“SYNTHESIS AND PARAMETRIC OPTIMIZATION OF Ni-Cu-P-TiO_2 ELECTROLESS COATING”

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR AWARDING THE DEGREE OF

MASTER OF MECHANICAL ENGINEERING

IN

FACULTY OF ENGINEERING AND TECHONOLOGY,

JADAVPUR UNIVERSITY

Submitted by

ATHMADEEP LALA

Exam Roll No. M4MEC24012

Registration No. 163714

Under the guidance of

Mr. Abhishek Mandal

Dr. Nabendu Ghosh

DEPARTMENT OF MECHANICAL ENGINEERING
JADAVPUR UNIVERSITY
KOLKATA-700032

MAY-2024

JADAVPUR UNIVERSITY

FACULTY OF ENGINEERING AND TECHONOLOGY

CERTIFICATE OF RECOMMENDATION

We hereby recommend that the thesis prepared under our supervision by Athmadeep Lala, entitled "**synthesis and parametric optimization of Ni-Cu-P-TiO_2 electroless coating**" be accepted in partial fulfilment of the requirements for awarding the degree of Master of Mechanical Engineering under Department of Mechanical Engineering of Jadavpur University., Kolkata - 700032.

Mr. Abhishek Mandal
Assistant Professor
Department of Mechanical Engineering
Jadavpur University, Kolkata-700032

Dr. Nabendu Ghosh
Assistant Professor
Department of Mechanical Engineering
Jadavpur University, Kolkata-700032

Dr. Swarnendu Sen
Professor and Head
Department of Mechanical Engineering
Jadavpur University, Kolkata-700032

Dr. Dipak Laha
Professor and Dean
Faculty of Engineering and Technology
Jadavpur University, Kolkata-700032

JADAVPUR UNIVERSITY

FACULTY OF ENGINEERING AND TECHONOLOGY

CERTIFICATE OF APPROVAL*

The foregoing thesis is hereby approved as a creditable study of an engineering subject carried out and presented in a manner of satisfactory to warrant its acceptance as a pre-requisite to the degree for which it has been submitted. It is understood that by this approval, the undersigned does not necessarily endorse or approve any statement made, opinion expressed, and conclusion drawn therein but the thesis only for the purpose for which it has been submitted.

Final Examination for ________________________

Evaluation of the Thesis

____

Signature of Examiners

*Only in case the thesis is approved.

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude to my supervisors **Mr. Abhishek Mandal and Dr. Nabendu Ghosh** for the continuous support of my study and research, for their patience, motivation, enthusiasm, and immense knowledge. Their guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my study.

I'd also like to take this opportunity to thank all of the faculty members in the Mechanical Engineering department for their mental support, invaluable assistance and cooperation throughout the course of this thesis work.

I'd like to express my gratitude to Jadavpur University research scholor Mr. Biplab baran Mandal, Mr. Vikash Kumar and Mr Rupam Mandal for their continuous academic support throughout the thesis work, without which it would not have been completely successful.

I am especially indebted to my parents, Mr. Manas Pada Lala and Mrs. Shashwati Lala for their love, sacrifice, and support towards my education. I would also like to thank my brother for their support at various stages of the thesis work.

Athmadeep Lala

Class Roll No. 002211202021

Exam Roll No. M4MEC24012

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1:

INTRODUCTION

From a perspective of surface engineering, a coating signifies a layer of material applied onto a substrate in order to improve surface characteristics aimed at providing protection against corrosion and wear. Selection of a suitable coating is influenced by various factors such as the operating environment, expected lifespan, compatibility with the substrate material, geometry and dimensions of the component, as well as the economic aspects.

There exists a diverse array of techniques for applying coatings involving a wide variety of materials ranging in thickness from a few microns to several millimeters. Categorization of different types of coatings can be approached in various manners, with one common classification based on the method of material deposition onto the substrate surface. Electroless deposition denotes a procedure in which metallic ions undergo reduction and are deposited onto a surface, without the requirement of an external power supply, in contrast to electroplating. The process entails the reduction of metal cations through the acceptance of electrons from a metal substrate or catalysts, wherein the reductant furnishes internal current for the reduction mechanism. Electroless nickel plating finds extensive application in the field of engineering owing to its remarkable characteristics such as corrosion resistance, wear resistance, ductility, lubrication, and electrical properties. These coatings consist of a blend of amorphous and microcrystalline nickel at low and moderate phosphorus concentrations, transitioning to completely amorphous at elevated phosphorus levels. The configuration of the deposits varies depending on temperature, with nickel phosphite emerging at higher temperatures, thereby enhancing corrosion resistance, hardness, and wear resistance. Tanks utilized in electroless plating may also undergo plating themselves, a phenomenon referred to as plate-out, necessitating proper management via routine upkeep and waste treatment.

1.1. Ni-P Electroless Coating

Ni-P electroless coating involves the deposition of a nickel-phosphorus alloy onto various surfaces without the need for an external power source, offering advantages like uniform thickness and coverage. This coating process has gained significant interest due to its excellent properties such as corrosion and wear resistance, making it suitable for a wide range of applications from macro to nano levels. The applications of Ni-P composite coatings include enhancing the life of molds for plastics and rubber, protecting against accelerated corrosion, and reducing wear in automobile components and foundry applications [1]. Electroless coatings can be categorized into alloy coatings, composite coatings, and metallic coatings, with the technology credited to Brenner and Riddell in 1946 [2]. The controlled chemical reduction reaction in electroless coating chemistry has become a significant area in surface engineering and metal finishing, growing at a rate exceeding fifteen percent annually. Electroless nickel coatings, particularly Ni-P coatings, are known for their excellent tribological properties such as high hardness, good wear resistance, and corrosion resistance. These properties make them highly desirable for various industries like aerospace, automobile, electrical, and chemical industries. Researchers have been exploring ways to enhance the tribological characteristics of Ni-P coatings by incorporating different elements and particles like SiC, TiO_2, Cu, and W. Additionally, modifying the coating process parameters has been a key focus to improve the performance of these coatings. The corrosion resistance of Ni-P coatings is influenced by factors like the phosphorus content, structure, and heat treatment. High phosphorous Ni-P coatings have shown excellent corrosion protection properties, forming a barrier against corrosive environments [3]. The components and parameter of bath and its function is shown in Table 1.1.

Table 1.1. The components and parameter of bath and its functions [1].

Sl. No.	Component/parameter	Functions
1	Metal ions	Source of metal
2	Reducing agents	Supply electrons to reduce the metal ions
3	Complexants	Prevent excess of free metal ions concentration
4	Accelerators	Accelerate the reducing agent and increase the deposition
5	Stabilizers	Stabilize the bath from decomposition by shielding catalytically active deposition
6	Buffers	Sustain the pH for long time
7	pH regulators	pH adjustment
8	Temperature	Energy for deposition

In electroless deposition, metal ions are reduced to metal by the action of chemical reducing agents, which are simply electron donors. The metal ions are electron acceptors, which react with electron donors. It is an autocatalytic process, which accelerates the electroless chemical reaction allowing oxidation of the reducing agent used as shown in Fig 1.1.

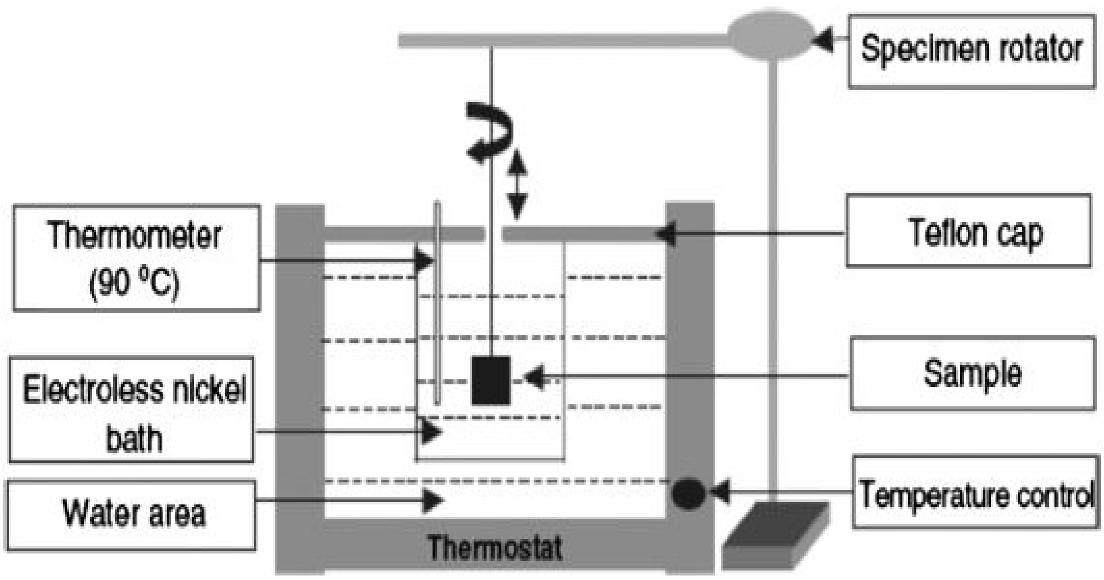


Fig 1.1. Basic Diagram of the apparatus usually used in electroless experiments[34].

1.2. Types of Electroless Nickel Coating

The versatility and reliability of electroless nickel nano coatings make them a valuable asset across diverse industries, showcasing their broad spectrum of beneficial properties and applications in engineering.

Electroless plating comprises a variety of forms determined by the composition and characteristics of the materials deposited. Electroless nickel coatings are the most economically significant within the realm of electroless coatings, providing diverse categories with varying attributes. Electroless nickel coatings can be categorized into three main groups: Low phosphorus coatings that deliver good corrosion resistance and hardness, medium phosphorus coatings that present a compromise between hardness and corrosion resistance, and high phosphorus coatings recognized for their outstanding corrosion resistance and non-magnetic properties.The configuration of electroless nickel deposits undergoes modifications with temperature variations, impacting traits such as corrosion resistance, hardness, and wear resistance. The favorable characteristics of electroless coatings can be customized by manipulating factors like pH, temperature, and bath composition etc. Fig 1.2 shows the different types of electroless coating that can be performed.

1.2.1. Pure Nickel

Pure nickel, in this context, denotes a metallic nickel deposit void of any additional elements originating from the reducing agent or bath additives, presenting specific advantages for certain applications. An autocatalytic nickel deposit categorized as 'pure' is especially valuable in fields such as semiconductor manufacturing. The process of depositing pure nickel is commonly accomplished through the utilization of precise bath compositions and operational parameters. In depositing pure nickel, a typical bath composition consists of nickel acetate, glycolic acid, EDTA, hydrazine, and sodium hydroxide, with specified pH and temperature ranges. The initial hardness of as-deposited pure nickel coatings is approximately 450 HV, imparting favorable mechanical properties. Subsequent to heat treatment at a designated temperature, the pure nickel coating undergoes a reduction in hardness and an increase in ductility, with a hardness of 125 HV. The characteristics of pure nickel coatings are amenable to customization through heat treatment and additional post-deposition procedures in order to fulfill specific application requirements.

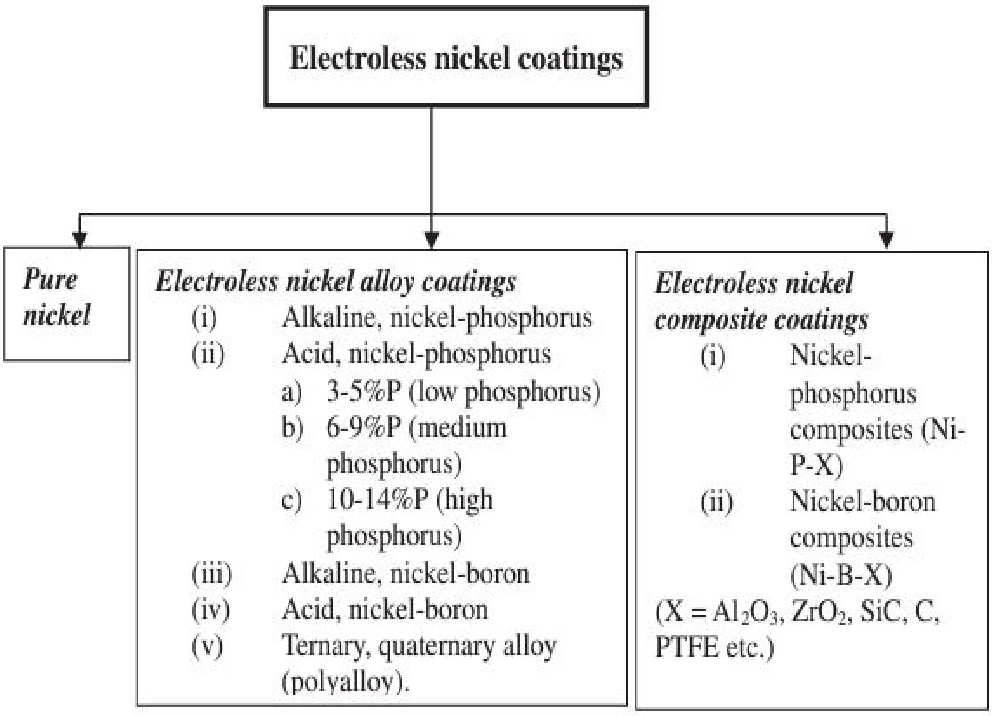


Fig 1.2. Types of Electroless Coating [1].

1.2.2. Black Nickel

It can be obtained from the surface of both electro and electroless deposition by etching the surface using oxidizing acid solutions. Due to the presence of phosphorus contents, the electroless nickel deposit is easy to etch by the oxidizing acids to get the ultra black surface. The blackening of electroless nickel deposit is obtained, when the deposit is dipped in a nitric acid (9 M) solution. The blackening resulting from the hole formation is visible first on the boundaries between the different nodules and the non the whole deposit surface on titanium alloy. This structure produced by selective etching traps the light and is capable of absorbing over 99% light in solar region (0.3–2μm). Moreover, these surfaces are extremely suitable in improving the absorption of thermal detectors and to minimize the effect of stray and scattered light in optical instruments and sensors. The optimum thickness of 35 ± 5 μm of electroless nickel is required to achieve the ultra high optical properties for blackening. Electroless nickel coatings with~ 7% phosphorus are good for further blackening. Higher phosphorus content alloys are not suit-able, because they are too corrosion resistant to blacken as a result of acid etching. The main components of the black coating are recognized to include NiO, Ni_2O_3 and some nickel phosphate. The blackened electroless nickel provides higher optical properties in the order of~ 0.85 αs (solar absorbance); this coating has good adhesion, uniformity, and stability in adverse space conditions. Hence, it is widely used in solar absorber for solar applications [1].

1.3. Electroless Nickel Alloy Coating

1.3.1. Acid bath Ni-P alloy

Acid bath Ni-P alloy designates an electroless nickel-phosphorus alloy that is deposited through the use of an acidic solution, providing distinct advantages when compared to alkaline solutions. Acidic baths are favored for the deposition of relatively thick coatings that exhibit superior quality and enhanced bath stability throughout the plating process. The manipulation of phosphorus levels in Ni-P alloy coatings allows for precise control, resulting in various classifications based on phosphorus content. Coatings with low phosphorus content (3-5% P) demonstrate exceptional resistance to wear and corrosion, particularly in concentrated caustic soda environments. Medium phosphorus coatings (6-9% P) are recognized for their effective corrosion protection and resistance to abrasion, making them suitable for a wide range of applications. High phosphorus coatings (10-14% P) are characterized by their high ductility and corrosion resistance, especially against chlorides and mechanical stress. By adjusting the phosphorus content, the properties of Ni-P alloy coatings can be customized to fulfill specific application requirements, including wear resistance, corrosion resistance, and ductility.

1.3.2. Alkaline bath Ni-P alloy

The utilization of alkaline bath Ni-P alloy in the deposition of nickel-phosphorus coatings via an electroless process presents a unique set of advantages and disadvantages when compared to alternative coating methodologies. This particular bath composition commonly consists of nickel chloride, sodium hypophosphite, as well as ammonium citrate and ammonium chloride. The operational parameters typically involve maintaining a pH range between 8 to 10 and a temperature range of 80 to 90°C, thereby facilitating a deposition rate of approximately 10 µm/h. The benefits associated with utilizing alkaline bath Ni-P alloy coatings encompass the ease of deposition on plastic substrates, favorable solderability characteristics particularly relevant to the electronic industry, and the economical nature of the processing involved. Nonetheless, it is imperative to acknowledge the drawbacks inherent in this coating method such as the comparatively lower resistance to corrosion, diminished adhesion capabilities when applied to steel surfaces, and the inherent challenges encountered when processing aluminum due to the elevated pH levels associated with the bath composition. A significant limitation worth highlighting is the instability exhibited by the alkaline solution when subjected to temperatures exceeding 90°C, resulting in a sudden decline in bath pH levels attributable to the loss of ammonia. In spite of these identified limitations, it is essential to recognize the pivotal role played by alkaline bath Ni-P alloy coatings in conferring specific properties such as solderability and facilitating cost-effective deposition processes, rendering them suitable for targeted applications within the industrial sector.

1.3.3. Alkaline bath Ni-B alloy

DMAB is usually used as a reducing agent in acid bath for electroless nickel–boron coatings where boron contents vary from 0.1%to 4%. The main advantage of the hot acid bath is its stability and deposits from this bath have a very high melting point of 1350 °C. They are very often used in industrial wear applications for their as-plated hardness, which is higher than that of nickel–phosphorus. They have good soldering, brazing and ultrasonic bonding characteristics, when boron is >1%. Boron can be usually reduced by alkyl amine, although up to 5% can be obtained by using some accelerator. A typical bath composition is 30 g/L nickel chloride, 3 g/L diethylamine borane, 40 g/L methanol, 4 g/L dimeth-ylamine borane (DMAB), 20 g/L sodium acetate, 20 g/L sodium succinate, and 10 g/L sodium citrate. Operating conditions are pH 5–6, temperature 50–60 °C, giving a deposition rate of 15–20 µm/h.

