

**Synthesis and Characterization of Nano-
Al₂O₃ Enhanced Ni-P-Mo Composite
Coatings on HSLA steel Substrates by
Electro-deposition Method**



Thesis by

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Dedication

I would like to dedicate this thesis to my creator and provider (i.e.) Allah Almighty.

After Allah to my entire family for their utmost patience, encouragement and support throughout my MS research journey.

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I would like to acknowledge the support of all the great people who passionately and selflessly helped me whenever and wherever it was needed. My supervisor i.e. Dr. Malik Adeel Umer has been the strongest guide throughout my entire research process along with encouragement he bestowed me with. My entire guidance committee members including Dr. Muhammad Shahid, Dr. Muhammad Aftab, and Dr. Farhan Javed supported me and provided me with valuable knowledge to lead my research successfully. Special thanks to Dr. Amna Safdar for being so considerate and facilitating in terms of encouragement and lab usage. My friends and family for always respecting and trusting my choices of work with whole-hearted support. I would also like to acknowledge Dr. Amir Azam Khan Principal, SCME, entire SCME faculty, lab assistants, lab colleagues, engineers and technical as well as non-teaching staff.

Genuinely,

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Abstract

HSLA (AISI 4340 alloy) steel has applications in industries like auto-motives, military, nuclear, aeronautical field, oil and gas sector etc. where it is mostly exposed to extreme conditions i.e., humidity, stress and high temperature etc. making it vulnerable to corrosion and wear issues raising the demand for more robust and effective materials having good surface properties and stability for protection purposes. This research project encompasses the scope to develop and analyze the electro-deposited nickel alloy and composite coatings with good mechanical stability and properties like low degradation in highly corrosive or high temperature applications, as the potential solution to the above mentioned problem when compared to bare HSLA steel. In this work, impact of different Al_2O_3 nano-particles (40~50nm in size) concentrations (i.e., 0.1, 0.3, 0.7, 1 g/L) on wear and corrosion resistive properties of Ni-P-Mo coatings on bare HSLA (AISI 4340) steel samples, was studied and analyzed via characterization techniques such as SEM, AFM, Micro-hardness, Nano-indentation, pin-on disk micro-testing for wear and potentiodynamic polarization method using 3.5 wt. % NaCl solution for corrosion testing. Electro-deposition technique was used to deposit Ni-P-Mo alloy and Ni-P-Mo/ Al_2O_3 composite coatings on steel substrates. SEM and AFM results reveal homogeneous, compact, denser and rougher coatings as nano-particles were incorporated in Ni-P-Mo alloy comparatively. Hardness was enhanced and improvement in mechanical wear resistant properties were witnessed as well from 5.28E^{-8} mm³/mm (Ni-P-Mo) to 0.373E^{-8} mm³/mm (Ni-P-Mo /0.3g/l Al_2O_3). Corrosion rates in mils-per-year of Ni-P-Mo coatings were also reduced significantly from 4.8mpy (Ni-P-Mo) to 0.3mpy (Ni-P-Mo /0.3g/l Al_2O_3) by the addition of Al_2O_3 particles. Positive results obtained suggest the potential use of these composite coatings in various industrial sectors.

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Abbreviations

Terms	Full form
C.R.	Corrosion rate
mpy	Mils per year
COF	Co-efficient of friction
EDS	Energy dispersive spectroscopy
HV	Hardness Vickers
AFM	Atomic force microscopy
CVD	Chemical vapor deposition
PVD	Physical vapor deposition
ALD	Atomic layer deposition
DC	Direct current
RF	Radio frequency
PECVD	Plasma enhanced chemical vapor deposition
MBE	Molecular beam epitaxy
TMAB	Tri-methyl-amine-borane
AB	Ammonia-borane
DMAB	Di-methyl-amine-borane
PSPD	Position sensitive photo-diode

Chapter # 1

Introduction

1.1 Background

Surfaces of different materials or structures are the first to physically or mechanically interact with the outer atmosphere or surroundings making them more vulnerable towards damage and wearing. Functionality of different surfaces deteriorate due to changes in the surroundings like temperature, humidity, stress etc. resulting eventually in system or structure failures. For instance surfaces interacting with harsh chemicals must have chemical stability against them to function properly without damage [2]. Usually they suffer from electrochemical corrosion and mechanical wear due to morphological changes caused by chemicals or extreme environments like humidity or temperature fluctuations etc. Therefore in order to solve these problems various coating systems and techniques (like evaporation, thermal spraying, deposition etc.) were developed and utilized for surface protection purposes. Coating is a centuries-old technique and is a finishing process for an object's surface, also known as the substrate. Coatings have been utilized to improve the surface qualities of materials (i.e. mechanical, adhesive, wettability, corrosion resistive, wear resistive, lubrication, and scratch resistance etc.) over years along with the advances [4]. Organic and inorganic materials can be applied to any substrate. It may form a hard, impervious film, a soft porous film, or a combination of the two after coating application. A single layer of coating or a multi-layer coating structure could be used for desired application [5].

Extended service life, greater tolerance to load or stress, low maintenance requirements, conservation of natural resources, excellent corrosion and wear resistance and use of reasonably priced structures etc. are some of most important functions of different diverse coatings. Most important feature in protective coatings is the hardness factor to withstand all the stress, load in order to avoid wear but corrosion protection is equally important in order to ensure long life. This could be achieved by having crack-free smooth coatings with lower to none surface defects. Another way to improve the wear and corrosion

resistance of the surface is the addition of nano-particles into the coating matrix. Coating adhesion to the substrate is another factor which is needed to be kept in mind which could be challenging as well due to presence of interface stresses. In order to make coating industrially viable adhesion strength must be considered essentially.

Nowadays, there are many other depositing techniques available like spin coating, sputtering, evaporation, closed sublimation etc. but all these methods are more intricate

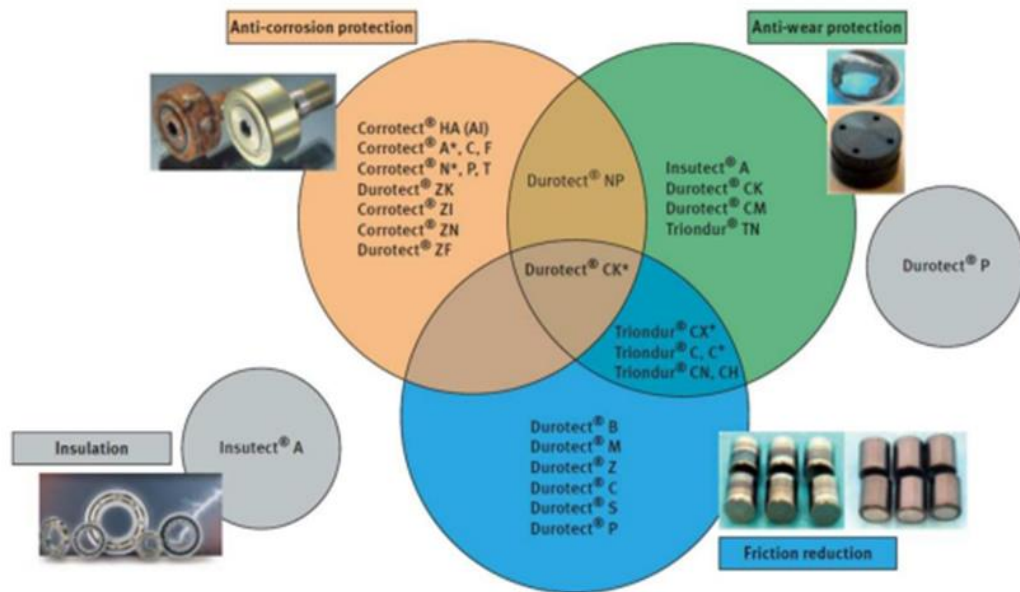


Figure 1: Applications of coatings being used in different industries on basis of material and properties [2]

and have limitation of poor deposition over complicated parts in contrast to electro deposition which is quite simple and effective. Electroplating is an immensely explored method in terms of coating, because of advantages like easy usage, cost-effectiveness and its utility to coat different compositional and structural coatings over samples of various sizes [6]. Properties can be tailored by changing the elemental composition and the process parameters or by heat treatment of coating systems [7]. Nevertheless surface properties of composite coatings prepared via electro-deposition need to be investigated thoroughly. Therefore, in this work analysis on surface and structural performance of Ni-P-Mo alloy and Ni-P-Mo/Al₂O₃ composite coatings is done with main focus on wear and corrosion resistance. This work will provide insight to the experimental set-up for Nano-composite coatings and impact of nano-particles on surface properties of coatings especially wear

and corrosion. Various characterization techniques were employed for the purpose of studying mechanical, morphological and corrosion resistive attributes of the resultant electro-deposited coatings.

These past years electroplated Ni metal and nickel alloy coatings like Ni-Mo-P, Ni-W-P, etc. have been developed by this method and utilized for purposes like corrosion resistant, stability at high temperatures and for protection [8, 9]. Particles like TiO₂, W, Al₂O₃, SiO₂, WS₂ etc. are mostly incorporated in Ni or Ni-alloy matrix for achieving improved coating properties like light weight, good thermal stability at high temperatures, and excellent wear and corrosive resistance [10, 11]. For achieving desired properties like hardness, wear and abrasive resistance and low coefficient of friction, different composite coatings like, Ni-P-Mo Ni-P-PTFE [12], Ni-SiC [13], Ni-Ti-P [14], were employed effectively [15, 16]. Further explanation is given in chapter 2 section 2.5 and 2.6.

1.2. Thin Surface Coatings; Deposition Types:

Thin coat is basically thin material covering of few microns or in nanometers regime and it could be aesthetic or functional depending upon the need or application and are of various types made up of diverse materials and methods complimenting the necessity [17, 18]. There are various physical and chemical methods that have been employed [1].

Table 1: Thin film deposition techniques [1]

Chemical deposition	Physical deposition
ALD	Sputtering methods (DC, RF etc.)
CVD	Ion plating
Sol- gel	MBE(molecular beam epitaxial)
Electro-chemical depositions	Laser beam plating
Spray-pyrolysis	Arc evaporation
PECVD	Electron beam
Chemical bath	Thermal vacuum evaporation

Some of commonly used methods are elaborated below:

1.3 Physical depositing methods

A. Evaporation processes:

It is one of the most commonly used practice for deposition of thin films. In this process material is evaporated from solid phase to vapors and then deposited onto specimen in a solid phase again. Therefore, a very measured and controlled environment is required to achieve good end coating and to run the method smoothly. This conversion of phases is achieved by the help of different energy sources like e-beam, heat and laser etc. Most common among these is the thermal evaporation technique. These different energy

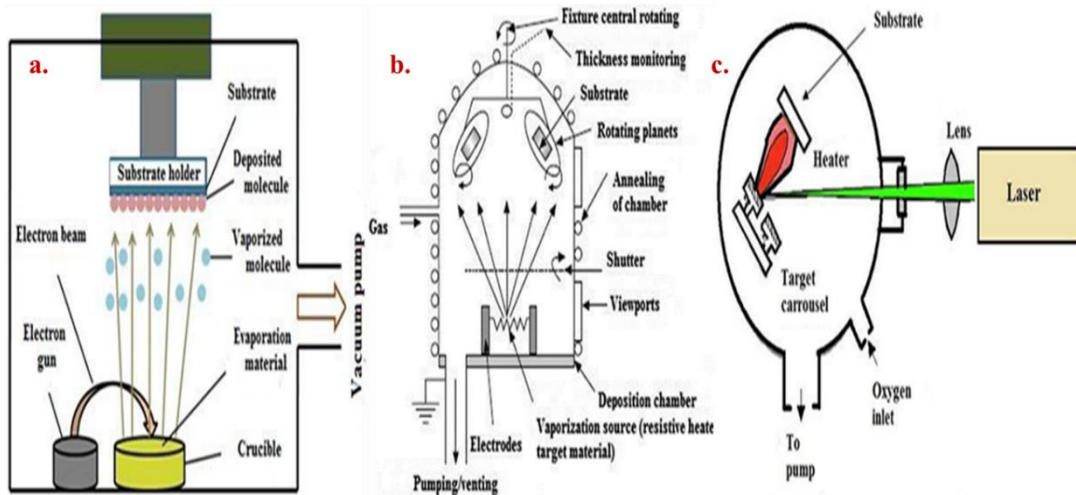


Figure 2: Different deposition methods by evaporation [1]

sources are preferred over other due to limitations in achieving the good quality film.

B. Sputtering:

Sputtering is used to deposit ultra-thin crystalline coatings in controlled/vacuumed atmosphere. In this method ions are bombarded on to the cathode with specific energy and momentum in order to displace the cathode molecules which in turn strike the substrate surface and deposition occurs there. Sputtering could be done either by using direct current which is cost effective and common or radio frequency power for deposition of dielectrics materials mainly.

