TRIBOLOGY OF DUPLEX ELECTROLESS NICKEL COATINGS

Thesis submitted by

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v. Palash Biswas, Suman Kalyan Das, and Prasanta Sahoo, “Duplex Electroless Ni-P/Ni-P-W coatings: Effect of Heat Treatment on Tribological and Corrosion Performance” International Conference on Recent Advances in Engineering Materials (ICRAEM 2022) March 3-5, 2022, Alva’s Institute of Engineering and Technology, Moodbidri, Karnataka, Paper ID: REAM 4088

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STATEMENT OF ORIGINALITY

I, Palash Biswas registered on 27.04.2018 do hereby declare that this thesis entitled **“Tribology of Duplex Electroless Nickel Coatings”** contains literature survey and original research work done by the undersigned candidate as part of Doctoral studies.

All information in this thesis have been obtained and presented in accordance with existing academic rules and ethical conduct. I declare that, as required by these rules and conduct, I have fully cited and referred all materials and results that are not original to this work.

I also declare that I have checked this thesis as per the “Policy on Anti Plagiarism, Jadavpur University, 2019”, and the level of similarity as checked by iThenticate software is 3%.

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About the Author

The author, Sri ***Palash Biswas*** was born in the village of West Barasat in North 24 Parganas District of West Bengal in the year 1985. He did his B. Tech in Mechanical Engineering from Kalyani Government Engineering College, (under West Bengal University of Technology, now Maulana Abul Kalam Azad University of Technology) Kalyani, in 2009. In 2011, he completed Masters of Mechanical Engineering under the specialization of Production Engineering from Bengal Engineering & Science University, Shibpur, (now Indian Institute of Engineering Science and Technology, Shibpur), West Bengal. He is currently engaged as an Assistant Professor in the Department of Mechanical Engineering, JIS College of Engineering, Kalyani, West Bengal.

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Palash Biswas

Palash Biswas

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To
Ma, Baba and my beloved son

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ABSTRACT

The present thesis deals with the tribological behaviour assessment of duplex electroless nickel coatings. To improve the hardness, wear, and corrosion resistance of substrate materials, the duplex electroless nickel coatings are developed on mild steel substrates. Duplex electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P and Ni-P/Ni-Mo-P coatings are developed using dual bath technique. For each set of coatings, two types of coatings are deposited with Ni-P as the inner layer and alternately with Ni-W-P or Ni-Cu-P or Ni-Mo-P as the outer layer. As heat treatment conditions are reported to influence the properties of the coating, the coatings are subjected to heat treatment at temperatures from 200 to 800°C and for 1-4h durations. The effect of heat treatment on the microstructural characteristics of the coatings was investigated by using scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) analysis. The influence of heat treatment conditions on microhardness, friction, wear, and corrosion behaviour is studied comprehensively. Heat treatment is found to have a beneficial impact on the coating with the formation of harder crystalline phases. Both microhardness and wear resistance of the electroless Ni-P/Ni-W-P and Ni-P/Ni-Cu-P coatings increase significantly when heat treated at 400°C temperatures for 1h duration. However, there is a degeneration in the microhardness when the coatings are heat treated beyond 400°C and for longer durations. This is due to coarsening of grains together with the formation of oxides, as indicated by the microstructural studies. For Ni-P/Ni-Mo-P (Ni-Mo-P as outer layer) coating, the highest microhardness, and the lowest wear rate however is obtained when heat treated at 600°C temperature for 1h duration. This is due to the formation of hard crystalline phases like nickel phosphide phase (Ni_3P) and nickel-molybdenum (Ni-Mo) phases. At a heat treatment temperature of 800°C for 4h, all the coatings exhibit cracks and tends to delaminate. The wear mechanism encountered during the sliding test under dry conditions and at room temperature is predominantly abrasive but there are signatures of adhesive wear as well. The electrochemical-based corrosion studies indicate that corrosion resistance of the present duplex coatings increases after heat treatment.

In general, it is found that the coatings with Ni-W-P, Ni-Cu-P or Ni-Mo-P as the outer layer outperforms those with Ni-P as the outer layer. The tribological behavior of these coatings is influenced by several factors which include the coating composition, heat treatment temperature, heat treatment time duration, etc. Above 400°C temperature, all the duplex coatings formed a hard Ni_3P, which is beneficial for developing wear resistance. At 400°C temperature for Ni-P/Ni-Cu-P coating, a few copper phosphide phases are obtained with Ni_3P and NiCu phases. For Ni-P/Ni-Mo-P coatings, Ni-Mo phases are also observed at the above conditions. At 400°C temperature for 1h

duration, Ni-P/Ni-W-P plating revealed the highest microhardness and lowest wear rate among all duplex coatings. In as-deposited coatings, Ni-P/Ni-Cu-P duplex coating obtained higher corrosion resistance than other duplex coatings. The comparison between the performances of the present duplex coatings to the constituent binary coatings reveals that the duplex coatings performed better in all aspects compared to their binary constituents. This may be attributed to each layer complementing the functions of the other as well as the excellent adhesion between the two layers.

To have a comparison with the conventional electrodeposited coatings, the overall best performer i.e. Ni-P/Ni-W-P duplex coating is developed though electrolytic method. The coating is also subjected to similar heat treatment conditions and all the mechanical and metallurgical characterisations are carried out. Mostly, the electroless and electrodeposited Ni-P/Ni-W-P coating display similar trends in terms of microhardness and wear performance. However, electroless Ni-P/Ni-W-P coating performed better than electrodeposited coating in all aspects and conditions. Both the system obtained optimal microhardness and lower wear rate at 400°C heat treatment temperature. At higher temperature (800°C) and for longer duration (4h), duplex electrodeposited coating also showed cracks and higher amount of oxide formation that negatively affects its mechanical, tribological and corrosion properties.

Overall, it is found that upon being subjected to the optimal condition of heat treatment, the duplex electroless coating presents an all-around performance that may be suitable for applications demanding both wear and corrosion resistance.

Chapter 1

Introduction

Outline of the chapter: *1.1 Introduction, 1.2 Popular Coating Techniques and their applications, 1.2.1 Electrodeposition, 1.2.2 Electroless nickel coating, 1.2.3 Anodizing, 1.2.4 Galvanizing, 1.3 Need for Duplex and Multilayer coatings, 1.3.1 Electroless Duplex coating, 1.3. Duplex Electrodeposited nickel and alloy coatings, 1.4 Present Work, 1.5 Structure of the thesis, 1.6 Closure.*

1.1 Introduction

Tribology is derived from the Greek word tribos which means to rub. Tribology is the science and technology of interacting surfaces in motion. It is an important part of mechanical engineering that deals with friction, wear, and lubrication. It is a multidisciplinary field that incorporates materials science, chemistry, physics, biology, mathematics, and engineering. Tribology is of utmost importance because it provides information that teaches how to regulate friction and wear with lubricants. It uses operational analysis to assess important economic features like maintainability, reliability, and wear on technological equipment ranging from simple domestic appliances to complex aircraft. Tribological behaviour is determined by the material's surface, with or without the influence of the environment. A material with adequate tribological features, on the other hand, may lack certain bulk properties, restricting its use. Hence, various surface engineering techniques are adapted which modify the surfaces suitably so that they imbibe favourable tribological characteristics.

1.2 Popular Coating Techniques and their applications

Coating is one of the widely utilized surface engineering approaches in order to protect or change surface characteristics based on need. Electroless nickel coating is one of the proven methods for improving the mechanical, corrosion, and tribological properties of surfaces **(Fayomi et al., 2019)**. Electroless nickel coating on mild steel protects it from corrosion and wear. This coating also improves the surface hardness of steel. This coating is very popular because of its splendid hardness, better resistance to corrosion and wear as well as consistent coating deposition. Electroless nickel coating is one of the best techniques to change the physical and mechanical properties of the surface of substrate materials (**Biswas et al., 2017).**

It can be uniformly deposited on any material even with irregular shape and size. The coating may be applied to ferrous and nonferrous surfaces as well as a wide spectrum of alloys.

However, the electroless technique has been recognized for its better wear and corrosion resistance. Special applications where the electrolytic method is inconvenient, include electronics, vehicles, turbines, motor machinery, valves, pumps, nuclear power generation, aerospace, electrical/mechanical tools, driveshafts, oil field valves, and engineering equipment, etc., (**Bell et al., 1998; Sahoo and Das, 2011**). In fact, electroless nickel deposits are found to be bio-compatible offering resistance against bacterial growth.

Coatings are mostly used in industries to prevent corrosion. Equipment's that has been subjected to corrosion may need to be repaired or replaced. Therefore, from an economic perspective, equipment corrosion is very harmful to every industry. Currently, a variety of methods are utilized to prevent metal from corroding, including metal spraying, vapor deposition, electroplating, and electroless deposition. Many metallic coatings are typically porous by nature and historically have been of little benefit in terms of their ability to prevent corrosion. Electroless nickel coating mostly prevents corrosion by barrier protection phenomenon besides forming passive films. Figure 1.1 shows the primary applications of electroless nickel coatings (source: www.pfonline.com).

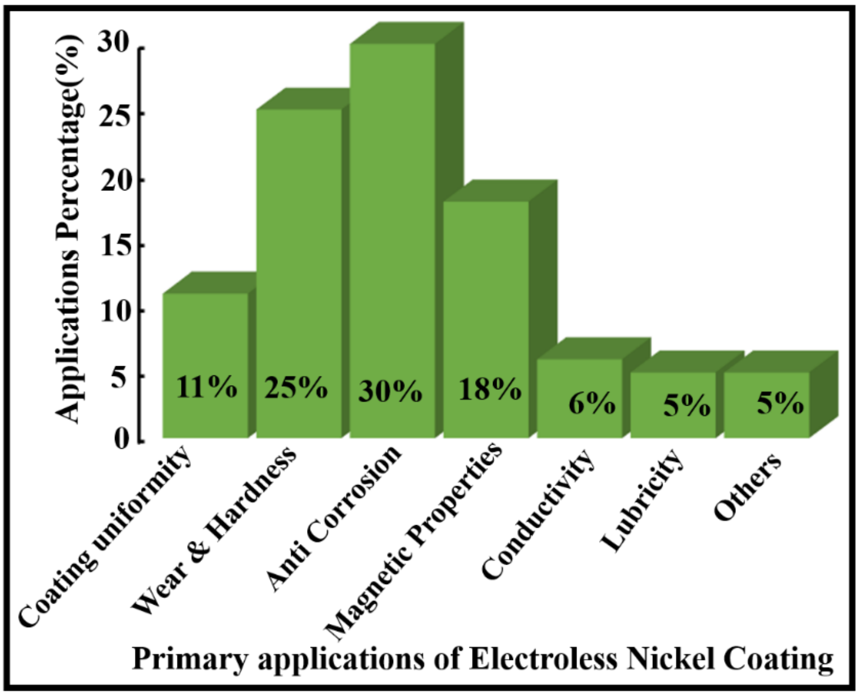

Figure 1.1 *Primary applications of electroless nickel deposits (source: www.pfonline.com)*

1.2.1 Electrodeposition

The electrolytic or electrodeposition approach is currently the most extensively utilised coating deposition technology. It is a process that uses an electric current to deposit a metal onto a substrate. The metal is dissolved in an electrolyte solution, and the current causes the metal ions to be reduced to metal atoms at the surface of the substrate. Electrodeposition is a versatile process that can be used to deposit a wide variety of metals, including copper, nickel, zinc, and chromium. The process is also relatively inexpensive and easy to scale up **(Nava et al., 2013; Yusuf et al., 2018)**. Here are some of the most common applications of electrodeposited coating:

- **Corrosion protection:** Electrodeposited coatings are often used to protect metals from corrosion. The coating can provide a barrier between the metal and the environment, preventing the metal from reacting with oxygen and other corrosive elements.
- **Wear resistance:** Electrodeposited coatings can also be used to improve the wear resistance of materials. The coating can fill in microscopic cracks and imperfections in the surface of the substrate, making it more resistant to wear.
- **Electrical conductivity:** Electrodeposited coatings can be used to improve the electrical conductivity of materials. The coating can provide a conductive path between different parts of the substrate, improving the electrical performance of the material.
- **Decoration:** Electrodeposited coatings can also be used for decorative purposes. The coating can be used to add colour, lustre, or other aesthetic features to a material.

1.2.2 Electroless nickel coating

Electroless nickel coating is a process for depositing a nickel alloy from aqueous solutions onto a substrate. Brenner and Riddell invented this method of deposition **(Brenner and Riddell, 1946)**. There is no electricity required for electroless nickel coating, due to an autocatalytic reduction process. The process involves dipping the substrate in a water solution containing nickel salt and a reducing agent, usually a hypophosphite salt. The nickel ions in the solution are reduced to metallic nickel by the reducing agent, and the metallic nickel is deposited on the surface of the substrate. The thickness of the coating can be controlled by varying the time the substrate is immersed in the solution, and the properties of the coating can be varied by adjusting the composition of the solution. Electroless nickel coating is practiced widely as it provides several advantages over conventional coating techniques. Electroless nickel coatings are typically used for their corrosion resistance, wear resistance, and electrical conductivity. They can be applied to a variety of metal substrates. Some of the benefits of electroless nickel coating are as follows:

- **Wear resistance:** Electroless nickel coatings are resistant to wear, making them ideal for use in high-impact or high-friction applications.
- **Corrosion resistance:** Electroless nickel coatings are highly resistant to corrosion, making them ideal for use in harsh environments.
- **Electrical conductivity:** Electroless nickel coatings are highly conductive, making them ideal for use in electronic applications.
- **Appearance:** Electroless nickel coatings can be applied to a variety of metal substrates, and they can be fabricated in various textures.

1.2.3 Anodizing

Anodizing is an electrolytic passivation technique used to give metal surfaces a thicker layer of natural oxide. Anodizing improves the material's resilience to wear and corrosion and improves paint primer and glue adhesion compared to bare metal. Anodic films can be utilized for a variety of cosmetic effects, such as adding reflected light wave interference effects or thick porous coatings that can absorb dyes. In addition, anodizing is utilized to provide dielectric coatings for electrolytic capacitors and stop threaded component galling. Although procedures for titanium, zinc, magnesium, niobium, zirconium, hafnium, and tantalum also exist, anodic coatings are most frequently used to protect aluminium alloys. When iron or carbon steel metal is oxidized under neutral or alkaline micro-electrolytic conditions, it exfoliates. This means that iron oxide, ferric hydroxide, or hydrated iron oxide, commonly referred to as rust, forms by large cathodic surfaces and anoxic anodic pits. These pits concentrate anions like sulfate and chloride, which accelerates the corrosion of the underlying metal. High-carbon steel, cast iron, and other iron and steel materials may contain carbon flakes or nodules that could interfere with coating or plating processes and create an electrolytic potential. To create hard, black Iron (II, III) oxide, ferrous metals are often anodized electrolytically in nitric acid or by treatment with red-fuming nitric acid. Even after plating this oxide onto the wiring and bending the wiring, it maintains its conformity.

The process of anodizing modifies the metal's surface's microscopic roughness as well as its surrounding crystal structure. Sealing is frequently required to achieve corrosion resistance because thick coatings are typically porous. Aluminium surfaces that have been anodized, for instance, have a higher hardness than aluminium but a low to moderate wear resistance that can be enhanced by adding thickness or using the right sealing agents. Most paints and metal platings are not nearly as robust and adhesive as anodic films, but they are also more brittle. This increases their vulnerability to thermal stress cracking but decreases their likelihood of peeling and cracking due to aging.

1.2.4 Galvanizing

Galvanizing is the process of applying a protective zinc coating on steel or iron, to prevent rusting. Zinc coated components are called galvanised components. The quality of coating depends on the process by which the zinc is applied and can be controlled by controlling the process parameters of that method. In general, electrodeposited coatings are thin and more uniform in thickness and have good reflectivity or shining. Hot dipped coatings are thick and slightly non-uniform in thickness.

These coating are anodic with respect to iron or steel and protection offered is of a sacrificial cathodic type. Even if the coating is porous, iron or steel is protected from corrosion and the protection continuous upto the last trace of zinc. This coating is widely used on corrugated sheets for building roofs, screws. nuts, bolts, drums and containers for water storages, wires, fencing wires, nails, pipe, tubes etc.

Large quantity of galvanised components are produced by hot-dip galvanizing process. It is the process of immersing iron or steel in a bath of hot, molten zinc to produce a corrosion resistant, multi-layered coating of zinc-iron alloy and zinc metal. While the steel is immersed in the zinc, a metallurgical reaction occurs between the iron in the steel and the molten zinc. This reaction is a diffusion process, so the coating forms perpendicular to all surfaces creating a uniform thickness throughout the part. The three main steps in the hot-dip galvanizing process are surface preparation, galvanizing, and post-treatment. The process is inherently simple, which is a distinct advantage over other corrosion protection methods.

1.3 Need for Duplex and Multilayer coatings

Duplex and multilayer coatings are advanced techniques used in various industries, primarily in engineering, manufacturing, and surface treatment applications. Both methodologies involve applying multiple layers of different materials onto a substrate for enhanced performance, protection, or aesthetic appeal. While they share similarities, there are distinct differences between the two. The two layers often complement each other, with one layer acting as a base or primer coat, while the other serves as a protective or decorative topcoat.

However, the duplex or multilayer electroless nickel coating gives a better performance to prevent corrosion. Also, the multilayer electroless nickel coating is used in various industries for better hardness, lower friction, and better wear resistance. From the tribological viewpoint, electroless nickel coatings provide lower friction and wear rate of the coated materials from the base metal and other deposition methods. Recently, multilayer or duplex coating has been found to improve the physical, mechanical, and tribological properties of monolayer coatings. Duplex electroless nickel coatings are employed in a variety of industries, including hydraulics, nuclear, machinery, automobile surfaces, computers, aircraft structures, pump parts, and engines, for their higher hardness and high wear and corrosion resistance. By using the double bath technique, duplex or graded electroless nickel coating is possible to prepare through consecutive immersions in the respective electroless nickel baths.

The best deposition method for a particular application will depend on the specific requirements of the application. In general, electrodeposition is used for applications where a high-quality coating is required, such as in the automotive and aerospace industries. Electroless deposition is a good choice for applications where it is difficult or impossible to use an electric current, such as in the medical and electronics industries.

1.3.1 Electroless Duplex Coatings

Duplex surface coating is a combined surface treatment method that involves the sequential deposition of two surfaces to produce a coating surface composite for improving the mechanical, tribological, and corrosion properties of the coated surface. A combined effect was obtained in the deposited coating due to the interactions of two different processes **(Bell et al., 1998)**. Electroless nickel plating has widespread applications due to high hardness values, lower wear rate, and better corrosion resistance for uniform coating deposition on any type of irregular shape, surface, or geometry. According to **Aleksinas M.J., 2019**, it has become clear that one type of electroless nickel coating cannot possibly match all the physical, mechanical, and tribological requirements that a particular application may have. This is because applications for electroless nickel coatings are constantly growing. Duplex coatings seem to be a viable answer to this issue. The combined properties of two coatings in a duplex system result in a finished product with enhanced qualities.

Duplex electroless nickel coatings provide a variety of qualities that can lead to the development of numerous novel applications both today and in the future. The metal finishing industry has already employed these coatings viz. [Ni-P/Ni-B, Ni-P/Ni-W-P]. Table 1.1 represents the classification of single layer, duplex and multilayer electroless nickel alloy coatings.

To enhance the below mentioned qualities duplex electroless nickel coating is preferred-

- Improved corrosion resistance
- Better wear resistance
- Better lubricity and release properties
- Longer bath life on aluminum
- More reflective deposits
- Blackening of the deposit

As opposed to single-layer electroless nickel deposits, which might satisfy only one feature listed above but duplex coatings can achieve multiple of them. Multilayer electroless nickel coatings provide better sliding and abrasive wear resistance as compared to any other mono-layer coating. The coefficient of friction is reduced slightly. It provides better corrosion resistance than monolayer coating **(Vitry et al., 2017)**. Today, multilayer electroless nickel coatings are more popular for different industrial applications like automobile, aerospace, food processing, electrical, chemical, etc. The duplex and multilayer electroless nickel coating have been used to improve the corrosion resistance and to modify the mechanical and tribological properties in all aspects. Some of the key features of duplex electroless nickel coating are as follows:

- **Corrosion Protection:** Duplex coatings are particularly effective in environments where corrosion is a concern, such as marine or industrial settings.
- **Adhesion:** The two layers are designed to adhere tightly to each other as well as to the substrate, ensuring long-lasting performance.
- **Versatility:** Duplex coatings can be customized based on the specific requirements of the application, allowing for flexibility in material selection and coating thickness.

Table 1.1 Classification of monolayer, duplex, and multilayer electroless nickel alloy coatings.

Alloy	Coating	References
Binary Alloy	Ni-P	Ramalho and Miranda, 2005; Sankara Narayanan et al., 2006; Palaniappa and Seshadri, 2008; Yan et al., 2008; Sahoo, 2009; Panja et al., 2016; Biswas et al., 2017; Kundu et al., 2018; Buchtík et al., 2019; Wang et al., 2021.
	Ni-B	Vitry et al., 2008; Kanta et al., 2010; Srinivasan et al., 2010; Das et al., 2012; Barman et al. 2019; Mukhopadhyay et al., 2019.
Ternary alloy	Ni-W-P	Lu and Zangari, 2002; Balaraju and Rajam, 2005; Balaraju et al., 2006; Huang et al., 2007; Palaniappa and Seshadri, 2008; Roy and Sahoo, 2013; Biswas et al., 2019.
	Ni-P-B	Stremsdoerfer et al., 2008; Srinivasan et al., 2010; Kundu et al., 2019; Biswas et al., 2021; Lakavat et al., 2022.
	Ni-Cu-P	Ashassi-Sorkhabi et al., 2002; Balaraju and Rajam, 2005; Georgieva et al., 2007; Huang et al., 2007; Liu et al., 2015; Biswas et al., 2021.
	Ni-Mo-P	Chou et al., 2008; Wang et al., 2013; Song et al., 2019; Rosas-Laverde et al., 2020; EL Haloui et al.,2022; Jia et al., 2022.
	Ni-Co-P	Klingenberg et al., 2005; Gao et al., 2007; Huang et al. 2007; Shaffer and Rogers, 2007; Sarkar et al., 2019; Sarkar et al., 2020.
	Ni-P-Sn	Zou et al., 2010; Sahoo and Das, 2011.
Quaternary alloy	Ni-W-Cr-P	Zhang et al., 2008.
	Ni-W-Cu-P	Balaraju and Rajam, 2005; Balaraju et al., 2006.
	Ni-Co-Fe-P	Yang et al. 2012; Sudagar et al., 2013.
Duplex	Ni–P/Ni–B	Sankara Narayana et al., 2003; Zhang et al, 2008; Subramanian and Palaniradja, 2015; Mindivan, 2019.
	Ni-P/Ni-W-P	Hong et al., 2012; Selvi et al., 2014.
	Ni-P/Ni-Mo-P	Liu et al., 2016; Liu and Liu, 2017; Song et al., 2017; Hong and QIAN, 2018; Fu et al., 2022.
	Ni-P-ZrO2/Ni-P	Wang et al., 2015.
Multilayer	Ni-P/Ni-B	Vitry and Bonin, 2017.
	Ni–P/Ni/Ni–P	Gu et al., 2005.

The duplex electroless nickel coating, which combines the properties of two coatings within a single system, is particularly find utility in applications necessitating high levels of wear resistance, corrosion resistance, and low friction. Here are some of the specific applications of duplex electroless coating:

- **Automotive Industry:** Duplex coatings are commonly used for automotive parts and components to improve corrosion resistance and prolong the lifespan of vehicles.
- **Oil and Gas Sector:** Pipelines, valves, and other equipment used in the oil and gas industry often undergo duplex coating to withstand harsh operating conditions.
- **Structural Steel:** Duplex coatings are applied to structural steel elements in buildings, bridges, and infrastructure to prevent corrosion and maintain structural integrity.

1.3.2 Duplex electrodeposited nickel and alloy coatings

Duplex electrodeposited nickel coating is a type of nickel coating that consists of two layers of nickel, a semi-bright layer and a bright layer. The semi-bright layer is typically thicker than the bright layer and it provides the coating with its wear resistance. The bright layer gives the coating its shiny finish. The coating protects from corrosion. They are often used in the automotive, aerospace, and electronics industries. Duplex electrodeposited nickel coatings are used in a variety of applications, including: corrosion protection, wear resistance, electrical conductivity and decorative purposes. The advantages of duplex electrodeposited nickel coatings include: excellent corrosion resistance, good wear resistance, high electrical conductivity and attractive appearance. The disadvantages of duplex electrodeposited nickel coatings include: relatively expensive, difficult to apply and can be susceptible to scratching.

Duplex electrodeposited nickel-phosphorus coatings represent an innovative and versatile surface treatment technique utilized in various industrial applications. This process involves the sequential deposition of two distinct layers of nickel-phosphorus onto a substrate, each layer serving specific purposes and offering unique properties. Duplex coatings typically consist of a lower layer of functional nickel-phosphorus alloy followed by a top layer of decorative nickel-phosphorus alloy.

The duplex electrodeposited process begins with the application of the functional nickel-phosphorus layer, which serves as a foundation for the subsequent decorative layer. This lower layer is typically deposited using a plating bath containing nickel and phosphorus ions, along with other proprietary additives. The composition of the nickel-phosphorus alloy can be tailored to meet specific requirements, with phosphorus content typically ranging from 5% to 15%. The functional nickel-phosphorus layer provides several key advantages, including excellent corrosion resistance, wear resistance, and hardness. It also offers good lubricity and solderability, making it suitable for a wide range of engineering and manufacturing applications, such as automotive components, hydraulic systems, and industrial machinery parts.

Following the deposition of the functional nickel-phosphorus layer, the decorative nickel-phosphorus layer is applied. This layer is deposited from a plating bath similar to the one used for the functional layer, but with adjustments made to achieve a bright and lustrous finish. The decorative nickel-phosphorus layer enhances the aesthetic appeal of the coated surface, providing a shiny and reflective appearance. It also offers additional corrosion resistance and wear resistance, further enhancing the durability and longevity of the coated parts. The phosphorus content in the decorative layer is often lower than that in the functional layer, typically ranging from 2% to 8%, to ensure good brightness and leveling properties.

The combination of the functional and decorative nickel-phosphorus layers in a duplex coating offers numerous advantages over single-layer coatings. By utilizing two distinct layers with complementary properties, duplex coatings can achieve superior performance in terms of corrosion protection, wear resistance, hardness, and aesthetics. The functional nickel-phosphorus layer provides robust protection and functionality, while the decorative layer enhances the surface finish and appearance.

Moreover, duplex electrodeposited nickel-phosphorus coatings can be further customized to meet specific application requirements through adjustments in composition, plating parameters, and post-plating processes. Additional treatments such as heat treatment, sealing, or passivation can enhance the performance and functionality of the coated parts, making them suitable for even more demanding environments and applications.

In conclusion, duplex electrodeposited nickel-phosphorus coatings offer a versatile and effective solution for enhancing the performance, durability, and aesthetics of metal components in various industries. By combining the benefits of functional and decorative nickel-phosphorus layers, duplex coatings provide superior corrosion resistance, wear resistance, hardness, and visual appeal compared to single-layer coatings. As such, they have become an integral part of modern surface finishing processes, contributing to the production of high-quality, long-lasting products. Overall, duplex electrodeposition nickel coatings are a versatile and effective type of coating that offers several advantages. They are often used in demanding applications where corrosion resistance, wear resistance, and electrical conductivity are important.

1.4 Present Work

The objective of the present work is to develop duplex electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P coatings and study their microhardness, friction, wear, and corrosion behaviour. The coatings are subjected to heat treatment at temperatures ranging from 200 to 800 °C and for 1-4 h duration. The effect of heat treatment on the microstructural characteristics of the coatings is investigated using Scanning Electron Microscope (SEM), Energy-dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) analysis. The influence of heat treatment conditions on coating performance are also investigated. Further, the best performing duplex combination is deposited electrolytically and its performance compared to that of the corresponding electroless coating.

1.5 Structure of the thesis

The present thesis has been divided into nine chapters. The first chapter introduces the electroless nickel coating, duplex or multilayer electroless nickel coating, and electrodeposited nickel coating. The second chapter presents the literature review of various duplex coatings based on tribological studies. The third chapter deals with the fundamental techniques and experimental details along with coating procedure, chemicals, equipment, and methods of measurement. The results of tribological and corrosion performance of duplex electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P coatings are discussed in chapters four, five and six respectively. The seventh chapter presents the comparative assessment of the developed duplex electroless nickel coatings. The eighth chapter covers the results and discussion of duplex electrodeposited Ni-P/Ni-W-P coating and a comparison with duplex electroless Ni-P/Ni-W-P coating. The final chapter nine provides the conclusion of the present work as well as the future scope in this area.

1.6 Closure

The present chapter gives an introduction to electroless nickel coating and duplex electroless nickel coating along with their advantages. Classification of monolayer, duplex, and multilayer electroless nickel alloy coatings are discussed in this chapter. Also, introduction to electrodeposition method along with its advantages and tribology-based application is presented. Finally, a short description of the current work has also been presented along with the structure of the thesis.

Chapter 2

Literature Review

Outline of the chapter: *2.1 Introduction, 2.2 Roughness evaluation of the coating, 2.3 Effect of heat treatment, 2.4 Hardness evaluation of the coatings, 2.5 Microstructural characterization, 2.6 Study of Tribological Behaviour, 2.7 Corrosion behaviour, 2.8 Applicability from tribological point of view, 2.9 Summary of the literature review, 2.10 Closure*

2.1 Introduction

Duplex electroless as well as electrodeposition nickel coating has evolved into a matured subject of research and development due to its wide range of applications. The choice of nickel as the base metal for deposition has been used by many industries. This is because both electroless and electrodeposited nickel coatings are very much suitable from tribological point of view. This can be attributed to the fact that electroless and electrodeposited nickel coatings can be used to reduce friction, wear, and corrosion rate in the system. It can also improve surface roughness and hardness properties.

2.2 Roughness evaluation of the coating

Roughness is commonly an uninvited attribute. It may cause friction, higher wear rate, fatigue, etc. However, sometimes roughness is more beneficial. Basically, the finished substrate materials are coated by electroless and electrodeposited nickel deposition techniques. Also, electroless and electrodeposited coatings are very uniform deposition process made on the substrate **(Mallory et al., 1990)**. Electroless nickel coatings are known to follow the substrate profile. However, after electroless nickel coating, the roughness becomes relatively lower. In duplex electroless Ni-P/Ni-B coating, the roughness is reported to be lower than in electroless Ni-B coating **(Vitry et al., 2008)**.

2.3 Effect of heat treatment

Heat treatment has a significant effect on the mechanical, tribological, corrosion, and morphological properties of duplex electroless nickel coating **(Ashassi-Sorkhabi et al., 2004)** and electrodeposited nickel coating **(Nava et al., 2013)**. The hardness increases with the increase in heat treatment temperature up to 400°C for 1h duration. Beyond this temperature, hardness decreases **(Biswas et al., 2017).** For Ni-P coating, hardness increases due to the formation of crystalline nickel phosphide (Ni_3P) phases. Higher heat treatment temperature and longer heating duration tend to decrease the hardness of Ni-P coating due to nickel oxide (NiO) formation. For duplex Ni-P/Ni-Mo-P coating, the crystalline nickel phosphide phases are produced at 400°C for 2h duration **(Li et al., 2020).** The corrosion resistance of electroless duplex and multilayer nickel coating is also affected by heat treatment. The higher hardness values and minimum wear rate are revealed at the heat treatment temperature range (from 400-450°C) for 1h duration. The coefficient of friction is also affected by the heat treatment conditions **(Biswas et al., 2017)**.

In the case of electrodeposited nickel coating, the microhardness value is reduced after heat treatment temperature of 500°C for 1h cycle (**Nava et al., 2013**). After 500°C, the hardness value falls drastically due to oxide formation. The coating starts to soften at higher temperatures as a result of the nickel phosphide particles clumping together producing fewer hardening sites. Additionally, the phosphorus present in the alloy is eliminated during this process, creating a distinct phase of soft nickel within the matrix, and lowering the alloy's bulk hardness.

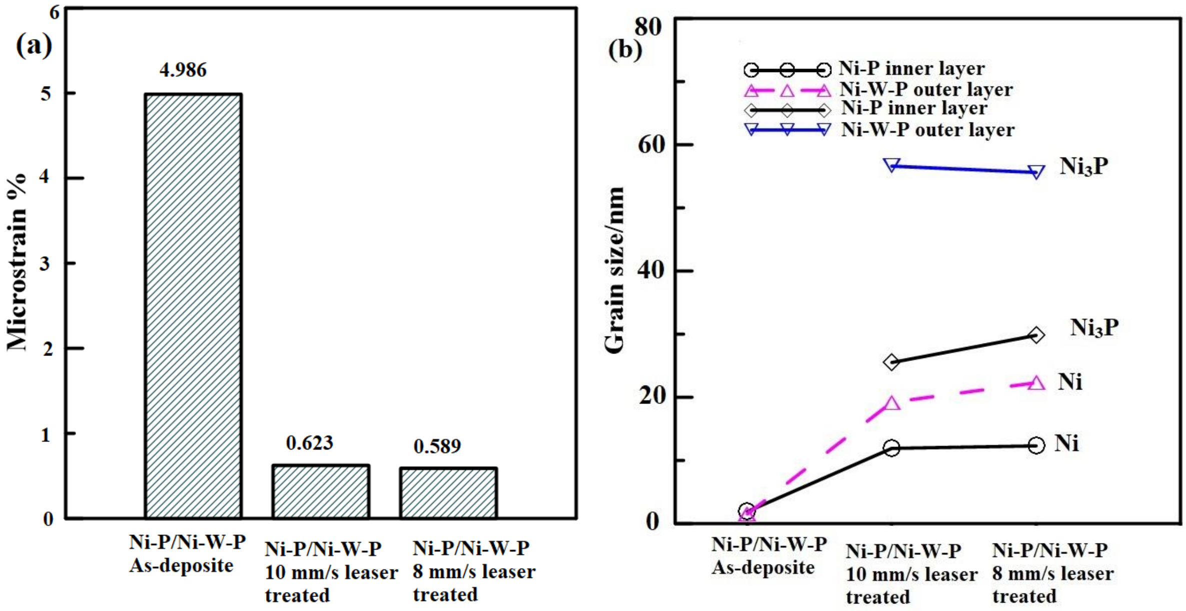

Figure 2.1 ***(a)*** *Microstrains and* ***(b)*** *Grain sizes of Ni-P/Ni-W-P duplex coatings before and after laser treatment* ***(Hong, et al., 2012)****.*

Laser treatment is a special surface treatment process which also affects the surface of the electroless nickel coating **(Tsujikawa et al., 2005)**. The hardness of Ni-P/Ni-W-P coating is increased after laser heat treatment. The maximum hardness value of duplex electroless Ni-

P/Ni-W-P coating is represented with low scanning velocity. The wear rate of duplex coating is reduced after laser treatment. The wear resistance of duplex electroless Ni-P/Ni-W-P coating is lower with low scanning velocity. The morphology of duplex Ni-P/Ni-W-P coatings has exhibited the appearance of a higher degree of crystallization and fine grain size. The percentage of micro-strain and grain size of Ni-P/Ni-W-P duplex coatings are shown in Figure 2.1 (a) and (b) before and after laser treatment conditions **(Hong et al., 2012).**

2.4 Hardness evaluation of the coatings

Hardness is one of the most important mechanical properties of a material essential for various applications. The wear and tear of semi-finished products depend on the surface hardness. Most of the tool materials have high hot hardness. Electroless as well as electrodeposited nickel coatings, are characterized by high hardness **(Keong et al., 2003; Kothanam et al., 2022)**. The hardness values of coatings are improved by heat treatment processes **(Keong et al., 2002).** The hardness values of electroless Ni-P and Ni-B coatings are dependent on the percentage of phosphorous (P) and boron (B) content respectively. For electroless Ni-P coating, the hardness is increased by decreasing the phosphorus content. The hardness values are increased with an increase in P content up to 8%. The hardness values are drastically reduced in Ni-P deposition due to increased phosphorus content above 8% **(Yan et al., 2008)**. For electroless Ni-B coating, the hardness values are increased with increasing boron content **(Mustafa et al., 2008).** For the multilayer Ni-P/Ni-B (ten successive layers deposited and Ni-B acts as an outer layer) coating, the hardness values are higher than the multilayer Ni-B/Ni-P **(Vitry et al., 2017)**. In duplex Ni-P/Ni-Mo-P coating, the hardness value is higher for Ni-Mo-P as an outer layer **(Liu et al., 2017 & Liu et al., 2016)**. Microhardness of duplex electroless Ni–P/Ni–B, Ni-B/Ni-P, and Ni-P, Ni-B monolayer coatings in as-plated and heat-treated (450°C for 1h) conditions are shown in Figure 2.2 **(Narayanan et al., 2003)**. The maximum hardness is obtained for Ni-P/Ni-B duplex coating in as-deposited conditions among all types of duplex and monolayer coatings as shown in Figure 2.2 (a). The hardness value is modified after heat treatment of the deposited coating. Figure 2.2 (b) shows the maximum hardness value of Ni-P/Ni-B duplex coating under heat-treated (450°C for 1h) conditions **(Narayanan et al., 2003)**.