1.3.4. Acid bath Ni-B alloy

The boron contents of the alkaline electroless nickel–boron de-posit range from 0.2 to 4 wt.% and from 4 to 7 wt.% when the reducing agents are aminoborane (N-alkyl amino boranes) and sodium borohydride, respectively. They are usually operated at tempera-ture in the range of 20–90 °C. Alkaline Ni–B cool bath has been preferred. At high temperature, bath becomes unstable and has limited industrial usage. These alkylamine borane baths generally have a much slower deposition rate. Complexing agents such as ethylendiamine are used to control nickel hydroxide precipitation. The main advantages of borohydride reduced electroless nickeldeposits are their hardness and superior wear resistance in the as-deposited condition. Dervos et al. proposed a vacuum heating technique within less than half an hour and leading to surface hardness values normally requiring processes of several months by the conventional approaches, i.e. heating in an inert atmosphere [61]. The 5 min thermal treatment in a high vacuum environment results in a chromium equivalent surface micro hardness, which in some cases reaches 2000 HV locally, without the environmental hazardous sewages of the hard chromium plating. The method can be used for a variety of industries, where they need to replace hard chromium plating. Kanta et al. investigated electroless Ni–B on mild steel with different post-treatments, including heat treatments in 95% Ar and 5% H_2 at 400 °C for 1 h, and thermo-chemical treatments. The thermo-chemical treatment was performed in a nitrogen based atmosphere, at 500 °C for 2 h, followed by a treatment based on ammonia. After heat and thermo-chemical treatments, Ni–B coatings crystallize and produce nickel and nickel borides in the coatings. The same authors prepared the Ni–P and Ni–B system onto, respectively, steel substrate and specially prepared aluminum substrate that was protected by an outer layer of Ni–P deposit, and found smoother surface, more noble electro-chemical comportment than the Ni–B.

1.3.5. Polyalloys

Polyalloys are alloy coatings composed of three or four elements, deposited through the electroless technique, renowned for their enhanced characteristics in comparison to binary alloys. Ternary alloys, such as Ni-Co-P, Ni-Fe-P, and Ni-Co-Fe-P, are extensively utilized due to their exceptional magnetic properties, featuring high-coercivity films for dense recording and low-coercivity alloys for rapid computers. Particular polyalloys like Ni-Cu-P provide heightened corrosion resistance and malleability when contrasted with the standard Ni-P alloy, rendering them suitable for diverse applications. The attributes of polyalloys can be customized to fulfill specific needs, including corrosion resistance, magnetic features, and malleability. Polyalloys are employed in sectors like dense recording and swift computers, among others, where distinct traits such as corrosion resistance and magnetic properties are vital. The electroless deposition technique enables precise management of the composition and characteristics of polyalloys, enhancing their adaptability for a variety of industrial uses. Its types and uses are illustrated in Table 1.2,

Table 1.2. Features and types of electroless metallic alloy coatings [1].

Sl No.	Use	Alloy types
1	Corrosion protection	Ni–P, Ni–P–Mo, Ni–Sn–P, Co–P, Co–P–Mo, Ni–Cu–P
2	Wear resistance	Ni–B, Ni–B–Tl, Ni–B–Mo, Ni–B–Sn, Co–P, Co–P–W, Co–B; Ni–P–SiC, Ni–P–WC (dispersion)
3	Magnetic	Au–Ni, Au–Co; Ni–Co–P, Ni–Co–B, Ni–Fe–P
4	Solderability	Sn–Pb, Ni–P
5	High temperature	Co–W–B, Ni–Re–P
6	Diffusion barrier	Ni-P

1.4. Electroless Nickel Composite Coating

The deposition process involves the impact and settling of particles on the surface of the workpiece, followed by the surrounding of these particles by the Ni-P matrix as it gets deposited, creating a significant interaction between the particles and the matrix. This interaction is crucial in determining the overall performance and properties of the composite coatings. The concept of electroless composite coatings refers to the co-deposition of composite materials, which can include hard particles or non-metallic substances, alongside the electroless coatings. This process is commonly known as electroless composite coatings and is aimed at producing wear-resistant composite materials through the incorporation of fine particulate matter. Various hard particles like diamond, silicon carbide, aluminum oxide, and solid lubricants such as polytetrafluoroethylene (PTFE) have been successfully co-deposited in this manner.

Additionally, small particles of intermetallic compounds and fluoro-carbons have been dispersed within an electroless nickel-phosphorus/boron matrix, showcasing the versatility of this process in creating diverse composite materials.

Initially, electroless composite coatings faced challenges and were not always successful due to issues such as bath decomposition. This was primarily caused by the dispersion of fine particles, which significantly increased the surface area loading of the electroless bath, leading to bath instability. However, through the utilization of suitable stabilizers, researchers were able to overcome these challenges and successfully prepare electroless nickel composite coatings. Unlike electro co-deposition, electroless coating offers the advantage of accurately reproducing surface features and shapes while avoiding the need for subsequent mechanical finishing processes. It is important to note that in electroless composite coatings, there is no direct molecular bonding between the metal matrix and the incorporated fine particles, highlighting the unique characteristics of these composite materials.

Researchers have developed mathematical models to better understand the electro-deposition process involved in creating composite coatings. Experimental findings have supported the proposed mechanisms, further validating the theoretical frameworks established in this field. For instance, Guglielmi's mathematical model has provided valuable insights into the electro-deposition process of composite coatings. Moreover, experimental setups like the one used by Grosjean et al. have been instrumental in producing electroless nickel-SiC composite coatings, demonstrating the practical applications of these theoretical concepts. By utilizing agitation induced by fluid circulation systems, researchers have been able to create laminar flows and maintain particle suspension within the solution, enhancing the quality and uniformity of the composite coatings.

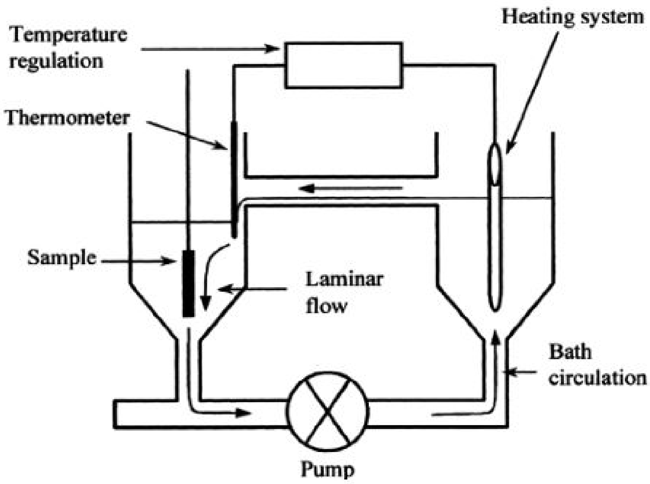


Fig 1.3. Experimental set-up recommended for producing electroless composite coatings [1].

1.5. Electroless Nickel Nanocoatings

Electroless nickel nanocoatings encompass the process of depositing extremely thin coatings of nickel that are free from voids and pores onto particles of micro, meso, and nano scales, which signifies a pioneering domain within the realm of nanotechnology. This advancement in technology facilitates the development of composite materials and coatings structured at the nano level, exhibiting customized properties that enable the manufacturing of miniature devices featuring elements of nanoscale dimensions composed of diverse materials and varying thicknesses. The utilization of this technique surpasses the functional capabilities of devices created through costly methods such as e-beam and X-ray lithography, establishing it as a cost-efficient and advantageous approach in the field of material engineering. The distinctive characteristics and potential applications of these nanocoatings are vast, ranging from enhancing properties like wear resistance, friction, corrosion resistance, ductility, tensile strength, hardness, soldering ability, to lubrication. The significance of electroless nickel nanocoatings extends to various industries due to their consistent thickness distribution, exceptional resistance to corrosion, wear, and abrasion, flexibility, soldering attributes, as well as their electrical characteristics, leading to their widespread adoption in a multitude of engineering applications.

1.6. Ni-P Electroless coating Properties
1.6.1. Physical Properties

- **Deposit uniformity**

This particular physical property holds great significance within the realm of electroless nickel process, presenting a notable advantage. The process showcases an exceptional capability in achieving a consistent thickness across components featuring intricate geometries and diverse shapes, as supported by literature. Unlike electroplating, the electroless nickel process operates independently of current density effects, thus eliminating concerns related to sharp edges, deep recesses, and blind holes. Through this method, a uniform thickness is effortlessly achieved. Unlike electrodeposition methods that often result in excessive material buildup at protrusions and edges, potentially necessitating finishing operations such as grinding, electroless deposits effectively circumvent these challenges.

- **Structure**

The coatings under consideration in this study are composed of a combination of amorphous and microcrystalline nickel when the phosphorus levels are low to medium; however, at high phosphorus levels, the coatings become entirely amorphous. Upon heating the coatings to 800 °C, the resulting deposits are found to be mixtures of Ni_3P and f.c.c. nickel stable phase. It is worth noting that intermediate metastable phases, such as NiP_2 may emerge when the phosphorus content is medium to high, before the stable Ni_3P phase forms. The structural transformation of Ni–P initiates at temperatures exceeding 220–260 °C, leading to the crystallization of the deposits and the loss of their amorphous nature. The formation of nickel phosphide (Ni_3P) commences within the alloy as the temperature surpasses 320 °C, and the structure attains maximum crystallization after being heated at 400 °C for 1 hour. This process is expected to enhance the corrosion resistance, hardness, and wear resistance of the coatings significantly. In cases where the phosphorus content exceeds 9%, a matrix primarily composed of nickel phosphide (Ni_3P) is formed, whereas deposits with lower phosphorus levels consist mainly of pure nickel. To prevent the development of a blue color on the samples after heat treatment, which results from the combination of an oxide layer with air exposure, it is crucial to maintain the samples in a vacuum furnace. While heat-treated samples exhibit increased hardness and wear resistance, their corrosion resistance tends to decrease.

- **Density**

The density of electroless Ni-P and Ni-B exhibits a close resemblance to that of an alloy with an equivalent content. This phenomenon demonstrates an inverse relationship with their respective phosphorus or boron composition as indicated by previous studies. The density levels manifest a notable variation within a specific range, ranging from 8.5 gm/cm3 for compositions with low phosphorus content to 7.75 gm/cm3 for those with high phosphorus content. In contrast, the density for compositions containing 5% boron is recorded at 8.25 gm/cm3.

- **Melting point**

The electroless Ni–P deposits exhibit a unique characteristic of not possessing a specific melting point; instead, they display a melting range, which distinguishes them from electrolytically deposited nickel. In contrast, pure nickel is known to have a precise melting point at 1455 °C. However, with an increase in the phosphorus content within the deposit, a phenomenon occurs where the deposit starts to undergo softening at temperatures lower than the melting point [83]. For instance, electroless Ni–P deposits that contain 11% phosphorus demonstrate the lowest melting point recorded at 880 °C. On the other hand, deposits with low phosphorus content, below 3%, exhibit the highest melting points, typically hovering around 1200 °C. In comparison, the melting point of Ni–B deposits is relatively high. Specifically, sodium borohydride-reduced electroless Ni–B deposits containing 5% boron reveal a melting point of 1080 °C, whereas in DMAB-reduced bath, the melting point ranges between 1350–1360 °C.

- **Electrical resistivity**

The electrical resistivity of electroless nickel alloys is reported to be higher compared to that of pure nickel as indicated in reference . Specifically, pure nickel exhibits a specific resistivity of 7.8×10^{-6} ohm cm. It is observed that with an increase in phosphorus content, there is a corresponding increase in the electrical resistivity as well. The range of resistivity values varies from 30 to 100 x 10^{-6} ohm cm depending on the conditions under which the deposition takes place. Furthermore, it is noted that through heat treatment of electroless Ni-P, there can be an enhancement in its conductivity which in turn impacts the resistivity measurements. For instance, the electrical resistivity of a sample containing 9% phosphorus is recorded as 89 x 10^{-6}ohm cm in the as-deposited state and decreases to 43 x 10^{-6}ohm cm after undergoing heat treatment at a temperature of 1100 °C. In the case of Ni-B alloys, the electrical resistivity property closely resembles that of Ni-P alloys with a resistivity value of 89 x 10^{-6} ohm cm for a composition containing 5% boron. The applications of Ni-B alloys are predominantly seen in electronic industries where low resistivity materials are required for optimal performance.

- **Magnetic property**

The primary application of electroless nickel lies in serving as a sublayer for computer memory disks. To meet the specific requirements of this application, it is imperative that the material retains its non-magnetic properties even after undergoing 1-hour bake cycles within the temperature range of 250 to 320°C. It is essential to subject the material to multiple baking processes to ensure its suitability. One of the critical characteristics of this high phosphorus coating is its non-magnetic nature, a quality that can only be attained with a phosphorus content exceeding 10.5 weight percent. The coatings must exhibit microcrystalline structure and maintain uniform grain sizes, especially at elevated bake temperatures, to optimize their thermo-magnetic properties. Nickel-phosphorus coatings are known for their non-magnetic behavior, while nickel-boron coatings display a very weakly ferromagnetic nature. Electroless nickel with a phosphorus content of at least 7 weight percent is typically amorphous, hence non-magnetic, making it a popular choice as an underlying layer for magnetic coatings. The storage systems utilizing these coatings operate in a challenging tribological environment due to the critical requirement of maintaining minimal distance between the read/write heads and the storage media.

1.6.2. Mechanical Properties

- **Internal stress**

The primary function of the coating composition in electroless nickel coatings is to manage internal stress. Tensile stresses ranging from 15 to 45 MPa emerge in deposits with lower phosphorus content due to dissimilar thermal expansion characteristics between the deposits and the substrate. The considerable stress levels observed in these coatings contribute to the development of cracks and porosity. When subjected to heat treatment above 220 °C, structural modifications lead to a volumetric contraction of electroless nickel deposits by as much as 6%, resulting in heightened tensile stress and diminished compressive stress within the coating. Co-deposition of orthophosphites or heavy metals, along with an excess of complexing agents in the plating solution, can further elevate deposit stress. Even minute quantities of certain metals have the potential to induce a significant stress escalation. Additionally, excessive internal stress levels detrimentally impact the ductility of the coating.

- **Ductility**

The ductility of the electroless Ni–P coating exhibits variation based on its composition. The incorporation of composites during deposition process can impact the ductile properties observed. Coatings with high phosphorus content in their as-deposited state typically demonstrate a ductility range of 1 – 1.5% (measured as elongation). While this level of ductility may be lower than that of many engineering materials, it proves to be sufficient for a wide array of coating applications. Notably, thin deposits can be bent fully without experiencing fracture. Conversely, coatings with low phosphorus content exhibit significantly reduced ductility, potentially approaching zero. In comparison, the ductility of electroless Ni–B is approximately one fifth (0.2%) of that seen in high phosphorus deposits. Interestingly, the impact of heat treatment on ductility is minimal.

- **Tensile strength**

The tensile strength of Ni–P deposits surpasses that of Ni–B deposits. The low phosphorus deposit exhibits a tensile strength value of 450–550 MPa in its as-deposited state. Following heat treatment, Ni–P demonstrates a decrease in tensile strength compared to its as-deposited form, accompanied by an increase in hardness, which ranges between 200–300 MPa.

- **Hardness**

Composite coatings such as electroless Ni-P demonstrate enhanced hardness characteristics, which are essential for tools utilized in diverse industrial settings at room temperatures. The level of hardness exhibited by these coatings is impacted by various factors including the quantity of co-deposited particles, phosphorus levels, and the process of heat treatment. An escalation in hardness is observed with an increased presence of rigid particles (e.g., SiC, Si_3N_4) within the coating, whereas the presence of soft particles such as PTFE leads to a reduction in hardness. The predominant contributors to the augmented hardness are the hard particles, regardless of the phosphorus content ranging from 2-14 wt.% P. The treatment involving heat plays a crucial function in determining the hardness, depicting an initial rise up to 400°C attributed to precipitation hardening facilitated by the emergence of intermetallic Ni_3P phase, followed by a decline post 400°C due to diminished lattice defects and the coalescence of Ni_3P particles. The integration of nanoparticles like SiO_2 or TiO_2 in the coating has the potential to significantly improve microhardness and resistance to wear, consequently enhancing the mechanical attributes of the composite coatings.

- **Surface Roughness**

Surface roughness (R_a) is a crucial factor that impacts the contact area between materials, thus influencing both friction resistance and coefficient. The modification of surface finish by co-depositing hard and soft particles in an electroless Ni-P matrix results in changes in brightness and R_a. The mechanical and tribological characteristics of composite coatings are markedly affected by the surface roughness, leading to alterations in properties such as wear, friction, corrosion, and other related aspects. Surface roughness plays a significant role in influencing the porosity of a coating, where increased porosity may potentially hamper the corrosion resistance of the material. It is imperative to conduct thorough examination and fine-tuning of the bath process parameters in order to effectively diminish surface roughness to the desired levels within composite coatings.

- **Wear resistance**

Composite coatings with fine diamond particles exhibit better wear resistance compared to those with coarse particles, emphasizing the importance of particle size and distribution in enhancing wear properties. The wear resistance of composite coatings is also affected by factors like heat treatment, particle size, and distribution, highlighting the complex interplay of material properties in determining wear performance.

- **Frictional properties**

The variations also differ depending on the phosphorus/boron levels and the specific heat treatment utilized. They exhibit similarities to the characteristics of chromium. The presence of phosphorus contributes to a natural lubricating property, proving advantageous in applications like plastic molding. When comparing the coefficient of friction between electroless nickel/boron and steel, it ranges from 0.12 to 0.13 under lubricated conditions and 0.43 to 0.44 under unlubricated conditions. The opposing surfaces consisted of diamond and plain carbon steel. It is observed that the coefficients of friction for electroless nickel coatings are elevated in comparison to those of chromium depositions.

1.7. Bath constituents

The fundamental requirement for an electroless plating solution consists of metal ions and their respective concentrations, as well as reducing agents, complexing agents, bath stabilizers, and the regulation of pH and temperature. Within the electroless deposition process, metal ions undergo reduction to form metal through the interaction with chemical reducing agents, known as electron donors. These metal ions function as electron acceptors that engage with electron donors, constituting an autocatalytic mechanism that expedites the electroless chemical reaction and facilitates the oxidation of the reducing agent employed.