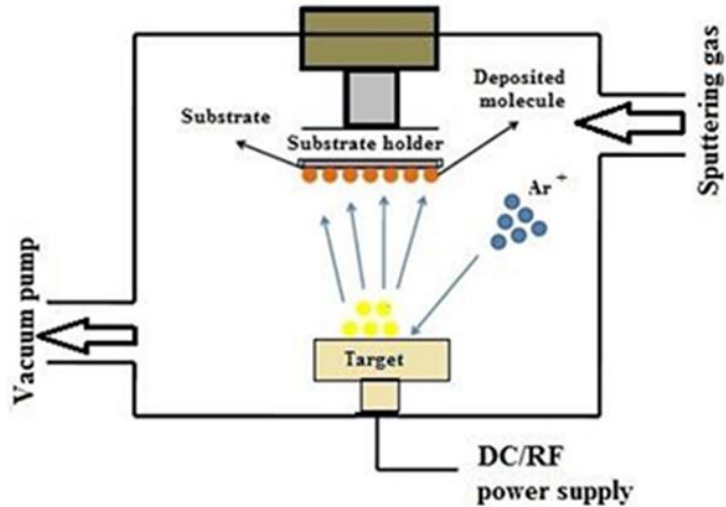


Figure 3: Sputtering mechanism [1]

1.4 Chemical deposition methods

In order to obtain the quality coating in more economical and effective ways, chemical deposition methods are opted rather than physical methods. These methods have lower equipment requirements as well. Chemical solution, solution viscosity and pH etc. are important factors that need to be kept in mind. CVD, ALD, sol-gel, dip, spin and electro-deposition are the mostly used chemical practices.

A. Sol gel:

It is considered as the wet-deposition method used at lower temperatures. In this process, colloidal suspension of various components are made followed by their gelation or conversion into solid substance on to the substrate surface.

B. Dip and Spin coating:

Dip coating comprises of different steps like dipping in coating solution then deposition of film and evaporation of solvent in order to get solid coat on to the surface of the substrate. Similarly spin coating also has the solution containing precursors which are then deposited on to the substrate while spinning for uniform distribution and deposition of coating.

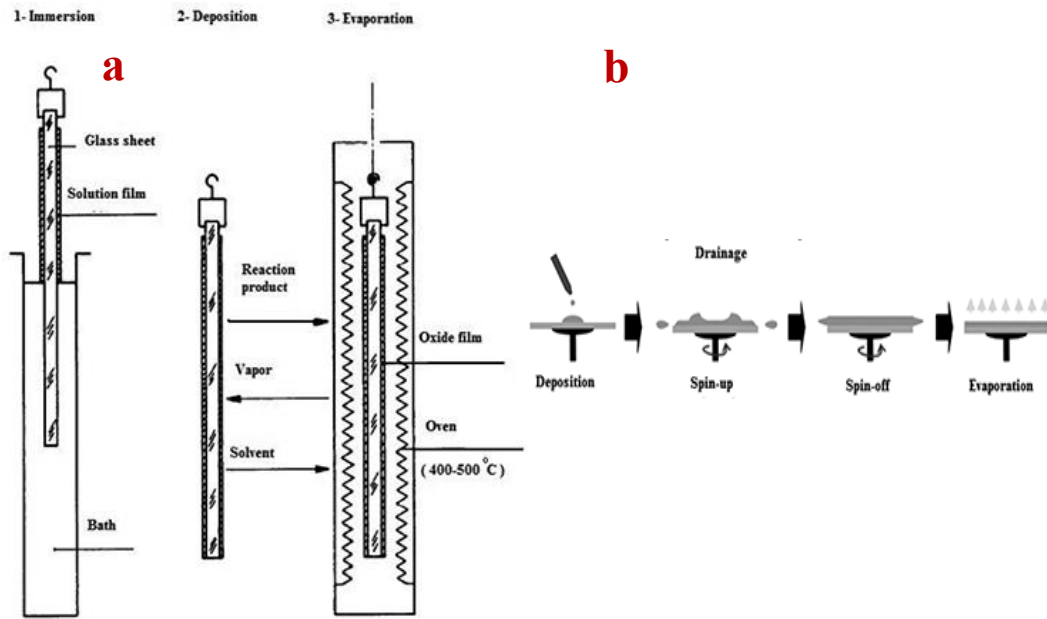


Figure 4: (a) Dip coating method (b) Spin coating [1]

C. Thermal battery enhanced deposition:

Thermo-battery deposition is quite relatable to the plating exchange that occurs when noble and nobler metals are submerged in to the solution. Due to its self-limiting nature thin coats are attained as the anode areas when covered stop the momentum of the process and plating stops as well. Many metals has been deposited by this method such as gold, copper. [19]

D. Chemical solution deposition:

Controlled precipitation technique for low temperature deposition mostly used for metal oxide films. Specimen is immersed into the solution containing chemical precursors, which is composed from complex ligands which act as source for anions.

E. Laser enhanced deposition

Laser enhanced deposition is another deposition method used to deposit the very refined and thin coatings. There are many deposition techniques that incorporate the usage of laser for coating thin films. Likes of which are laser ablation, pulsed laser deposition, direct laser deposition, and laser chemical vapor deposition etc. [20]. Laser plating has also been used for depositing the gold coatings effectively [19]. Laser enhanced deposition has 3 main types which are laser enhanced electro-less deposition, laser enhanced electro-deposition and laser enhanced thermal deposition [21].

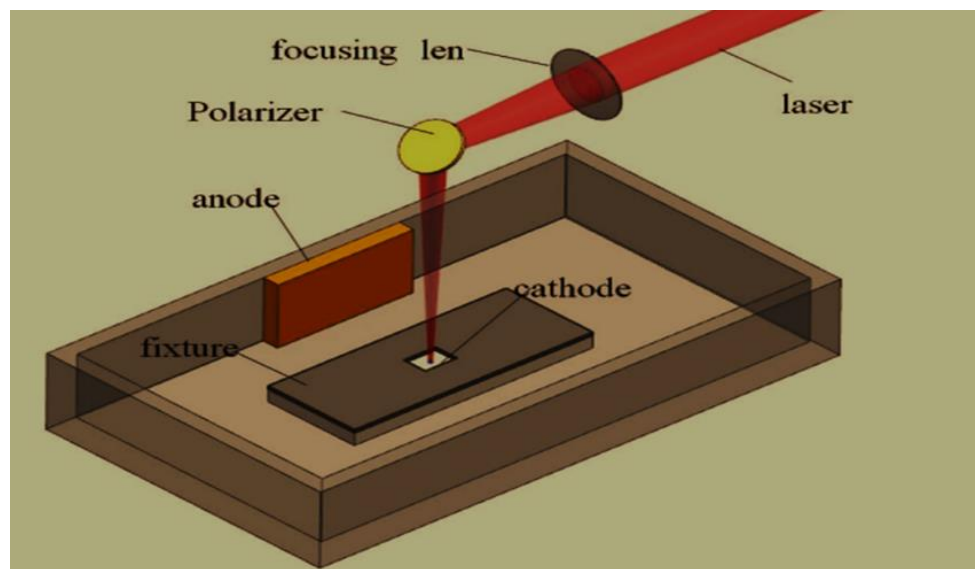


Figure 5: Illustration of laser enhanced deposition [22]

Different types of lasers are being used for the desired purposes. For instance, Nd: YAG, CO₂ and fiber lasers etc. for sintering purpose [23]. Following are some of the laser parameters that are meant to be kept in mind while operating the deposition processes[24]:

- **Laser power**

One of the most important parameters is the laser power which is calculated in watts (W). This unit is used in order to measure the energy transferred to the area being irradiated.

- **Scan speed**

Scan speed is another important parameter in terms of getting and controlling the final desired results. It is expressed in mm/s unit.

- **Laser wavelength being irradiated**

Wavelength needs to be considered while operating lasers as different materials have variant absorption coefficient and wavelength plays pivotal role here [24]. Different types of lasers influence the resultant product binding in different ways depending upon above given parameters.

1.5 Electro-less deposition

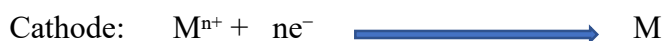
This deposition method involves the metallic ion reduction on to the specimen surface simply by chemical or auto-catalytic means without any external current involvement. And also used for brazing and soldering. Some common reducing agents used are TMAB (tri-methyl-amine-borane), AB (ammonia-borane), and DMAB (di-methyl-amine-borane) etc.[25]. Process is time consuming and auto/self-catalyzed [26]. Chemicals to avoid the oxidation are used as finishers to complete the process which leads to improvement in corrosion and friction resistive properties [27].

1.6 Electro-deposition

Electroplating is a convenient and widely used method to prepare variant coatings of different shapes and sizes along with its economic importance which cannot be neglected or undermined. Amorphous coatings can also be prepared with ease, of different compositions and thicknesses by this method just by controlling the process conditions and parameters [6].

Main principle

Oxidation occurs at anode which is of pure Ni where electrons are being liberated and directed towards the cathode comprises of the material which is being coated. Metal ions from electrolytic solution accept the electrons to become reduced on surface of the cathode (reduction occurs). Following reactions occur particularly on surfaces of anode and cathode interface with electrolytic solution:



Here M denotes the metal, M^{n+} represent the metal ion and ne^{-} denotes the electrons present in electrolytic solution.

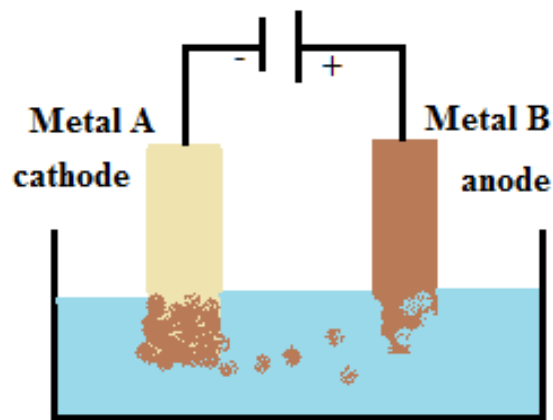


Figure 6: Schematic electroplating

<https://www.toppr.com/ask/content/concept/electroplating-261349/>

Parameters that effect electro-deposition process and resultant coat:

Electrolytic solution comprises of dissolved ions of metallic salts in desired solvent which could be water or other than water and plays the role of ionic conduction. Electrical conductance improves as **pH** is adjusted by inorganic base or acid results in reduction of voltage, which eventually enhancing the deposited material's uniformity and thickness throughout the substrate surface. pH should be constant around the electrode surface as well as to improve adhesion. **Buffering agents** are added specially to improve adhesion and stable pH of solution especially during hydrogen evolution. Different agents are added for different purposes such as for brightening the coating surface without polishing, for smoothing the coating surface, for avoiding the pit formation, for decreasing the internal stresses and to enhance the current efficiency etc. **Current density** directly effects the quality of depositing material and film quality. As we increase the current density mass transport of material will accelerate decreasing the growth of crystallites which eventually results in grain refinement as nucleation rate will be enhanced. **Deposition time** of coating greatly affects the coating thickness, reaction completion, grain growth and quality of resultant coat etc. as process starts with nucleation progressed with the metal growth from

stable metal clusters ultimately followed by the normal growth of coating by the attachment of more atoms from the solution.

1.7. Types of electro-deposition

A. DC current

Method using direct current or constant current/potential to deposit the desired material on to the specimen surface is known to be the direct current deposition which is the conventional type of deposition and used more frequently. These variables are manipulated in a manner to get desired deposit morphology and thickness along with the quality [28]. Despite having issues like hydrogen evolution or porosity, this type is still a leader in production due to its easy to use nature and economical [29].

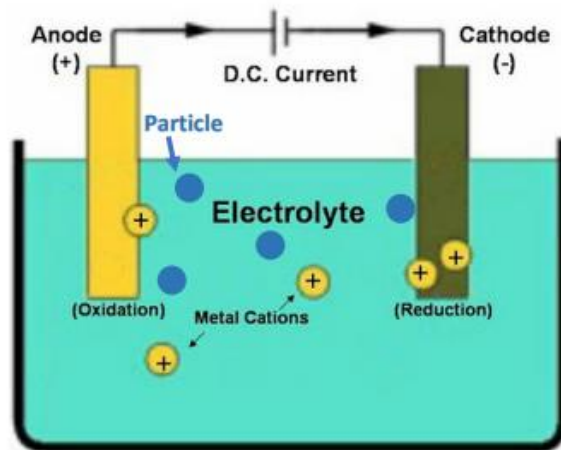


Figure 7: Electro-deposition using direct current

<https://www.slideshare.net/shailaja183/electric-field-and-electroplating>

B. Pulsed and pulsed reversed current (PC, PRC)

In this type of electro-deposition, modulation waves of potential or current are applied to get the deposition. Apart from the variables used in DC approach some more variables are utilized in this type to control the deposition process such as on and off time denoted as t

(on) and t (off) respectively. Variation in these two times is defined by a common factor namely duty cycle. Following equation is used to express the duty cycle:

$$\% \text{ Duty-Cycle} = \frac{t(\text{on})}{t(\text{on}) + t(\text{off})} * \text{frequency (Hz)} * 100,$$

Where, frequency = 1 / t (on) + t (off)

Variation of duty-cycle in a controlled manner helps to achieve the effective deposition results by influencing the nucleation rate, layer being diffused or grain size etc. [30].

