanical, and electrical engineering principles to design protective layers or surface treatments that can extend service life while maintaining cost efficiency. The ultimate objective is to create surfaces that are more durable, more resistant to corrosion, and better suited to demanding service environments, without compromising the desirable properties of the underlying bulk material.

Among the various coating technologies; such as Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), electroplating, electroless coating, and spray coating; electroless coating has gained significant prominence due to its ability to produce uniform and reliable metallic deposits. In contrast to electroplating, which requires an external electrical current, electroless deposition operates solely through chemical reactions occurring within the plating solution [1, 2]. Metal ions are reduced by a suitable reducing agent, enabling the controlled deposition of metallic atoms onto the substrate surface.



Electroless coating, often described as autocatalytic deposition, begins with the activation of the substrate surface using an appropriate catalyst. This activation step generates the required potential for initiating metal deposition. During the redox reaction, the reducing agent (R^{n+}) donates Z electrons, reducing metal ions (M^{Z+1}) from the solution to form a solid metal layer on the substrate, while the reducing agent itself is oxidized to R^{n+Z} [2]. The overall autocatalytic process is represented in Eqs. (1.1)–(1.3), where M , R , and O denote the metal, reducing agent, and oxidized byproducts, respectively. This mechanism provides predictable coating rates, excellent surface uniformity, and improved resistance to corrosion and wear, establishing electroless deposition as a highly effective surface-modification technique for engineering applications.

1.1.1 Importance of Electroless Coating in Modern Industry

Electroless coating, particularly electroless nickel plating, has become increasingly important in modern industry due to its unique ability to deposit a uniform metal layer without using an external electrical current. This autocatalytic chemical process enables consistent coating thickness across complex geometries, including internal surfaces and sharp edges areas where traditional electroplating often fails. One of the key advantages of electroless coating is its exceptional corrosion and wear resistance [3–5]. Industries such as aerospace, automotive, oil and gas, and electronics rely on these coatings to protect critical components operating in harsh environments. For example, in the aerospace sector, electroless coatings help extend the service life of turbine blades, fuel system parts, and fasteners by resisting corrosion and reducing friction.

Electroless coatings also offer excellent adhesion and surface hardness, which are crucial for parts exposed to mechanical stress. They are especially valuable in precision engineering and tooling, where dimensional accuracy is critical. The process allows for the deposition of thin, even layers, ensuring parts meet tight tolerances without the need for extensive post-processing.

Additionally, electroless coating is compatible with a wide range of substrates, including metals[3, 5], ceramics[6], and certain plastics (with suitable pretreatment)[7, 8], making it highly versatile. It also supports the incorporation of materials like phosphorus or boron, enabling the tuning of properties such as hardness, magnetic behavior, and corrosion resistance.

As industries increasingly demand high-performance, reliable, and cost-effective surface treatments, electroless coatings stand out for their consistency, efficiency, and adaptability. With growing interest in automation and miniaturization, electroless technology continues to play a vital role in improving product durability, reducing maintenance costs, and enhancing functionality across diverse industrial sectors.

1.1.2 Advantages of Electroless Coating

Electroless coatings provide a range of advantages that make them highly valuable for protecting and enhancing engineering materials, especially in applications where uniformity, precision, and durability are essential. One of the most important benefits of electroless deposition is its ability to produce a consistent coating thickness across the entire surface of a component, regardless of its shape or complexity[1, 2]. Because the process relies on a chemically driven reduction reaction rather than an external electrical current, the coating can penetrate recessed areas, internal passages, sharp edges, and irregular contours with equal effectiveness[4]. This capability is particularly useful for components that cannot be uniformly coated by traditional electroplating or spray-based methods. In addition to uniformity, electroless coatings, especially electroless nickel, offer excellent mechanical and chemical properties. They provide high hardness, substantial wear resistance, and strong corrosion protection, making them suitable for harsh industrial environments or parts exposed to friction, chemicals, or fluctuating temperatures.

Another advantage of electroless coatings is the high degree of control over coating composition and thickness[9, 10]. By adjusting bath chemistry and operating conditions, it is possible to tailor the coating's microstructure and properties,

including hardness, ductility, and corrosion resistance. The process also supports the incorporation of alloying elements or ceramic particles[5], allowing for the creation of composite coatings with enhanced functional characteristics such as improved lubricity, magnetic properties, or thermal stability[11]. Electroless coatings generally exhibit excellent adhesion to the substrate due to the autocatalytic nature of the reaction, which helps form a strong metallurgical interface. Furthermore, the process is relatively simple, cost-effective, and suitable for batch or mass production without requiring complex electrical setups. Overall, the combination of uniform deposition, superior functional performance, versatility, and high reliability makes electroless coatings a preferred choice in applications ranging from automotive and aerospace components to electronics, precision machinery, and corrosion-sensitive alloys.

Additionally, electroless plating adheres well to a variety of substrates, including non-conductive materials (with surface activation), unlike electroplating, which requires conductivity. Overall, electroless coatings are ideal for high-performance, precision, and engineering-critical applications, where traditional coatings may fall short.

1.2 Wettability of Surface and its Importance

Wettability describes how readily a liquid spreads across or retracts from a solid surface[12], and it is largely influenced by the surface's chemical composition and microscopic texture[13]. This behavior is commonly evaluated through the water contact angle[14]: surfaces that encourage spreading are hydrophilic, while those that repel water are considered hydrophobic. In recent years, the concept of superhydrophobicity has gained significant attention. A Superhydrophobic surface (SHS) typically exhibits a contact angle above 150° and allows water droplets to slide off with almost no resistance. Such behavior arises from a combination of low surface energy materials and hierarchical surface structures, similar to those found on lotus leaves. When droplets roll across these surfaces, they pick up dust and contaminants,

naturally cleaning the material[15].

The development of superhydrophobic coatings has become increasingly important across scientific and industrial fields because of their ability to impart self-cleaning and protective properties. By minimizing the interaction between a surface and water, these coatings help prevent the build-up of dirt, organic matter, and chemical residues, which in turn reduces maintenance efforts and extends the service life of the underlying material. In metals such as Magnesium (Mg) alloys—known for their lightweight nature but sensitive to corrosion—superhydrophobic layers can act as a barrier that limits contact with moisture and aggressive ions. Beyond self-cleaning, SHS technology enables benefits in anti-icing[16], fluid drag reduction, and resistance to biological fouling[17]. Surfaces that shed water quickly also hinder ice formation, improve energy efficiency in fluid systems, and restrict the attachment of microorganisms. Because of this broad range of advantages, superhydrophobic coatings are increasingly viewed as a key strategy for enhancing durability, performance, and sustainability in modern surface engineering.

1.3 Mg AZ31 Alloy as Substrate

In the contemporary landscape of materials engineering, Mg and its alloys occupy a position of unique strategic importance. With a density of approximately 1.74 g/cm^3 , magnesium is the lightest structural metal available to industry, being roughly 33% lighter than aluminum and 75% lighter than steel [18]. This has made it a material of choice for "lightweighting" initiatives in the automotive, aerospace, and medical device sectors [19]. The drive to reduce fuel consumption and carbon emissions in transportation, and the demand for ultra-lightweight portability in laptops and smartphones, has catalyzed a massive surge in the application of magnesium alloys. Beyond gravimetrics, magnesium alloys offer excellent vibration damping, electromagnetic shielding, and high thermal conductivity [20–22].

However, magnesium is exceptionally vulnerable to corrosion due to its high chemical reactivity [23]. The very properties that make magnesium chemically

distinct also make it exceptionally vulnerable. Magnesium is chemically active, with a standard electrode potential of -2.37 V versus the Standard Hydrogen Electrode (SHE) [18]. It resides at the anodic end of the galvanic series, making it sacrificial to almost every other structural metal.

The motivation for applying electroless coatings to Mg alloys lies in extending the alloy's functional life and enabling its use in more demanding environments. By improving surface durability and reducing corrosion susceptibility, manufacturers can maintain Mg's lightweight advantage while overcoming its main weakness—chemical instability. This opens up new opportunities for lightweight structural components, housings, and connectors, particularly in automotive and aerospace sectors where weight savings translate directly into energy efficiency and performance gains.

Additionally, electroless coatings can serve as an effective base layer for subsequent painting or composite bonding, improving adhesion and aesthetic finish. As industries push for materials that balance performance, durability, and environmental resistance, electroless coatings on Mg alloys provide a cost-effective, scalable, and technically reliable solution. With further optimization in pretreatment and bath chemistry, this technique is poised to play a key role in the broader adoption of Mg alloys in high-performance applications.

Within this context, the present research focuses on two major innovations: the development of electroless alloy coatings with superior mechanical performance, and the introduction of an environmentally benign pretreatment method to replace hazardous chemical processes.

1.4 Aim of the Study

The aim of the present study is to develop and evaluate electroless and superhydrophobic coatings on AZ31 Mg alloy in order to enhance its surface integrity and functional performance. The research focuses on optimizing the electroless plating bath parameters using Taguchi analysis and systematically characterizing the re-

sulting coatings to understand their structural, mechanical, and corrosion-resistant properties. Surface morphology and phase composition are examined through SEM, EDS, optical microscopy, and XRD, while performance assessments are carried out using micro- and nano-hardness measurements, corrosion test, adhesion strength tests, and wettability analysis. Electroless coating is selected as the principal surface modification technique for its ability to deposit uniform, adherent metallic layers on Mg alloys, which are otherwise susceptible to rapid degradation. Superhydrophobic coating developed to improve water repellency for the self-cleaning applications. Additionally, the dynamics of water droplet impact on the treated surfaces are investigated to gain insights into their self-cleaning potential and durability. Overall, the study seeks to establish an efficient and sustainable coating strategy that can significantly extend the applicability of AZ31 Mg alloy in engineering environments.

1.5 Structure of the Thesis

The subsequent chapters of this thesis are structured as follows:

- Chapter 2** reviews the literature related to electroless coatings on Mg alloys, pre-treatment methods, and predictive modeling techniques.
- Chapter 3** details the experimental setup, materials used, and methods for coating synthesis, characterization, and testing.
- Chapter 4** discusses fundamentals of wettability, contact angle measurement, and the effects of surface roughness and chemistry on wetting behavior.
- Chapter 5** presents the results and discussion on the optimization of Ni-Zn-Cu-P coatings using Taguchi and ANN methods.
- Chapter 6** discusses the development and evaluation of eco-friendly Ni-W-P coatings, including microstructure, mechanical properties, and corrosion behavior.
- Chapter 7** presents the experimental investigation of droplet impact on SHS, including the experimental setup and analysis of the impact dynamics.
- Chapter 8** concludes the thesis with a summary of findings, contributions to knowledge, and recommendations for future work.

LITERATURE REVIEW

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Mg alloys are highly attractive for structural applications in industries such as automotive, aerospace, and electronics due to their excellent strength-to-weight ratio, and good thermal conductivity. Despite these advantages, Mg alloys exhibit poor corrosion resistance due to their highly negative standard electrode potential and the spontaneous formation of a loose and porous oxide layer. Surface modification is therefore essential to enhance the durability of Mg alloys in aggressive environments. Among various surface treatments, electroless nickel coating has gained attention due to its uniform deposition, independence from component geometry, and the superior corrosion and wear resistance of the resultant film. Unlike electroplating, electroless plating proceeds via autocatalytic chemical reduction, which allows for the deposition of nickel-phosphorus alloys without external current sources.

2.1 Electroless Coating on Magnesium

As outlined in previous chapter, electroless coatings have gained attention as an effective route to enhance the surface durability. Because this process develops a uniform coating layer that exhibits improved corrosion resistance, increased surface hardness, and better wear performance. Also, it develops consistent coating thickness across edges, recesses, and irregular geometries, which is difficult to achieve with electroplating.

Despite these advantages, electroless plating on Mg alloys faces several persistent challenges. The high chemical reactivity of magnesium, difficulty in establishing a stable catalytic activation layer, and rapid hydrogen evolution during deposition all complicate the process. Additionally, the pretreatment steps are often hazardous, highly sensitive, and require multiple stages. These factors can result in bath instability, reduced deposition rates, weak coating adhesion, and the formation of surface defects such as pores or pits. Furthermore, electroless baths generally have limited operational lifetimes and impose higher processing costs compared with traditional plating systems. Environmental and safety concerns also arise due to the reliance on complex reducing agents, stabilizers, and other chemical additives.

2.1.1 Challenges Associated with Electroless Coating on Magnesium

Applying electroless nickel (EN) coatings to magnesium substrates is inherently difficult due to the highly reactive nature of magnesium. A major obstacle arises from the rapid displacement reaction between magnesium and nickel ions in solution, expressed as: $\text{Mg} + \text{Ni}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Ni}$. This reaction leads to the formation of a loosely bonded, porous nickel layer that lacks adhesion and disrupts the onset of the desired autocatalytic deposition process. As a result, direct EN deposition on untreated magnesium surfaces is impractical. Comprehensive pretreatment steps are therefore essential to eliminate surface contaminants, dissolve unstable intermetallic phases, and establish a stable and catalytically active surface for coating initiation.

Despite the benefits, electroless plating on Mg alloys is technically challenging

[23] due to:

- Spontaneous formation of a porous oxide/hydroxide layer that hinders adhesion .
- High susceptibility to galvanic corrosion, especially under nickel coatings.
- Rapid dissolution of Mg in many plating baths.

These issues necessitate meticulous pretreatment procedures to enable successful and durable coating applications.

2.1.2 Pretreatment Strategies for Electroless Nickel Deposition

Pretreatment is a critical step in electroless nickel-phosphorus deposition on Mg alloys due to the inherently reactive nature of the substrate [24]. Mg surfaces are covered by a non-protective, porous oxide/hydroxide film that impairs coating adhesion and uniformity. Moreover, the microstructural heterogeneity and high dissolution rate of Mg in aqueous plating baths necessitate surface conditioning to achieve chemical and electrochemical stability. Effective pretreatment removes surface oxides, suppresses substrate degradation, and promotes uniform nucleation, ensuring the formation of adherent, pore-free coatings essential for corrosion and wear resistance. Without pretreatment, the integrity and functional performance of the electroless deposit are significantly compromised. The pretreatment strategies that are broadly adopted are zincating and fluoride activation [25, 26].

The traditional zincating approach involves sequential steps of cleaning, degreasing, acid pickling, zinc immersion, and copper plating prior to electroless deposition. Zinc provides a temporary barrier, improving coating uniformity and adhesion. However, this method is associated with several limitations. Poor adhesion is observed on alloys with high aluminum content. The process relies on cyanide-based copper solutions, raising environmental and safety concerns. Furthermore, non-uniform zinc distribution, particularly on β -phase regions, compromises coating integrity [27, 28].

To circumvent the need for cyanide and reduce the number of processing

steps, various direct electroless plating methods employing fluoride-based activation have been developed [29, 30]. This sequence typically began with alkaline cleaning then a chromic acid/nitric acid pickling/etching, followed by HF or Ammonium bifluoride (NH_4HF_2) activation. Treatment with HF or NH_4HF_2 forms a thin, adherent MgF_2 layer that acts as a barrier which slows the displacement reaction and provides a base for the subsequent nickel coating to anchor through mechanical interlocking for electroless deposition. Subsequently, alternative surface conditioning strategies emerged in the form of chemical conversion coatings. Pretreatments based on phosphate, stannate, rare-earth elements, titanium, zirconium, and molybdenum compounds were developed to generate low-solubility interfacial layers between the magnesium substrate and the surrounding environment. These conversion coatings are commonly employed as primer layers [31] and are frequently combined with HF activation to facilitate electroless coatings.

Phosphate-based pretreatments (phosphating) refers to the deposition of phosphate compounds, such as zinc phosphate, iron phosphate or strontium phosphate, on the base metal from the phosphating solution [32]. These layers enhance corrosion resistance, increase nucleation site density, and support better adhesion of the electroless coating. However, phosphating often requires multiple process steps and relatively complex chemical control [32, 33].

Rajabalizadeh and Seifzadeh used titanate conversion bath [34] and hexafluoroantimonic acid [35] limiting HF for the pretreatment in their studies, but the solutions contain fluorides in it and also Nitric acid (HNO_3) is used for etching.

Rare Earth Based Conversion Coatings also emerged as an alternative, as non-chromate pretreatment options, offer promising results as corrosion-resistant pretreatments [36]. These layers promote strong mechanical interlocking and electrochemical compatibility between the substrate and Ni-P coating. Studies demonstrate comparable or better corrosion resistance than traditional chromate pretreatments [37].

While effective, these methods suffer from safety concerns due to the use of

fluorides and toxic acids like CrO_3 , Palladium chloride (PdCl_2), Sulfuric acid (H_2SO_4) and HNO_3 . Moreover, the MgF_2 layer can act as a diffusion barrier, potentially limiting the coating's mechanical adhesion.

Huo et al. [38] used stannous chloride and HCl for the sensitization and PdCl_2 for the activation. Sudagar et al. [39] studied Ni-P deposition via a vanadium based coating as pretreatment. Yang et al. [40] used a molybdate based pretreatment.

As an alternative to conventional pretreatment, earlier studies had used Plasma Electrolytic Oxidation (PEO) followed by sensitization before coating [41–43]. PEO or Micro arc oxidation (MAO), operates above the dielectric breakdown potential, creating micro-discharges that form a dense, ceramic-like oxide layer. MAO layers are excellent bases for electroless plating because the plating solution infiltrates the pores, creating a "rivet" interlocking mechanism. Although effective, it requires high voltage and special equipment, limiting its widespread use. Although MAO pretreatment is free of CrO_3 and HF, it is extremely time-consuming and along with the MAO treatment, the pretreatment process for the electroless coating consists of alkaline cleaning, sensitization, and activation.

Apart from these above methods there are several studies that explore the electroless coating on Mg alloys through a chromium/fluoride free pretreatment. To avoid hazardous chemicals, some alternative methods have been explored by the researchers. Lei et al. [81] proposed an eco-friendly procedure with multiple steps for electroless plating of magnesium alloy, including degreasing under ultrasonic waves in isopropanol solution, alkaline washing in a special solution, acidic pickling in a solution containing phosphoric acid and sodium molybdate, activation in NH_4HF_2 solution, and finally nickel-phosphorus electroless plating in sulfate bath.

Furthermore, in many studies along with the chemical conversion, the substrate undergoes an activation process in solutions of HNO_3 , H_3BO_3 , HCl, and PdCl_2 , etc in the treatment process and these chemicals fall under Category 1 toxicity. The toxicity level and H-statements of the chemical compounds are mentioned in **Table A.2** as per their safety data sheets (SDS) by Regulation (EC) No 1272/2008.

2.2 Super Hydrophobic Coating on Magnesium Alloy

Electroless coatings are well known for providing high hardness and improved corrosion resistance; however, they generally do not impart superhydrophobic functionality. Mg alloys are widely considered for lightweight structural applications and biomedical components due to their favorable strength-to-weight ratio and biocompatibility. Despite these advantages, their usage is severely constrained by rapid degradation, which arises from their high chemical reactivity and poor stability in corrosive environments. An effective approach to mitigate this issue is the development of superhydrophobic coatings, which reduce the solid–liquid contact area and facilitate droplet roll-off, thereby limiting electrolyte residence time on the surface.

The fabrication of SHS on Mg alloys typically involves generating hierarchical micro/nano structures combined with a low surface energy modification layer, which together minimize interactions with water and physiological fluids [44]. Several methods have been explored for producing such surfaces, including electroless plating [45], electrodeposition [46], chemical vapor deposition (CVD) [47], **mao!** (**mao!**) [48], and wet chemical etching [49]. Nevertheless, many of these strategies face challenges due to the use of hazardous reagents, complex multistep processing, and concerns regarding environmental sustainability and large-scale implementation.

For example, Zhang et al. [50] developed an electroless Ni–B/GO coating on AZ91 Mg alloy that demonstrated favorable hydrophobic behavior; however, the procedure relies on toxic chemicals such as nickel chloride, raising environmental and handling concerns. Likewise, Zhang and Chen [51] produced superhydrophobicity using Zn–Ni electrodeposition followed by chemical dealloying, but this approach required the use of potassium fluoride. Wan et al. [52] reported a wet chemical route for fabricating superhydrophobic coatings on AZ31 alloy through sequential immersion in HF, H₂SO₄, and hydrogen peroxide (H₂O₂), followed by stearic acid modification. Although the surface exhibited desirable roughness and wettability, the involvement

of highly corrosive and toxic acids such as HF and H₂SO₄ introduces serious safety risks and environmental concerns.

2.2.1 Wettability and Droplet Impact

When a liquid comes into contact with a solid surface, the initial gas-liquid and gas-solid interfaces are replaced by a solid-liquid interface, a process referred to as wetting. Wetting describes the ability of a liquid to maintain contact with a solid surface, governed by intermolecular interactions between the two. This process is determined by the balance between adhesive and cohesive forces. Adhesive forces between the liquid and the surface promote droplet spreading, while cohesive forces within the liquid favor the droplet's spherical shape[53].

The wettability of a solid surface is governed mainly by its surface chemistry and morphological structure [54–56]. Conventionally, surfaces exhibiting a static contact angle (CA) below 90° are classified as hydrophilic, whereas those with CA above 90° are hydrophobic. Surfaces with CA exceeding 150° are categorized as Superhydrophobic surface (SHS). Such SHS display extremely low wettability and typically exhibit minimal contact angle hysteresis. Compared to hydrophilic surfaces, SHS have attracted considerable research interest owing to their broad technological relevance. Their utility has been demonstrated in diverse applications, including reducing pesticide or raindrop retention on plant leaves in agriculture [57], mitigating icing on aircraft fuselages in aerospace systems [58], functioning as antifog coatings for automotive glass [59], and suppressing rust-related electrical short circuits in electronic devices [60].

Droplet impact on solid surfaces is a common phenomenon[61] and holds significant relevance across various industries. The outcome of a droplet impacting on a surface; whether it bounces, spreads, or splashes; is largely determined by the surface's wetting characteristics. For instance, a water droplet striking a hydrophilic surface typically deposits, while on a hydrophobic or SHS, it may deposit, bounce, or splash depending on the impact velocity [62]. Splashing arises from the breakup

of a fine liquid sheet that is ejected radially along the surface.

Typically, a bouncing droplet undergoes three stages during impact: spreading, retraction, and separation. In the spreading phase, the droplet gets compressed and flattens to its maximum diameter, reaching a minimum height. During retraction, the droplet begins to pull inward; and in the separation phase, rises to a maximum height before the droplet lifts off from the surface. Key parameters for evaluating the dynamic behavior of droplet impact include the spreading factor ($\beta = D/D_0$), the height factor ($\varepsilon = h/D_0$), and the contact time (t_c), where D and h are the instantaneous droplet diameter and height, respectively. Each parameter plays a critical role in determining surface performance in practical scenarios.

2.2.2 State of the Art in Droplet Impact on SHS

When a liquid droplet impacts a surface, complex interfacial dynamics unfold, governed primarily by inertial, capillary, and viscous forces. These interactions are generally characterized in terms of dimensionless numbers; Weber number ($We = \rho U_0^2 D_0 / \sigma$), Reynolds number ($Re = \rho U_0 D_0 / \mu$), and Ohnesorge number ($Oh = \sqrt{We} / Re$). Here, ρ is the density, U_0 is the impact velocity, D_0 is the initial droplet diameter, σ is the surface tension, and μ is viscosity of liquid. SHS, which exhibits very low wettability (contact angle, $\theta > 150^\circ$) and low contact angle hysteresis, have been widely studied for their unique impact behavior. These surfaces are of particular interest due to their self-cleaning, antifogging, and anti-icing properties [16, 17, 63].

Substantial studies[64–75] have investigated the behavior of droplets impacting SHS, especially focusing on spreading dynamics, contact time, and rebound phenomena. Various studies had established models for maximum spreading factor (β_{max}) based on scaling laws[64–67] and energy conservation[68–73]. Richard et al.[74] proposed a velocity-independent scaling law for contact time ($t_c = (2.6 \pm 0.1) \sqrt{\rho D_0^3 / 8\sigma}$) and found that t_c varies with droplet size. Later, Chen et al.[75] and Yang et al.[67] in their study discovered that the t_c decreases with U_0 for

very low We . Other works have examined the influence of surface microstructure formed by coatings [16, 76], nano-texturing[77–80], and substrate flexibility [81, 82].

Since the impact dynamics is generally characterized by We and Re , various empirical correlations have been established for β_{max} in terms of We and Re [72, 83]. These empirical correlations are formulated considering a large number of experimental[66, 76, 84] and numerical[76, 81] data statistically without considering the surface wettability and energies associated. Hence a theoretical analysis is required to obtain in depth physical insight in the droplet dynamics. Of which, the conservation of energy approach is used predominantly. The energy conservation approach incorporates balance between the kinetic energy, surface energy, and viscous losses. Previous works[68–73] that established/developed theoretical models, are distinguishable from each other on the basis of the approximation of surface energy or viscous losses. The basic models for β_{max} considering different geometry approximations are presented in Eqns.(2.1)–(2.3) [68, 70, 73].

$$\frac{3We}{2Re}\beta_{max}^4 + (1 - \cos\theta)\beta_{max}^2 - \left(\frac{1}{3}We + 4\right) = 0 \quad (2.1)$$

$$(We + 12)\beta_{max} = 8 + \left[3(1 - \cos\theta) + 4\frac{We}{\sqrt{Re}}\right]\beta_{max}^3 \quad (2.2)$$

$$(We + 12)\beta_{max} = 1.302 + [2.841 + 3(1 - \cos\theta)]\beta_{max}^3 + \frac{1.29We}{\sqrt{Re}}\beta_{max}^{4.454} - 0.947\sqrt{9\beta_{max}^6 - 20.64\beta_{max}^3} \quad (2.3)$$

Where the droplet is assumed to be a cylindrical disk at its maximum spread in Eqns.(2.1)[68] and (2.2)[70]. Eqn.(2.3)[73] assumes the droplet to be a lamella surrounded by a rim, whose cross section presents one quarter of ellipse. However, most of these studies [65, 70, 72] have concentrated on moderate-to-high We ($We > 20$) considering viscous dissipation. Conversely, the low We regime ($We < 20$), where surface tension force is more significant, remains comprehensively unexplored. Ex-

isting studies[67, 84, 85] in this regime often focus on spreading behavior (β_{max}) via empirical correlations. Hence it is necessary to fill up this gap by studying on theoretical analysis for impact dynamics at low We .

In the present work, we address this gap by elucidating several previously under-reported aspects of droplet impact on SHS at low We . Specifically, we report three key findings that advance current understanding of inertial-capillary interactions in this regime. First, we identify and characterize two distinct minima in the height evolution of the droplet during spreading. Second, we introduce and quantify the holding time (t_h) over which the droplet maintains its maximum spread before initiating retraction. This timescale is shown to exhibit a decreasing trend with We , revealing new temporal dynamics in the contact phase. Lastly, we proposed an improved geometric approximation for β_{max} in the theoretical framework of energy conservation model. These contributions offer new physical insights into the morphological transitions and rebound dynamics of water droplets impacting SHS under low We conditions.