1.7.1. Stabilizing agent

Stabilizers play a crucial role in electroless nickel (EN) plating processes, particularly on magnesium alloys, influencing bath pH, coating quality, and bath life. acetate, as a pH stabilizer, outperforms other stabilizers in buffer capacity, enhancing EN coating quality and corrosion resistance. Proper usage of ammonium acetate can extend the bath life pH stabilizers like ammonium acetate and ammonium succinate exhibit better buffer performance in the pH range of 4-6, crucial for maintaining optimal plating conditions. Stabilizers help in preventing corrosion spots on coatings, ensuring compact and uniform Ni-P alloy coatings on magnesium substrates. The addition of stabilizers helps in controlling bath pH within the desired range, enhancing the overall quality and longevity of the plating solution.Stabilizers like ammonium acetate are essential for constructing a strong buffer couple in the bath, maintaining the required pH for efficient EN plating processes [11].

1.7.2. Complexing Agent

In order to prevent the decomposition of the solution and to make the bath stable the complexing agents are added to the electroless bath. It also controls the reaction mechanism, deposition rate so that the deposition occurs only over the catalytic surface. Complexing agents are generally organic acids or their salts; however there are two exceptions. The first one is the inorganic pyrophosphate anion which is used as a complexing agent exclusively in alkaline EN (Electroless-Nickel) solutions, and the second one is ammonium ion, which is usually added to the plating bath for pH control or maintenance [13]. The complexing agents serve as a buffering agent that prevents the pH of the solution from falling too fast; they prevent the precipitation of nickel salts, e.g., basic salts or phosphites and also reduce the concentration of free nickel ions by forming meta-stable complexes.

1.7.3. Reducing agent

The reducing agent, sodium hypophosphite, is a key component in the electroless nickel phosphorous (Ni-P) coating process, influencing various properties of the coatings. Increasing the reducing agent concentration enhances the deposition rate of the coatings up to a certain limit, beyond which it can lead to bath decomposition. The concentration of the reducing agent affects the surface roughness of the coatings, with higher concentrations resulting in increased roughness. The reducing agent influences the formation of an amorphous phase in the Ni-P coating, impacting its microhardness. Heat treatment post-coating leads to the formation of an intermetallic nickel phosphide (Ni_3P) phase, improving the hardness of the coating .Incorporation of nano alumina particles in the Ni-P coating results in a composite coating with increased hardness, attributed to the resistance of alumina to nickel deposition and the formation of a hard matrix with Ni_3P phase [13].

1.7.4. Surfactants

Surfactants are compounds that lower the surface tension between two substances, such as a liquid and a solid or between two liquids. They are amphiphilic molecules, containing both hydrophilic (water-attracting) and hydrophobic (water-repelling) regions.In the context of electroless nickel (Ni-P) coating, surfactants like sodium dodecyl sulfate (SDS) play a crucial role in influencing the surface roughness, microhardness, and microstructure of the coated samples. The addition of these surfactants at a concentration of 0.6 g/l results in a smoother surface finish with reduced average roughness values compared to coatings without surfactants. The presence of surfactants during the deposition process enhances the hardness of the coated layers significantly. For instance, with the addition of SDS, the microhardness value increased to 685 Hv, for coatings without surfactants. Surfactants like SDS also impact the microstructure of the deposited layers. They help in dispersing fine nickel particles uniformly on the substrate surface, leading to improved surface finish and quality of the deposits, ultimately enhancing properties like corrosion resistance [12].

1.7.5. Temperature

Temperature plays a crucial role in the electroless deposition process, affecting the quality and characteristics of the deposited films. Higher temperatures generally lead to increased deposition rates and improved adhesion of the deposited material to the substrate. The study observed that the optimal temperature range for Ni-P deposition on AISI 1045 steel was between 70°C to 80°C, resulting in very bright and uniform film deposition. Beyond 80°C, bath instability was noted, especially for Ni-P deposition, leading to a decline in the weight of deposited material and a dark appearance on the plated surface. The amount of material deposited per unit area increased linearly with temperature until 85°C - 100°C for Zn-P, while a decline was observed for Ni-P at higher temperatures, indicating the need for higher concentrations for bath stability. Overall, maintaining the temperature within the optimal range is essential for achieving bright, uniform, and wear-resistant coatings on the substrate [15].

1.7.6. Time

Different coating times result in varying thicknesses and phosphorus contents of the deposits, affecting their hardness and corrosion resistance. The hardness of the coatings increases with an increase in coating time due to decreased phosphorus content, ranging from approximately 502-650 HV. The correlation between coating time and the properties of electroless Ni-P alloy deposits underscores the importance of optimizing this parameter for tailored coating characteristics. Heat treatment further enhances the hardness of Ni-P deposits, reaching a maximum of 1045 HV at 400°C, indicating the impact of heat treatment on the mechanical properties of the coatings. Coating time influences the corrosion behavior of the deposits, as observed in the shift in corrosion potential and anodic current density with different plating times. Coating time plays a crucial role in determining the composition, structure, hardness, and corrosion characteristics of electroless Ni-P alloy deposits, highlighting its significance in tailoring the properties of the coatings [16].

1.7.7. pH value

The pH of the plating bath significantly impacts the electroless nickel (EN) plating rate and coating quality, influencing the overall performance of the process. Different pH values result in variations in the chemical composition of the coatings, with higher pH values leading to increased nickel content in the coatings formed. pH also influences the corrosion resistance of the coatings, with coatings formed at pH 5.5 exhibiting better corrosion resistance compared to those formed at pH 7.0, indicating the importance of pH control for achieving optimal coating properties .

Acid: pH<7

Base: pH>7

1.8. Application of Electroless Nickel Coating

The main application of electroless composite coatings is for machining and finishing tools requiring maximum wear resistance, surface friction coefficient, and hard surface. The applications are shown in Table 1.3

Table 1.3 Application of electroless Ni–P coatings [2].

Sl No.	Application	Components
1	Automotive	Heat sinks, carburettor components, fuel injection, ball studs, differential pinion ball shafts, disk brake pistons and padholders, transmission thrust washers, synchromesh gears, knuckle pins, exhaust manifold sand pipes, mufflers, shock absorbers, lock components,hose couplings,gear and gear assemblies. Fuel pump motors, aluminium wheels,water pump components,steering column wheel components, ,air conditioning compressor components,decorative plastics and slip yokes
2	Aircraft/ aerospace	Bearing journals,servo valves, compressor blades,hot zone hardware, pistons heads, engine main shafts and propellers, hydraulic actuator splines, seal snap sand spacers, landing gear components, pilot tables, gyro parts, engine mounts, oil nozzle components, turbine front bearing cases,engine mount insulator housing, flanges, sun gears,
3	Chemical & Petroleum	Pressure vessels, reactors, mixer shafts, pumps and impellers, heat exchangers, filters and components, turbine blades and rotor assembles, compressor blades and impellers, spray nozzles, valves, chokes and control valves, oil field tools, oil well valves: ball, gate, plug, check and butterfly, stainless steel packers and equipment, oil

		well turbine and pumps, drilling mud pumps, hydraulic systems actuators blowout
4	Electrical	Motor shafts, rotor blades of stator rings
5	Electronics	Head sinks, computer drive mechanisms, chassis memory drums and discs, terminals of lead wires, connectors, diode and transistor cans, interlocks, junction fittings and PCB
6	Food	Pneumatic canning machinery, baking pans, moulds, grills and freezers, mixing louts, bun warmers and feed screw and extruders
7	Marine	Marine hardware, pumps and equipment
8	Material Handling	Hydraulic cylinders and shafts, extruders, link drive belts, gears and clutches
9	Medical & Pharmaceutical	Disposable surgical instruments and equipment, sizering screens, pill sorters and feed screws and extruders
10	Military	Fuse assemblies, tank tarred bearings, radar wave guides, mirrors, motors, detonators and firearms
11	Mining	Hydraulic systems, jetting pump heads, mine engine components, piping connections, framing hardware
12	Moulds & dies	Zinc dies, cast dies, glass moulds and plastic injection moulds of plastic extrusion dies
13	Printing	Printing rolls and press beds
14	Rail road	Tank cars, diesel engine shafts and car hardware
15	Textiles	eeds and guides, fabric knives, spinnerets, loom ratchets and knitting needles
16	Wood & paper	Knife holder corer plates, abrading plates and machine parts
17	Miscellaneous	Chain saw engine, Precision tools, Shower blades and heads, Pen tips

CHAPTER 2:

LITERATURE REVIEW AND RESEARCH OBJECTIVES

2.1. Literature Review

The research paper focuses on the application of Ni-P-(Cu) composite coatings on St37 steel using an acidic hypophosphite composite bath. It explores the impact of Cu particle concentration and solution pH on the coating's Ni and P content, morphology, and hardness. XRD and SEM-EDS analyses were conducted to study the phases, microstructure, and alloying elements in the coatings. Heat treatment at 400ºC for 1 hour resulted in a crystalline structure, enhancing coating hardness. EDS analysis revealed increased element percentages, with Ni and P present due to particle entrapment in the Ni-P matrix. Coating thickness increased with higher pH levels, transitioning from amorphous to crystalline structures, impacting hardness. The hardness of the composite coatings is lower than the hardness of the simple coating of Ni-P. The hardness of Ni-P coating is 482.4 VH while the hardness of the Ni-P-Cu composite coating with 7 gr/lit Cu particles is 380.7 VH. The main reason for the lower hardness of the composite coating compared to the simple Ni-P coating is the softening nature of Cu. Therefore, the hardness of the coating increased as the amount of Cu particles increased [5].

Electroless coatings play a crucial role in protecting machine parts from corrosion and wear. Incorporating soft or hard particles in the electroless Ni-P matrix can enhance properties like lubrication effect, corrosion resistance, and hardness. Successful co-deposition of particles depends on factors like bath composition, reactivity, and particle size distribution. Hardness of electroless nickel coating improves with the inclusion of hard composite particles, leading to enhanced tribological properties. Annealing the composite coating at 400°C significantly enhances hardness and tribological properties by modifying the coating structure. The study focuses on the impact of TiO_2 particles on micro-hardness, wear resistance, corrosion resistance, and friction of Ni-P-TiO_2 composite coatings at different annealing temperatures. Experimental trials involve varying process parameters like nickel sulphate, sodium hypophosphite, TiO_2 particles, and annealing temperature to deposit coatings with specific characteristics [6].

The research paper focuses on optimizing coating parameters and annealing temperature to enhance the microhardness and corrosion resistance of Ni-P-TiO_2 composite coatings .Four process parameters are selected for the coating deposition process: nickel sulphate, sodium hypophosphite, titania particles, and annealing temperature. These parameters were chosen based on a literature survey and experimental trials. Grey relational analysis is used to determine the optimal combination of coating parameters, with a focus on the significant impact of annealing temperature and the amount of titanium particles on the corrosion properties and microhardness of the coatings .The study also involves examining the surface morphology, phase transformation, and chemical composition of the Ni-P-TiO_2 composite coatings using scanning electron microscopy, X-ray diffraction analysis, and energy dispersive analysis, respectively .The research paper emphasizes the importance of the annealing temperature (parameter D) as having the most significant impact on the corrosion properties and hardness of the TiO_2 composite coating, as confirmed through response tables and main effect plots [7].

Electroless Ni-P coatings are widely used in engineering applications to enhance surface properties of steel substrates. The research focuses on optimizing microhardness of (Ni-P), (Ni-Cu-P), and (Ni-Cu-P-TiO_2) coatings using Taguchi method. Taguchi method is employed to optimize process parameters like stirring speed, temperature, and time for enhanced microhardness .The addition of TiO_2 nanoparticles in the coating increases microhardness, as observed in the (Ni-P-TiO_2) nanocomposite deposition. Taguchi modeling is utilized to optimize input parameters based on the signal-to-noise ratio, with the aim of maximizing microhardness. Bath temperature and time significantly impact the hardness regulation features of electroless (Ni-P-TiO_2) deposition. Previous studies have explored the effects of TiO_2 nanoparticles on the microstructure and corrosion resistance of electroless Ni-P coatings [8].

The study focuses on the impact of nickel, phosphorus, and second phase particles on the hardness, tribological properties, and microstructure of electroless composite coatings. Researchers have used surfactants to lower surface tension, aiding in the spread of particles and reducing interfacial tension between solid and liquid surfaces .Various factors like nickel source concentration, reducing agent, and TiO2 particle amount are crucial in controlling the properties of composite coatings .This literature survey highlights the significance of surfactants, optimization of coating parameters, and key factors influencing composite coating properties as discussed in the paper [9].

The paper discusses the development of metal deposition processes based on electroless nickel, alloy, and composite coatings, highlighting the surge in interest among researchers in recent years. It reviews the methods of formation of electroless nickel-phosphorus boron, polyalloys, composite coatings, and nanocoatings, emphasizing their effects on coating characteristics, applications, and recent developments. Interest in magnetic metal nanotubes for applications in nano medicine, high-density magnetic recording media, and sensing devices is discussed, showcasing recent findings on end-closed Ni-Co-Fe-B nanotubes and Ni-NiO core-shell nano-arrays **.**The paper also explores the deposition of electroless coatings incorporating nano-sized particles like ZrO_2, Al_2O_3, and barium hexaferrites, highlighting their influence on microstructure, hardness, corrosion resistance, and microwave absorption properties [1].

The paper discusses the inception of electroless coating by Brenner & Riddell in 1946, which has since been a subject of research interest, with a shift towards studying properties and applications in the last two decades. The co-deposition of particulate matter within the growing film has led to the development of electroless composite coatings with excellent wear and corrosion resistance, expanding the potential applications of these coatings. Various characterisation studies have been conducted on electroless nickel-based coatings, focusing on wear and corrosion properties, showcasing the importance of these coatings in surface engineering and metal finishing. The paper highlights the market expansion of electroless alloy/composite coatings due to their ability to coat a wide range of materials, including electrically conductive materials, fabrics, insulators, and more, emphasizing the versatility and growing demand for these coatings [2].

The paper focuses on reviewing the tribological advancements of different electroless nickel coatings, particularly Ni-P coatings, based on bath types, structure, and tribo testing parameters in recent years. Electroless nickel coatings are distinct from electrolytic coatings as they do not require electricity for operation, offering benefits like uniform coating and the ability to coat nonconductive materials. These coatings exhibit excellent tribological properties such as high hardness, good wear resistance, and corrosion resistance, making them widely used in industries like aerospace, automobile, electrical, and chemical industries. Researchers have been exploring newer variants of electroless nickel coatings like Ni-W-P, Ni-Cu-P, Ni-P-SiC, and Ni-P-TiO_2 to enhance their tribological characteristics. Additionally, modifying the coating process parameters has been a key focus to improve the wear and tear resistance of these coatings .The study emphasizes the importance of developing newer coating materials with improved wear resistance to meet the demands of technological advancements. Electroless nickel coatings, especially Ni-P coatings, have shown significant potential in this regard, warranting a comprehensive study of their tribological advancements [3].

The research paper emphasizes the importance of controlling properties of composite coatings through key parameters like nickel source concentration, reducing agent, and TiO_2 particle amount, as identified in previous studies. Various factors such as nickel source quantity, reducing agent quantity, pH, bath temperature, TiO_2 composite particles amount, complexing agents, and stabilizers influence coating characteristics in composite coatings. Prior research has shown that incorporating different types of hard/soft composite particles in Ni-P matrix results in a uniform distribution of particles, enhancing coating properties. The study utilizes Grey relational analysis and the Taguchi method to investigate the influence of process parameters on surface roughness, highlighting the significance of TiO_2 particle concentration and reducing agent amount in controlling roughness parameters of composite coatings [10].

Electroless nickel (EN) plating on magnesium alloys has been a subject of study over the last two decades, aiming to enhance the corrosion resistance of magnesium alloys for various applications. The stability of the plating bath is crucial, as the concentration of bath components fluctuates during the plating process, impacting coating quality and bath stability .pH stabilizers like ammonium acetate play a vital role in maintaining bath stability and controlling coating quality and bath life, leading to the formation of a uniform and dense coating .The ideal operating pH for an acid Ni-P plating bath is typically between 5.0 to 7.0, with stabilizers like acetic acid, succinic acid, ammonium acetate, and ammonium succinate exhibiting good buffer performance in the pH 4-6 range. This literature survey highlights the importance of bath stability, pH stabilizers, and optimal pH ranges in EN plating processes on magnesium alloys [11].

Electroless nickel (EN) coating is a well-established surface engineering process that involves depositing a metal-metalloid alloy coating on various substrates, providing high hardness and excellent resistance to wear, abrasion, and corrosion. The effect of surfactants, specifically sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB), on the surface roughness, microhardness, and microstructure of EN coatings is a key focus of this study. Researchers have reported that the addition of SDS in the EN coating process results in a smoother surface at higher concentrations, leading to improved surface roughness and microhardness of the coating. Studies have shown that surfactants like SDS and CTAB can influence the surface topography of EN deposits, promoting smoother surfaces and altering the microstructure of the coatings .The research aims to investigate the impact of surfactants on EN coatings to enhance their mechanical properties and surface characteristics, contributing to the existing knowledge in the field of surface engineering and coating technologies [12]

Previous research focused on co-deposition of nano TiO_2 in Ni-P matrix using electroless plating technique, lacking information on surfactant effects on tribological characteristics. The study aimed to achieve Ni-P-nano-TiO_2 coatings on low carbon steel substrates via electroless deposition and assess the impact of anionic (SDS) and cationic (DTAB) surfactants on wear and friction behavior. Investigations revealed that optimal surfactant concentrations led to smoother surfaces, lower friction coefficients, enhanced microhardness, and improved wear resistance in the composite coatings. The presence of surfactants contributed to higher critical load tolerance and lower penetration depth in scratch tests, attributed to the reinforcing effect of TiO_2 nanoparticles in the coatings. Surfactants, especially DTAB, increased the weight percentage of TiO_2 in the Ni-P matrix significantly, with the highest TiO_2 incorporation observed at critical micelle concentration (CMC) of DTAB [14].

Electroless coating of mild steel with nickel-phosphorus alloy was conducted using a bath containing sodium hypophosphite and glycincitrate complexing agents. Heat treatment of specimens improved hardness and corrosion resistance, with coatings containing 11.7 - 12.2% phosphorus exhibiting the least corrosion rate. The formation of an adsorbed layer of hypophosphite anion on the alloy surface provided passivity in the aqueous environment, contributing to increased weight observed during the first month of immersion tests. The microstructure analysis revealed that different phosphorus compositions led to variations in grain size and intermetallic phases, affecting corrosion resistance. Coating time influenced the phosphorus content, thickness, and structure of the deposits, with longer coating times resulting in increased thickness and decreased phosphorus content [16].