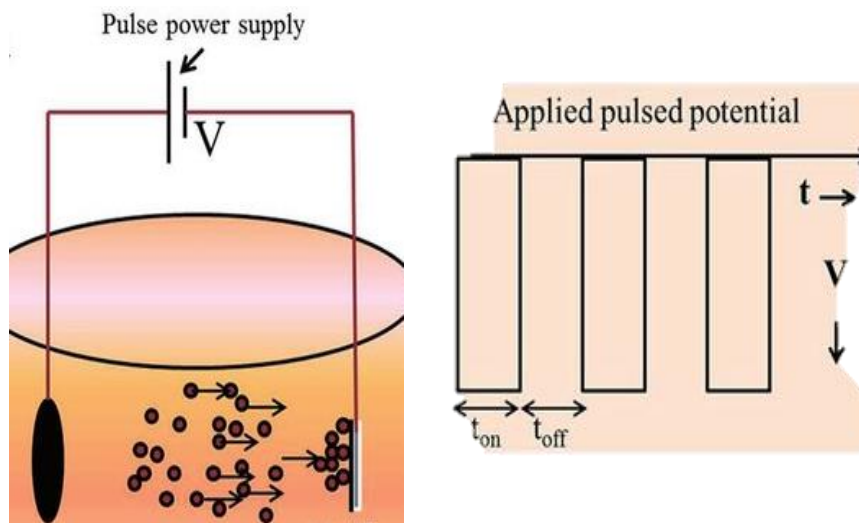


Figure 8: Diagram displaying the PED process[30]

While in this process due to the periodic on and off of potential or current cycle, negatively charged layer formed during t (on) will get discharged during t (off) which facilitates the ionic passage towards the cathode. Off time facilitates the homogeneous distribution of ions in electrolytic bath so that they could be readily available for use while t-on [31].

C. Pulse reversed electro-deposition:

This type is more novel and effective than the above explained for deposition of quality coatings. In this process small anodic pulses are used along with cathode ones in alternating way during whole applied current cycle [32]. Just like PED (pulsed electro-deposition), careful control and modulation of additional variables such as t (a) and t (c) results in getting desired properties in the resultant film nullifying the fear of compromised

quality [3]. Variation in anodic and cathodic pulses is expressed by the factor duty cycle

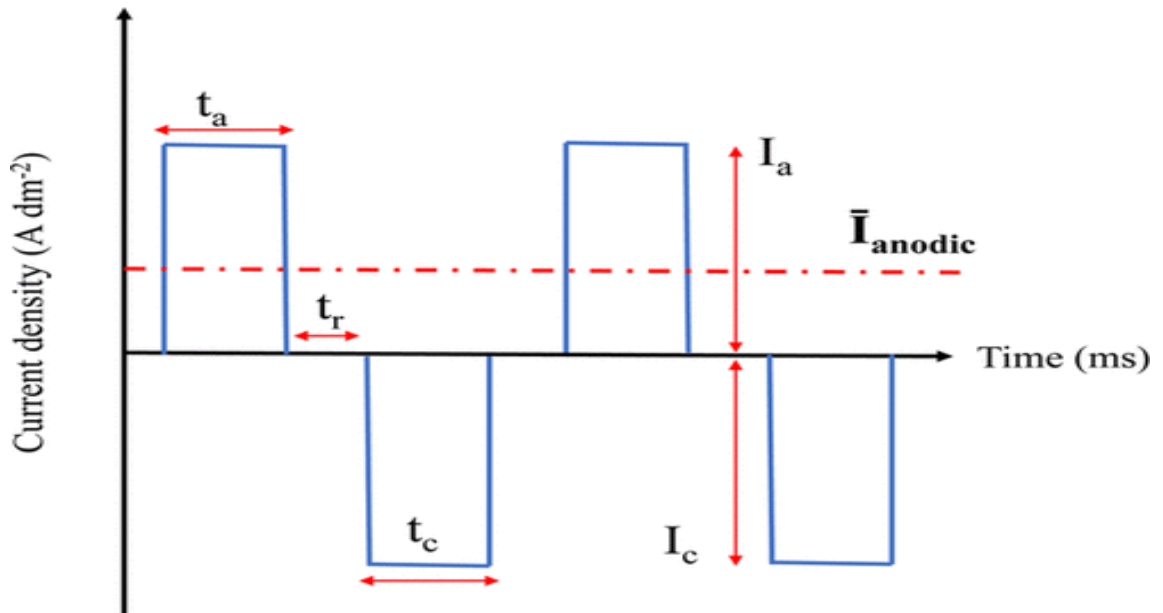


Figure 9: Illustration of pulse reversed current [3]

as utilized in PED technique[33]. Equation is as follows:

$$\% \text{ Duty-Cycle} = \frac{t(c)}{t(a) + t(c)} \times 100$$

Where, t (c) is cathodic pulse time and t (a) is reversed anodic pulse time.

Industries usage of the coated products obtained by electro-deposition:

Due to effective economic and operational advantages of using this method, many industrial sectors opt for using this process for deposition purposes. For instance electro-deposited protective films are used on specimens with low wear or corrosion resistant and are more sensitive towards the environment in which they are being used.

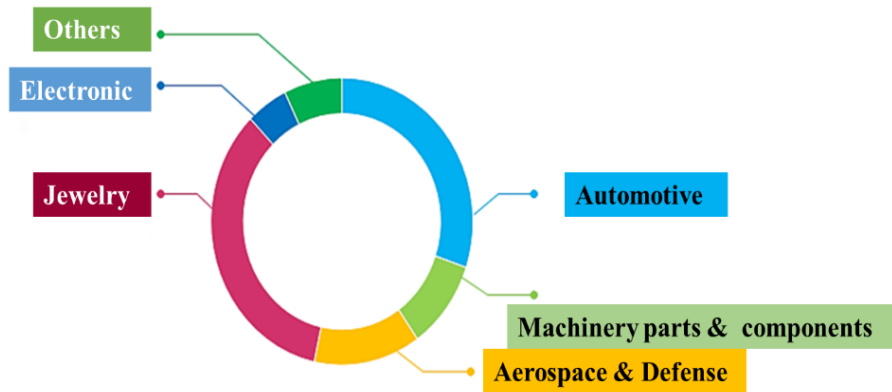


Figure 10: Industries that are utilizing the electroplated coatings

(<https://www.verifiedmarketresearch.com/product/electroplating-market.>)

Table 2: Coatings and their industrial usage

Coatings	Industrial usage
Pd and Ni-Pd	In electrodes, for storing H ₂ and evolution, distillation purposes, fuel cells etc.
Ni-Al₂O₃, Ni-SiC, Ni-Ti	For wear and corrosion resistive purposes
Ti-Al-N, Cr-Al-N	Hard coatings + thermal stability applications
Co-P, Co-W	Hard + Magnetic
Ni-Mo-P, Ni-P, Ni-Mo, Ni-W etc.	For wear and corrosion resistance applications in extreme conditions
Ni-Cr-Fe	For cracking impedance and catalysis purpose, also employed as soft magnets

1.8 Electrochemical deposition; why?

This method is particularly cheaper and simple to use than other available options for deposition of metal, metal alloy and nano-composite coatings. Following are some of advantages of utilizing this method over others for deposition purposes [34]:

- Economical and easy to use

- Time efficient
- Production of coatings with low porosity
- Easy to control various parameters such as pH, current density, operating temperature, deposition time etc. for achieving required deposit
- High nucleation and fine grain size could be achieved by controlling the parameters because of electric crystallization
- Can be used for deposition of complex structures
- Versatile and high rates of deposition hence increasing overall production [35, 36].

Further research on this method is recommended, due to the material operational cost in an industrial setting that is projected to be over 200 times cheaper than electro-less deposition method [37].

1.9 Research Aim

This research project aims to deposit Ni-based Nano-composite coatings on HSLA steel substrates by electro-deposition method and to improve the mechanical and corrosion resistive performance of resultant coatings.

Chapter # 2

Literature review

This chapter deals with prior work done on nickel base alloy or composite coatings. Apart from coatings a little insight to HSLA substrates and their choice would be given as well. Nickel coatings provide very promising alternative to other counter parts due to various other limitations, one of them is major environmental deterioration due to waste production. Distinct properties and various compositional combinations resulting pleasing performance as compared to other materials embarks a competition making nickel coatings undeniably a potential candidate for industrial applications. Nickel is preferred due to its amazing properties like good mechanical strength, light weight, corrosion resistive, good finisher, good thermal and electrical conductance, and good surface properties as well. Novel combinations are being introduced in simple nickel coatings to get more application friendly properties.

Second phase micro or Nano particles (such as Al_2O_3 , TiO_2 , CNTs, SiC etc.) are incorporated successfully using electro-deposition technique, in Ni or Ni-alloy matrix showing enhancement in tribological properties and more mechanically and chemically stable coatings [5]. Nano composite coats are a major topic in materials scientific research and as the industry moves towards the Nano science, our understanding of rudimentary components of coatings as well as potential to modify them at atomic scale is rising. Thin hard PVD coatings (mono, multilayer, and composite such as TiN, TiAlN, AlTiN coatings, nanocoating nACo, etc.) and other diverse coating diverse coating systems like (hard metal + coatings, high speed steel + coatings, nitrided steel + coatings) were explored respectively. Duplex coatings and duplex treatments (self-lubricated films on PVD coatings, laser hardening of PVD coated surfaces) were investigated to expand the application regions of thin hard coatings [38]. These thin coatings were also prepared by chemical deposition processes mentioned in detail in first chapter.

2.1. HSLA steel; substrates:

Although HSLA steels have almost relatable chemical composition to plain carbon steels still they have higher (twice) strength, (due to light weights and high strength) have higher load-bearing abilities which sits well with their engineering applications. This higher strength is due to the grain refinement (by precipitation hardening) caused by micro alloying with elements like vanadium, Nb, Ti etc. Manufacturing processes (like rolling and cooling) in a controlled manner also impact their strength value as compared with simple steel [39]. These steels are considered as micro-alloyed steels as minute amounts of alloying additions are used as compared with other steel types [40]. For example Nb, Ti [41], Mo, Cr, or Si etc. are some of the elements that are being used as alloying additions due to the impartment of their unique properties in steel such as ductility, strength, stiffness, machinability, wear or corrosion resistance etc. [42]. Ni is an effective ferrite solid solution strengthening metal which imparts the strength to the structure [43]. However it does not have any impact on austenitic formation and refinement. Therefore it could not be a favorable choice while needing the austenitic grain refinement. Cr as Ferrite grain refinement can be effectively catered by chromium carbide than nickel [44]. Cr impartment also enhances the corrosion resistive properties in the steel [45].

Table 3: Commonly used alloying elements in steels and their functionalities [46].

Alloying Element	Function
Nickel	Stabilises the austenitic structure during the austenisation treatment.
Manganese	Stabilises the austenitic structure during the austenisation treatment.
Nitrogen	Increases the tensile strength through solid solution strengthening.
Niobium	Stabilises carbon and improves the creep strength by forming NbC carbides.
Carbon	Increases the tensile strength through solid solution strengthening.
Copper	Improves the creep strength by the precipitation of a copper rich phase. Also has an austenitic stabilising effect.
Chromium	Improves the oxidation/corrosion resistance. Resistance increases with increasing chromium content.
Silicon	Improves the oxidation/corrosion resistance.
Phosphorus	Involved in increasing hardenability and strength.

Comprehensive understanding and investigation of elemental impact on each other needs to be done prior to the development of structure with required properties [47]. For example Nb is the most favorable element used for the purpose of precipitation hardening in the steel and also resists the transformation of phases from $\gamma \rightarrow \alpha$ increasing strength of steel. It also imparts the grain refinement properties to the steel by creating the pinning effect to the grain boundaries [48, 49] [50, 51]. Mo could serve the same purpose as Nb and also provides Nb sites to nucleate when both are used in combinations [52-54].

2.1.1: HSLA coating; why?

HSLA (high strength low alloy) steels are frequently used in the industrial areas like construction industry, locomotive industry, transportation, oil and gas industry etc. [55, 56]. Therefore they are more subjected to the extreme environments/atmospheres which causes deterioration of their wear or corrosive performance. Hence different coatings containing different elemental compositions are used for protecting them in extreme

conditions[57]. For example Cu also serves the purpose of corrosion resistance just like Nickel and chromium in order to enhance the HSLA steels durability to be used in more poignant and aggressive conditions [56].

Table 4: Coatings that have been deposited on HSLA steels over years [58-65].

Coatings	Purpose	Method	Year
Ni-Cr-P	Corrosion, fatigue and crack resistance	Electro-deposition	1992
Ni-W-SiC	For protection against H ₂ Embrittlement	Electro-deposition	1992
N-ion implantation	To resist contamination by hydrogen	Ion implantation	1993
Ni / Cr alloys	For resistance against H attack	Thermal spraying	2003
Galvano-Alcotec	For corrosion resistance and air craft applications	Electro-plating	2003
Zn-14% Ni & SermeTel 1140/962	For H embrittlement resistance	Electro-deposition	2008
Ni-P/WS₂	For better tribological performance	Electro-less deposition	2012
Ni-Co layers	For impact resistance, hardness and corrosion resistance as well	Thermal spraying (HVOF)	2015
Ni-P/PTFE	For self-lubrication	Electro-less	2017
Ni-WC	For wear and friction resistance	Laser deposition	2019
Cu, Cr, Ni, Zn	For improved mechanical and corrosion resistance	Electro-deposition	2019
Ni-P-Ti	For wear and corrosion resistance	Electro-less deposition	2020
Ni-P/TiC	For grain refinement, hardenability	Pulsed electro-deposited	2021

2.2. Ni coatings

Nickel deposition is done by means of different types of electrolytic baths which are as following:

- Watts's bath
- Sulphate bath
- Chloride bath
- Fluoborate bath

This has led to greater focus on the development of novel nickel processing techniques. Ni's key advantages includes its lightness accompanied with high strength to weight ratio. Good corrosion resistance, erosion and deposition and other chemical containments, high thermal and electrical conductivity, good light birefringence and finishing in variant shades and textures on its surface [5]. For certain applications, hard 'nickel' coatings are recommended. Therefore some hard elements are added such that Co, W, Mo etc. in order to enhance the performance as well as its numerous industrial applications, has boosted its use in a variety of new industries, putting it in direct rivalry with other materials. Electroforms, in particular, benefitting from their enhanced wear attributes [66]. Dry gases such as carbon dioxide, hydrogen and ammonia are impervious to nickel coatings. Carbon tetrachloride, fuel, soap and petroleum are all resilient to it. Ni coatings enhances fatigue resistance. Corrosion fatigue also mitigated by Ni- coatings. Ni coatings are just not impervious to nitric acid or chlorides conditions [67]. Ni coatings have huge industrial usage whether they are alloys or composite coatings. Ni plated coatings were mainly used for the corrosion resistance purposes and for bright ornate look of different specimens [67]. The study about Ni and its alloy or composite coatings is not the novel idea in process instead it is well established field and reason for this are the continuous improvements that were being witnessed because of different compositional combinations of Ni (nickel) with other elements. Each composition shows distinct and favorable properties enhancing the overall coating potential [8].