2.3 Research Gaps

1. Development of a defect free electroless coating:

Electroless coatings on Mg alloys commonly exhibit defects such as micropores and pits, which act as initiation sites for coating degradation and eventual failure through delamination. Therefore, it is essential to systematically investigate the mechanisms responsible for pore/pit formation and to develop strategies for producing defect-free electroless coatings.

2. Environmental Concerns in Synthesis of coatings:

Conventional pretreatments involve toxic chemicals like HF and CrO_3 . While some alternatives exist, comprehensive evaluations of one-step, green pretreatment strategies remain underexplored and are not widely adopted in industrial settings.

3. Proper adhesion of the coatings on substrate:

Although a lot of research has been done on synthesis of electroless coating on Mg alloy, in many cases the adhesion of deposits are not adequate and in some cases there are porosity observed on the coatings.

4. Optimization of process parameters:

Systematic optimization of key process parameters is required to achieve improved coating quality and enhanced performance.

5. Characterization of coatings:

A comprehensive characterization of the deposited coatings is required to quantify coating quality and performance. This includes surface and microstructural analysis using techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD), along with performance evaluation through micro/nano-hardness, corrosion resistance, and coating adhesion strength measurements.

6. Fabrication of superhydrophobic coating:

Electroless coatings generally lack superhydrophobic behaviour, which restricts their potential use in advanced functional applications such as anti-icing, self-cleaning, and anti-fogging surfaces. Therefore, developing a Superhydrophobic surface (SHS) remains an important research gap.

7. Understanding the droplet impact on SHS at low We ($We < 20$):

While droplet impact dynamics on SHS have been widely investigated at moderate and high impact conditions, the low We regime ($We < 20$) remains comparatively underexplored. In this regime, the evolution of interfacial morphology during spreading, retraction, and lift-off is not yet well established. Therefore, a systematic investigation is required to quantify impact outcomes and to correlate key response metrics, such as the spreading factor (β), height factor (ε), and contact time (t_c), with We .

8. Improvement of theoretical model for β_{max} at low We :

Existing models for β_{max} are largely formulated for $We > 20$, where viscous effects dominate. However, the low- We regime, governed primarily by cap-

illary forces, remains insufficiently understood and is often described only through empirical fits. Therefore, a physics-based theoretical model for β_{max} in the low- We regime is still needed.

2.4 Research Objectives

The overarching aim of this research is to enhance the mechanical and electrochemical performance of Mg AZ31 alloy through innovative surface engineering approaches. The specific objectives include:

1. To identify the mechanisms responsible for pore/pit formation in electroless deposits and establish routes for defect suppression.
2. To synthesize a defect free electroless coating on AZ31 Mg alloy and optimize key process parameters using Taguchi-based DOE.
3. To develop a sustainable pretreatment protocol using hazard-free chemicals as alternatives to HF and CrO_3 .
4. To characterize coating morphology, phase constitution, and elemental distribution using SEM, XRD, and EDS, and to evaluate functional performance via hardness, corrosion, and adhesion tests.
5. To fabricate a chemically safer SHS on AZ31 alloy using hazard-free reagents.
6. To examine droplet impact dynamics on the prepared SHS and develop an improved theoretical model for β_{max} .

2.5 Scope of This Thesis

Magnesium (Mg) alloys offer significant potential as lightweight structural materials owing to their low density and high specific mechanical performance. However, their practical deployment in long-term engineering applications remains strongly constrained by poor corrosion resistance in chemically aggressive environments. The present thesis addresses this critical limitation through the development of functional surface modification strategies, with emphasis on electroless coatings and environmentally benign surface engineering routes for AZ31 Mg alloy.

This work develops a quaternary electroless Ni-Zn-Cu-P coating system aimed at enhancing surface mechanical properties and corrosion resistance. Coating parameters are optimized using Taguchi design of experiments (L27 orthogonal array), focusing on the influence of key bath constituents and plating conditions on coating quality and hardness. The microstructural and elemental distribution of the coatings are investigated, and a processing limit associated with coating instability at extended plating duration is identified.

The scope further includes investigating the mechanisms responsible for coating failure, particularly the role of hydrogen evolution during rapid deposition, which contributes to coating defects such as cracking and delamination. To address environmental and safety concerns associated with conventional pretreatments, an eco-friendly single-step aqueous iron sulfate pretreatment route is proposed for enabling electroless Ni-W-P coatings on AZ31. The influence of bath modification on deposition kinetics, defect formation, and coating integrity is systematically assessed. The coatings yield superior hardness, good adhesion, and corrosion protection.

Since electroless coatings do not intrinsically provide superhydrophobicity, the thesis also extends toward multifunctional surface technologies. An environmentally benign chemical method is employed to fabricate SHS on AZ31 alloy with CA > 155°. The behavior of water droplet impact on these surfaces is examined in the low We regime, which remains less explored in existing literature. An improved theoretical formulation for β_{max} is proposed based on geometric approximation of the droplet profile at maximum deformation. Detailed droplet morphology analysis reveals transient toroidal configurations and dual minima in height evolution, and a holding time parameter at maximum spread is introduced and correlated with We . These findings provide new physical insight and design guidelines for superhydrophobic coatings intended for low-energy liquid–surface interactions.

Part II

Methodology and Theory

MATERIALS AND METHODS

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This chapter outlines the materials, preparation methods, and experimental procedures employed in the electroless coating study. It details the substrates and chemicals used, surface preparation techniques, and the formulation of electroless plating baths. The chapter also describes the characterization techniques used to analyze coating morphology, composition, structure, and performance, including SEM, EDX, XRD, AFM, hardness, corrosion, and wear testing. Finally, it presents the statistical design methods applied, such as Taguchi and ANOVA, to optimize the process and analyze the experimental results systematically.

3.1 Materials Used

This section outlines the primary materials involved in this study, including the metal substrate and the various chemicals utilized during surface treatment and coating processes.

3.1.1 Substrate

Magnesium (Mg) and its alloys are increasingly favored in automotive, aerospace, biomedical, and electronics industries due to their exceptional strength-to-weight ratio, high specific stiffness, and excellent damping capabilities [86–88]. However, the widespread application of Mg alloys remains constrained by their inherently poor corrosion resistance and limited wear durability [89, 90]. These drawbacks necessitate the development of robust surface modification techniques that can not only enhance mechanical and electrochemical performance but also meet the growing demand for sustainability in materials processing. Electroless plating has emerged as one of the most promising surface engineering strategies to address these limitations [33, 91]. In this study, Mg AZ31 alloy is used as substrate.

3.1.2 Chemicals

The list of all the chemicals used in the research work and their corresponding purity are listed below:

- Ammonia (NH_3)
- Ammonium bifluoride (NH_4HF_2)
- Chromic anhydride (CrO_3)
- Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)
- Hydrofluoric acid (HF)
- Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$)
- Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$)
- Nitric acid (HNO_3)
- Maleic acid ($\text{C}_4\text{H}_4\text{O}_4$)

- Sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$)
- Sodium carbonate anhydrous (Na_2CO_3)
- Sodium hypophosphite ($\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$)
- Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$)
- Stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$)
- Trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2 \text{H}_2\text{O}$)
- Zinc chloride (ZnCl_2)
- Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$)

3.2 Surface Preparation

The preparation of substrates for electroless coating involves a precise and systematic series of steps designed to ensure a clean, uniform, and reactive surface suitable for successful metal deposition. Proper surface conditioning is essential to achieve good adhesion, consistent thickness, and desirable coating properties.

In this procedure, sheet metal specimens were first mechanically cut into square pieces measuring $20 \text{ mm} \times 20 \text{ mm}$. The cut samples were then polished mechanically to produce smooth and uniform surfaces. Polishing was performed using emery papers of successively finer grit sizes, starting from 220 grit and progressing through to 2000 grit. This step effectively removed surface irregularities, scratches, and native oxide layers. After polishing, the samples were subjected to ultrasonic degreasing in ethanol to eliminate residual grease, oil, and particulate contaminants.

Following degreasing, the samples underwent an etching treatment in a suitable acidic solution. The etching process served to further clean the surface, increase surface roughness at the microscopic level, and prepare the substrate for activation. This was immediately followed by an activation step, where the etched specimens were immersed in a catalytic solution to create active sites on the surface. These active sites are crucial for initiating the electroless deposition reaction. After each individual step; polishing, degreasing, etching, and activation; the samples were thoroughly rinsed with de-ionised water (DI water) to remove residual chemicals

and prevent cross-contamination between treatment baths. Rinsing was performed promptly and effectively to ensure that no intermediate residues interfered with the coating quality.

The complete set of processing steps, along with specific operating parameters such as reagent composition, immersion durations, and temperatures, is detailed in following sections. Adhering strictly to these procedures is essential for achieving reliable and reproducible results in the electroless coating process.

3.3 Formulation of Plating Baths

The formulation of a coating bath plays a pivotal role in determining the microstructure, mechanical performance, and functional characteristics of the final deposited layer. In general, an electroless plating bath is composed of metal ion sources, a chemical reducing agent, complexing agents, stabilizers, and pH regulators, each selected and balanced according to the specific requirements of the coating system.

3.3.1 Formulation of Electroless Plating Baths

Metal salts serve as the source of metallic constituents that are to be deposited on the substrate. Reducing agent facilitates the chemical reduction of metal ions in solution, enabling their deposition without the application of external current. Complexing agents are included to regulate the availability of free metal ions, ensuring their gradual and uniform release, which is essential for consistent deposition rates. Stabilizers are added in trace amounts to suppress spontaneous decomposition of the bath, thereby enhancing its longevity and operational reliability. pH regulators are employed to maintain the bath within a defined pH range, as the deposition kinetics and coating quality are highly sensitive to pH variations.

The process parameters, such as bath composition, temperature, pH, and deposition time, must be meticulously optimized to produce coatings with desirable attributes such as uniform thickness, high adhesion, enhanced hardness, and corrosion resistance. The formulation strategy also considers environmental and safety

Table 3.1: Detailed processes with their working conditions for Ni-Zn-Cu-P coating.

Process	Chemical	Conc.	Operating Condition
Ultrasonic Cleaning	Acetone		10 min, RT
Etching	HNO ₃	70 mL/L	60 s, RT
Acidic activation	C ₄ H ₄ O ₄	4 g/L	150 s, RT
Electroless coating	NiSO ₄ · 6 H ₂ O	25–35 g/L	Temp = 70 ± 2°C, Time = 600 s, pH = 9.8 ± 0.2
	ZnSO ₄ · 7 H ₂ O	2–3 g/L	
	CuSO ₄ · 5 H ₂ O	0.2 g/L	
	NaH ₂ PO ₂ H ₂ O	30–40 g/L	
	NaC ₂ H ₃ O ₂	45 g/L	
	NH ₄ HF ₂	8 g/L	
	HF	12 mL/L	
	NH ₃	pH regulator	
	Thiourea	1 ppm	

aspects, particularly in the selection of chemicals to minimize toxicity. This foundational framework provides the basis for tailoring specific bath compositions, such as those used for ternary or quaternary electroless coatings, which are discussed in the subsequent sections. The details of coating process, bath composition, and working conditions for Ni-Zn-Cu-P and Ni-W-P coatings are provided **Table 3.1** and **Table 3.2**, respectively.

3.3.2 Formulation of Hydrophobic/Super-Hydrophobic Plating Bath

The coating bath for fabricating Superhydrophobic surface (SHS) on AZ31 Mg alloy was formulated via a solution-based chemical method at 65°C. Prior to coating, the alloy substrates are mechanically polished and ultrasonically cleaned in acetone to remove surface contaminants; no etching or chemical pretreatment is applied, distinguishing this method from conventional electroless coatings. The coating

Table 3.2: Detailed processes with their working conditions for Ni-W-P coating.

Process	Chemical	Conc.	Operating Condition
Ultrasonic Cleaning	Ethanol		10 min, RT
Pretreatment	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	0.1 M	20–25 min, RT
T1 coating	$\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$	25–35 g/L	Temp = 50–70°C, pH = 10 ± 0.3 , Time = 25–55 min
	$\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$	2–3 g/L	
	$\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$	30–40 g/L	
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2 \text{H}_2\text{O}$	45 g/L	
	Na_2CO_3	12 mL/L	
	NH_4HF_2	8 g/L	
	NH_3	pH regulator	
T2 coating	$\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$	25–35 g/L	Temp = 50–55°C, pH = 8 ± 0.3 , Time = 2 hour
	$\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$	2–3 g/L	
	$\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$	30–40 g/L	
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2 \text{H}_2\text{O}$	45 g/L	
	Na_2CO_3	12 mL/L	
	NH_4HF_2	8 g/L	

solution is prepared by dissolving Stearic acid (0.1 M) in ethanol and Zinc chloride (0.1 M) in de-ionised water. The Zinc chloride solution was then added dropwise to the stearic acid solution under constant stirring until a volumetric ratio of 1 : 4 (Zinc chloride : Stearic acid) is achieved, forming a stable precursor solution. Cleaned substrates are immersed in this solution for 1.5 h, facilitating the formation of a hydrophobic layer. This formulation enabled the deposition of zinc–stearate coordination complexes, crucial for achieving low surface energy and hierarchical surface morphology necessary for superhydrophobicity.

3.4 Characterization Techniques Used

This section presents the characterization techniques used to evaluate the structural, mechanical, and electrochemical properties of the electroless coatings. Scanning Electron Microscopy (SEM) is employed to investigate the surface morphology and reveal details of the coating's microstructure, while Energy Dispersive Spectroscopy (EDS) provides qualitative and quantitative information about the elemental composition. X-ray Diffraction (XRD) is used to identify the crystalline phases and to assess the structural integrity of the coatings. Mechanical properties are examined through Vickers microhardness testing, which determines the hardness and uniformity of the deposited layers. Corrosion resistance is assessed using electrochemical methods, which offer insight into the coating's protective performance in corrosive environments. Adhesion strength is evaluated by both pull-off and scratch tests to determine the coating's bonding capability and its resistance to mechanical failure. Each of these techniques is discussed in detail in the following subsections to provide a comprehensive understanding of the coating performance.

The surface and cross-sectional morphologies of the samples were characterized by SEM (Model: ZEISS EVO-MA10). The elemental composition of the samples was evaluated using EDS (Energy resolution: ≤ 125 eV), which was coupled with SEM. To examine the atomic structure of the coatings, an XRD (Bruker, D8 Advanced, 30 kV, 30 mA Cu anode) emitting Ni-filtered Cu-K radiation ($\lambda = 1.540598\text{\AA}$) was used to generate an XRD pattern of the samples with a scanning range of 20 to 80°. The optical images were taken using a microscope (Olympus BX53M, attached with Streambasic 2.0 software).

3.4.1 Micro and Nano Hardness

Vickers microhardness testing is a widely employed technique for assessing the hardness of materials by evaluating their resistance to localized plastic deformation under a low applied load. This method is particularly suited for thin films, surface coatings, and micro-scale features. A diamond indenter with a pyramidal geometry

with a 136° face angle is pressed into the surface of specimen under a controlled load. Typically, the load is set between 10 to 100 gf, depending on the thickness. The load is maintained for a specific dwell time ≈ 10 to 15 sec, to ensure consistent indentation. Upon load removal, the diagonals of resulting impression are measured using optical microscopy, and the Vickers hardness number (HV) is then calculated using $HV = 1.8544P/d^2$, where P is the applied load in kgf and d is the average diagonal length in mm. All measurements in this thesis work are carried out on a UHL-VMHT micro-indentation hardness tester.

To accurately measure the microhardness of electroless coatings without interference from the underlying substrate, it is essential to ensure that the indentation depth (h_i) remains below 10 % of the coating thickness[92]. This criterion prevents the indenter from penetrating through the coating and influencing the measurement with the substrate's mechanical properties. Oraon et al. [93] established a geometric correlation between h_i and d , given by $h_i = d/2\sqrt{2} \tan 68^\circ \approx d/7$. This relationship enables estimation of the indentation depth based on the measured diagonal length, thereby facilitating the appropriate selection of applied load to maintain the indentation within allowable depth range.

The nanoindentation tests of coatings were conducted using a Hysitron nanoindenter equipped with a standard Berkovich tip. The experiments were performed on the polished coating cross-section with a loading rate of $300 \mu N s^{-1}$, with a peak load fixed at 10 mN. The Oliver and Pharr method was employed to determine the values of hardness and Young's modulus from load versus indentation depth curves.

3.4.2 Corrosion

Electrochemical corrosion studies are conducted using a potentiostat (Metrohm μ Stat 400i) in a 3.5 % NaCl solution at ambient temperature and atmospheric pressure conditions. A conventional three-electrode configuration was employed, consisting of an Ag/AgCl reference electrode, a graphite counter electrode, and the test specimen as the working electrode with an exposed surface area of 1 cm^2 . Prior to

polarization tests, specimens were immersed in the NaCl solution for 30 minutes to reach a stable open circuit potential (OCP). Potentiodynamic polarization measurements were subsequently performed over a potential range extending ± 350 mV from the stabilized OCP, employing a scan rate of 2 mVs^{-1} . Electrochemical impedance spectroscopy (EIS) analyses were conducted by applying a sinusoidal perturbation signal with an amplitude of 5 mV RMS over a frequency range of 10^{-2} to 10^5 Hz, recording 10 measurement points per frequency decade.

3.4.3 Adhesion Tests

The adhesion strength between a coating and its substrate directly affects the durability and overall performance of the coated surface. In this study, adhesion strength was assessed using two distinct methods. The pull-off adhesion test, performed following ASTM D4541 [94], quantitatively measures the coating's adhesion strength by applying a tensile force perpendicular to the substrate. Additionally, the tape-test adhesion method, conducted according to ASTM D3359 [95], qualitatively evaluates adhesion by examining the coating's resistance to peeling after adhesive tape removal. These tests collectively provide a comprehensive understanding of coating adhesion, offering both numerical data and qualitative insights into coating-substrate interactions and coating durability.

Pull-off Adhesion Test

The pull-off adhesion test quantitatively evaluates the adhesion strength between coating and base substrate. Tests in this study adhere to the ASTM D4541 standard. The methodology comprises following steps:

- 1. Surface Preparation**

The coated surface is initially cleaned thoroughly. Subsequently, an aluminum dolly (diameter: 25 mm) is adhered to the coated surface using an epoxy adhesive. The adhesive is then allowed to cure at ambient temperature for 48 hours to ensure adequate bonding strength.

- 2. Force Application**

A calibrated pull-off adhesion tester (Positest Adhesion Tester) applies a controlled perpendicular tensile force to the dolly. This force is gradually increased until detachment or failure occurs.

3. Failure Analysis

Upon failure, the maximum force required to detach the dolly is recorded. The failure mode is systematically categorized into one of three types:

- (a) **Adhesive failure:** Detachment occurs at the interface between the coating and substrate, or between coating layers.
- (b) **Cohesive failure:** The coating itself fractures internally.
- (c) **Substrate failure:** Fracture occurs within the substrate material itself.

Tape-test

The tape-test adhesion method provides a qualitative evaluation of adhesion for coatings by assessing their resistance to peeling upon removal of adhesive tape. This method is particularly applicable for thin coatings, typically in the micrometer thickness range, and is conducted following ASTM D3359 guidelines. The tape-test procedure comprises the following principal steps:

1. Surface Preparation

The coated surface is thoroughly cleaned to eliminate contaminants and ensure accurate test conditions.

2. Cross-cut Pattern Application

A precision cutting tool is utilized to create a standardized lattice pattern of intersecting parallel and perpendicular cuts penetrating through the coating down to the substrate.

3. Application of Adhesive Tape

Standardized adhesive tape (3M Scotch Tape) is firmly pressed onto the cross-cut region. Uniform adhesion of the tape is ensured by applying consistent pressure using a suitable tool such as a rubber eraser.

4. Removal of tape

After allowing sufficient dwell time, the tape is rapidly peeled from the coating

Surface of cross-cut area from which flaking has occurred						
Classification	5B	4B	3B	2B	1B	0B

Figure 3.1: Adhesion performance scale as per ASTM D3359.

surface at a standardized angle (typically around 180° or 90°), at a controlled, uniform speed.

5. Inspection and Evaluation

The tested area is inspected using microscope to identify any coating removal or detachment. Adhesion quality is classified according to the criteria established by ASTM D3359, as shown in **Figure 3.1**.

3.4.4 Wettability Test

The wettability of the specimens is characterized by static water contact angle (WCA) measurements using a contact angle goniometer (Model: HO-IAD-CAM-01A) shown in **Figure 3.2** at ambient conditions. DI water droplets ($\sim 7 \mu\text{L}$) are gently placed on the sample surface using a micro-syringe to avoid dynamic effects. The contact angle hysteresis (CAH) is determined using the tilting plate method: a droplet was deposited on the surface, and the stage was gradually tilted until the droplet began to move. The advancing and receding angles at the front and rear of the droplet were recorded at the onset of motion, and their difference was taken as the hysteresis value.

Uncoated AZ31 substrates exhibited a hydrophilic nature, with a mean CA below 80° , attributed to the native oxide layer and high surface energy of magnesium. In contrast, coated surfaces displayed significantly enhanced water repellency. The electroless coated surfaces exhibited hydrophobic with $\text{CA} \approx 100^\circ$ while the zinc-stearate coating samples showed a static contact angle exceeding 150° , confirming the achievement of superhydrophobicity.



Figure 3.2: Digital image of the experimental setup: (A) Laptop for controlling the imaging and dispensing system; (B) drop dispenser controller; (C) rigid workbench for stable mounting of components; (D) substrate holder; (E) high-resolution camera; (F) micro-syringe; (G) LED light source with diffuser for uniform back-lighting.

3.5 Statistical Techniques Used

Statistical techniques are fundamental tools for analyzing and optimizing experimental processes, particularly in complex systems like electroless plating. This section outlines the use of two key methods: Design of Experiment (DOE) and ANOVA. The DOE approach, based on the Taguchi method, allows for the systematic investigation of multiple parameters with a reduced number of experimental runs, ensuring both efficiency and reliability. It facilitates the identification of the most influential factors and the determination of their optimal levels to enhance coating characteristics such as microhardness. ANOVA is employed to quantify the contribution of each process variable to the overall variation in results, helping to distinguish statistically significant factors from those with minimal effect. Together, these techniques provide a structured and evidence-based framework for improving process performance and ensuring consistent outcomes.

3.5.1 Design of Experiments

The electroless plating bath consists of a mixture of metal salts and various chemicals, including a reducing agent, stabilizer, buffer, and accelerator. Each component, along with the operating conditions, plays a critical role in determining the quality and characteristics of the deposited coating. To investigate the influence of bath parameters (specifically the concentrations of metal salts and reducing agent) on coating performance, a design of experiments (DOE) approach based on the Taguchi method is employed. This method uses orthogonal arrays to study multiple factors simultaneously with a limited number of experiments, ensuring both efficiency and statistical reliability [96]. Control parameters and their levels are selected based on preliminary experimental observations and established literature. An appropriate orthogonal array is chosen to construct the experimental runs, facilitating the identification of most influential factors and their optimal levels. The Signal to noise ratio (S/N ratio)s are calculated for each variable, with the "**larger-the-better**" criterion applied in accordance with the objective of maximizing microhardness. Taguchi analysis is carried out using MINITAB 20 software to determine the optimal parameter combination for improved coating microhardness. The equation used for "larger-the-better" type analysis is:

$$\text{S/N ratio} = -10 \times \log_{10} \left(\frac{1}{10} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (3.1)$$

3.5.2 ANOVA

Analysis of Variance (ANOVA) is a statistical tool widely applied in Taguchi design methodology to evaluate the effects of various control factors on the response. It provides a quantitative basis for determining the contribution of each factor by partitioning the total observed variation into components associated with individual parameters and experimental error. This analysis is essential for identifying the most significant factors affecting performance and for guiding the optimization of

process conditions. By applying ANOVA to the results of a Taguchi experiment, it becomes possible to distinguish between influential and negligible factors, thereby enabling a more efficient and robust design of experiments.

In ANOVA, the p-value is a statistical metric used to assess the significance of each factor. It represents the probability that the observed differences could have occurred by random chance under the null hypothesis, which assumes no real effect. A lower p-value indicates stronger evidence against the null hypothesis, suggesting that the factor has a statistically significant influence on the response. Typically, a factor is considered statistically significant when the p-value is less than 0.05 (95% significance level), although the threshold may be adjusted based on the required confidence level.

In ANOVA, the influence of factors are identified by examining the percentage of contribution of each factor to total variation in the response variable. The steps include:

1. Sum of Squares (SS)

Quantifies the variation in the response attributable to each factor. SS is calculated as:

$$SS_{total} = \sum_{i=1}^N ((y_i - \bar{y})^2) \quad (3.2)$$

$$SS_A = \sum_{j=1}^a n_j ((\bar{y}_j - \bar{y})^2) \quad (3.3)$$

$$SS_{error} = SS_{total} - \sum SS_A \quad (3.4)$$

where N is total number of observations, y_i individual response value, $\bar{y}$ is overall mean of all responses, $\bar{y}_j$ is mean response at level j of factor A , n_j is number of observations at level, and a is the number of levels of the factor.

2. Degrees of Freedom (DOF)

It is associated with each factor and used in subsequent calculations. DOFs are calculated as:

$$\text{DOF}_{total} = N - 1 \quad (3.5)$$

$$\text{DOF}_A = a - 1 \quad (3.6)$$

$$\text{DOF}_{error} = \text{DOF}_{total} - \text{DOF}_{factors} \quad (3.7)$$

3. F-value

F-value for each factor is calculated using $F = \text{MS}_{factor} / \text{MS}_{error}$ where Mean square (MS) = SS/DOF. A higher F-value typically indicates a more significance.

4. Percentage of Contribution

It reflects each factor's influence on the total variation. It is calculated using the following equation.

$$\% \text{Contribution} = \frac{\text{SS}_{factor}}{\text{SS}_{error} \times 100} \quad (3.8)$$

5. p-value

Once the F-value is obtained, the corresponding p-value is determined using the F-distribution with DOF for factor and error. If the calculated p-value is below the chosen significance level (e.g., 0.05), the factor is considered to have a statistically significant effect on the response.

3.6 Computational Learning Model

The neural network model developed in this study serves as a robust computational approach for capturing the complex nonlinear relationships between electroless coating parameters and resulting microhardness. The interdependence of process variables such as the concentrations of Nickel sulfate hexahydrate, Zinc sulphate heptahydrate, and Sodium hypophosphite necessitates a data-driven method capable of accurately correlating inputs with output performance. By training the network on experimental data, a predictive relationship was established, allowing for the estimation of coating microhardness under varied process conditions. This significantly reduces the reliance on exhaustive experimental trials. The model's performance

was evaluated using indicators such as mean squared error (MSE) and correlation coefficient (R), ensuring both precision and generalizability. The computational approach demonstrated here offers a reliable method for forecasting outcomes and optimizing process parameters in surface engineering applications.