The study focuses on the nucleation and growth processes of Ni-P deposition influenced by a complexing agent, specifically aminoacetic. Aminoacetic is selected as the main complexing agent in the electroless nickel deposition bath. The initial stages of Ni-P electroless depositions were analyzed using atomic force microscopy (AFM) and scanning electron microscopy (SEM).The research methodology includes the preparation of the deposition bath with specific reagents and water quality standards. Copper substrates were prepared by mechanical polishing before the electroless nickel deposition process. Characterization techniques such as AFM, SEM, and X-ray diffraction were employed to study the morphology and microstructure of the deposits. The study also investigates the electrochemical reactions in the bath solution and the impact of the complexing agent on the deposition rate and composition of the Ni-P alloy [17].

Electroless Ni-P coatings have been widely studied for their ability to improve the mechanical properties of substrates, such as mild steel. The addition of $CuSO_4$ to the coating solution has been explored to create Ni-P-Cu composite coatings, enhancing properties like microhardness. Heat treatment of coated samples at 400°C has been shown to enhance the mechanical properties of the coatings compared to as-plated substrates.SEM and XRD techniques were utilized to analyze the surface morphology and structure of the coatings, providing insights into the composition and characteristics of the Ni-P-Cu particles [18].

Electroless deposition of ternary nickel-based alloys has attracted attention due to their remarkable attributes such as corrosion resistance, wear resistance, thermal stability, and favorable magnetic properties. The research is centered on investigating the influence of copper and tungsten in alkaline electroless nickel solutions for the plating of Ni-Cu-P, Ni-W-P alloys, and the combined impact of ions in depositing Ni-W-Cu-P alloys. The introduction of copper into Ni-W-P solutions leads to the formation of a quaternary coating, Ni-W-Cu-P, exhibiting enhanced crystalline structure and a highly polished surface. Incorporating copper into Ni-W-P coatings does not bring about a significant alteration in hardness, albeit it slightly enhances corrosion resistance in comparison to ternary alloys. Moreover, the investigation delves into the effects of heat treatment on the hardness of electroless Ni-P, Ni-Cu-P, Ni-W-P, and Ni-W-Cu-P layers, alongside their electrochemical performance in diverse environments [19].

Electrodeposited Ni coating is commonly used in various industries due to its excellent properties, such as corrosion resistance and durability. To enhance the mechanical properties of Ni coatings, forming duplex composite coatings is an effective strategy. In this approach, Ni-P coatings are often used as the outer layer to improve mechanical strength, while Ni coatings serve as the inner layer for corrosion protection. Previous research has focused on improving the mechanical properties of Ni-P coatings by incorporating nanosized hard particles into the electrolyte. However, challenges like particle agglomeration have been encountered due to the small size and high surface energy of nanoparticles. A novel sol-enhanced plating method has been developed to address the issue of particle agglomeration. By adding a small amount of oxide-containing sol to the traditional electrolyte, in situ composite coatings with well-dispersed nanoparticles can be produced, leading to significantly enhanced mechanical properties [20].

The metastable Ni_2P_5 precipitates in Ni_3P coatings have been primarily studied using XRD tests due to their small proportion.TEM has been identified as a powerful tool to investigate the evolution of metastable NixPy nanophases during the crystallization of NieP amorphous coatings. Previous studies have focused on the addition of third elements like Cu, Mo, W, Sn, and Re, as well as composite particles to NieP coatings to enhance their performance. Ni-Cu-P coatings, a popular ternary NieP-based coating, have been extensively studied for their crystallization process, including the precipitation of nanoecrystalline Ni(Cu) and phase transformations to Ni_5P_2, Ni_12P_5, and Ni_3P phases. The mechanism of phase transformation between different phases in Ni-Cu-P coatings remains unclear, prompting this study to investigate the crystallization process and phase transformation mechanisms using XRD and TEM techniques [4].

Electroless Ni-P alloys are widely used in industry due to their exceptional properties like wear resistance, corrosion resistance, and unique physical characteristics, making them valuable for various applications. Studies have shown that Ni-Cu-P alloy deposits exhibit superior characteristics compared to Ni-P deposits, including better thermal stability, corrosion resistance, solderability, magnetic, and electrical properties, making them promising for applications like underbump metal (UBM) of solder bumps. Previous research has focused on the technology of Ni-P deposits and the effect of deposition parameters on the elemental contents and deposition rate of electroless Ni-Cu-P deposits, emphasizing the importance of composition and microstructure control in electroless deposits.The crystallization behavior of electroless Ni-P and Ni-Cu-P deposits has been studied using techniques like differential scanning calorimetry and X-ray diffractometry, revealing differences in transformation sequences and crystallization temperatures based on phosphorus content and composition [21].

The paper reviews the mechanism of the third element co-deposition in electroless Ni-P plating and its impact on ternary coatings' properties. It proposes a model explaining the role of copper in electroless nickel plating, suggesting that Cu (II) ions are reduced into Cu (co-deposited in the alloy) and Cu (I) ions by reactions with hypophosphite. It discusses the challenges and ambiguities surrounding the co-deposition of tin and copper during electroless plating of Ni-P, highlighting the unclear mechanisms and the role of disproportionation reactions of Cu (I).The paper also explains the formation of Cu-rich zones near the substrate due to the nobility of copper compared to Ni, emphasizing the delicate balance required in the composition of the solution for electroless Ni-Cu-P plating [22].

Electroless nickel alloys are widely used in various industries due to their desirable physical and mechanical properties. Addition of copper into electroless Ni-P matrix enhances the thermal stability and solderability of coatings. Ni-Cu-P coatings with copper content above 28% exhibit non-magnetism properties. Previous studies have shown that the addition of copper improves the corrosion resistance of electroless Ni-P coatings. Wang et al. found that electroless Ni-Cu-P coatings have better corrosion resistance in NaOH solution compared to Ni-P or stainless steel. Yu et al. and Chen and Lin have investigated the deposition parameters and behaviors of Ni-Cu-P coatings on different substrates. The optimal conditions for preparing corrosion-resistant Ni-Cu-P coatings involve specific pH, temperature, and CuSO4 concentrations [23].

Citrate is identified as a suitable complexing agent for electroless Ni-Cu-P deposits. Autocatalytic deposition of nickel and its alloys holds significant industrial applications. Prior studies have focused on achieving Ni-Cu-P alloy layers with varying nickel and copper percentages. Investigations have aimed at obtaining compact Ni-Cu-P alloys with high deposition rates, comparable to Ni-P deposition rates. Copper plays multiple roles in electroless plating solutions, acting as a stabilizer, accelerator, and affecting solution stability. The research aims to develop Ni-Cu alloy layers with high deposition rates and superior deposit properties through autocatalytic deposition [24].

The research paper investigates the microstructure evolution and corrosion resistance of Ni-Cu-P alloy coatings. X-ray diffraction (XRD), transmission electron microscope (TEM), and electrochemical examination were used to study the effects of Cu on the alloy's properties. XPS analysis was conducted to investigate the composition of corrosion products on the samples, revealing that Cu incorporation enhanced the stability of the Ni-Cu-P amorphous coating. The semiconductor characteristics of passivation films on the alloys were studied, showing that the Ni-Cu-P passivation film had n-type semiconductor features due to the presence of phosphorus and nickel phosphate. Microstructural analysis using XRD showed that Cu incorporation delayed the crystallization process in the Ni-Cu-P samples compared to Ni-P coatings [25].

The paper emphasizes the significance of SEM analysis in understanding the physical and mechanical behaviors of improved clays, highlighting the importance of microstructural analysis. Various studies in the literature focus on clay microstructure and improved clay microstructure, showcasing the relevance of SEM in soil improvement works. SEM tests are commonly conducted in material engineering laboratories, translating materials science tests into practical applications for soil improvement projects. Studies have shown that SEM images reveal reaction products, variations in microstructures, and micro-macro pores, providing detailed insights into the effects of additives, curing time, freeze-thaw cycles, etc., on soil properties. The interpretation of SEM analysis is based on grain size changes before and after improvement, offering a better understanding of soil behavior compared to traditional mechanical tests [29].

The paper extensively discusses X-ray diffraction (XRD) techniques as powerful tools for characterizing materials, providing information on phases, crystalline structure, crystallite size, strain, orientation, texture, crystallinity, and defects. Various growth techniques like molecular beam epitaxy, chemical vapor deposition, and sputtering are employed to prepare thin films, with X-ray radiations used for characterization due to their rapid and non-destructive nature. XRD analysis is crucial for understanding the structural properties of materials, including bulk materials, polycrystalline thin films, and multilayer structures, with applications in phase analysis, stress evaluation, texture coefficient analysis, and depth profiling. The paper also highlights the significance of XRD in characterizing different forms of materials, from simple bulk materials to complex structures like nanostructures and non-crystalline materials such as glasses and liquids [30].

2.2. Objective of the present work

The present work shall deal with the study of hardness and mass deposition rate of electroless Ni-Cu-P-TiO_2 quaternary alloy coating on Mild Steel substrate. It has been observed that there is very little specific research on the study of hardness and mass deposition rate. Therefore, the objective of this research shall focus on the following points:

1. Synthesis of Electroless Ni-Cu-P-TiO_2 composite coating on Mild Steel substrate.
2. Measurement of hardness of electroless Ni-Cu-P-TiO_2 composite coating.
3. Optimizations of one variable, i.e, hardness of the coating by varying the coating process parameters.
4. Use of Taguchi method for parametric optimization.
5. Study of microstructure and composition of Ni-Cu-P-TiO_2 coating with the help of Scanning Electron Microscopy (SEM) and Energy dispersive X-ray analysis (EDAX) respectively.

CHAPTER 3:

EXPERIMENTAL DETAILS

3.1. Introduction

The present study considers preparation and characterization of Ni-Cu-P-TiO_2 electroless composite alloy coatings. These coatings are deposited on Mild steel substrates. The coating deposition along with different parameter and hardness behavior have been evaluated on these coatings and the optimization of these coatings was performed. The surface morphology, phase transformation behavior and chemical composition of the coatings have been studied by scanning electron microscope (SEM), X-ray diffraction analysis (XRD) and energy dispersive X-ray analysis (EDX) respectively.

3.2. Deposition of Electroless Ni-Cu-P-TiO_2 Coating

3.2.1. Preparation of substrate sample

Wire-cut EDM was used to cut the Mild steel plate into coupons of 10 mm × 6 mm × 2 mm and were used as substrate for the electroless coating. All the substrates were mechanically polished using different grade of SiC papers with grit size ranging from 220, 400, 600, 800, 1000, 1200 and 1500 to achieve a smooth surface finish and to ensure the surface to be dirt and abrasive free. After polishing the samples were put in acetone and cleaned ultrasonically in a sonicator (MAKERS name) for 8-10 minutes to remove any oxide or unwanted foreign matters, then the substrate was rinsed with distilled water (DI) for 2-3 minutes. Second step of cleaning was followed by alkaline cleaning using 10 wt.% NaOH for 10-12 minutes using sonicator operating at ambient temperature.

3.2.2. Experimental set up for Ni-Cu-P-TiO_2 Electroless Coating

The following instruments and chemical were required for obtaining electroless coating deposition:

(i) Electronic Balance: High precision electronic balance was used to measure weights of substrates and chemicals. AFCOSET, Model No. ER-182A, SL. No. 0108017, Maximum range 180 g, Minimum range 0.01 mg shown in Figure 3.1

Fig 3.1. Electronic Balance

(ii) Magnetic Stirrer cum heater : Magnetic stirrer cum heater was used for proper mixing of the bath solution and to heat the bath to the required temperature. 2MLH Magnetic stirrer, Manufactured by Remi Instruments shown in fig 3.2 was used.

Fig 3.2. Magnetic Stirrer cum heater

(iii) Mercury in glass Thermometer: Thermometer is used to maintain the bath temperature during the coating process.

(iv) Glass Beakers: It is used to hold the bath solution (BOROSIL).

(v) pH meter: A digital pH meter was used to measure the pH of the electroless bath. Electronics India, Model No. 181, SL. No. 11505265, Maximum range 14 pH, Minimum range 0.01 pH shown in Figure 3.3.

Fig 3.3. pH meter

(vi) Ultrasonic cleaner: Ultrasonic cleaners are used to clean many different types of objects, including industrial parts, tools, coins,The ultrasonic cleaner effectively removes contaminants from various objects, ensuring a thorough cleaning process in industrial applications.

Fig 3.4. Ultrasonic cleaner

3.2.3. Reagents Used and Electroless coating procedure

Nickel Sulphate ($NiSO_4.6H_2O$) was used as a *source of nickel ions*. The nickel sulphate solution was crucial in providing nickel ions for the electroless coating deposition process. Copper Sulphate ($CuSO_4.5H_2O$) was uesd as a *source of copper ions*. The copper sulphate solution played a vital role in supplying copper ions essential for the electroless coating deposition process alongside the nickel sulphate solution. Sodium Hypophosphite ($NaH_2PO_2.H_2O$) was used as a *reducing agent*. It was employed as the reducing agent providing the source of phosphorus. The electroless plating process is based on a reduction reaction in which the reducing agent is oxidized and Ni^{2+} ions are reduced and gets deposited on the substrate surface [13]. Tri-sodium Citrate Dihydrate ($Na_3C_6H_5O_7.2H_2O$) was used as a *complexing agent* to control the rate of release of free metal ions for the reducing reaction. Sodium Acetate (CH_3COONa) acts as a *buffering agent* which is uesd to maintain the bath self-adjust pH value so that the pH value can be kept stable during the electroless plating process. Titanium Oxide (TiO_2) nanoparticles were used to obtain composite coating. Sodium dodecyl sulfate (SDS) was used as a *surfactant* to promote suspension, stable dispersion of nanoparticles and to avoid agglomeration of nano-particles, and to control the size of the nanoparticles due to their electrostatic repulsion properties. The bath constituent details is provided in Table 3.1.

<u>Steps for Electroless coating deposition:</u>

Step 1 - Nickel sulphate and copper sulphate with 80 ml of distilled water (DI).

Step 2 – Step 2 involves carefully stirring the solution until the Nickel sulphate is completely dissolved in the distilled water.

Step 3 - Then mix Sodium Hypophosphite, Tri-sodium Citrate Dihydrate, Sodium Acetate with 80 ml of DI with the help of stirrer until it completely dissolves, ensuring a homogeneous solution for the electroless plating process.

Step 4 - Now heat the solution to reach a temperature of 85 ± 2 *℃* and maintain the the bath pH of around 5.8 ± 1.

Step 5 - The samples were activated in palladium chloride ($PdCl_2$) solution for 8-10 seconds at 55 ^{o}C temperature followed by rinsing with distilled water for few seconds.

Step 6 - Ensuing proper temperature and pH the activated samples were introduced in the electroless bath and allowed to start the deposition process for 30 minutes to obtain electroless Ni-Cu-P alloy coating.

Step 7 - The nanosized TiO_2 particles was then mixed with SDS and DI and was sonicated for 30- 45 minutes to obtain better dispersion of TiO_2 nanoparticles.

Step 8 - The well dispersed TiO_2 nanoparticle+SDS solution was then stirred at 300-350 rpm for subsequent 15 minutes.

Step 9 - This TiO_2 solution was poured slowly in the electroless Ni-Cu-P bath to obtain TiO_2 embedded Ni-Cu-P electroless coating which resulted in a composite coating.

Step 10 - After completion of the coating, samples were cleaned with distilled water (DI) followed by air-drying and went for subsequent mechanical as well as morphological characterization.

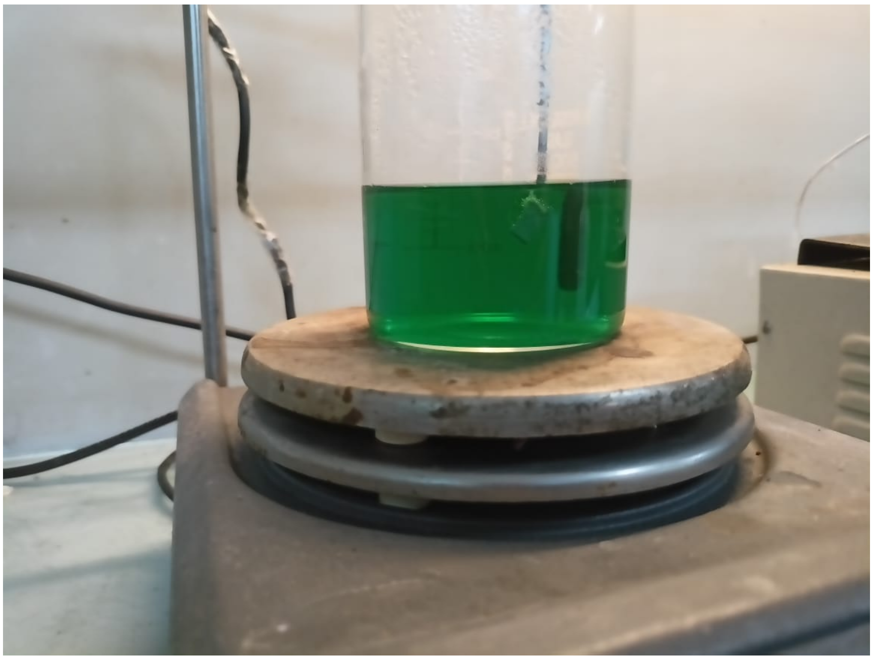


Fig 3.5. Schematic diagram of electroless setup

Table 3.1. Chemical compositions of the Ni-Cu-P-TiO_2 electroless bath

Bath composition	Quantity (gm/L)
Nickel Sulphate ($NiSO_4.6H_2O$)	4-6 gm/L
Copper Sulphate ($CuSO_4.5H_2O$)	0.08-0.24 gm/L
Sodium Hypophosphite ($NaH_2PO_2.H_2O$)	4-6 gm/L
Tri-sodium Citrate Dihydrate ($Na_3C_6H_5O_7.2H_2O$)	8 gm/L
Sodium Acetate (CH_3COONa)	5 gm/L
Titanium Oxide(TiO_2)	0.2-1 gm/L
Sodium dodecyl sulfate (SDS)	0.02 gm/L
pH values	5.8-6
Time	1hr
Temperature	85℃
Bath volume	200 cm^3

3.2.4. Heat treatment

Heat treatment plays a crucial role in altering the properties of Ni-Cu-P-TiO_2 composite coatings [6]. Heat treatment of the Ni-Cu-P-TiO_2 amorphous coating involves annealing of the coated samples in present study the optimized sample obtained from Taguchi Analysis was heat treated at three different temperatures: 200, 400 and 600 ^{o}C to induce microstructure evolution and phase transition. The mechanical properties of the coating, including hardness, elastic modulus, and wear resistance, are significantly influenced by the microstructure evolution and phase transition during crystallization induced by heat treatment. The suitable heat treatment process results in the improvement of hardness and wear resistance of the coating. The formation rate of crystallization products in the Ni-Cu-P-TiO_2 coating is dependent on the temperature and duration of heat treatment, with higher temperatures accelerating atom diffusion and promoting nucleation and growth rates of precipitates [4]. The process of heat treatment is essential for understanding the behavior of composite coatings under different thermal conditions. Scanning electron microscopy (SEM) is used to observe the surface morphology changes post heat treatment, revealing alterations in grain structure. Energy dispersive X-ray analysis (EDX) helps in verifying the presence of different elements like nickel, copper, phosphorus, titanium, and oxygen in the coatings after heat treatment. Heat treatment affects the friction coefficient of the composite coatings. Friction coefficient increases with the incorporation of TiO_2 particles and higher annealing temperatures, impacting the tribological performance [6].