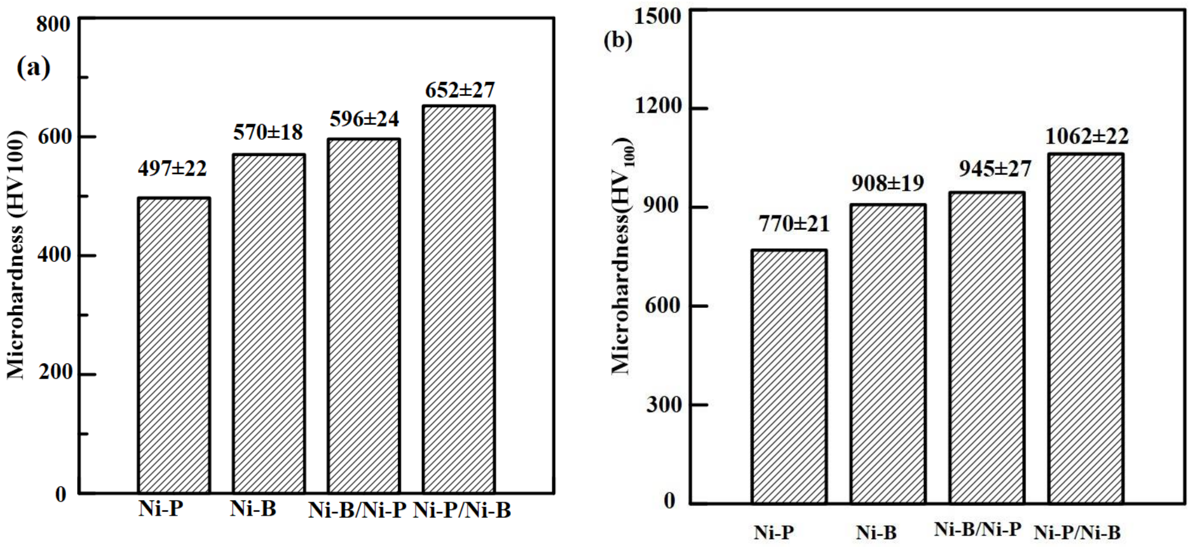

Figure 2.2 *Microhardness of duplex electroless Ni-P/Ni-B and monolayer coatings deposit in (a) as-plated and (b) heat-treated (450°C for 1h) conditions* ***(Narayanan et al., 2003)***.

2.5 Microstructural characterization

In the case of film deposition by electroless and electrodeposited nickel coating, the deposition initiates at the isolated area of the substrate. During the deposition period, lateral growth of the coating covers the whole substrate **(Agarwala and Agarwala, 2003).** Ni-P plating generally exhibits nodular formation. The nature of the nodular structure of electroless nickel coating is inherently lubricious (**Delaunois and Lienard, 2002)**. The microstructure of electroless nickel coating is mainly controlled by the phosphorous content. A nanocrystalline structure hints at the presence of a low quantity of phosphorus in the coating. The amorphous phase structure indicates high-phosphorus deposition. The presence of phosphorus content in the coating is responsible for their splendid mechanical and tribological properties. These medium-phosphorus coatings exhibit moderated structures with high hardness and abrasive wear resistance. The amorphous phase in as-deposited coating is converted into crystalline phase after heat treatment. Phosphides and borides are precipitated during heat treatment temperature range of 400-450°C. Duplex electroless Ni-P/Ni-W-P coating revealed less nodular formation along with a dense and smooth surface appearance (Figure 2.3). After laser treatment, the morphological structure of duplex Ni-P/Ni-W-P coating appears to have larger grain size with a higher degree of crystallization for Ni-W-P as outer layer than Ni-P as inner layer **(Hong et al., 2012)**.

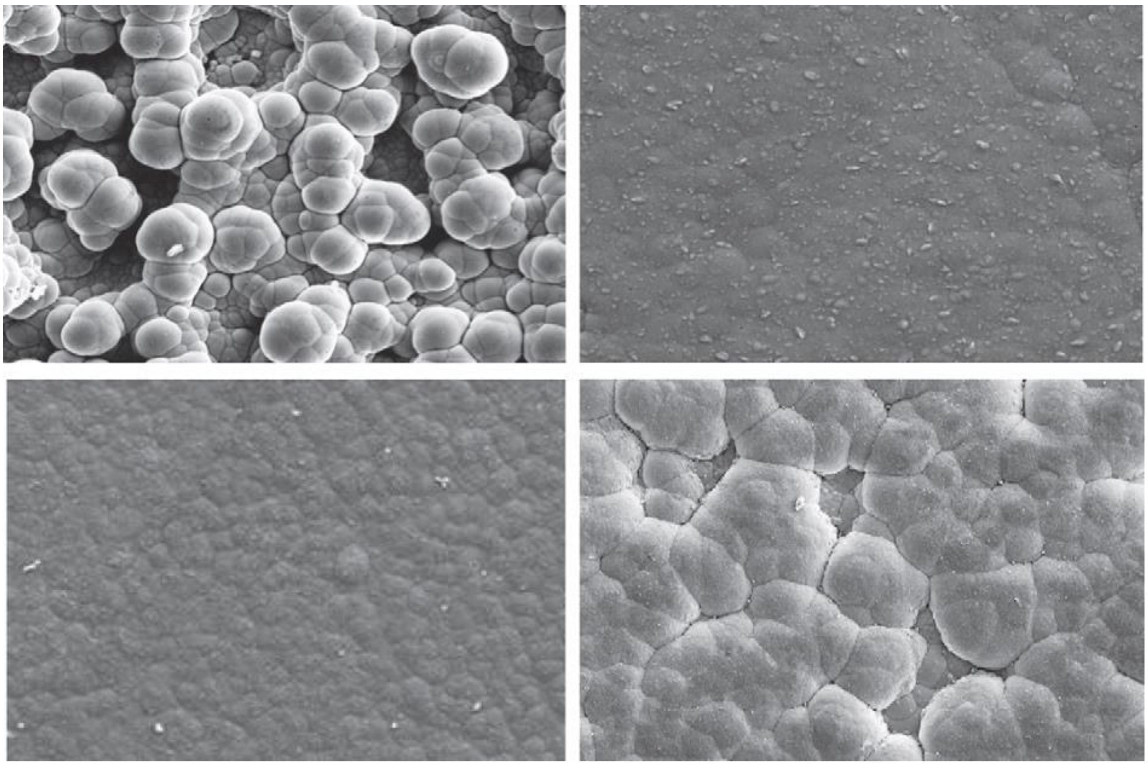

Figure. 2.3 *FESEM images of as-deposited samples AZ31B Mg samples at 1000× magnification: (a) Ni-P, (b) Ni-P/Ni-W-P (c) passivated Ni-P/Ni-W-P and (d) heat treated passivated Ni-P/Ni-W-P* ***(Selvi et al., 2014)***

2.6 Study of Tribological Behavior

To evaluate the wear rate and coefficient of friction (COF) of duplex and multilayer electroless and electrodeposited nickel coating, researchers have used various tribometers and contact arrangements. For the tribological test of electroless nickel coating, popular arrangements are found to be pin-on-disc, ball-on-disc and block-on-the-ring. Researchers have selected sliding speed range of 10cm/s to 50 cm/s and normal load range of 10N to 50N. Duplex or multilayer electroless nickel coatings are mainly designed to offer better friction performance and high wear-resistant behaviour. Duplex or multilayer coatings existence relatively smooth and hard offer both these attributes. The COF of multilayer electroless Ni-B/Ni-P nickel coating is lower in individual single-layer coating. It has been reported by **Vitry and Bonin (2017).** The COF is dependent on the surface roughness.

The wear rate of duplex coatings is much lower than monolayer coatings due to their higher hardness. The wear rate of monolayer Ni-P and Ni-B as well as duplex Ni-B/Ni-P and Ni-P/Ni-B coatings are shown in Figure 2.4 **(Sankara Narayanan et al., 2003)**. The maximum wear resistance is obtained for duplex Ni-P/Ni-B coating among all types of duplex and monolayer coatings. The lowest wear rate of duplex electroless Ni-P/Ni-W-P deposition appeared at the laser scanning velocity of 8 mm/s due to high hardness **(Hong et al., 2012).** When put through a wear test against hardened steel material, the laser-treated duplex Ni-P/Ni-W-P coating exhibited an adhesive wear mechanism. In addition to hardness, the degree of duplex Ni-P/Ni-B coating crystallization and quantity of Ni_3P phases had a significant impact on the adhesive wear behaviour **(Hong et al., 2012).**

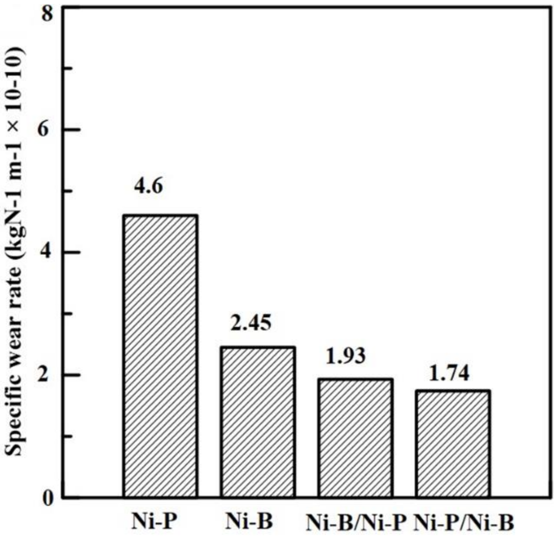

Figure 2.4 *Wear rate for duplex coating* ***(Sankara Narayanan et al., 2003)***.

2.7 Corrosion behaviour

The corrosion performance of the coating is mostly evaluated by electrochemical methods, such as the potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). In a variety of environment, the electroless Ni-P alloy coating is mainly used for protection against corrosion. The substrate is protected from corrosive environment by the sealing action of the deposition which acts as a barrier. Ni-(high) P coating provides excellent corrosion resistance. For several corrosive environment, Ni-(low) P and Ni-(medium) P coating is not recommended **(Bigdeli and Allahkaram, 2009).** The corrosion resistance mainly dependent on the capability of the formation of surface-protection film. It is explicitly understood from the literature survey on electroless Ni-P coating that preferential dissolution of nickel occurred which leads to the prosperity of phosphorous content on the external layer. In the as-deposited circumstances and with laser annealing, the duplex Ni-P/Ni-Mo-P coatings offered an even greater corrosion protection to the steel substrate than the single Ni-P coating. The corrosion process of a coating is found to be governed by a mixture of uniform and pitting corrosion. When pitting corrosion reached the surface of substrate, spilling action occurred, causing the corrosion protection to be rendered ineffective. The highest corrosion resistance of the duplex coating is achieved at laser annealed speed of 14 mm/s **(Liu and Liu, 2017).** The corrosion behaviour of coatings is influenced by stress situation **(Hong and Qian, 2018).** The corrosion process of the single Ni-P coating is dominated by uniform corrosion. On the contrary case of the single Ni-Mo-P coating corrosion process is mostly in the form of pitting, which is adversely impacted by tensile stress **(Hong and Qian, 2018)**. The duplex Ni-P/Ni-Mo-P coatings demonstrated higher corrosion resistance with respect to their respective single layer coatings **(Hong and Qian, 2018)**. The duplex Ni-P/Ni-Mo-P coatings were subjected to compressive stress, which limited the growth of corrosion-cracking around the pits and enhanced the compactness and completeness of the hypophosphite layer. This served as a passive protection at high potential range during anodic polarisation **(Hong and Qian, 2018).** Electroless Ni-W-P/Ni-P nano-ZrO_2 composite coating was found to have better corrosion resistance in chloride solution **(Luo et al., 2018).**

2.8 Applicability from tribological point of view

In order to accommodate the huge requirement in industrial application, electroless nickel coatings underwent a few revisions since Brenner and Riddell's development in 1946. Due to its microhardness, lubricity (low friction coefficient), wear and corrosion resistance properties, electroless nickel coatings are mostly used in tribological applications. Electroless nickel coatings are utilized in a variety of industries, including mining, aviation, aerospace, oil and gas, automotive, radio electronics, microelectronics, computer engineering, chemical processing, food processing, processing, textiles, equipment, and plastic metallization (**Lee, 2008; Sahoo, 2008b**). In addition to its engineering benefits, electroless nickel provides a useful coating that can be seen as a problem-solving finish surface finish technique offering a cost-effective alternative to more expensive metal alloys. The coating may be applied to non-conductive surfaces such as glass, ceramics, plastics, and graphite. The wear and corrosion properties of CFRP (**carbon-fiber-reinforced plastic**) materials have been improved by electroless nickel coating. This CFRP material is frequently used in the aerospace, aviation, and automotive industries due to its lightweight **(Lee, 2009)**. Ni-P-PTFE provides high dry-lubricity, non-galling, non-sticky, low friction, good wear and corrosion-resistant surfaces. It is used for precision instrument parts, butterfly valves for the oil and gas industry, pumps, valves, carburettor, and choke shafts **(Mallory and Hajdu, 1990).**

Duplex electroless Ni-P/Ni-W-P coating has good wear-resistant properties, making it ideal for applications where parts are subjected to high levels of friction and abrasion **(Oloyede**

et al., 2019). This includes applications such as gears, bearings, and cutting tools. This coating has good electrical conductivity, making it ideal for use in electrical contacts. These coatings are biocompatible, making them suitable for use in medical applications. These coatings are used to protect metal parts in marine applications, such as ships, boats, and offshore platforms. These components are to be protected against corrosion in salt water and other harsh environment**.** The duplex coating is used to protect metal parts in automotive applications, such as engine components, brake rotors, and fuel lines. The duplex electroless nickel coatings are used to protect metal parts in medical applications, such as implants, surgical instruments, and dental appliances **(Aleksinas M.J., 2019)**. Moreover, due to its deposition uniformity and good bio-compatibility, coatings have been applied to medical devices for protection against corrosion. Some medical components on which electroless nickel coatings have been applied include anaesthesia delivery components, laryngoscope handles, radiation focus plates, radiation lead, etc. These coatings are used to protect against wear and corrosion of metal parts in aerospace applications, as well as aircraft engines and landing gear **(Sankara Narayanan et al., 2003)**. Duplex electroless Ni-P/Ni-Mo-P coating is used to protect against wear and corrosion of metal parts in energy applications, such as power plants and oil rigs **(Hong and Qian, 2018)**.

In addition, electrodeposited coatings can also be used in a variety of specific applications. For example, these coatings are used in the marine industry to protect ship propellers and hulls against corrosion. In the automotive industry, it is used to protect brake rotors and other wear-prone components. In the chemical industry, duplex electrolyte coating is used to protect reactors and other equipment against corrosion. In the medical industry, it is used to protect implants and other medical devices from corrosion and infection. Different industrial tools and equipment, such as the surface of industrial shafts, gears, cylinders, and pistons, cutting tools, pulleys, crankshafts, engine valves, car wheels, roll and ball bearings, gun grooves, injection screws, ball valves, engraving rollers, textile rollers, dental and medical tools, etc., are traditionally electroplated with monolithic layers **(Aliofkhazraei et al., 2021)** due to protection against wear and corrosion.

2.9 Summary of the literature review

Previous researchers have already mentioned, that electroless nickel coating is a suitable coating deposition method. This method is more suitable for providing better tribological, mechanical, and corrosion resistance properties. Duplex or multilayer electroless nickel coating can provide improved properties like hardness, friction performance, corrosion, and wear resistance compared to monolayer coatings. The hardness of the coatings are increased with increasing heat treatment temperature up to 450°C for an hour duration. The duplex or multilayer electroless nickel coating is more applicable for corrosion and wear resistance related applications. These properties make electroless nickel coatings ideal for applications where tribology is important, such as valve gates, plugs, butterfly types bearings, machining tools, and steel valves of the ball. However, a compressive study addressing the tribological behaviour of these coatings relating to heat treatment is found to be lacking. Hence, the motivation to study the tribological behavior of duplex electroless nickel coating is obtained.

2.10 Closure

In the present chapter, an extensive literature review has been presented on the duplex electroless nickel coatings from a tribological point of view. From the review, the research gap is identified and the motivation for the current work is presented.

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Chapter 3

Fundamental Considerations and Experimental Details

***Outline of the chapter:** 3.1 Introduction, 3.2 Fundamental aspects of electroless nickel coating, 3.2.1. Substrates preparation, 3.2.2 Source of Nickel, 3.2.3 Reducing agents, 3.2.4. Complexing agents, 3.2.5 Buffers, 3.2.6 Stabilizers, 3.2.7 Surfactants, 3.2.8 Bath Temperature, 3.3 Fundamental aspects of electrodeposited nickel coating, 3.3.1 Electrolyte solution, 3.3.2 Working electrode, 3.3.3 Counter electrode, 3.3.4 Power supply, 3.3.5 Stirring system, 3.3.6 Temperature controller, 3.3.7 Safety equipment and cleanliness, 3.4 Deposition of Various Duplex Coatings, 3.4.1 Chemicals used for deposition, 3.4.2 Duplex electroless Ni-P/Ni-W-P coating, 3.4.3 Duplex electroless Ni-P/Ni-Cu-P coating, 3.4.4 Duplex electroless Ni-P/Ni-Mo-P coating, 3.4.5 Duplex electrodeposited Ni-P/Ni-W-P coating, 3.5 Equipment used for coating deposition, 3.5.1 Digital Balance, 3.5.2 Magnetic Stirrer, 3.5.3 Glass Beakers, 3.6 Heat Treatment in Muffle Furnace, 3.7 Evaluation of the coating, 3.7.1 Measurement of coating thickness, 3.7.1.1 By weight gain method, 3.7.1.2 By microscopic observation, 3.7.2 Measurement of microhardness, 3.7.3 Tribological testing of duplex coatings, 3.7.4 Measurement of friction and wear, 3.7.5 Corrosion test, 3.7.6 Characterization of Duplex Coatings, 3.7.6.1 Microstructure study, 3.7.6.2 Compositional study, 3.7.6.3 Phase structural analysis, 3.8 Closure*

3.1 Introduction

Surface coating is the most common surface engineering technique used for protecting the base material against wear and corrosion. The electroless nickel deposition procedure is widely practiced, providing several advantages over electrolytic coating techniques relevant to industries due to their superior tribological, mechanical and corrosion properties and unique applications where electrolytic procedures are impractical. A nation's economy continues to suffer greatly from the corrosion and wear of industrial equipment and facilities. They have an impact on maintenance expenses and spending on replacement parts, in addition to shortening the lifespan of equipment and increasing downtime. Therefore, these losses can be reduced by creating coatings with enhanced corrosion and wear resistance. Duplex or multilayer coating shows the potential to outperform monolayer coatings. Thus, coating is becoming an essential component of modern engineering. Additionally, improved duplex coatings with more recent technology are continually being created to fit our needs of today.

3.2 Fundamental aspects of electroless nickel coating

Electroless nickel coating is a popular autocatalytic deposition method today. The substrate develops a potential when it is dipped in electroless solution called bath. This bath typically comprises an aqueous solution of metal ions, complexing agent, reducing agent, stabilizer and other components operating in a specific metal ion concentration, temperature, and pH ranges. Due to the developed potential, both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process. The bath components of duplex electroless nickel coatings and their functions are given in Table 3.1.

Table 3.1 Electroless nickel bath composition and their functions

Bath Component	Function
Nickel Ion	Source of metal
Reducing agent	Source of electrons
Complexants	Stabilizes the solution by forming nickel complexes
Accelerators	Activates reducing agent and accelerates the deposition
Buffers	Controlling pH
pH regulators	Regulates pH of solution
Stabilizer	Prevents solution breakdown
Wetting agents	Increases wettability of the surfaces to be coated

3.2.1 Substrate preparation

Mild steel substrate is used to deposit duplex electroless nickel coating. Mild steel is chosen as the substrate is cheap and readily available. Moreover, the material provides necessary rigidity in case of hardness test as well as friction and wear test of the coatings. As electroless nickel coating follows the substrate surface profile, substrates with similar roughness values are chosen for deposition. The cylindrical pin samples measuring Φ6×30 mm is used for the tribological test. Square samples measuring 15×15×2 mm is used for metallurgical characterization. To prepare a smooth surface, the samples are polished with various grades of emery paper after several machining operations like turning, facing, parting, etc. As surface interactions are dependent on the shape of the contacting surfaces (**Davim, 2011**), all substrates are ground to about the same roughness value. The samples were carefully cleaned with running water. After rinsing, the samples were degreased with acetone, and the final wash is made with distilled water. After that, the samples are submerged in 50 % HCl solution for 2 minutes and washed in distilled water. Before immersing in electroless nickel bath for the inner layer of deposition, the samples are dipped into a warm palladium chloride solution for activation.

3.2.2 Source of Nickel

The main source of nickel ion is nickel sulfate ($NiSO_4(H_2O)_6$) and nickel chloride ($NiCl_2.6H_2O$) salts. Nickel acetate is used as a source of nickel (Ni) ion in a very limited application. However, nickel hypophosphite [$Ni(H_2PO_2)_2$] is the ideal source of nickel ion **(Mallory and Hadju, 1990).** The use of nickel hypophosphite would eliminate the addition of sulphate and chloride ions and hence suppresses the build-up of alkali metal ions. The salt would also help in the replenishment of the reactants consumed during the metal deposition **(Delaunois et. al., 2000).**

3.2.3 Reducing agents

The reducing agent is one of the most important components of the electroless nickel bath. A reducing agent is an element or compound that donates an electron to an oxidizing agent in a reduction-oxidation chemical reaction. Pure nickel is not deposited on the substrate. The deposition combinations are Ni-P, Ni-W-P, Ni-B, Ni-Mo-B etc. depending on the reducing agents.

Table 3.2 Application of various reducing agents **(Agarwala and Agarwala, 2003).**

Coating Deposition	Used of reducing agent	Bath types
Ni-P	($NaH_2PO_2.H_2O$)	Acid or alkaline bath (2-17%P)
Ni-B	($NaBH_4$)	Acid or alkaline bath
	(DMAB)	Alkaline bath (0.5-10%B)
Only Ni	(NH_2NH_2)	Alkaline bath

In nickel plating, many reducing agents are used like sodium hypophosphite ($NaH_2PO_2.H_2O$), amino-boranes (DMAB) sodium-borohydride ($NaBH_4$), and hydrazine (NH_2NH_2). Acidic and alkaline baths are mainly used for deposition of electroless nickel alloys based on the different reducing compounds which are shown in Table 3.2 **(Agarwala and Agarwala, 2003).**

3.2.4 Complexing agents

The complexing agent plays is an important role to prevent the bath decomposition and plating deposition rate. Depending on the different baths, the choice of complexing agents and their concentration is very important. It affects the reaction processes and coating deposition rate. To prevent bath decomposition and control chemical reactions, the complexing agent is added to the solution. In electroless nickel plating solutions, complexing agents are additives of organic acid and its salts. Complexing agents are employed for three main purposes in the electroless nickel plating bath **(Mallory and Hadju, 1990).** It also acts as primary buffers to control the pH of the solution. They prevent the formation of nickel phosphite. Complexing agents have reduced concentrations of free nickel ions. With the addition of a complexing agent up to the optimal concentration, the deposition rate is gradually increased but falls beyond a certain limit. For the reduction of hypophosphite, the complexing mediator is sodium citrate (about 30 g/l). Ethylenediamine (around 90 g/l) is used to reduce borohydride. The quality of the deposition can be improved with the use of a complexing agent.

3.2.5 Buffers

Hydrogen ions are formed during electroless coating deposition. Due to the progression of hydrogen, the pH of the solution tends to decrease which sequentially makes the bath unstable. To maintain a constant pH count in the electroless solution, the buffer is added to the electroless bath. Electroless nickel-plating solutions contain buffering agents such as potassium or sodium salts of carboxylic acids such as glycolic, citric, lactic, or malic acids.

3.2.6 Stabilizers

The stabilizer is a chemical that is used to prevent degradation of the electroless bath. For the presence of any types of foreign particles, the bath reagents breakdown spontaneously and decompose the electroless bath during the coating deposition process. By addition of a stabilizer in the electroless nickel bath, the rate of reductions is controlled properly which stabilizes the electroless plating bath. The electroless coating bath is influenced by several parameters viz. concentration of chemicals, pH, temperature, concentration of reducing agents, and presence of foreign bodies. The characteristics of the metallic coating depend on each stabilizer and their optimal concentration.

3.2.7 Surfactants

Surfactants are used to improve the wetting property, reduce surface tension, and ensure uniform distribution of bath constituents **(Gadhari and Sahoo, 2014).** The presence of surfactant in the electroless nickel plating bath promotes the deposition reaction on the dipping substrate surface and the bath solution. Mechanical properties and corrosion resistance is improved, with the addition of two surfactants like Sodium dodecyl sulfate (SDS) and Cetrimonium bromide (CTAB) during electroless Ni-P coating deposition, which also improves the deposition rate **(Elansezhian et.al., 2008)**. For the composite coating of Ni-P-nanometer Al_2O_3, a cationic surfactant (triethanolamine) ensures a faster deposition rate, uniform spreading of Al_2O_3 particles, and good abrasion resistance **(Zhou et.al., 2007).**

3.2.8 Bath Temperature

Bath temperature is very important for the coating deposition rate. At the optimal temperature, the coating deposition rate is increased. If the temperature fluctuates during the deposition period, the bath is decomposed spontaneously. The temperature is varied between 75°C to 95°C **(Biswas et al., 2018).**

3.3 Fundamental aspects of electrodeposited nickel coating

3.3.1 Electrolyte solution

The electrolyte solution is a liquid that contains the nickel ions that will be deposited on the substrate. The electrolyte solution must contain the correct concentration of nickel ions, as well as other ions that help to improve the properties of the nickel coating. The purity of the electrolyte solution is important for ensuring that the nickel coating is uniform and free of defects.

3.3.2 Working electrode

The working electrode is the substrate that will be coated with nickel. The working electrode must be made of a material that is compatible with the electrolyte solution, and it must have a good surface finish. The cleanliness of the working electrode is important for ensuring that the nickel coating has good adhesion.

3.3.3 Counter electrode

The counter electrode is used to complete the electrical circuit. The counter electrode can be made of any conductive material, such as platinum or graphite.

3.3.4 Power supply

The power supply provides the electrical current that is used to reduce the nickel ions in the electrolyte solution. The power supply must be able to provide a constant DC current, and it must be able to deliver the correct amount of current for the desired thickness of the nickel coating.

3.3.5 Stirring system

The stirring system stirs the electrolyte solution stirred, which helps to ensure that the nickel ions are evenly distributed throughout the solution.

3.3.6 Temperature controller

The temperature controller is used to control the temperature of the electrolyte solution, which can affect the rate of deposition.

3.3.7 Safety equipment and cleanliness

Safety equipment, such as gloves, goggles, and a face mask, should be worn when working with electrolyte solutions, as they can be corrosive and harmful to the skin and eyes. In addition to the required components, there are several other factors that can affect the quality of the nickel coating, such as the purity of the electrolyte solution, the cleanliness of the working electrode, and the operating conditions. It is important to follow the manufacturer's instructions carefully when applying electrodeposited nickel coating to ensure that the coating meets the desired specifications.

3.4 Deposition of Various Duplex Coatings

Duplex electroless nickel coating is a type of electroless nickel coating that consists of two layers of nickel, with a different composition in each layer. The two layers are typically bonded together by a diffusion process. The procedures for deposition of various duplex coatings are discussed in the following sections.

3.4.1 Chemicals used for deposition

The following chemicals are used for depositing duplex electroless nickel coating:

1) Nickel (II) sulfate hexahydrate purified ($NiSO_4$, $6H_2O$): Merck Life Science Pvt. Ltd., Mumbai, India.
2) Nickel (II) chloride hexahydrate purified ($NiCl_2$, $6H_2O$): Merck Specialities Pvt. Ltd., Mumbai, India.
3) Sodium hypophosphite (NaH_2PO_2, H_2O): Loba Chemie Pvt. Ltd., Mumbai, India.
4) Trisodium citrate dihydrate ($Na_3C_6H_5O_7$, $2H_2O$): Merck Life Science Pvt. Ltd., Mumbai, India.
5) Sodium succinate ($C_4H_4Na_2O_4$, $6H_2O$): Loba Chemie Pvt. Ltd., Mumbai, India.
6) Ammonium sulfate ($NH_4)_2SO_4$): Merck Life Science Pvt. Ltd., Mumbai, India.
7) Lactic acid ($C_3H_6O_3$): Merck Specialities Pvt. Ltd., Mumbai, India
8) Sodium tungstate (Na_2WO_4): Merck Life Science Pvt. Ltd., Mumbai, India.
9) Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$): Merck Life Science Pvt. Ltd., Mumbai, India.
10) Citric acid ($C_6H_8O_7$): Merck Specialities Pvt. Ltd., Mumbai, India.
11) Sodium molybdate (Na_2MoO_4): Merck Life Science Pvt. Ltd., Mumbai, India.
12) Ammonium chloride (NH_4Cl): Merck Specialities Pvt. Ltd., Mumbai, India.
13) Sodium fluoride (NaF): Merck Specialities Pvt. Ltd., Mumbai, India.
14) Sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$): Merck Specialities Pvt. Ltd., Mumbai, India.
15) Paladium (II) Chloride anhydrous ($PdCl_2$): Merck Specialities Pvt. Ltd., Mumbai, India.
16) Acetone (CH_3COCH_3): Merck Specialities Pvt. Ltd., Mumbai, India.

17) Hydrochloric acid about 35% (HCL): Merck Specialities Pvt. Ltd., Mumbai, India**.**

18) Sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$): Merck Specialities Pvt. Ltd., Mumbai, India.

3.4.2 Duplex electroless Ni-P/Ni-W-P coating

Duplex electroless Ni-P/Ni-W-P (Ni-P as inner layer and Ni-W-P as outer layer or vice versa) coatings are deposited successfully by sequential deposition. The bath compositions of duplex electroless nickel coatings are given in Table 3.3 **(Biswas et.al., 2017; Kundu et.al., 2019)**. The setup used for the electroless nickel deposition is shown in Figure 3.1. After performing the entire surface treatment of the substrate (as mentioned in the previous section), the samples are dipped in a previously prepared Ni-P bath for 2 h duration for the deposition of the inner layer. Then, the Ni-P coated samples are dipped in Ni-W-P baths for developing duplex Ni-P/Ni-W-P coating again for 2h duration. Nickel and tungsten are obtained from Nickel (II) sulfate hexahydrate [$NiSO_4(H_2O)_6$], and Sodium tungstate [Na_2WO_4], respectively. Sodium hypophosphite ($NaPO_2H_2$, H_2O) acts as the reducing agent and the source of phosphorus. Depending on the inner and outer layers, the sequence of immersion of the substrates in electroless baths are altered.

Table 3.3 Bath Composition and deposition conditions for Ni-P/Ni-W-P coating **(Biswas et.al., 2017; Kundu et.al., 2019)**

Sl No	Component/condition	Concentration/value (Ni-W-P) Bath	Concentration/value (Ni-P) Bath
1	Nickel sulfate (g/l)	20	20
2	Nickel chloride (g/l)	-	20
3	Sodium hypophosphite(g/l)	20	24
4	Trisodium citrate dehydrate (g/l)	35	-
5	Sodium succinate (g/l)	-	12
6	Ammonium sulfate (g/l)	30	-
7	Lactic acid (g/l)	5	-
8	Sodium tungstate (g/l)	20	-
9	Temperature (°C)	90±2	82±2
10	pH	7-8	4.5-5.5

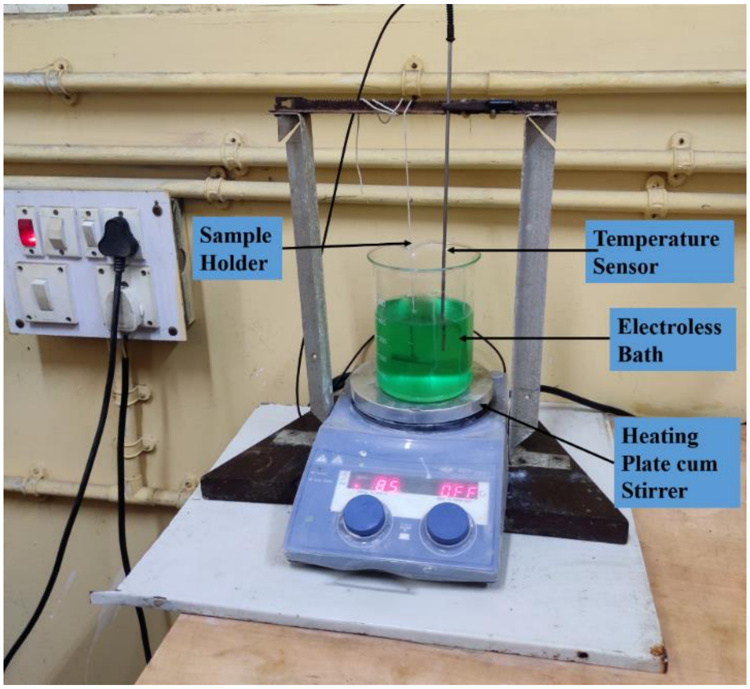

Figure 3.1 *Setup for electroless nickel coating deposition*

3.4.3 Duplex electroless Ni-P/Ni-Cu-P coating

Electroless deposition of duplex Ni-P/Ni-Cu-P coating is also developed in a similar manner by dipping the substrate sequentially in Ni-P and then in Ni-Cu-P bath for the duplex system with Ni-

Table 3.4 Bath Composition and deposition condition for Ni-P/Ni-Cu-P coating (**Biswas et al., 2017; Biswas et al., 2021)**

Sl No	Component/condition	Concentration/value (Ni-P)	Concentration/value (Ni-Cu-P)
1	Nickel chloride (g/l)	20	-
2	Nickel sulfate (g/l)	20	25
3	Trisodium citrate dehydrate (g/l)	-	45
4	Sodium hypophosphite (g/l)	24	25
5	Copper sulfate pentahydrate(g/l)	-	1
6	Sodium Succinate (g/l)	12	-
7	Temperature (°C)	82±2	90±2
8	pH	4.5-5.5	7-8

Cu-P as the outer layer for the deposition of the first set of duplex systems. And in a reverse sequence for Ni-P as the outer layer. The deposition conditions as well as bath compositions are provided in Table 3.4 (**Biswas et al.,2017; Biswas et al.,2021).** In the case of Ni-Cu-P coatings, the source of nickel and copper were nickel-sulfate ($NiSO_4$, $6H_2O$) and copper sulfate pentahydrate ($CuSO_4.5H_2O$), respectively. Sodium hypophosphite ($NaPO_2H_2$, H_2O) was used as the reducing agent for both coatings. The deposition time was fixed at 2h for deposition of each layer.

3.4.4 Duplex electroless Ni-P/Ni-Mo-P coating

Duplex electroless Ni-P/Ni-Mo-P (Ni-P as inner layer and Ni-Mo-P as outer layer or vice versa) coatings are deposited successfully by sequential deposition. The bath compositions of duplex electroless Ni-P/Ni-Mo-P coatings are given in Table 3.5 **(Biswas et al., 2017; Liu and Liu, 2017)**. In the case of Ni-Mo-P coatings, the source of Nickel and Molybdenum are obtained from Nickel-sulfate ($NiSO_4(H_2O)_6$) and Sodium molybdate, ($Na_2MoO_4,\cdot 2H_2O,$) respectively. The deposition was carried out for 2h duration for each layer.