Therefore, for further enhancement in properties like hardness, wear and abrasive resistance and low coefficient of friction, different compositions of alloy and composite coatings like Ni-P, Ni-B (binary alloys), Ni-P-Mo, Ni-P-Sn etc. (ternary alloys), Ni-SiC,

Ni-TiP, Ni-Mo-P-Al₂O₃ (composites) etc. were employed effectively. These ternary and quartet systems are studied mainly to get improved coating properties and to boost this industry towards more effective and robust solution [68].

Nickel instead of Cr:

Functional Cr coatings are extensively used in aeronautical, automobile, and engineering industries due to their remarkable mix of abilities, which include excellent mechanical properties, exceptional corrosion, wear, or heat resistance, and low impact resistance. The most commercially available Cr electrodepositing treatment, on the other hand, uses an aqua bath incorporating hexavalent Cr. It is regarded as a carcinogen, which, when coupled with its strong oxidizing properties, poses substantial health and environmental risks to humans and the environment. As a result, hexavalent Cr's use has been restricted. Furthermore, due to its outstanding stability, the common wetting agent per Fluor-o-octane-sulfonic acid (PFOS) used in Cr electroplating to minimize the hazard of the procedure by limiting the mists produced during electroplating is being outlawed, posing an issue for the environment [69].

2.3. Ni-P Coatings:

Because of their superior qualities Ni-P coatings are used favorably for corrosion and wear resistive purposes. As plated deposits of this alloy have many significant properties like mechanical, rheological and electrochemical properties as well as catalytic properties and favorable magnetic characteristics depending upon their composition and structure. Processing of these alloy coatings can result in excellent hardness properties than Cr coatings. Mechanical, tribological, corrosion, catalytic and magnetic properties as well as key process variables influenced by P-content in coated deposit and the presence of certain bath constituents are all taken in to account. In view of the foregoing, researchers are concentrating their efforts on discovering alternatives to Cr while keeping the demand for outstanding functional qualities in manufactured deposits. The electric current flowing between the electrodes drives the electro-deposition process (plating substrate) where standard Ni (-0.25 V) and P (-0.28 V) reducing potentials are closer to one other, enabling for effortless co-deposition. By electroplating nickel with phosphorus, it gains greater hardness (500 HV as-plated Ni-P), corrosive and wear resistance, and a lower friction

coefficient (0.4-0.7 as-plated Ni-P), as well as a changeover to paramagnetic properties. Coatings having low phosphorus level exhibit high hardness and wear resistance than with a greater phosphorus content even though they have strong protection against corrosion but poor mechanical performance due to a shift to amorphous structure. The majority of amorphous Ni-P deposits are brittle having limited ductility. Pulse plating, rather than direct current plating, can preserve Ni-P crystalline structure while at greater phosphorus concentrations, resulting in good mechanical qualities distinctive of low-phosphorus deposits [70].

Because of no significant specification of several process parameters in the Ni-P electroplating process, determining the primary influencers, their method, and the magnitude of their impact is tedious job. By adjusting process parameters like current density, electrodeposition of Ni-P allows for good control over deposit thickness, appropriate shape, and appealing physical characteristics of the coating. The formation of metal phosphides inside the microstructure after subsequent heat treatment might increase hardness. Electro-less plating on Ni-P might be chosen when precise finishes are required on complicated, demanding profiles, such as tiny fittings, despite rising electrolyte costs, additional maintenance requirements, and considerably shorter bath spans [71]. More research on throw power and current distribution on basic and more intricate geometries, including the impact of solution/cathode action, are essential for both methods of deposition [72]. During the electro-deposition of NiP alloys, the interrelationship of four aspects is considered to be important which are as follows: [73]

- Substrate state,
- Electrolyte composition,
- Process parameters, and
- Deposit characteristics

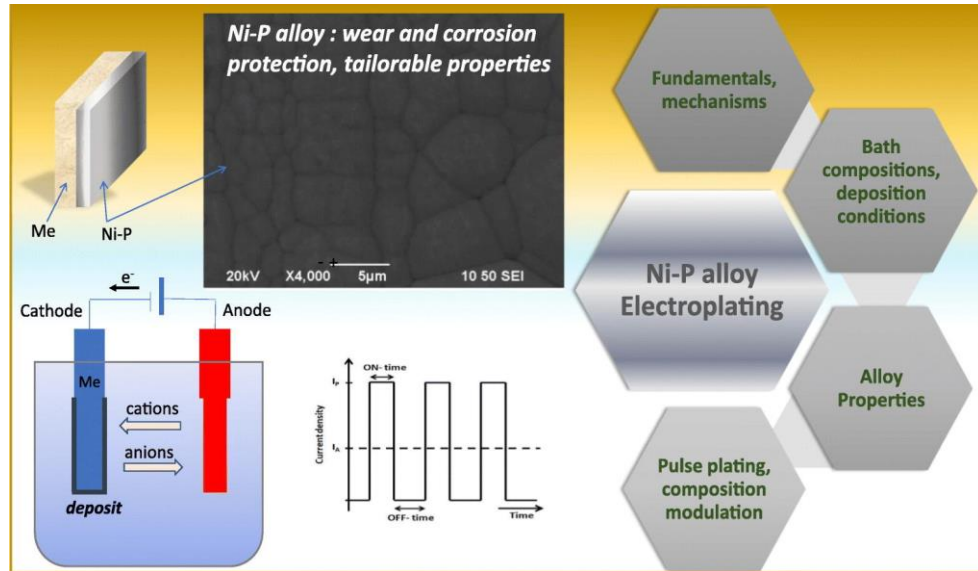


Figure 11: Ni-P electrolytic deposition process and needed factors [72]

Ni-P alloy electrodeposited coatings have various field applications such as automobiles, aerospace, for functional and decorative purposes and other such industrial products with remarkable properties like high precision constituents, diffusion obstructions, micro-batteries, catalytic coatings for hydrogen evolution in water electrolysis, magnetic memory discs (thin films) and sensors etc. [72].

2.4. Addition of Mo in Ni-P alloy:

Because of its great corrosion resistance, high hardness and wear resistance, ease of operation, and economic advantage, (Ni-P) plating is widely used in coating industry. It also improves the surface's solder ability and buffing properties, prolonging the serviceability. With the rise of strong industrial demands, binary Ni-P alloys are no longer able to handle applications requiring unique conditions, such as machine manufacturing and corrosion-resistant constituents in saline water. As a result, several investigations have focused on the ternary alloy, or the co-deposition of additional metal into the Ni-P coating, such as Zn, Cu, Co, Fe, Sn, W, and Mo etc. (mostly electro-less). By modification of the microstructures and grain size, the ternary alloy improves the physical as well as chemical properties of resultant coating. Generally, hardness and corrosion resistive properties of ternary Ni-Mo-P alloy are better than binary Ni-P alloy coatings. And due to Mo

incursion crystallization temperature as well as deposition rate of ternary alloy are lower than binary ones [18]. Furthermore, when the coating reaches a significant thickness, the Mo–P co-deposition enhances the coating's hardness and internal stress concentration, making it more brittle and susceptible to cracking and stripping [74]. Due to the restricted mobility of refractory elements in their alloys, alloying with refractory metals, such as molybdenum, is a very well strategy to raise the thermal properties and enhance the thermodynamic properties of crystallization and transformation of many metals and alloys [75]. Mo also has an effective edge over Cr while micro-alloying in HSLA steel as it causes the dislocation recovery interruption and take part in impeding the phase coarsening effect [76]. Electro-deposited Ni-Mo coatings are considered due to the corrosion resistant and good harness properties, but their properties (neither corrosive nor hardness) were not up to the par with chrome coatings. Yet their properties were not only enhanced but were superior to that of chrome coatings upon heat -treatment above 100 degrees Celsius [77]. Another advantage of nickel-moly (Ni-Mo) coatings over chrome was the harmless waste while Cr⁶⁺ ions in chrome coatings cause serious health problems [78]. Amount of Mo could be only used up to certain limit to get better results above 17 at. (Atomic) % of Mo in coating was having the deteriorated effect on properties like corrosion or hardness due to crack formation [79]. Phosphorus (P) therefore, is the most used element among all due to its role in enhancing corrosion resistive properties [80]. Mo and P both elements could not be electrodeposited separately in their own molten salt solution, but their co-deposition occurs due to the presence of iron, nickel group salts but not in higher amounts due to enhancement of cracks in film possibly because of hydrogen evolution. Co-deposition results after multiple steps of molybdenum salt reduction to molybdic oxide which would be further reduced by the atomic hydrogen residing on the surface of metal introduced [81]. Owing to the Phosphate anion surface protection layer formation in aqueous environment dissolution of such coats (i.e., Ni-P, Co-P) becomes limited kinetically. So, P incorporation in Ni-Mo coatings displays increment in properties like hardness and corrosion. P amount should be more than 14 at. (Atomic) % for coating to be amorphous [82]. In the table given below are the Ni-Mo-P coatings that are being deposited by various methods on various substrates.

Table 5: Ni-Mo-P deposition over years

Sr. no.	Substrate	Deposition method	Journal & publication year
1	Ceramic tiles	Electro-less deposition	Coatings / 2020
2.	Graphite	Electro-deposition	Surf. Interface anal. 2013
3.	Copper	Electro-less deposition	Korean J. Chem. Eng., (2012)
4.	Copper plate	Electro-deposition	The royal society of chemistry 2016
5.	Disc-shaped Cu	Electro-deposition	J. Braz. Chem. Soc., 2012
6.	Mild steel (Q235)	Electro-less deposition	Tribology international (2016)
7.	3D Ni foam	Electro-deposition	Electro-chimica acta 335 (2020)
8.	The mild steel (Q235)	Electro-less deposition	Surface engineering 2019
9.	Stainless steel	Electro-deposition	Fuel cells 16, 2016
10.	Copper	Electro-deposition	Plating & surface finishing, 1995
11.	Stainless steel and brass	Electro-less deposition	Bulletin of Electrochemistry, 2001

2.5. Ni-composite coatings and their electro-deposition:

Composite coating is a type of coating that employs a blend of two or more compounds to protect the substrate. The strengthening granules in the coating matrix are being used to generate this unique type of coating. It is manufactured in a wide range of means to satisfy the needs of diverse industries. These composite coatings provide further corrosion, wear, and mechanical characteristics as well as protection [5]. Attempts have been undertaken to enhance the characteristics of nickel coatings by including a second phase in the form of scattered non-metallic particles into them known as composite coatings. The particles can be included to provide the coatings more wear resistance, especially at elevated temperatures. Hard refractory particles like silicon or chromium carbides, or tungsten or zirconium borides etc. are used for the purpose. For self-lubricating and low friction nickel coatings Mica or graphite are utilized. Nickel deposits can contain oxides such as alumina, thoria, silica, or titania for their dispersion-strengthening qualities. Nickel, its alloys, and compounds are the most researched matrix due to its great brightness, hardness, corrosion resistance and less hazardous nature. For

example, studying the progress of the hydrogen reaction during electro-co-deposition of a Ni and MoS₂ particles [83].