3.3. Measurement of Hardness

3.3.1. Hardness properties

Hardness is a critical mechanical property often used to assess the quality of coatings. The Vickers hardness number (VHN) is a common measure of hardness, defined as the ratio of load to the total area of the indentation produced .The absolute hardness (H0) is the macrohardness independent of the load, and it varies with the applied load according to a specific relation. The hardness test is widely used due to its simplicity in estimating the mechanical properties of coatings. The hardness number varies with the applied load, especially in the microhardness characterization range, impacting the measured values. Composite hardness calculations involve considering the film thickness, indentation print, substrate hardness, and their variations with the applied load .The area law of mixture for microhardness is suitable for thick hard coatings or indentation depths similar to the film thickness when using modified models [26]. The ratio of indentation depth to film thickness is essential in determining the behavior solely due to the coating properties. Hardness properties play a significant role in material characterization, especially in coatings and thin films, impacting various industrial applications and material design processes [27]. The composite hardness is influenced by the relative indentation depth and the hardness of the substrate and coating. A mathematical model is proposed where the composite hardness is a function of the relative indentation depth and the substrate and coating hardnesses, with a fitting parameter X describing various properties like coating brittleness and indenter geometry**.** The hardness can be expressed in terms of the total indentation energy [28]. **Vickers test** uses a square-based diamond pyramid of apex angle 136° as the indenter and is able to measure the hardness of very soft materials. Vickers hardness number is obtained using the formula

$$\mathbf{VHN = 1.854 \times (F/d^2)}$$

Where, d = Diagonal of the indentation made on the test specimen.

F = Load in gram

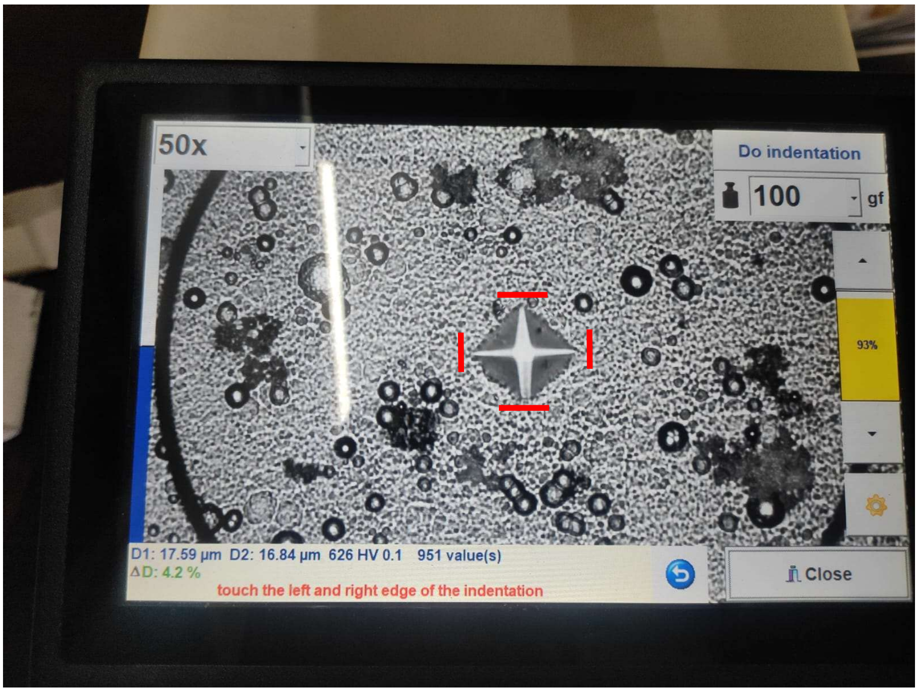


Fig 3.6. Vickers Micro Hardness Tester (VMHT) Machine.

3.3.2. Hardness measuring machine

As the name indicates, a Vickers hardness tester is specialized for hardness testing according to the Vickers method. These instruments support standard compliant testing of different materials and component geometries across a wide range of industries. A typical Vickers hardness testing instrument includes a load application feature, an indenter, a test anvil and an optical system. Vickers hardness testers can be manually operated, where the indentation is measured using an ocular device, or they can be software- controlled Vickers hardness testing machines with fully automated evaluation of the test indentation. With the software-controlled Vickers hardness testing machines you benefit from a wide range of functions including a template function, user-defined specimen grips, a high-resolution camera system and electronically controlled load application. These Vickers hardness testing instruments can be used to create hardness curves (hardness profile measurements) and hardness maps of complete specimens. Measuring hardness helps designers Activate Windows and manufacturers determine material properties, including after hardening and forming processes. Therefore evaluate how they will behave in their intended application.

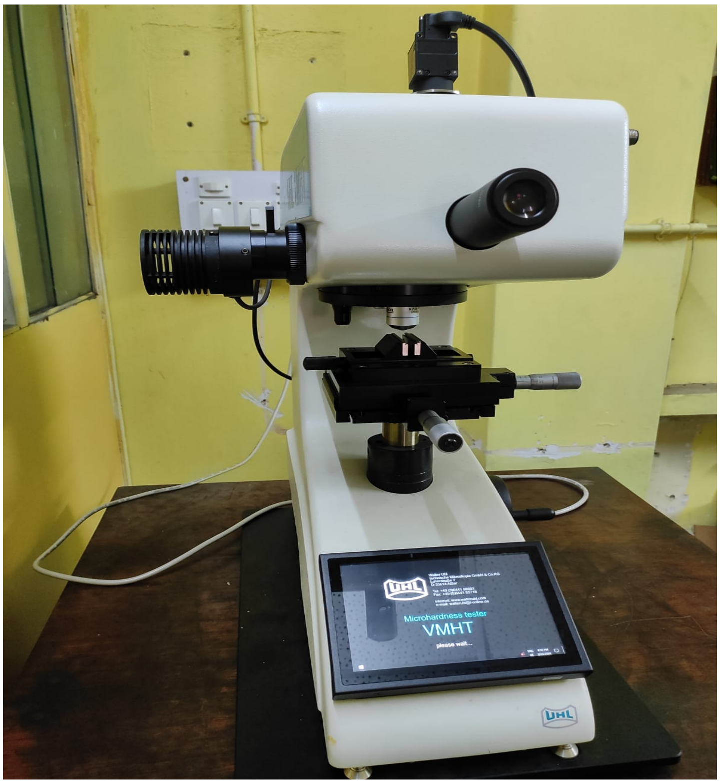


Fig 3.7. Vickers Micro Hardness Tester (VMHT) Machine

3.4. Scanning Electron Microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS)

The SEM gives the magnified images of the particle or grain size, shape and provides visual understanding of the surface morphology. During SEM imaging a sample surface can be magnified upto nanometer (nm) level to understand the surface structures and also to evaluate the difference on the surfaces. SEM offers the opportunity to analyze the material to be examined with an electron beam generated in a vacuum environment and thinned with electromagnetic lenses in the same situation to create a high-resolution image. The images found in the microscope are created by counting the reflections or electrons reflected from the interaction of the electron beam with the material [29]. To evaluate a coating in detail, it is essential to determine parameters such as grain size, alignment of grains to the substrate, the presence of inclusions and voids between the substrate and the coating. The fundamental features to search for in a typical microstructure study of a coating are: (i) the grain structure, (ii) change in the grain structure of the substrate and the coatings, (iii) the interface between coating and substrate to obtain coating thickness by cross-section SEM, (iv) the exterior surface of the coating.

Effective micro-structural evaluation will depend in most cases on the combined use of several forms of microscopy, e.g. Optical Microscopy and Scanning Electron Microscopy (Fig 3.7).

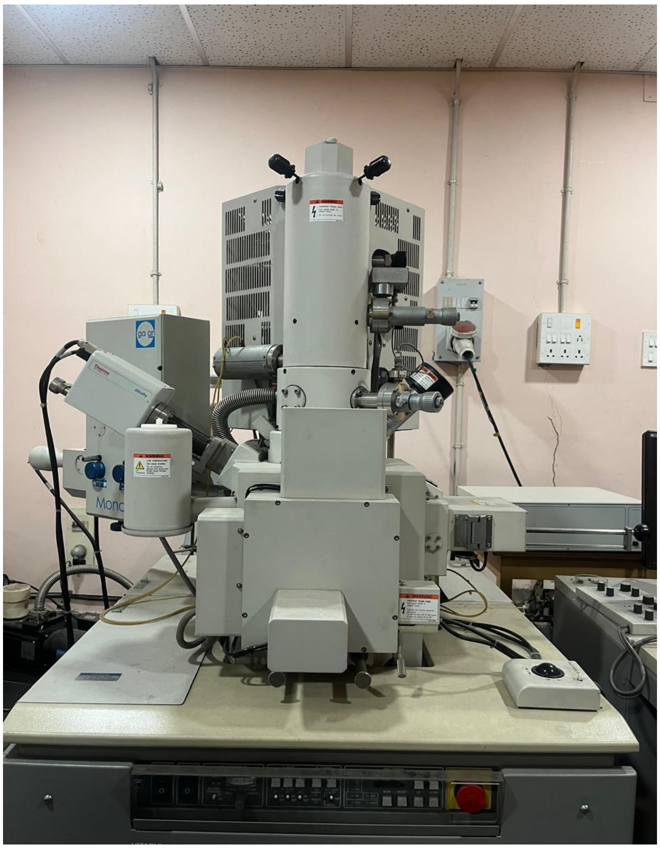


Fig 3.8. Scanning Electron Microscopy (SEM) equipped with EDS

The primary function of Energy Dispersive X-ray analysis (EDAX) is to perform elemental analysis of materials by detecting characteristic X-rays emitted when the sample is bombarded with high-energy electrons. It helps in determining the elemental composition and the weight percentage of elements present in the sample. EDAX provides quantitative information about the elemental composition of the material being analyzed. It allows researchers to identify and quantify the elements present in the sample, aiding in understanding the material's properties and characteristics [10]. In present study EDAX is done for the compositional analysis of the electroless nickel coating. This will indicate the presence of nickel and the primary alloying element (phosphorous, nickel or copper) by their weight percentages which further helps in determining the characteristics of the coating.

3.5. Phase Analysis using XRD

X-ray diffraction techniques are powerful and non-destructive tools used for material characterization with minimal sample preparation. XRD provides crucial information about various aspects of materials, including phases, crystalline structure, average crystallite size, micro and macro strain, orientation parameter, texture coefficient, degree of crystallinity, and crystal defects [30]. X-ray diffraction applies the ability of X-rays to be diffracted by a crystalline lattice since the wavelength of X-rays is comparable to inter-planar spacing of a crystal. The diffraction pattern formed is characteristic to a specific crystalline structure and XRD is particularly useful for inorganic chemical analysis. XRD has a wide variety of applications in materials characterization, such as determination of crystal structure and orientation, phase identification, and detection of trace compounds in a material. Oxides, nitrides, carbides and sulphides of metals can usually be clearly distinguished by this technique. A diffractometer consists of an X- ray source, a sample holder with ability for rotation and a series of counter to monitor the diffracted intensity. The X-rays used are monochromatic which is different from the X-rays used in imaging. Rotation of the sample facilitates detection of the diffracted pattern, which is a series of dark and light bands that denote destructive and constructive interference between scattered X-rays. The angular spacing between dark and light bands indicates the size of the inter- planar spacing, which is used to determine the compounds.

3.6. Design of Experiment (DOE)

In the field of statistics and research, the design of experiment (DOE) is defined as a systematic approach of planning, conducting, analyzing, and interpreting the possible outcome of an experiment by considering the input process parameters at different levels. It is an efficient method that enables us to study the relationship between factors (input variables) and responses (output variables), thus helping in the optimization of process parameters with the help of which we can take data-driven decisions. This information is useful for building statistical models to predict the process performance. Thus, it defines the specific setting levels of the combinations of elements at which the different runs in the experiment are to be done.

3.6.1. HISTORY OF DESIGN OF EXPERIMENT (DOE)

The history of DOE can be traced back to the early 20th century when statisticians and scientists recognized the need for a more efficient and structured approach to experimentation. However, in the year the 1920s and 1930s, Ronald A. Fisher, a British statistician, invented the design of experiments at the Roth Amsted Experimental Station which was located 25 miles north of London. He made significant contributions to the development and popularization of DOE and his work laid the foundation for modern DOE. The most well-known of a group of Japanese scientists, Genichi Taguchi, is known for his quality-improvement techniques. Toyota was one of the first firms to implement Taguchi's techniques. Some basic concepts of the design of experiments were described by Ronald A. Fisher and those fundamental principles are

- **Randomization:** It is a technique for preventing an unknown bias from affecting the outcomes of an experiment and it also ensures that the groups are comparable. It helps in controlling the effects of extraneous variables and allows for valid statistical inferences.
- **Replication:** It involves running multiple independent experimental runs or observations for each treatment combination with identical experimental conditions. It helps in estimating the experimental error, assessing th variability, and obtaining more precise and reliable results. When the noise comes from uncontrollable nuisance variables, replication improves the signal- to-noise ratio.
- **Blocking:** It is a technique used to reduce variability in the experimental units caused by sources that are not of primary interest. It involves grouping similar experimental units together and randomly assigning treatments within each group.
- **Orthogonality**: Orthogonal designs are those in which the effects of different factors are uncorrelated or independent of each other. It thus helps in the efficient estimation of the main effects and interaction between factors. They help in obtaining clear and unambiguous information about the effects of individual factors on the response variable.

3.6.2. APPLICATIONS OF DOE

DOE finds applications in various fields, including manufacturing, engineering, healthcare, agriculture, and social sciences. Some common uses of DOE include:

- **Process optimization:** DOE helps identify the critical process factors that affect the outcome of a process and determine the optimal levels for these factors, thus optimizing the manufacturing processes. By systematically varying the factors and measuring the response, researchers can uncover the optimal settings that lead to improved product quality, efficiency, or cost savings.
- **Product development:** DOE is used to optimize product formulations or designs by studying the effect of various factors, such as materials, design parameters, or production methods, on the final product's quality or performance. This helps in creating better products with reduced development time.
- **Quality improvement:** DOE can be employed to identify the critical process parameters and their optimal settings that have the most significant impact on product quality. By reducing variability and understanding the impact of different factors, organizations can enhance product reliability and consistency, reduce defects, and ensure customer satisfaction.
- **Root cause analysis:** When troubleshooting a process or system, DOE can be used to systematically investigate the potential causes of a problem. varying the factors suspected of contributing to the issue, researchers can determine the root cause and develop appropriate solutions.
- **Sensitivity analysis**: DOE allows for the evaluation of the sensitivity of a process or system to different factors. By systematically varying the factors, researchers can assess which ones have the most significant impact and focus resources on those that matter the most.
- **Robustness testing**: DOE helps in testing the robustness of a process or product design by intentionally introducing variations in operating conditions or component specifications. This helps in identifying the range of conditions within which the process or product performs reliably.

- **Cost optimization:** DOE aids in optimizing costs by identifying the key factors that contribute to cost variations and determining their optimal levels. This helps in achieving cost savings without sacrificing quality or performance.
- **Scientific research**: In scientific studies, DOE helps researchers investigate hypotheses, explore relationships between variables, and determine cause-and- effect relationships. It allows for controlled experimentation, reducing bias and confounding factors, and enabling more reliable conclusions.

3.6.3. Taguchi Method

- **Taguchi's method:**

Taguchi's techniques have been used widely in engineering design (Ross 1996 & Phadke 1989). The Taguchi method contains system design, parameter design, and tolerance design procedures to achieve a robust process and result for the best product quality (Taguchi 1987 & 1993). The main trust of Taguchi's techniques is the use of parameter design (Ealey Lance A.1994), which is an engineering method for product or process design that focuses on determining the parameter (factor) settings producing the best levels of a quality characteristic (performance measure) with minimum variation. Taguchi designs provide a powerful and efficient method for designing processes that operate consistently and optimally over a variety of conditions. To determine the best design, it requires the use of a strategically designed experiment, which exposes the process to various levels of design parameters.

Taguchi has used Signal-Noise (S/N) ratio as the quality characteristic of choice. S/N ratio is used as measurable value instead of standard deviation due to the fact that, as the mean decreases, the standard deviation also deceases and vice versa [31].

However, classical experimental design methods are too complex and not easy to use. Furthermore, a large number of experiments have to be carried out when the number of the process parameters increases. To solve this problem, the Taguchi method uses a special design of orthogonal arrays to study the entire parameter space with a small number of experiments only. The experimental results are then transformed into a signal-to-noise (S/N) ratio. Taguchi recommends the use of the S/N ratio to measure the quality characteristics deviating from the desired values. Usually, there are three categories of quality characteristic in the analysis of the S/N ratio, i.e. **the-lower-the better, the-higher-the-better, and the-nominal-the-better.** The S/N ratio for each level of process parameters is computed based on the S/N analysis. Regardless of the category of the quality characteristic, a greater S/N ratio corresponds to better quality characteristics. Therefore, the optimal level of the process parameters is the level with the greatest S/N ratio. Further more, a statistical analysis of variance.