Table 3.5 Bath composition and deposition condition for Ni-P/Ni-Mo-P coating **(Biswas et al., 2017; Liu and Liu, 2017)**

Sl No.	Component/condition	Concentration/value (Ni-P)	Concentration/value (Ni-Mo-P)
1	Nickel chloride (g/l)	20	-
2	Nickel sulphate (g/l)	20	20
3	Sodium hypophosphite (g/l)	24	40
4	Tri sodium citrate (g/l)	-	16
5	citric acid (g/l)	-	8
6	Sodium Succinate (g/l)	12	-
7	Sodium molybdate (g/l)	-	5
8	ammonium chloride (g/l)	-	14
9	NaF (g/l)	-	0.002–0.004
10	sodium dodecyl sulfate (g/l)	-	0.006–0.008
11	Temperature (°C)	82±2	90±2
12	pH	4.5-5.5	9.5

3.4.5 Duplex electrodeposited Ni-P/Ni-W-P Coating

The typical direct current electrodeposition technique is used to deposit duplex Ni-P/Ni-W-P coating on mild steel substrates. Pure Ni plates are used as the anode. The substrate is used as the cathode. The substrates are initially cleaned with soap and water. Acetone is used to eliminate any organic debris that may have remained. Before coating, the substrates are pickled in a 50% HCl solution for one minute to remove oxide and rust. The plating conditions and electrolyte concentration that were employed in the current study are summarized as shown in Table 3.6. To create the necessary internal and external layers, substrates are sequentially immersed in corresponding baths (for thirty minutes each). After deposition, the samples are taken out of the bath, rinsed with deionized water, and dried. Duplex Ni-P/Ni-W-P coating, one set of Ni-W-P as the outer layer as well as Ni-P as the inner layer, and another set of duplex coating Ni-W-P as the inner layer and Ni-P as the outer layer. The stirrer is rotated at 250 rpm to proper movement of the electron and smooth coating deposition.

Table 3.6 Bath composition and deposition conditions for electrodeposited Ni-P/Ni-W-P coating

Sl No	**Component/condition**	**Concentration/value (Ni-P)**	**Concentration/value (Ni-W-P)**
1	Nickel-sulfate (g/l)	20	25
2	Sodium-hypophosphite (g/l)	20	20
3	Trisodium citrate dehydrate (g/l)	35	35
4	Ammonium sulfate (g/l)	30	30
5	Lactic acid (g/l)	5	5
6	Sodium tungstate (g/l)		20
7	Sodium lauryl sulfate (g/l)	0.002	0.002
8	Current density (A/cm^2)	0.1-0.15	0.1-0.15
9	Temperature (°C)	50±2	50±2
10	pH	4.5-5.5	7-8

3.5 Equipment used for coating deposition

3.5.1 Digital Balance: High-precision electronic balance was used to measure the weight of substrates and chemicals. Afcoset, Model No. ER-182A, SL. No. 0108017, Maximum range 180 g, Minimum range 0.01mg (refer to Figure 3.2).

Figure 3.2 *Digital balance*

3.5.2 Magnetic Stirrer: To prepare the solution, the magnetic Stirrer is used for the proper mixing of chemicals with the bath solution**.** 1MLH Magnetic stirrer is manufactured by Remi Instruments is employed.

3.5.3 Glass Beakers: Glass beakers from Merck of suitable sizes are used.

3.6 Heat Treatment in Muffle Furnace

The various properties of duplex electroless and electrodeposition coatings, *viz.* phase structure, morphology, *etc*., are influenced by the heat treatment process. Above a specific heat treatment temperature, electroless and electrodeposition nickel coatings are observed to change phase (from amorphous to crystalline). After this phase transformation, the hardness value is increased, and the wear rate of electroless and electrodeposition coatings is reduced. Heat treatment of the coatings is carried out at temperatures ranging from 200°C to 800°C with time durations of 1 to 4h in a muffle furnace by Electro Scientific Equipment, Howrah (India) (Model No. ESE, Temperature range: RT-1450°C) with no special environment as shown in Figure 3.3. The rate of heating is kept fixed at 10°C per minute. The samples are removed from the muffle furnace after the completion of heat treatment and air-cooled to room temperature.

Figure 3.3 *Muffle furnace*

3.7 Evaluation of the coating

The various properties of the duplex electroless and electrolyte nickel coatings viz. coating thickness, phase structure, morphology, microhardness coefficient of friction wear rate, and corrosion performance are evaluated by various test equipment. The following discussion covers the principles of the characterization tools and coatings considered for the current investigation:

3.7.1 Measurement of coating thickness

The developed coating thickness is measured in the following two ways.

3.7.1.1 By weight gain method

Thickness of coating was measured by measuring the gain in weight after coating. The calculations are as follows:

W_b = Mass of sample in g before deposition

W_a = Mass of sample in g after deposition.

W_a-W_b = W, Deposited mass in g.

A = surface area covered by coating in cm^2

Deposition rate $= \frac{\mathrm{W}}{2A} = \frac{Wa-Wb}{2A}$ in $\mathrm{g/cm}^2$

Deposition thickness$= Y = \frac{\mathrm{W}\times 10}{2\times\rho\times\mathrm{A}}$ in cm

ρ = density of the coating in g/cc [taken 8.0g/cc as per existing literature (**Panja et al., 2014**)].

(It is to be noted that the weight gain method is used to only determine the approximate thickness of the coating just after the deposition. For this, the value of density of about 8.0 g/cc as reported in previous studies on such coatings have been employed. In fact, studies on different ternary variants of the coating also report densities near about the same value **(Biswas et al., 2019; Panja et al., 2014; Sudagar et al., 2013)**. For this reason, even though the present system being a duplex one the density has been calculated as in a single layer coating in order to get a rough estimate about the thickness. However, the precise thickness of the coating is determined using microscopic observation (by SEM) which is a standard method to measure coated layer thickness.)

3.7.1.2 By microscopic observation

The cross-cut surface of the coated sample can be seen in SEM, which further confirms the coating thickness. To get a smooth section and a realistic representation of the coating thickness, the cross-cut surface is at first properly ground before being examined under the microscope.

3.7.2 Measurement of microhardness

The Vickers test is frequently simpler to apply than other hardness tests because the calculations needed are independent of the indenter's size and the indenter can be used with any material, regardless of hardness. The microhardness of the duplex coating is measured by a Vickers hardness tester (UHL-VMHTOT, Technische- Mikroskopie, Asslar- Germany) for samples in as-deposited and heat-treated conditions. Microhardness is important to get an idea about the coating's resistance to deformation so that the tribological behavior of the coating could be interpreted. The test is conducted by employing the following test parameters: a constant load of 100 gf, speed of 25 µm/s, and dwell time of 15s. In both coated samples with or without heat treatment, the microhardness is measured immediately after developing the coating. Also, for each sample, an average of at least five hardness values is recorded. An optical microscope is used to measure the diagonals of the square indentation. Figure 3.4 displayed the Vicker's microhardness tester.

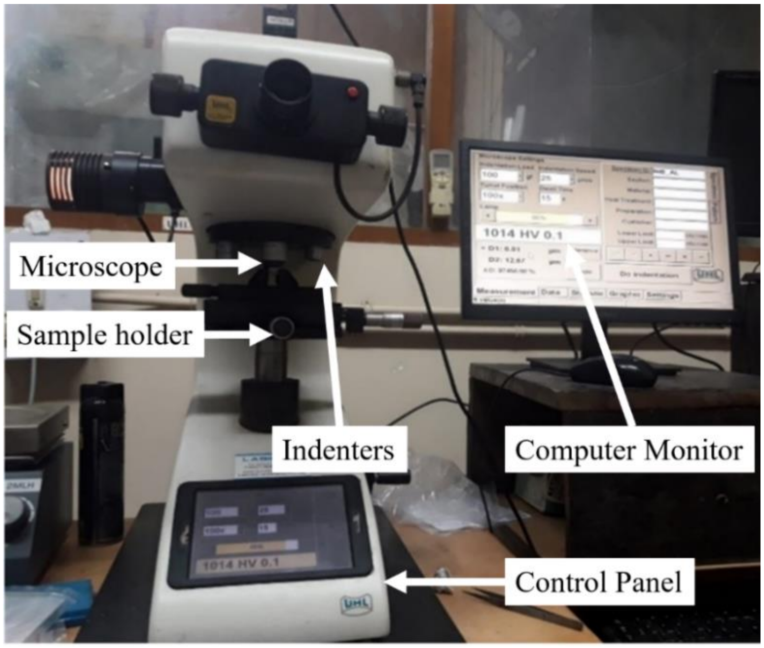

Figure 3.4 *Vicker's microhardness tester*

3.7.3 Tribological testing of duplex coatings

Duplex electroless and electrodeposited nickel coatings are typically applied to surfaces as a shroud. Therefore, any coating must provide protection from friction and wear in order to work well. The resistance to sliding exists when two surfaces are pressed together and are in contact. A single coefficient of friction is frequently used to describe friction, and it is calculated by dividing the force that resists sliding by the force that normally pushes two surfaces together. This COF is frequently regarded as a material characteristic that is applicable throughout a wide range of velocities, pressures, and temperatures. Wear is commonly understood to be the loss of material or dimension, or even both, from a surface as a result of the mechanical action of the interacting opposite surface. The limiting factor in device service life is frequent wear, a crucial component of tribology. Therefore, wear needs to be reduced, if not eliminated, save in a few rare circumstances, as it is an undesirable phenomenon. The study of friction and wear processes using laboratory-based tribometer apparatuses, test specimens with simple geometry, and precisely described test conditions is one of the key parts of tribology. A rotating cylinder or disc is typically used in a laboratory tribometer against a solid object that is fixed in place. The commonly used test instruments for laboratories are:

- Pin on flat (reciprocating or linear motion)
- Flat on flat (reciprocating or linear motion)
- Rotating pins on disc (face-loaded)
- Pin on the rotating disc (face-loaded)
- Cylinder on cylinder (face-loaded)
- Cylinder or pin on a rotating cylinder (edge-loaded)
- Rectangular flat on rotating cylinder (edge loaded)
- Disc on disc (edge loaded)

In addition, it is important to carefully choose the operational variables for friction and wear tests performed in laboratories so that they are appropriate for the type of investigation being conducted.

3.7.4 Measurement of friction and wear

The tribological behaviour assessment of both the duplex coatings in the as-deposited and heat-treated states is carried out on a pin-on-disc tribometer (TR-20LE-CHM-400, Ducom, India) at ambient conditions (30°C temperature and 50 percent RH) in a dry state. Pictorial view of the tribometer is shown in Figure 3.5. The close-up view of the pin and disc attachment is shown in inset. The tests are performed in accordance to ASTM G99. The duplex-coated pin samples are kept fixed and aligned with a revolving counterface disc of hardened EN 31 (58- 62 HRC) steel.In comparison to the coated samples, the counterface disc material shows negligible wear. Tribological tests are performed with a constant speed of 50 RPM, a normal load of 20N, and a fixed sliding distance of 94.2m (**Biswas et al., 2017**). A track diameter of 60 mm is maintained. The responses considered are: wear in terms of mass loss and COF. A precision weighing machine with a reading of 0.01 mg is used to measure the mass loss of the duplex coatings immediately after the tribo-test. The frictional force is recorded by a button-type load cell with a capacity of 10kg and a precision of 0.1±1% of the measured force.

However, for determining the wear rate (K), the weight loss of the samples after each test is measured, and the following relation is employed: $K = V / (S \times F)$, where S, F, and V are as sliding distance (m), normal load (N), and wear volume (mm^3), respectively. The wear volume (in mm^3) is calculated as V = mass loss / density of the coating.

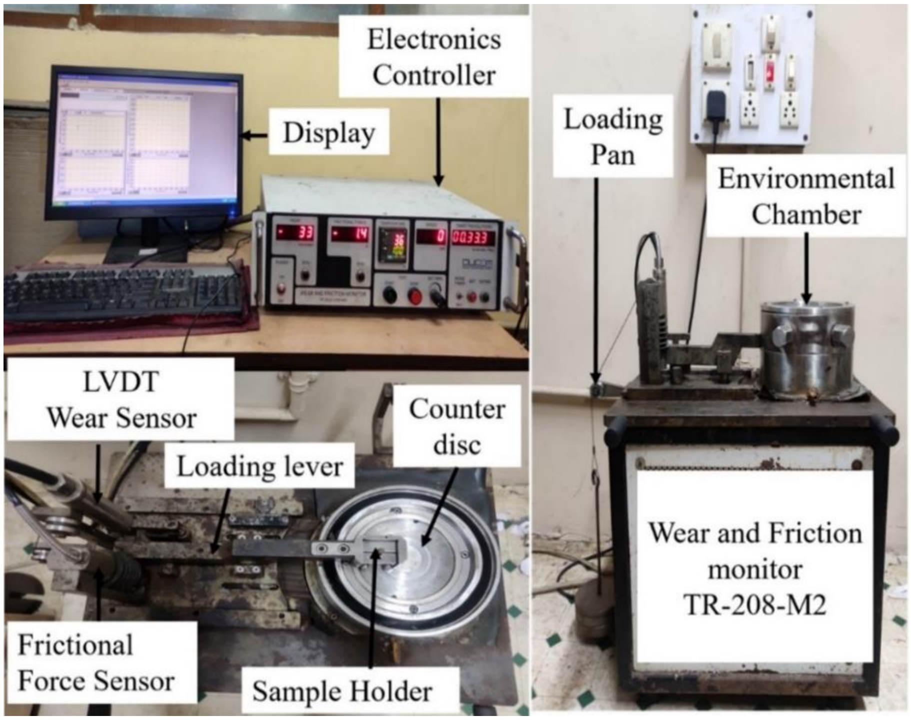

Figure 3.5 *Pictorial view of wear and friction monitor setup and close up view (inset)*

3.7.5 Corrosion test

A potentiostat (Gill AC by ACM Instruments, UK) is used to conduct potentiodynamic polarization (PDP) and Electrochemical impedance spectroscopy (EIS) testing on the duplex coatings. Tests are conducted using a 3.5-weight percent NaCl solution as the electrolytic medium at room temperature (32°C). For all tests, the surface area of the samples that meet the electrolyte solution is fixed at $1 cm^2$. Three electrodes are utilized to perform corrosion tests. At first, coated samples are connected to the potentiostat as working electrodes. There are two additional electrodes: a reference electrode and an auxiliary electrode. Due to its ability to maintain a constant voltage, the saturated calomel electrode is utilized as the reference electrode. To provide an alternative path for the applied current in the electrolyte solution, a platinum electrode is used as an auxiliary electrode. The open circuit potential (OCP) stabilization period is set at 10 minutes. Corrosion tests are performed by setting the start and reverse potential as -250 mV and 250 mV, respectively, and the sweep rate to 1 mV/s for both directions **(Mukhopadhyay et al., 2017; Banerjee et al., 2019).** The EIS test employed frequencies between 10 kHz and 0.01 Hz. However, the EIS analysis provides comprehensive information on the corrosion behavior of coated material. Double-layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) are determined by analyzing the Nyquist plots (**Mukhopadhyay, and Sahoo, 2021).** The anodic and cathodic portions of the Tafel plot are used to extrapolate output parameters such as E_{corr} (corrosion potential) and I_{corr} (current density). Figure 3.6 illustrates the electrochemical corrosion test setup.

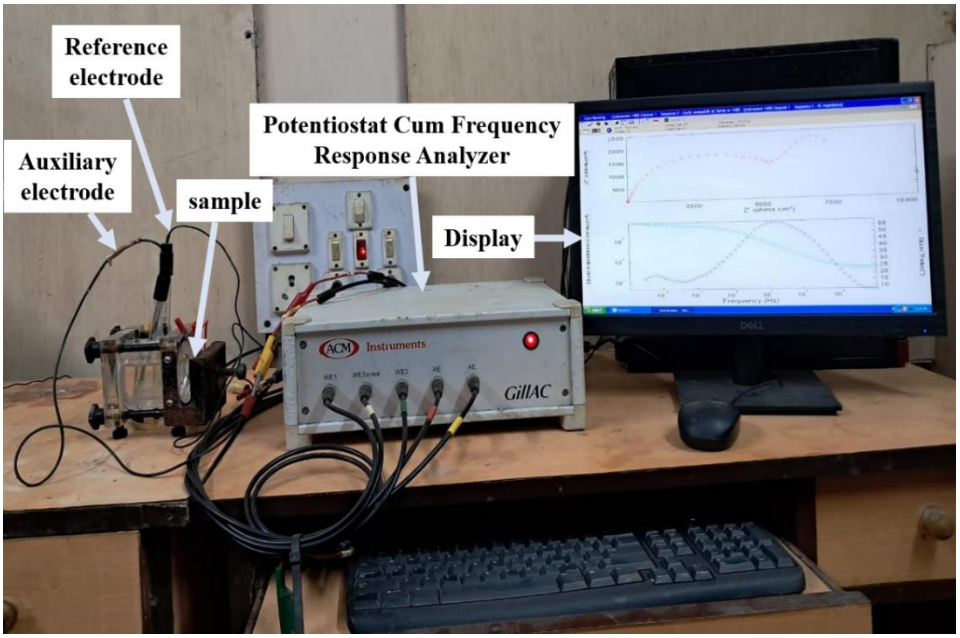

Figure 3.6 *Photograph of electrochemical corrosion test setup*

3.7.6 Characterization of Duplex Coatings

Characterization of the duplex coating is necessary to ensure that it is formed correctly as well as to gain insights into its microstructure and composition. The choice of characterization techniques will depend on the specific properties of the coating and the information that is needed. SEM is used for observing the surface morphology. If the chemical composition is to be determined of coatings, Energy dispersive X-ray analysis will be used. With the use of these techniques, the designer can create new materials with novel property combinations. Additionally, they aid in determining whether a material has been correctly heat-treated. The following texts outline the approaches specifically used in this investigation.

3.7.6.1 Microstructure study

SEM images are frequently used in the microstructure characterization of materials and are highly helpful for observing a material's microstructure or surface morphology in detail. In this technique, an electron beam is used to scan the surface of a specimen to be inspected. The reflected (or secondary electrons) electron beam is then collected and displayed on a CRT (cathode ray tube) monitor or an LCD screen at the same scanning rate. The surface characteristics of the item are represented by the image on the screen and are photographed for more in-depth analysis. In SEM, the magnification varies between 10 to 50000 times. As part of a microstructural study of the coatings, the surface morphology is observed with the help of a Scanning Electron Microscope by Carl Zeiss, Germany (Model No. EVO LS 10). Figure 3.7 displays the Scanning Electron Microscope instrument. Everhart-Thornley Detector is used to detect the secondary electrons (SE). The cross-section of duplex coating is observed to ensure the coating thickness and uniformity of deposition.

Figure 3.7 *Photograph of Scanning Electron Microscope*

3.7.6.2 Compositional study

The elemental composition (and proportions) of a sample may be determined using energy-dispersive X-ray analysis (EDX). In EDX, electron penetration into a sample range from 0.1 to 1m; as a result, the elemental composition can be precisely determined within this range of coating thickness. SEM and an EDX are used together since they both use the same electron source. The composition of a point or line or over a large area can both be examined using EDX. Scanning for X-ray emissions at certain energies can also be used to map specific elements over a test surface.

Since carbon and hydrogen emit X-rays with very low energy that are difficult to detect, EDX is often employed for inorganic coatings. In the current investigation, an EDX analyzer is used under a high vacuum at 20 kV to obtain systematic observation of the composition of electroless monolayer and duplex coatings. EDX is used to determine phosphorus, tungsten, nickel, etc content in the coatings.

3.7.6.3 Phase structural analysis

X-ray diffraction analysis (XRD) is a flexible, non-destructive method that provides detailed crystalline structure of manufactured and natural materials. This method is based on diffraction, which is the energy-free elastic scattering (change of direction) of electromagnetic wave motion. To properly analyze crystalline solids, diffraction techniques must be used. The phase structure of the present coatings is examined using the X-ray diffraction (XRD) setup Ultima III by Rigaku, Japan (refer to Figure 3.8). Scanning is done at a diffraction angle (2Θ) ranging from 20-80° based on the available literature (**Palaniappa and Seshadri, 2007).** The following parameters are used to measure phase structure: a scan width of 0.02° and a scanning speed of 1.0°/min. The sharp peak in XRD plots represents the crystalline phase, while the diffused peak indicates the amorphous phase **(Lewis and Marshall, 1996).**

Figure 3.8 *Photograph of X-ray diffraction (XRD) setup*

3.8 Closure

In this chapter, the fundamental considerations along with the experimental details are discussed. The chapter starts with the theory of duplex electroless and electrodeposition nickel coatings and their characteristics, along with a discussion on the equipment used for deposition of the coatings. Several types of duplex electroless (Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P) and duplex electrodeposited Ni-P/Ni-W-P coatings have been developed. The procedure of deposition is discussed in detail for both electroless and electrodeposited coatings. The bath compositions for the development of the coatings are presented. The different testing methods, like hardness testing, tribological testing (friction and wear) and corrosion tests are explained. Moreover, different microstructural characterization techniques, viz., SEM, EDX and XRD are described in detail.

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Chapter 4

Duplex Electroless Ni-P/Ni-W-P Coatings

Outline of the chapter: *4.1 Introduction, 4.2. Results and Discussion, 4.2.1 Microstructure characterization and composition analysis, 4.2.2 Phase structure, 4.2.3 Microhardness study, 4.2.4 Friction performance, 4.2.5 Wear performance, 4.2.5.1 Wear behaviour, 4.2.5.2 Wear mechanism, 4.2.6 Corrosion performance, 4.2.7 Performance comparison with single layer coatings, 4.3 Closure*

4.1 Introduction

In this chapter the evaluation of microhardness, friction, wear, and corrosion performance of duplex electroless Ni-P/Ni-W-P coatings is presented. Electroless Ni-W-P being harder is expected to provide resistance against wear. At the same time, Ni-P provides the necessary corrosion resistance. Duplex Ni-P/Ni-W-P coatings acquire the constituent coatings' best properties and are expected to have enhanced mechanical and tribological properties. Duplex electroless Ni-P/Ni-W-P coating is developed in-house over steel substrates as discussed in the previous chapter. The coatings are heat-treated at different temperatures and durations. The tribological testing of coated samples is carried out on a pin-on-disc setup. Microhardness test is carried out to evaluate the mechanical properties of the coated samples. Corrosion tests are conducted by PDP and EIS techniques. To carry out a comprehensive analysis, one set of coating is developed with Ni-W-P as the outer layer (denoted as Ni-P/Ni-W-P) and another set with Ni-P as the outer layer (denoted as Ni-W-P/Ni-P). The performances of the two set of coatings are compared.

4.2 Results and Discussion

4.2.1 Microstructure characterization and composition analysis

The surface morphology of duplex electroless Ni-P/Ni-W-P coatings is investigated with the aid of SEM micrographs (Figure 4.1). The coating in general appears to be defect free. As deposited coatings display nodular structure with nodule size ranging between 5 -10 μm (refer to Figure 4.1a). With heat treatment, however, the size of the nodule changes (Figure 4.1b-h).

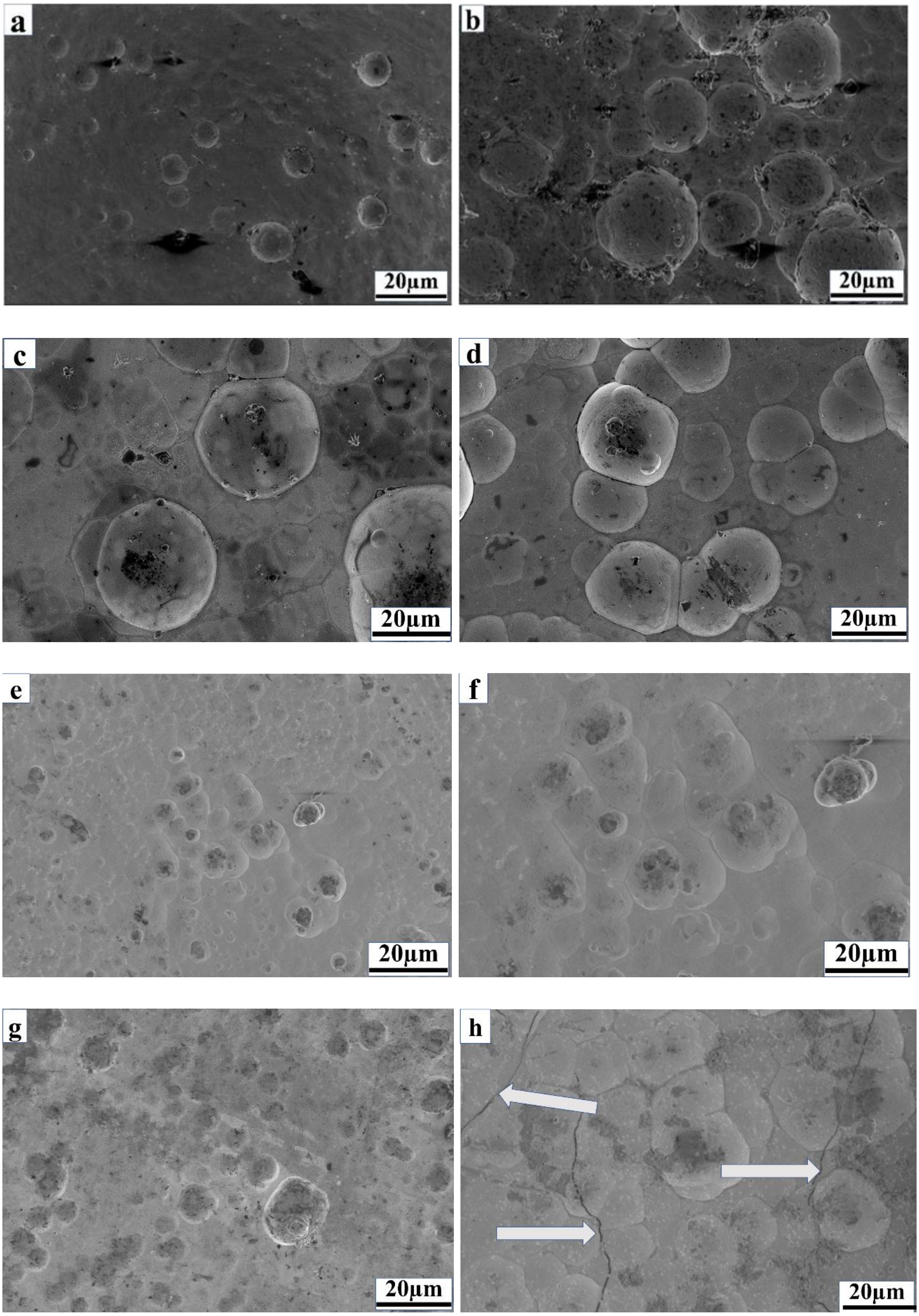

Figure 4.1 *SEM images of duplex Ni-P/Ni-W-P coating for (a) as-deposited coating; (b) 400°C for 1h duration; (c) 400°C for 2h duration; (d) 400°C for 4h duration (e) 600°C for 1h duration; (f) 600°C for 2h duration; (g) 800°C for 1h duration; (h) 800°C for 4h duration.*

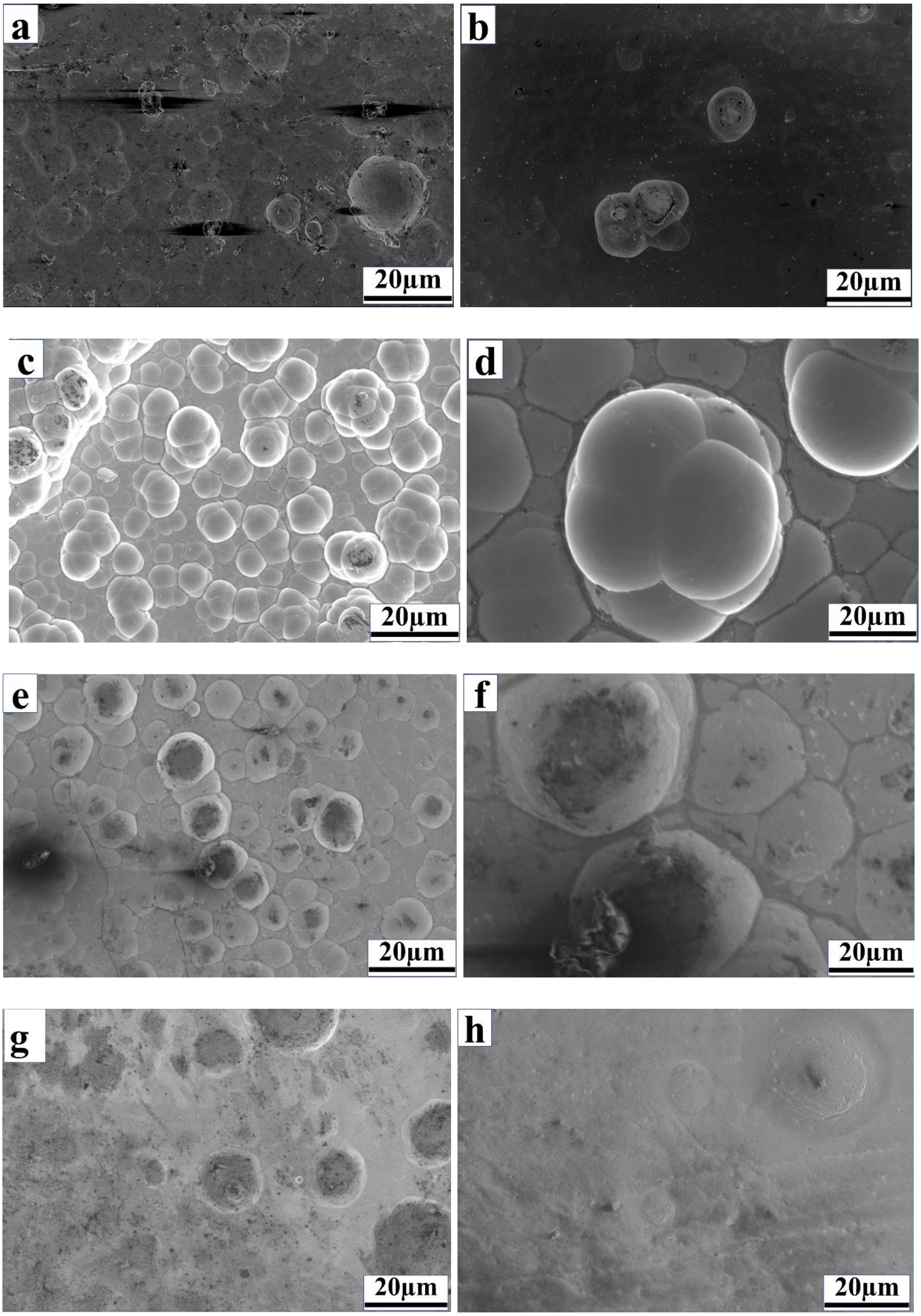

Figure 4.2 *SEM images of duplex Ni-W-P/Ni-P coating for (a) as-deposited coating; (b) 400°C for 1h duration; (c) 400°C for 2h duration; (d) 400°C for 4h duration (e) 600°C for 1h duration;(f) 600°C for 2h duration; (g) 800°C for 1h duration; (h) 800°C for 4h duration.*

This may also be indicative of changes in its microstructure. It is found that with heat treatment, the nodules undergo bulging (Figure 4.1b). The bulging is more prominent for prolonged heat treatment time (Figure 4.1c & 4.1d). At 400°C heat treatment temperature for a 2h duration, there are some black spots (refer to Figure. 4.1c) on the coating which may imply the formation of a minor level of oxides. However, upon heat treatment at 600°C and beyond, the nodules seem to undergo flattening (Figure 4.1g). The sample heat treated at 800°C for 4h develops cracks (indicated by arrows) on the surface (Figure 4.1h) which is due to the relief of the accumulated thermal stress in the coating microstructure.

Apart from these, dark spots are noticed on the coating surface. For samples heat treated at 600°C and 800°C, these dark spots are more prominent. The presence of dark patches may indicate that oxides may have formed on the coating surface. In the case of duplex Ni-W-P/Ni-P coating, the existence of nodular form may be seen in the surface characteristics of the as-deposited coating as illustrated in Figure 4.2a. The effect of heat treatment is prominently observed in microstructure, *i.e.*, the size of the nodule increases (Figure 4.2b-h). This is due to the grain coarsening effect of longer exposure to heat. For heat treatment temperature of 800°C and 1h holding time (Figure 4.2g), the coating surface reveals blackish patches which are anticipated to be formed due to oxidation. At 800°C temperature and 4h duration, the oxide layer is more prominent.

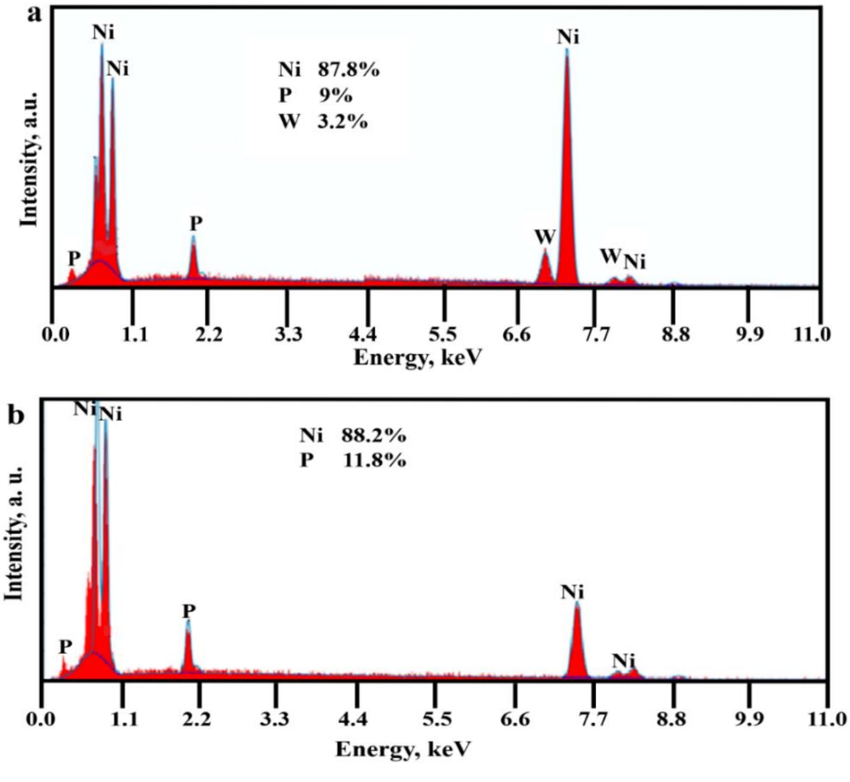

Figure 4.3 *EDX spectrum of as-deposited (a) Ni-P/Ni-W-P coating; (b) Ni-W-P/Ni-P coating*

The EDX spectrum of Ni-P/Ni-W-P coating is presented in Figure 4.3, along with the constituents' percentage composition. It is observed that both the duplex electroless nickel coating has a moderately higher percentage of phosphorous (Figure 4.3). Hence, the deposit is expected to be amorphous/micro-crystalline **(Narayanan et al., 2006).** In case of electroless Ni-P/Ni-W-P (Ni-W-P as outer layer) coating, tungsten content is found to be around 3.2% (refer to Figure 4.3a).