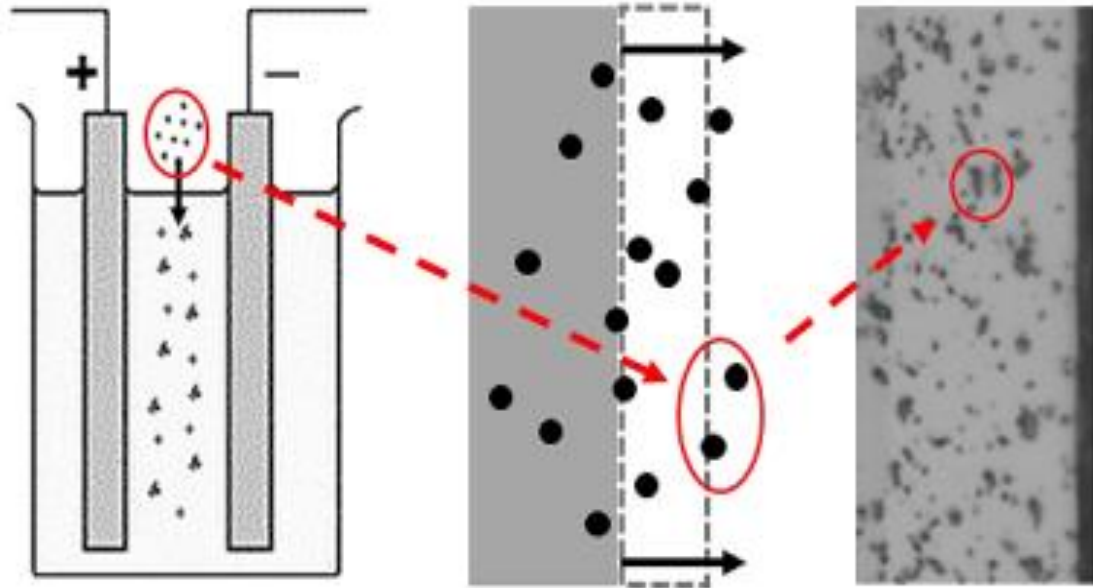


Figure 12: Diagram representing the co-deposition of particles in to Ni-Matrix [84].

The process of co-deposition consists of five stages:

1. On the particles, ionic clouds formation occurs.
2. Convection in the direction of the cathode
3. Transmission in the boundary layer of a hydrodynamic generated in solution
4. Then passing through concentration boundary layer occurs i.e. diffusion
5. Finally adsorption of particles occur at the cathode (within the metal deposit).

Brownian motion occurs continuously among particles fully dispersed in an electrolyte solution. Whenever two particles approach each other, their separation or aggregation is fundamentally decided by the energies existing between them. Particles face agglomeration when attraction energy between them exceeds the repulsion one, while opposite occurs otherwise. The quantity of net force for the creation of agglomerated structures is largely determined by the system's state and character. As a result, knowing the structure of the interfacial area is serious to understand the dispersion stability of solid

particles in electrolyte [85]. Metal ions with undissolved particles of oxides (SiO_2 , TiO_2 , CeO_2 , Al_2O_3 , ZrO_2 , MoS_2 , and SrSO_4), carbides (SiC , B_4C), nitrides (Si_3N_4), polymers (PTFE), and even metals are reduced by electro-deposition. This results in a metal/alloy matrix with micro/Nano solid particles implanted in it. The size, nature, and type of particles present in solution strongly impact the composite coating's properties. This can improve the vital characteristics of substrate metals and alloys. Composite coating is primarily used to improve wear and corrosion resistance as they have better yield strength, hardness and toughness than pure metals [5, 86-94]. Different nanoparticles are also incorporated in these coating for enhancement of properties for advance industrial applications like light weight, good thermal stability at high temperatures, excellent wear, and corrosive resistance. Particles like Ti, W, Al_2O_3 , SiO_2 , WS_2 etc. are used for achieving properties like high hardness, toughness, and corrosion resistance in Ni-composite coatings. These coating type still need to be investigated further for more revolutionary progress as different compositions and combinations impart distinct properties in resultant coatings [95].

2.6. Al_2O_3 nano-particles:

Alumina Nano-particles incursion into the coatings (like other hard Nano particles) is due to improved properties like wear resistance and hardness as these particles are hard in nature. The composite coatings with alumina nanoparticles have improved hardness and corrosion resistance qualities [96]. Coating surfaces containing alumina particles can be smooth and dense, but they can also be rough. The surface particle size has also been reduced to micrometer which eventually results in grain refinement. These findings reveal that the addition of alumina in the coatings bath substantially refines the surface morphology [97]. Proper dispersion of particles is very important for their adsorption on to the cathode surface due to higher particle density and more chances for loose particles to adsorb. The smaller the agglomerated alumina particle groups, the greater the electric field's ability to attract them, resulting in effective and strong adsorption [98]. For example Nano-Ni/ Al_2O_3 composite coating is largely utilized in microelectronics to boost the wear resistance of metal surfaces [98]. The inclusion of nano- Al_2O_3 causes increase in hardness, which increased erosion and wear resistance. The high level of hardness, wear, and

oxidation resistance of nano- Al_2O_3 ceramic material has piqued curiosity for further research [99].

2.7. Research gap

Nano-composite coatings are been used in various industries for protection purposes. And Ni-composite coatings have a special importance in this regard because of their eco-friendly advantages along with excellent surface wear and corrosion resistive properties. But pure Ni metal coatings has some disadvantages at extreme conditions as they become unstable. Therefore, many studies are being done to explore various elemental combinations and compositions with Ni in order to achieve more economical and better performing coatings systems.

Ni-Mo-P ternary alloy has been extensively used for corrosion and wear resistive protection coatings. Whereas, ceramic alumina nano or micro particles also have good stability thermally and chemically [100]. They also have good corrosion as well as wear resistance and have been incorporated in Ni and other Ni-alloy matrixes before for the same purposes [101]. But these ceramic particles have not been incorporated in Ni-P-Mo alloy matrix prior. Hence we investigated their effect on surface, mechanical and electro-chemical properties of this ternary alloy in order to improve further research.

2.8. Research Objectives

Following are the main objectives of this research project:

- To develop Ni-P-Mo nano-enhanced composite coatings, having improved wear and corrosion properties for usage in extreme conditions, by means of an effective and economical method.
- To investigate the effect of different alumina nano-particles concentrations on mechanical and structural properties of resultant coatings
- To thoroughly investigate and identify the optimized experimental parameters to electrodeposit Ni-Mo-P alloy and Ni-Mo-P/ Al_2O_3 composited coatings on HSLA steel substrates

2.9. Novelty in project

In this project novelty comes by the co-depositing alumina nano-particles in Ni-P-Mo alloy matrix. Prior Ni-P-Mo alloy coatings have been investigated extensively in terms of wear and corrosion resistive properties. And alumina nanoparticles have also been used in various nano-enhanced composite coating systems. Still their impact on Ni-P-Mo alloy system is yet to be explored. Therefore we incorporated and study their impact on properties of Ni-P-Mo alloy coatings.

Chapter # 3

Methodology

3.1 Experimental Methods

A. Sample Preparation

HSLA (high strength low alloy steel AISI 4340) substrates of having 2.5x2.5cm² size were used for fabrication of coatings by electro deposition method. All samples were cut from a full HSLA steel sheet. After cutting the samples (of 2.5x2.5cm² size), they were prepared by grinding with Si-C emery papers of multiple grades (starting from 180 to 2000), prior to the coating. After grinding the substrates they were polished by 0.5 microns Alumina solution to get surface free of dirt, scratches and to lower the surface roughness in order to achieve good coating adhesion. Sonication of substrates was done using acetone (electrolyte) for 20 minutes prior to coating. Before dipping the substrate in solution it was chemically activated by utilizing 20% H₂SO₄. And then distilled water was utilized for thorough rinsing the substrate before dropping into the solution (electrolyte) bath [102]. Chemical Composition of HSLA steel is given below in **Table 6**.

Table 6: Chemical composition of HSLA steel

Elements	C	Si	Mn	Ni	Cr	S & B	Fe
Wt%	0.28	1.2	0.9	0.3	1.1	0.025	balance

B. Bath Composition and set-up

Electro-deposition was performed using common 2 electrode system where electrodes were hanged parallel to each other in 250ml solution beaker. Whole experimental set-up is given in figure 13. All the chemicals used were purchased from Sigma Aldrich. These were dissolve in 150ml distilled water in 250ml beaker. Continuous stirring was achieved

by using a small sized magnetic stirrer and additive such as Ammonium hydroxide (NH_4OH) was introduced to the electrolyte for pH maintenance. KXN-3020D, DC power supply (as voltage source) was used for the experiment to occur. Bath composition included Nickel sulfate hexa-hydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) reagent >98%, Nickel hypophosphite monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) reagent > 99 %, Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), Tri-sodium citrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})$) reagent > 99% for Ni-P-Mo alloy coatings and then same composition was utilized for Ni-P-Mo/ Al_2O_3 composite coatings along with the addition of different concentrations of Al_2O_3 nanoparticles of size 40~50nm. pH of solution was in acidic regime 4.5 to 5 which was adjusted by addition of few drops of concentrated H_2SO_4 . Boric acid was also added to ensure good coating adhesion.

Apparatus Set-up

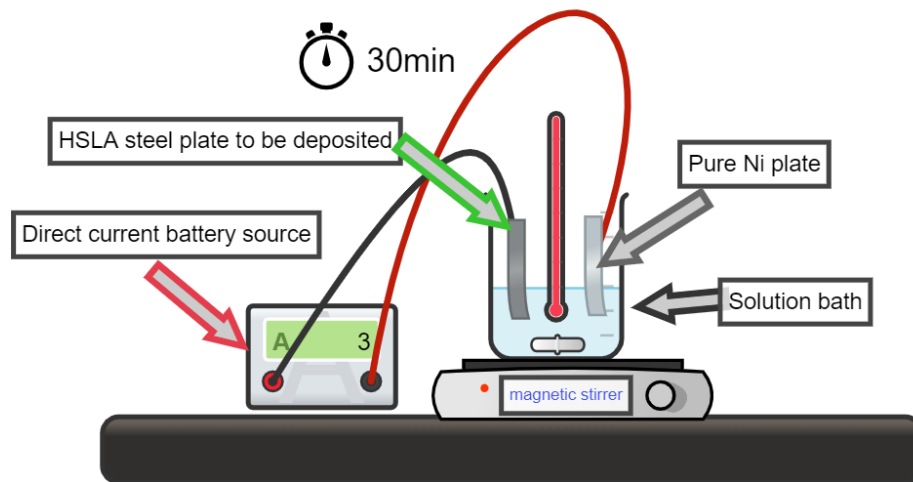


Figure 13: Experimental set-up

Bath compositions of Ni-P-4.48g/l Mo alloy and Ni-P-Mo/ Al_2O_3 composite coatings are shown in **Table 6** and **Table 7**.

Table 7: Bath composition of Ni-P-Mo coatings

Sr. No.	Chemicals used	Quantity in 150ml solution bath
1	Nickel sulphate hexahydrate	8.0925 grams
2	Sodium hypophosphite	1.59 grams
3	Sodium citrate	13.236 grams
4	Sodium molybdate	0.726 grams, 0.52 grams, 0.96 grams

Table 8: Bath composition of Ni-P-Mo/Al₂O₃ composite coatings

Sr. No.	Chemicals used	Amount in 150ml solution bath
1	Nickel Sulphate Hexahydrate	8.0925 grams
2	Sodium Hypophosphite	1.59 grams
3	Sodium Citrate	13.236 grams
4	Sodium Molybdate	0.726 grams
5	Alumina powder (50nm)	0.1 grams, 0.05 grams, 0.02 grams
6	Boric acid	3 grams

C. Electro-deposition Parameters and Conditions

In order to ensure the uniformity and resultant improved properties of coatings, parameters play key role and need to be controlled and optimized carefully. The conditions and process parameters for electro-deposition are enlisted in **Table 9**.

Table 9: Optimized plating parameters

Temperature range	30~35°C
pH	4~5 (Acidic)
Current	0.3A
Etching time	30 secs in 15% conc.H ₂ SO ₄
Deposition time	50 min

3.2. Characterization techniques

Following characterization methods were employed to study and analyze the obtained results.

A. SEM (scanning electron Microscope)

To overcome the short comings from optical Microscope like resolution and magnification, electron microscopes were originated. Electrons are used as incident beam to interact with the sample surface. These interactions results in diverse discharges such as: Back scattered electrons, Auger electrons, Secondary electrons emissions and X-rays. Scanning electron microscope works as the high energy electron beam is projected onto

the specimen using objective lens and these electrons then interact with surface of sample resulting in various discharge. “SEM” as the foremost technique in field of research was used to analyze coating surfaces, for thoroughly studying the fractured or effected areas and different such characterizations. We also used this technique in order to analyze the composition of samples. Coatings were cleansed thoroughly before SEM testing as to avoid the distractions while data reading due to surface impurities.

B. EDS

Energy dispersive spectroscopy (EDS) is the most used technique in the field of analytical testing. This technique is mainly based on using characteristic x-rays emission process when atomic energy imbalances by the bombardment of high speed electrons and the electron from innermost shell gets knocked out leaving a vacancy behind which is then filled by the electron from the outer higher energy shell emitting energy in form of x-rays. Each characteristic x-ray corresponds to specific energy, so different elements could be identified verily by the energy peak signal and amount/content of element in compound can also be identified by the analyses of peak intensity (energy signal) [103]. We used EDS analysis for compositional study of elements deposited in coatings and their resultant impact on coating properties. In spot EDS analysis, due to the possibility that certain element might not be detected because of lower concentrations therefore, line EDS spectrum was utilized for getting the clear idea about compositional distribution of all present elements along specific line area of coating surface.

C. Surface roughness (Optical Profilometer)

Roughness measurements are obtained by various equipment like AFM, STM or other optical methods. This is a faster way to measurement roughness and readings are recorded in Ra (mean roughness) and Rz (roughness depth) in microns. Mainly there are 2 ways to calculate roughness of various samples which are as follows:

- Contact mode method
- Non –contact mode method

Rough surfaces are more prone to cracks and wear out more quickly, also corrode more but helps in bonding than smooth surfaces so surface roughness is an important parameter of material to be measured before any application.