Eight-Steps in Taguchi Methodology

Step-1: Identify the main function, side effects, and failure mode

Step-2: Identify the noise factors, testing conditions, and quality characteristics

Step-3: Identify the objective function to be optimized

Step-4: Identify the control factors and their levels

Step-5: Select the orthogonal array matrix experiment

Step-6: Conduct the matrix experiment

Step-7: Analyze the data and predict the optimum levels and performance

Step-8: Perform the verification experiment and plan the future action

- **Analysis of variance (ANOVA)**

ANOVA is statistical technique, which can infer some important conclusions based on analysis of the experimental data. The method is very useful for revealing the level of significance of influence of factor(s) or interaction of factors on a particular response. It separates the total variability of the response into contributions of each of the factors and the error. Using Minitab, ANOVA is performed to determine which parameter and interaction significantly affect the performance characteristics. ANOVA calculates the F-ratio, which is the ratio between the regression mean square and the mean square error. The F-ratio, also called the variance ratio, is the ratio of variance due to the effect of a factor and variance due to the error term. This ratio is used to measure the significance of the parameters under investigation with respect to the variance of all the terms included in the error term at the desired significance level, a. If the calculated value of F-ratio is higher than the tabulated value of F-ratio, then the factor is significant at desired α level. In general, when F value increases the significant of the parameter also increases. ANOVA table shows the percentage contribution of each parameter [33].

(ANOVA) is performed to see which process parameters are statistically significant. With the S/N and ANOVA analyses, the optimal combination of the process parameters can be predicted. Finally, a confirmation experiment is conducted to verify the optimal process parameters obtained from the parameter design [32].

3.6.4. Experiment Parameters and Response for Taguchi Method

For conducting the experimental analysis, three levels and four control factors were selected, as presented in Table 3. Taguchi L9 (3ˆ4) orthogonal design given in Table 4 was selected to understand the effect of individual factors on Hardness. The four input factors are Nickel Sulphate (A), Sodium-hypophosphate (B), Copper sulphate (C), TiO_2 nanoparticles (D). Three different levels low (-1), medium (0), and high (+1) were considered based on some preliminary experiments. MinitabR2019 was used for the analysis of Taguchi's design. The response, Hardness of the composite coating was considered for maximum hardness thus S/N ratio (dB) with the "larger-the-better" characteristic was calculated using Equation. Finally, a confirmation test (at optimum parameter combination) was performed for validation of the Taguchi optimal parameters.

$$S/N\,\text{ratio, ``larger - the - better''} = -10 \times \log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right)$$

where n is the total number of experiments and y_i is the observed response for the *i*th number of experimental data for each experiment.

Table 3.2. Control factors and levels of the parameters (*Mid-level combination as the initial parameter)

Control Factors	Designation	Unit	Parameter Level		
			-1	0	1
Nickel Sulphate	A	g/L	4	6*	8
Sodium-hypophosphate	B	g/L	4	5*	6
Copper Sulphate	C	g/L	0.08	0.16*	0.24
TiO_2 Nanoparticle	D	g/L	0.2	0.6*	1

Table 3.3. Un-coded experimental plan as per Taguchi L9 design

Run No	A	B	C	D
1	4	4	0.08	0.2
2	4	5	0.16	0.6
3	4	6	0.24	1
4	6	4	0.16	1
5	6	5	0.24	0.2
6	6	6	0.08	0.6
7	8	4	0.24	0.6
8	8	5	0.08	1
9	8	6	0.16	0.2

CHAPTER 4:

RESULTS AND DISCUSSION

4.1. Introduction

This chapter presents the results and discussions for the optimization of coating process parameters of electroless Ni-Cu-P-TiO_2 coating. The analyses are done for optimizing the coating process parameters for optimum micro hardness. The analysis are done in order to find out the suitable coating process parameters combination for each response. Then with the Taguchi method of optimization of single performance characteristics for micro hardness is done and suitable process parameters combinations are reported accordingly.

After obtaining the suitable process parameters combination, confirmation tests for all the optimum combinations are done in comparison with the initial process parameters combination in order to validate the optimum parametric combinations. Finally the results of Energy dispersive x-ray analysis (EDX), and Scanning electron microscopy (SEM) analysis are discussed. The EDX analysis is carried out to find the actual composition of elements which present at the coating.

4.2. EFFECT OF COATING ON MICRO-HARDNESS

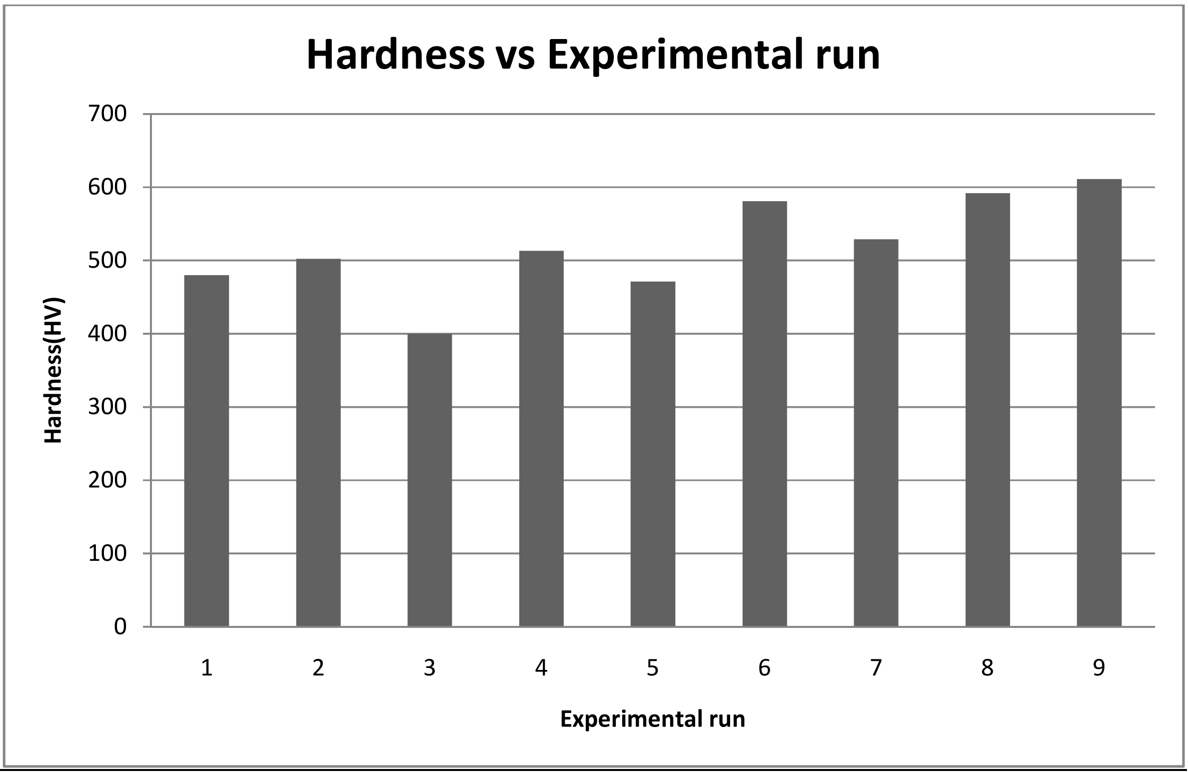
4.2.1. Micro-Hardness of Ni-Cu-P-TiO_2 using Taguchi Method

The present study investigates the hardness of Ni-Cu-P-TiO_2 coating which was deposited over Mild steel electrolessly. The hardness for each experiment has been shown in Table 4.1.

Table 4.1. Taguchi L9 Orthogonal Array design with input parameters and response

Run No.	A	B	C	D	Hardness ($HV_{0.1}$)
1	4	4	0.08	0.2	480
2	4	5	0.16	0.6	502
3	4	6	0.24	1	400
4	6	4	0.16	1	513
5	6	5	0.24	0.2	471
6	6	6	0.08	0.6	581

7	8	4	0.24	0.6	529
8	8	5	0.08	1	592
9	8	6	0.16	0.2	611



Hardness Vs Experimental run

Taguchi Analysis

- **Analysis of Signal to Noise Ratio:**

Signal to Noise ratio (S/N) is the ratio of the valuable information to irrelevant data. The more positive the value of S/N the better the quality. Taguchi method uses S/N ratio to investigate the performance of the coating. The S/N ratio can be applied in three different ways for checking the performance. There are:

- Lower the better
- Nominal the best
- Larger the better

The higher the hardness of the coating the better is the performance of the coating. So we apply 'larger the better' S/N ratio to find the optimal coating parameters.

S/N ratio for larger the better is given by:

$$\mathbf{S/N = -10\ Log_{10}\ (1/n * (\Sigma 1/y^2))}$$

Where y is the measured hardness and n is the number of the experiment.

4.2.2. Signal to Noise Ratio

The Signal to Noise ratio is used to optimize the bath parameters and obtain a particular combination of the levels of three different factors. Signal to Noise (SN) ratio is calculated by Larger is better.

Table 4.2. The S/N ratio corresponding to each experiment.

Experiment Number	Hardness($VHN_{0.1}$)	S/N ratio
1	480	53.6248
2	502	54.0141
3	400	52.0412
4	513	54.2023
5	471	53.4604
6	581	55.2835
7	529	54.5691
8	592	55.4464
9	611	55.7208

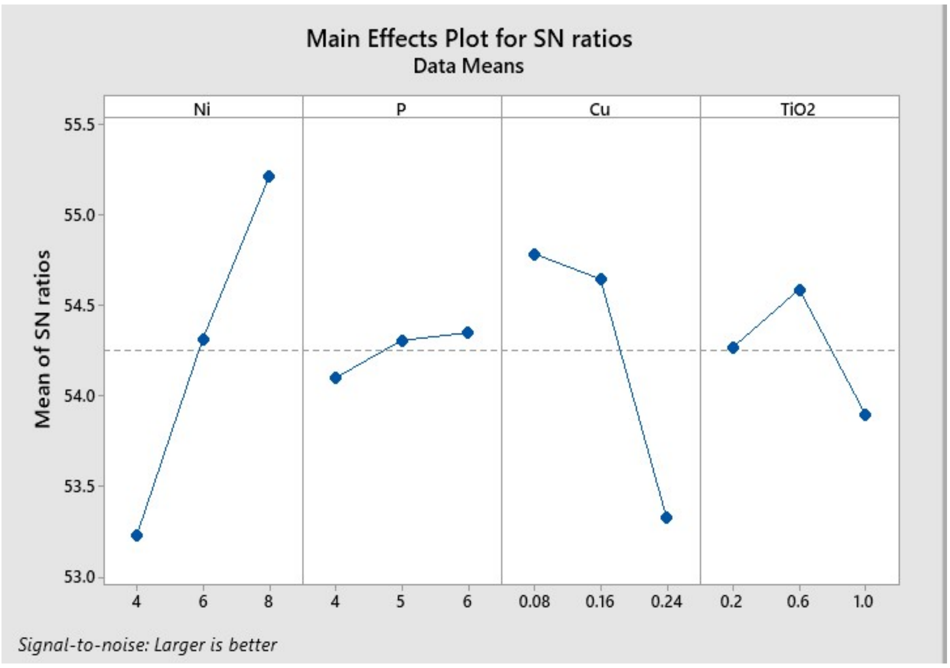


Figure 4.1. Shows the main effect plot for signal-to-noise ratios.

The main effects of hardness plot (Fig. 4.1) can be interpreted to find which factors play a more significant term in determining the hardness of the coating.

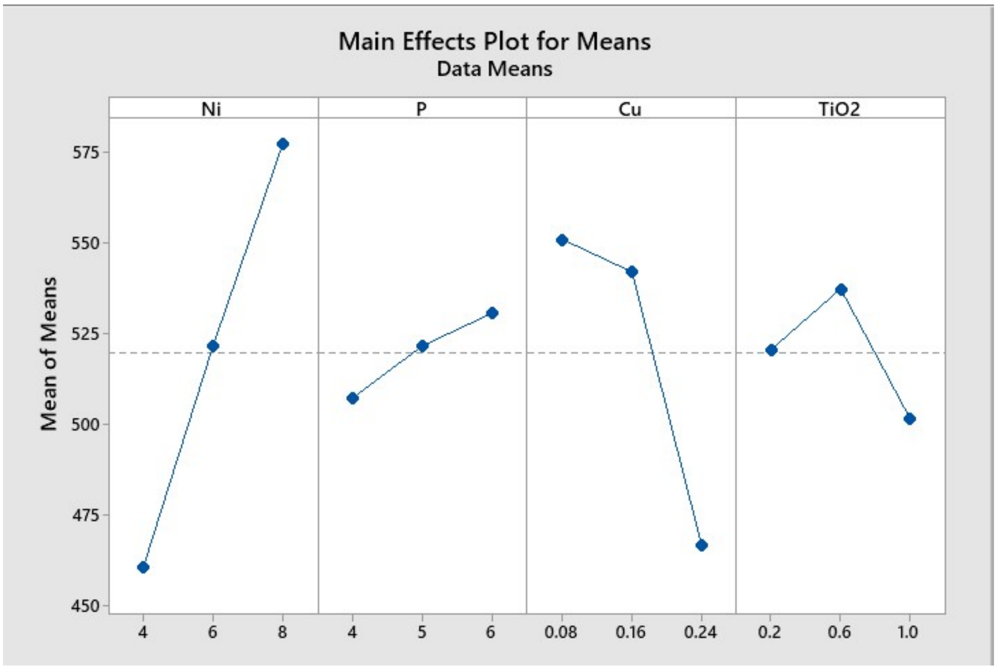


Fig 4.2. Main effects plot for hardness

Figure 4.2 shows the main effect plot for means,which depicts the influence of control factors on the hardness of Ni-Cu-P-TiO_2 coatings. The increase in Nickel sulphate, increases the hardness. The effect of Sodium hypophosphite shows that maximum hardness was obtained at a higher level of Sodium hypophosphite content. The hardness decreases with the decrease of copper sulphate content. The hardness increases with the increase of nano TiO_2 particles but further increment beyond the mid-level it begins to decline.

Table 4.3. Mean signal-to-noise ratio for Hardness (larger is better).

Level	A	B	C	D
1	53.23	54.10	54.78	54.27
2	54.32	54.31	54.65	54.59
3	55.21	54.35	53.32	53.90
Rank	1	4	2	3

Table 4.3 depicts the rank of each parameter, which shows that the Nickel sulphate (A) has the most significant effect, the second most influential parameter is Copper sulphate (C) followed by the TiO_2(D) nanoparticles and the Sodium hypophosphite (B) content has the least significance. Therefore, the Taguchi (A3-B3-C1-D2) (optimum predicted parameter) combination achieved the maximum hardness, i.e., higher level of A (Nickel sulphate = 8g/L), higher-level of B (Sodium hypophosphite= 6g/L), the highest level of C (Copper sulphate = 0.08 g/L), and mid level of D (nanoTiO_2 = 0.6g/L),

4.3. ANOVA analysis

Table 4.4. Analysis of variance (ANOVA) for deposition rate

Parameters	DOF	Sum of Square	Mean square	F-ratio	% Contribution
A	2	5.9313	2.96565	-	55.63
B	2	0.1075	0.05373	-	1.008
C	2	3.9031	1.95153	-	36.61
D	2	0.7201	0.36007	-	6.75
Error	0	-	-	-	
Total	8	10.6620			100

Table 4.5. Pooled ANOVA for deposition rate (the pooled factor is shown in {})

Parameters	DOF	Sum of Square	Mean square	F-ratio	P-value	% Contribution
A	2	5.9313	2.96565	55.19	0.02	55.63
{B}	{2}	{0.1075}	-	-		-
C	2	3.9031	1.95153	36.32	0.03	36.61
D	2	0.7201	0.36007	6.70	0.13	6.75
Polled Error	2	0.1075	0.05373	-	-	1.008
Total	8	10.6620	-	-	-	100

Confidence level = 95%, *Significant (P-value < 0.05)

The ANOVA provides performance characteristics of the process parameters. ANOVA for the SN ratio based on hardness is shown in Table 4.2. It suggests that the hardness is highly influenced by the Nickel sulphate content with a 55.63% contribution followed by copper sulphate, and TiO_2 nanoparticles content, respectively. The least influential factor indicated by the ANOVA result in Table 4.5 is B (Sodium hypophosphite content) which contributed 1.008%. Each parameter has 2 degrees of freedom (DOF), the *F*-ratio could not be calculated, as the *F*-ratio is defined as the mean square of individual factors divided by the mean square of polled error term. To exclude the zero DOF from the error term, a pooled ANOVA is applied. The process of ignoring the least contributing factor is called pooling.

Pooled ANOVA shown in Table 4.5 indicates that factor A and factor C was highly significant (P-value < 0.05). The *P*-value is the probability of the parameters having a significant effect on the responses. According to the ANOVA, a factor will be considered statistically significant if its *P*-value is less than 0.05 at a 95% confidence level. The results of the confirmation test with the optimum parameter (A3-B3-C1-D2) combination predicted by the Taguchi method are shown in Table 4.3. **The optimal hardness obtained from this experiment is (A3-B3-C1-D2). The hardness for these optimal parameters was found to be 584$HV_{0.1}$.**

4.4. Scanning Electron Microscopy (SEM) Study

For SEM observation in the present research we have taken two sample conditions one is the optimized coating (A3-B3-C1-D2) and other one is the initial parameters (A2-B2-C2-D2) setting which was set as the mid-level parameter setting in the Taguchi design. Surface morphology reveals a compact coating was achieved on both the samples. The coating morphology also reveals nodular type surface morphology on the bottom which is for the initial layer of Ni-Cu-P as seen in Fig 4.3. Above the initial Ni-Cu-P layer some flakes type of portions are also visible which is due to the induction of TiO_2 nanopaticles. Hence, SEM morphology reveals a typical composite coating where TiO_2 embedded nanopaticles is clearly visible on the surface of ternary Ni-Cu-P coating which reveals a composite coating microstrure.