3.6.1 Artificial Neural Network

A neural network is a distributed network that consists of simple processing units that store and distributes experimental data in a parallel fashion. Artificial neural network (ANN) are computer programs that replicate how the human brain processes data [97]. The network gathers experimental data through a learning process, and synaptic weights, or connecting neuron strength, are used to retain the information in ANN.

A neuron is a computational element and is the building block of an ANN. The mathematical representation of a neuron is

$$V_i = \sum_{j=0}^n w_{ij}x_j \quad (3.9)$$

$$y_i = \varphi(V_i) \quad (3.10)$$

where x_j and y_i are inputs and outputs, w_{ij} synaptic weights and φ is the activation function.

There are three layers in a neural network: input, output, and one or more hidden layers. The ANN just needs input and output data to train, and it develops a relationship between the two through the learning process. After the network has been trained, the ANN can predict the output for the input variables. The neural network's inputs are weighed nickel sulphate, zinc sulphate, sodium hypophosphite concentrations, and microhardness of coatings as a single output. The neural network toolbox in MATLAB R2016a was used to implement the neural network algorithm. In this approach, data samples were randomly separated into three categories: training, validation, and testing, with an 80:10:10 ratio [98, 99].

The training data are fed into the network during training, and the network is adapted depending on its inaccuracy; the validation data are used to assess network generalization and to terminate training when generalization fails to improve further; and the testing data do not have any influence on training, providing an unbiased estimate of network efficiency during and after training. As a result, 80% of the data was used for training, 10% for validating that the network is generalized and terminated before overfitting, and the remaining 10% for testing the network. The Levenberg-Marquardt (LM) backpropagation algorithm, a two-layered feed-forward network with sigmoid hidden neurons and linear output neurons, had been used to train the network.

3.7 Error Analysis and Model Evaluation

The performance of the Taguchi method and artificial neural network (ANN) was assessed using several widely accepted statistical error metrics to ensure the reliability and accuracy of model predictions. These metrics include mean absolute error (MAE), mean absolute percentage error (MAPE), MSE, root mean squared error (RMSE), and the coefficient of determination (R^2). MAE measures the average magnitude of absolute errors between predicted and actual values, while MAPE expresses this error as a percentage, allowing for scale-independent evaluation. MSE calculates the average of the squared differences between predictions and actual outcomes, and RMSE is the square root of MSE, which provides error information in the same units as the original data.

The mathematical expressions for these metrics are provided in the following equations.

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^n \left| \frac{A_i - P_i}{A_i} \right| \quad (3.11)$$

$$\text{MAPE} = \frac{1}{n} \sum_{i=1}^n \left| \frac{A_i - P_i}{A_i} \right| \times 100 \quad (3.12)$$

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (A_i - P_i)^2 \quad (3.13)$$

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (A_i - P_i)^2} \quad (3.14)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (A_i - P_i)^2}{\sum_{i=1}^n (A_i - \bar{A})^2} \quad (3.15)$$

where A_i and P_i are actual and predicted value for the i^{th} data, and $\bar{A}$ is the average value of actual data.

R^2 , or the coefficient of determination, indicates the strength and direction of the linear relationship between predicted and actual values. A higher R^2 value, approaching 1, signifies a strong correlation and model performance, whereas a value near 0 indicates weak or no correlation. In contrast, lower values of mean absolute error (MAE), mean absolute percentage error (MAPE), mean squared error (MSE), and root mean squared error (RMSE) suggest higher model accuracy and better predictive ability. By applying these metrics, the study quantitatively validates the effectiveness of both the Taguchi and ANN models, enabling a robust comparison of their prediction capabilities and fitting accuracy.

WETTABILITY AND CONTACT ANGLES: THEORY, MEASUREMENT, AND APPLICATIONS

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This chapter discusses wettability, which describes how a liquid behaves when it comes into contact with a solid surface. Wettability is central to surface science because it influences a wide range of practical applications, from printing technologies and oil recovery processes to the development of water repellent materials and medical devices. A key parameter in understanding wetting behaviour is contact angle (CA), which provides a measurable indication of how strongly a liquid interacts with a surface. The chapter outlines the principles behind contact angle formation, common methods of measurement, and the ways in which surface chemistry and textures affect wetting characteristics.

4.1 Fundamentals of Wettability

Wettability, the ability of a liquid to maintain contact with a solid surface, is a fundamental concept in surface science and interfacial phenomena. This property plays a crucial role in surface science and the study of interfaces between materials. It directly impacts a wide range of practical applications, such as inkjet printing [100], enhanced oil recovery [101], the development of water-resistant fabrics [102], and the design of biomedical devices [60]. At the core of wettability lies the concept of contact angle (CA), a parameter that quantitatively describes the interaction between liquid and solid surfaces. This chapter explores both the theoretical background and practical implications of wettability, focusing on how contact angles are measured, how surface texture and chemical composition affect wetting behavior, and how these principles are applied in various modern technologies.

Wettability is a key factor in fluid dynamics and the study of interfaces, and a solid grasp of this concept is essential for designing surfaces with targeted interaction characteristics. Whether the aim is to develop water-repellent, self-cleaning materials, enhance the bonding of coatings, or analyze biological surface behavior, wettability directly influences how materials perform. As technologies continue to shrink—particularly in fields like microfluidics and biomedical engineering—the ability to precisely manage how liquids interact with surfaces becomes increasingly important. This has made the control of wettability at both the micro- and nano-scale a critical area of focus in material science and engineering.

Wettability is determined by the balance of adhesive and cohesive forces. Adhesive forces between the liquid and solid promote wetting, while cohesive forces within the liquid resist it. When a droplet is placed on a solid surface, its shape and the angle it forms with the surface, known as the contact angle, indicate the extent of wetting.

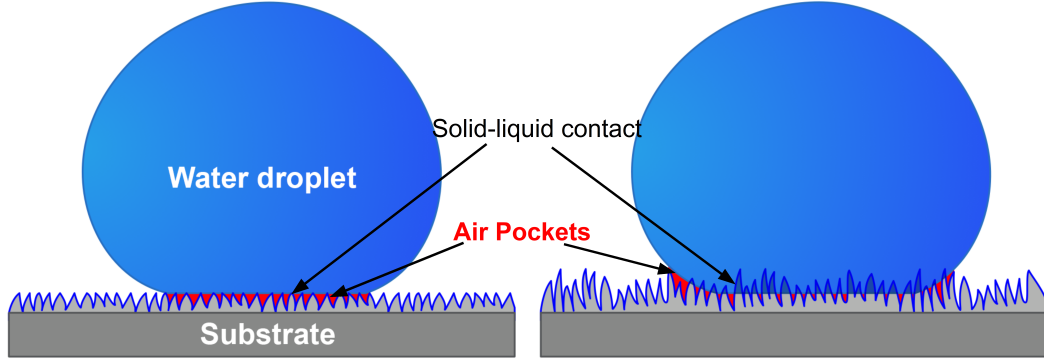


Figure 4.1: Illustration of contact angle (θ) formed by a liquid droplet on a solid surface.

4.1.1 Surface and Interfacial Tensions

Wetting behavior is governed by surface tension (σ), which is the energy required to increase the surface area of a phase. The key interfacial tensions associated with surface wetting are Solid-vapor (σ_{sv}), Solid-liquid (σ_{sl}), and Liquid-vapor surface tension (σ_{lv}). The relationship between these three is described by Young's equation.

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos \theta \quad (4.1)$$

Where θ is the equilibrium contact angle. A lower interfacial tension between the solid and liquid phases leads to better spreading and a lower contact angle, indicative of hydrophilicity. Conversely, a high solid-liquid interfacial tension results in poor spreading and a higher contact angle, indicating hydrophobicity.

These distinctions are crucial in understanding how liquids behave on surfaces in natural and engineered systems. For example, superhydrophobic surfaces, such as those mimicking lotus leaves, can lead to selfcleaning behavior, while superhydrophilic surfaces can enhance the wicking of fluids in medical diagnostics.

4.2 Contact Angle and Its Measurement

The contact angle is the primary metric for assessing wettability. It is defined geometrically as the angle formed at the junction of liquid, solid, and vapor phases shown in **Figure 4.1**.

4.2.1 Static and Dynamic Contact Angles

The static contact angle is measured under equilibrium conditions and reflects the intrinsic wettability of the surface. It is affected by surface heterogeneity, contamination, and ambient environmental conditions. In practice, multiple droplets are measured to determine an average contact angle, increasing the reliability of results.

When a droplet is manipulated to either grow, shrink or move on a surface, the contact angle changes dynamically. These measurements are essential for understanding droplet mobility and adhesion.

1. **Static contact angle or CA (θ):** The angle formed at the junction of liquid, solid, and vapor phases
2. **Advancing Angle (θ_a):** The maximum angle when the liquid front advances.
3. **Receding Angle (θ_r):** The minimum angle when the liquid front recedes.
4. **Hysteresis ($\Delta\theta$):** The difference between θ_a and θ_r . High hysteresis often indicates strong pinning forces and surface roughness or chemical heterogeneity.

4.2.2 Measurement Techniques

Several experimental methods exist to measure contact angles, Sessile Drop Method: The most common technique, where a drop is placed on a surface and imaged from the side. Tilting Plate Method: A drop is placed on a surface that is slowly tilted until the drop begins to slide. Accurate contact angle measurement is crucial for characterizing surface modifications and predicting wetting behavior.

4.3 Effect of Surface Roughness on Wettability

Surface roughness plays a pivotal role in altering the apparent contact angle on a substrate. A smooth surface behaves differently from a textured or rough one, even if both are chemically identical. The apparent contact angle is typically different from the theoretical value predicted by Young's equation when surface roughness is introduced.

4.3.1 Wenzel Model

Wenzel proposed that roughness amplifies the inherent wettability of a surface. If a surface is naturally hydrophilic, increasing its roughness decreases the contact angle, making it more wettable. Conversely, for hydrophobic surfaces, roughness increases the contact angle, enhancing water repellency. This relationship is presented as:

$$\cos \theta^* = r \cos \theta \quad (4.2)$$

Where θ^* is the apparent contact angle r and is the roughness ratio, defined as the ratio of the true surface area to the projected area. Real world applications that use the Wenzel model include the design of hydrophilic catalysts and sensors.

4.3.2 Cassie-Baxter Model

In contrast to Wenzel, the Cassie–Baxter model describes the case where the liquid droplet rests on a composite surface made of both solid and air. This model explains the superhydrophobic nature of surfaces like lotus leaves, where droplets sit atop microscopic air pockets:

$$\cos \theta^* = f_s \cos \theta - (1 - f_s) \quad (4.3)$$

Here, f_s is the fraction of solid in contact with the liquid. Surfaces designed under this regime exhibit very high contact angles and low sliding angles, allowing droplets to roll off easily.

4.4 Influence of Surface Chemistry

While surface topography is known to strongly influence wettability, the chemical composition of a substrate plays an equally critical role. The surface energy, which governs the extent of liquid spreading, is inherently linked to the surface chemistry. The presence of specific functional groups can markedly alter wettability polar or hydrophilic groups (e.g., $-\text{OH}$, $-\text{COOH}$) promote strong interactions with water, resulting in low contact angles and enhanced wettability, whereas non-polar or hydrophobic groups (e.g., $-\text{CH}_3$, fluorinated chains) lead to high contact angles

and reduced wettability. By tailoring surface chemistry through methods such as coatings, chemical treatments, or grafting, it is possible to systematically control wetting behavior. This chemical modulation is central to the design of functional interfaces in applications ranging from self-cleaning materials to microfluidic devices and biomedical surfaces. In the present study, Superhydrophobic surface (SHS)s are fabricated via a coating-based approach, with the details of the coating process described in **subsection 3.3.2**.

4.5 Applications

Wettability manipulation is central to numerous technological and industrial applications:

1. **Self Cleaning Surfaces:** Inspired by the lotus leaf, SHSs enable water droplets to pick up dirt particles and roll-off. This has led to commercial products such as self-cleaning paints, solar panels, and textiles.
2. **Microfluidics:** Microfluidic systems use wettability gradients to guide fluid motion without pumps. Patterned wettability also supports droplet-based chemical reactions and diagnostics in lab-on-chip platforms.
3. **Oil Water Separation:** Selective wetting membranes, typically superoleophobic in water or vice versa, enable efficient separation of oil and water. These are vital in environmental cleanup and wastewater treatment.
4. **Biomedical Devices:** Surface wettability influences cell adhesion, proliferation, and protein adsorption on biomedical implants. Hydrophilic surfaces often reduce biofouling and enhance biocompatibility.
5. **Anti-icing:** Superhydrophobic surfaces delay ice formation and reduce adhesion strength of ice, benefiting aerospace and power grid applications. Similarly, reduced drag in marine vessels is achieved by controlling wettability.

Part III

Result and Discussion

SYNTHESIS OF ELECTROLESS Ni-Zn-Cu-P COATING

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This chapter systematically examines the fabrication, optimization, and characterization of electroless Ni-Zn-Cu-P coatings on AZ31 Mg alloy. The chapter begins by detailing the electroless deposition process and establishing suitable operating conditions to obtain uniform and adherent Ni-Zn-Cu-P coatings. Particular attention is given to the influence of deposition time on coating integrity and mechanical properties. Subsequently, a systematic optimization of bath composition is carried out using the Taguchi design of experiments approach, with microhardness selected as the primary response parameter. The relative significance of individual process variables and their interactions is quantified through signal-to-noise ratio analysis and ANOVA.

Finally, the optimized coating is extensively characterized using XRD, SEM, EDS, and microhardness measurements to elucidate their structural, compositional, and morphological features. The insights gained in this chapter provide a robust basis for tailoring electroless Ni-Zn-Cu-P coatings aimed at improving the surface performance of magnesium alloys.

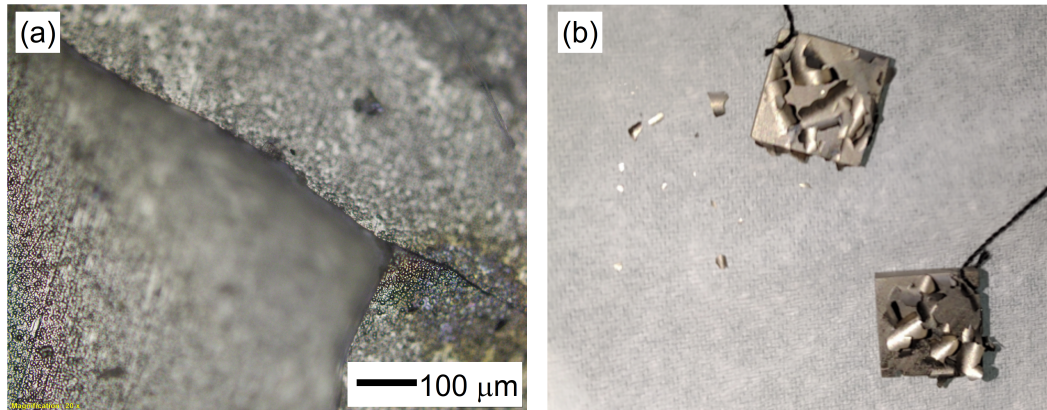


Figure 5.1: Optical and macroscopic images illustrating crack formation and propagation in the coating: (a) optical micrograph showing the initiation of a crack at the early stage of failure, and (b) digital camera image displaying progressive crack propagation leading to layer-by-layer delamination and peeling of the coating.

5.1 Ni-Zn-Cu-P Coating

The methodology adopted for the preparation of the Ni-Zn-Cu-P coating, including the plating bath composition and operating parameters, is described in detail in **section 3.3** of **chapter 3**. The deposited coating exhibits an average thickness of approximately $\sim 6 \mu m$ and a microhardness ranging from about 390 and 635 $HV_{0.01}$. The deposition process is carried out for nearly 10 min; however, extending the plating duration beyond this threshold cracks began to form in the coating layer. Further increases in plating time promoted crack growth, leading to delamination and eventually layer-by-layer peeling of the coating, as shown in **Figure 5.1**. The underlying mechanism responsible for this behavior is discussed in **subsection 6.3.1** of **chapter 6**. Consequently, coatings produced with a deposition time of 10 min were selected for optimization of process parameters to achieve maximum microhardness. Under the optimized conditions, the coating attained a microhardness of approximately $\sim 632 HV_{0.01}$, representing a significant improvement compared to the substrate hardness of about $\sim 85 HV_{0.01}$.

Table 5.1: Control parameters and their levels for Taguchi DOE of Ni-Zn-Cu-P coatings.

Factors	Levels (all concentrations are in g L ⁻¹)		
	1	2	3
A : NiSO ₄ · 6 H ₂ O	25	30	35
B : ZnSO ₄ · 7 H ₂ O	2	2.5	3
C : NaH ₂ PO ₂ H ₂ O	30	35	40

5.2 Optimization of Process Parameters

The electroless bath for Ni-Zn-Cu-P coating is a mixture of chemical compounds containing various metal salts (NiSO₄ · 6 H₂O, ZnSO₄ · 7 H₂O, and CuSO₄ · 5 H₂O) as well as other chemical compounds such as reducing agent NaH₂PO₂H₂O, stabilizer (thiourea), NH₄HF₂, NaC₂H₃O₂ etc. Each of these chemical compounds has an impact on coating quality. Even the working conditions have an impact on coating quality. Taguchi analysis was performed using MINITAB software and Taguchi L27 Orthogonal Array for three elements with three levels each in the current technique. The three factors are NiSO₄ · 6 H₂O (A), ZnSO₄ · 7 H₂O (B), and NaH₂PO₂H₂O (C) which are used as control parameters in the Taguchi design to create an L27 orthogonal array and their levels are mentioned in **Table 5.1**. The microhardness of a coated or plated metal is one of its most important mechanical properties, and thus it was chosen as a response parameter in the present investigation. The analysis type was set "Larger is better" in the MINITAB software from the available options, since the larger S/N ratio, the better will be microhardness.

The equation used for the "Larger is better" type analysis for microhardness is

$$S/N \text{ ratio} = -10 \times \log_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (5.1)$$

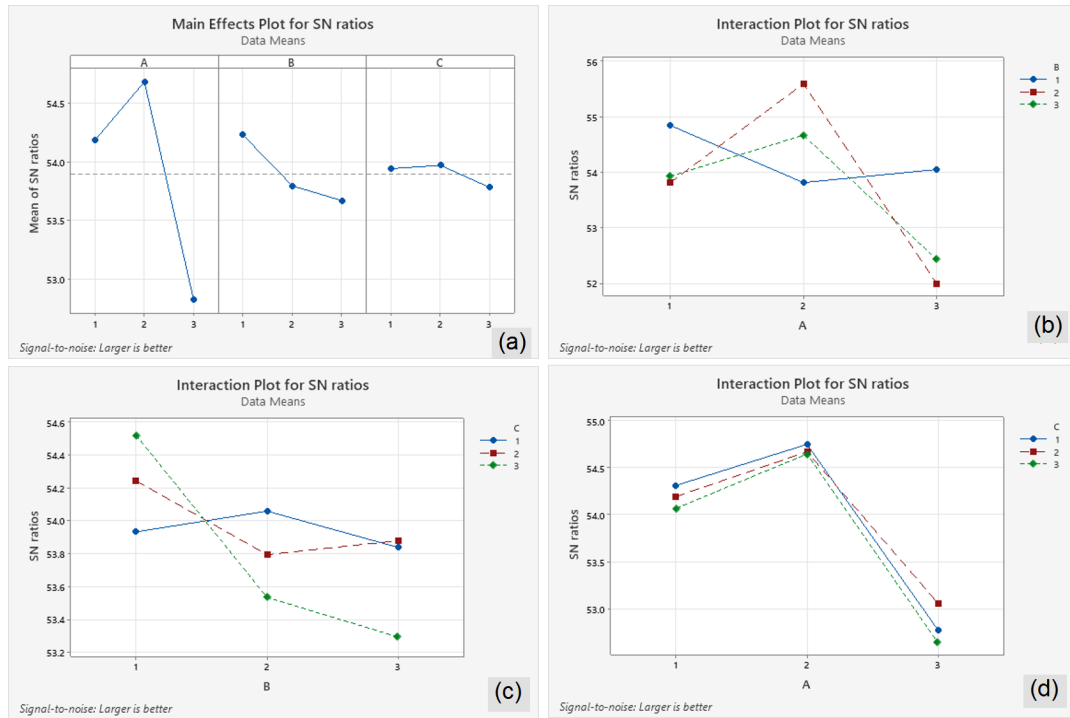


Figure 5.2: S/N ratio plots for (a) main parameters, (b) Interactions of A and B, (c) B and C, and (d) A and C.

5.2.1 Taguchi Analysis

According to Taguchi, Signal to noise ratio (S/N ratio) should be employed to turn experimental results into a number for the optimization problem's evaluation characteristic [10]. Where, mean is the signal, and standard deviation is the noise. Coating quality improves as S/N ratio rises. MINITAB statistical software was used to perform Taguchi analysis, and the study took into account by taking both the main and interaction effects of the controllable factors. The control parameters are provided together with their respective response and S/N ratio in **Table A.1**.

Figure 5.2a depicts the main effects graph for S/N ratio. The ideal parameter combination, the levels linked with the highest S/N ratio, is A2B1C2, i.e., the middle level of factor $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, low level of factor $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, and middle level of factor $\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$, as seen in the main effect graph. The main effect graph also gives a fair notion of the parameter's relative importance in terms of hardness. The higher the delta value (the difference in mean values from the highest to the lowest) of a factor, the greater will be its influence [103, 104]. The delta values for S/N ratio

Table 5.2: *Response table for S/N ratio.*

Level	A	B	C
1	54.19	54.23	53.94
2	54.68	53.79	53.97
3	52.82	53.67	53.78
Delta	1.86	0.56	0.19
Rank	1	2	3

at each level for each parameter are presented in **Table 5.2** and can also be observed in **Figure 5.2a**. The delta values for S/N ratio show that factor $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ has a very high level of significance whereas factors $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ are less significant. **Figure 5.2b, c, and d** show the interaction graph for S/N ratio. If the plots are not parallel, there is an interaction between the associated parameters, and if two plots intersect, the interaction is believed to be highly substantial [96, 103]. It is clear from the interaction graphs from **Figure 5.2b, c, and d** that there is an interaction impact between the parameters.

5.2.2 ANOVA Analysis

An ANOVA analysis was subsequently employed to evaluate the statistical significance of the main factors and their interactions. The results of the ANOVA analysis are summarized in **Table 5.3**. According to the F-distribution chart, $F_{0.05,2,8}$ equals 4.46 and $F_{0.05,4,8}$ equals 3.84 respectively. It may be inferred that A and its interaction impact with B are significant because their corresponding F-values are $14.27 > 4.46$ and $5.59 > 3.84$. The P-value is below 0.05, which further confirms that $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and its interaction with $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ significantly affect the microhardness of the coatings with a 95 % confidence level [9, 105]. It indicates that A is highly important among the major components, while the AB interaction is highly significant among the interactions, with 44.42 % and 34.83 % contributions, respectively, and a P-value of 0.002 and 0.019. Therefore, by re-examining the optimum parameter derived from the main factors, A2B1C2, from **Figure 5.2b** we can see that A2B2 has a greater value

Table 5.3: Results from ANOVA analysis for L27 orthogonal array.

Source	DOF	SS	% Contribution	F-Value	P-Value
A	2	51439	44.42	14.27	0.002
B	2	4356	3.76	1.21	0.348
C	2	630	0.54	0.17	0.843
A×B	4	40334	34.83	5.59	0.019
A×C	4	598	0.52	0.08	0.985
B×C	4	4022	3.47	0.56	0.700
Error	8	14419	12.45		
Total	26	115797	100.00		

than A2B1. The optimum parameters are thus A2B2C2 based on the interaction analysis.

5.3 Characterization of Ni-Zn-Cu-P Coating

XRD plot of the substrate (Mg AZ31) after polishing and coating (M) for the optimum combination A2B2C2, which corresponds to the experiment no. 14 in **Table A.1** is presented in **Figure 5.3**. XRD pattern for the base substrate is similar to a typical magnesium alloy XRD pattern showing around 10 peaks near 33.3° , 34.5° , 36.7° , 48° , 57.5° , 63.2° , 68.8° , 71° , 72.6° , and 78° [106]. A low intensity broad peak was observed with a wide angular range between 420 to 480 , which corresponds to Ni (111) of Ni-coatings. Using the 'Match 3' software, XRD patterns of the substrate and coating are matched to the JCPDS card numbers 96-901-3058 and 96-900-9863, respectively. The crystalline peaks in the XRD pattern of coating are from the Mg substrate, implying that the thickness of coating is thin [107–109]. The cross-sectional image of the coating for A2B2C2 captured by the optical microscope is presented in **Figure 5.4** and the coating thickness obtained was 5.39-5.88 microns.

The elemental composition of coatings from the experiment no. 1, 14, and 27 is provided in **Table 5.4**. The weight percentage of phosphorus observed here is

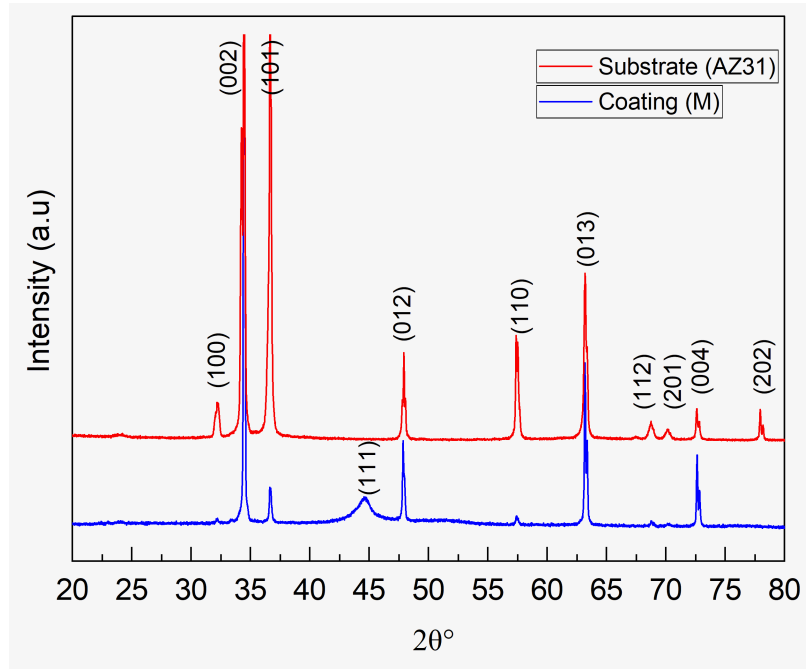


Figure 5.3: XRD pattern of the base substrate (AZ31) and coating (M).