D. AFM

This method is used for the precise and detailed study of the topography at atomic scale. We can get analysis of substrates in both air and liquid surroundings. It could be used to image the surfaces of variety of substrates such as ceramics, composites, polymers and biological etc. [104-109]. Topographical features of different surfaces is captured by AFM by the help of a cantilever. The difference in heights due to the features present on the surface of specimen. These differences in features causes the change in deflection of laser beam as well generating the resultant data and all of this is recorded by means of PSPD. Feedback loop is used to govern the tip height from surface for maintaining steady laser site. We can get the map of all features present on surface of specimen by use of AFM [4, 110]. AFM analysis was done in order to get the precise image of surface roughness values of all coatings to study their behavioral changes and properties in different applications like wear and corrosion studies. Surface of specimen should be prepared or cleaned before testing as the dust particles or any such impurity could generate false deflections so influencing the resultant readings.

E. Micro-Vickers Hardness

In this instrument diamond knoop or Vickers indenter is utilized to apply load of up to one thousand (1000) grams against the sample surface. This application of force onto the material surface cause deformation permanently of materials by the size and shape of indenter. The measurements taken from the indent are then used in specific formulas to determine hardness values for Vickers and knoop both methods. Micro testing scope is used to examine the indent due to its extremely small size [111].

$$HV = \frac{2F \sin \frac{136^\circ}{2}}{d^2} \quad HV = 1.854 \frac{F}{d^2} \text{ approximately}$$

Figure 14: Formulae for HV hardness calculations [111].

F denotes force in Kgf,

d stands for mean value of diagonals d 1 and 2 calculated arithmetically

And HV stands for hardness Vickers.

Micro hardness testing was used to determine the hardness of coating surfaces. Surface of coating should be smooth and free from impurities in order to get the accurate results. 10 to 15 indent readings were taken from different points, in order to get detailed surface hardness measurements. After tabulating these reading, their average value was calculated to get overall hardness of entire coating surface.

F. Nano-indentation

Nano-indentation as the name describes used to measure hardness various materials in sub nano-accuracy by the application of indenter tip [112]. Nano tester tests the materials properties (elastic and plastic), utilizing EMF (electromagnetic force) and capacitive depth extents. Due to depth sensing high accuracy and precision of penetration and load can be made possible in a very controlled manner while experimenting. This testing was utilized in order to find nano-accuracy hardness values of coating surfaces

Following measurements were taken from this method of all coatings:

- Young's Modulus
- Hardness

Above measurements are done by using following calculative formulas:

- 1- For calculating hardness of materials

$$H = \frac{P_{max}}{A_c}$$

2- For the calculation of Reduced Elastic Modulus

$$E_r = S \times \sqrt{\pi} / 2\sqrt{Ac}$$

3- For calculating testing material and probe poisson ratios and Young's Modulus of probe:

$$E_{IT} = \frac{1 - (\nu_s)^2}{\frac{1}{E_r} - \frac{1 - (\nu_i)^2}{E_i}}$$

G. Pin on disc: tribometer for wear analysis

Wearing of the materials which is basically (displacement of material) occurs when 2 bodies comes in contact with each other while relatively moving. Friction and wear are not related to material properties rather belong to the system. Pin on the disc test is very important characterization tool for the measurements of wear and wear coefficient especially the hard coatings [113]. This COF (coefficient of friction) can also be determined by the sensor at pivot of the arm as it records the changes in torque. Wear rate is then calculated by the measurement of loss of material while testing [114]. This testing was then done to determine the tribological properties of all coatings. In the light of above mentioned testings' results like AFM, optical profilometry, SEM/EDS, Micro and Nano-hardness, wear rates and COF values of all coatings were determined and analyzed accordingly.

H. Corrosion testing: Tafel plots

Due to difference in any 2 electrode potentials at equilibrium while they are in contact either electrically or electrolytically corrosion ensues. Rate at which material corrodes could be predicted by Tafel plots [115, 116]. Corrosion testing was performed in order to check the coating life in drastic conditions as in tribological testing. Corrosion rates in miles per year were calculated using icorr values of all coatings. Following is the formula used for the purpose:

$$\text{Corrosion rate (mpy)} = (0.13) (I_{\text{corr}}) (\text{E.w.})/d$$

Where E.w. represent equivalent weight, and d is density in g/cm^3 .

Chapter # 4

Results and discussion

Different characterization techniques were employed in order to analyze the resultant samples data. Chemical elemental composition and coating morphology was obtained and studied using EDS and SEM testing respectively. SEM was performed by Instrument JSM-6490 Joel Model SEM set-up using tungsten (W) thermionic emission. 401MVD model of Wolpert group digital micro Vickers hardness instrument was utilized for testing the Micro-hardness of all samples. 980 mN force with 5 seconds dwell time was used for indentation purpose. AFM testing was performed using JSPM-5200 SPM PARAMs. Reference voltage of -3.8V (cantilever contact mode) was selected for testing to get surface roughness values at nano-scale. Surface roughness was measured using optical profilometer. 2 μ m tip roughness of instrument Surfcoorder SE1700 α was utilized having (M. speed 0.500mm/s and length 4mm). Gamry PCI4G750-52089 (electrochemical potentiostat) was utilized to study corrosion rate in 3.5% salt (NaCl) solution. Pin on disk tribometer instrument was used to study tribological micro-properties of coatings, of model MT/60/NI. Nano-indentation by using Berkovich diamond indenter was performed in order to get the hardness and elastic strain values of coatings (having poisson ratio value 0.07 and elastic modulus of 1140 GPa). 5mN and 0.2s⁻¹ was the target load and target strain rate values used respectively for running the test.

4.1 Micro-structural analysis

Different concentrations of alumina particles of around 50nm in size were used to check their impact on coating properties and morphology. In **Figure 15 (a)** surface morphology of Ni-P-Mo alloy coating shows the nodular grain structure throughout the coating surface. Nodular size of grains in alloy coating is larger and coarser than those of composite coatings. Nodular morphology of Ni-P-Mo alloy coating become more refined and homogenously compact in Ni-P-Mo/Al₂O₃ composite coatings which can be seen from **Figure 15 (a)** to (d). Due to the presence of alumina nanoparticles more uniform and

denser surfaces of coatings are attained validating the successful incorporation of nanoparticles in composite coatings. This refinement in grain structure occurs due to increment in nucleation rate as nano-particles act as potential sites for nucleation to take place, mentioned in studies by Islam et al, Yu et al [117, 118] and Mohanty et al [119] as well. Here alumina nanoparticles serves the same purpose for nodular grain refinement of composite coatings. Although composite coatings are not entirely free of defects i.e., micro-cracks or porosity but decrement in their density and size was observed as Al₂O₃ Nano-particles were introduced in to the coatings. Nano-particles cover the pore interior walls and fill the gaps in between to reduce them in density and size also observed by S.sarbishei et al [120] and Naizi, H., et al [121] in their respective researches. However particles addition in a coating should be kept in a certain range for good results as if they exceed a certain concentration their incorporation in the coating gets restricted and agglomeration becomes serious problem curtailing the much needed coating performance [122].

In **Figure 15 (d)** morphology seems inclining towards coarser surface as the amount of Alumina nanoparticles increases might be due to Nano-particles agglomeration and increase in surface asperities like cracks, micro porosity etc.. Best results were obtained by the coating containing the 0.3g/l of alumina nanoparticles with fewer defects. Surface morphology of composite coatings cannot be only attributed to the incorporation of nanoparticles, concentration of other elements like P and Mo plays important role as well [96].

Therefore, other factors must be considered as well while explaining the behavioral changes in resultant coatings. Size of nanoparticles, added, was in Nano regime, therefore, they could not be seen at this magnification in SEM images. But the changes in the coating morphology indicate towards their successful incursion in the coatings. From **Figure 15 (b to d)** clear difference in composite coating morphology can be seen as the Nano-particles concentration is varied.

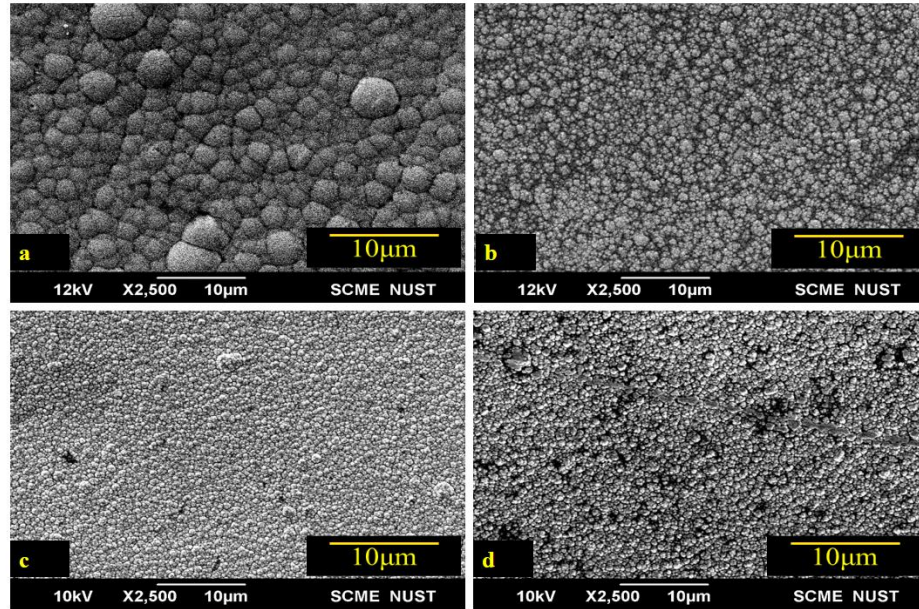


Figure 15: Composite coating morphology: (a) shows the morphology of Ni-P-(4.48g/l) Mo coating (b) Morphology of comp. 0.1g/l alumina (c) Morphology of Comp. 0.3g/l alumina coating (d) morphology of 0.7g/l alumina coating

EDS testing was done to get the elemental composition of coatings and to assure the successful incursion of alumina nanoparticles in the Ni-Mo-P alloy matrix. Increment in Aluminum At. % was observed along with increased concentration of Al_2O_3 nanoparticles. Also from the data shown in **Figure 16** it is very much evident that the presence of alumina nanoparticles effects the deposition of other elements like P, Mo and Ni in the resultant coatings which in turns effects the overall coating properties. As the alumina concentration was enhanced in the electrolytic bath, other elements like Ni, P and Mo deposition became lesser. This behavior is observed earlier in the research done by Rahimi et al as well [96]. Presence of nanoparticles in electrolytic bath prohibit the diffusion of other metallic ions towards the electrode (affecting their deposition) and their higher concentration makes this effect more profound in composite coatings which added to the reason why there appears a drastic propertied change in coatings containing the varied nanoparticle concentrations [123]. Other studies regarding this effect has been reported as

well by Boonyongmaneerat, Y., et al and Low, C.T.J., et al [124, 125]. Results obtained in our case are in accordance with the above mentioned effect.

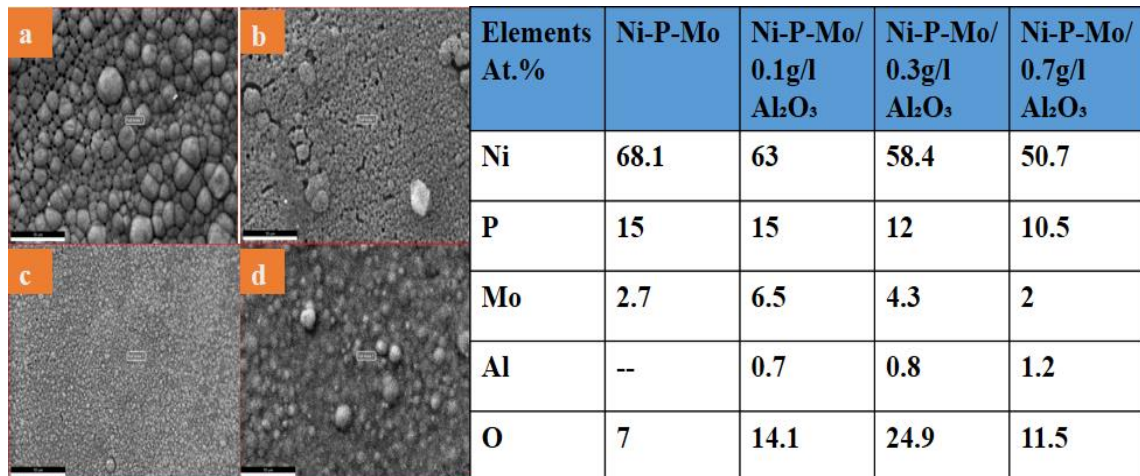


Figure 16: EDS images of (a) Ni-P-Mo alloy coating (b) Ni-P-Mo/0.1 g/l Al₂O₃ (c) Ni-P-Mo/0.3 g/l Al₂O₃ (d) Ni-P-Mo/0.3 g/l Al₂O₃ along with atomic percentages of elements present in all coatings

Figure 17 shows the elemental peaks of a composite coating confirming the alumina presence in the coating. Fe and Cu presence came from the substrate.