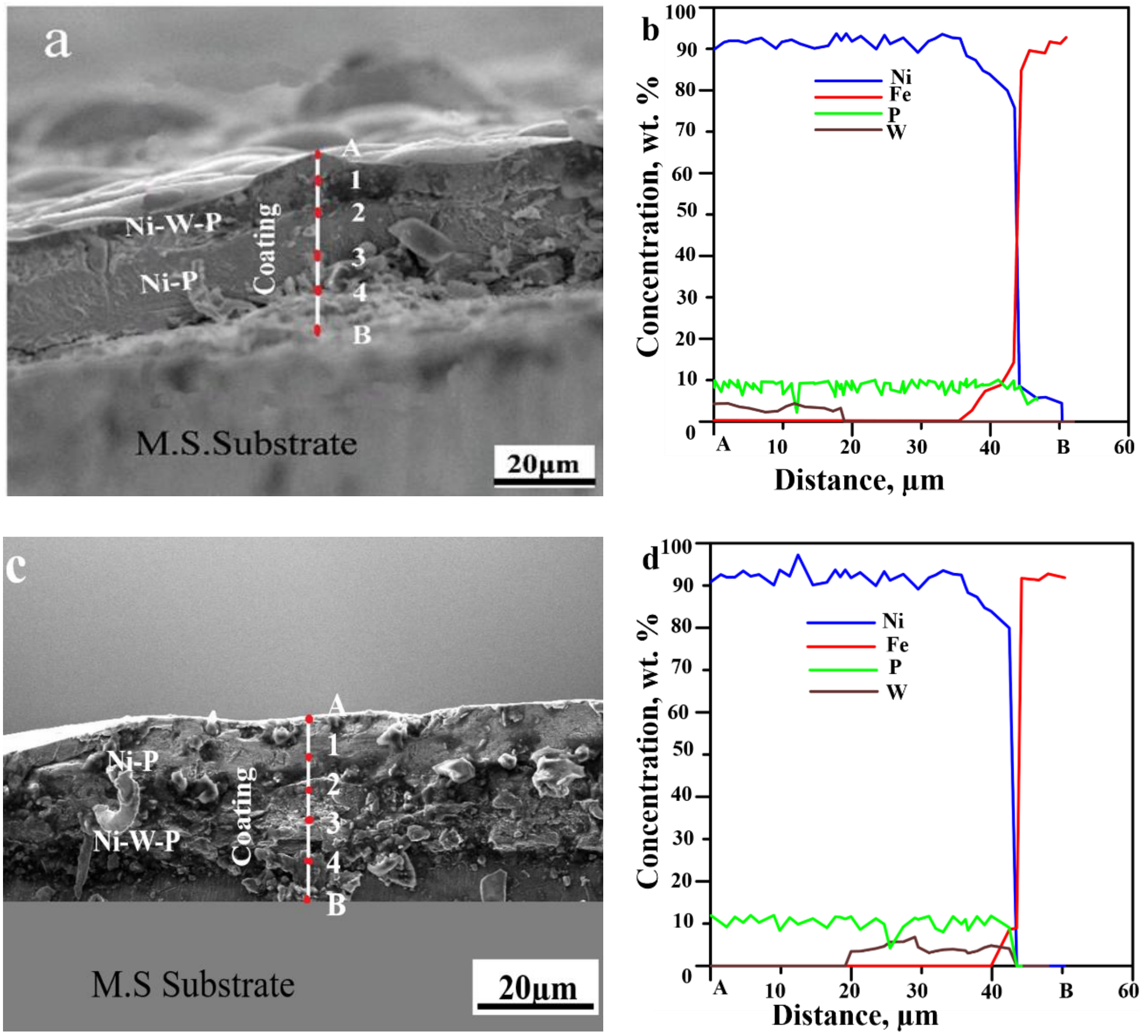

Figure 4.4 *Coating cross-section showing line EDX results of: (a, b) Ni-P/Ni-W-P coating and (c, d) Ni-W-P/Ni-P coating*

Additionally, the line EDX is performed on the cross-section of the coating, as shown in Figure 4.4a and Figure 4.4c, and the corresponding concentration of wt.% plot is presented in Figure 4.4b and Figure 4.4d respectively. From the cross-cut micrograph, the overall thickness of the present coating is found to be around 40µm. However, there is no visible demarcation between the two layers of the coating. From line EDX results, it can be seen that W is detected from the top surface of the duplex Ni-P/Ni-W-P coating up to about a depth of

18µm. Beyond this zone, only Ni and P are detected at their usual concentration until about 40µm after which Fe becomes the dominant phase. Similarly for Ni-W-P/Ni-P coating, W is detected from the inner layer, and the thickness is around 21 µm. This confirms the successful deposition of two layers of the coating as expected. The absence of visible demarcation in the cross-cut micrograph may indicate splendid adhesion and compatibility between the two layers of the deposit.

4.2.2 Phase structure

XRD analysis of both the duplex coating is presented in Figures 4.5 and 4.6. The as-deposited sample exhibits mainly an amorphous structure typical to any high phosphorous electroless nickel deposit. This is represented by the XRD plot exhibiting a single broad peak ranging between 2θ values of 35-55°(Figure 4.5a and 4.5b). Now, when heat treated at 200°C, there is not much change in the XRD plots. However, when the samples are heat treated at/beyond 400°C, there is a marked change in the samples' XRD profile with multiple peaks of various phases combining Ni, P, W, and even O. This shows a phase transformation in the coating microstructure when heat treated at a temperature between 200 and 400°C. One of the previous literature dealing with similar coating reports the phase transformation occurring at a temperature of around 350°C **(Biswas et al., 2019).** The primary phase detected in the present coating after heat treatment is the stable nickel phosphide (Ni_3P) phase, which is responsible for the increase in hardness and wear resistance of the coatings. In fact, for duplex Ni-P/Ni-W-P coated samples heat treated at 400°C, 1h, many nickel phosphide (Ni_3P) phases are detected in different planes like (301), (321), (330), and (141). As a transformation to Ni_3P occurs more at around 400°C temperature, these samples are expected to possess higher hardness and wear resistance than other treated samples (refer to Figure 4.5a). Apart from that, Ni (111) phase is also detected. No metastable phases of nickel and phosphorous are detected. One of the interesting phases to be detected is the WP phase. With an increased duration of heat treatment at 400°C, the number of crystalline peaks is found to be somewhat reduced. When the heat treatment temperature increases or even for a higher treatment duration, the peaks in the XRD profiles get sharper, this sharpening of the peaks may occur because of relaxation in the surface strain and increased grain size growth **(Zhao and Zhang, 2008).**

Heat treatment at 600°C and 800°C reveals oxide phases of nickel oxide (NiO). NiO being dark black, generates visible dark patches on the coating surface. A significant difference is not observed in comparing the XRD plots of 1h, 2h, and 4h heat treated samples. However, the increased detection of the oxide phase at higher temperatures for 4h duration cycles may moderately influence the tribological and corrosion behavior of the present duplex coatings.

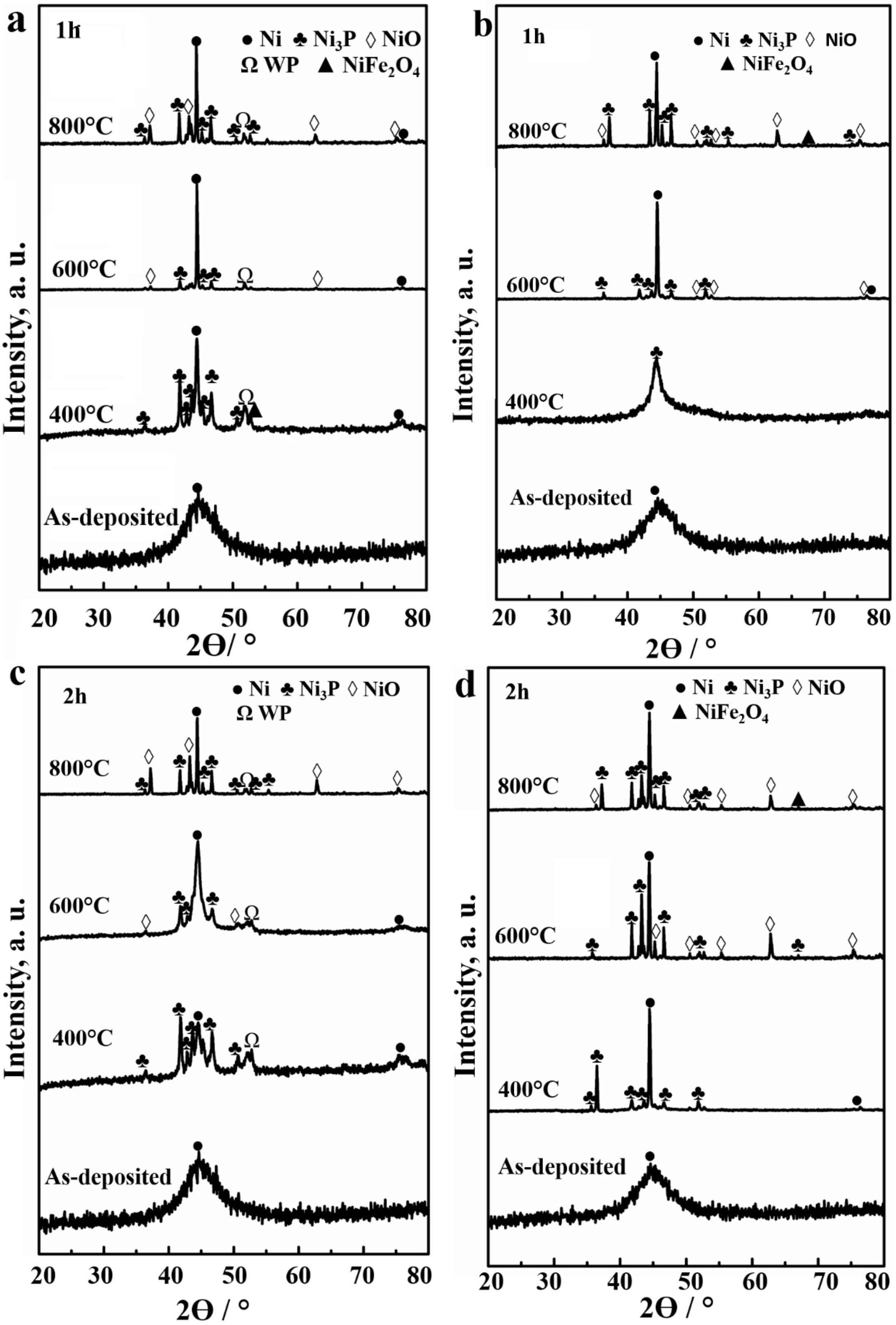

Figure 4.5 *XRD plots of (a) Ni-P/Ni-W-P coating, 1h; (b) Ni-W-P/Ni-P coating, 1h; (c) Ni-P/Ni-W-P coating, 2h;(d) Ni-W-P/Ni-P coating, 2h*

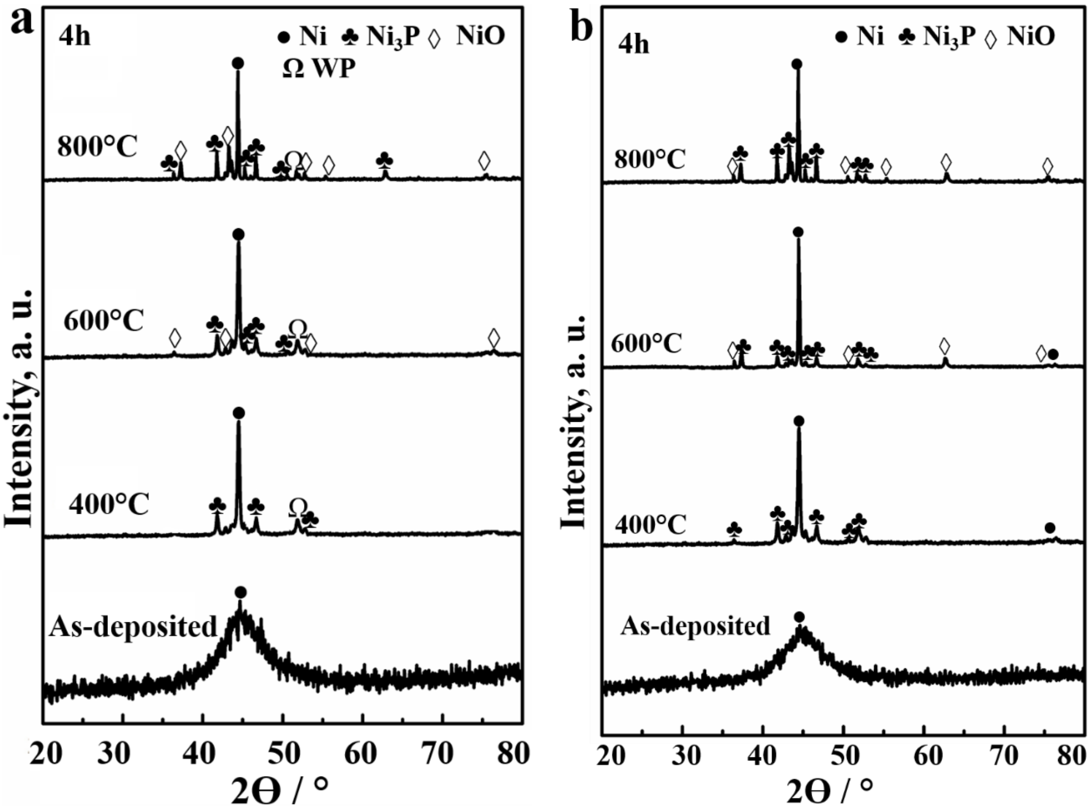

Figure 4.6 *XRD plots of: (a) Ni-P/Ni-W-P coating, 4h; (b) Ni-W-P/Ni-P coating, 4h*

For duplex Ni-W-P/Ni-P coating, the precipitation of phases is almost similar to duplex Ni-P/Ni-W-P Coating. Upon heat treatment, the coating turns crystalline as can be observed in the case of heat-treated samples (Figure 4.5b). At 400°C heat treatment temperature for 1h duration, the coated samples display a single sharp peak of Ni_3P in the (111) plane. There are peaks of Ni (111) (200) and Ni_3P (321) (112) (420) for 2h heat treatment duration (refer to Figure 4.5d). At 600°C heat treatment temperature with a two-hour duration exposes single sharp peak with diffraction angle of 44.51° on the Ni phase in the (111) plane. Crystalline Ni_3P phases are also detected in (321), (112), and (141) planes. At high temperatures (600°C or 800°C) and at time duration of 1h-4h few oxides phase (NiO) is detected. This oxide phase is responsible for reduced hardness values for samples heat treated at high temperatures.

Not much difference between the phase structure between the two sets of coating is observed indicating that the insertion of a ternary element viz. Tungsten does not affect the phase structure of the coatings. Also, the duplex coatings do not exhibit a highly varied behaviour w.r.t. the individual single-layer coatings **(Sankara Narayanan et al., 2003; Kundu et al., 2019).**

4.2.3 Microhardness study

In the present investigation, the microhardness of as-deposited duplex Ni-P/Ni-W-P coatings is reported as 724 $HV_{0.1}$. In fact, for better visualization, the microhardness results for both the coated samples are presented in Figure 4.7. Heat treatment seems to have a direct impact on the microhardness of the coating. The microhardness almost doubles that of as-deposited microhardness at a heat treatment cycle of 400°C and 1h. This shows the microhardness of the coating is highly impacted by the phase transformation regime and the formation of various crystalline phases, particularly the Ni_3P phase. Ni_3P phase being a hard phase, comes in the way of dislocation resisting them. Moreover, dislocations, which find a favorable situation for progressing in amorphous substance, get impeded by the grain boundaries in crystalline

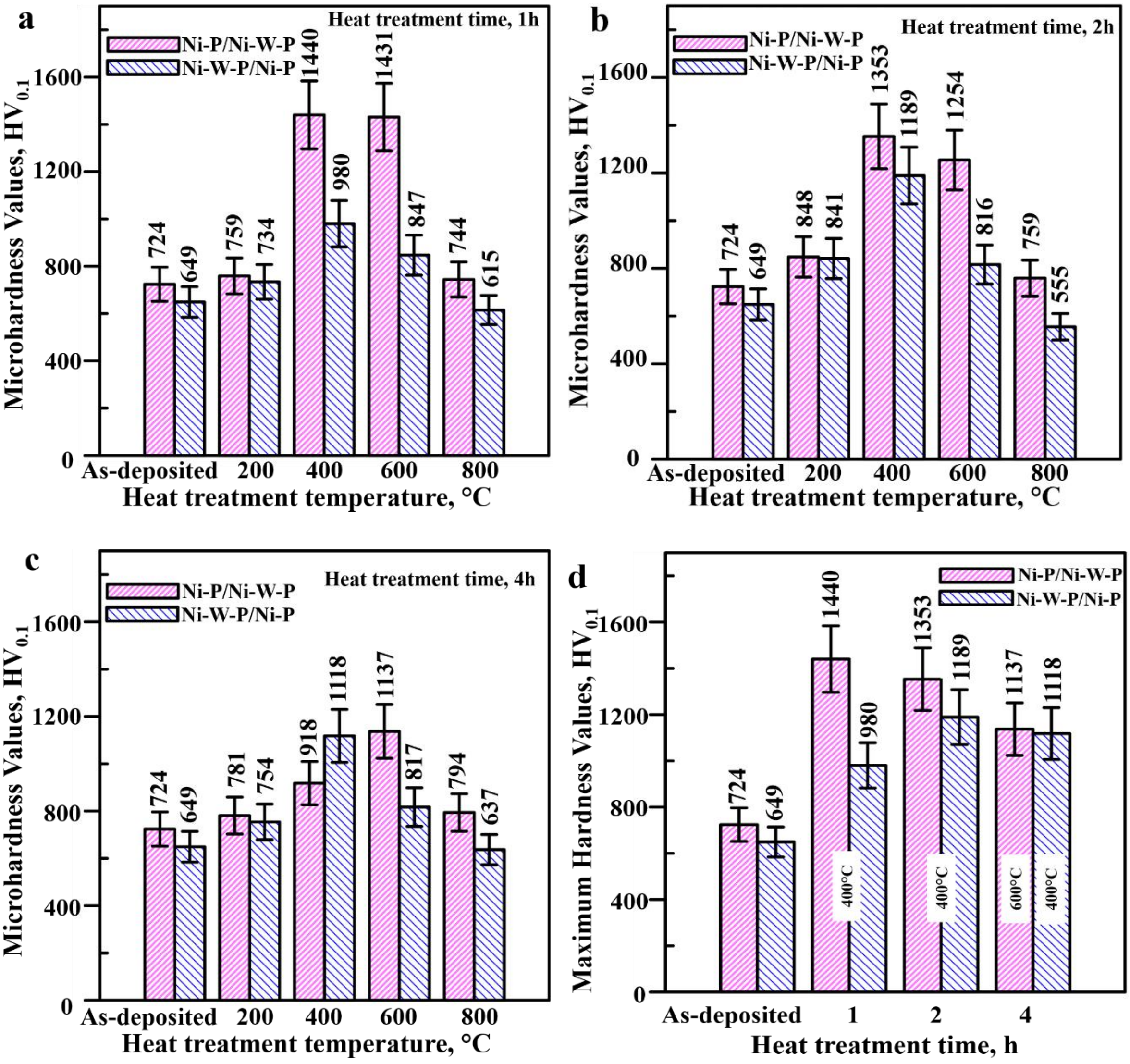

Figure 4.7 *Microhardness plots for heat treatment temperature of 200-800°C for: (a) 1h; (b) 2h; (c) 4h; and (d) maximum hardness value plot*

structures. These combined phenomena result in the samples being heat treated at 400°C and 1h to display the best microhardness. It is interesting to see that despite oxidation getting initiated at 600°C, 1h heat treatment cycle, the microhardness of the deposit does not suffer much (refer to Figure 4.7a). However, when heat treated at 800°C, 1h, the microhardness of the coated sample reduces drastically. This is mainly due to grain coarsening as well as oxide formation.

When the heat treatment temperature is kept at 400°C for 2h duration, the coating also shows the highest microhardness value (Figure. 4.7b) due to the creation of a crystalline Ni_3P phase. XRD analysis has previously established the formation of this phase. The hardness increase is about 87% when compared to the as-deposited state, which is significant. The hardness values drop as the heat treatment temperature rises beyond 400°C due to grain softening and oxide formation. The development of oxides is observed at temperatures exceeding 600°C, which may result in a reduction in microhardness The coating's microhardness value plummets around 800°C for 2h duration.

Upon heat treatment for 4h duration, the microhardness is found to be more than that of as-deposited microhardness. However, the values are significantly lesser than those observed for 1h and 2h heat-treated specimens. For a 4h sample, the formation of Ni_3P phases may be lesser, as indicated in XRD results. At the same time, for a 4h heat treatment cycle, there is a higher accumulation of thermal stresses, which act as residual stresses and hence result in a quicker formation and movement of dislocations. The best microhardness achieved for 1h, 2h, and 4h heat treatment cycles are compared to as-deposited microhardness and presented in Figure 4.7d. It can be observed that w.r.t. microhardness, the 1h heat treatment duration seems to be the optimum choice.

For as-deposited duplex Ni-W-P/Ni-P coating, the microhardness is obtained as $649HV_{0.1}$. At 400°C temperature treated samples revealed the maximum hardness values among all treated samples (Figure. 4.7a) due to the formation of crystalline hard Ni_3P phase structure **(Biswas et al., 2017)**. The hardness value is increased by about 50 percent from the as-plated coating. For heat treatment temperature of 600°C or 800°C, the microhardness decreases due to grain coarsening but the coating is still harder compared to the as-deposited one. For higher heat treatment temperatures, the hardness reduces drastically due softening of the coating and the formation of oxides.

For a 2h duration heat treatment cycle, the increment in microhardness compared to the as-deposited state is observed to be around 83% which is significant. After 400°C, the hardness values decrease as the heat treatment temperature rises due to the grain softening phenomenon.

Further above 600°C temperature and 2h and 4h duration, the formation of oxides is noticed which may result in lowering of the microhardness.

As compared to Ni-W-P/Ni-P coating, Ni-P/Ni-W-P coating possesses relatively higher microhardness. This is due to the incorporation of W in the coating. The peak microhardness level of Ni-W-P outer layer coating seems to be maintained even at 600°C (Figure. 4.7a-c) which may be due to higher thermal stability of W. The hardness of the coating falls drastically at 800°C due to the combined effect of grain coarsening as well as oxide formation. Thus, according to the microhardness study, the Ni-W-P as the top layer coating is the preferable choice in all aspects.

4.2.4 Friction performance

Electroless nickel coatings are uniform and smooth and normally display a low COF. In the present study, the friction of both the coating is also found to be low, as presented in Figure 4.8. It is interesting to see that COF of the coating decreases after heat treatment due to the rise in microhardness of the coating. The harder coating leads to a lower area of contact resulting in low COF. However, the lowest COF is displayed by coatings undergoing heat treatment at 200°C, 1h for both the systems (which doesn't yield the best microhardness). For Ni-W-P top layer coating, the COF reduction is almost 50% (w.r.t. as-deposited coating) as seen in Figure. 4.8a. In case of 400°C, 1h, reduction in COF is almost 40%. The highest COF is observed for the heat treatment cycle of 600°C, 1h, which is quite hard but also has oxide patches. The COF again decreases for sample heat treated at 800°C, 1h, which may be because of the formation of the higher amount of oxide film, which presents lower shear strength, thus reflecting as low COF.

In fact, the changes in COF due to heat treatment is not too much significant. This may be attributed to the higher thermal stability of the W as the ternary element. For Ni-W-P top layer coating systems, COF drops at 600°C heat treatment temperature for 2h. The tribooxide layer formed for those particular samples may be responsible for presenting a surface layer with low shear stress which may result in the coatings displaying lower friction.

For 4h heat treatment cycles, the COF values are marginally lower for 600°C and 800°C. This may be due to the formation of a higher amount of oxidation which presents a layer of low shear strength. Overall, COF is found to be more or less consistent for samples particularly heat treated at 400°C. The COF values over the testing period are also found to be quite consistent (refer to Figure 4.9). These plots exhibit an initial period of increasing COF, post which the COF attains almost a stable value. This initial period is known as the run-in period and is a characteristic feature of any friction test in sliding mode.

For Ni-W-P/Ni-P coating COF is found to be 0.53 in as-deposited state(refer to Figure 4.8a). At 200°C temperature and 1h time period treated sample displayed minimum COF (Figure 4.8d). At higher temperatures (600°C and 800°C), the friction behaviour of the coated samples is additionally governed by the oxide layer formed on the coated surface. For 2h duration at 200°C temperature, the COF is reduced by around 47% with respect to as-plated coating (Figure 4.8b). The COF of the coating heat treated at 400°C is found to be maximum for the higher hardness values of the coating which presents an incompatible surface to the counterface during the sliding process. For Ni-W-P/Ni-P coating systems, COF drops at 600°C or 800°C, 2-4h duration (refer to Figure 4.8c) as compared to as-deposited coating. The

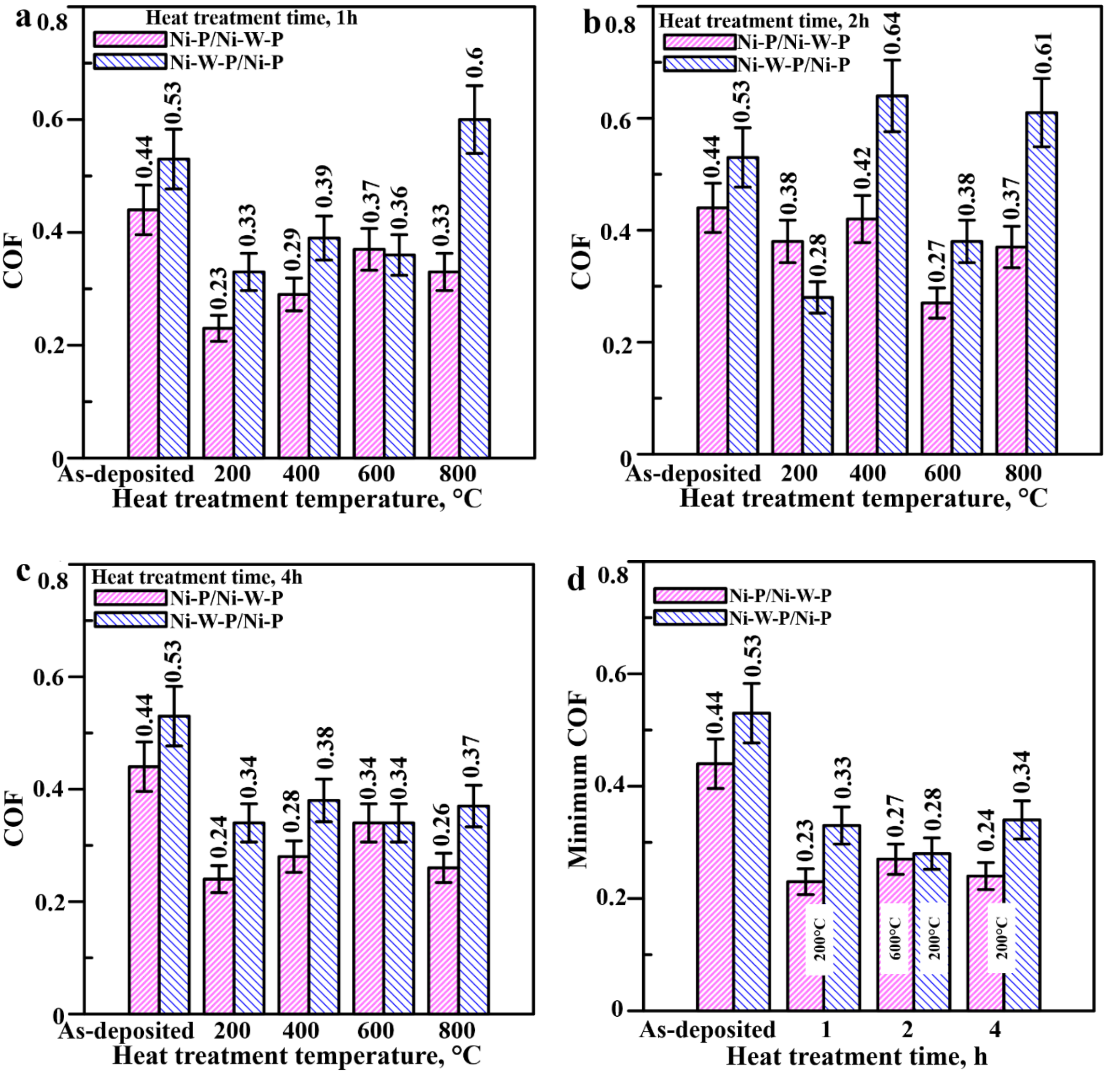

***Figure 4.8** COF plots for heat treatment temperature of 200-800°C: (a) 1h; (b) 2h;(c) 4h; and (d) minimum COF plot*

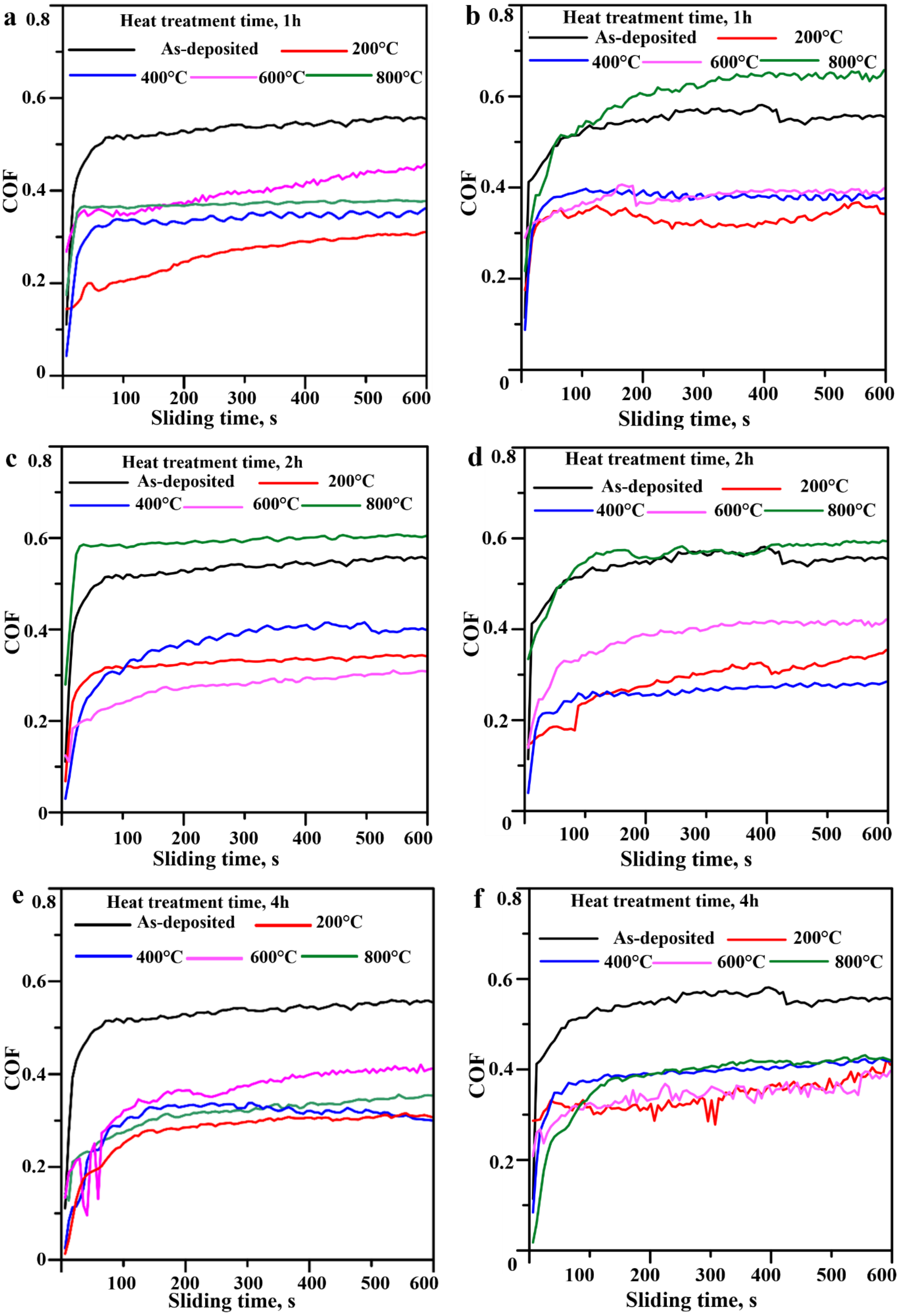

Figure 4.9 *COF vs. sliding duration plots of: (a) Ni-P/Ni-W-P coating, 1h; (b) Ni-W-P/Ni-P coating, 1h; (c) Ni-P/Ni-W-P coating, 2h;(d) Ni-W-P/Ni-P coating, 2h (e) Ni-P/Ni-W-P coating, 4h; (f) Ni-W-P/Ni-P coating, 4h*

tribooxide layer formed for those particular samples may be responsible for presenting a surface layer with low shear stress which may result in the coatings displaying lower friction. Overall Ni-W-P as outer layer coating exhibits a more stable friction behavior compared to Ni-P as outer layer coating.

4.2.5 Wear performance

4.2.5.1 Wear behaviour

The results of the wear test are shown in Figure 4.10. The top Ni-W-P layer is hard and quite wear-resistant compared to the Ni-P coatings. This is because tungsten, when introduced in the Ni-P matrix, results in solid solution strengthening. Apart from that, both coatings have a similar wear pattern. The wear rate is reduced with increased heat treatment temperature in

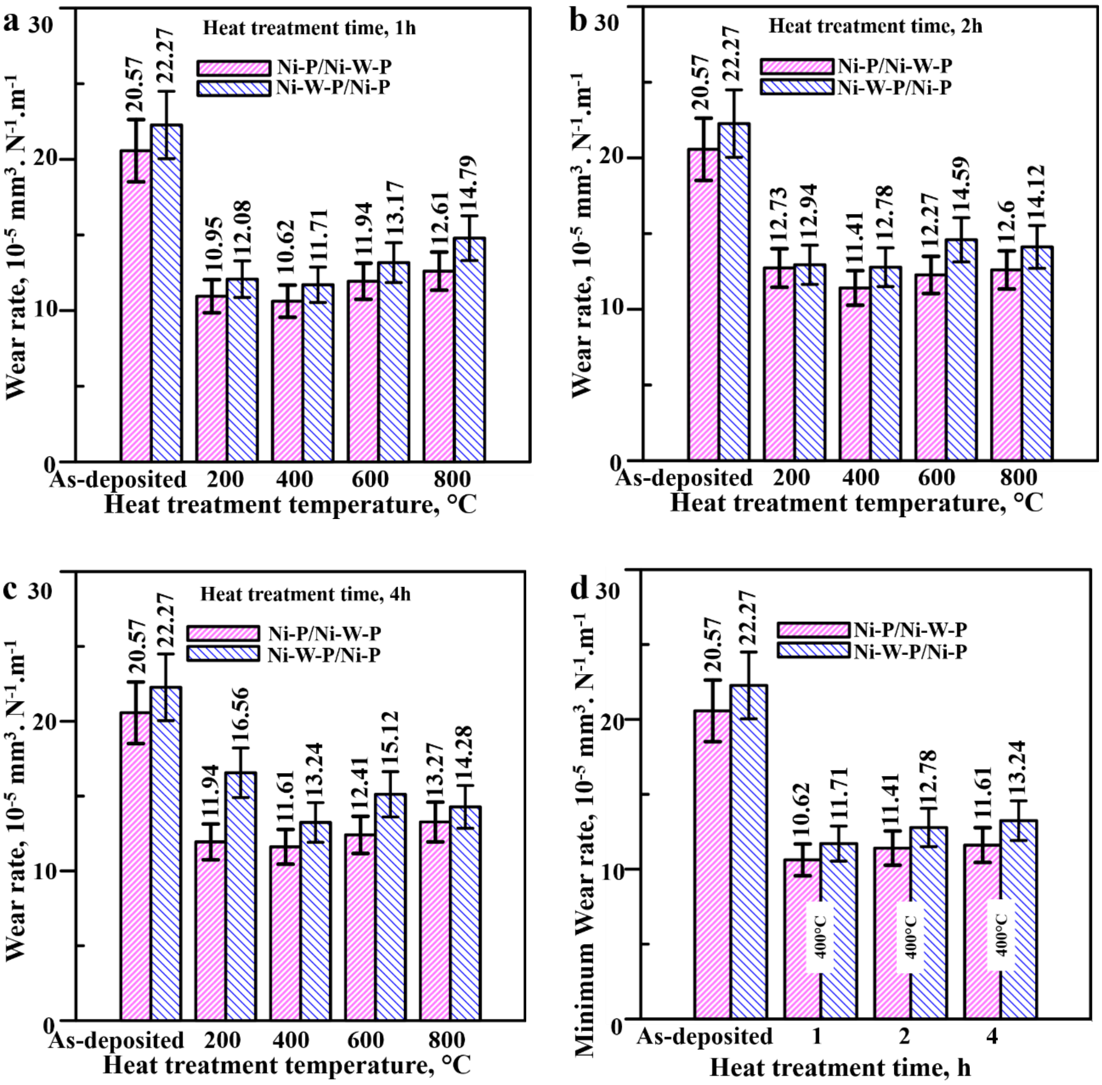

Figure 4.10 *Wear rate for heat treatment temperature of 200-800°C for: (a) 1h; (b) 2h; (c) 4h and (d) minimum wear rate*

both the duplex coating (Figure 4.10a-4.10d). It is observed that the wear rate of both the duplex coatings decreases after heat treatment for 1h duration. In fact, the Ni-W-P as outer layer coating, the best wear resistance, as anticipated, is seen for the sample heat-treated at 400°C, 1h (about 50% decrease in the wear rate compared to the as-deposited sample (refer to Figure 4.10a). After heat treatment, harder nickel phosphide phases precipitate (as observed in diffraction results), which increases the microhardness of the coating. Moreover, upon heat treatment at 400°C, the coating system attains complete crystallization resulting in optimum grain size as well as the correct amount of Ni_3P precipitation. With heat treatment temperature beyond 400°C, the wear rate increases, which may be due to a combination of phenomena, viz. grain coarsening, oxide formation, and interdiffusion of elements. The minimum wear rate is obtained at 400°C among all time durations (1-4h duration) (Figure 4.10d).