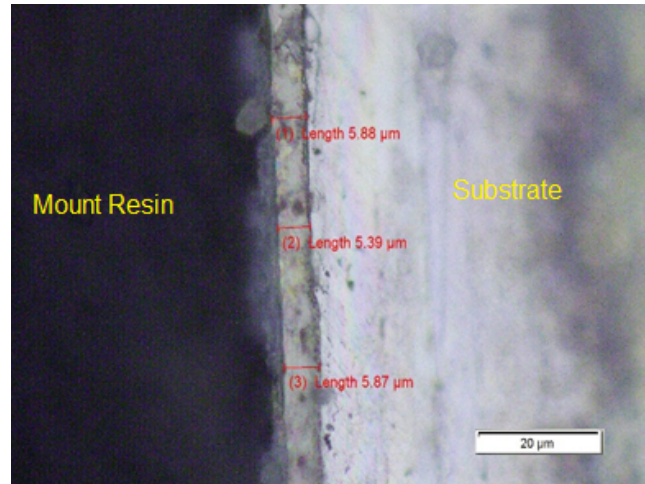


Figure 5.4: Cross-sectional image of coating showing thickness.

Table 5.4: Results from EDS analysis of Ni-Zn-Cu-P coatings.

Expt. No.	Composition of elements by weight (%)			
	Ni	P	Zn	Cu
1	81	11	4	4
14	83	10	4	3
27	79	12	3	5

10 %, which corresponds to the broad XRD peak of Ni, indicating that the Ni-Zn-Cu-P coatings are amorphous. When the phosphorus level in electroless nickel coatings exceeds 7 wt.%, the coatings become amorphous [11, 107, 110, 111]. As determined by the EDS technique, a lesser amount of Zn (3-4 %) and Cu (3-5 %) atoms are co-deposited with the nickel matrix, therefore no XRD peak matching the microstructure of zinc and copper was found separately. This is most likely due to Ni atoms being replaced with co-deposited Zn and Cu atoms in nickel's lattice structure [112].

Figure 5.5a and **b** depict the elemental mapping for the Ni-Zn-Cu-P coating at optimal parameter combination; **Figure 5.5a** depicts the overlay maps of all elements (Ni, P, Zn, and Cu), whereas **Figure 5.5b** depicts the maps of individual elements and **Figure 5.5c** shows SEM image of the area from where EDS data is obtained. The surface morphology of Ni-Zn-Cu-P coating (expt. no. 14) is shown in **Figure 5.6** with different magnifications, where **Figure 5.6a** and **b** display low and high magnifications, respectively. **Figure 5.6** indicates that the coating is compact and has a cauliflower-like appearance, with nodular grains generally of the same size distributed homogeneously. The nodule sizes were measured using ImageJ software for the coatings with a copper content of 5, 4, and 3 wt.%. The average grain size was reported to be inversely proportional to the copper content, with the largest nodules measuring 1.972, 3.317, and 3.561 μm for coatings with a copper content of 5, 4, and 3 wt.%, respectively. That is, when the copper content rises, the size of nodules reduces, as reported earlier [113]. Because of the high nickel content and the presence of zinc [112], the coating color is greyish. **Figure 5.5** shows that the elements are distributed uniformly across the surface.

As described in **subsection 3.4.1**, the indentation load has to be chosen carefully to avoid the indenter penetrating the coating layer and striking the substrate. Since the thickness of coatings are $\sim 6 \mu\text{m}$, therefore, the indentation load was set to 10gf. Microhardness of the substrate after polishing was found to be 87 $\text{HV}_{0.01}$, while that of the coated samples ranged between 390 and 635 $\text{HV}_{0.01}$. The coatings exhibit a

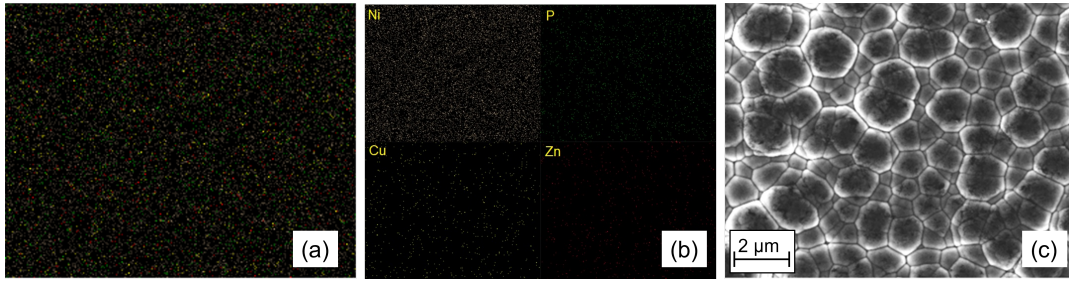


Figure 5.5: EDS elemental mapping (a) overlay of Ni, Zn, Cu, and P, (b) Ni, P, Cu, and Zn, and (c) SEM image of collected EDS data of coating (expt. no. 14).

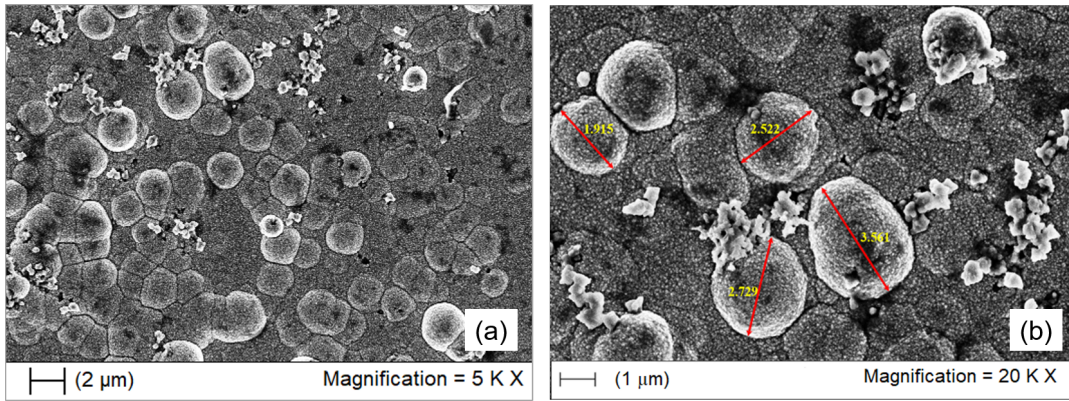


Figure 5.6: SEM images with magnifications (a) 5 K X, and (b) 20 K X of coating (expt. no. 14).

microhardness of 4 to 7 times that of the substrate. The microhardness values of the coated samples are presented in presented in **Table A.1**. It is observed from **Table A.1** that, the coating with lowest phosphorus content in the bath, has a higher microhardness value and vice versa. That agrees with previous related works for phosphorus content above 8% [114].

5.4 ANN Results

The network was trained using a two-layered feed-forward network containing sigmoid hidden neurons and linear output neurons. The network was initially trained with one neuron in the hidden layer numerous times until the best trained network was obtained. The hidden neurons are gradually raised to 10, and the network is trained several times, each time until it is better trained. **Table 5.5** displays the R(regression)-values for training, validation, and testing of each model for the best trained network (where 3-1-1 indicates that the model has three input vertices in the input layer, one hidden node in the hidden layer, and one output variable in the

Table 5.5: *Regressions of different ANN models.*

ANN Model	R_{Train}	R_{Val}	R_{Test}	R_{All}
3-1-1	0.64346	0.99374	0.941739	0.66631
3-2-1	0.91063	0.97821	0.85188	0.86193
3-3-1	0.79552	0.99937	0.96256	0.84578
3-4-1	0.8984	0.99518	0.92753	0.87091
3-5-1	0.98826	0.96615	0.9998	0.96528
3-6-1	0.99375	0.98974	0.94103	0.97187
3-7-1	0.9935	0.98754	0.99904	0.99105
3-8-1	0.99064	0.9888864	0.97682	0.98384
3-9-1	1	0.98511	0.99241	0.98017
3-10-1	0.999	0.99616	0.9935	0.96207

output layer). **Figure 5.7** summarizes the ANN performance in terms of R^2 and MSE. An increase in the number of hidden-layer neurons resulted in improved predictive capability, as reflected by the progressive rise in R^2 . The optimum performance was obtained at 7 neurons, yielding the highest R^2 (0.982) along with a comparatively low MSE. Accordingly, ANN 3-7-1 was selected as the most suitable model among the evaluated architectures. The predicted microhardness values obtained from the ANN (3-7-1) model and Taguchi analysis are summarized in **Table A.1**. At the optimal conditions, the ANN and Taguchi approaches predicted microhardness values of 631.41 and 599.48 $HV_{0.01}$, corresponding to absolute percentage errors of 0.0288 and 5.084%, respectively.

The predictive performance of the ANN and Taguchi approaches was evaluated using statistical error metrics (MSE, RMSE, MAE, MAPE, and R^2) defined in **Equation 3.11-15**, based on the dataset in **Table A.1**. The calculated values are summarized in **Table 5.6**. Performance plots comparing relative error and R^2 are presented in **Figure 5.8**. As shown in **Figure 5.8b**, the ANN predictions closely follow the ideal parity line ($Y = X$), whereas the Taguchi predictions exhibit a no-

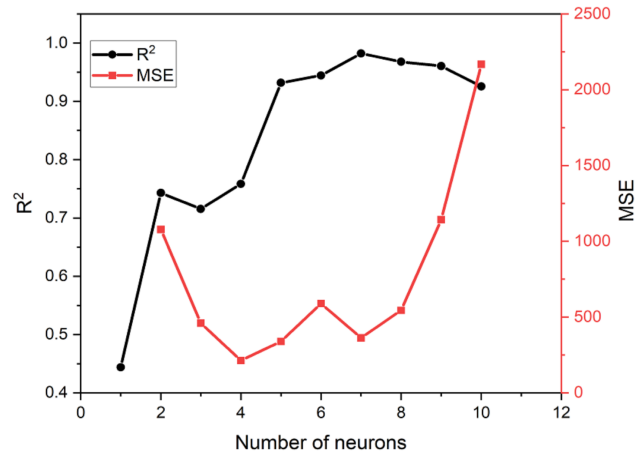


Figure 5.7: Effect of number of hidden neuron on ANN accuracy in terms of R^2 and MSE

Table 5.6: Statistical parameters of ANN and Taguchi analysis in prediction of microhardness

Model	MAE	MAPE	MSE	RMSE	R^2
ANN	4.88	0.99	78.28	8.84	0.982
Taguchi	19.42	3.836	534	23.10	0.875

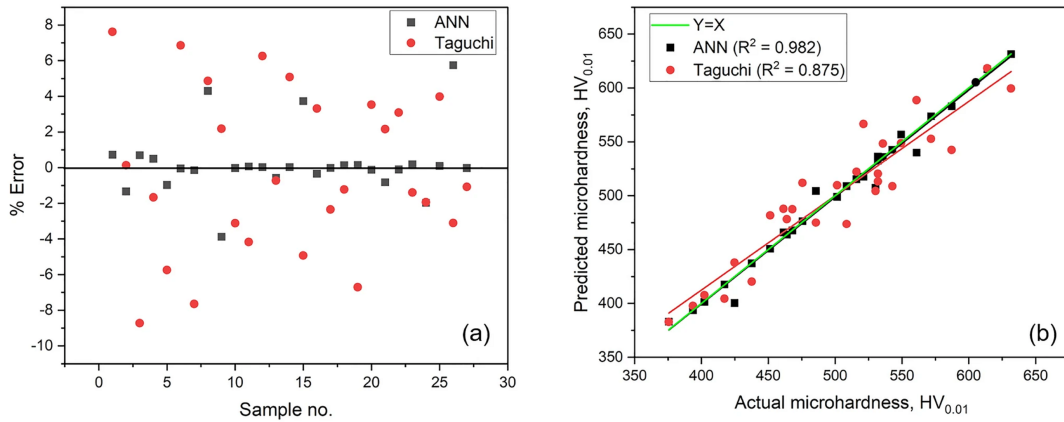


Figure 5.8: Performance plots in terms of (a) relative error, and (b) R^2 for ANN and Taguchi analysis.

ticeable deviation. Overall, **Table 5.6** and **Figure 5.8** confirm that ANN provides superior predictive accuracy compared to Taguchi analysis, yielding lower error values and higher goodness-of-fit (R^2). Specifically, the ANN model achieved MSE = 8.84, RMSE = 78.28, MAE = 4.88, MAPE = 0.99, and R^2 = 0.982, while the Taguchi method resulted in MSE = 23.10, RMSE = 534, MAE = 19.42, MAPE = 3.836, and R^2 = 0.875.

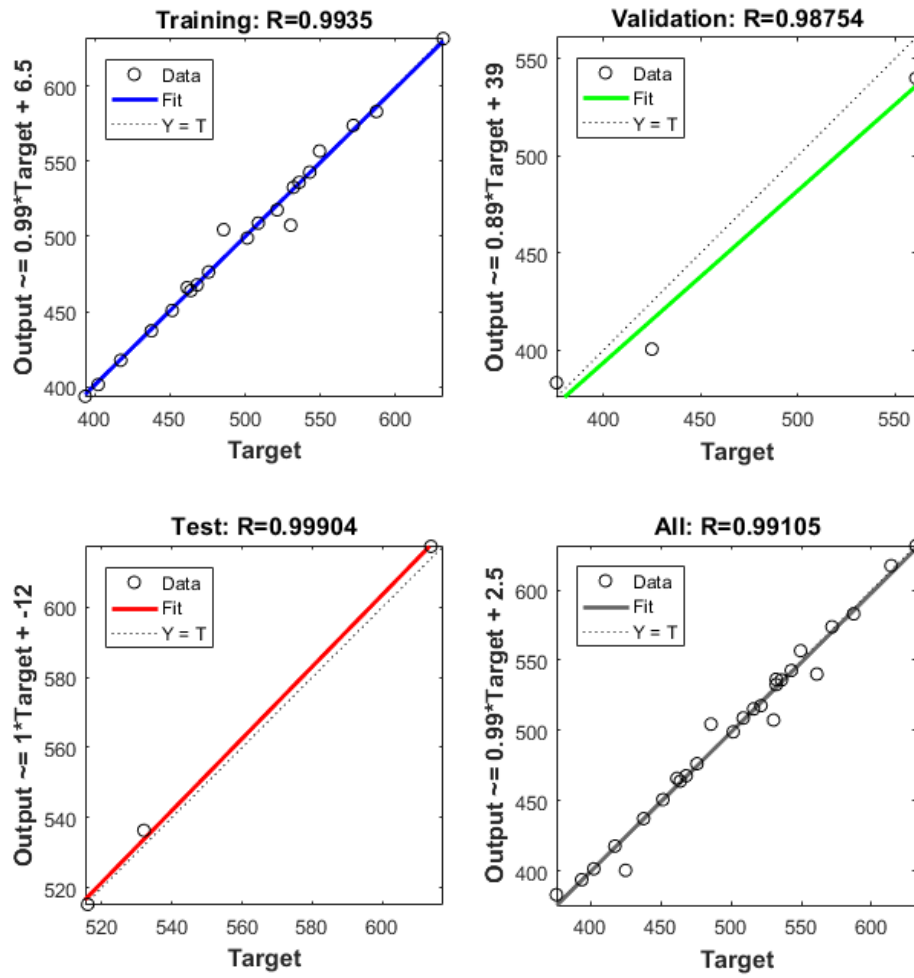


Figure 5.9: Regression plots of ANN 3-7-1.

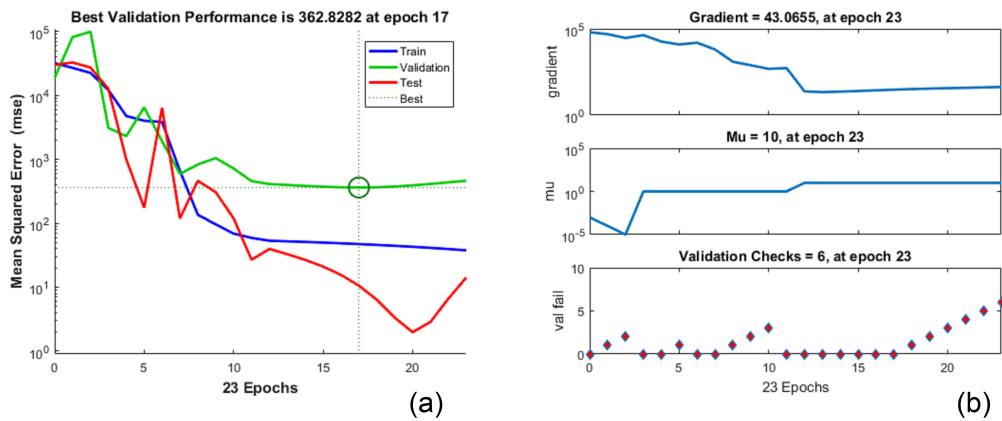


Figure 5.10: (a) MSE versus epochs, and (b) network performance plot of ANN 3-7-1.

The regression graphs of the trained network outputs of the ANN 3-7-1 are shown in **Figure 5.9**. The data should fall along a 45° line, i.e., the R-value should be near 1, with network outputs equal to targets, for a perfect match [115, 116]. The fit for all data sets is satisfactory for this model, with R values greater than 0.987 in each case, and the overall R (R_{all}) is 0.99105. The MSE versus epoch plot in **Figure 5.10a** indicates that ANN 3-7-1's greatest validation performance is 362.8282 at epoch 17. **Figure 5.10b** shows the gradient, Mu, and validation fail plots. The validation fail plot in **Figure 5.10b** shows that beyond epoch 17, the validation fail starts to rise, which corresponds to the circle representation of optimal validation performance in **Figure 5.10a**.

5.5 Concluding Remarks

This chapter establishes a systematic framework for the development and optimization of electroless Ni-Zn-Cu-P coatings on AZ31 magnesium alloy, with emphasis on achieving high hardness and coating stability. A uniform coating with a thickness of approximately 6 μm was obtained when the deposition time was carefully controlled, while prolonged plating was shown to induce crack formation and interfacial failure. Statistical optimization using Taguchi methodology, supported by ANOVA, identified the nickel source concentration as the most influential factor affecting microhardness, along with its significant interaction with zinc concentration. The optimized bath composition yielded a maximum microhardness of $\sim 632 \text{ HV}_{0.01}$, representing a marked enhancement over the untreated substrate. Structural and compositional characterization revealed an amorphous Ni-rich matrix with minor, uniformly distributed Zn and Cu co-deposits, consistent with the observed broad XRD features and EDS results. The coatings exhibited a dense, nodular surface morphology with homogeneous elemental distribution.

ECO-FRIENDLY SYNTHESIS OF ELECTROLESS COATING

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This chapter presents the synthesis and evaluation of electroless Ni-W-P coatings on AZ31 Mg using a modified pretreatment eco-friendly route. The revised surface preparation enables extended deposition beyond 10 min, producing continuous coatings with increased thickness and improved mechanical performance. The underlying causes of coating delamination observed in earlier systems are identified and discussed. Two bath conditions are investigated: T1, deposited from an NH_3 -containing bath, and T2, deposited without NH_3 . The resulting coating thicknesses were $\sim 10 \mu\text{m}$ (T1) and $\sim 14 \mu\text{m}$ (T2), obtained after deposition times of ~ 50 and ~ 120 min, respectively. The coatings exhibit substantially enhanced hardness relative to the substrate, with microhardness values of $550 \pm 50 \text{ HV0.01}$ for T1 and $710 \pm 50 \text{ HV0.01}$ for T2. The sections that follow describe the eco-friendly pretreatment

concept, coating synthesis, and the resulting microstructural, mechanical, adhesion, and corrosion characteristics.

6.1 Ni-W-P Coating

As discussed in the previous chapter, the coatings undergo failure through delamination after a critical deposition time. To address this limitation, an electroless coating is synthesized using an alternative pretreatment approach, enabling deposition durations exceeding 10 minutes. The preparation methodology for the Ni-W-P coatings, including bath composition and operating parameters, is detailed in **section 3.3 of chapter 3**. The measured coating thickness is approximately $10\text{ }\mu\text{m}$ for coating T1, prepared using a bath containing NH_3 , and about $14\text{ }\mu\text{m}$ for coating T2, produced without NH_3 . The corresponding deposition times are approximately 50 minutes for T1 and 120 minutes for T2. Microhardness measurements reveal values of $550 \pm 50\text{ HV}_{0.01}$ for T1 and $710 \pm 50\text{ HV}_{0.01}$ for T2.

6.2 Development of a One-Step Eco-friendly Pretreatment Method

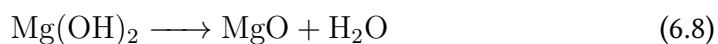
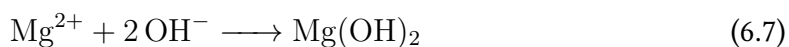
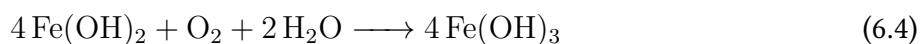
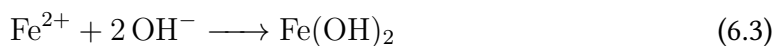
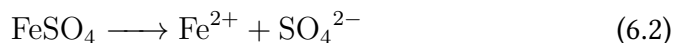
Conventional pretreatment methods for electroless coating on magnesium alloys often involve multistep processes utilizing highly toxic chemicals such as Hydrofluoric acid, Chromic anhydride, or cyanide-based solutions. These substances not only pose significant environmental and safety concerns but also make the overall process labor-intensive, expensive, and less sustainable. To address these limitations, this study proposes a novel, eco-friendly, and cost-effective one-step pretreatment approach that ensures adequate surface preparation of AZ31 magnesium alloy for subsequent electroless Ni-W-P coating without the use of hazardous chemicals. The hazard statements of the chemical substances generally used are given in **Table A.2**.

The developed pretreatment method employs an aqueous solution of Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as the sole chemical agent for surface conditioning. This single-step process eliminates the need for conventional acidic pickling and

fluoride activation steps. The underlying mechanism relies on the redox interaction between the magnesium substrate and the iron sulfate solution. During the immersion process (20–25 minutes at room temperature), a displacement reaction occurs where magnesium atoms are oxidized and dissolve into the solution, while iron ions are reduced and form surface by-products such as iron hydroxides and oxides. These reaction products are weakly bonded to the substrate and are subsequently removed by ultrasonic cleaning in DI water. The process not only etches the surface but also modifies it physically and chemically to enhance coating adhesion.

6.2.1 Pretreatment Mechanism

When the magnesium alloy is immersed in an aqueous iron sulfate solution, oxidation of Mg occurs with hydrogen evolution. In an aqueous solution, FeSO_4 dissociates into Fe^{2+} and SO_4^{2-} , and in the presence of Mg a displacement reaction takes place between Mg and FeSO_4 . Iron by-products formed during the pretreatment adsorb on the Mg alloy surface, and Mg^{2+} transforms into MgSO_4 and $\text{Mg}(\text{OH})_2$. The iron by-products (dark appearing) adsorbed over the substrate were removed by ultrasonication in deionized water. Immediately after the ultrasonication, the samples were hot air dried and immersed in the electroless bath for deposition. Upon drying, the $\text{Mg}(\text{OH})_2$ dehydrates to form MgO [34]. The reaction of Mg in the aqueous solution of Iron (II) sulfate [117] is as follows:



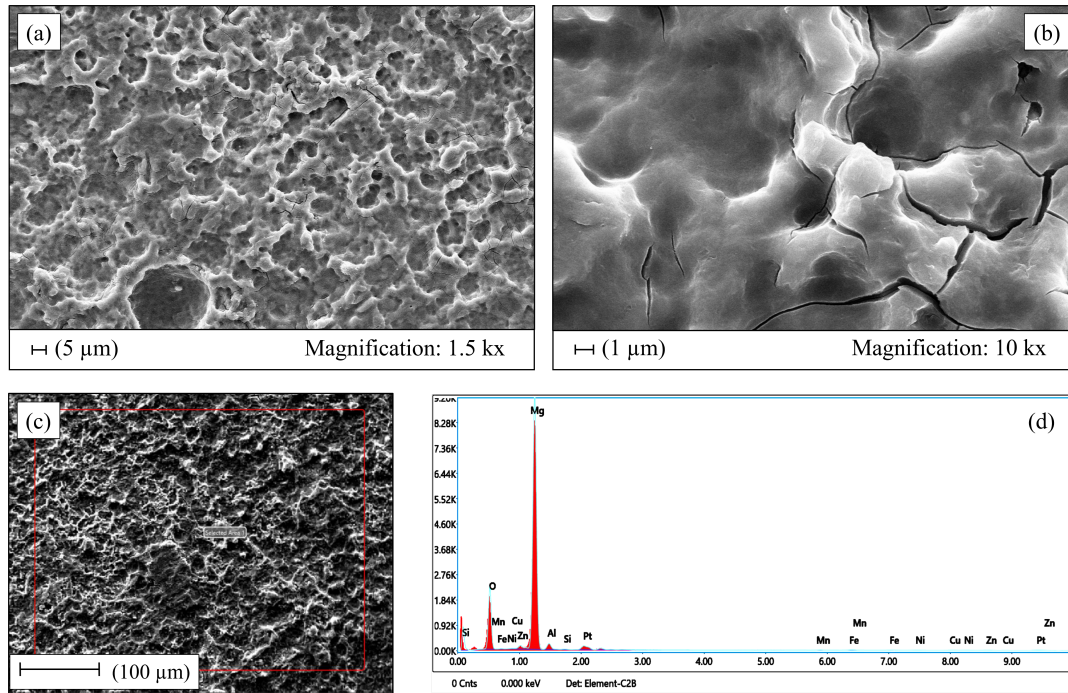


Figure 6.1: (a), (b) SEM images, and (c), (d) EDS analysis of sample pretreated sample; (c) area from where EDS data was collected, and (d) EDS spectrum.

Table 6.1: Elemental composition of polished and pretreated substrate.

Specimen↓	Elements→	O	Al	Zn	Fe	Mg
Base	Wt.%	8.18	3.35	1.2	0.02	Balance
	Atomic %	11.99	2.65	0.6	0.01	Balance
Pretreated substrate	Wt.%	19.9	3.1	1.6	1.3	Balance
	Atomic %	29.4	2.7	0.6	0.6	Balance

The pretreatment process in this study used an aqueous solution of Iron (II) sulfate heptahydrate, having category 2 toxicity. The polished Mg AZ31 specimen is treated in it for 20-25 min at room temperature. Since iron sulfate is salt of a strong acid H_2SO_4 and a weak base $\text{Fe}(\text{OH})_2$, hence the aqueous solution of iron sulfate is acidic in nature. As it is well known that magnesium is reactive in acids, the aqueous solution of iron sulfate acts as an etching solution, and the treated specimen post ultrasonication (A), developed a rugged texture, shown in **Figure 6.1a**. The magnified image, **Figure 6.1b**, revealed elongated cracks (width less than $1\ \mu\text{m}$) of different lengths. It was believed that cracks appearing on the treated sample were

caused by the combined effect of stress induced by ultrasonication[118, 119] and dehydration of the base substrate upon drying[34]. Prior to the electroless deposition, a rough surface was desired since that enhances the adhesion of coatings and enables deposits to interlock mechanically with the substrate[112, 120]. **Figure 6.1c** shows the area from where the EDS data was collected, and **Figure 6.1d** shows the EDS spectrum of sample A. The elemental composition obtained by EDS analysis of the polished substrate is presented in **Table 6.1**. A notable rise in iron (Fe) content (from 0.02 to 1.3 wt.%) was reported on the sample after treatment, indicating that iron hydroxides might have been present on the surface of sample A. Additionally, there was significantly more oxygen (from 8.18 to 19.9 wt.%) detected on the treated sample, which suggests the formation of MgO and Mg(OH)₂ over the surface.