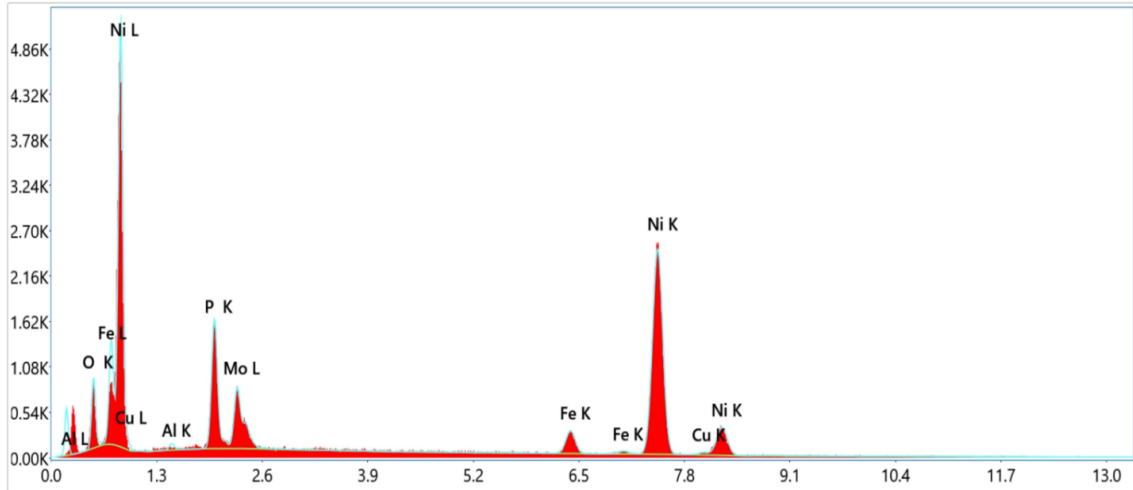


Figure 17: Elemental peaks of Ni-P-Mo/0.3 g/l Al₂O₃ composite coating

4.2 Surface roughness

Roughness is an important factor while describing the coating surface properties. Two different scales were utilized while taking the Roughness measurements of all samples.

One is in micro-meter (Optical Profilometry) and other is in more precise nanometer scale (AFM). Roughness values obtained on both scales show the composite coatings to be rougher than alloy one. Ni-P-Mo 0.3g/l Al₂O₃ has the lowest roughness among all composite coatings but greater than the Ni-P-Mo alloy coating. Alumina nanoparticles deposition in Ni coatings causes the disturbance in Ni coating's usual surface structure resulting in enhancement of surface roughness along with micro-crystallinity [126]. Presence of nano-particles causes the nucleation rate to enhance as can be seen in **Figure 15** (b to d) which in return increases the surface roughness. From **Figure 18**, Ni-P-Mo 0.3g/l Al₂O₃ coating has the lowest Ra (μm) value among composite coatings due to comparatively homogeneous and smooth surface with lowest asperities (i.e., cracks, porosity, pinholes). In Ni-P-Mo 0.3g/l Al₂O₃ composite coating, due to nano-particles agglomeration, surface asperities and coarseness enhances causing the roughness values to increase as well. Our results are in accordance with the studies done by Allahyarzadeh, M., et al. [127, 128] [129], Borkar, T., et al. by the addition of reinforcements in Ni composite coatings [130], Nicolenco, A., et al. by the addition of alumina sub-micron particles in Fe-W matrix [101], and Karthikeyan, et al., by incorporation of alumina nanoparticles into Ni-P coatings [131] as well.

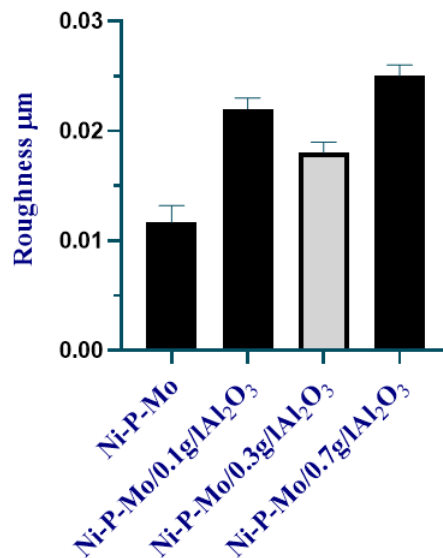


Figure 18: Surface roughness trend of all samples

AFM studies were conducted in order to have a lucid idea about the change in surface roughness values at smaller scale i.e., in nanometers of composite coatings as the amount of alumina nanoparticles increased from 0.1 to 0.7 g/L. Results obtained from AFM show similar trend as obtained from profilometry. AFM images of all coatings are given in **Figure 19**. From these images differences in surface morphologies of all samples could be seen. Among composite coatings, Ni-P-Mo/0.3g/l Al₂O₃ has the lowest Ra (nm) value, compared with Ni-P-Mo/0.3g/l Al₂O₃ and Ni-P-Mo/0.7g/l Al₂O₃ therefore, showing smooth surface morphology. The reason could be higher grain refinement, dense and comparatively lesser surface defects like cracks or micro-porosity than the rest of composite coatings as can be seen from **Figure 15 (c)**. In Ni-P-Mo/0.7g/l Al₂O₃ because of particles agglomeration (due to increase in their concentration), generating micro porosity and cracks which also led to increase in roughness value from **figure 19 (d)**, where surface clearly has more spikes than the rest. Supported by research done by Grewal, H.S., et al. who states the brittle nature of Al₂O₃ nanoparticles and their possible effect over coating appliance which results in high surface roughness and porosity as the content keeps on increasing [132].

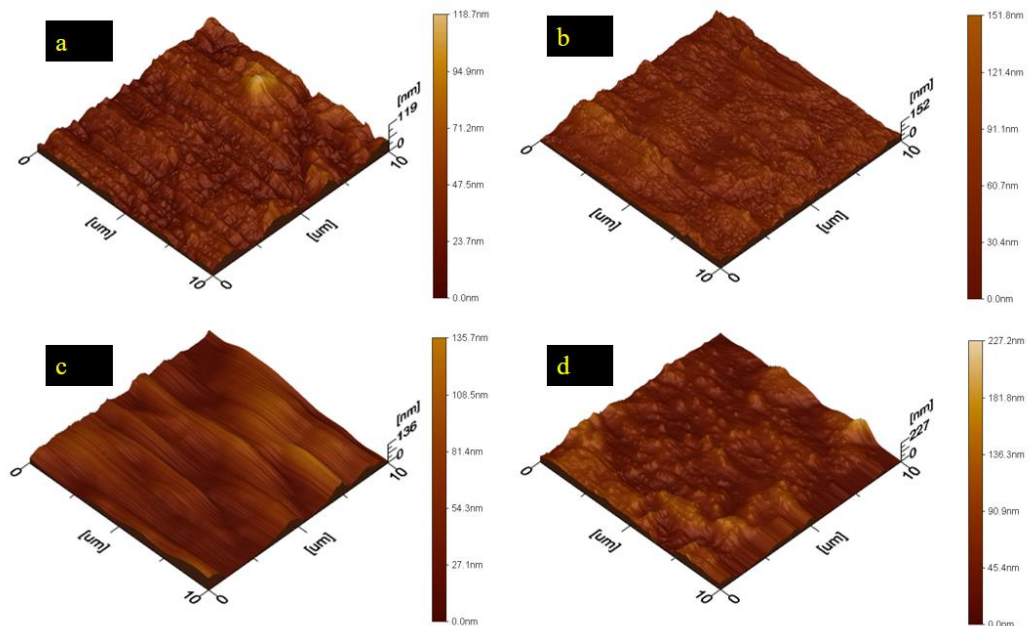


Figure 19: AFM analysis (a) AFM image of Ni-P-Mo alloy coating (b) AFM image of Ni-P-Mo/0.1g/l Al₂O₃ (c) AFM image of Ni-P-Mo/0.3g/l Al₂O₃ (d) AFM morphological image of Ni-P-Mo/0.7g/l Al₂O₃

Roughness increases with alumina presence as compared with coating without alumina but difference in values is not high. As increment in reinforced particles beyond certain concentration occurs surface roughness does not vary much due to low heterogeneity according to Shi, X., et al. [133]. Which is in accordance with our results as there is not much difference between the roughness values of composite coatings as shown in **Figures 18 and 19** as well. Therefore the amount of alumina nanoparticles must be in a certain range to get best possible results as over incursion causes issues like porosity due to agglomeration and micro cracking declining the coating properties. Roughness values obtained from AFM are given in **Table 10**.

Table 10: Ra (nm) values obtained from AFM testing

Samples	Ra (nm)
Ni-P-Mo	11.9
Ni-P-Mo/ 0.1g/l Al ₂ O ₃	23.1
Ni-P-Mo/ 0.3g/l Al ₂ O ₃	18.1
Ni-P-Mo/ 0.7g/l Al ₂ O ₃	26.1

4.3 Mechanical testing

Micro-Vickers hardness

Similarly, by the addition of alumina nanoparticles in coatings, hardness increases enviably. As all composite coatings have higher hardness values than the Ni-P-Mo alloy coating. In composite coatings increment in hardness values with the alumina nanoparticles concentration is because they are hard in nature, and impede the movement of dislocations by residing at grain boundaries limiting the plastic deformation to occur in the coatings. Supported by the research done by Goral, A., which stated that addition of Al₂O₃ nanoparticles in to Ni-based coatings led to increment in hardness considerably. This increase in micro-hardness is attributed to the effect of dispersion hardening caused by Alumina nanoparticles in Ni-matrix explained by Orowan theory [134]. Another reason for this increase in micro-hardness values of composite coatings than alloy coatings is the increase in nucleation rate and grain refinement by the addition of nano-reinforcements. As previously reported by Mousavi, S.R., that enhancement in nucleation sites occurs due

to increment of Alumina nanoparticles which causes the grain refinement resulting in hardness enhancement of coatings [135]. In composites due to dominance of directional covalent bonds, plastic deformation and movement of dislocations gets restricted which is another reason for hardness enhancement in coatings [136]. Li, C., et al. [137] explained the similar pinning effect by the addition of Nano-reinforcements.

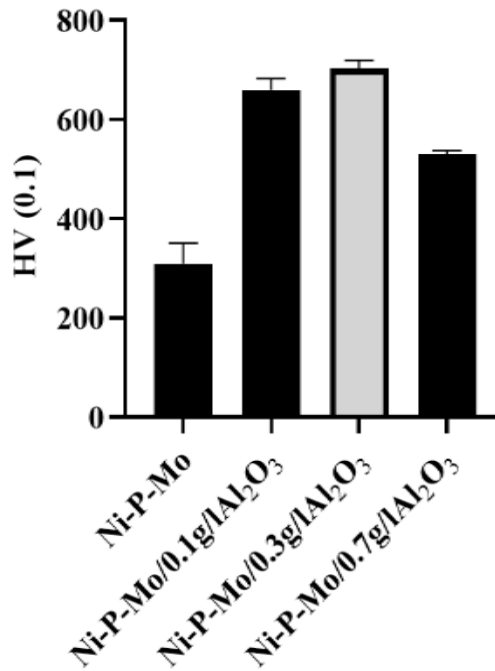


Figure 20: Micro-hardness trend

From **Figure 20**, graph shows the hardness values of all composite coatings obtained from Vickers hardness tester compared with alloy hardness value. Coating containing highest alumina particle concentration shows dip in hardness value to 530 (HV 0.1) as compared with rest. This decrement in hardness value is due to higher surface roughness and asperities caused by particle agglomeration due to increased particle concentration.

Nano-indentation

Hardness values were obtained in nanometer scale by Oliver and Pharr method which is a load controlled depth sensing instrument for more precise results. In composite coatings

alumina Nano particles play pivotal role in hardness and elastic strain increment. Hardness, Elastic Modulus and strain values of composite coatings are given in **Table 11**.