A longer heat treatment period also does not seem to have a positive effect on the wear performance of the coating. However, a good correlation between the wear and microhardness results can be observed for the present coatings, especially for the 1h heat treatment cycle.

The coating displaying the highest microhardness displays the lowest wear rate. And as the hardness decreases with higher heat treatment temperature and longer duration (from 1-4h), the wear rate also increases.

For Ni-P outer layer coating in as-deposited state, the wear rate is observed as 22.27×10^{-5} mm^3 N^{-1} m^{-1} (Figure. 4.10). The minimum wear rate for Ni-W-P/Ni-P coating is obtained at 400°C due to formation of hard Ni_3P phase. At heat treatment temperatures beyond 400°C, the wear rate is increased due to more oxide formation and grain coarsening. At 800°C, the wear rate is increased marginally compared to that at 400°C temperature in 1h, 2h and 4h time duration. In the meantime, at 800°C for 2h and 4h duration, wear rate is reduced from 600°C temperature (refer to Figure 4.10b & 4.10c). According to tribological based application the Ni-W-P as the outer layer seems to be the preferred.

4.2.5.2 Wear mechanism

The wear mechanism and wear behaviour of Ni-W-P outer layer coating is revealed by the SEM micrograph of the samples after tribological test for both as-deposited and heat-treated conditions as shown in Figure 4.11. In as-deposited condition a few deep grooves are obtained on the surface along the sliding direction (refer to Figure 4.11a). It indicates abrasive wear mechanism. Adhesive wear is also noticed in the forms of pits and prows. Adhesive wear is caused by experimental settings that create a strong attraction between the coating and the counterface surfaces. Moreover, nickel and iron are known to have high mutual solubility and hence adhesion between the coating and counterface is strong. Few wear debris is also noticed on both the coating surfaces. The 400°C for 1h heat-treated sample (refer to Figure 4.11b) shows the presence of wear tracks, indicating that an abrasive wear mechanism exists. Some remnants of the original nodular structure of the coating are visible. Apart from the wear tracks, some debris is found to be scattered on the tested surface (marked by arrows). This debris seems to get welded to the surface. A few pits and prows are observed on the worn surface. These imply the occurrence of adhesive wear alongside. The wear debris naturally gets pressed between the sample and the counter face. The worn surface of 400°C for 2h heat treated samples shows a few cracks and ploughing on the surface (refer Figure 4.11c). The ploughing is seen in the sliding direction.

The worn surface of 800°C for 4h heat-treated sample shows a lot of damage (refer to Figure 4.11d). Apart from wear tracks, a part of the coating layer seems to have delaminated, exposing the interlayer of the coating. This strongly points out to the heavy oxidation suffered

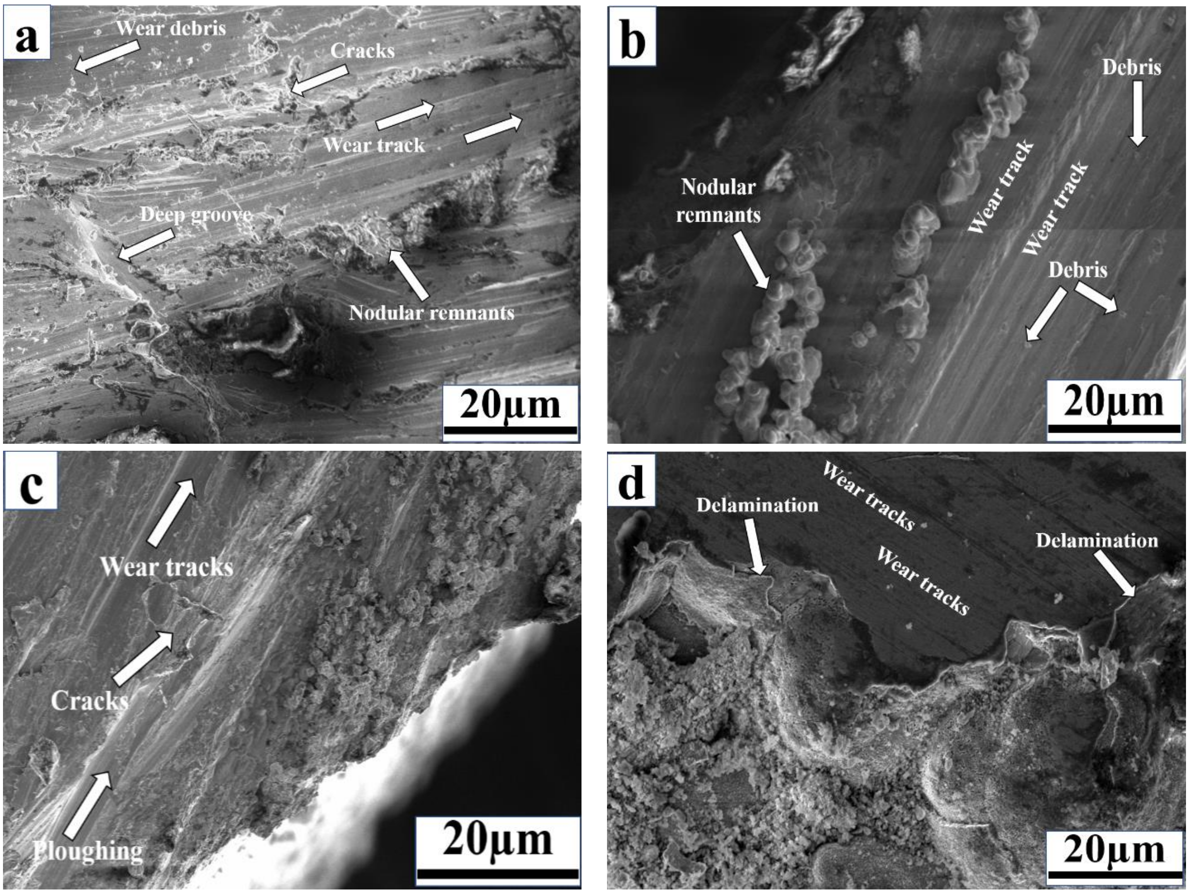

Figure 4.11 *SEM of Ni-P/Ni-W-P coating after wear test of (a) As-deposited coating (b) heat treated at 400°C for 1h, (c) heat treated at 400°C for 2h, (d) heat treated at 800°C for 4h*

by the sample during heat treatment, as already discussed before. Now, the top oxide layer obviously doesn't have the necessary adhesive strength with the coating interlayer making it vulnerable to flaking and delamination under contact pressure. Wear debris in patches is also found to be smeared on the worn surface of the sample. The SEM micrograph of the sample is quite commensurate with its higher wear rate, as observed during the wear test.

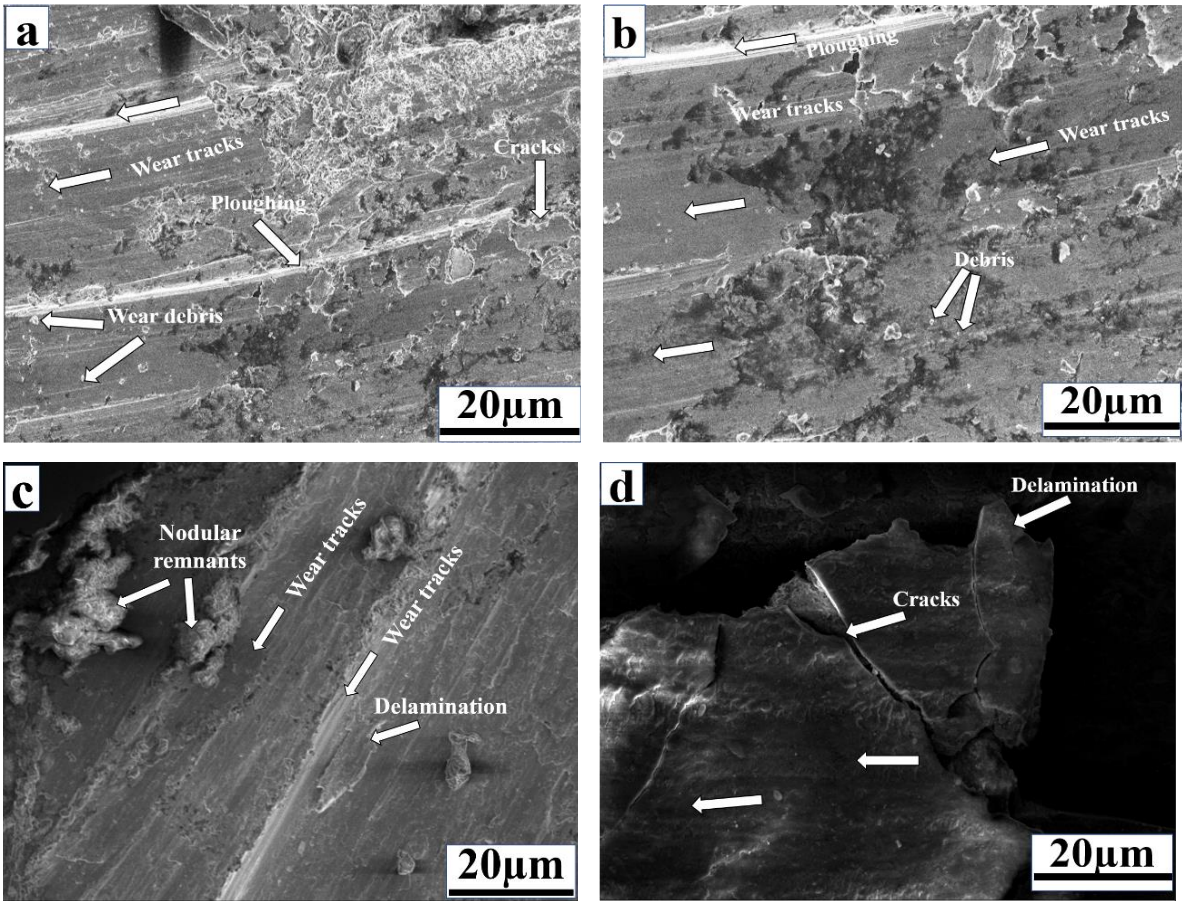

***Figure 4.12** SEM of Ni-W-P/Ni-P coating after wear test of (a) As-deposited coating (b) heat treated at 400°C for 1h, (c) heat treated at 400°C for 2h, (d) heat treated at 800°C for 4h*

The wear mechanisms are revealed by the SEM micrograph of Ni-P outer layer coatings after tribological test for as-deposited and heat-treated conditions as shown in Figure 4.12. The surface of coating is characterized by fine longitudinal grooves running along the length of the surface, indicating that an abrasive wear mechanism has occurred. The occurrence of grooves is as a result of micro ploughing and micro cutting effect. Apart from the groove, a few partial irregular pits are observed which are indicative of adhesive wear. The wear debris in both as-deposited and worn samples (at 400°C,1h) are indicated in the Figure 4.12a & 4.12b. Instead of breaking completely, the attached substance deforms plastically and adheres to the surface (at 400°C,2h). These characteristics point to the occurrence of delamination wear as shown in Figure 4.12c. A similar type of observation is reported by **Banerjee et.al 2019**. At 800°C for

4h duration, the worn surface displays more crack and delamination. Also, oxide layer has been seen on the worn surface. Formation of oxide also deteriorates the tribological performance of both the coatings.

4.2.6 Corrosion performance

The PDP plots of both the duplex systems are presented in Figure 4.13. The results of PDP and EIS tests for the present duplex Ni-P/Ni-W-P and Ni-W-P/Ni-P coatings are listed in Table 4.1. The plots exhibit proper Tafel region with distinct anodic and cathodic sections. The PDP results show that, in general, the corrosion potential moves towards the positive region after heat treatment. This implies that as-deposited coatings have the least corrosion resistance in both the coatings. This is interesting, considering present as-deposited coating is believed to possess an amorphous structure. In fact, heat treatment induces crystallinity in the coating that may aid corrosive media to penetrate the coating by traveling through the grain boundaries. This observation may be explained by the fact that the present coating has more of a nanocrystalline structure rather than completely amorphous. After heat treatment, the coating

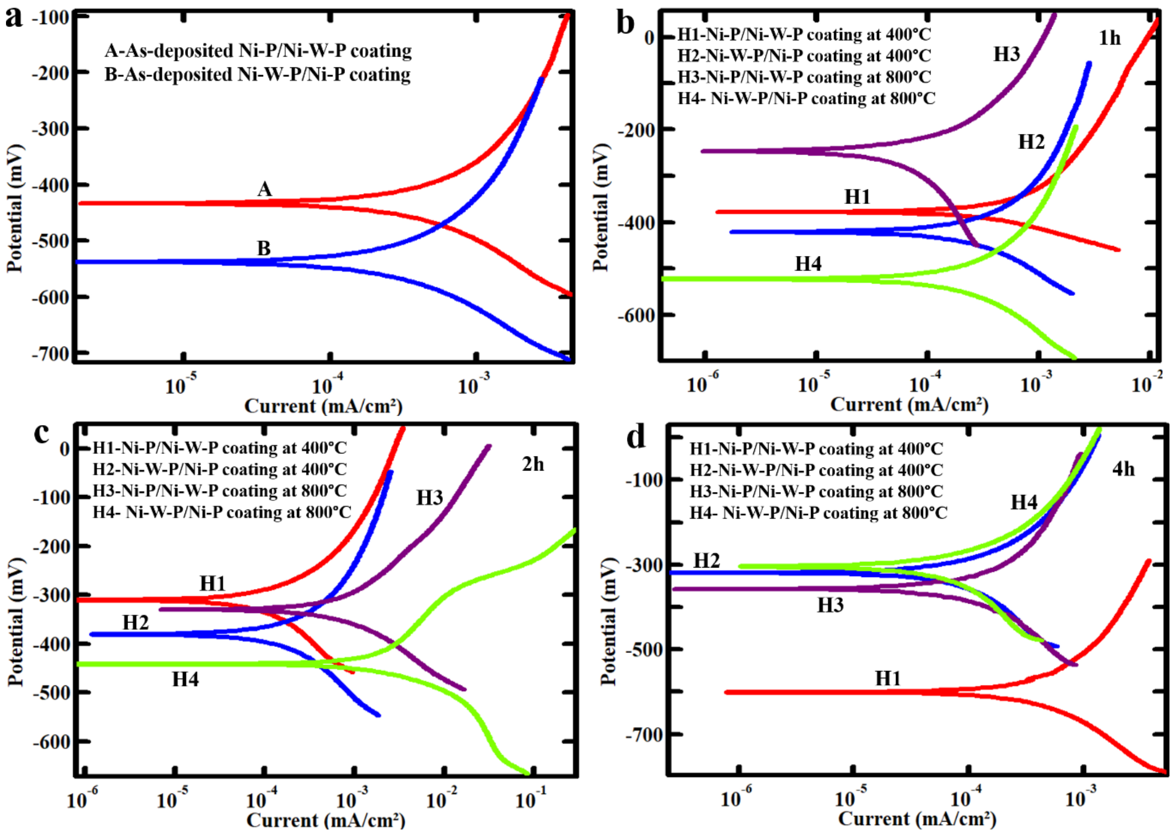

Figure 4.13 *PDP plots for: (a) as-deposited condition; (b) heat-treated samples 1h duration; (c) heat-treated samples 2h duration; (d) heat-treated samples 4h duration*

becomes denser and more compact. This type of observation has been reported by some other researchers as well **(Rabizadeh et al., 2010)**. Besides, as the present coating is a duplex coating system, heat treatment may help attain a splendid adhesion between the two layers of deposit. Another interesting thing to observe is that the corrosion potential moves towards the positive direction with higher heat treatment temperature, especially Ni-P/Ni-W-P coating for a 1h heat treatment cycle (Figure 4.13b). This may be because of the fact that with higher heat treatment temperatures, grain coarsening of the coating occurs. Now, coarser grains are always favourable w.r.t. resisting the corrosive media.

In the meantime, both the duplex coating in 2h heat treatment cycle, the plot shift towards positive potential. This implies that the corrosion resistance of the coating increases post heat treatment which is further evident from lower corrosion current than as-deposited coatings except for the Ni-W-P/Ni-P coated sample heat-treated at 800°C, 2h (refer to Table 4.1). Nanocrystalline structure definitely have higher grain boundary density. More grain boundaries mean more sites for attack by the corrosive media. Hence, as grain boundary density in heat treated samples are bound to be lesser, they show increased corrosion resistance than their as-deposited counterparts. Similar observation has been made by **Rabizadeh et al. (2010),** and **Mukhopadhyay et al. (2017)**. Among Ni-P/Ni-W-P and Ni-W-P/Ni-P coating, the former is found to be possessing a higher corrosion resistance. The presence of W on the top layer may be resisting the formation of micro corrosion cells or promoting the formation of passive layer

Table 4.1 Corrosion data obtained from PDP and EIS tests

Samples	**E_{corr} (mV)**	**i_{corr} (mA/cm^2) ×10^{-5}**	**R_{ct} (Ohm. cm^2) ×10^5**	**C_{dl} (10^{-6}F)**
Ni-P/Ni-W-P Coating, as-deposited	-433	34.88	1.108	21.08
Ni-W-P/Ni-P Coating, as-deposited	-537	24.73	1.047	21.45
Ni-P/Ni-W-P Coating, at 400°C 1h	-379	18.54	1.415	13.03
Ni-W-P/Ni-P Coating, at 400°C 1h	-421	13.96	1.607	13.06
Ni-P/Ni-W-P Coating, at 800°C 1h	-243	9.1	2.34	0.324
Ni-W-P/Ni-P Coating, at 800°C 1h	-522	6.294	1.45	4.809
Ni-P/Ni-W-P Coating, at 400°C 2h	-310	4.87	2.44	1.11
Ni-W-P/Ni-P Coating, at 400°C 2h	-381	3.75	1.88	0.106
Ni-P/Ni-W-P Coating, at 800°C 2h	-328	32.08	1.36	4.52
Ni-W-P/Ni-P Coating, at 800°C 2h	-441	58.24	1.34	0.142
Ni-P/Ni-W-P Coating, at 400°C 4h	-602	32.18	1.26	28.34
Ni-W-P/Ni-P Coating, at 400°C 4h	-321	3.495	2.86	3.95
Ni-P/Ni-W-P Coating, at 800°C 4h	-357	8.18	2.31	1.48
Ni-W-P/Ni-P Coating, at 800°C 4h	-303	1.878	3.03	2.2

which prevent the attack by the corrosive media. In the case of the 4h heat treatment cycle, the samples display higher corrosion resistance than as-deposited coatings except for the Ni-P/Ni-W-P coated sample heat-treated at 400°C, 4h.

The Nyquist plots for both the present duplex coatings are shown in Figures 4.14a to 4.14d, while the equivalent circuit employed is illustrated in Figure 4.14e. The EIS plots for the samples processed with a 1h heat treatment cycle display one semicircle. The semicircle is specifically located in the high-frequency region at OCP of the respective coatings (refer to Figure 4.14). The existence of a single semicircle in the Nyquist plots specifies that the corrosion process encountered in the present duplex coatings contains a fixed time constant. Moreover, the semicircles are almost similar in shape but vary in size. This implies the same fundamental process must have been encountered during corrosion for all the samples. R_{ct} and C_{dl} values almost reflect the same story as seen in the case of PDP test. Compared to as-deposited coating, heat-treated samples show higher R_{ct} and lower C_{dl} values. The highest R_{ct}

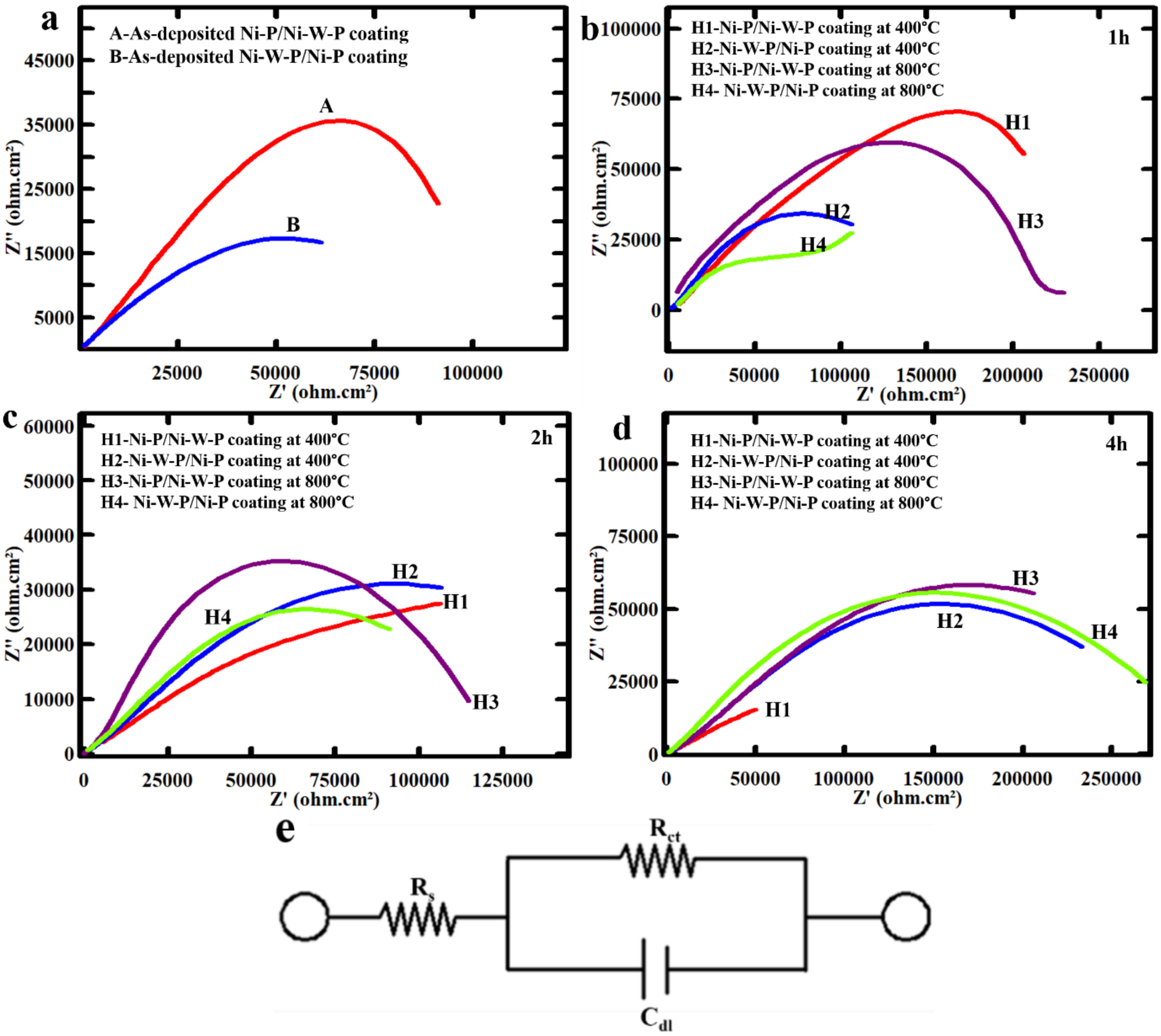

***Figure 4.14** Nyquist plots of the coatings (a) as-deposited (b) 1h duration, (c) 2h duration, (d) 4h duration, and (e) equivalent circuit diagram*

value is seen for the Ni-W-P outer layer sample heat-treated at 800°C, 1h. The results indicate that there may be some minor porosity in the as-deposited coating, which gets reduced after heat treatment. This is supported by the fact the C_{dl} values decrease with an increase in the heat treatment temperature.

For 2h heat treatment cycle , Ni-W-P as the outer layer coating, the higher R_{ct} value is obtained at 400°C heat treatment temperature. The low R_{ct} and high C_{dl} values for the Ni-W-P as outer layer coating heat-treated at 400°C, 4h, is a bit intriguing. Now, during heat treatment, several phases are precipitated in the coating microstructure. This results in inhomogeneities in the material, making it prone to be attacked by corrosive media. For the concerned sample, the resulting microstructure may be vulnerable to this attack, displaying poor corrosion resistance. Among all the heat treatment temperature and time duration, both the coating have almost similar trends of corrosion performance. It is very interesting to see that the higher R_{ct} value is obtained for Ni-P outer layer coating at 800°C,4h duration.

4.2.7 Performance comparison with single-layer coatings

The discussion of the present work remains incomplete without a performance comparison between the duplex coatings with the constituent single-layer coatings. A comparison of the microhardness and wear results is given in Table 4.2, while the corrosion results are compared in Table 4.3. It can be observed that the microhardness of both the present duplex coating is significantly higher than single-layer Ni-P coating but marginally lower than single-layer Ni-W-P coating for both as-deposited as well as the heat-treated case. In fact, Ni-W-P as the top layer also increases the wear resistance of Ni-P coatings, further enhancing through heat treatment. This is quite logical, considering tungsten in the Ni-P matrix induces a solid solution-strengthening mechanism, as already discussed before.

Table 4.2 Comparison of microhardness and wear for single-layer and duplex coatings

Coating Type	**Microhardness ($HV_{0.1}$)**		**Wear rate (10^{-5} $mm^3.N^{-1}.m^{-1}$)**	
	As-deposited	Heat Treated (400°C,1h)	As-deposited	Heat Treated (400°C,1h)
Single layer Ni-P	585	1082	25.32	14.52
Single layer Ni-W-P	735	1435	18.46	7.53
Duplex Ni-P/Ni-W-P	724	1440	20.57	10.62
Duplex Ni-W-P/Ni-P	649	980	22.27	11.71

Interestingly in the case of corrosion performance, however, the present duplex coatings perform inferiorly relative to single-layer Ni-P coatings with lower E_{corr} and higher R_{ct} values. Now, the corrosion behaviour in the Ni-P system is affected by the P content as the same decides the formation of passive film on the coating surface, thus providing protection to it. Hence, the single-layer Ni-P coating used for the comparison study is developed with approximately the same P percentage as the present duplex coatings. The duplex coatings, however, performed fairly well when compared to single-layer Ni-W-P coatings. Thus, it can be seen that the duplex coatings combine the advantages of the individual constituent layers, thus being able to provide a decent combination of wear and corrosion resistance. This makes them ideal material candidates for demanding applications.

Table 4.3 Comparison of corrosion performance for single-layer and duplex coatings

Coating Type	**E_{corr} (mV)**		**R_{ct} (ohm.cm^2)**	
	As-deposited	Heat Treated (400°C,1h)	As-deposited	Heat Treated (400°C,1h)
Single layer Ni-P	- 386	- 346	1.820×10^5	2.252×10^5
Single layer Ni-W-P	- 452	- 403	0.092×10^5	1.125×10^5
Duplex Ni-P/Ni-W-P	- 433	- 379	1.108×10^5	1.415×10^5
Duplex Ni-W-P/Ni-P	- 537	- 421	1.047×10^5	1.607×10^5

4.3 Closure

The present chapter attempts to systematically evaluate the effect of varying heat treatment temperature (200°C to 800°C) and time duration ranging from 1-4h on the tribological and corrosion performance of developed duplex Ni-P/Ni-W-P coating and also correlating the same with the microstructural observations. Suitable microstructural evaluations are carried out to study the morphology, phase structure and composition of the duplex coatings. Microhardness, COF and wear rate are evaluated to obtained the high hardness, lower COF and higher wear resistance of coatings. The wear mechanisms are found to be adhesive as well as abrasive in nature in both the duplex coatings. Also, corrosion behaviour is studied in the present chapter. Finally, comparison is made between the performances of the present duplex coatings to the constituent single-layer coatings. Overall, it is found that upon being subjected to the optimal condition of heat treatment, the duplex coating presents an all-around performance that may be suitable for applications demanding both wear and corrosion resistance.

Chapter 5

Duplex Electroless Ni-P/Ni-Cu-P Coatings

Outline of the chapter: *5.1 Introduction, 5.2 Results and Discussion, 5.2.1 Microstructure characterization and composition analysis, 5.2.2 Phase structure, 5.2.3 Microhardness study, 5.2.4 Friction performance,5.2.5 Wear performance, 5.2.5.1 Wear behaviour, 5.2.5.2 Wear mechanism, 5.2.6 Corrosion performance, 5.2.7 Performance comparison with single layer coating, 5.3 Closure*

5.1 Introduction

The present chapter studies the microhardness, friction, wear, and corrosion performance of duplex electroless Ni-P/Ni-Cu-P coatings. Ni-Cu-P having higher corrosion resistance is expected to provide good anti-corrosion performance while Ni-P will provide the necessary hardness and wear resistance. The effect of heat treatment temperature and its time duration on the hardness, friction, and wear behaviour of both coatings are evaluated and compared. This would help in understanding how heat treatment influences the duplex system of coatings and help identify the suitable condition of heat treatment for optimal performance of the coating. Also, the corrosion performance of duplex electroless Ni-P/Ni-Cu-P coatings is discussed in detail. To carry out a comprehensive analysis, one set of coating is developed with Ni-Cu-P as the outer layer (denoted as Ni-P/Ni-Cu-P) and another set with Ni-P as the outer layer (denoted as Ni-Cu-P/Ni-P). The performances of the two set of coatings are compared.

5.2 Results and Discussion

5.2.1 Microstructure characterization and composition analysis

The SEM micrographs of as-plated and heat-treated duplex Ni-P/Ni-Cu-P coating are shown in Figure 5.1. The heat treatment temperature and the amount of phosphorous content influence the phase structure of the coatings **(Sahoo and Roy, 2017)** leading to changes in their surface morphology. The as-plated coating reveals a cauliflower-like morphology, as seen in Figure 5.1a, which is also reported by several researchers **(Sahoo and Das, 2011; Agarwala and Agarwala, 2003).** The average size of the nodules is found to be around 5 µm. Almost no visible pores imply that the formed coating is highly dense. The heat treatment effect is observed prominently in the microstructure. After heat treatment of the duplex coating, the size

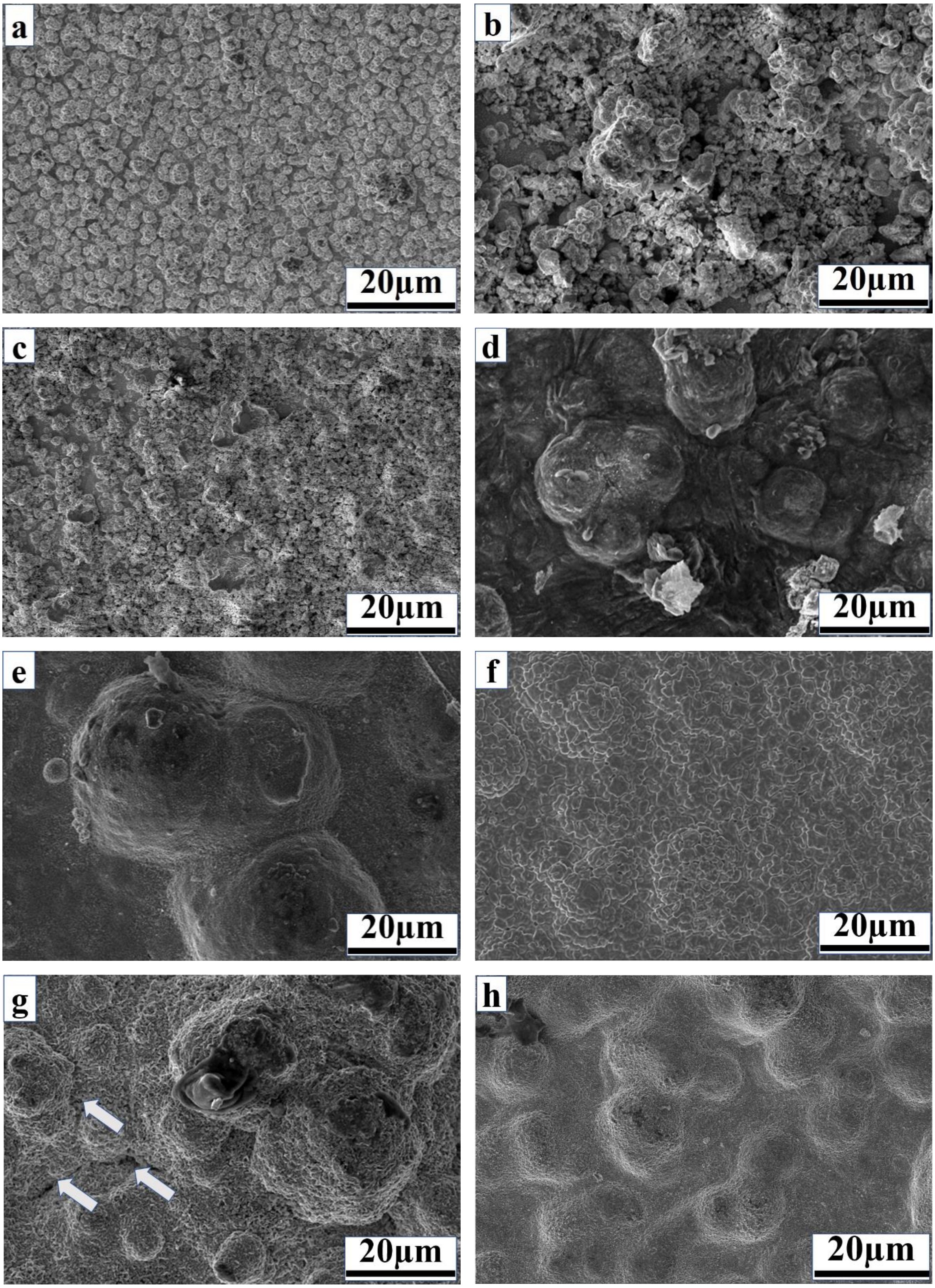

Figure 5.1 *SEM images of duplex Ni-P/Ni-Cu-P coating: (a) as-deposited; (b) heat treated at 400°C, 1h; (c) heat treated at 400°C, 2h; (d) heat treated at 400°C, 4h; (e) heat treated at 600°C, 1h; (f) heat treated at 600°C, 4h; (g) heat treated at 800°C, 1h; (h) heat treated at 800°C, 2h*

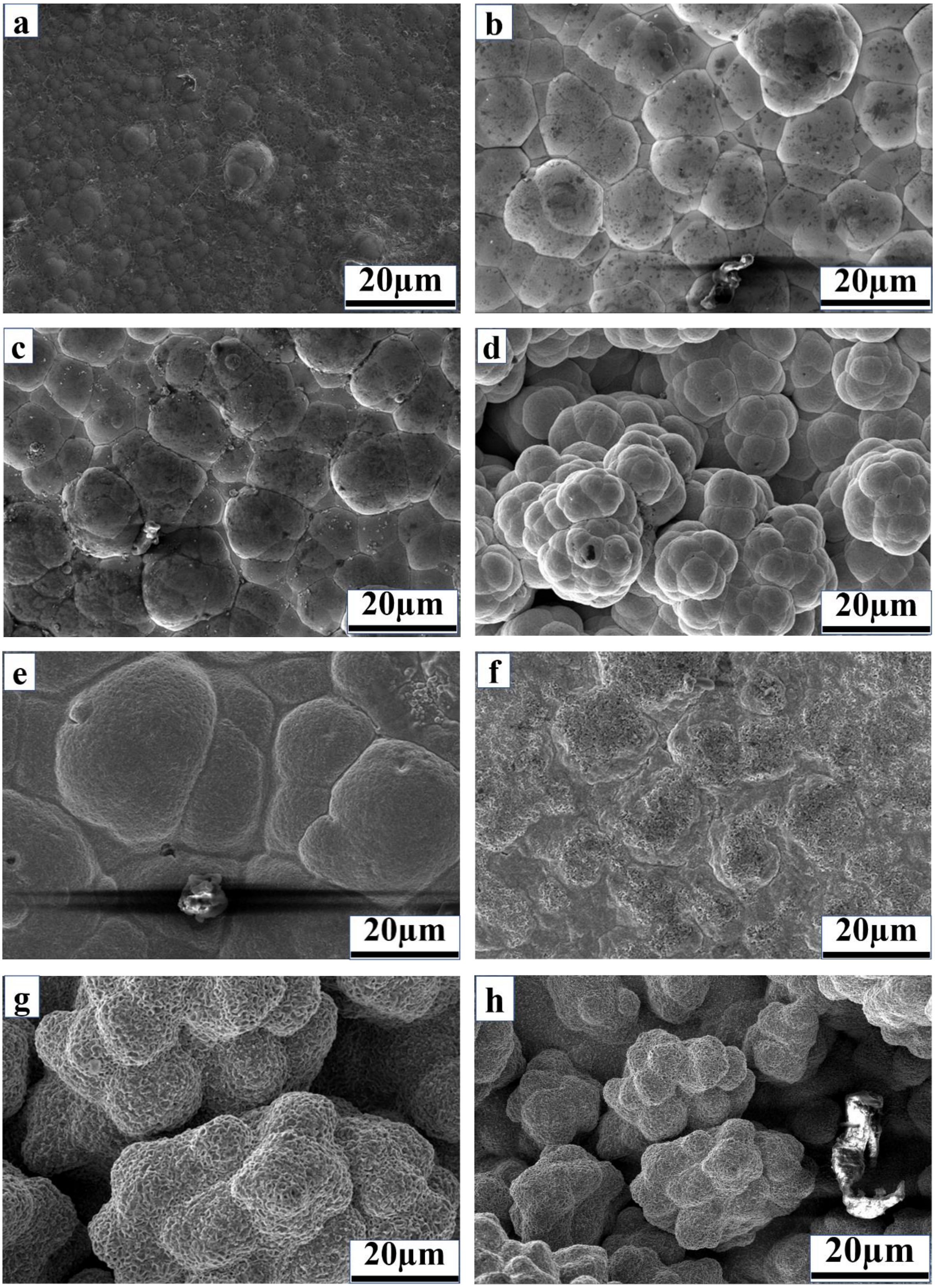

Figure 5.2 *SEM images of duplex Ni-Cu-P/Ni-P coating: (a) as-deposited; (b) heat treated at 400°C, 1h; (c) heat treated at 400°C, 2h; (d) heat treated at 400°C, 4h; (e) heat treated at 600°C, 1h; (f) heat treated at 600°C, 4h; (g) heat treated at 800°C, 1h (h) heat treated at 800°C, 2h*

of the nodules grows larger (Figure 5.1b-h). Figure. 5.1(c) shows that when heat treatment is done at a temperature of 400°C for 2h duration, the morphology of the duplex coating is rather different, with the presence of island like features. At 600°C temperature for 1h duration, the nodule is found to be flattened (refer to Figure 5.1e). In fact, the flattening is more prominent for higher heat treatment temperature and prolonged duration of heating. At 800°C temperature for 1h duration, the surface of the coating develops a few cracks, which may be due to the relief of the accumulated thermal stress, which is also reported in earlier work **(Biswas et al., 2017).** At 600°C and 800°C temperatures, both the coating show diffused nodules due to the relief of the accumulated thermal stress in the coating microstructure. Furthermore, at high temperatures (at 600 or 800°C) for a 2h cycle, few dark spots are observed on the surface (refer to Figure 5.1h). This may indicate the formation of oxide phases on the samples. The coating thickness is obtained around 40 µm as observed from the cross-cut samples.