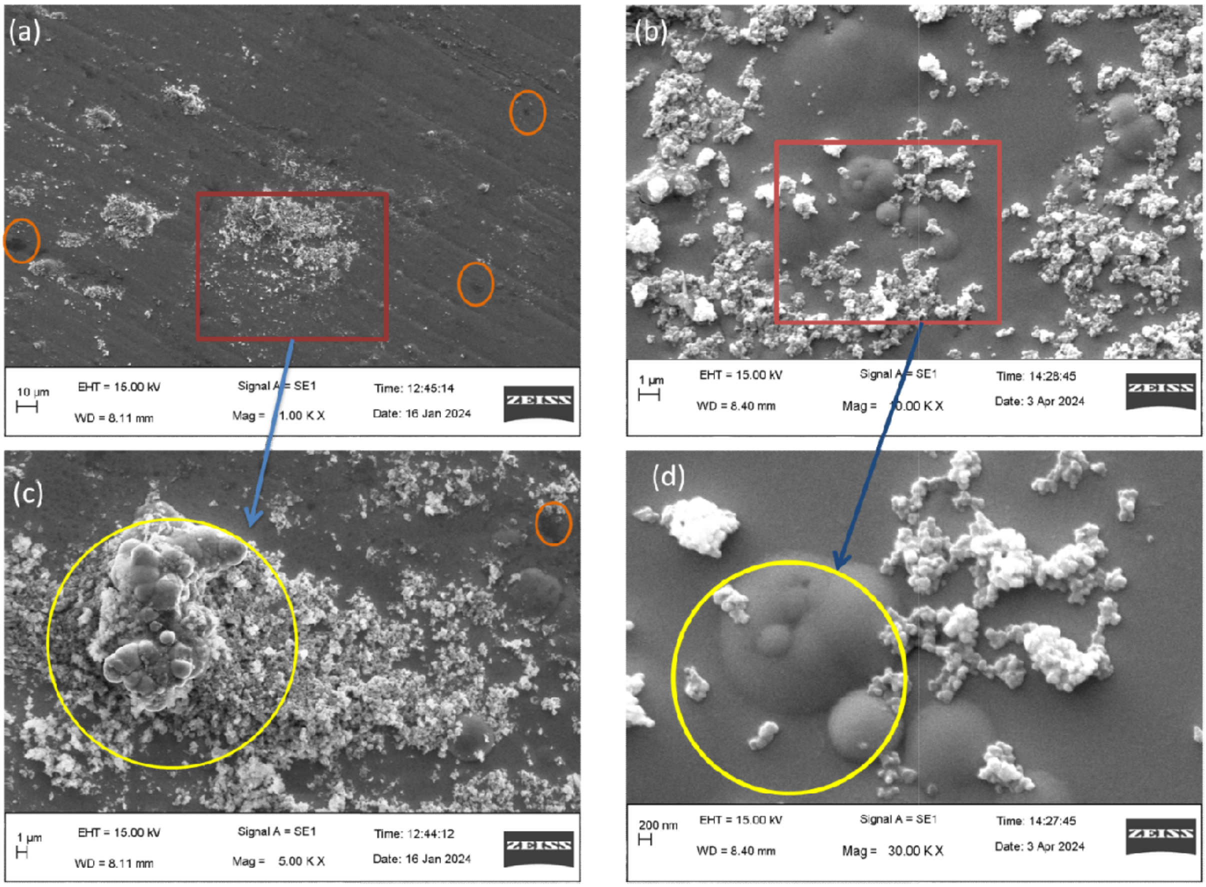
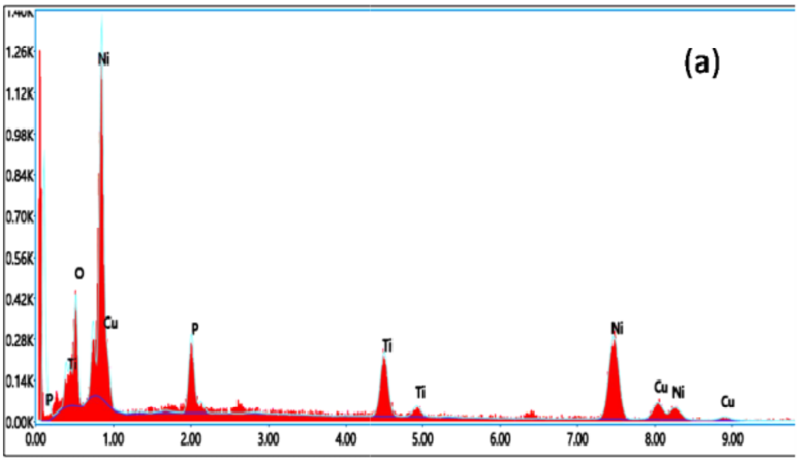
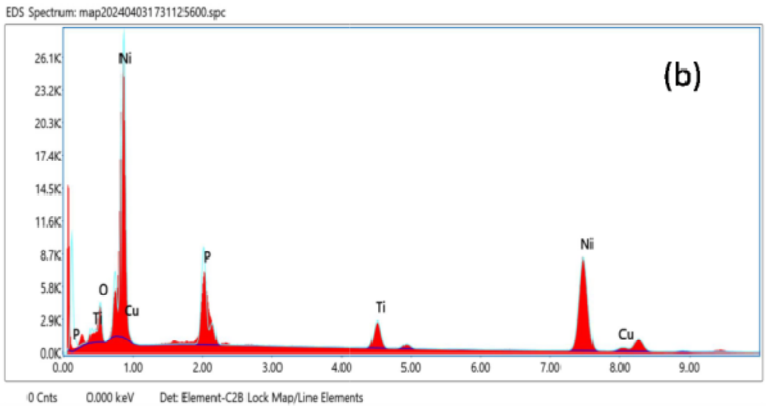


Fig 4.3. SEM morphology of Ni-Cu-P-nanoTiO_2 composite coatings **a**, **c** initial run (A2-B2-C2-D2), and **b**, **d** confirmation run (A3-B3-C1-D2)

Apart from this observation, the initial parameter setting (A2-B2-C2-D2) reveals some porous site which are marked with orange circle, the possible cause is due to the reduction process in which hydrogen is entrapped due to lack of surface energy but at that time another layer is deposited on the hydrogen entrapped portion and due to stress relieving that entrapped portion was break and form a hole. On the contrary, the optimized parameter setting coating SEM morphology reveals a smooth coating microstructure with no holes and uniformly distributed TiO_2 nanoparticles on the entire surface of the Ni-Cu-P ternary alloy coating. In both the coating TiO_2 particles are visible as clusters of particles.



Element	Weight%
O	8.6
P	6.5
Ti	12.1
Ni	56.9
Cu	16



Element	Weight%
O	3.1
P	9.6
Ti	6.1
Ni	77
Cu	4.2

Fig 4.4. EDS spectrum of Ni-Cu-P-nanoTiO2 composite coatings **a** initial run (A3-B3-C3-D3), and **b** confirmation run (A3-B3-C1-D2)

Refer to Fig. 4.4. The EDS value the deposition of nano TiO_2 content is decreased for optimized (A3-B3-C1-D2) sample. From here we can say that the visual inspection of SEM can be justified by EDS that in optimized sample TiO_2 particle are deposited in few areas as compared to the initial condition. EDX (energy dispersive x-ray analyzer) is used to find out the quantity nickel, phosphorus, copper, oxygen and titanium oxide in the composite coating.

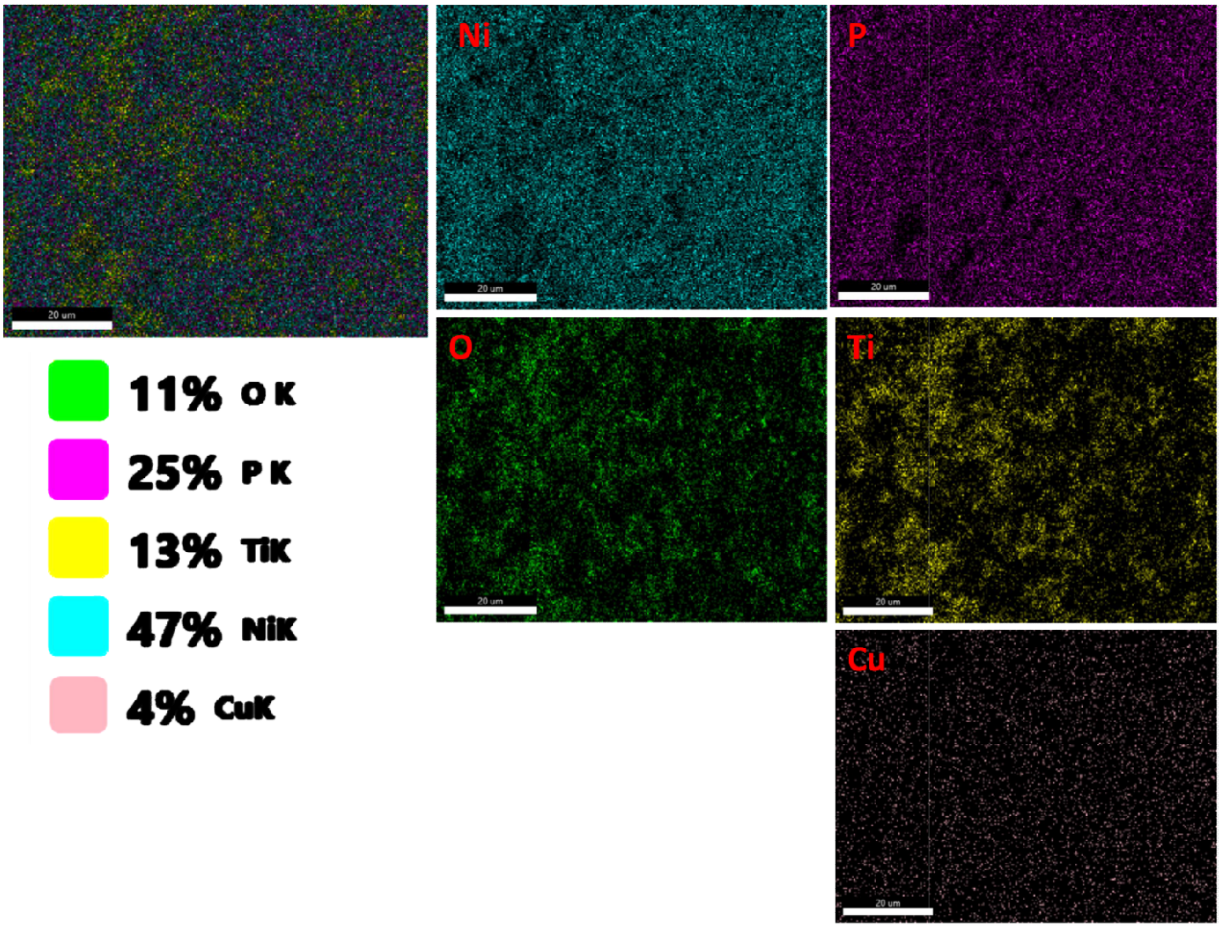
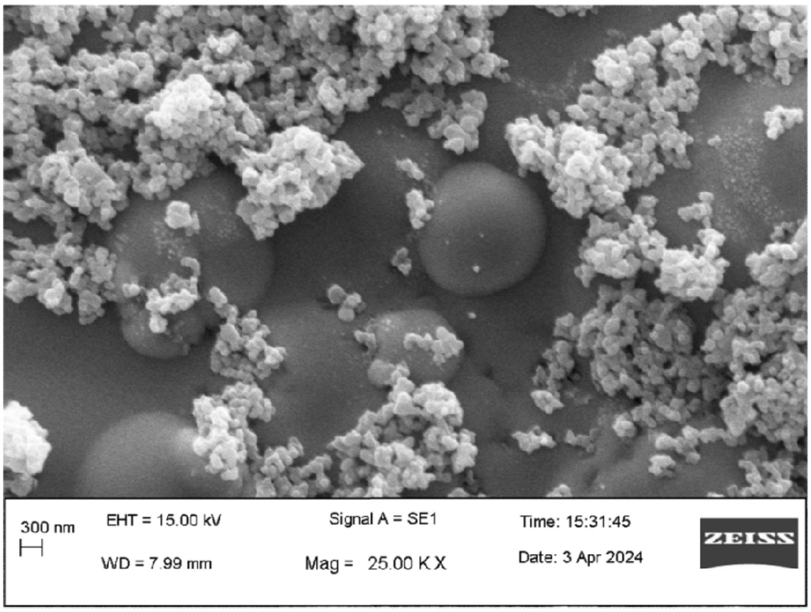


Fig 4.5. Elemental mapping of electroless Ni-Cu-P-nanoTiO_2 composite coating.

4.4.1. Morphology of Heat-Treated Ni-Cu-P-TiO_2 coatings

Based on the results obtained from Taguchi optmization the optimum parameter setting obtained was A3-B3-C1-D2. In present study we have taken the optimized coated sample and done heat treatment of this coating at three different temperatures viz. 200 ^oC, 400 ^oC and 600 ^oC to assess a better understanding of the morphological behavior of the elctroless composite coatings. Fig. 4.6, 4.7 and 4.8. reveals the morphology of Ni-Cu-P-TiO_2 coating heated treated at 200 ^oC, 400

°C and 600 °C. SEM morphology clearly shows that no evident changes occurred in the coatings heat treated at 200 °C shown in Fig. 4.6. The coatings seems to be similar in morpholgy as obtained for the as-plated Ni-Cu-P-TiO_2 electroless coated samples as shown in Fig. 4.3.



Element	Weight%
O	2.9
P	12.8
Ti	6.1
Ni	72.5
Cu	5.7

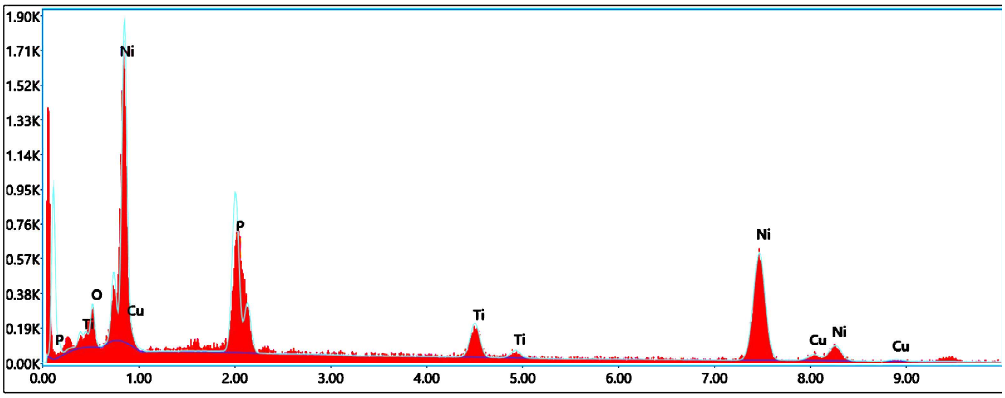
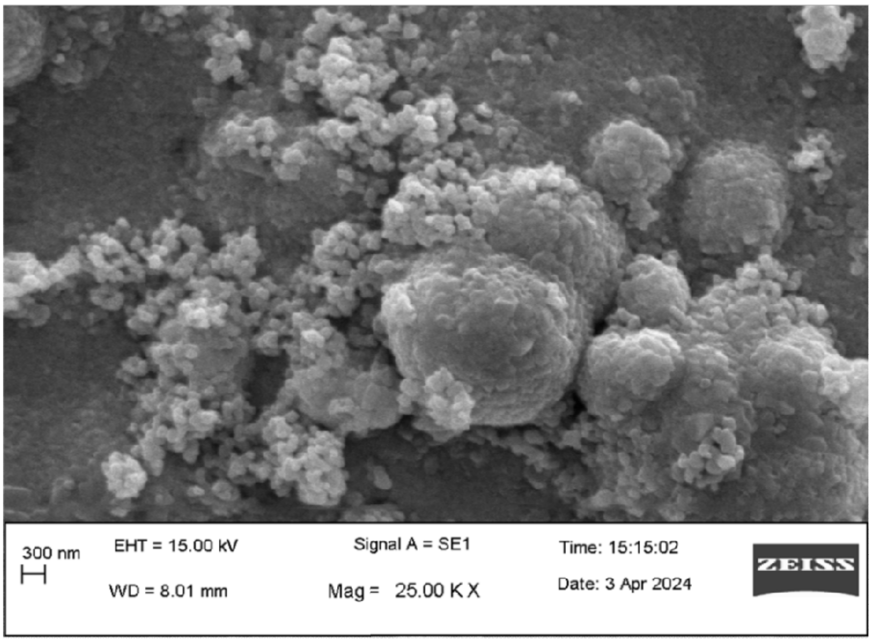


Fig 4.6. SEM morphology and EDS of heat treated Ni-Cu-P-nanoTiO_2 composite coatings at 200 °C.



Element	Weight%
O	9.8
P	9.5
Ti	11
Ni	63.6
Cu	6

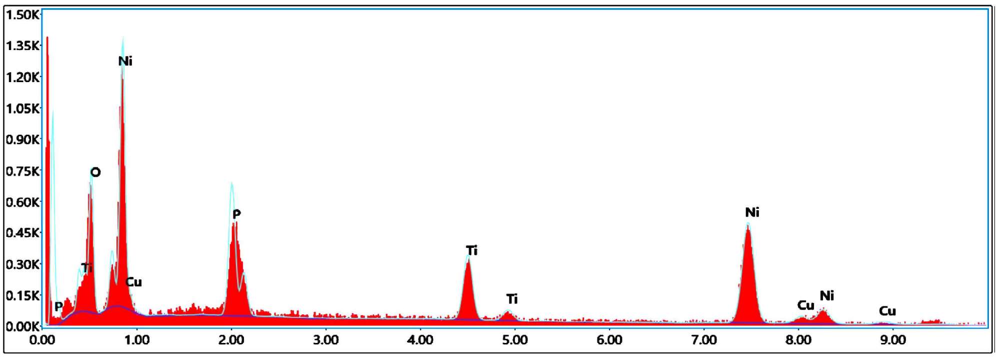
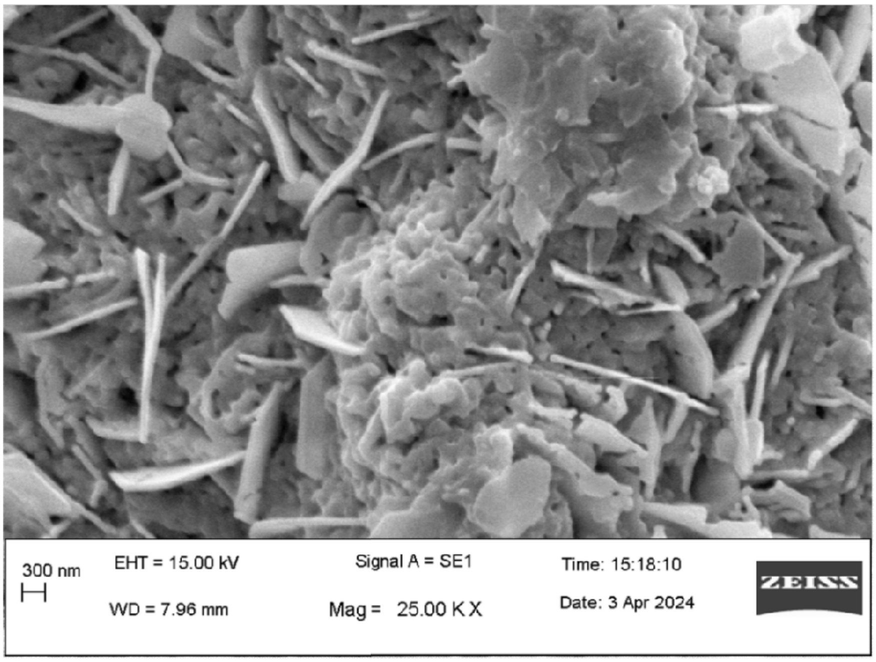


Fig 4.7. SEM morphology and EDS of heat treated Ni-Cu-P-nanoTiO_2 composite coatings at 400 ^{o}C.