6.3 Synthesis of Coatings by Eco friendly Pretreatment

The detailed coating process is discussed in **section 3.3**, and the plating bath composition with operating condition for the synthesis with FeSO₄ · 7 H₂O is provided in **Table 3.2**. The pH of the bath was regulated by adding NH₃, but as shown in **Table A.2**, it is a category 1 hazardous substance. Hence, to eliminate the toxicity of plating bath another bath was prepared that did not contain NH₃. As a result, the plating baths prepared are categorized into two types: one with NH₃ (pH ≈ 10.0) and one without NH₃ (pH ≈ 8.0). The coating from the bath containing NH₃ is named T1 coating, and that does not contain NH₃ is named T2.

6.3.1 Development of Cracks in Coating

During the experiment, we observed that the T1 coatings developed coating fractures, while the T2 coating showed no evidence of coating failure. Therefore, to study the effect of plating conditions (plating bath temperature and plating time) on the crack initiation for T1 coating, the T1 coating was performed by varying the temperature, and time was noted when a crack is observed in the coating. As the temperature of bath rises, the rate of hydrogen evolution was intensified due to the acceleration of reaction rate at higher temperatures. It is observed that an increase in bath

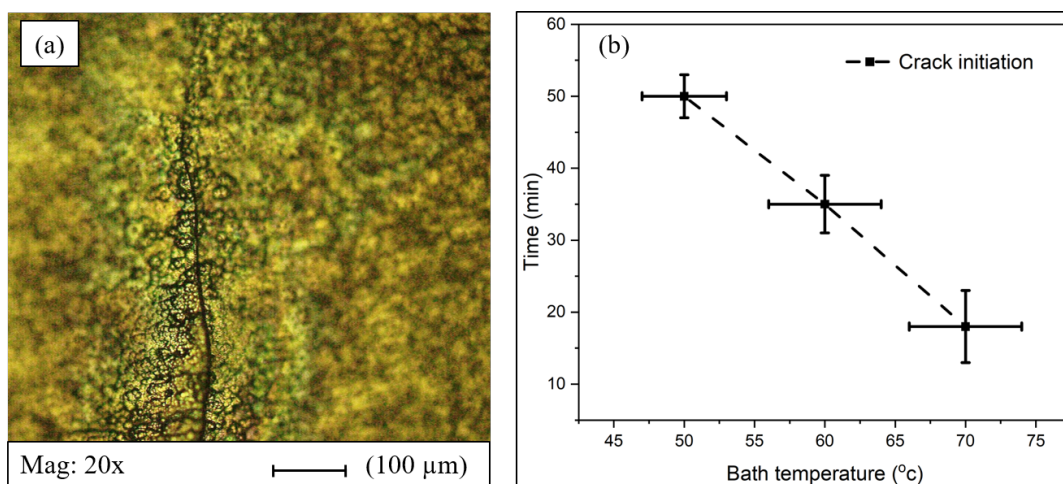


Figure 6.2: (a) Optical image of a crack in deposit, and (b) temperature and time dependency of crack initiation in T1 coatings.

temperature resulted in a quicker appearance of cracks in T1 coatings. **Figure 6.2a** shows the optical image of a crack in the coating, while the graph in **Figure 6.2b** illustrates the relationship between time and temperature for the earliest stages of crack formation. It is noticed that if the coating process persisted even after the formation of cracks on the surface, the deposit layers would fracture in form of chips. **Figure 6.3** displays the cross-sectional image of both coatings along with the EDS mapping of the cross-sectional morphology, which shows that the coatings exhibit homogeneity throughout their thickness. The T1 coating process exhibited the ability to apply coatings without any cracks for a duration of one hour. The measured thickness of the coatings for T1 and T2 was approximately $10.02 \pm 0.14 \mu\text{m}$ and $13.93 \pm 0.31 \mu\text{m}$, for a plating time of 55 and 120 minutes respectively. The deposition rate for T1 was $10 \mu\text{mh}^{-1}$, while for T2 it was $7 \mu\text{mh}^{-1}$.

6.4 Coating Characterization

Figure 6.4a,b display SEM images of T1 and T2, respectively. The T1 and T2 coatings exhibit surface morphologies that are typical for electroless coatings, which are nodular structures that resemble the appearance of cauliflower. In **Figure 6.4a**, micro-pits were observed, in some regions of the deposits in between nodules (identified in red circles). The inset in **Figure 6.4a** shows the enlargement of one

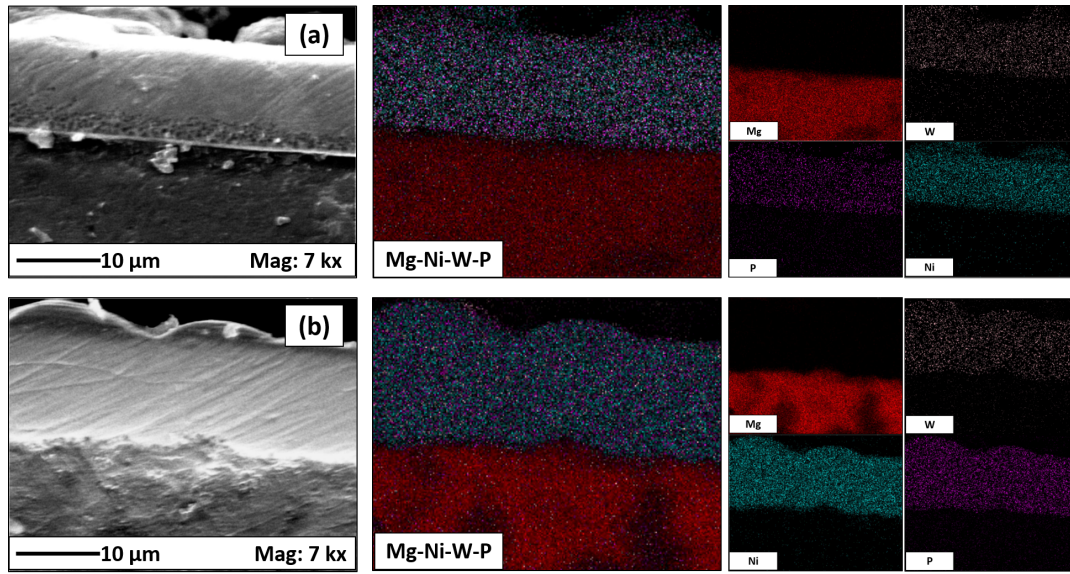


Figure 6.3: Cross-sectional image and their corresponding EDS maps of cross-sectional morphologies of (a) T1 after 55 min, and (b) T2 after 120 min of deposition.

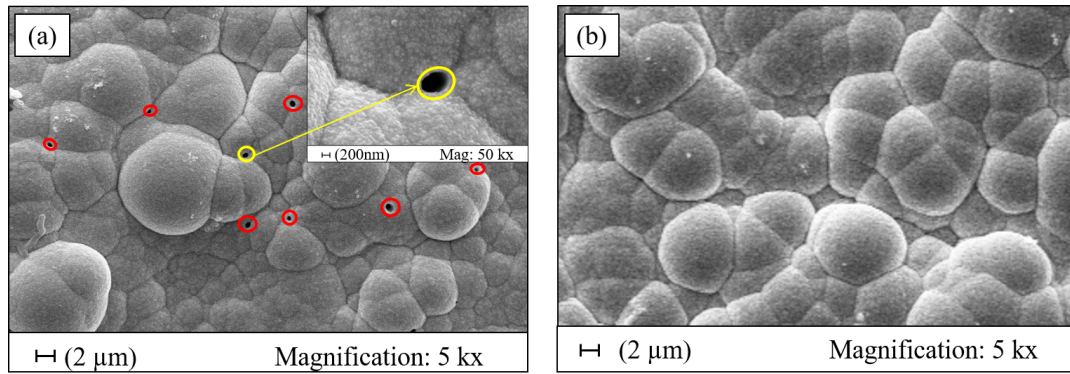


Figure 6.4: FESEM image of (a) T1 and (c) T2 coating.

of the pits, which is marked by a yellow outline. The morphology of the pits was predominantly circular or oval, with an area ranging from 0.2 to 0.3 μm^2 . Whereas, the T2 coating showed no evidence of observable pits within the deposits. The existence of pits is attributed to the intense evolution of hydrogen ions from the surface during the deposition process. The experimental findings indicate that the initiation of cracks was solely observed in T1 deposits at a coating time of 50-55 minutes, while maintaining the bath temperature at approximately 50-55°C. So it can be elucidated, although the pit-density in the surface is not high eventually these pits became the sites of crack initiation after a certain period of coating[41].

The XRD graphs of the polished Mg alloy before treatment (P), after treatment

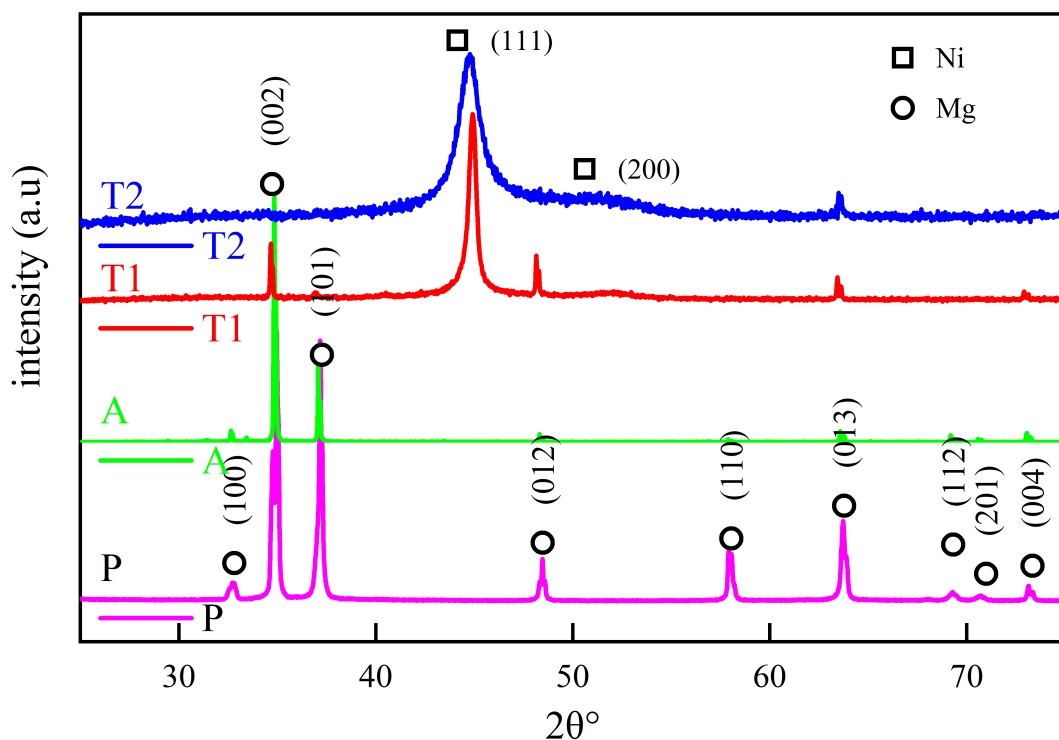


Figure 6.5: XRD patterns of Mg alloy before treatment (P), after treatment (A), T1, and T2 coating.

in aqueous solution of iron-sulfate (A), T1, and T2 coatings were presented in **Figure 6.5**. XRD patterns of specimens P and A show nine distinct peaks at about 33° , 34.5° , 37° , 48° , 57.5° , 63° , 69° , 71° , and 72.5° . XRD pattern of specimens P and A is similar to that of a magnesium alloy[106, 121]. Two broad peaks around 45° and 52° are observed for both T1 and T2 coatings, corresponding to the Ni (111) and Ni (200), respectively. **Figure 6.6** presents the EDS data of both the coatings; red rectangles (**Figure 6.6a,c**) represent the area from where the EDS data was collected; and **Figure 6.6b,d** show the EDS spectrum including the elemental weight, and atomic percentage.

High phosphorus (> 11 wt.%) deposits are completely amorphous, while medium phosphorus deposits contain a mixture of amorphous and crystalline nickel phases, and low phosphorus (< 4 wt.%) deposits consist of microcrystalline phases[3, 5]. As phosphorus content increases, the deposits structure changes from crystalline to amorphous. Therefore, considering the phosphorus concentration (9–10 wt.%) and the broad peak in the XRD pattern, the deposits exhibit a mixture of crystalline and

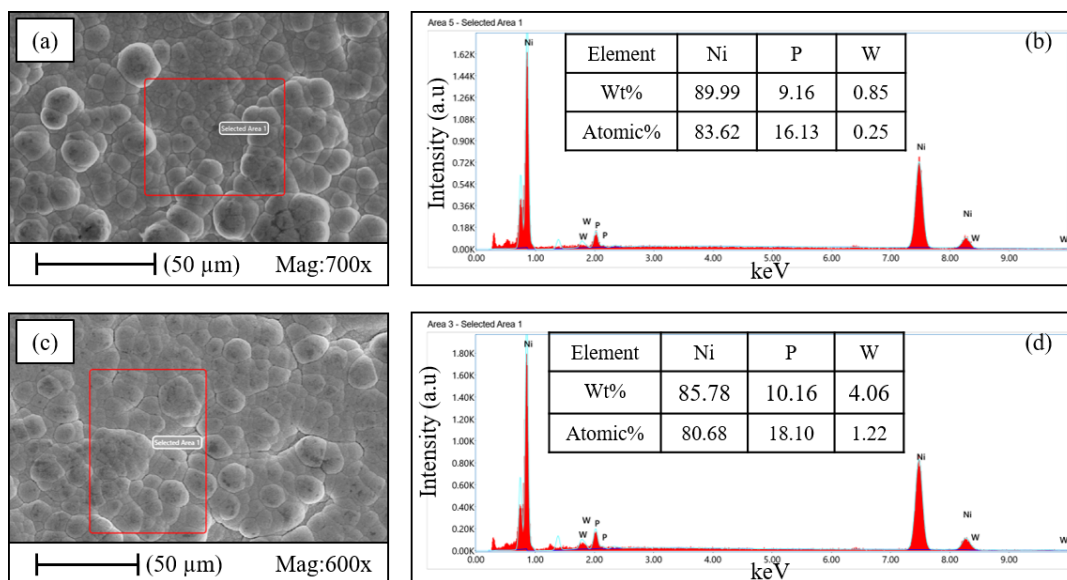


Figure 6.6: EDS analysis of (a, b) T1 coating, (c, d) T2 coating, the table shows the corresponding wt% of elements; (a, c) SEM image of the area from where EDS data is collected, and (b, d) EDS spectrum.

amorphous structures. A similar type of study is reported by E. Georgiza et al.[22] The peaks in XRD pattern corresponding to magnesium (Mg) and nickel (Ni) were identified by comparison with the JCPDS reference cards numbered 96-901-3056 and 96-901-1604, respectively.

The XRD pattern of T1 coating displays a few low intensity peaks that corresponding to the base substrate. Comparatively, in case of T2 coating the peaks of base substrate were heavily suppressed (only one peak for magnesium was observed). This was obvious as the disparity in coating time between T1 and T2 coatings, which was 55 minutes and 120 minutes, respectively, had an impact on the resulting coating thickness. The tungsten (W) content deposited in T2 coating (4.06%) is significantly higher than that of T1 coating (0.85%). Similar results have been reported in relation to an alkaline electroless solution, wherein the co-deposition of phosphorus and tungsten was observed to be more prominent in a bath with a pH of 8 compared to a pH of 10[93].

6.5 Micro and Nano-Hardness

Figure 6.7 displays the microhardness values of P, T1, and T2. Both coatings

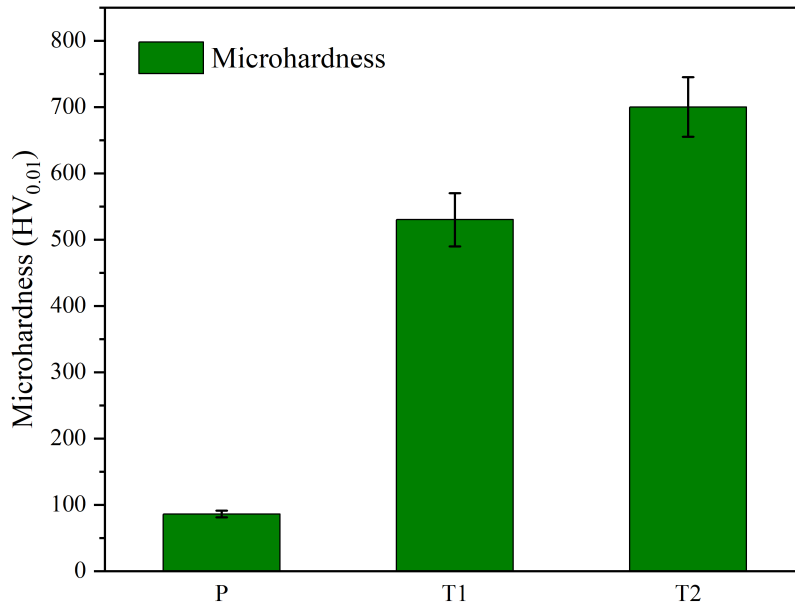


Figure 6.7: Microhardness of specimens.

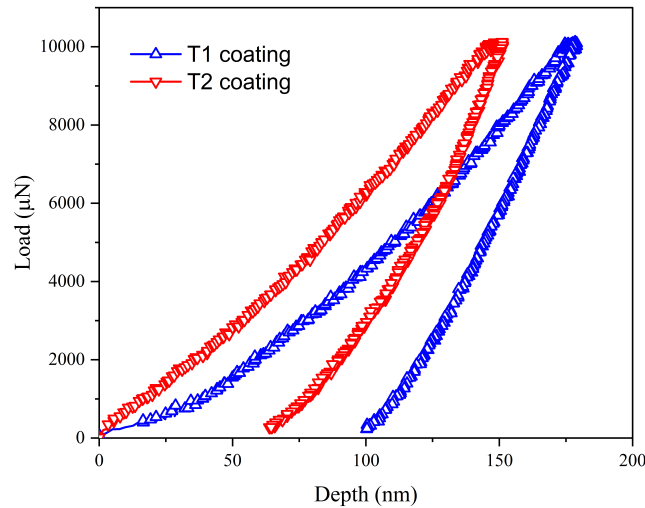


Figure 6.8: Load vs indentation depth of coatings.

showed an enormous rise in microhardness compared to the base alloy. According to previous studies[121], there is a tendency for the microhardness of binary Ni-P coatings to decrease as the phosphorus content increases. Despite T2 having a greater phosphorus content than T1, its increased microhardness can be attributed to the higher co-deposition of tungsten compared to T1. This indicates that tungsten exerts a greater influence on microhardness compared to phosphorus, and the third alloying constituent (W) has a significant impact on the hardness of the coatings.

Figure 6.8 displays the load versus indentation depth curve for the coatings

Table 6.2: *Hardness and reduced elastic modulus of coatings.*

Specimen	H(GPa)	E_r (GPa)	H/E_r
T1	5.06 ± 0.526	121.73 ± 14.08	0.0415
T2	7.735 ± 0.421	139.13 ± 12.94	0.0556

obtained during the nano-indentation test. **Table 6.2** shows the hardness and reduced elastic modulus of the coatings obtained from the nano-indentation test. The obtained curves demonstrate the coating's elastoplastic behavior. The residual depth (h_r) of T1 and T2 coatings were measured under the same load, revealing values of approximately 100 and 65 nm, respectively. This indicates a nearly 35% reduction in h_r for the T2 coating, implying a higher level of hardness compared to T1. A previous study with a tungsten content of 2.7% showed a hardness value of approximately 6.8 GPa[122]. The results of the nano-indentation test reveal that the T1 and T2 coatings (tungsten content 0.85 and 4.16%) exhibit average hardness values of 5.06 ± 0.526 and 7.735 ± 0.421 GPa, respectively. This shows that the effect of tungsten content is more significant for hardness than that of the microstructure of the coatings, as previously reported in a study of varying tungsten content in Ni-P coatings[123]. As evidenced by the microhardness test, it can be observed similar results (hardness of $T1 \leq T2$) from the nano-indentation test. Additionally, the corresponding reduced modulus (E_r) values for T1 and T2 coatings are 121.73 ± 14.08 and 139.13 ± 12.94 GPa, respectively. The index of coatings durability, known as the ratio H/E_r , has been widely acknowledged and this ratio can also be associated with the coatings capacity to withstand strain leading to failure, as per existing studies[124, 125]. The value of H/E_r for both the coatings is listed in **Table 6.2**.

The plastic work ratio (W_p/W_t) and elastic recovery (R) are evaluated as described in the literature[126]. Where W_p and W_t are plastic and total work done during indentation, and R is given by $R = (h_m - h_r)/h_m$. Where h_r and h_m are residual and maximum depth of indentation. This W_p/W_t ratio provides valuable insights into the magnitude of plastic deformation experienced by the specimen.

A value of 1 or 0 indicates that the deformation is completely plastic or elastic, respectively. The R and W_p/W_t values for T1 are 0.44 and 0.5354, respectively. For T2, the values are 0.57 and 0.4987, respectively. It can be inferred that T2 deposits show a higher elastic recovery when compared to T1.

6.6 Corrosion Study

Electrochemical corrosion tests were carried out to evaluate the corrosion performance of both the base substrate and the coated samples. open circuit potential (OCP) of the specimens was first assessed and displayed in **Figure 6.9a**. OCP on the base surface showed a gradual rise before stabilizing at approximately -1375 mV, followed by a small dip of 25 mV, whereas OCP on T1 and T2 surfaces is mostly stable at -325 mV and -330 mV, respectively. The ascending trend of OCP for the base can be attributed to the formation of protective $\text{Mg}(\text{OH})_2$ film at the surface, and since the film grows thicker as the water comes in contact with the metal, the passivity of the surface also increases, resulting in a higher OCP [127]. However, the presence of Cl^- ions in the solution also reacts with the hydroxide film to dissolve it, and the dynamic equilibrium of these two counteracting reactions is reflected by the fluctuations in OCP. However, the stable OCP values show that the coated surfaces are generally passive and highly resistant to such reactions.

The polarization curves for the base substrate and both the coatings in 3.5% NaCl solution are presented in Fig. 9b. The Tafel extrapolation method was used to analyze the polarization curves and determine the corrosion potentials (E_{corr}), corrosion current densities (i_{corr}). **Table 6.3** presents the corrosion parameters derived from Tafel extrapolation, for both the substrate and coatings. The corrosion parameters suggest an enhancement in the corrosion resistance of the coatings. The corrosion potential of both coatings exhibited a significant shift towards more positive values in comparison to the substrate. The corrosion current density values for T1 and T2 are approximately 3.94 and 1.92 $\mu\text{A}/\text{cm}^2$, respectively. These values are roughly three orders of magnitude greater than the substrate. In contrast, the bare substrate's

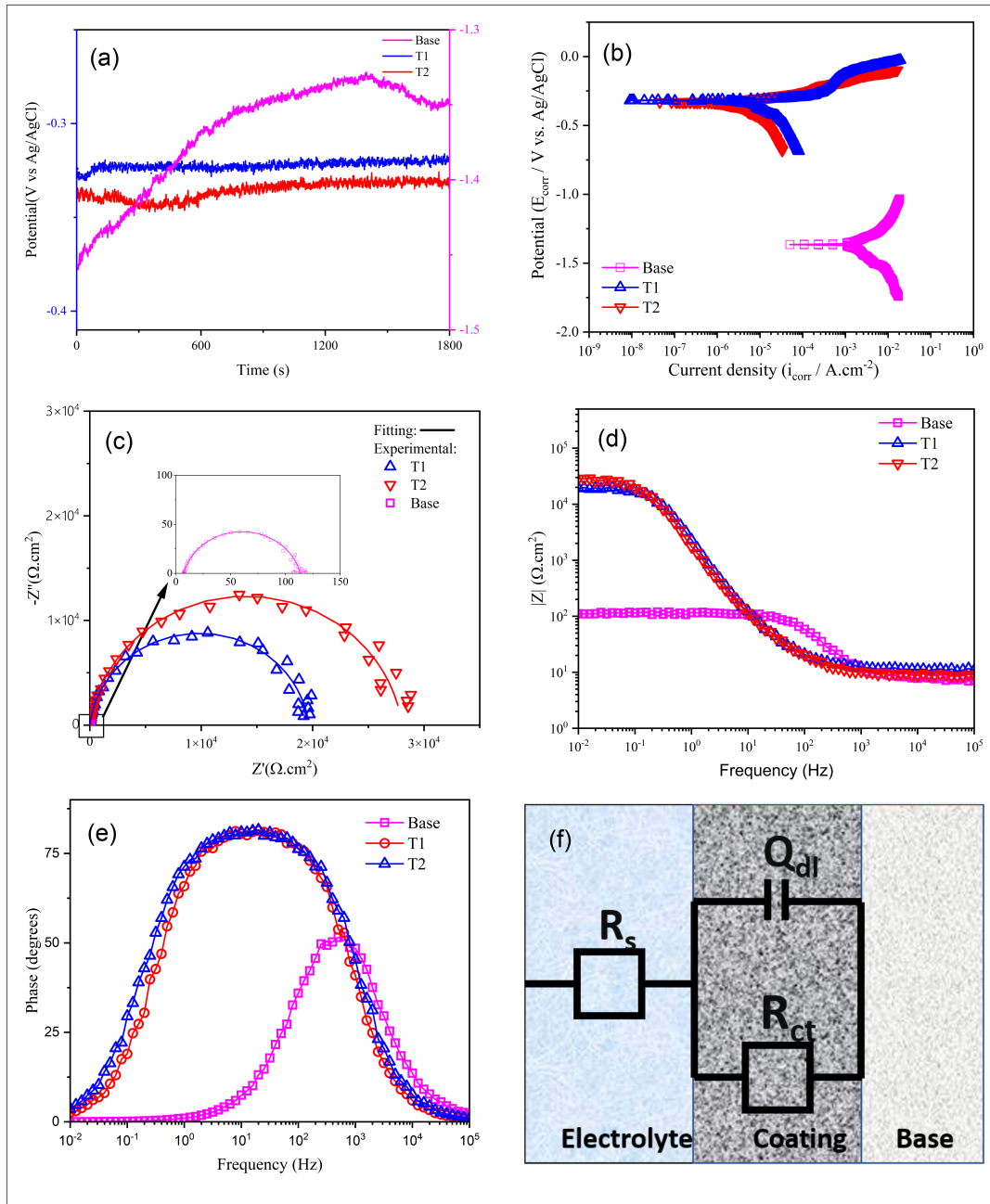


Figure 6.9: (a) Open-circuit potential, (b) Tafel plots, (c) Nyquist plots, (d) Bode impedance plots, (e) Bode phase plots, and (f) proposed equivalent circuit.

corrosion current density was found to be 1.368 mA/cm². This demonstrates an enhancement of the corrosion resistance in the coatings. Due to the moderate phosphorus content (T1 $\approx$ 9 and T2 $\approx$ 10 wt.%) present in the coatings, the resulting deposits exhibit a mixture of micro-crystalline and amorphous characteristics, which leads to a noticeable improvement in corrosion resistance [22, 128]. Both coatings

Table 6.3: Corrosion Parameters obtained from Tafel plot.