In the case of duplex Ni-Cu-P/Ni-P coating, as-deposited coating reveals a similar nodular structure (Figure 5.2a). However, the nodules are more prominent compared to duplex Ni-P/Ni-Cu-P coating. The effect of heat treatment is prominently observed in the microstructure, *i.e.*, the size of the nodule increases (Figure 2b-h). When heat treated at 400°C, duplex Ni-Cu-P/Ni-P coating prominently displays cauliflower-like morphology. At higher temperatures (600 or 800°C) and prolonged time duration (1 to 4h), the smoothness on the surface of the nodules is lost and some pores are visible (Figure 5.2f). At a temperature of 600°C, the duplex Ni-Cu-P/Ni-P coating displays flaking in the morphology. According to one of the earlier investigations, high heat treatment temperature appears to increase the coating's porosity **(Biswas et al., 2021).**

The composition of the coatings was determined using EDX and the results are displayed in Figure 5.3. For both coatings, the phosphorous content indicates that the coatings belong to the high phosphorous category. The high phosphorus content in the duplex coating indicates its amorphous nature, as reported in the literature **(Sahoo and Das, 2011; Chen and Lin, 1999).**

Additionally, line EDX (refer to Figure 5.4) is conducted along the coating cross-section to get an idea about the variation of the coating composition. From Figure 5.4, it is found that the duplex system of coatings is successfully developed. This is mainly inferred from the marked variation in wt. % of copper near the middle of the combined deposit thickness. This implies a change from Ni-P to Ni-Cu-P layer or *vice versa*. Also, the top and bottom layers almost have the same thickness. The absence of a visible demarcation between the top and the bottom layer indicates excellent adhesion and compatibility between the two

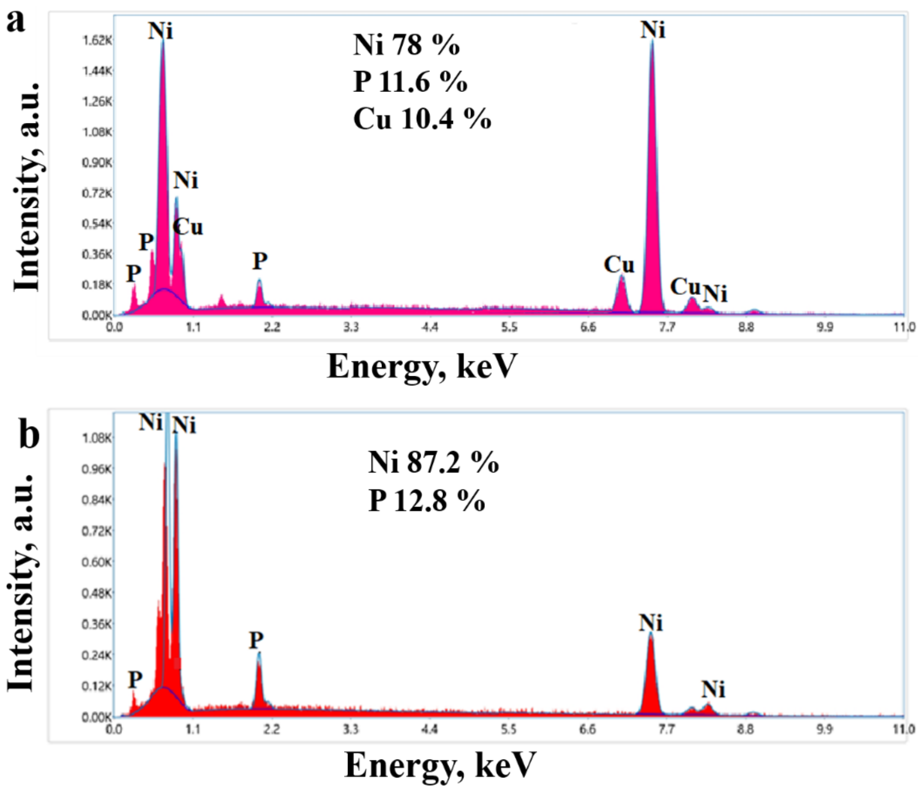

Figure 5.3 *EDX spectra of duplex e(a) Ni-P/Ni-Cu-P coating and (b) Ni-Cu-P/Ni-P coating*

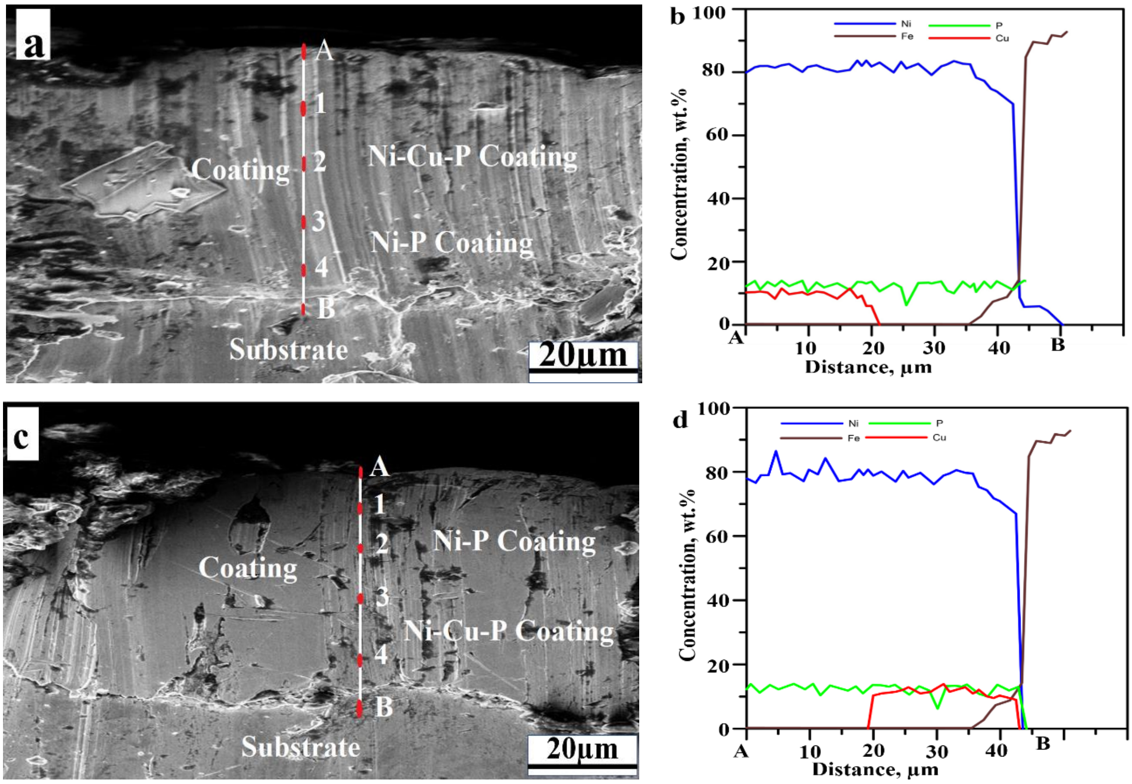

Figure 5.4 *Coating cross-section showing line EDX results of: (a, b) duplex Ni-P/Ni-Cu-P coating and (c, d) duplex Ni-Cu-P/Ni-P coating*

layers of the deposit. In the case of Ni-Cu-P coating, the deposition process is influenced by the incorporation of Cu. Due to the redox potential difference between Ni and Cu, copper will be deposited first and foremost. The addition of Cu to a single layer Ni-P alloy coating improves the crystallinity of the coating **(Duari et al., 2016)**. The copper content of the Ni-Cu-P layer remains around 9-10 % for both the deposits. The cross-section of the coating shows the absence of porosity and other defects. This implies that the coating is expected to possess good corrosion resistance.

5.2.2 Phase structure

Figure 5.5 & 5.6 depicts the XRD analysis of both the duplex Ni-P/Ni-Cu-P and Ni-Cu-P/Ni-P coating. The as-deposited coating has a broad peak, implying that it is amorphous. The single broad peak implying Ni (111) plane is observed at a diffraction angle (2ϴ) between 40-50°. As no significant change is noticed in the phase structure for the sample heat-treated at 200°C, the corresponding XRD plot is not presented. As per **Biswal et al. (2017),** phase transformation occurred in electroless nickel coatings above 362°C heat treatment temperature. Because of heat treatment effect, the coatings turn crystalline. For heat treatment at temperatures of 400°C and above, the coating displays many crystalline peaks, mostly nickel phosphide (Ni_3P) phases in (321), (112), (141), and (322) planes. At 400°C temperature, due to the higher diffusivity of Cu, it enters the Ni lattice to form NiCu. Because of the larger atomic radius of Cu (compared to Ni), the dissolution of copper in the nickel lattice increases the size of the lattice structure. At high temperatures, dark cupric oxide (CuO) is obtained. Furthermore, at high temperatures (at 600 or 800°C) and 1 to 4h duration, a variety of oxides with Ni and Cu have been detected (refer to Figures 5.5a-5.6b). Apart from these, a few hard and brittle crystalline copper phosphide (Cu_3P) phase is obtained. The formation of the phosphide Ni_3P is expected to enhance the hardness of the coating. The primary reason for these oxide formations is the entrapped air within the furnace.

At high temperatures, there is also an increase in peak intensity and sharpening, visible at 600°C and 800°C for 1h, 2h, and 4h duration. Grain refining at higher temperatures shows up as increased peak intensity in the XRD plot. A metastable Ni_8P_3 phase is obtained at high temperatures for the deposition with Ni-Cu-P as the outer layer.

For duplex Ni-Cu-P/Ni-P coating, the precipitation of phases is almost similar to duplex Ni-P/Ni-Cu-P coating. It is interesting to note the presence of Cu_3P as one of the phases considering the top layer being Ni-P. This may be explained by the fact that Cu ion may have

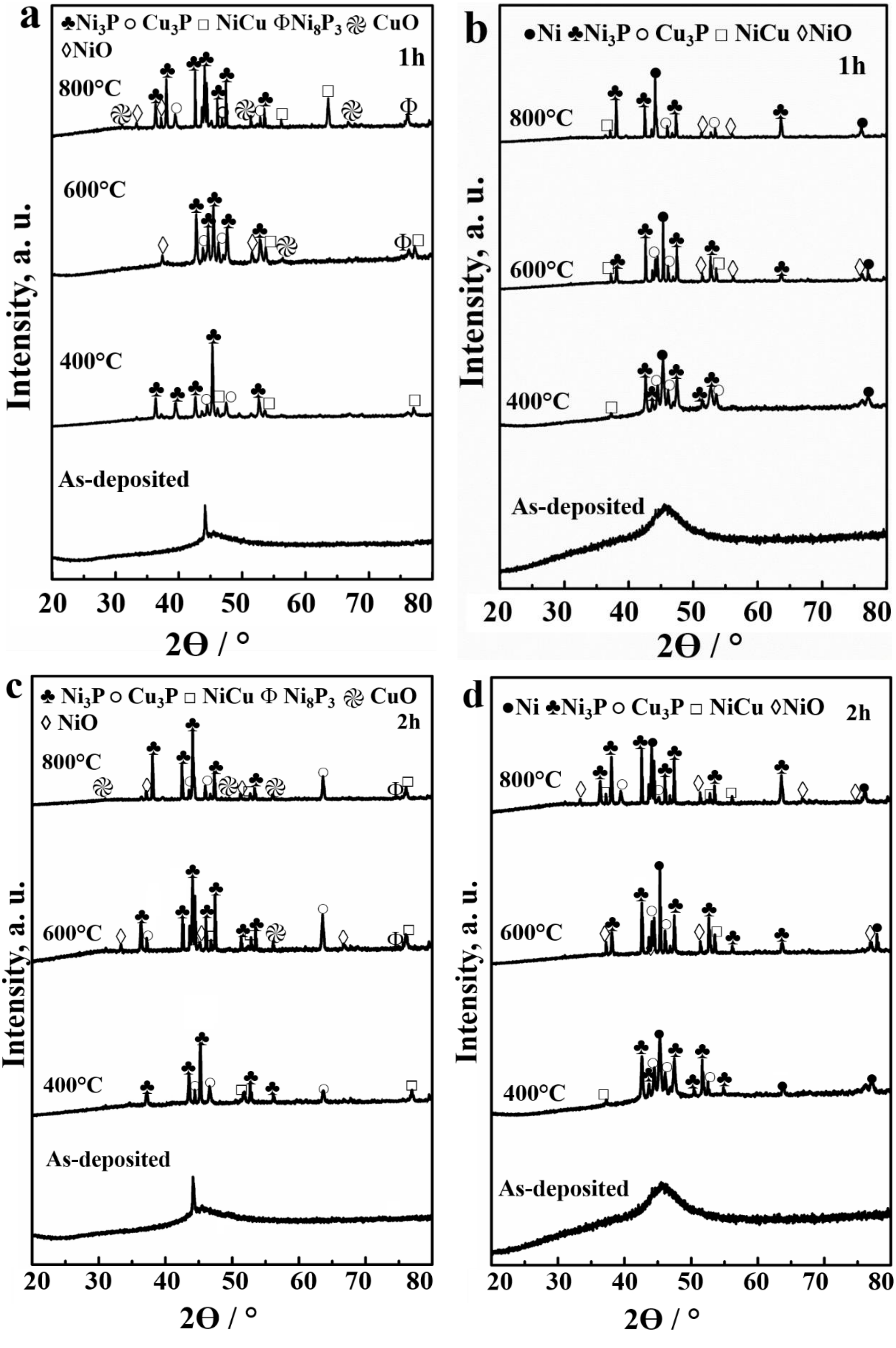

Figure 5.5 *XRD plots of duplex: (a) Ni-P/Ni-Cu-P coating, 1h; (b) Ni-Cu-P/Ni-P coating, 1h; (c) Ni-P/Ni-Cu-P coating, 2h;(d) Ni-Cu-P/Ni-P coating,2h*

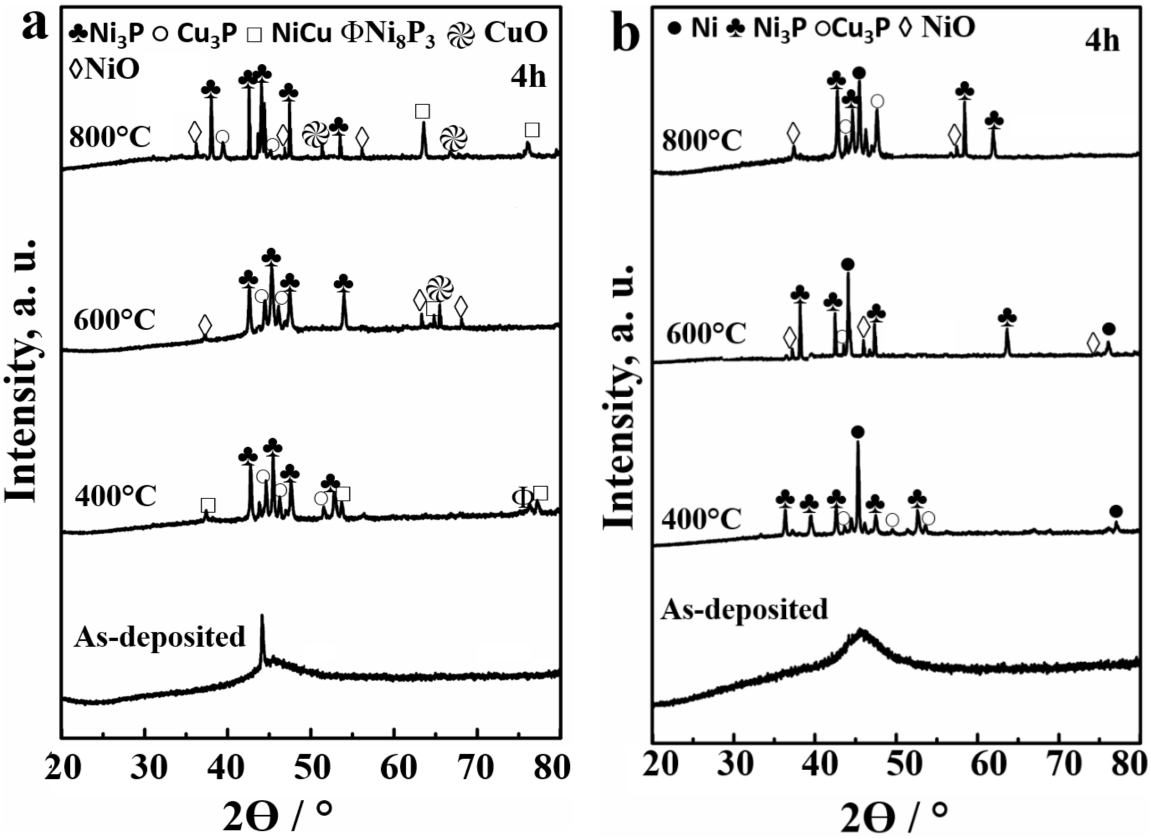

Figure 5.6 *XRD plots of duplex: (a) Ni-P/Ni-Cu-P coating, 4h; (b) Ni-Cu-P/Ni-P coating, 4h*

travelled near the surface of the coating by diffusion when the sample was exposed to high temperatures in the furnace. At 800°C temperature and 1h, 2h and 4h duration, NiO phase is obtained.

5.2.3 Microhardness study

The microhardness results of the present duplex coating is displayed in Figure 5.7. For duplex Ni-P/Ni-Cu-P coating, the microhardness value is 568 $HV_{0.1}$ in the as-deposited state. To improve the microhardness value, the coating is heat treated at various temperatures ranging from 200 to 800°C and time durations of 1 to 4h. At 200°C heat treatment temperature, minimal change is observed due to lesser microstructure change. The maximum microhardness is obtained at 400°C heat treatment temperature and 1h duration mainly due to the formation of hard nickel phosphide (Ni_3P) along with copper phosphide (Cu_3P) phases. Hence, the higher microhardness of duplex electroless nickel coatings is attributed to both solid solutions strengthening and precipitation hardening during heat treatment (above phase transition temperature). The hardness value is increased by around 92% compared to as-deposited coating

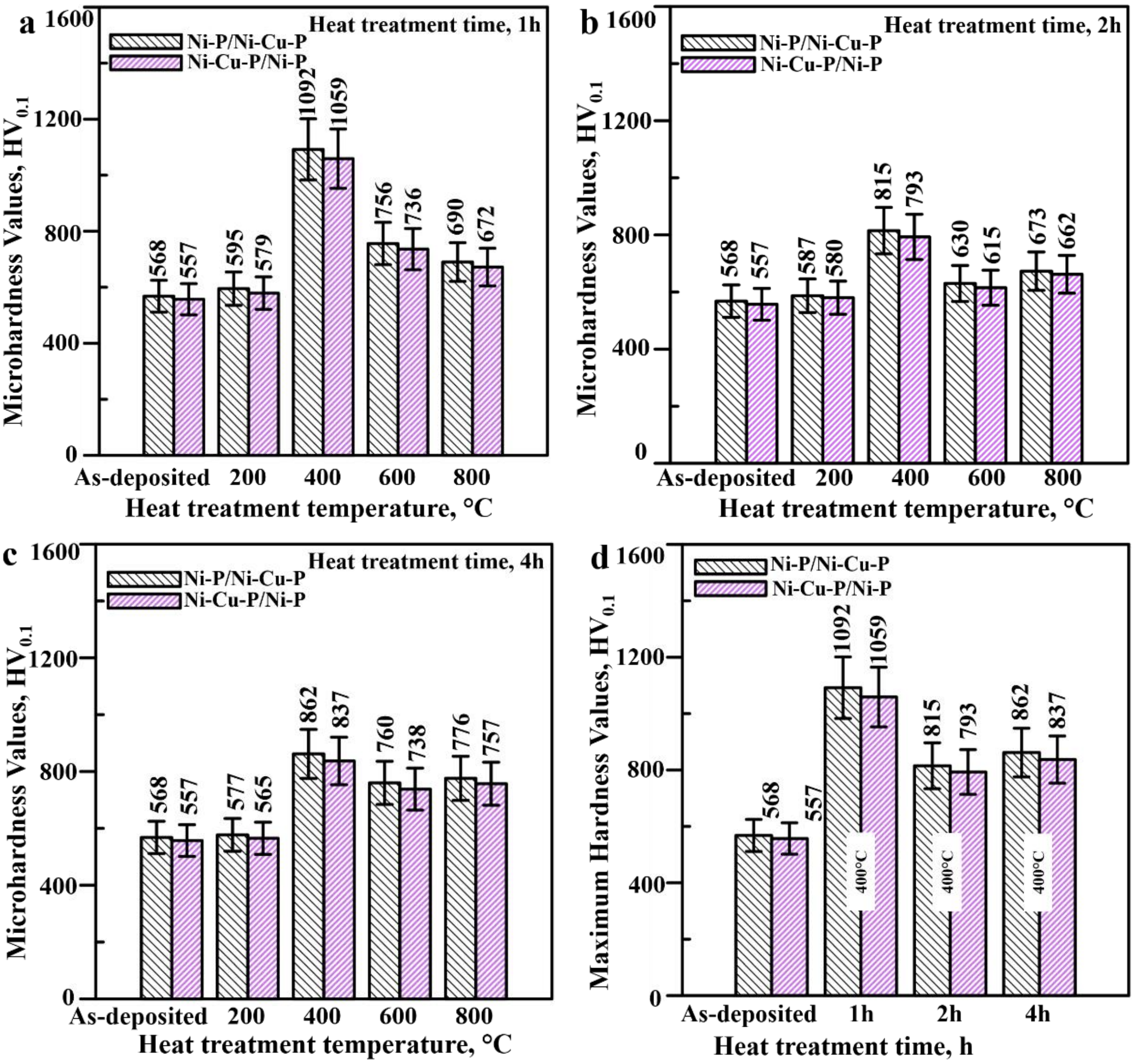

Figure 5.7 *Microhardness plots for heat treatment temperature of 200-800°C for (a) 1h; (b) 2h; (c) 4h and (d) maximum hardness value plot*

(Figure 5.7a). At 400°C temperature for 2h duration, the microhardness is increased by around 43% compared to the as-deposited coating. Due to grain coarsening, the hardness reduces by about 23% at 600°C heat treatment temperature for a 2h duration, although the coating is still harder than as-deposited one (refer to Figure 5.7b). At 800°C, the hardness values reduce as compared to 400°C because of the formation of nickel oxide phases. But the same sample shows higher hardness compared to as-deposited coating because the harder phases are still present on the coating surface.

When the heat treatment duration was increased from 1 to 4h at 400°C temperature, the microhardness value was reduced by around 21%, which may be due to grain coarsening. Above 400°C temperature, the microhardness value falls probably due to the same reason (Figure 5.7c). However, the increased porosity of the coating may also be responsible for this decrease in the microhardness of the coating. It is noted that if the porosity in the materials is increased, the load-bearing area decreases **(Sinha and Farhat, 2015).** The chances for crack nucleation increase due to an increase in the subsurface porosity of the coating. This causes the weakening of the duplex coating and a decrease in its strength. Furthermore, the significant fall in P concentration when heat treated at high temperatures may also be contributing to a loss in microhardness. Finally, oxide formation at higher temperatures, like NiO and CuO (which are relatively soft and dispersed over the coating surface) is also responsible for lowering the microhardness.

In the case of duplex Ni-Cu-P/Ni-P coating, the microhardness value is obtained as 557 $HV_{0.1}$ in the as-deposited coating. The maximum microhardness value is again obtained at 400°C temperature for 1h duration. The microhardness value is increased by around 90% from as-deposited coating due to the formation of the hard phase. Similar trend in microhardness change with heat treatment temperature indicates that the same underlying mechanisms are active as discussed for duplex Ni-P/Ni-Cu-P coatings. Overall, it can be said that heat treatment increases the microhardness of the coating. However, heat treatment at higher temperatures and longer duration is not beneficial for the microhardness of both the coating systems. In the current investigation, the microhardness of Ni-Cu-P as an outer layer is higher than that of Ni-P as the outer layer in all aspects.

5.2.4 Friction performance

The average COF of both duplex coatings is shown in Figure 5.8 for both as-deposited and heat-treated samples. The first thing to note is that the COF of as-deposited coating is higher than the heat-treated coatings. In fact, COF is reduced by half upon heat treatment. The heat-treated coatings display more or less a stable COF value ranging between 0.14 and 0.25, for both the coating systems. In case of 2h heat treatment cycle, COF ranges between 0.22-0.39. For 4h duration heat treatment, COF ranges between 0.12 and 0.28, which is also stable. The decrease in COF value post-heat treatment is mainly due to the gain in hardness of the coatings. However, some variation in the COF is also observed because of the formation of various phases on the coating surface, including oxides. The COF *vs*. time plots shown in Figure 5.9 also shows quite stable friction behaviour of the current coatings. Some variation is noticed, especially for 4h duration heat-treated samples with Ni-P as the outer layer, which may be testimony to the fact that due to phenomena *viz*. oxide formation and grain coarsening, the integrity of the top layer is somewhat lost, which is not the case for coating with Ni-Cu-P as the top layer. Overall, it can be said that duplex Ni-P/Ni-Cu-P coating displays relatively lower COF compared to Ni-Cu-P/Ni-P coating.

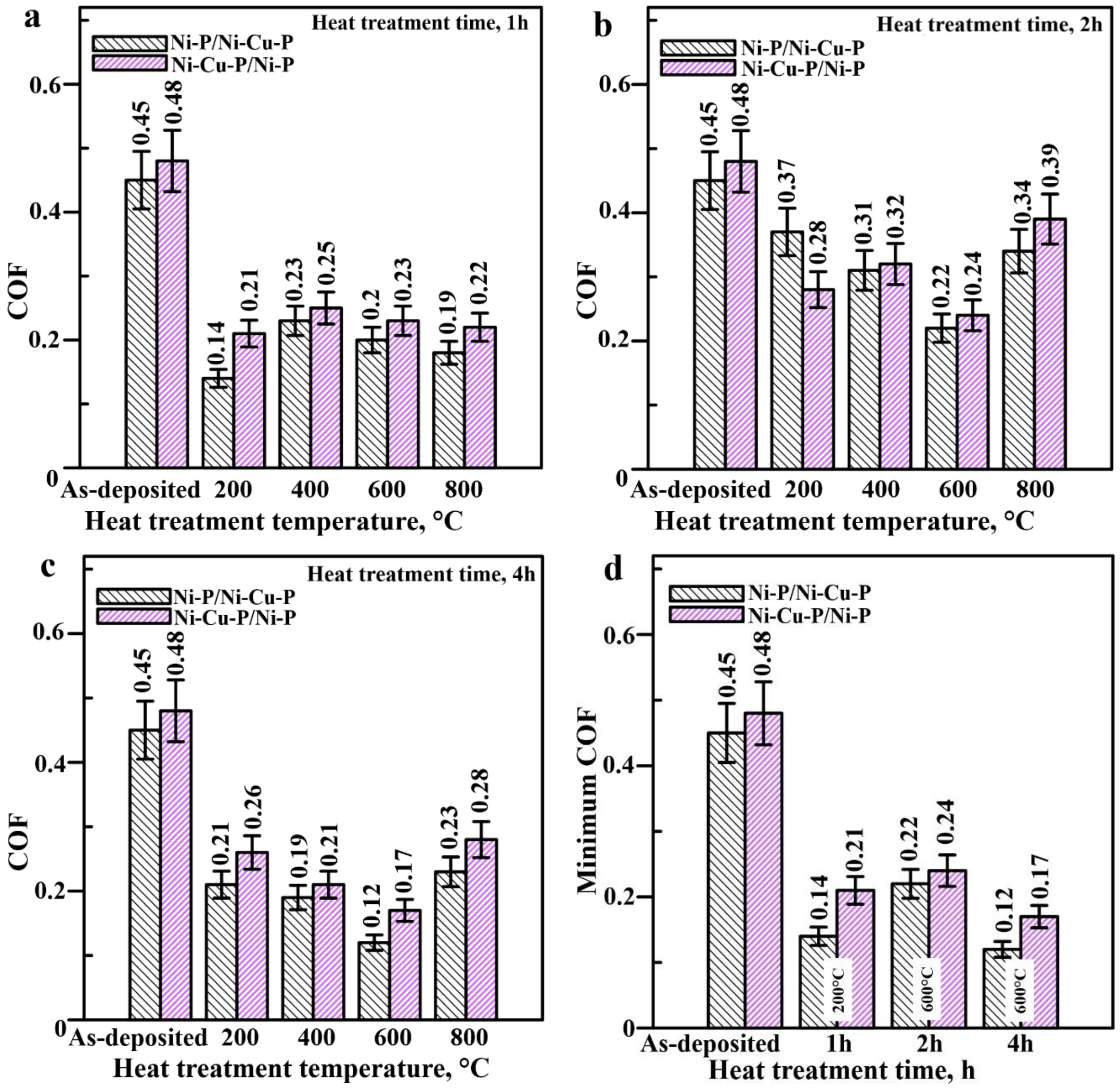

Figure 5.8 *COF plots for heat treatment temperature of 200-800°C: (a) 1h; (b) 2h; (c) 4h; and(d) minimum COF plot*

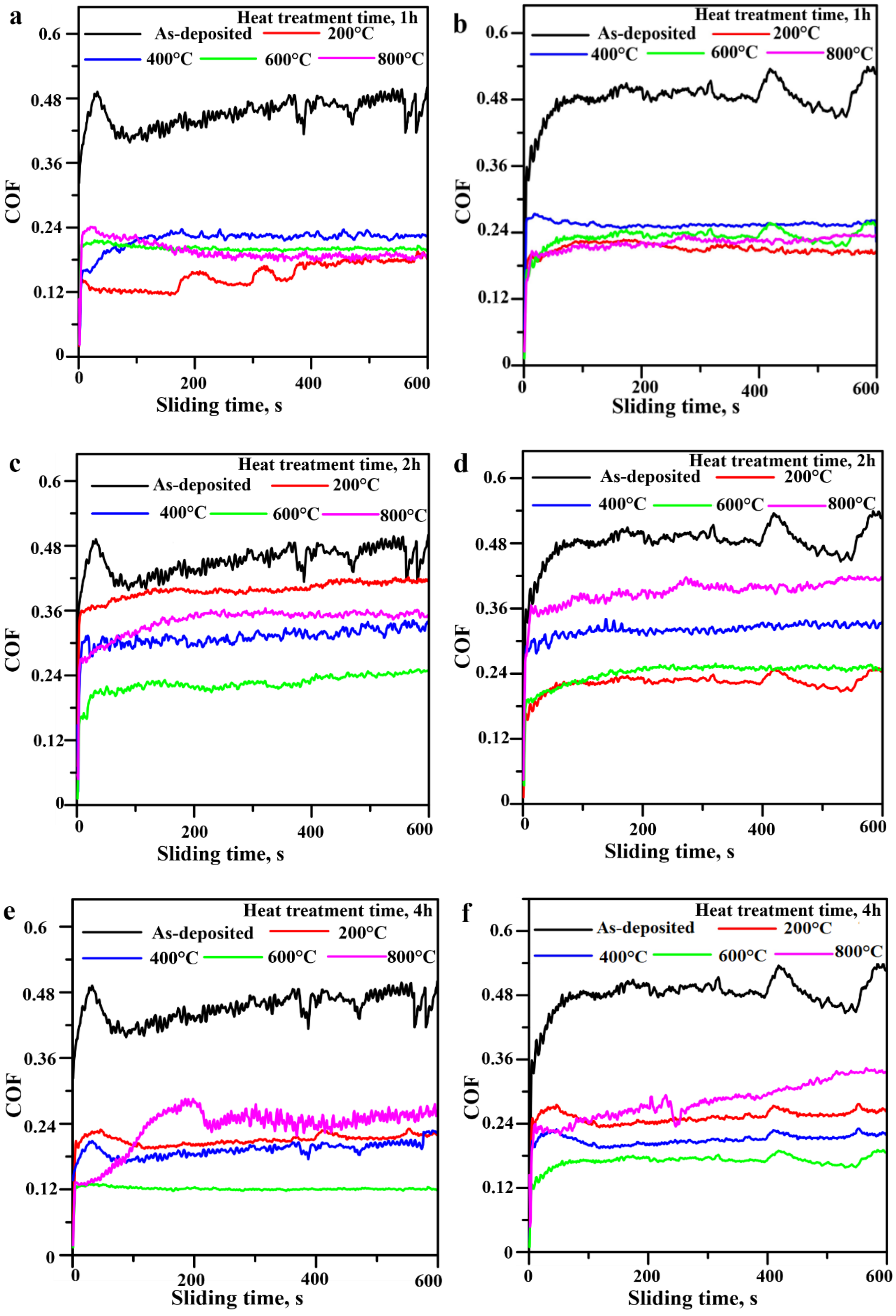

Figure 5.9 *COF vs. sliding duration plots of duplex electroless: (a) Ni-P/Ni-Cu-P Coating, 1h; (b) Ni-Cu-P/Ni-P Coating, 1h (c) Ni-P/Ni-Cu-P Coating, 2h;(d Ni-Cu-P/Ni-P Coating, 2h (e) Ni-P/Ni-Cu-P Coating, 4h; (f) Ni-Cu-P/Ni-P Coating, 4h*

5.2.5 Wear performance

5.2.5.1 Wear behaviour

The wear behaviour of duplex coatings is shown in Figure 5.10. The first thing to note is that heat treatment definitely lowers the wear rate of as-deposited coatings. The lowest wear rate is observed for the heat treatment state of 400°C, beyond which the wear rate increases. In fact, a very good correlation is observed between the hardness and wear results. The samples displaying higher hardness show lower wear rates or higher wear resistance. The wear rate is reduced with increase in heat treatment temperature due to the formation of the hard Ni_3P and Cu_3P phases.