However, referening to Fig. 4.7 the morphology of Ni-Cu-P-TiO_2 heat treated at 400 ^{o}C shows a larger nodular morphology accompanied by nanoporous appearnce and the grain recrystallization also occurred at 400 ^{o}C. Moreover, the mophology of Ni-Cu-P-TiO_2 heat treated at 600 ^{o}C given in Fig. 4.8 shows that the nodules are intensified and appeared as sheet like or flaky appearance when heat treated at a higher temperature of 600 ^{o}C. Also, the heat treated sample at 600 ^{o}C shows defects such as holes.



Element	Weight%
O	11.4
P	7.5
Ti	1.7
Ni	62.9
Cu	16.5

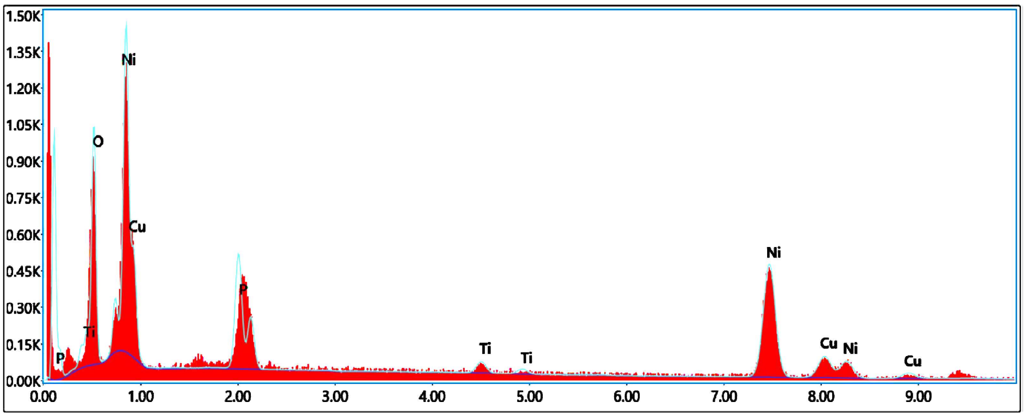


Fig 4.8. SEM morphology and EDS of heat treated Ni-Cu-P-nanoTiO_2 composite coatings at 600 ^oC.

4.5. XRD Analysis

The XRD profile test was performed on the optimized (A3-B3-C2-D2) as-pated coating and 400 ^{o}C heat treated sample as shown in Fig. 4.9 (A), (B). Match software was used to match the peak position to find the crystal plane and JCPDS number was assigned as obtained from the Match software.

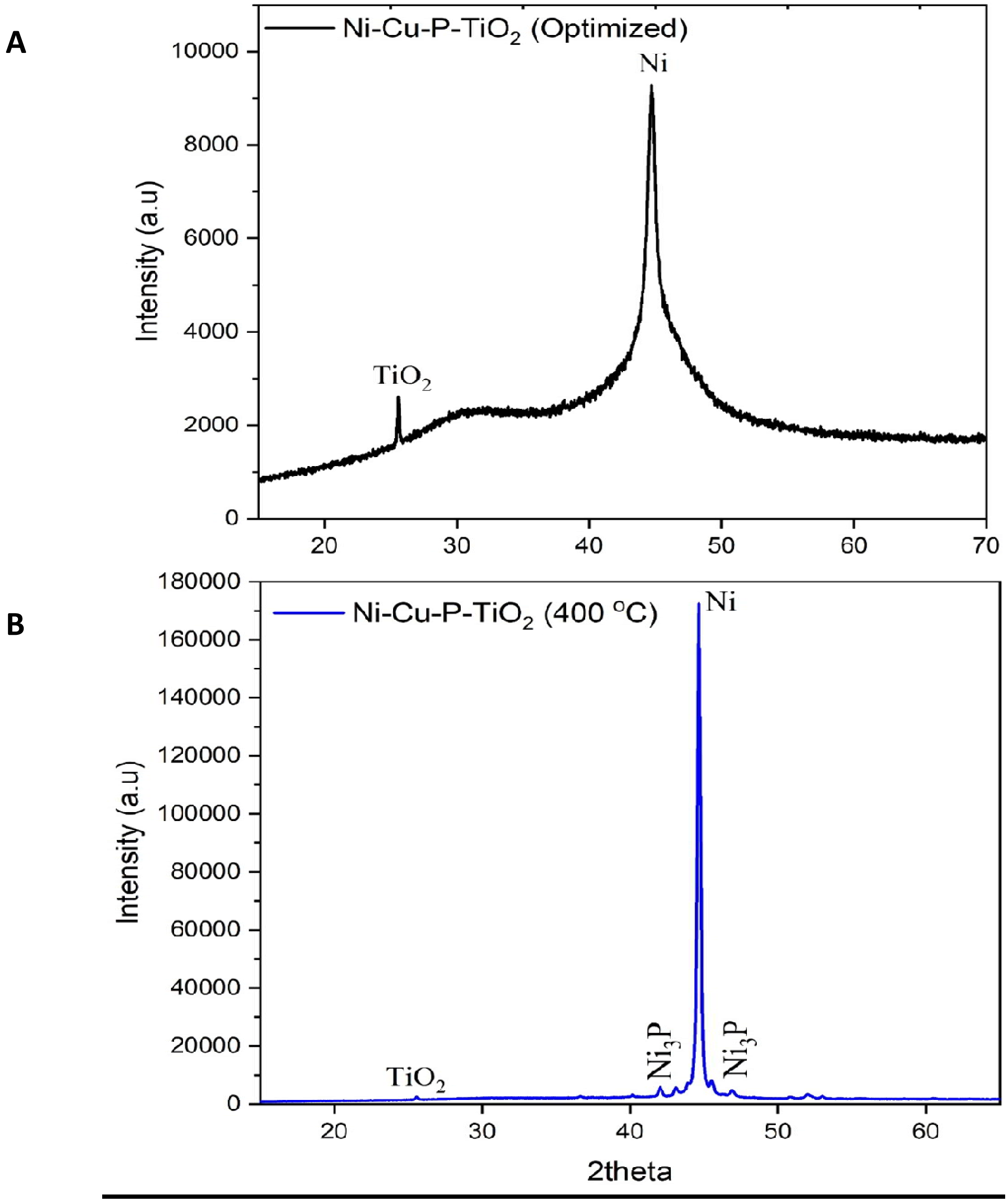


Fig 4.9. XRD of As-plated (A3-B3-C1-D2) and heat treated (at 400 ^{o}C) Ni-Cu-P-nanoTiO_2 composite coatings.

The XRD profiles reveals a semi-crystalline nature that means a mixture of the crystalline and amorphous phases present in the as-plated coated sample shown in Fig. 4.9. A. Meanwhile the XRD profile of heat treated sample as shown in Fig. 4.9. B. reveals sharp and high intense crystalline peak. A wide range of angles (2θ) at around 45° corresponds to Ni (111) was obtained in both the coated samples (Heat treated and Optimized). Fig. 4.9. B. shows that due to recrystallization of the grain at 400 ^{o}C an Ni_3P phase was formed on the coated which obtained in the XRD profile of heat treated sample.

Furthermore, apart from Ni (111) and Ni_3P phase another single weak peak at around 2θ = 25.5° confirms the presence of TiO_2 corresponding to JCPDS number 96–500-0224. Due to the dispersive distribution of nanoparticles in the coatings, a very small TiO_2 peak was observed. TiO_2 exhibits 011 plane and a tetragonal crystal system with unit cell a = b = 3.7892 Å, c =9.5370 Å. This validates that TiO_2 nanoparticles are incorporated into the Ni-Cu-P matrix to develop Ni-Cu-P-TiO_2 composite coatings.

CHAPTER 5:

CONCLUSION AND FUTURE SCOPE OF WORK

5.1. Conclusion

In the present study Taguchi **L9** Orthogonal Array is employed to study the effect of hardness of the coating . The electroless Ni-Cu-P-TiO_2 composite coating has been successfully deposited on mild steel substrate by varying four coating parameters, namely nickel sulphate, copper sulphate, sodium hypophosphite, concentration of TiO_2 particles. The optimum parameter combination is found as A3B3C1D2. At optimum level the hardness is increased as compared to the substrate. The SEM micrograph as-deposited composite has a smooth surface with uniform distribution of TiO_2 particles whereas heat treated coating has larger nodules. From XRD plot it is confirmed that the as-deposited coating has a semi-crystalline nature that means a mixture of the crystalline and amorphous phases present in the as-plated coated sample and heat treated coating has a crystalline structure with peaks of Ni and Ni_3P hard particles, which are responsible for the increase in hardness of coating.

5.2. Future scope of work

In the present study we have developed Ni-Cu-P-TiO_2 composite coating by electroless deposition and also focused on the influence of coating parameters to optimize the hardness. However there is ample of scope for future work which is given as follows:

a) To study the roughness behavior of Ni-Cu-P-TiO_2 coatings.
b) To study the wear behavior of Ni-Cu-P-TiO_2 coatings.
c) To study the deposition rate and coating thickness of Ni-Cu-P-TiO_2 coatings.
d) To study the corrosion behaviour of Ni-Cu-P-TiO_2 coatings.
e) To study the wettability of Ni-Cu-P-TiO_2 coatings.
f) Characterization using Nano-indentation, TEM of the Ni-Cu-P-TiO_2 coatings.
g) Couple the Taguchi method with Grey relation analysis for multi-objective optimization of the process parameters.

REFERENCES

1. Sudagar, J., Lian, J., & Sha, W.. (2013). *Electroless nickel, alloy, composite and nano coatings – A critical review*. *571*(571). https://doi.org/10.1016/J.JALLCOM.2013.03.107
2. Agarwala, R. C., & Agarwala, V.. (2003). *Electroless alloy/composite coatings: A review*. *28*(3). https://doi.org/10.1007/BF02706445
3. Sahoo, P., & Das, S.. (2011). *Tribology of electroless nickel coatings – A review*. *32*(4). https://doi.org/10.1016/J.MATDES.2010.11.013
4. Chen, J., Zhao, G., Zhang, Y., Duan, S., Matsuda, K., & Zou, Y.. (2019). *Metastable phase evolution and nanoindentation behavior of amorphous Ni–Cu–P coating during heat treatment process*. *805*. https://doi.org/10.1016/J.JALLCOM.2019.07.068
5. Mousavi Anijdan, S. H., Sabzi, M., Roghani Zadeh, M., & Farzam, M.. (2018). *The Effect of Electroless Bath Parameters and Heat Treatment on the Properties of Ni-P and Ni-P-Cu Composite Coatings*. *21*(2). https://doi.org/10.1590/1980-5373-MR-2017-0973
6. Gadhari, P., & Sahoo, P.. (2016). *EFFECT OF TiO2 PARTICLES ON MICRO-HARDNESS, CORROSION, WEAR AND FRICTION OF Ni–P–TiO2 COMPOSITE COATINGS AT DIFFERENT ANNEALING TEMPERATURES*. *23*(01). https://doi.org/10.1142/S0218625X15500821
7. Gadhari, P., & Sahoo, P.. (2015). *Study of Hardness and Corrosion Resistance of Electroless Ni-P-TiO2 Composite Coatings*. *3*(2). https://doi.org/10.4018/IJSEIMS.2015070102
8. Carraro, C., Maboudian, R., & Magagnin, L.. (2007). *Metallization and nanostructuring of semiconductor surfaces by galvanic displacement processes*. *62*(12). https://doi.org/10.1016/J.SURFREP.2007.08.002
9. Gadhari, P., & Sahoo, P.. (2015). *Optimization of Coating Process Parameters to Improve Microhardness of Ni-P-TiO2 Composite Coatings☆*. *2*. https://doi.org/10.1016/J.MATPR.2015.07.303
10. Gadhari, P., & Sahoo, P.. (2014). *Influence of Process Parameters on Multiple Roughness Characteristics of Ni–P–TiO2 Composite Coatings*. *97*. https://doi.org/10.1016/J.PROENG.2014.12.268
11. Hu, B., Hu, B., Sun, R., Yu, G., Liu, L., Xie, Z.-H., He, X., & Zhang, X.. (2013). *Effect of bath pH and stabilizer on electroless nickel plating of Magnesium alloys*. *228*(228). https://doi.org/10.1016/J.SURFCOAT.2013.04.011
12. Elansezhian, R., Ramamoorthy, B., & Kesavan Nair, P.. (2008). *Effect of surfactants on the mechanical properties of electroless (Ni–P) coating*. *203*(5). https://doi.org/10.1016/J.SURFCOAT.2008.08.021
13. Karthikeyan, S., & Ramamoorthy, B.. (2014). *Effect of reducing agent and nano Al2O3 particles on the properties of electroless Ni–P coating*. *307*. https://doi.org/10.1016/J.APSUSC.2014.04.092

14. Tamilarasan, T. R., Rajendran, R., Siva shankar, M., Sanjith, U., Rajagopal, G., & Sudagar, J.. (2016). *Wear and scratch behaviour of electroless Ni-P-nano-TiO2: Effect of surfactants*. *346*. https://doi.org/10.1016/J.WEAR.2015.11.015
15. C. O. Osifuye1, A.P.I. Popoola1,*,C.A. Loto1,2 and D.T. Oloruntoba1 (2014). https://doi.org/10.1016/S1452-3981(23)10871-6
16. Ashassi-Sorkhabi, H., & Rafizadeh, S. H.. (2004). *Effect of coating time and heat treatment on structures and corrosion characteristics of electroless Ni-P alloy deposits*. *176*(3). https://doi.org/10.1016/S0257-8972(03)00746-1
17. Huang, Y. S., & Cui, F. Z.. (2007). *Effect of complexing agent on the morphology and microstructure of electroless deposited Ni–P alloy*. *201*(9). https://doi.org/10.1016/J.SURFCOAT.2006.07.189
18. Hareesh P1, S. Karthikeyan1*, K. Raja1, P. A. Jeeva1, *Performance Characteristics of Electroless Ni-P-Cu and Ni-P-Cu-Pvp Composite Coatings*
19. Balaraju, J. N., & Rajam, K. S.. (2005). *Electroless deposition of Ni–Cu–P, Ni–W–P and Ni–W–Cu–P alloys. 195(2). https://doi.org/10.1016/J.SURFCOAT.2004.07.068*
20. *Zhang, W., Cao, D., Qiao, Y., Wang, Y., Li, X., & Gao, W.. (2019). Preparation and properties of duplex NI-P-TIO2/NI nanocomposite coatings. 33. https://doi.org/10.1142/S0217979219400198*
21. Hui-Sheng Yu*, Shou-Fu Luo, Yong-Rui Wang, *A comparative study on the crystallization behavior of electroless Ni–P and Ni–Cu–P deposits*
22. *Georgieva, J., & Armyanov, S.. (2007). Electroless deposition and some properties of Ni–Cu–P and Ni–Sn–P coatings. 11(7). https://doi.org/10.1007/S10008-007-0276-6*
23. *Liu, Y., & Zhao, Q.. (2004). Study of electroless Ni–Cu–P coatings and their anti-corrosion properties. 228(1). https://doi.org/10.1016/J.APSUSC.2003.12.031*
24. *Ashassi-Sorkhabi, H., Dolati, H., Parvini-Ahmadi, N., & Manzoori, J.. (2002). Electroless deposition of Ni–Cu–P alloy and study of the influences of some parameters on the properties of deposits. 185(3). https://doi.org/10.1016/S0169-4332(01)00464-0*
25. *Chen, J., Zhao, G., Matsuda, K., & Zou, Y.. (2019). Microstructure evolution and corrosion resistance of Ni–Cu–P amorphous coating during crystallization process. 484. https://doi.org/10.1016/J.APSUSC.2019.04.142*
26. *Iost, A., & Bigot, R.. (1996). Hardness of coatings. 80. https://doi.org/10.1016/0257-8972(95)02697-5*
27. *Fernandes, J. V., Trindade, A. C., Menezes, L., & Cavaleiro, A.. (2000). A model for coated surface hardness. 131. https://doi.org/10.1016/S0257-8972(00)00839-2*
28. *Korsunsky, A. M., McGurk, M. R., Bull, S., & Page, T. F.. (1998). On the hardness of coated systems. 99. https://doi.org/10.1016/S0257-8972(97)00522-7*

29. *Ural, N.. (2021). The significance of scanning electron microscopy (SEM) analysis on the microstructure of improved clay: An overview. 13(1). https://doi.org/10.1515/GEO-2020-0145*
30. *Pandey, A., Dalal, S., Dutta, S., & Dixit, A.. (2021). Structural characterization of polycrystalline thin films by X-ray diffraction techniques. 32(2). https://doi.org/10.1007/S10854-020-04998-W*
31. *An Overview on Taguchi Method*
32. *Yang, W. H., & Tarng, Y. S.. (1998). Design optimization of cutting parameters for turning operations based on the Taguchi method. 84(1). https://doi.org/10.1016/S0924-0136(98)00079-X*
33. *Sahoo, P.. (2009). Wear behaviour of electroless Ni–P coatings and optimization of process parameters using Taguchi method. 30(4). https://doi.org/10.1016/J.MATDES.2008.06.031*
34. *Li, L., An, M., & Wu, G.. (2006). A new electroless nickel deposition technique to metallise SiCp/Al composites. 200(16). https://doi.org/10.1016/J.SURFCOAT.2005.05.031*