Sample	E_{corr} (V)	i_{corr} ($\mu A cm^{-2}$)
AZ31	-1.368	1102.6
T1	-0.320	3.94
T2	-0.330	1.92

show similar polarization curves, although certain distinctions are discernible. At equivalent over-potentials, the T2 coating displays a marginally reduced cathodic current compared to the T1 coating and shows a corrosion current density with half of the T1 coating. The T1 coating exhibited a pseudo-potential, whereas the T2 coating did not.

The passivation phenomenon in T1 coating was observed within the potential range of -0.25 to -0.13 V, which suggests the growth of a passive film and the corrosion current density was approximately $300 \mu A.cm^{-2}$. The observed phenomenon may be attributed to the electrolyte's infiltration into the micro-pits found in the T1 coating (**Figure 6.4**). The phenomenon of pseudo-passivation is typically observed in the anodic polarization of nickel alloys or nickel coatings [129, 130]. In nickel-phosphorus coatings, this behavior is attributed to the presence of micro-pits or defects within coatings [15,20]. However, the anodic polarization curve for T2 coating does not display any passivation. This corroborates the existence of pore-free deposits on the surface of the T2 deposit, as shown in **Figure 6.4**. The rapid oxidation of an active element above nickel content can result in a significant anodic current during anodic polarization. It is observed from the studies conducted by various authors[112, 118] that the presence of a third element in nickel-phosphorus coatings can affect passivation. The passivation ability is reduced in the presence of an element that is more active than nickel. When a coating contains an element that is nobler than nickel, the slope of the passivation zone becomes steeper. The T1 and T2 coatings contain tungsten in concentrations of 0.85 wt.% and 4.06 wt.%, respectively. This could be the reason for the disappearance of pseudo-passivation

Table 6.4: Fitted equivalent circuit component from EIS test.

Sample	$R_s (\Omega.cm^2)$	$R_{ct} (\Omega.cm^2)$	$Q_{dl}(F.s(\alpha - 1).cm^{-2})$
AZ31	7.336	106	38.19×10^{-6}
T1	11.09	19645	28.66×10^{-6}
T2	8.865	28011	31.64×10^{-6}

observed in the anodic polarization curve. Several authors have conducted studies indicating that ternary and quaternary electroless nickel coatings containing 4.5 wt.% tungsten exhibit optimal corrosion resistance[128, 131].

The EIS plots of the electrochemical corrosion test are presented in Fig. 9. The Nyquist plots (**Figure 6.9c**) of the EIS data reveal that the base surface has a very low impedance value, indicating low corrosion resistance, while the coated surfaces have impedance values two orders of magnitude higher than the base substrate. Therefore, the coatings are expected to improve the corrosion resistance of the Mg alloy substrate. Among the two coatings, T2 showed significantly higher impedance than T1, this could be attributed to the thicker deposits of T2 coating indicating more effective corrosion protection. Also, in the Bode plots (**Figure 6.9d**), the admittance of the T1 coating is higher than that of the T2 at the lower frequencies, and the trend changes at higher frequencies with the T2 showing a relatively higher admittance. At lower frequencies, the system behavior is more resistive, and the low admittance is a result of the overall high impedance, mainly due to the charge transfer resistance. As the frequency of the applied signal increases, the system's capacitive reactance decreases, allowing more current to pass[132].

For fitting the EIS data, a simple Randles cell consisting of the solution resistance (R_s) in series with the charge transfer resistance (R_{ct}) and a constant phase element (Q_{dl}) for the double layer capacitance was considered as the equivalent circuit (**Figure 6.9f**). From the fitted values (presented in **Table 6.4**) of the circuit components, both coatings had a much stronger capacitive nature compared to the Mg alloy surface, as reflected by the high exponents of the constant phase element,

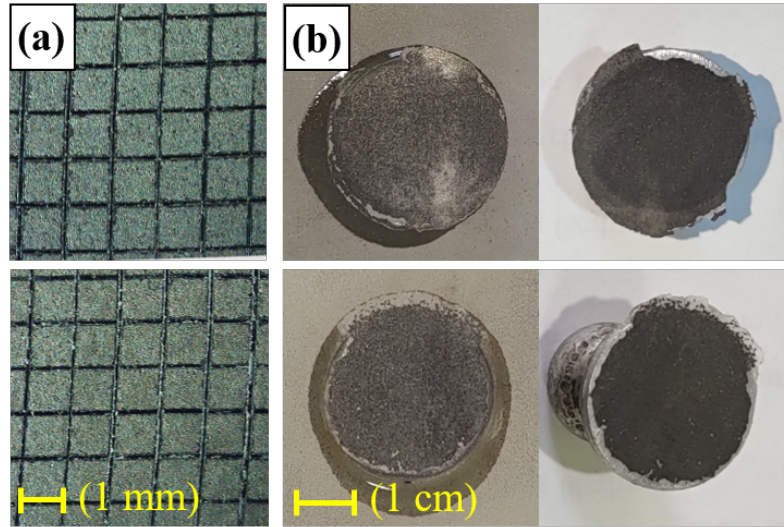


Figure 6.10: Images of coatings after (a, c) the tape test, (b, d) the pull-off adhesion test; (a, b) T1, and (c, d) T2 coatings.

and the R_{ct} of the T2 coating is almost 50% higher than that of the T1. The developed coatings demonstrate superior corrosion resistance, with the T2 coating expected to offer a higher protective ability among the two coatings.

6.7 Adhesion Strength of Coatings

Figure 3.1 displays the categorization of adhesion performance according to the ASTM D3359 standard [95]. The scale ranges from 5B to 0B, where 5B represents no removal and 0B represents more than 65 percent of the coated area. The adhesive strength of the coatings falls within the 4B category. **Figure 6.10a,c** display the images of the samples after the tape test. The pull-off adhesion test showed that the adhesion strength at the interface between the substrate and the coating is around 6 ± 0.24 and 8.1 ± 0.15 MPa for T1 and T2, respectively. **Figure 6.10b,d** display images of the coatings after the adhesion pull-off test. Both coatings showed satisfactory adhesive strength, yet T2 displayed slightly higher strength. When comparing the NiP coating on the Mg AZ91D alloy with pickling in HF + HCl and HF activation, it exhibits higher strength[21]. However, compared to pickling and pretreatment with molybdate (on the AZ91D alloy) and titanate (on the AM60 alloy), its strength is moderate[21, 34].

Table 6.5: Control parameters and their levels for Taguchi DOE of Ni-W-P coatings.

Factors	Levels (all concentrations are in g L ⁻¹)		
	1	2	3
Ni : NiSO ₄ · 6 H ₂ O	15	20	25
W : Na ₂ WO ₄ · 2 H ₂ O	15	20	25
P : NaH ₂ PO ₂ H ₂ O	20	25	30

6.8 Optimization of T2 Coatings

The factors considered in the Taguchi design are NiSO₄ · 6 H₂O (Ni), Na₂WO₄ · 2 H₂O (W), and NaH₂PO₂H₂O (P); and microhardness of the coating is chosen as the response parameter. Taguchi analysis is conducted to optimize the process parameters, employing a Taguchi L9 orthogonal array for three factors each at three levels. The specific levels of these factors are presented in **Table 6.5**.

6.8.1 Taguchi and ANOVA Analysis

Taguchi analysis was conducted, focusing on the main effects of the controllable factors. The control parameters along with their response and S/N ratio is presented in **Table 6.6**. From the main effects plots in **Figure 6.11**, the optimal parameter combination is identified as Ni3-W3-P1 i.e. the high level of Ni, the high level of W, and the low level of P. This plot also provides insight into the relative importance of each parameter in relation to response depending on the delta value. The delta values for S/N ratios of the control factors mentioned in **Table 6.7** reveal that factor W is highly significant, whereas factors Ni and P have comparatively lower significance.

According to the F-distribution chart, $F_{0.05,2,2}$ equals 19.0. **Table 6.8** presents the outcomes of ANOVA. It may be inferred that W is significant because its corresponding F-value is $40.91 > 19.0$ and P-value is below 0.05, which confirms that Na₂WO₄ · 2 H₂O significantly affect the microhardness of coatings with a 95.0 % confidence level. It is clearly observed from the delta, F, and P values, that the effect of W dominates among the three control factors. The microhardness value of

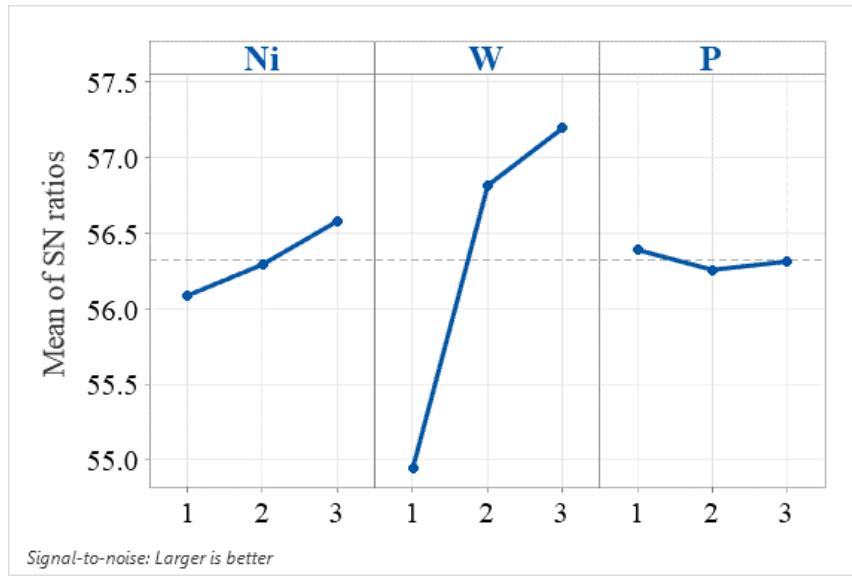


Figure 6.11: S/N ratio plots for main parameters.

Table 6.6: The L9 orthogonal array with microhardness and S/N ratio.

No.	Ni	W	P	Microhardness	S/N ratio
1	1	1	1	535	54.5671
2	1	2	2	676	56.5989
3	1	3	3	715	57.0861
4	2	1	2	562	54.9947
5	2	2	3	673	56.5603
6	2	3	1	734	57.3139
7	3	1	3	581	55.2835
8	3	2	1	731	57.2783
9	3	3	2	722	57.1707

coatings increases significantly with $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and when we look in to the effect of P, it is observed the microhardness decreases with increasing $\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$ in the bath.

Confirmation Test

A confirmation test was performed to validate the experimental findings, the results presented in **Table 6.9**. The S/N ratio for the optimal combination was higher

Table 6.7: Response table for S/N ratio.

Level	Ni	W	P
1	56.08	54.95	56.39
2	56.29	56.81	56.25
3	56.58	57.19	56.31
Delta	0.49	2.24	0.13
Rank	2	1	3

Table 6.8: Results from ANOVA analysis for L9 orthogonal array.

Source	DOF	SS	F-Value	P-Value
Ni	2	1970.9	1.47	0.363
W	2	45881.6	40.91	0.024
P	2	293.6	0.26	0.793
Error	2	1121.6		
Total	8	49267.6		

Table 6.9: Confirmation test results.

	Initial Combination	Optimal Combination	
		Predicted	Experimental
Level	Ni1W1P1	Ni3W3P1	N3W3P1
Hardness (HV _{0.01})	535	750	736
S/N ratio	55.31	57.52	57.34

than that of the initial combination. An increase of 2.03 dB in the S/N ratio was observed, corresponding to a 37.57% improvement in hardness of the coating at optimal combination compared to the initial combination and the predicted hardness value being close to the experimental result.

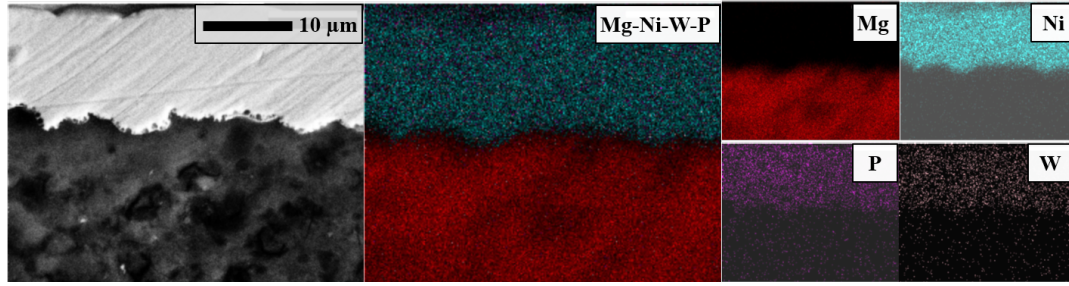


Figure 6.12: Cross-sectional SEM image and corresponding EDS maps of the coating at optimal run.

Table 6.10: Results from EDS analysis of T1 coatings.

Experiment	Composition of elements by weight (%)		
	Ni	W	P
Initial Combination	86	2.6	11.4
Optimal Combination	86.6	3.5	9.9

6.8.2 Characterization

The elemental composition of the coating from initial combination (Ni1W1P1) and the optimal combination (Ni3W3P1) is presented in **Table 6.10**. In the Ni3W3P1 bath combination, the concentration of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, tungsten source, is higher compared to the Ni1W1P1 bath, while the $\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$ concentration, phosphorus source, remains constant across both baths. This results in greater availability of tungsten ions in the Ni3W3P1 bath, leading to higher tungsten incorporation and reduced phosphorus deposition in the resulting coatings. Our findings are consistent with the investigation reported in the review article [23], who observed an inverse relationship between tungsten and phosphorus content in electroless Ni–W–P coatings, indicated by negative slopes in W vs P content plots. The increased tungsten and lower phosphorus content is likely responsible for the enhanced hardness observed in the coating. **Figure 6.12** shows the cross-sectional image of the coating at the optimal run, accompanied by EDS mapping of the cross-sectional morphology, demonstrating that the coatings exhibit homogeneity throughout their thickness.

6.9 Concluding Remarks

The present study successfully synthesized low-cost Ni-W-P coatings on magnesium alloy via a one-step eco-friendly pretreatment process. The pretreatment process produced a suitably coarse surface morphology that is essential prior to the application of electroless coating. The microstructure of coatings exhibit cauliflower-appearing nodular structures consisting of a mixture of microcrystalline and amorphous components. NH_3 in the plating bath cause micro-pits in the coating (T1) due to the higher rate of hydrogen formation. The presence of micro-pits in T1 and its high reaction rate led to the growth of crack formation sites in the coatings after a specific duration of deposition. The appearance of cracks in T1 coatings can be characterized as a dependent variable of both the time of coating and the temperature of the plating bath. An increase in bath temperature was observed to result in an earlier crack formation.

The T2 coatings co-deposited more tungsten and phosphorus (4.06 and 10.16 wt.%) in the deposits than in T1 coatings (0.85 and 9.16 wt.%). The T1 coatings reflected a higher plastic work ratio, lower elastic recovery, and lower H/E_r values. The effect of tungsten content dominates the effect of phosphorus content present on the hardness of the coatings. T2 coatings exhibited better hardness and corrosion resistance when compared to T1 coatings. The hardness of the coatings improved six to eight times compared to the base substrate. In terms of corrosion resistance, both T1 and T2 coatings have significantly higher corrosion resistance than the base alloy. The electrochemical impedance of coatings is two orders of magnitude higher than that of the base alloy. T2 has an impedance value that is 50% higher than T1.

According to the ASTM D3359 standard, the coatings adhesive strength falls under the 4B category. The coatings exhibited an adhesion strength of approx. 6 ± 0.24 and 8.1 ± 0.15 MPa for T1 and T2, respectively, as determined by pull-off adhesion test.

STUDY OF DROPLET IMPACT ON SHS

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Superhydrophobic surface (SHS) are distinguished by apparent water contact angles exceeding 150° and low contact angle hysteresis, arising from the combined effects of low surface energy chemistry and hierarchical micro/nanotexturing. Such surfaces favor the Cassie–Baxter wetting regime, in which an intervening air layer minimizes solid–liquid contact. As a result, droplets impacting SHS display limited adhesion, rapid recoil, and frequent rebound.

Understanding droplet impact on SHS is essential because impact events dictate the performance of these materials in applications such as self-cleaning, anti-icing, and spray-based thermal management. Unlike hydrophilic surfaces, where droplets spread and dissipate kinetic energy through viscous losses and wetting, SHS are governed primarily by inertia–capillary balance and interfacial energy exchange. These mechanisms lead to reduced contact times, suppressed wetting, and altered splashing behavior. Systematic investigation of impact dynamics therefore provides

critical insight for designing surfaces with tailored wetting and energy dissipation characteristics.

In this chapter, we investigate the dynamics of droplet impact on fabricated Superhydrophobic surface (SHS). The key aspects covered include: (i) visualization of the droplet morphology transitions during impact, up to and including the bounce-off phase, (ii) temporal evolution of spreading and height factors, (iii) derivation of correlations for maximum spreading factor (β_{max}) through both theoretical analysis and empirical scaling laws, (iv) the dependence of contact time on Weber numbers (We), (v) the velocities associated with spreading and retraction of the droplet, and (vi) the elastic response of the droplet as a function of We .

7.1 Fabrication of the Super-Hydrophobic Surface

SHS is fabricated on magnesium AZ31 alloy substrate via a solution based chemical coating process conducted at 65°C as described in **subsection 3.3.2 of chapter 3**. The resulting surface demonstrated a static contact angle of approximately 155° with contact angle hysteresis of less than 3°, as shown in the inset of **Figure 7.1a**.

Surface morphology is characterized by SEM, and is presented in **Figure 7.1**. **Figure 7.1a** reveals a homogeneous distribution of micro/nanostructure composed of randomly oriented, flake-like features resembling vertically aligned petals. This topography facilitates a non adhesive superhydrophobic behavior by promoting a Cassie-Baxter wetting state [133, 134], wherein trapped air pockets at the liquid-solid interface significantly reduce the actual contact area and thus minimize adhesion.

In contrast, **Figure 7.1b** shows localized aggregation of the petal-like structures into dense, flower-like clusters, indicating a heterogeneity in surface morphology. These morphological irregularities induce pinning of water droplets, resulting in a sticky superhydrophobic behavior. This behavior is attributed to the Wenzel wetting state [135], where the surface roughness induces increased wetting of microtextures, thereby increasing solid-liquid interfacial area and preventing easy detachment. A schematic depiction of the Cassie-Baxter and Wenzel wetting states are presented in

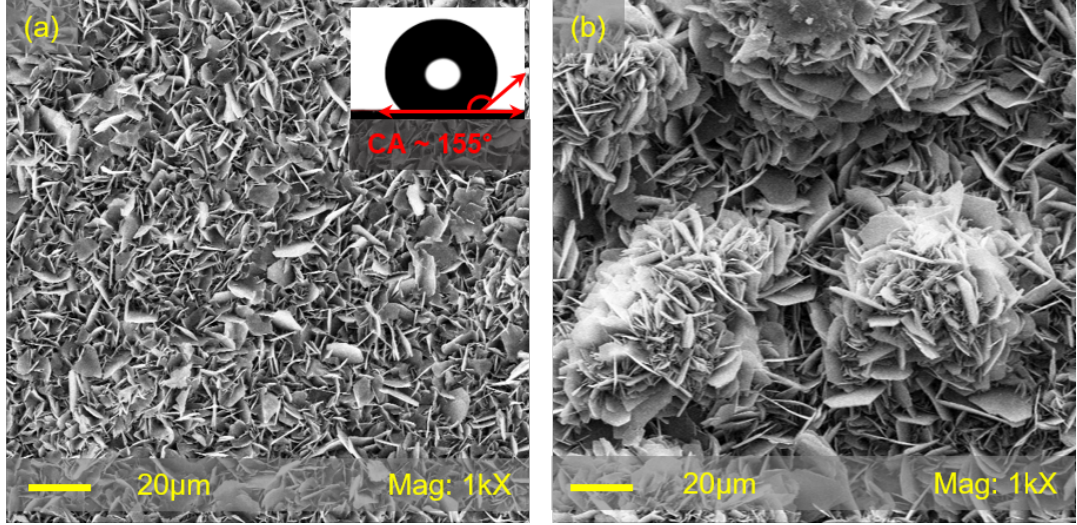


Figure 7.1: SEM image of the fabricated SHS showing (a) uniformly distributed microtextures promoting a Cassie-Baxter wetting state and (b) aggregated, flower-like clusters indicative of Wenzel type droplet pinning. The inset shows measured contact angle from the wettability test.

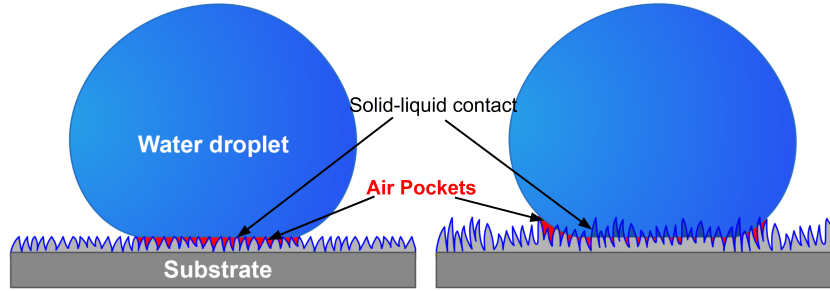


Figure 7.2: Schematic representation of Cassie-Baxter (left) and Wenzel (right) wetting states of a droplet exhibiting superhydrophobicity, illustrating differences in droplet-surface interactions.

Figure 7.2.

7.2 Experimental Setup for Droplet Impact

Droplet impact experiments are performed on the fabricated SHS to examine the dynamic behavior of water droplets upon impact. A microsyringe, mounted vertically on a precision stand, is employed to dispense water droplets with a controlled volume of approximately $7.5 \mu\text{L}$, corresponding to $D_0 \approx 2.6 \pm 0.05 \text{ mm}$. The droplets fall freely under the influence of gravity and impact on the SHS at room temperature (25°C). Impact velocity (U_0) is varied by adjusting the vertical distance between the syringe tip and the substrate surface, yielding velocities in the range of 145 to 700

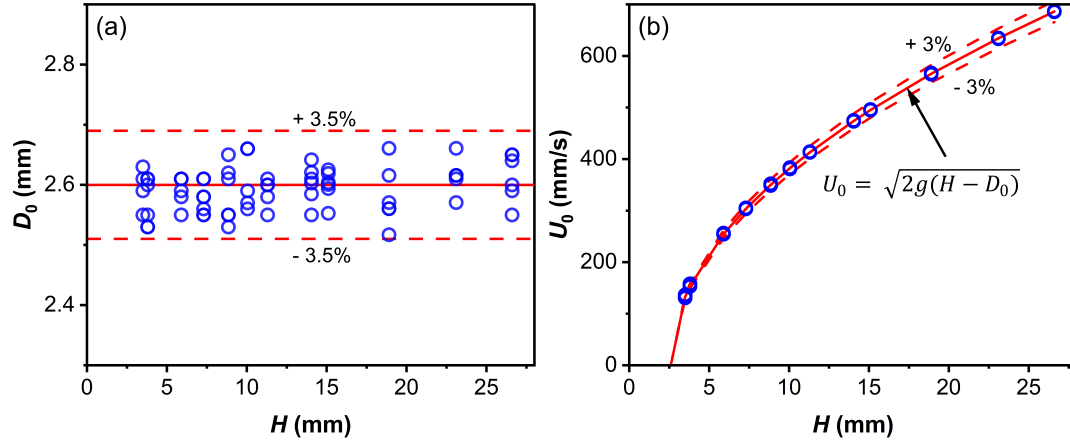


Figure 7.3: Uncertainty analysis for (a) D_0 and (b) U_0 at different release height.

mm/s. The corresponding We range from 0.75 to 17.

The droplet impact and spreading dynamics are recorded using a highspeed camera operating at 8000 frames per second. A uniform LED backlight with a diffuser is positioned behind the droplet to ensure sharp imaging. The experimental setup includes a laptop interfaced with the control software, a drop dispenser controller, and a rigid workbench that supports all components. The substrate is secured on an adjustable holder aligned beneath the dispensing needle. An image of the experimental setup with labeled components is provided in **Figure 3.2**.

7.2.1 Uncertainty analysis

The outer diameter of the dispensing syringe needle is measured to be 4.5×10^{-4} m. The needle is captured and used to calibrate the droplet snapshots, resulting in a conversion factor of $45 \mu\text{m}/\text{pixel}$. The maximum error in determining the droplet shape is estimated to be 3 pixels, corresponding to an uncertainty in droplet diameter of $135 \mu\text{m}$. Following the previous studies[136, 137], the relative error for We is calculated using equation $\Delta We/We = \Delta D_0/D_0 + 2\Delta U_0/U_0$. Accordingly, the repeatability of measurements for the initial droplet diameter (D_0) and impact velocity (U_0) is evaluated. The associated uncertainties are determined to be $\pm 3.5\%$ for D_0 and $\pm 3\%$ for U_0 , as illustrated in **Figure 7.3**, resulting in a relative error for We of 9.5%. U_0 is calculated by using the relation $U_0 = \sqrt{2g(H - D_0)}$. Where H denotes the release height and g is the gravitational acceleration ($g \sim 9.81\text{m/s}^2$).

7.3 Results and discussion

Experiments are performed to investigate the droplet impact dynamics on SHS. In each experiment, a droplet of deionized water is freely suspended over the surface from a certain height. Experiments are performed by varying the impact height, resulting in $U_0 \approx 145 - 700 \text{ mm/s}$ that corresponds to $We \approx 0.75 - 17$.

The temporal evolution of spreading factor (β) and height factor (ε), and t_c are analyzed from time resolved experimental snapshots. Upon impact, the contact diameter (D) and droplet outer diameter (d) gradually increases to their maximum value due to inertial forces, while the droplet height (h) decreases to a minimum. This is followed by a retraction phase, during which the contact diameter begins to retract while the droplet height increases under the effect of surface tension. Ultimately, the droplet detaches from the surface due to the residual kinetic energy [83].