The minimum wear rate is obtained at 400°C heat treatment temperature for 1h duration due to higher microhardness. The wear rate is reduced by around 38% as compared to as-

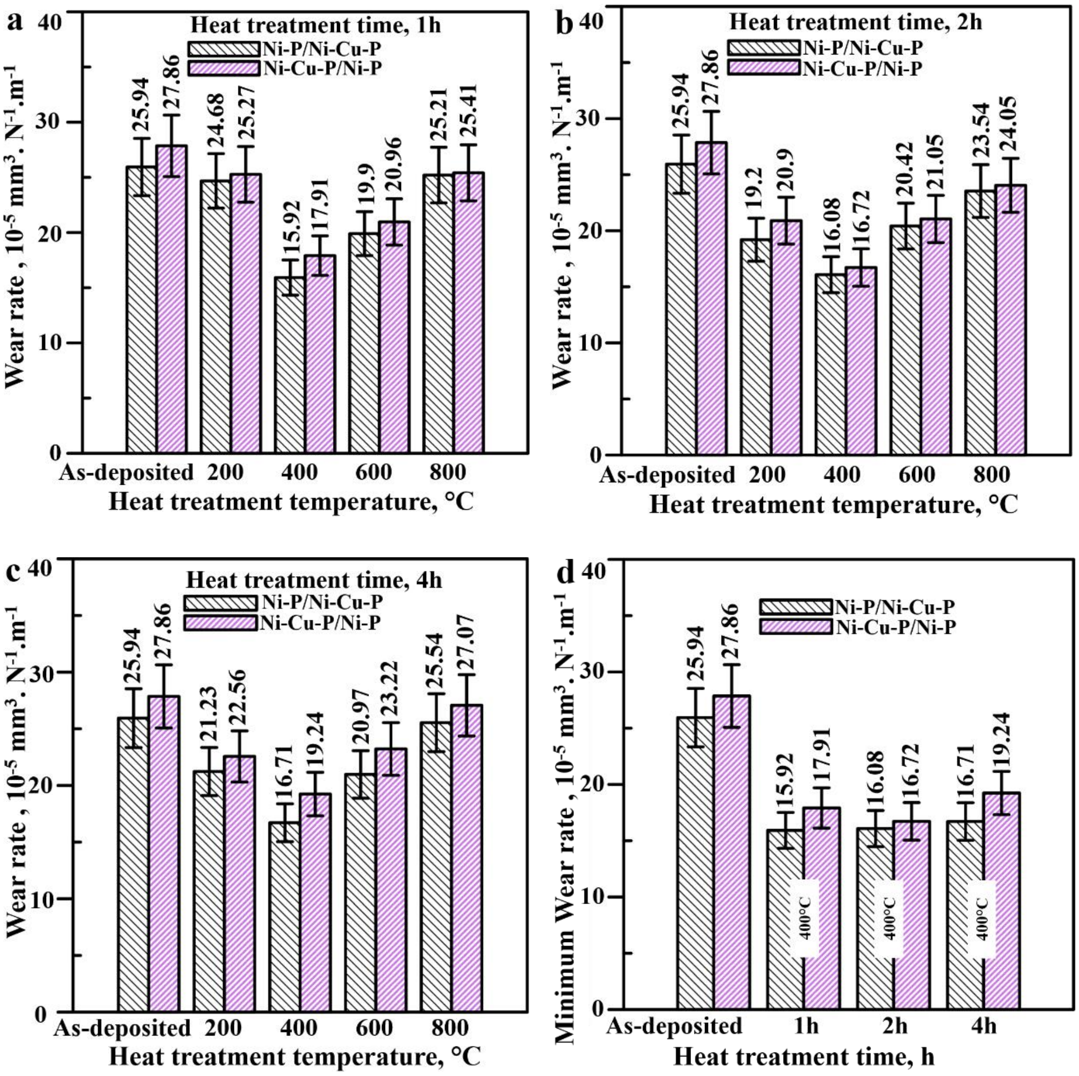

Figure 5.10 *Wear rate plots for heat treatment temperature of 200-800°C: (a) 1h; (b) 2h; (c) 4h; and(d) Minimum wear rate plot*

deposited coating (Figure 5.10a &5.10b). At 600°C or 800°C for 1h & 2h duration, the wear rate is increased due to grain coarsening. The increase in wear rate post 400°C temperature is also due to the formation of oxide phase. But still at this temperature, the wear rate is lesser compared to the as-deposited coatings. At high temperatures (600 or 800°C) and longer time duration, the wear performance of the coating degrades due to spallation and delamination of the coating. At this temperature, the wear rate increases due to the formation of oxides, *viz*. NiO and CuO. This oxide layer is normally unwanted. This oxide layer has lower shear strength and presents poor adhesion to the interlayer of duplex coatings, tending to cause delamination of the top layer. Porosity encountered at higher temperatures and longer duration heat treatment may also affect the wear behaviour of the coatings, as seen in Figure 5.10c. This is also reported in one of the previous studies **(Dubrujeaud et.al., 1994).** In fact, the wear performance of coatings heat treated at 800°C is almost the same as as-deposited coatings. Another significant observation is that among both the coating systems, coating with Ni-Cu-P as the outer layer exhibits a lower wear rate. This is due to the higher microhardness of the Ni-Cu-P layer, as already seen in the hardness study. However, for both coatings, the minimum wear rate is observed at 400°C heat treatment temperature as shown in Figure 5.10d. In both types of coatings, similar wear behaviour is observed. Duplex coating with Ni-Cu-P as the outer layer displays the best wear performance in all aspects.

5.2.5.2 Wear mechanism

The detailed wear mechanism is studied with the help of SEM and EDX of the wear-tested samples and presented in Figures 5.11 to 5.14. The wear behaviour of duplex Ni-P/Ni-Cu-P coating in an as-deposited state is shown in Figure 5.11a. The worn surface morphology of the as-deposited coating shows ploughing due to sliding under the applied load. Ploughing marks are shown by white arrows, indicating the occurrence of an abrasive wear mechanism **(Davim 2012 & Davim 2018)**. Some pits and prows are also observed, indicating that adhesive wear might have occurred. The presence of Fe in the EDX plot (Figure 5.11b), confirms the occurrence of adhesive wear. This is because the only possible source of Fe is the ferrous counterface (material against which the sample is rubbed during the test) and this exchange occurs due to the high mutual solubility of iron and nickel. A small amount of oxygen is also detected in the sample showing oxidation at the sliding interface.

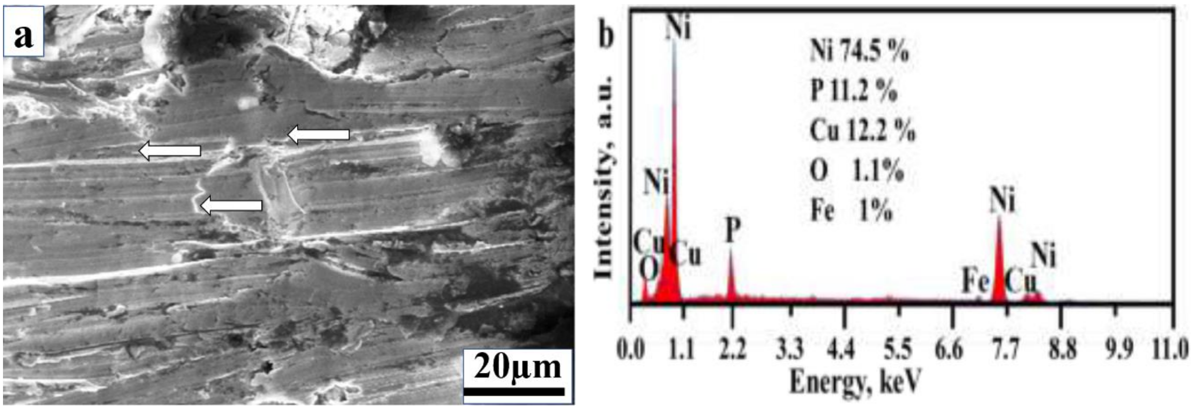

Figure 5.11 *Worn surface of as-deposited duplex Ni-P/Ni-Cu-P coating: (a) SEM image; (b) EDX plot*

For 400°C, 1h treated sample (Figure 5.12a), the worn surface exhibits plastic deformation due to sliding under the applied load. Abrasion marks in the sliding direction are also present. Few deep grooves and micro-cracks are also observed on the surface of the coated sample. This indicates a mixture of adhesive and abrasive wear mechanisms. For 600°C, 1h treated sample (Figure 5.12b), some spallation of the coating is observed apart from the presence of abrasive marks.

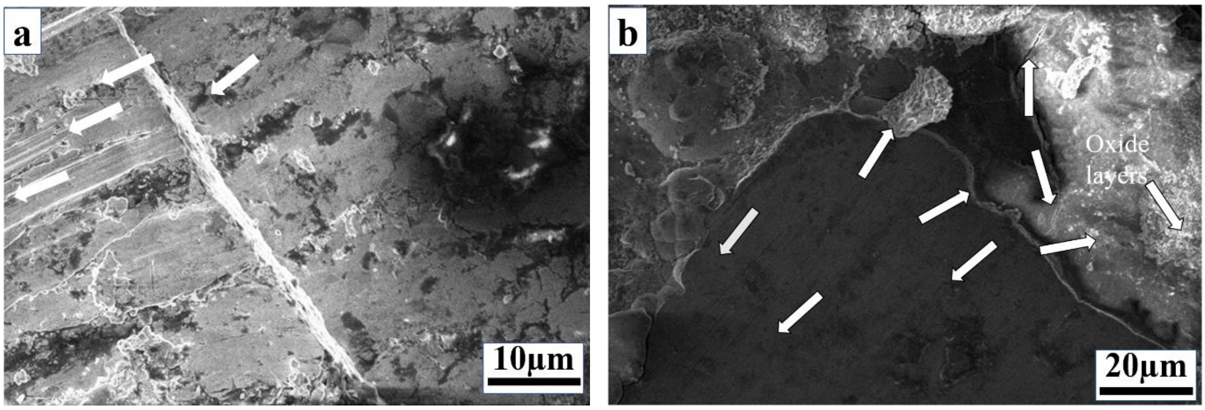

Figure 5.12 *SEM images of worn surface of duplex Ni-P/Ni-Cu-P coating heat treated at: (a) 400°C, 1h; (b) 600°C,1h*

The worn surface of duplex Ni-P/Ni-Cu-P coating displays few cracks and micro-cracks in the sliding direction at 400°C temperature for 2h duration. These characteristics point to the occurrence of delamination wear as shown in Figure 5.13a. A similar type of observation is reported by **Banerjee et.al (2019)**. In the sliding direction, a few flanks are obtained on the worn surface of the coating.

In the case of 800°C, 2h the tested surface displays significant damage in spallation, plastic deformation, cracking, *etc.*, including abrasive marks as shown in Figure 5.13b. For the 800°C, 4h sample (Figure 5.14a), the tested surface shows significant damage in the form of

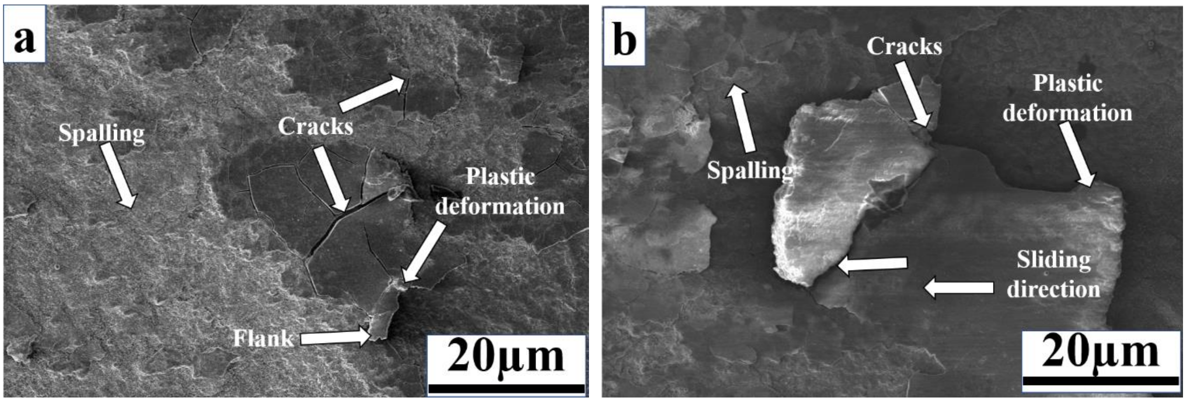

Figure 5.13 *SEM images of worn surface of duplex Ni-P/Ni-Cu-P coating heat treated at: (a) 400°C, 2h;(b) 800°C, 2h*

spallation, delamination, cracking, *etc.*, while abrasive marks are not visible. This implies that the abrasive wear mechanism is not the governing mechanism. Rather, the wear behaviour of the sample is impacted by the formation of an oxide layer on its surface. This is supported by the EDX results, where about 17.1 % oxygen is detected on the tested surface (Figure 5.14b).

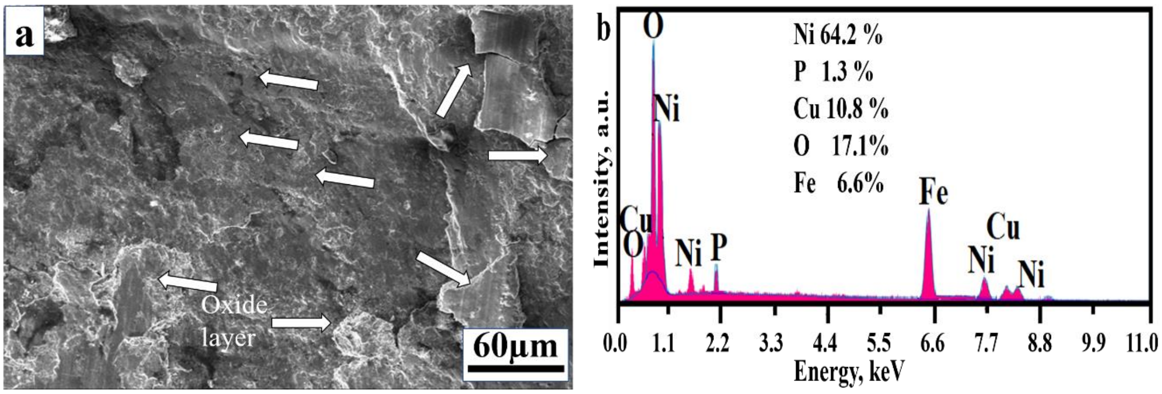

Figure 5.14 *Worn surface of duplex Ni-P/Ni-Cu-P coating heat treated at 800°C, 4h: (a) SEM image and (b) EDX plot*

The results of wear-tested samples of Ni-Cu-P/Ni-P coating are shown in Figures 5.15 to 5.18. The as-deposited sample (Figure 5.15a) shows abrasion marks (indicated by white arrows) along the sliding direction. Besides, there is much pressed wear debris almost welded to the surface. This indicates the occurrence of 2-body abrasion. It is interesting to see the presence of Cu in the EDX results (Figure 5.15b), as the coating under consideration has Ni-P as the outer layer. Now, discreet cuts and damages are observed on the coating surface, through which Cu from the bottom layer might have been detected. Adhesive wear also occurs, which is supported by the presence of pits and prows as well as the detection of Fe.

For the sample heat-treated at 400°C, 1h (Figure 5.16a), the worn surface exhibits abrasion marks along with the smeared wear debris patches. However, for the sample heat treated at 600°C, 1h, some spallation of the coating is observed again due to the formation of oxides on the top surface.

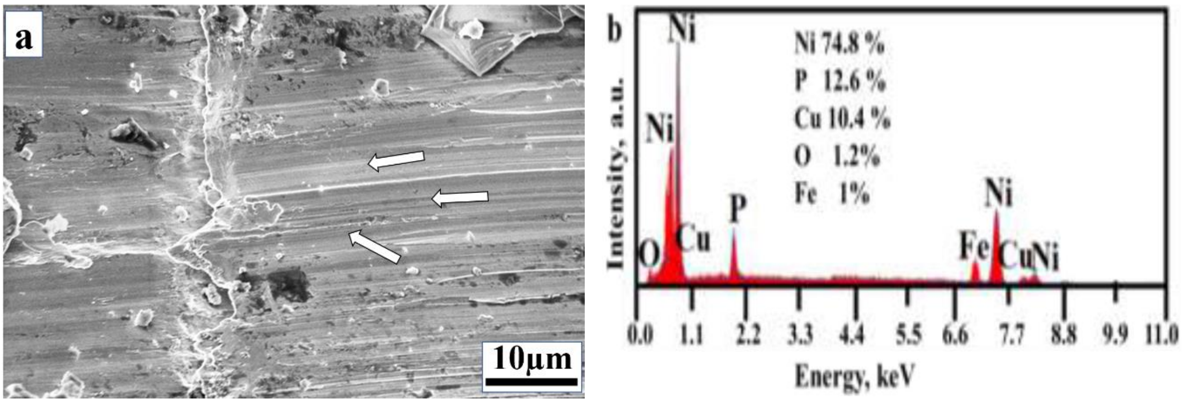

Figure 5.15 *Worn surface of as-deposited* Ni-Cu-P/Ni-P coating*: (a) SEM image; (b) EDX plot*

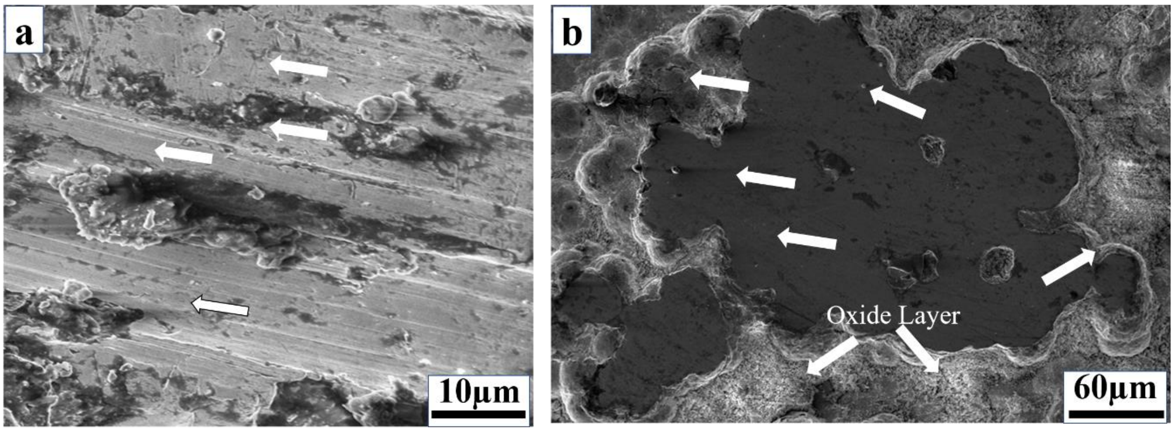

Figure 5.16 *SEM image of worn surface of Ni-Cu-P/Ni-P heat treated at: (a) 400°C, 1h; (b) 600°C, 1h*

At 400°C, 2h duration, the worn surface of duplex Ni-Cu-P/Ni-P coating shows few damaged nodules in the sliding direction due to micro-cutting and crack formation (Figure 5.17a). Plastic deformation occurs due to high contact pressure at the sliding interface. Separately few wear debris is also noticed on the coating surfaces. At 800°C heat treatment temperature for 2h duration, the tested surface shows significant damage in the form of plastic deformation, micro-cutting, micro-cracks, oxide formation, *etc.* Abrasive marks are also seen along with sliding direction (refer to Figure 5.17b). More wear debris seemed to be welded on the worn surface.

At 800°C for 4h duration, the worn surface morphology displays more oxide formation and crack formation as shown in Figure 5.18a. Spallation occurs due to sliding under applied normal load. A higher amount of oxygen and iron is also detected in the sample showing

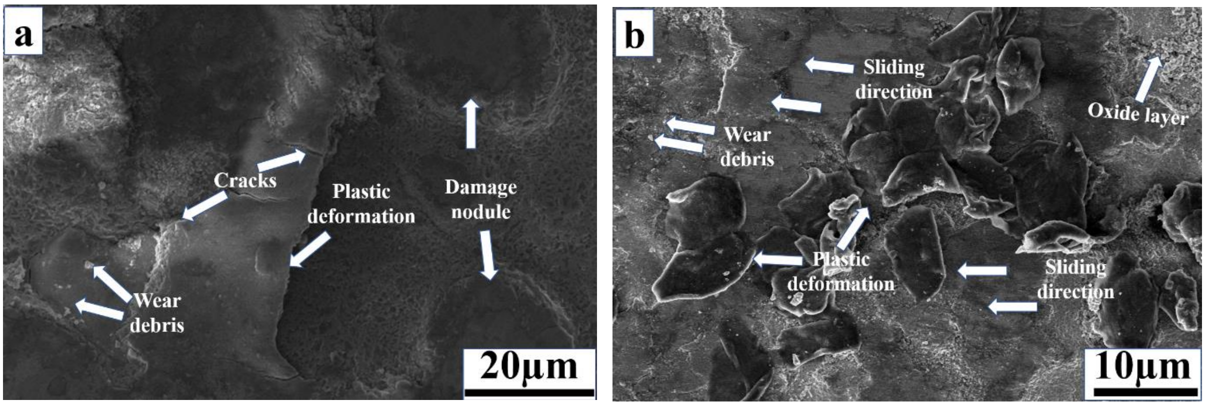

Figure 5.17 *SEM image of worn surface of Ni-Cu-P/Ni-P heat treated at: (a) 400°C, 2h; (b) 800°C, 2h*

oxidation at the sliding interface. This is confirmed by the EDX results, where about 8.1% iron and 9.1% oxygen is noticed on the worn surface (Figure 5.18b). As the worn surface of Ni-Cu-P/Ni-P coating depicts features almost similar to duplex Ni-P/Ni-Cu-P coating, it may be concluded that similar types of wear mechanisms are underlying both duplex coating systems.

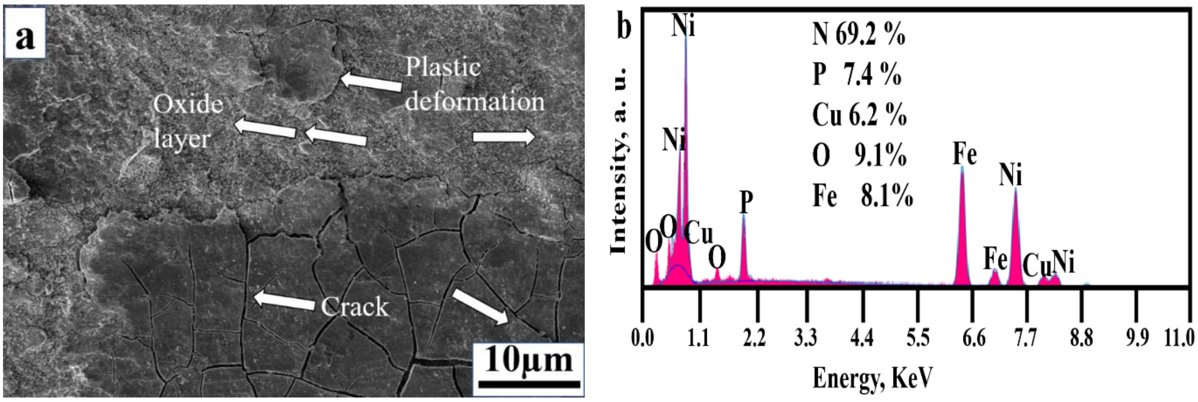

Figure 5.18 *Worn surface of duplex Ni-Cu-P/Ni-P coating heat treated at 800°C, 4 h: (a) SEM image and (b) EDX plot*

5.2.6 Corrosion performance

The potentiodynamic polarization performance of mild steel substrates is compared to the coated specimens in the form of Tafel plots, as presented in Figure 5.19a. The cathodic and anodic portions of the plots are distinctly visible for all the samples. Figure 5.19a shows that duplex coating has a higher corrosion potential than uncoated samples, indicating significant protection against corrosion. Again, the system with Ni-Cu-P as the outer layer of deposition displays a passivation phase in the polarization curve, as was also reported by **Chen et al. (2019).** This leads to the conclusion that the performance of duplex Ni-P/Ni-Cu-P coating is relatively better compared to the system with Ni-P as the outer layer. Generally, it has been demonstrated that the presence of P can raise E_{corr} and decrease i_{corr} in Ni–P coatings and their variations by boosting anodic and cathodic processes and accelerating Ni dissolution. The present duplex coating achieves a significant reduction of i_{corr}. Moreover, the presence of Cu inhibits the corrosion process in Ni-P, as Cu has a higher reduction potential than Ni **(Chen et al., 2017).**

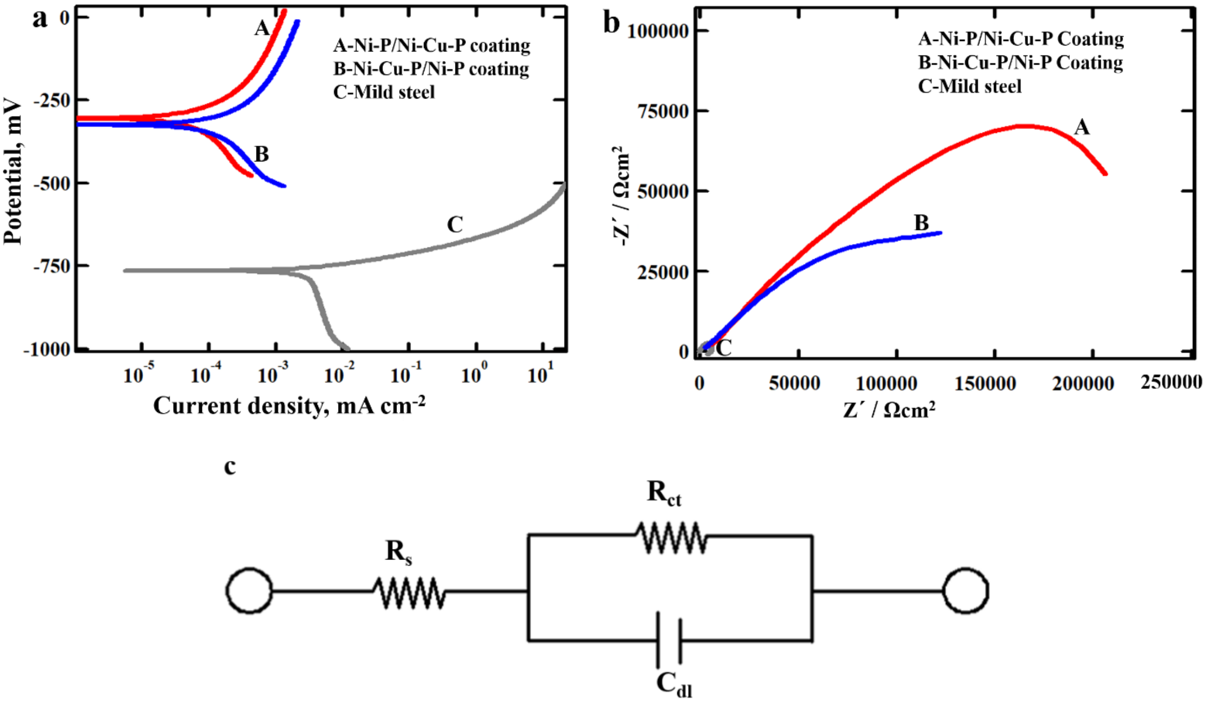

Figure 5.19 *(a) Polarization plots; (b) Nyquist plots; (c) equivalent circuit diagram for steel and coated samples*

The impedance results of mild steel are also compared to its coated counterparts in the form of Nyquist plots, as presented in Figure 5.19b. The assumed circuit is a simple Randles circuit, as illustrated in Figure 5.19c, where Rs, R_{ct}, and C_{dl} refer to solution resistance, charge transfer resistance due to corrosion, and interfacial double-layer capacitance, respectively. Nyquist plot of this combination would present a semicircle response with the diameter determined by the value of charge transfer resistance, R_{ct}. Higher diameters of Nyquist plots shown in Figure 5.19a for duplex coatings compared to the mild steel substrate suggest better corrosion protection provided by the coatings. This implies an increase in impedance magnitude and, thus, enhanced resistance against corrosion. The higher corrosion resistance of duplex Ni-P/Ni-Cu-P coating compared to Ni-Cu-P/Ni-P coating is also evident from the plots. The actual values of the corrosion parameters, as determined from the tests, are listed in Table 5.1.

The effect of heat treatment conditions on the corrosion behaviour of the coatings is also studied and presented in Figures 5.20 and 5.21. The Tafel polarization plots of heat-treated samples are displayed in Figure 5.20. The potentiodynamic polarization results show that, in general, the corrosion potential moves towards a more negative region after heat treatment. This indicates a loss in corrosion resistance after heat treatment. This is quite understandable as the amorphous structure in as-deposited coating turns crystalline after heat treatment, and their grain boundaries act as active sites for attack by corrosive media **(Chen et al., 2019).** It is interesting to find that the E_{corr} value of the duplex coating is reduced and i_{corr} value increases with increasing heat treatment temperature and time duration (Table 5.1). This implies that crystallinity is not the only factor impacting the corrosion resistance of the present coatings after heat treatment.

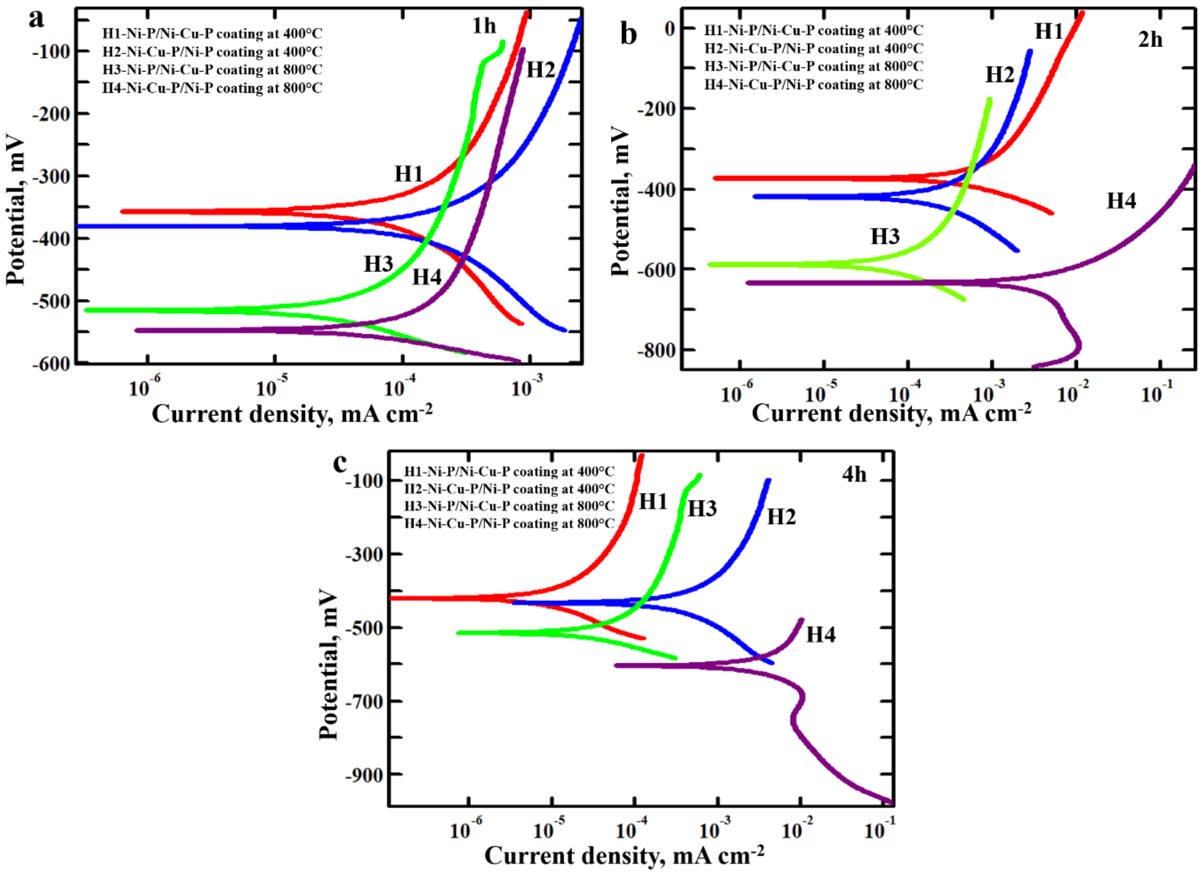

__Figure 5.20__ Polarization plots for heat-treated samples: (a) 1h duration; (b) 2h duration and (c) 4h duration

The passivation phenomenon observed for the as-deposited systems seems to be weakened due to heat treatment **(Chen et al., 2019).** Moreover, at higher temperatures, due to grain coarsening and higher stresses, there is visible cracking on the surface of the coating, as observed previously. Through these damages and microcracks, Cl- ions can enter and the corrosion resistance of the coatings is compromised. Moreover, the formation of oxide phases at these heat treatment conditions also presents a heterogeneous surface having local variation in corrosion potential leading to an intense attack by NaCl solution.

Table 5.1 Corrosion data obtained from Tafel extrapolation and Nyquist plots

Samples	**E_{corr} (mV)**	**i_{corr} (mA/cm^2) ×10^{-5}**	**R_{ct} (Ohm cm^2) ×10^5**	**C_{dl} (10^{-6}F)**
Mild steel	-764	46.19	0.0794	18.76
Ni-P/Ni-Cu-P coating, as-deposited	-302	1.83	2.650	3.541
Ni-Cu-P/Ni-P coating, as-deposited	-323	2.11	1.890	5.018
Ni-P/Ni-Cu-P coating, at 400°C 1h	-358	2.77	9.203	4.901
Ni-Cu-P/Ni-P coating, at 400°C 1h	-382	6.84	4.780	10.29
Ni-P/Ni-Cu-P coating, at 800°C 1h	-514	3.42	3.205	1.075
Ni-Cu-P/Ni-P coating, at 800°C 1h	-545	2.28	1.403	2.354
Ni-P/Ni-Cu-P coating, at 400°C 2h	-380	6.49	18.75	1.832
Ni-Cu-P/Ni-P coating, at 400°C 2h	-421	2.721	3.375	2.91
Ni-P/Ni-Cu-P coating, at 800°C 2h	-587	4.09	2.877	4.54
Ni-Cu-P/Ni-P coating, at 800°C 2h	-629	26.7	1.290	1.076
Ni-P/Ni-Cu-P coating, at 400°C 4h	-420	13.72	38.20	1.353
Ni-Cu-P/Ni-P coating, at 400°C 4h	-432	1.52	8.502	18.57
Ni-P/Ni-Cu-P coating, at 800°C 4h	-548	2.21	3.140	2.659
Ni-Cu-P/Ni-P coating, at 800°C 4h	-607	9.80	1.062	6.477

Nyquist plots for the heat-treated coatings are shown in Figure 5.21. Almost similar patterns are observed for all samples. However, the curves vary in size. This implies that the same underlying mechanism acts over a different effective area. Similar reporting has been made by earlier studies **(Banerjee et al., 2021)**. Ni-P/Ni-Cu-P coating, in general, displays higher impedance values compared to Ni-Cu-P/Ni-P coating (Table 5.1). As already discussed, this is because Ni-P/Ni-Cu-P coating has Ni-Cu-P as the outer layer, which is reported to have higher corrosion resistance ability than Ni-P coatings. Ni-Cu-P/Ni-P coating heat treated at 400°C, 4h has the largest diameter (in Nyquist plot), which indicates its highest resistance against corrosion. This is followed by Ni-P/Ni-Cu-P coating heat treated at 400°C, 1h. Both the coatings, when heat treated at 800°C, display lower impedance values compared to samples treated at 400°C This implies that corrosion resistance is compromised at higher heat treatment temperatures. In fact, at 800°C oxide formation occurs on the coating surface and micro-cracks are generated, as seen from the microstructural studies. The duration of heat treatment induces a different impact on the corrosion behaviour of the coating at different heat treatment temperatures. At 400°C, the increased duration of heat treatment resulted in increased corrosion resistance. However, for 800°C, the corrosion resistance decreases with the increased duration of heat treatment. This may be due to the increased thermal stress related manifestations on the coating surface at these conditions apart from the oxide and crack formation. 800°C, 4h heat treatment condition results in the lowest corrosion resistance among the coated samples, but still, the same is better than the base substrate. This implies the coating is still able to provide protection to the steel substrate. But in heat-treated samples, the results are consistent. Overall, duplex electroless Ni-P/Ni-Cu-P coatings have the highest corrosion resistance both in the as-deposited and heat-treated states.