Table 11: Nano-indentation data

Samples	Hardness (GPa)	Elastic modulus (GPa)	H/E
Ni-P- Mo	3.39	107	0.03
Ni-P-Mo/0.1g/l/Al ₂ O ₃	7.02	132.27	0.052
Ni-P-Mo /0.3g/l/Al ₂ O ₃	7.20	120.28	0.06
Ni-P-Mo /0.7g/l/ Al ₂ O ₃	5.41	115.35	0.04

While analyzing the nano-indentation data the foremost factors that we need to consider are area under the curve and the indentation depth by berkovich tip in to the coating surface. Max. Load of 5mN was applied for the indentation purposes. According to **Figure 21 (b)**, Ni-P-Mo alloy coating with Max. Depth of 290nm has more indentation depth and area under the curve as compared with the composite coatings. Min. Depth penetration was 181nm of composite coating containing 0.3 g/l alumina nanoparticles concentration. This decrease in penetration depth and area under curve of composite coatings depict their higher resistance towards the plastic deformation and high mechanical strength as compared to bare HSLA and Ni-P-Mo alloy coatings [57]. Turbulence in curves shows that coatings have high surface roughness and are not entirely free of defects. These hard alumina particles impede the dislocation movement and provide coating resistance to deform to have higher strain values as well. Apart from this in composite coatings nano or micro particles addition fills the gap or porosity if present hence making the coatings more compact and dense

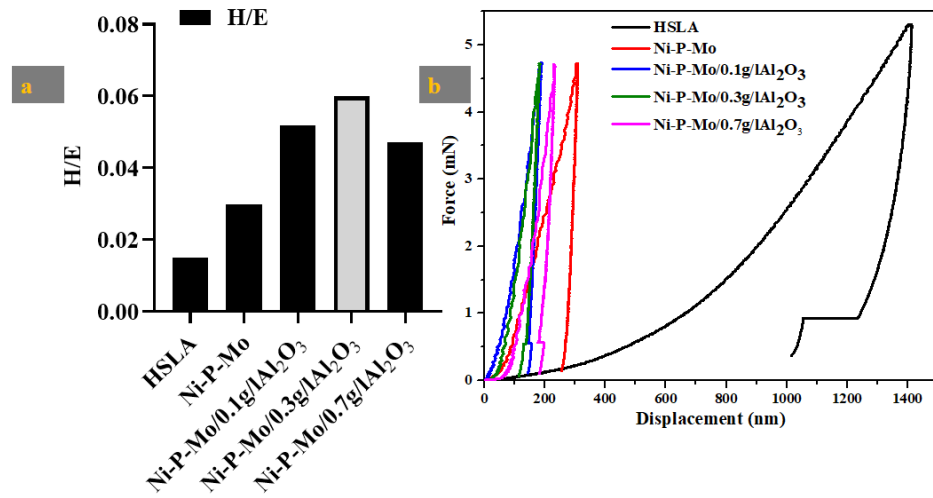


Figure 21 (a) Elastic strain (H/E) trend (b) Force vs. Displacement curves of all samples

structured which results in increase of hardness values and modulus as well [138] as can be seen from **Figure 15**. From **figure 21** (a) Ni-P-Mo/0.3g/l Al₂O₃ has the highest elastic strain value. Increment in hardness values is due to lower surface discontinuous and dispersion hardening by the presence of hard reinforced phase in the matrix. How much reinforcement is added and how uniformly it is distributed are among the deciding factors while discussing enhancement in hardness as explained by Balaraju, J.N., et al [139] as well. In Ni-P-Mo/0.7g/l Al₂O₃ having highest alumina content depreciation in hardness and strain values is distinct because of rise in surface roughness and surface asperities. If higher hard particles insertion occurs, particles agglomeration and internal stress relaxation occurs in coating surface results in decrement or gradual fall of properties. Locking and unlocking theory of dislocations explains the yielding phenomenon that occurs during applied stress. As liberation of dislocations and formation of new ones and their multiplication process extends from grain to grain in presence of stress leading to low areas (or areas such as pop-ins) or decrease in values [140]. In order to determine the wear resistant properties of a material, H/E elastic strain to failure factor considered to be an important indicator. More robust and long lasting coatings would have higher H/E value that it has more resistance to deformation or wear [141, 142]. Study done by

Nicolenco, A., et al. shows H/E ratio to be an important parameter as well in determining wear resistance of materials i.e. higher H/E ratio should have lower wear rates and deformation [101]. Which are very much in accordance to our wear results from **table 12** as Ni-P-Mo/0.3g/l Al₂O₃ alumina has the highest H/E ratio as well as highest wear resistance among composite coatings.

4.4 Tribological testing wear analysis

According to the obtained results, Ni-P-Mo/Al₂O₃ composite coatings proves to be more wear resistant than Ni-P-Mo alloy coating. Relatively in composite coatings grain refinement and nucleation rate increases due to incursion of nanoparticles in the coatings which impede the dislocation movements and hence enhances the hardness and wear resistance would be higher as compared with alloy coatings. Wear rates and Co-F values of composite coatings are given in **Table 12**.

Table 12: Wear rate and Co-F values of all samples

Samples	Wear rates (mm ³ /mm)	Av. CoF
HSLA	5.0081E ⁻⁶	0.1166
Ni-P-Mo	5.28E ⁻⁸	0.4369
Ni-P-Mo/0.1g/l Al ₂ O ₃	1.04E ⁻⁸	0.69
Ni-P-Mo/0.3g/l Al ₂ O ₃	0.373E ⁻⁸	0.459
Ni-P-Mo/0.7g/l Al ₂ O ₃	19.4E ⁻⁸	0.747

Wear rate of Ni-P-Mo/0.7g/l Al₂O₃ is highest due to its higher surface roughness and Co-friction which led to higher micro-asperities than the rest of composite coatings and it has lowest hardness and modulus as well. Higher wear rates could be due to micro-cracks, stresses and higher coefficient of friction value as explained by delamination theory stated by Suh et al. [143] as well. Another reason for high coefficient of friction and wear rate could be the presence of debris which enhances the sternness among contacting surfaces [101]. According to study done by Luo, et al. nanoparticles are highly reactive that their chemical interactions and agglomeration could occur if higher amount is incorporated in coatings. Dislocations unlocking and locking and nucleation could be an issue as well in

decrement of mechanical properties if hard particles are incorporated [144]. Singh, et al. and Zawawi et al. suggested the certain incorporation of nanoparticles concentration in coatings for better performance as well [145, 146]. In our results wear phenomenon transforms from abrasive-adhesive to abrasive as the incorporation of alumina in coating is enhanced along with hardness which is similar to the findings by Luo, et al. [142] and by Allahkaram, et al. [147] as well who states that Abrasive wear is dominant at higher alumina nanoparticles concentration. H/E (elastic strain) of Ni-P-Mo/0.3g/l Al₂O₃ is higher among other coatings (in figure 21) which in turns comparable to the wear results as wear resistance of this sample amplified as can be seen in **Figure 22 (b)**.

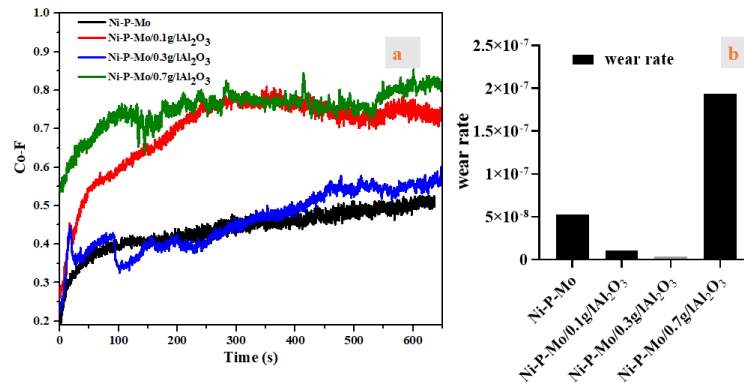


Figure 22: (a) Co-F vs. time plot for all samples (b) wear rates of all samples

Furthermore, this improvement in wear resistance is mainly due to dispersion hardening restricting the deformation or wear and grain refinement as could be seen in **figure 15 (c)**. However static Co-F rise in alumina reinforced coatings could be due to the high surface roughness values as previously reported by Allahyazadeh, et al. [128]. Increase and decrease in different sliding speeds could influence the friction as well, so it could not be constant [148]. Alumina particles transform the wear process from adhesive to rolling one which in turn reduces the wear rate [149].

4.5 Electrochemical Corrosion Behaviour

In Ni-P-Mo alloy and composite coatings, Mo and Alumina nanoparticles play an important role in improving the corrosion performance. Here Mo amount is kept constant so the improvement in corrosion performance is certainly because of Alumina nanoparticles. Icorr and C.R. (mpy) values of composite coatings are given in **Table 13**. Composite coatings have more chemical stability than alloy coatings hence help prevent localized corrosion as reported by Ranganatha, et al. [150].

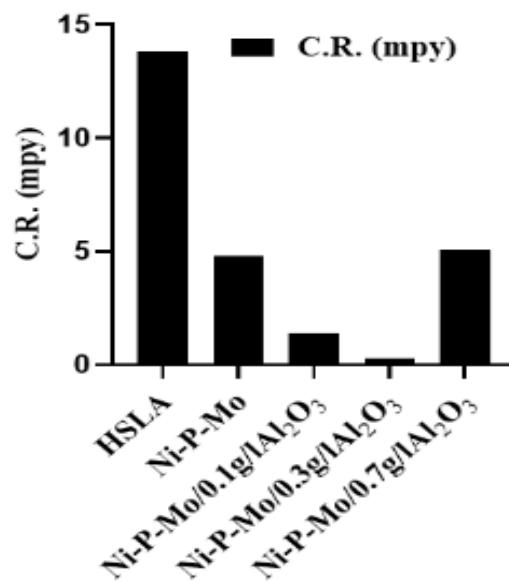


Figure 23: Comparison of corrosion rates of all samples

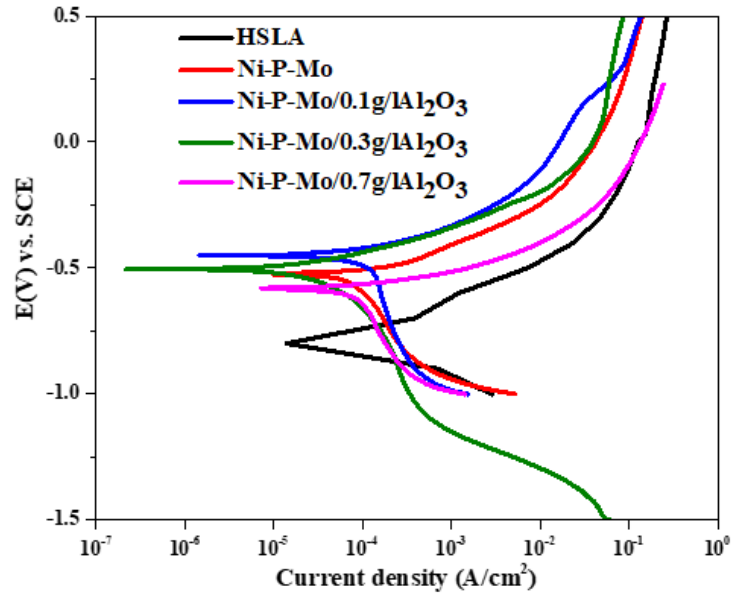


Figure 24: Tafel plots of all coatings

Corrosion mechanism in pores enhances preferentially as cationic dissolution occurs leading to formation of metal hydroxide and ultimately becoming a source for hydrogen evolution as in formula 5 [151, 152] given below:



Corrosion further deepens along the pore as salt solution acidity increases. Therefore more the pores a surface has, more would be the initialization points for localized corrosion to occur [153]. In composite coatings, alumina nanoparticles fill up the coating gaps, cracks or free areas making it to be denser and compact which results in improvement in hardness as well as corrosion values can be seen from **Figure 23** where lowest corrosion value is of Ni-P-Mo/ (0.3g/l) Al₂O₃ having smoother surface compared with rest of composite coatings. Small concentrations of alumina nanoparticles act as a barrier for corrosive media by minimizing the path ways through the coatings [154]. Alumina nanoparticles act as controlling species for electrochemical reactions by reducing the pore density and sizes hence decreasing the rise of corrosion [121]. Ni-P-Mo/ (0.7g/l) Al₂O₃ has the highest corrosion rate of 5.1 mpy and major reasons could be higher surface defects and agglomeration of nano-particles given in **Table 13**. Corrosion improvement in composite coatings could be due to labyrinth effects as well caused by the presence of nano-particles

[155]. Addition of second phase particles could cause more corrosion if not incorporated in certain concentrations due to high surface roughness. When the coating is crack free or more compact and finer, then it would be more water-repellent so surface would be less likely exposed to the aqueous environment [137]. That's why coating having high surface roughness values are drier and would be less water repellent hence corrosion performance will be compromised.

Table 13: Electrochemical testing values

Samples	I_{corr} (A/cm²)	C.R (mpy)
HSLA	30E ⁻⁶	13.8
Ni-P-Mo	10.5 E ⁻⁶	4.8
Ni-P-Mo /0.1g/l Al ₂ O ₃	3.4E ⁻⁶	1.4
Ni-P-Mo /0.3g/l Al ₂ O ₃	0.28E ⁻⁶	0.3
Ni-P-Mo /0.7g/l Al ₂ O ₃	11E ⁻⁶	5.1

Conclusions:

Successful electro-deposition of Ni-P-Mo alloy and Ni-P-Mo/Al₂O₃ composite coating on HSLA steel samples was achieved along with promising and positive results in terms of its mechanical wear and corrosive properties. Following conclusions were drawn:

- Nucleation rate enhances as we add alumina nano-particles as they act as nucleation sites hence helps to improve the grain refinement of composite coatings
- Hardness and wear properties were considerably improved by addition of Alumina Nano-particles in Ni-P-Mo coatings as compared with bare HSLA steel and simple Ni-P-Mo alloy coatings.
- Comp. 0.3g/l showed the best hardness and wear resistant values. Whereas Comp.0.7 g/l showed the lowest hardness and wear resistant values among composite coatings mainly due to agglomeration of particles due to high concentration and high surface Co-F and roughness
- Corrosion resistive properties were also enhanced by the addition of these Nano-particles.
- Comp. 0.3g/l has best corrosion resistant value of 0.3 mpy and Comp. 0.7g/l has highest value of 5.1 mpy
- Excessive amount of these particles proved to be detrimental to properties.

Further studies need to be done on effects of heat treatment and change of different process parameters on properties of these composite films.

Future recommendations

Following are some of the recommendations for future work/research in this field of study:

- Effect of heat treatments on the behavior and properties of these alloy and composite coatings on HSLA substrates needs to be explored further.
- Effect of different processing parameters while coating of substrates needs to be checked as well. For example, current density plays a crucial role in coating quality and adhesion, temperature needs to be consider as well.
- Double layered coatings using this composite and alloy on different substrates could be studied showcasing the dynamics among multiple interfaces and their overall impact on the coating properties.

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