7.3.1 Droplet impact visualization

We start with the case of very low U_0 where bouncing starts to occur. In our studies, the droplet rebound occurs with a critical U_0 of approximately $U_0 \approx 145 \text{ mm/s}$ ($We \approx 0.75$). Below this critical U_0 , the droplet sticks to the surface and oscillates (**Figure 7.4(i)**). The oscillation continues until it completely dissipates its kinetic energy [76]. As the U_0 increases beyond the critical value, the droplet gains sufficient kinetic energy to undergo a complete rebound (**Figure 7.4(ii-vi)**). In some cases partial bouncing of the droplet is observed above this critical value of U_0 , it could be because of the irregularities on the surface morphology as discussed in Section "Fabrication of the superhydrophobic surfaces". These irregularities on the surface may cause an impaled state in which the droplet attains a transition from Cassie to Wenzel state [134, 138, 139].

A complete rebound phenomenon includes three important stages namely spreading, retraction, and detachment. Droplet contact begins upon initial surface interaction and ends at the point of detachment. Based on the variation in spreading

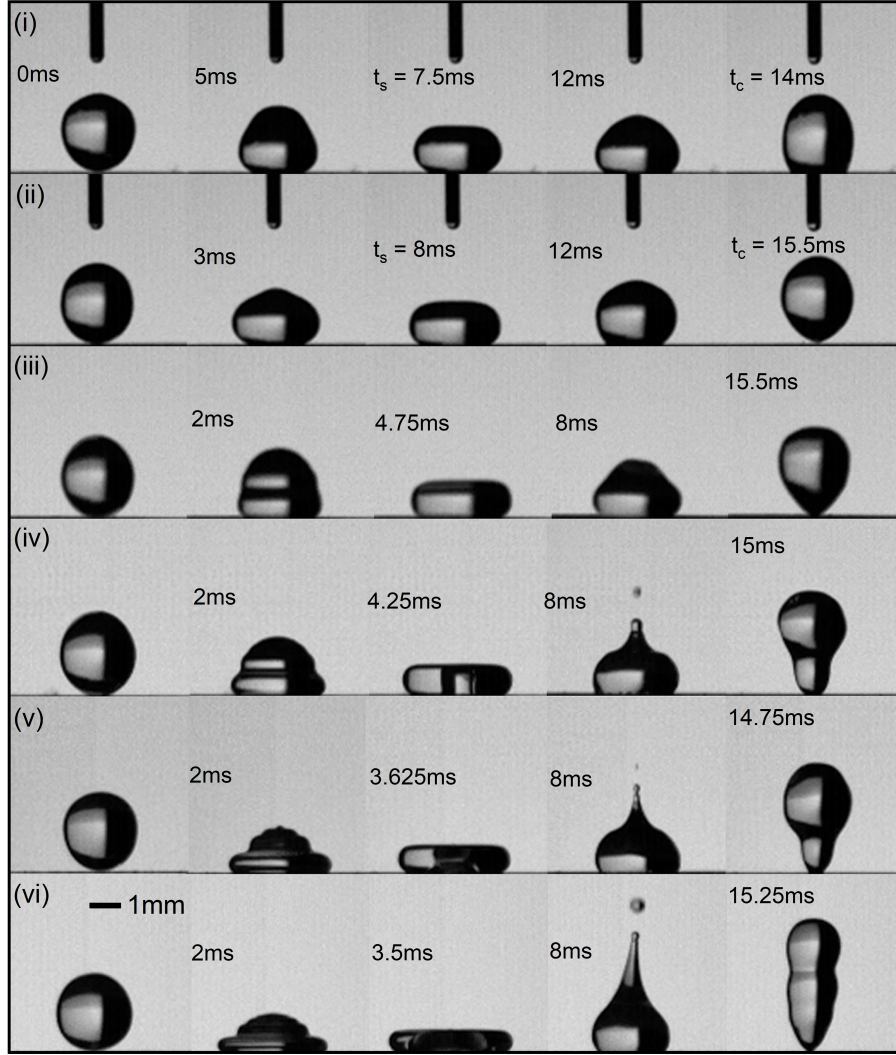


Figure 7.4: Sequence of water droplets impacting on the SHS at low to moderate $We \approx$ (i) 0.6, (ii) 0.75, (iii) 2.25, (iv) 6.1, (v) 11.7, and (vi) 14.5.

length, the contact phase is categorized into spreading and retraction stages. Due to inertial effects, the droplet extends outward during the spreading phase as its height decreases. When a droplet hits the solid surface, a capillary wave always arises (the second image of the sequence in **Figure 7.4**) and travels down the surface as it spreads. At $We > 3$, a cylindrical air cavity is developed at the droplet center simultaneously transforming into a toroidal shape (3rd image in **Figure 7.4**(iv-vi) and **Figure 7.5a**) due to the downward oscillation of capillary waves[140–142]. Eventually, the droplet morphology transforms from a spherical to a hat-like structure, generating a toroidal shape for $We > 3$ and a thin disk for $We < 3$. Once

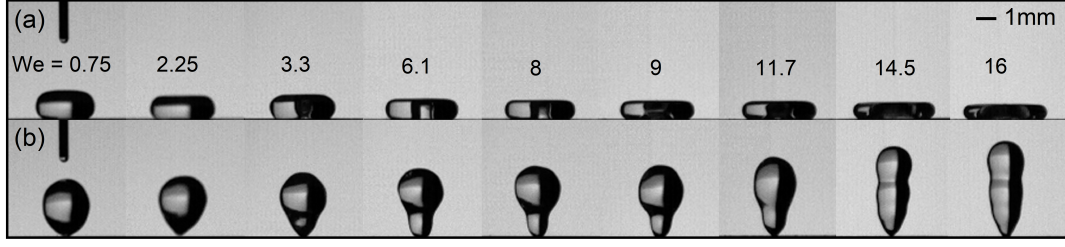


Figure 7.5: Snapshots of droplets, demonstrating the droplet's morphology (a) at maximum spreading (disc or toroid shape) and (b) at detachment, impacting on SHS at low to moderate We .

the droplet spreads to its maximum value, the retraction stage begins, and surface tension causes the droplet to compress towards its center, decreasing its spreading length while increasing its height. The rebound occurs when the spreading length becomes zero, leading to droplet detachment from the surface.

For cases exhibiting complete rebound, droplet detachment typically initiates near the center of the contact area, resulting in a largely axisymmetric morphology about the vertical axis as shown in **Figure 7.5**. This phenomenon exists for a few milliseconds, prior to the droplet's lift off. The morphology of the droplet at the point of detachment is strongly dependent on U_0 . The shape of the droplet upon detachment is presented in **Figure 7.5b**. The droplet shape is nearly spherical resembling a parachute with minimal deformation at very low We . With increasing We , the droplet begins to elongate vertically taking on a reminiscent of a pear shape, and for $We > 14$, the droplet is significantly stretched resembling an elongated ellipsoid shape. At very low We , the surface tension dominates over the inertial forces, maintaining the droplet shape. In contrast at higher We the inertial forces are stronger relative to the surface tension, causing more significant deformation. During the receding stage for $We > 4$, secondary droplets were observed (**Figure 7.4(iv-vi)**) ejecting with a higher speed from the primary droplet known as Worthing jet [53, 82]. The maximum diameter during spreading and the droplet height after rebound increases with the We . This demonstrates the increasing role of inertia with We showing the transition from a spherical to a stretched/elongated morphology upon detachment from the SHS. At maximum spreading, D_{max} increases and h decreases with We and upon detachment h increases with We .

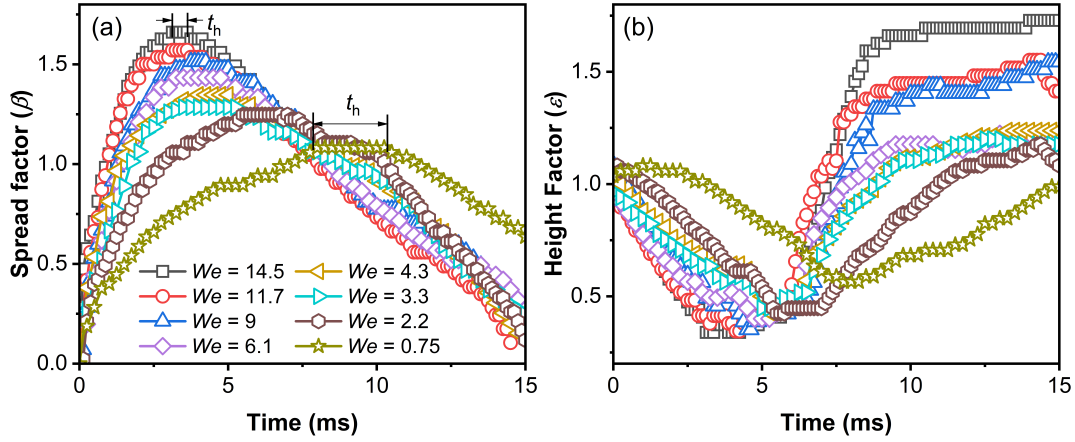


Figure 7.6: Temporal evolution of (a) β and (b) ε for different We .

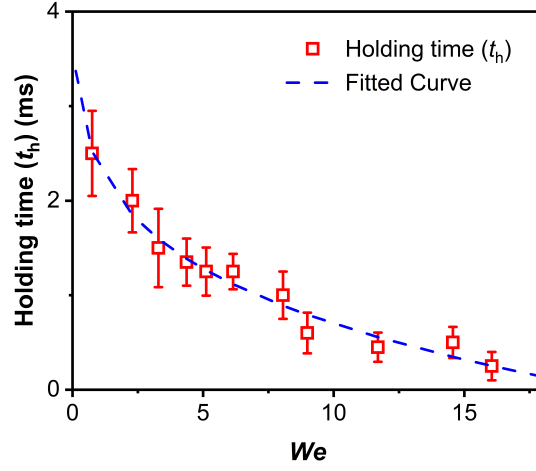
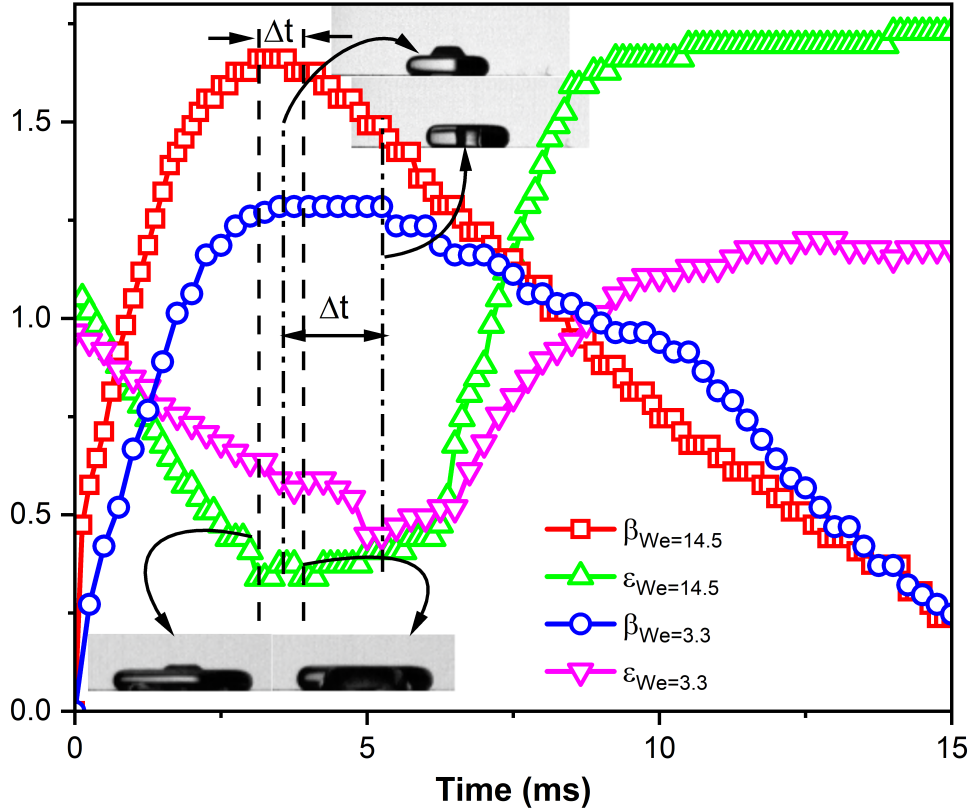
7.3.2 Time evolution of spreading and height factor

The temporal evolution of the β , presented in **Figure 7.6a**, indicates that the time required to reach the maximum spread (t_s) decreases with increasing We . Upon droplet impact on the surface, β , representing the contact length, undergoes a rapid increase driven by the initial kinetic energy until reaching its peak value (β_{max}), followed by a slower retraction phase. During the spreading phase, the kinetic energy is predominantly converted into surface energy. At very low We , both spreading and retraction occur at a slower rate due to the dominance of surface tension forces [65], whereas at higher We , the droplet attains maximum spreading more rapidly.

A noteworthy observation emerging from the temporal evolution of β is the transient holding of the droplet configuration at maximum spread, which persists for a finite interval termed as holding time (t_h). t_h is larger for low We and smaller for high We . The corresponding trend is quantified in **Figure 7.7**, where t_h exhibits a decreasing trend with We , suggesting more rapid transition dynamics at higher impact energies. The empirical relation of t_h with We can be expressed as

$$t_h = 5.2 - 2.84We^{0.2}; \quad R^2 \sim 0.971 \quad (7.1)$$

Time evolution of ε follows a distinct trend, as illustrated in **Figure 7.6b**, where it


 Figure 7.7: Variation of t_h with We .

 Figure 7.8: Temporal evolution of β and ε for $We = 3.3$ and 14.5 showing $\varepsilon_{min,1}$, ε_{min} , and the time difference of occurrence of the two (Δt).

initially decreases rapidly to a minimum value and subsequently increases during the retraction phase. Prior to detachment, the droplet undergoes maximum elongation. For impact at $We < 3$, the droplet transforms into a disk shape of thickness h_{min} at maximum spread. However, at higher We ($We > 3$), a toroidal shape is formed as

depicted in **Figure 7.5**, with two distinct minima as observed in the height evolution. To further analyze these morphological transitions, the temporal evolution of ε for $We \sim 3.3$ and 14.5 is presented in **Figure 7.8**. The first minimum ($\varepsilon_{min,1}$) transpires during the transition of droplet from hat-like shape to a thin disk during the spreading phase. Following maximum spreading, the droplet morphology transforms from a thin disk to a toroidal shape at the onset of retraction, resulting in second minimum (ε_{min} , which is also the global minima). These morphological transitions follow the sequence: $\varepsilon_{min,1} \rightarrow \beta_{max} \rightarrow \varepsilon_{min}$ (or equivalently, $h_{min1} \rightarrow d_{max} \rightarrow h_{min}$). The first minima appear shortly before maximum spreading (β_{max}), while the second one follows β_{max} , indicating the onset of retraction. The time interval (Δt) between the first (t_{e1}) and second minima (t_e) decreases with increasing We . The Δt reduces from 2 ms to 0.75 ms as We increases from 3.3 to 14.5. Additionally, the time corresponding to maximum spreading (t_s) and minimum elongation (t_e) decreases with increase in We , as shown in **Figure 7.9**. For the impacts at $We < 3$, the time to reach maximum spread (t_s) exceeds the time of minimum elongation (t_e), indicating that the minimum elongation occurs before the droplet attains its maximum spread. In contrast, for $We > 3$, the relationship reverses ($t_s < t_e$), meaning that the minimum elongation occurs after the droplet has reached its maximum spread.

7.3.3 Theoretical analysis for maximum spreading factor

We propose a theoretical estimate on the maximum spreading factor of a droplet. According to the principle of energy conservation, the total energy of a droplet prior to impact, comprising its kinetic and surface energies, should be equal to the sum of the kinetic energy, surface energy at maximum spreading, and the energy dissipated due to viscous losses during the spreading phase [72, 73]. Accordingly, the energy equation of a freely falling droplet can be expressed as

$$E_{k,0} + E_{s,0} = E_{k,f} + E_{s,1} + E_v \quad (7.2)$$

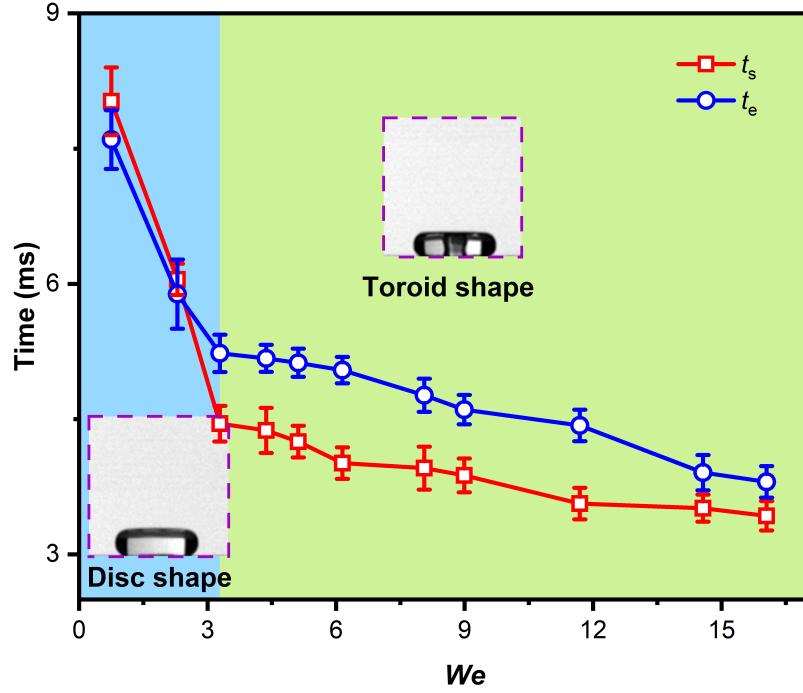


Figure 7.9: Variations in times of maximum spreading (t_s) and minimum height (t_e) with We showing the shape of droplet at maximum spread.

Where, E_k , E_s , and E_v are kinetic energy, surface energy, and energy loss due to viscous dissipation, respectively. The subscripts 0 and f refer to the states before impact and at maximum spreading. Oh (oh) quantifies the relative importance of viscous force to surface tension force, and the viscous effects can be neglected for a droplet impacting on SHS if $Oh \ll 0.1$ [140, 143, 144]. Furthermore, Clanet et al. [64] introduced an impact number, $P = We/Re^{4/5}$, to characterize whether the droplet impact dynamics on a SHS is governed by viscous forces or capillary forces. When $P > 1$, β_{max} is influenced by the interplay between inertial and viscous forces. While for $P < 1$, β_{max} is primarily determined by the balance between inertial and surface tension forces. In our study, $0.75 \leq We \leq 17$ and $370 \leq Re \leq 1750$, this yields $Oh \ll 0.1$ and $P \ll 1$. Therefore, neglecting E_v , Eqn.(7.2) becomes

$$E_{k,0} + E_{s,0} = E_{k,f} + E_{s,1} \quad (7.3)$$

The surface energy depends on the surface area of the droplet, hence the droplet geometry approximation plays an important role in estimating the surface energy

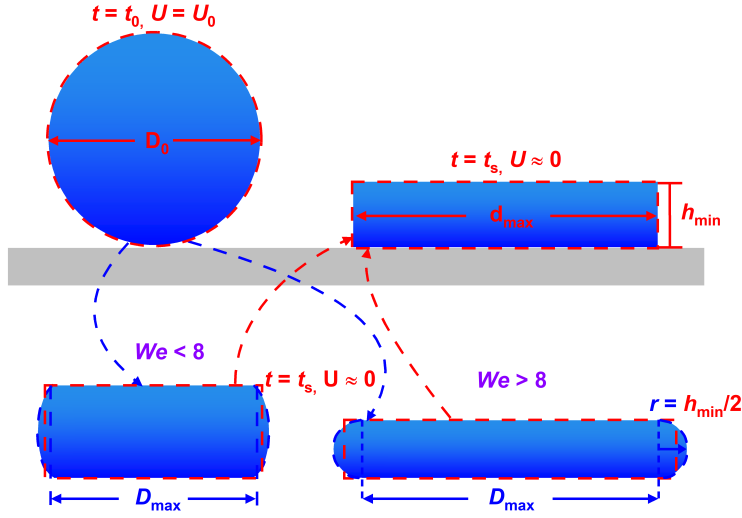


Figure 7.10: Schematics of droplet impact at $t = 0$ and maximum spread ($t = t_s$).

accurately. Theoretical models for β_{max} , with different geometry approximations of the droplet shape at maximum spreading, are presented in Eqns.(2.1)–(2.3). Eqns.(2.1) and (2.2) are based on a cylindrical disk assumption, whereas Eqn.(2.3) assumes a lamella surrounded by a rim, whose cross section presents one quarter of ellipse.

Motivated by our experimental findings, we assumed the droplet shape to be a cylindrical disk with curved edges like a coin, as presented in **Figure 7.10**. The droplet with initial diameter D_0 and velocity ($U = U_0$) adopts cylindrical disk shape at maximum spreading, with a diameter d_{max} and height h_{min} . At the maximum spread $U \approx 0$, the terms $E_{k,0}$, $E_{s,0}$, $E_{k,f}$, $E_{s,1}$ will become

$$E_{k,0} = \frac{1}{2}mU_0^2 = \frac{1}{2} \left(\rho \frac{\pi D_0^3}{6} \right) U_0^2 \quad (7.4)$$

$$E_{k,f} = 0 \quad (7.5)$$

$$E_{s,0} = \sigma A_0 = \sigma \pi D_0^2 \quad (7.6)$$

$$E_{s,f} = \sigma A_f = \sigma \left(\frac{\pi}{4} d_{max}^2 (1 - \cos \theta) + \pi d_{max} h_{min} \right) \quad (7.7)$$

Here, h_{min} can be expressed in terms of d_{max} by applying the volume conservation of the droplet, assuming there is no volume loss during spreading. We obtain,

$$\frac{\pi}{4} d_{max}^2 h_{min} = \frac{\pi}{6} D_0^3 \quad (7.8)$$

$$h_{min} = \frac{2D_0^3}{3d_{max}^2} \quad (7.9)$$

Substituting Eqns.(7.4)-(7.7) and (7.9) in Eqn.(7.3),

$$\frac{1}{2} \left(\rho \frac{\pi D_0^3}{6} \right) U_0^2 + \sigma \pi D_0^2 - \sigma \left(\frac{\pi}{4} d_{max}^2 (1 - \cos \theta) + \pi d_{max} \frac{2D_0^3}{3d_{max}^2} \right) = 0 \quad (7.10)$$

$$\frac{1}{12} \left(\frac{\rho D_0 U_0^2}{\sigma} \right) + 1 - \left(\frac{d_{max}^2}{4D_0^2} (1 - \cos \theta) + \frac{2D_0}{3d_{max}} \right) = 0 \quad (7.11)$$

$$\left(\frac{d_{max}^2}{4D_0^2} (1 - \cos \theta) + \frac{2D_0}{3d_{max}} \right) = 1 + \frac{We}{12} \quad (7.12)$$

$$3(1 - \cos \theta) \left(\frac{d_{max}}{D_0} \right)^3 + 8 = (12 + We) \frac{d_{max}}{D_0} \quad (7.13)$$

For $We < 8$, the width of curved shape is very small, and hence D_{max} can be approximated as d_{max} . However, for higher We , the width is significant and the curved shape is similar to semicircle of radius $r = h_{min}/2$. Thus, the actual diameter D_{max} deviates from the apparent diameter d_{max} , and can be related by the conservation of droplet volume as,

$$\frac{\pi}{4} (d_{max}^2 - D_{max}^2) h_{min} = \frac{\pi^2}{8} (D_{max}) h_{min}^2 + \frac{\pi}{6} h_{min}^3 \quad (7.14)$$

Substituting the value of h_{min} from Eqn.(7.9) yields,

$$\frac{1}{2} (d_{max}^2 - D_{max}^2) = \frac{\pi}{4} (D_{max}) \left(\frac{2D_0^3}{3d_{max}^2} \right) + \frac{1}{3} \left(\frac{2D_0^3}{3d_{max}^2} \right)^2 \quad (7.15)$$

Normalizing with respect to D_0 ,

$$\left(\frac{d_{max}}{D_0} \right)^2 - \left(\frac{D_{max}}{D_0} \right)^2 = \frac{\pi}{3} \left(\frac{D_{max}}{D_0} \right) \times \frac{1}{\left(\frac{d_{max}}{D_0} \right)^2} + \frac{8}{27} \times \frac{1}{\left(\frac{d_{max}}{D_0} \right)^4} \quad (7.16)$$

$$\beta_{max}^2 = \left(\frac{d_{max}}{D_0} \right)^2 - \frac{\pi \beta_{max}}{3 \left(\frac{d_{max}}{D_0} \right)^2} - \frac{8}{27 \left(\frac{d_{max}}{D_0} \right)^4} \quad (7.17)$$

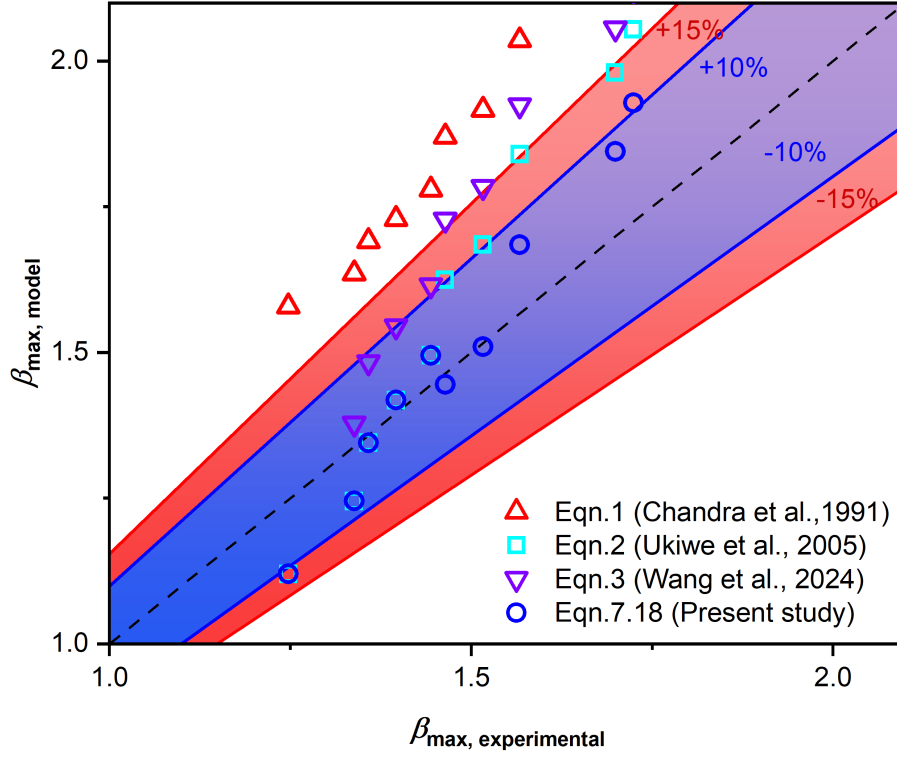


Figure 7.11: Comparison of the experimental β_{max} with the estimated β_{max} of present and previous theoretical models.

Finally, the modified expression for β_{max} can be written as

$$3(1 - \cos \theta)B^3 + 8 = (12 + We)B; \quad \begin{cases} \beta_{max} = B, & \text{for } We \leq 8 \\ \beta_{max}^2 = B^2 - \frac{\pi\beta_{max}}{3B^2} - \frac{8}{27B^4}, & \text{for } We > 8 \end{cases} \quad (7.18)$$

We assess the applicability of the present model using our experimental data and compare it with previous models reported in the literature. As shown in **Figure 7.11** the experimental data aligns closely with the present model, which estimates β_{max} more accurately than earlier models.

7.3.4 Empirical scaling laws for spreading and height factor

As shown in **Figure 7.9** and **Figure 7.12a**, β_{max} and ε_{max} increase with We , while ε_{min} and timescales to reach both β_{max} and ε_{min} decrease correspondingly. The droplet maintains its maximum spreading state for a few milliseconds before retraction. Due to the superhydrophobic characteristic of the surface and the efficient

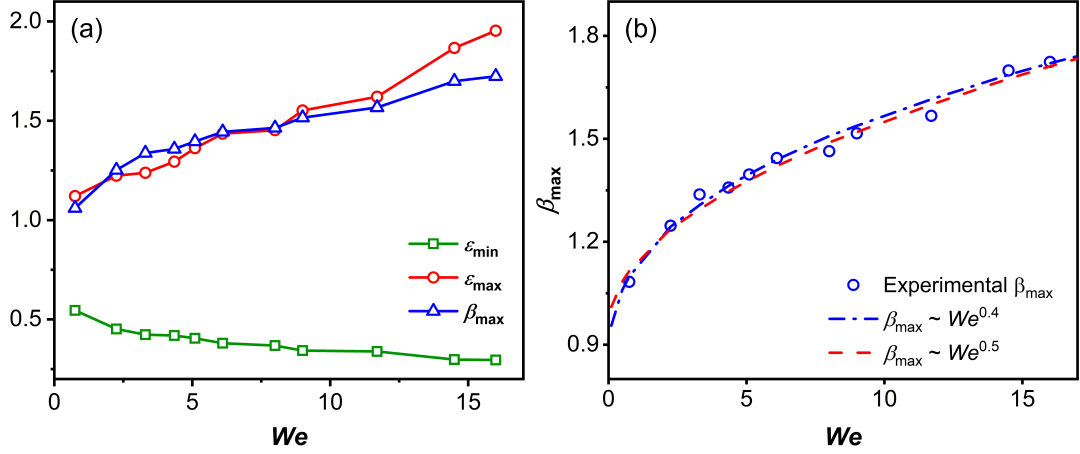


Figure 7.12: Variations of β_{max} , ϵ_{min} , and ϵ_{max} and (b) Correlation of β_{max} with We .

rebound at low We , viscous dissipation during impact is minimal [64, 76], suggesting that the kinetic energy of the droplet is predominantly converted into surface energy. Accordingly, β_{max} is governed by the balance between inertial and surface tension forces and exhibits a dependence on the We . Previous investigations[66, 76] have proposed scaling laws as $\beta_{max} \sim We^{0.5}$ and $\sim We^{0.25}$ with numerical coefficients 0.18 and 0.9, respectively. The dependence of β_{max} on We in this study is presented in **Figure 7.12b**, where the best fit power law relation yields $\beta_{max} \sim We^{0.4}$ with a coefficient of determination of $R^2 \approx 0.985$. When constraining the exponent to 0.5, as predicted in previous studies [76], the quality of the fit slightly decreases to ($R^2 \sim 0.98$), and the scaling coefficient decreases from 0.29 to 0.19. Based on experimental data obtained from droplet impacts on the fabricated SHS, the empirical relationship can be expressed as:

$$\beta_{max} = 0.84 + 0.29We^{0.4} \quad (7.19)$$

$$\beta_{max} = 0.95 + 0.19We^{0.5} \quad (7.20)$$

Additionally, we presented correlations for ϵ_{min} and ϵ_{max} . ϵ_{min} follows a scaling relation of $\sim We^{-0.33}$, while the ϵ_{max} exhibits a linear dependence on We with a slope of 0.05.

$$\epsilon_{min} = 0.4We^{-0.33} - 0.15; R^2 \sim 0.95 \quad (7.21)$$

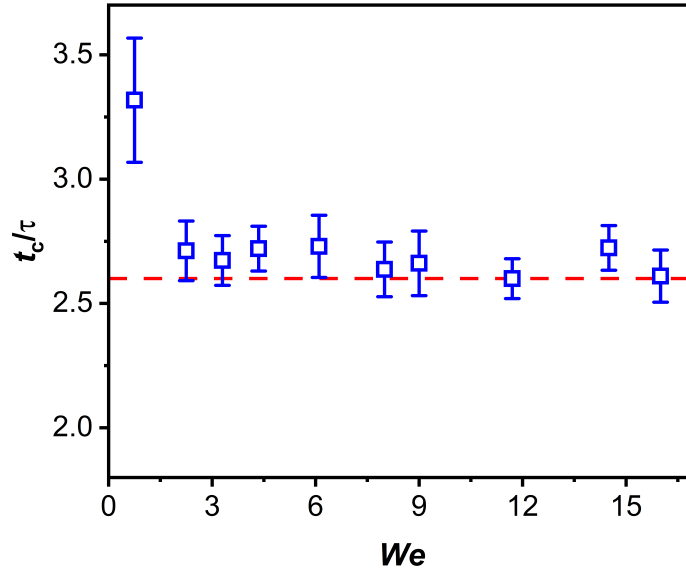


Figure 7.13: Dimensionless contact time for different We .

$$\varepsilon_{max} = 1.08 + 0.053We; R^2 \sim 0.983 \quad (7.22)$$

7.3.5 Contact time (t_c)

t_c of a droplet rebounding from a SHS has been shown to follow the scaling law $t_c = (2.6 \pm 0.1)\sqrt{\rho D_0^3/8\sigma}$, as originally proposed by Richard et al. [74]. This expression highlights the dependence of fundamental droplet properties, surface tension (σ), density (ρ), and initial droplet diameter (D_0) through inertial-capillary timescale $\tau = (\rho D_0^3/8\sigma)^{1/2}$. Notably, t_c is independent of U_0 , indicating that t_c is governed by fluid properties and interfacial forces rather than kinetic energy of the droplet. In the present study, the dimensionless contact time, defined as the ratio of t_c to τ , was determined to be approximately 2.7, shown in **Figure 7.13**, in close agreement with the reference value of 2.6 ± 0.1 . Across We ranging from $We \sim 0.75$ to 17, this normalized contact time remained constant. However, at $We \sim 0.75$, a slightly larger value ($t_c/\tau \sim 3.3$) was observed, consistent with the previous findings [76, 145, 146]. These results further confirm that t_c remains independent of U_0 for low-viscosity droplets such as water on SHS, as originally predicted by Richard et al [74].

7.3.6 Influence of toroidal deformation on spreading and retraction velocities

To investigate the droplet spreading and retraction dynamics upon impact, the spreading velocity (v_s) and retraction velocity (v_r) were evaluated using the relations $v_s = d_{max}/2t_s$ and $v_r = d_{max}/2(t_c - t_s)$ as given by Biroun et al.[136]. The variation of spreading velocity (v_s) and retraction velocity (v_r) with We is presented in **Figure 7.14**. v_s increases rapidly as We is increased, whereas v_r remains relatively constant. The data reveal a distinct transition in the spreading dynamics near $We \approx 3$, where v_s follows a piecewise linear trend. For $We < 4$, the slope of v_s versus We curve is approximately 0.08, indicating a rapid increase in v_s . Beyond this threshold, the slope decreases to ≈ 0.021 , reflecting a reduced rate of increment in v_s . This transition correlates with a morphological shift in the droplet shape during impact as shown in **Figure 7.5**. Clanet et al. [64] demonstrated that the impact-induced internal flow in droplets is primarily vortical in nature. They argued that the droplet's initial kinetic energy is partitioned not only into surface energy but also into internal kinetic energy. The formation of a toroidal morphology at high We facilitates more complex internal flows[142, 147], diverting a greater fraction of kinetic energy away from lateral spreading toward internal motion.

At $We < 3$, droplets deform extensively upon impact and show behavior analogous to elastic body. Conversely, at $We > 3$, toroid formation facilitates more complex internal motion, causing increased conversion of the initial kinetic energy into internal motion. This redistribution of energy explains the observed reduction in the rate of increase in v_s at higher We . The observations are further supported by β_{max} (or equivalently, D_{max}). At $We < 3$, a pronounced rise in β_{max} (**Figure 7.12**) coupled with a rapid decline in time to reach maximum spread (t_s) (**Figure 7.9**) results in a sharp increase in v_s . Conversely, at elevated We , both the increment in β_{max} (**Figure 7.12**) and the decline in t_s (**Figure 7.9**) are moderate, resulting in a less pronounced rise in v_s . Despite the continuous growth of D_{max} with We , v_r is nearly constant, which agrees with the previous study by Bartolo et al.[141] where

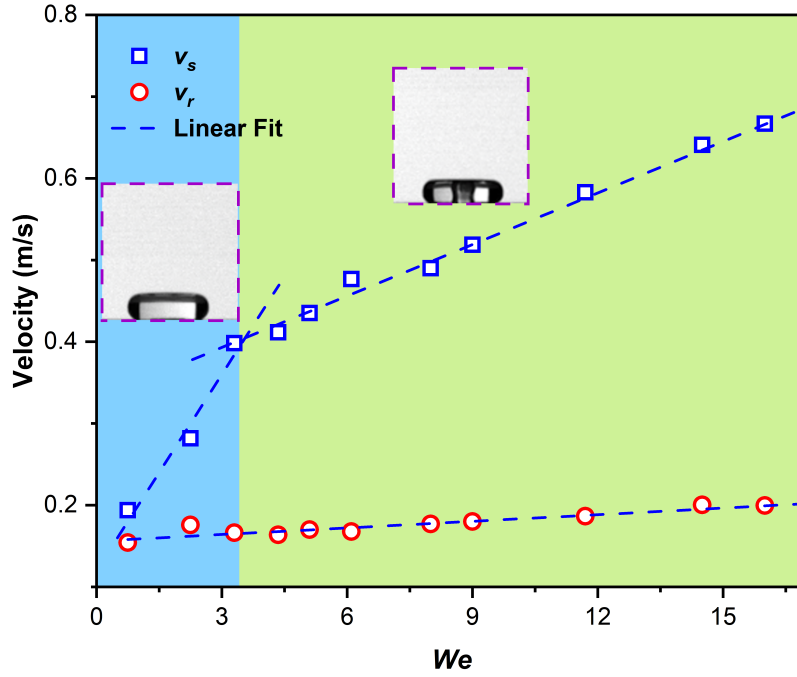


Figure 7.14: Variation of v_s and v_r with We . The dashed blue lines represent linear fits to the data, indicating a transition in spreading dynamics.

v_r has been found to be independent of U_0 . This is attributed to the simultaneous increase in the retraction time ($t_c - t_s$), which compensates for the change in D_{max} and yields a near-constant v_r over the examined We range.

7.3.7 Elastic response of droplet impact as function of Weber number

The energy loss associated with droplet impact is quantified by the coefficient of retraction (c_r), defined as the ratio of rebound velocity ($v_{rebound}$) to U_0 [81, 146, 148]. Experimentally, c_r can be estimated from the relation $c_r = (h_r/H_i)^{1/2}$, where h_r is maximum rebound height of primary droplet and H_i is the impact height of the droplet. Since energy dissipation is inevitable during the impact-rebound process, c_r is always less than unity. For $We < 1$, corresponding to impact velocities ($U_0 \sim 145 \text{ mm/s}$), c_r reaches a maximum value (~ 0.85). c_r decreases with We as shown in **Figure 7.15**. This finding aligns with observations by Biance et al.[149], who reported peak restitution at velocities near 200 mm/s for millimetric droplets.

The impact phenomenon involves dynamic energy conversion; the kinetic energy of the droplet is partly stored as surface energy during spreading, then reconverted

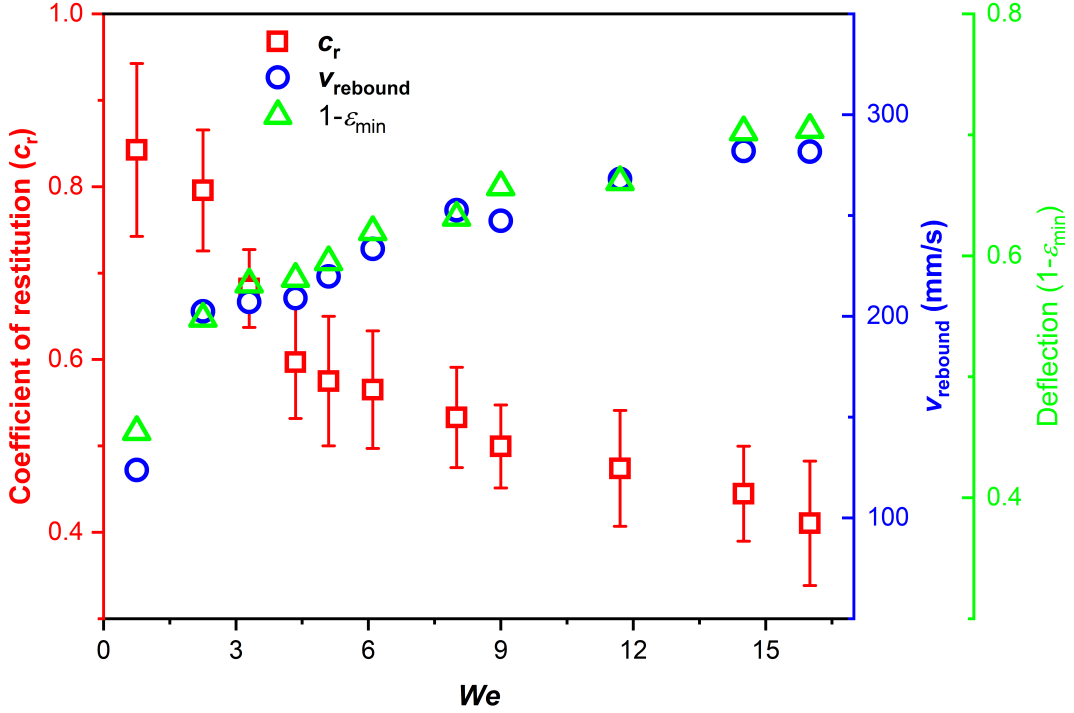


Figure 7.15: Variation of c_r , $v_{rebound}$, and droplet deflection ($1 - \epsilon_{min}$) with We .

to translational energy during retraction enabling the rebound [149]. This process is analogous to a spring system, where the elastic energy is stored during compression and released upon relaxation. The compression of the droplet can be quantified from $(D_0 - h_{min})/D_0 = 1 - \epsilon_{min}$, which provides a measure of this elastic storage.

The evolution of rebound velocity ($v_{rebound}$) and droplet deflection is presented in **Figure 7.15**, where both $v_{rebound}$ and deflection increases concurrently with We . In the low We regime ($We \approx 3$), deflection increase steeply, accompanied by a corresponding rise in rebound velocity. This regime reflects strong elastic behavior, with c_r exceeding 0.8. Above $We \approx 3$, further increase in We result in diminishing changes in deflection and $v_{rebound}$, indicating a loss of elastic recovery. The complex internal flow in the toroidal droplet morphology with increased We , reduces the energy available for rebound. Furthermore, at $We > 4$ the rebounding droplet undergoes fragmentation, generating secondary droplets, implying that a part of momentum in primary droplet transits into the secondary droplets[146]. This leads to a reduction in the rebound velocity of primary droplet consequently decreasing the c_r .

7.4 Concluding Remarks

The study provides a comprehensive experimental investigation of impact dynamics of water droplets on chemically coated SHS at low We . The fabricated SHS exhibits a uniform and heterogeneous micro-nano structures, promoting predominantly Cassie-Baxter wetting with localized areas of Wenzel wetting. The SHS exhibit a static contact angle of $\sim 155^\circ$. A critical impact velocity, $U_0 \sim 145 \text{ mm/s}$ ($We \approx 0.75$) is identified as the threshold for droplet rebound. The study reveals key insights in droplet behavior, including two distinct minima in the height evolution during spreading. The time difference between the occurrence of two minima decreases with We . Furthermore, the study introduced the holding time (t_h), which quantifies the duration for which the droplet maintains its shape at maximum spreading. t_h shows a decreasing trend with We ($t_h = 5.2 - 2.84We^{0.2}$), indicating more rapid transition dynamics at higher impact velocities. The theoretical model for the maximum spreading factor β_{max} is improved, using a more precise geometrical approximation. The proposed model closely matches with experimental data and estimates β_{max} more accurately. Empirical correlations between We and $\beta_{max} \sim We^{0.4}$, as well as minimum and maximum height factors, are established. The contact time for rebounding droplets remained effectively constant and independent of U_0 , consistent with inertial-capillary scaling laws. The observed reduction in spreading (v_s) growth at higher We is attributed to the redistribution of energy into complex internal flows and toroidal deformation. The c_r decreased monotonically with increasing We , reflecting enhanced energy dissipation and internal energy redistribution. These findings contribute to a deeper understanding of droplet dynamics on SHS, particularly in the low We regime. Which offer valuable design criteria for optimizing SHS in applications such as self-cleaning surfaces, anti-icing coatings, and microfluidic devices.

CONCLUSIONS AND FUTURE SCOPE

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This chapter summarizes the key findings of the thesis and discusses their scientific significance. It also outlines potential directions for future research, highlighting opportunities to extend the present work and explore new applications and underlying mechanisms.

8.1 Conclusions

This thesis investigates the development of environmentally benign surface coatings for multifunctional enhancement of AZ31 magnesium alloy. Two distinct coating systems are explored: hard electroless coatings aimed at improving mechanical performance, and soft chemical superhydrophobic coatings designed for self-cleaning and anti-icing applications. Emphasis is placed on minimizing the use of hazardous chemicals to ensure eco-friendly synthesis routes. The work is structured into three main components: (i) synthesis, optimization, and comprehensive characterization of electroless coatings, (ii) fabrication and characterization of superhydrophobic coatings, and (iii) experimental investigation of droplet impact dynamics on Superhydrophobic surface (SHS).

In **chapter 5**, the characterization and parametric optimization of electroless Ni-Zn-Cu-P coatings are presented with the objective of maximizing microhardness. The study further reveals that, beyond a critical plating duration, coating failure occurs predominantly through delamination of the deposited layers. The key findings

are summarized below.

- Electroless Ni-Zn-Cu-P coatings exhibit a microhardness approximately four to seven times higher than that of the base metal, with a measured coating thickness $\sim 6 \mu\text{m}$.
- The microhardness of coatings shows a clear inverse dependence on phosphorus content. Taguchi optimization identifies the A2B2C2 (Ni2-Zn2-P2) parameter combination as optimal for achieving maximum microhardness ($\sim 630 \text{ HV}_{0.01}$).
- ANOVA analysis reveals that $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ concentration is the dominant individual control parameter influencing microhardness, contributing 44.42%, while the interaction between $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ is the most significant interaction effect, accounting for 34.83% of the contribution.

In **chapter 6**, a novel eco-friendly pretreatment technique for electroless coating on Mg alloys. It identifies the key factors responsible for coating failure and examines their relationship with plating bath temperature. A defect-free electroless Ni-W-P coating is successfully developed, its performance is evaluated, and the plating parameters are optimized to achieve maximum hardness. The key findings are summarized below.

- A low-cost Ni-W-P coating was successfully deposited on a magnesium alloy using a single-step, eco-friendly pretreatment, which generated a sufficiently roughened surface morphology necessary for effective electroless deposition.
- The coatings exhibit a nodular, cauliflower-like microstructure composed of a mixed microcrystalline–amorphous phase, characteristic of electroless Ni-based alloys.
- Increased deposition rates enhance hydrogen evolution, leading to micro-pit formation and crack development. Higher bath temperatures accelerate these effects, resulting in coating failure and delamination.
- T2 coatings contain higher W and P contents than T1 coatings. T2 exhibits significantly improved hardness and corrosion resistance compared to T1.

- Adhesion testing classifies both coatings within the 4B adhesion category, with pull-off strengths of 6.0 ± 0.24 MPa for T1 and 8.1 ± 0.15 MPa for T2.

In **chapter 7**, the fabrication process and surface morphology of SHS are described. In addition, droplet impact experiments are conducted to investigate the dynamic response of the surfaces. The key findings are summarized below.

- The SHS exhibits uniform and heterogeneous micro-nano structures, showing a CA of $\sim 155^\circ$. A critical impact velocity, $U_0 \sim 145 \text{ mm/s}$ ($We \approx 0.75$) is identified as the threshold for droplet rebound.
- A characteristic holding time (t_h) defined as the duration over which the droplet maintains its shape at maximum spreading, is introduced. t_h shows a decreasing trend with We ($t_h = 5.2 - 2.84We^{0.2}$), indicating more rapid transition dynamics at higher impact velocities.
- A first-principles-based theoretical model for the maximum spreading factor (β_{max}) is formulated which exhibits excellent agreement with experimental results and estimates β_{max} with higher accuracy.
- The contact time for rebounding droplets remains effectively constant and independent of the impact velocity, consistent with inertial–capillary scaling.
- The coefficient of restitution decreases monotonically with increasing We , reflecting enhanced energy dissipation and internal energy redistribution during impact.

8.2 Future Scope

- Future research can be directed toward the design of multifunctional surface coatings that simultaneously achieve high mechanical robustness, improved resistance to corrosive environments, and sustained superhydrophobic behavior, enabling systematic investigation of trade-offs among these properties.
- Additional experimental studies involving droplet impacts across a broader range of droplet sizes and velocities would help clarify scale effects and broaden the applicability of impact dynamics to varied operational conditions.

- Extending impact studies to liquids with different physicochemical characteristics, including complex and biologically relevant fluids, may provide new insights into wetting transitions, internal flow evolution, and self-cleaning mechanisms on engineered surfaces.
- The development of advanced computational and theoretical frameworks capable of capturing transient interfacial deformation, multiphase flow, and dynamic wetting states during impact remains an important direction for future work.
- Integrating experimental data with numerical simulations and predictive modeling approaches may enable improved understanding of inertia–capillary interactions and support the rational design of surfaces with tailored impact and rebound responses.

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APPENDIX

A.1	Experimental Runs of Ni-Zn-Cu-P Coating	124
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A.1 Experimental Runs of Ni-Zn-Cu-P Coating

The S/N ratio from the Taguchi analysis and the prediction of microhardness for each run from Taguchi and ANN model is given in **Table A.1**.

Table A.1: The L27 orthogonal array with microhardness, S/N ratio and ANN predictions.

No.	A	B	C	Hardness (HV _{0.01})	S/N ratio	Predictions		Absolute % error	
						Taguchi	ANN	Taguchi	ANN
1	1	1	1	587.2	55.3757	542.47	582.96	7.618	0.722
2	1	1	2	549.4	54.7978	548.67	556.75	0.133	1.338
3	1	1	3	521.2	54.3401	566.67	517.58	8.723	0.694
4	1	2	1	501.4	54.0037	509.78	498.91	1.671	0.496
5	1	2	2	461.4	53.2816	487.91	465.89	5.746	0.972
6	1	2	3	508.6	54.1275	473.71	508.82	6.860	0.044
7	1	3	1	475.6	53.5448	511.96	476.29	7.644	0.145
8	1	3	2	530.2	54.4888	504.42	507.39	4.862	4.303
9	1	3	3	485.6	53.7256	475.02	504.45	2.178	3.881
10	2	1	1	463.8	53.3266	478.24	463.91	3.114	0.024
11	2	1	2	468.0	53.4049	487.51	467.72	4.169	0.059
12	2	1	3	542.8	54.6928	508.84	542.65	6.256	0.028
13	2	2	1	613.8	55.7605	618.29	617.30	0.731	0.570
14	2	2	2	631.6	56.0088	599.49	631.42	5.084	0.029
15	2	2	3	561.0	54.9793	588.62	540.09	4.924	3.728
16	2	3	1	571.8	55.1449	552.87	573.76	3.311	0.342
17	2	3	2	535.8	54.5801	548.40	535.90	2.352	0.018
18	2	3	3	516.0	54.2530	522.33	515.29	1.227	0.137
19	3	1	1	451.4	53.0912	481.69	450.71	6.710	0.153
20	3	1	2	532.0	54.5182	513.22	532.63	3.530	0.118
21	3	1	3	532.0	54.5182	520.49	536.36	2.164	0.819
22	3	2	1	417.2	52.4069	404.33	417.63	3.084	0.102
23	3	2	2	402.2	52.0888	407.80	401.45	1.392	0.186
24	3	2	3	375.6	51.4945	382.87	383.03	1.935	1.977
25	3	3	1	437.6	52.8215	420.18	437.18	3.981	0.096
26	3	3	2	424.8	52.5637	437.98	400.39	3.102	5.747
27	3	3	3	393.6	51.9011	397.84	393.69	1.078	0.022

A.2 Hazard Statement of Chemical Compounds

The toxicity level and H-statements of the chemical compounds was mentioned in **Table A.2** as per their safety data sheets (SDS) in accordance with Regulation (EC) No 1272/2008. The SDS of the chemical compounds was fetched from website of the chemical provider. As per Regulation (EC) No 1272/2008, the chemicals were classified into four levels based on their toxicity: Category 1, 2, 3 and 4. Where Category 1 refers to the most toxic and severely irritating substances, and Category 4 refers to the practically non-toxic and non-irritant substances.

Table A.2: Chemical substances and their H-statement according to Regulation (EC) No 1272/2008.

Chemical	Toxicity level	Hazard statement
Ethanol	Category 2	H225, H319
FeSO ₄ · 7 H ₂ O	Category 2	H302, H315, H319
NiSO ₄ · 6 H ₂ O	Category 1	H302+H332, H315, H317, H334, H341, H350, H360D, H372, H410
Na ₂ WO ₄ · 2 H ₂ O	Category 4	H302
NaH ₂ PO ₂ H ₂ O	Not Hazardous	NA
Na ₃ C ₆ H ₅ O ₇ · 2 H ₂ O	Not Hazardous	NA
Na ₂ CO ₃	Category 2	H319
NH ₄ HF ₂	Category 1B	H301, H314, H315, H318, H319
NH ₃	Category 1	H221, H280, H314, H318, H331, H400, H410, H411
HF	Category 1	H300, H300+H310+H330, H310, H314, H318, H319, H330
CrO ₃	Category 1	H271, H272, H301, H311, H312, H314, H317, H318, H330, H334, H335, H340, H350, H361F, H372, H400, H410
PdCl ₂	Category 1	H290, H302, H317, H318, H400, H410
HNO ₃	Category 1	H272, H290, H314, H331
H ₂ SO ₄	Category 1	H290, H314

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