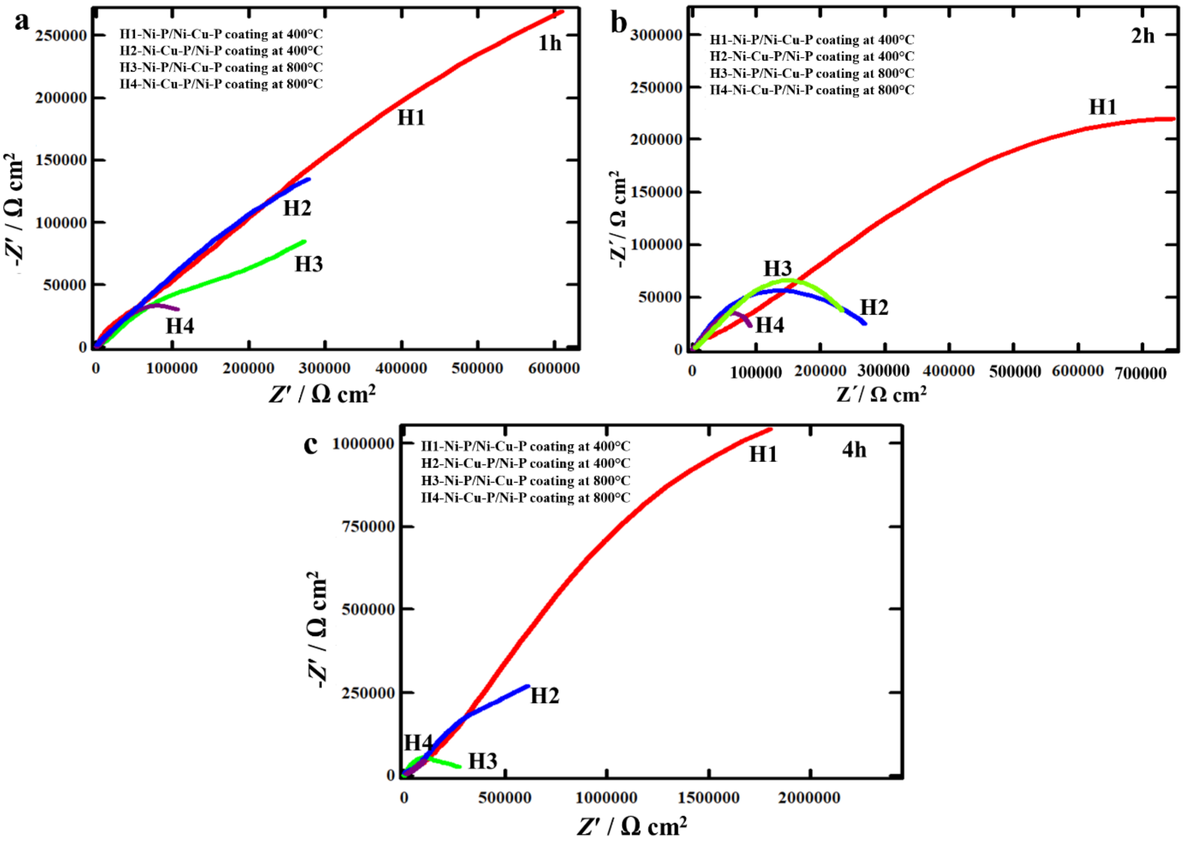

Figure 5.21 *Nyquist plots for heat-treated samples: (a) 1h duration; (b) 2h duration and (c) 4h duration*

From the present study, it is seen that duplex Ni-P/Ni-Cu-P is a promising coating for surface protection. Particularly the system with Ni-Cu-P as the outer layer displays higher wear resistance which improves further after heat treatment due to the phase transformation of the coating and precipitation of harder phases. The as-deposited coating can give good protection to the substrate surface against corrosion due to the former’s amorphous structure and ability to generate a passive film. In fact, Cu inhibits, to some extent, the crystalline transformation of the coating during heat treatment and results in enhanced corrosion resistance. Apart from this, Cu aids in the formation of the passive film. After heat treatment, the corrosion resistance ability of the coating increases in general. Heat treatment at 400°C results in the highest corrosion resistance. However, heat treatment beyond 400°C seems to have a negative impact on the coating, considering both the wear and corrosion resistance. Oxide formation, and generation of cracks and pores leads to a significant lowering of the wear and corrosion resistance of the present duplex coatings.

5.2.7 Performance comparison with single layer coating

When compared to single-layer coatings as studied by other researchers, the present set of duplex coatings exhibits lower hardness compared to single-layer Ni-P coating but higher hardness than single-layer Ni-Cu-P coatings **(Vitry and bonin, 2017; Hong and QIAN, 2018; Tan et al., 2014).** The wear performance of the present duplex coatings is found to be quite correlated to their hardness behaviour displaying lower wear rate compared to single layer Ni-Cu-P coatings but higher wear rate compared to single layer Ni-P coatings (**Tan et al., 2014).** However, in case of corrosion performance, the present duplex coatings outperform both the single layer counterparts. Hence, it may be concluded that the present set of duplex coatings combine and complement the advantages and limitations of the individual layers. In fact, the duplex system with Ni-Cu-P as the outer layer performs well and may be suitable for applications requiring both wear resistance as well as corrosion resistance.

5.3 Closure

The current chapter focuses on the evaluation of duplex electroless Ni-P/Ni-Cu-P coating. The coated samples were characterized by SEM, EDX, and XRD. The effect of heat treatment temperature and its time duration on the hardness, friction, and wear behaviour of both coatings are evaluated and compared. This would help in understanding how heat treatment influences the duplex system of coatings and helps in identifying the suitable condition of heat treatment for optimal performance of the coating. The corrosion behaviour of the coatings is also assessed with the help of electrochemical techniques, viz. PDP and EIS. Heat treatment is found to have a significant influence on the corrosion behaviour of duplex coatings. Finally, comparison is made with the constituent single-layer coatings and both the duplex coating systems. Overall, the duplex coating with Ni-Cu-P as the outer layer displays better results in both as-deposited and heat-treated conditions.

Chapter 6

Duplex Electroless Ni-P/Ni-Mo-P Coatings

Outline of the chapter: *6.1 Introduction, 6.2 Result and Discussion, 6.2.1 Microstructure characterization and composition analysis, 6.2.2 Phase structure, 6.2.3 Microhardness study, 6.2.4 Friction performance, 6.2.5 Wear performance, 6.2.5.1 Wear behaviour, 6.2.5.2 Wear mechanism, 6.2.6 Corrosion performance, 6.3 Closure*

6.1 Introduction

Duplex electroless Ni-P/Ni-Mo-P coatings provide a variety of qualities that can lead to the development of numerous novel applications both today and in the future. The metal finishing industry has already employed these coatings in several applications. For instance, research was done to improve corrosion resistance by applying duplex coatings. The effect of heat treatment conditions on the hardness, friction, wear and corrosion behaviour is studied in this chapter. To carry out a comprehensive analysis, one set of coating is developed with Ni-Mo-P as the outer layer (denoted as Ni-P/Ni-Mo-P) and another set with Ni-P as the outer layer (denoted as Ni-Mo-P/Ni-P). The performances of the two set of coatings are compared.

6.2 Results and Discussion

6.2.1 Microstructure characterization and composition analysis

The as-deposited duplex coating needs to be investigated to confirm that the coating is deposited appropriately. Figure 6.1 shows the SEM microstructure of duplex electroless Ni-P/Ni-Mo-P coating. The morphology of duplex coatings in as-deposited state shows tiny nodular structure (Figure 6.1a). Additionally, the duplex coating seems uniform throughout without any flaws or defects. The coated surface has some pores, which are visible. Because of the evolution of hydrogen during the reduction of nickel throughout the coating, these pores are typically generated in electroless nickel coatings. These pores do not extend up to the substrate surface because they are too tiny. As a result, the coating's ability to defend against corrosion is not compromised **(Biswas et al., 2017)**. The amount of phosphorous present and the heat treatment temperature influence the phase structure of the coatings,

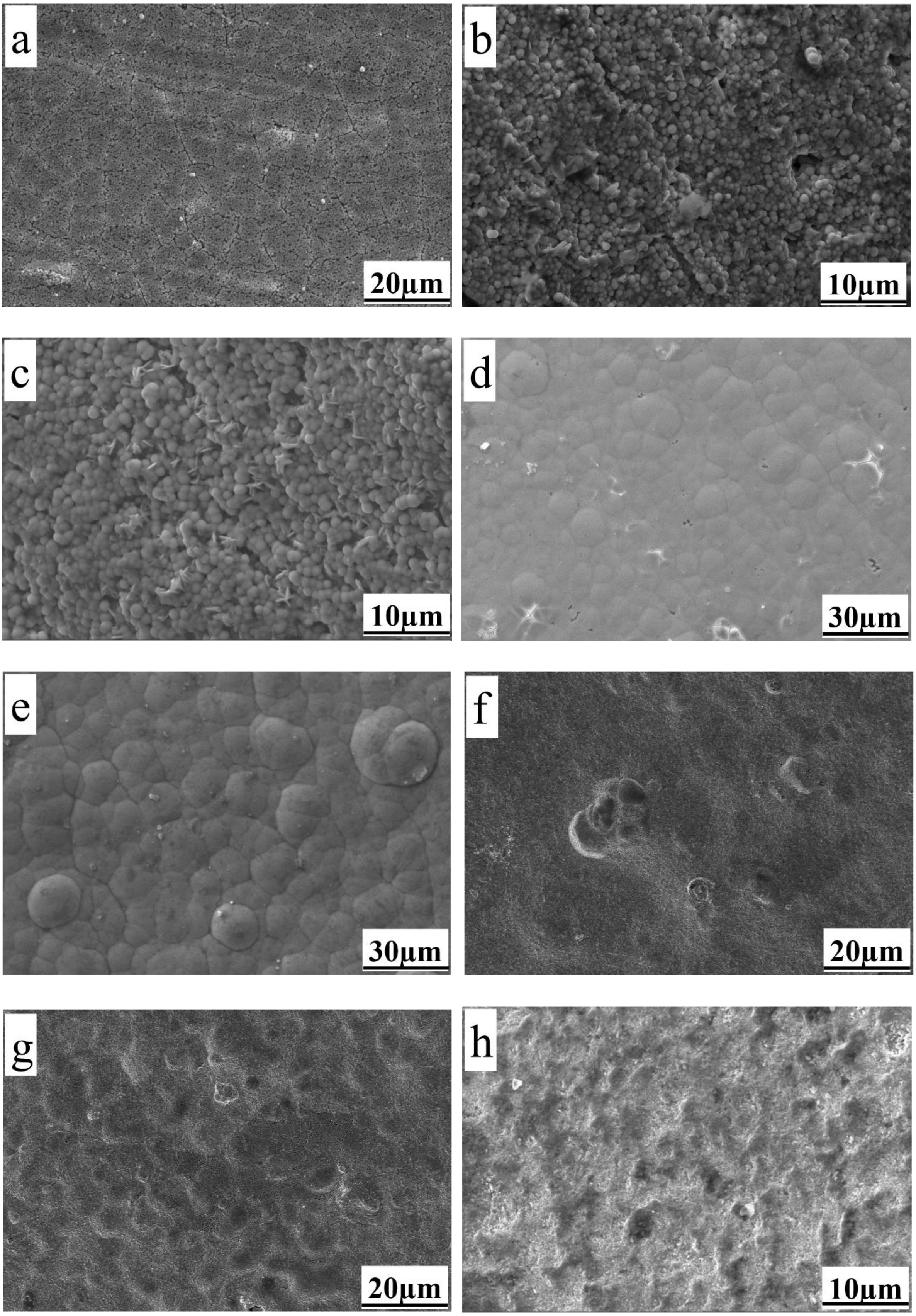

Figure. 6.1 *SEM images of duplex Ni-P/Ni-Mo-P coating for (a) as-deposited coating (b) at 400°C, 1h duration (c) at 400°C, 2h duration (d) at 400°C, 4h duration, (e) at 600°C, 1h duration, (f) at 600°C, 4h duration, (g) at 800°C, 1h duration, (h) at 800°C, 4h duration*

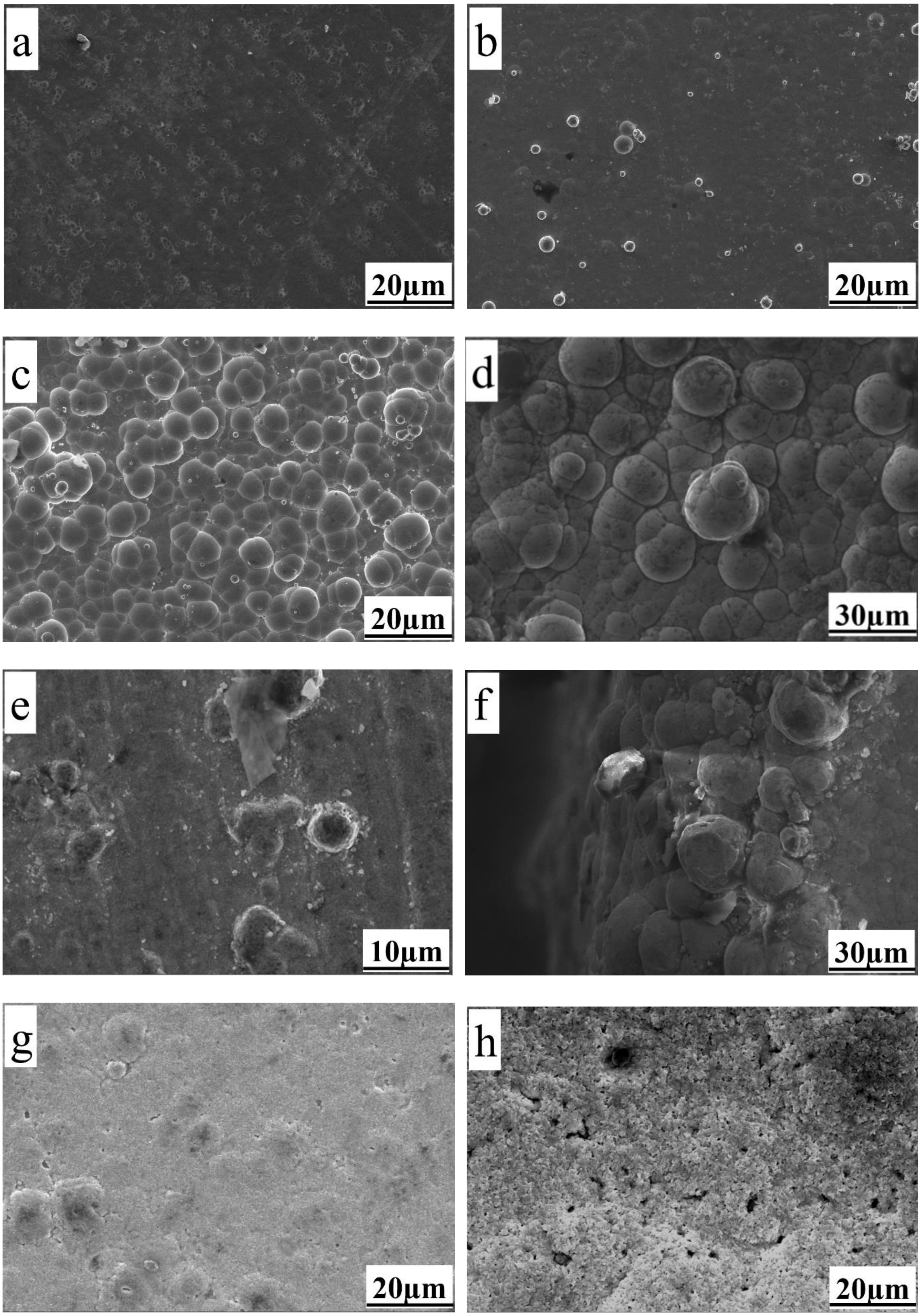

Figure. 6.2 *SEM images of duplex Ni-Mo-P/Ni-P coating for (a) as-deposited coating (b) at 400°C, 1h duration (c) at 400°C, 2h duration (d) at 400°C, 4h duration, (e) at 600°C, 1h duration, (f) at 600°C, 4h duration, (g) at 800°C, 1h duration, (h) at 800°C, 4h duration*

which changes the surface morphology to some extent **(Sahoo and Roy, 2017)**. The nodule's size increases post heat treatment of the duplex coating (Figure 6.1b-h). The coatings heat treated at 400°C also exhibit nodular structure, with nodule sizes ranging between 5 to 10 µm. However, after being heated to 600°C and above, the nodules appear to flatten (Figure 6.1e & 6.1f). In fact, the flattening is more noticeable at higher heat treatment temperature and longer heating periods. In addition, only a few white and dark spots are seen on the surface at high temperatures (around 800°C). This can mean that various phases have formed on the samples. As per micrograph of the cross-cut samples, the coating thickness is obtained as 38 µm.

In the case of duplex Ni-Mo-P/Ni-P coating too nodular structure can be visible in the as-deposited state (Figure 6.2a). The size of the nodule grows as a result of the heat treatment, as in the case of duplex Ni-P/Ni-Mo-P coating (Figure 6.2b-h). The nodules are determined to be approximately 15µm in size on average. At 400°C temperature, there is no porosity evident on the surface. The smoothness on the nodules' surface is lost at higher heat treatment temperatures (around 800°C) and over longer heat treatment periods (Figure 6.2f-h). For high heat treatment temperatures, the coating's porosity appears to be increased. At 800°C temperature for 4h duration, oxide formation is observed on the surface (Figure 6.2h). The mechanical and tribological properties are influenced by the presence of oxide layer.

Figure 6.3 displays the EDX spectrum of the coatings along with the percentage composition of the elements in as-deposited conditions. According to their phosphorus-

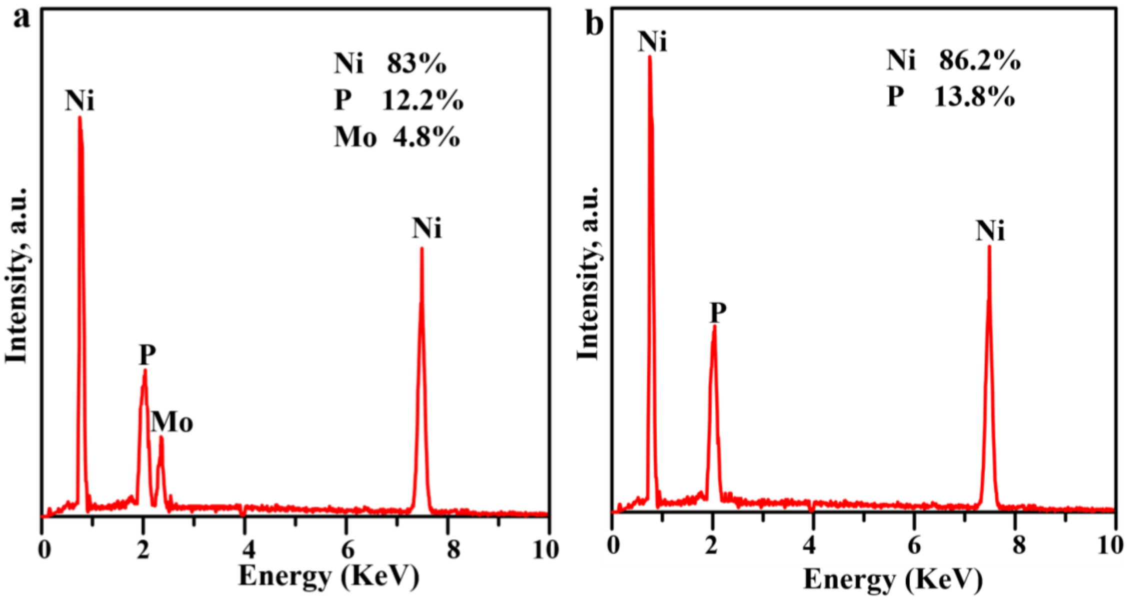

Figure 6.3 *EDX plot of duplex electroless (a) Ni-P/Ni-Mo-P coating and (b) Ni-Mo-P/Ni-P coating*

content, both coatings fall under the high phosphorous category. As is already reported **Sahoo and Das (2011); Keong and Sha (2002),** the duplex coating's high phosphorus content (> 8 wt%) indicates that it is having an amorphous phase structure. Similarly, the existence of Mo with the P and Ni on the duplex coating, indicates that the coating's top layer is a Ni-Mo-P layer. The Mo percent is found to be around 4.8% on duplex Ni-P/Ni-Mo-P coating. The elements of Ni and P are found on the surface of the duplex coating with a distribution of 86.2 wt% Ni and 13.8 wt% P, indicating that the coating's top layer is a Ni-P coating.

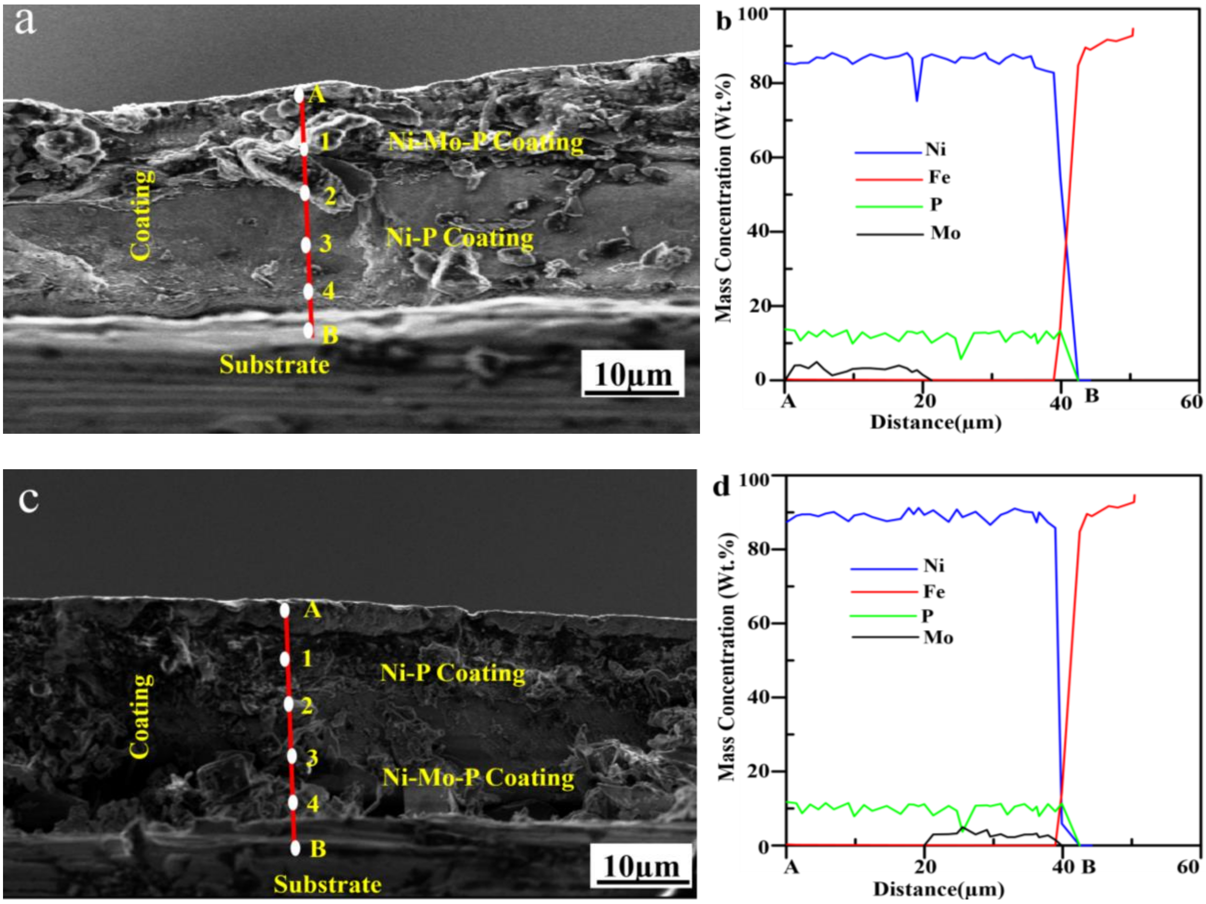

Figure 6.4 *Cross-section of the coating including line EDX result of duplex Ni-P/Ni-Mo-P coating (a, b) and duplex Ni-Mo-P/Ni-P coating (c, d)*

To get insight into the changes in the coating composition, line EDX is also performed along the coating cross-section as shown in Figure 6.4. The duplex coatings are successfully deposited, as seen in Figure 6.4. This is mostly deduced from the noticeable variation in molybdenum wt % near the interface of the top and bottom layers (near 20µm depth). This indicates a change over from Ni-P to Ni-Mo-P layer or vice versa. Additionally, the thickness of both the layers are nearly identical. The top and bottom layers of the coating exhibit excellent adhesion and compatibility since there is no discernible boundary between them. The coating's cross-section demonstrates that there are no pores or other defects. For these, the coating is expected to have excellent corrosion resistance.

6.2.2 Phase structure

The XRD results of the duplex coatings are displayed in Figures 6.5 and 6.6. The as-deposited duplex Ni-P/Ni-Mo-P coating exhibits a sharper peak at a 2Ɵ angle of 45° compared to the as-deposited duplex Ni-Mo-P/Ni-P coating, which has diffused peak indicative of an amorphous structure. This suggests that duplex electroless Ni-P/Ni-Mo-P coating is more crystalline than Ni-Mo-P/Ni-P coating. In this work, the composition of P and Mo indicates that it may be a mixture of amorphous and crystalline states that has been reported in the literature (**Koiwa et al., 1988).** There is not much of a difference in the XRD plots of samples heat treated at 200°C. However, there is a noticeable shift in the XRD profile of the samples when the heat treatment temperature is 400°C or above, with several peaks of different phases comprising of Ni, Mo, P, and even O. In Ni-P/Ni-Mo-P coating, heat treated at 400°C for 1h duration, the highest peak is found at 45° for nickel-molybdenum (Ni-Mo). The nickel diffraction peaks are connected to the two sharp peaks at 45° and 51°. Ni-Mo diffraction peak is associated with the peak at 75°. A similar type of investigation has been conducted by **Koiwa et al. (1988).** At this temperature, the precipitation of Ni, Ni_3P, and Ni-Mo phases are obtained. When the samples are heated to 600°C for 1h, the diffraction peaks are more clearly defined, showing that the Ni-P/Ni-Mo-P coating has been crystallized. But at higher temperature (at 800°C), a few NiO phases is obtained along with Ni-Mo, Ni, and Ni_3P phases. The coating exhibits several crystalline peaks during heat treatment at 400°C and above, predominantly Ni_3P phases in the (321), (112), (141), and (322) planes. According to the XRD patterns (Figure 6.5c), 400°C heat treatment temperature for a 2h period causes Ni-Mo to be a significant phase in Ni-P/Ni-Mo-P coating along with Ni_3P.

Further, by increasing the temperature of the Ni-P/Ni-Mo-P coating, the nickel oxide phase is found to be present with the precipitation of Ni, Ni_3P, and Ni-Mo phases. For high temperatures and longer duration (at 800°C with 2& 4h duration), higher amount of nickel oxide is formed. The trapped air in the furnace is the main contributor to these oxide forms.

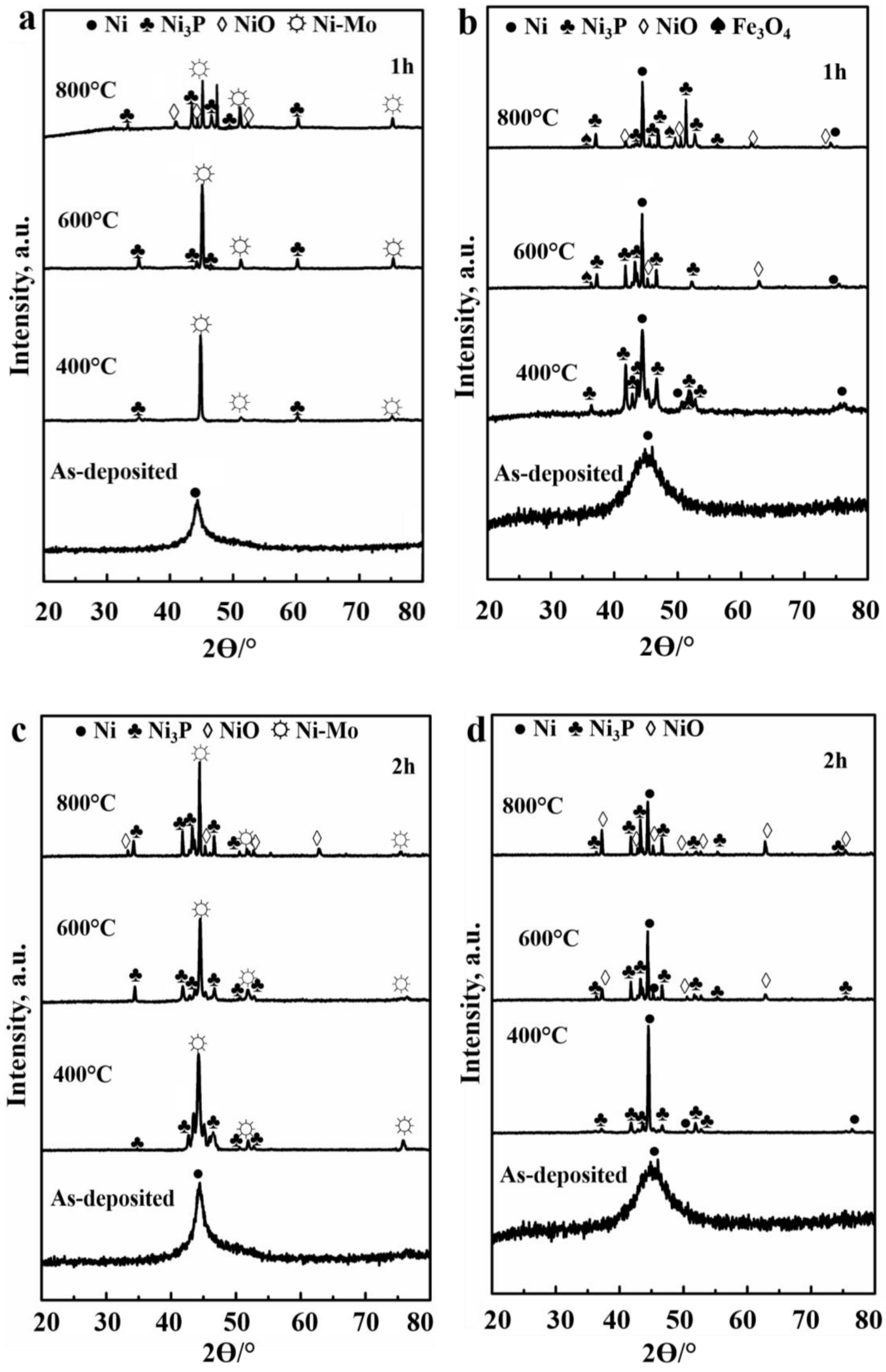

Figure 6.5 *XRD plots of: (a) Ni-P/Ni-Mo-P coating for 1h duration, (b) Ni-Mo-P/Ni-P coating for 1h duration, (c) Ni-P/Ni-Mo-P coating for 2h duration, (d) Ni-Mo-P/Ni-P coating for 2h duration*

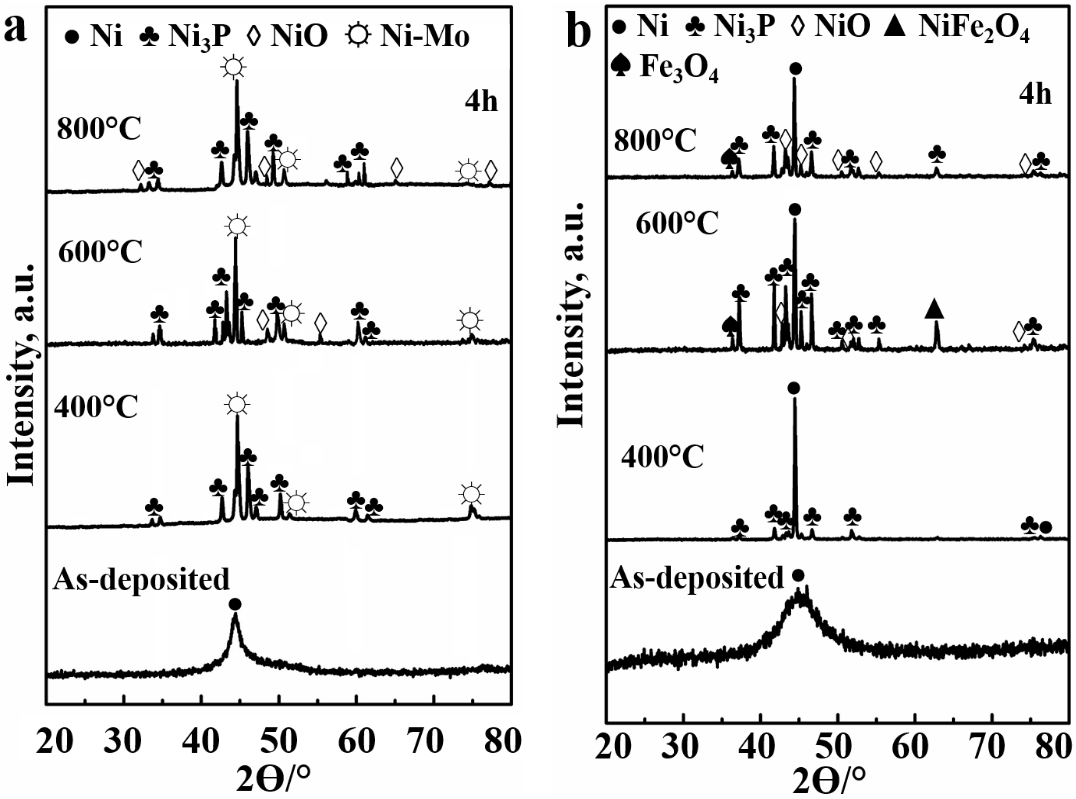

Figure 6.6 *XRD plots of: (a) Ni-P/Ni-Mo-P coating for 4h duration, (b) Ni-Mo-P/Ni-P coating for 4h duration*

For Ni-Mo-P/Ni-P coating, the precipitation of the Ni_3P phase and residual Ni phase is obtained at 400°C temperature as shown in (Figures 6.5b, d, and Figure 6.6b). At high heat treatment temperatures (600°C or 800°C) for 1h duration, Fe_3O_4 phase is obtained together with the Ni_3P and Ni phases. A few NiO phases are also revealed at these temperatures. At 600°C temperature and 4h duration, Ni and Fe_2O_4 phases are obtained. The development of hard crystalline Ni_3P phase is the primary factor to responsible for improving the hardness after heat treatment. For high temperatures (at 600°C or 800°C) with prolonged time duration (2 & 4h), NiO phase is formed with Ni_3P phase. The NiO reduced the hardness values. At 600°C and 800°C for 2 and 4h, there is also a sharpening and rise in peak intensity.

6.2.3 Microhardness study

Microhardness tests are performed to determine the influence of duplex coating composition and heat treatment temperature on the coating's microhardness. Figure 6.7 shows the microhardness of the current duplex coating. The microhardness value for Ni-P/Ni-Mo-P coating is found to be 587 $HV_{0.1}$ in the as-deposited state. When the sample is heat-treated at 200°C, no discernible alteration is found in the phase structure. Due to minor microstructure change, there is little variation in microhardness values as seen at 200°C heat treatment temperature.

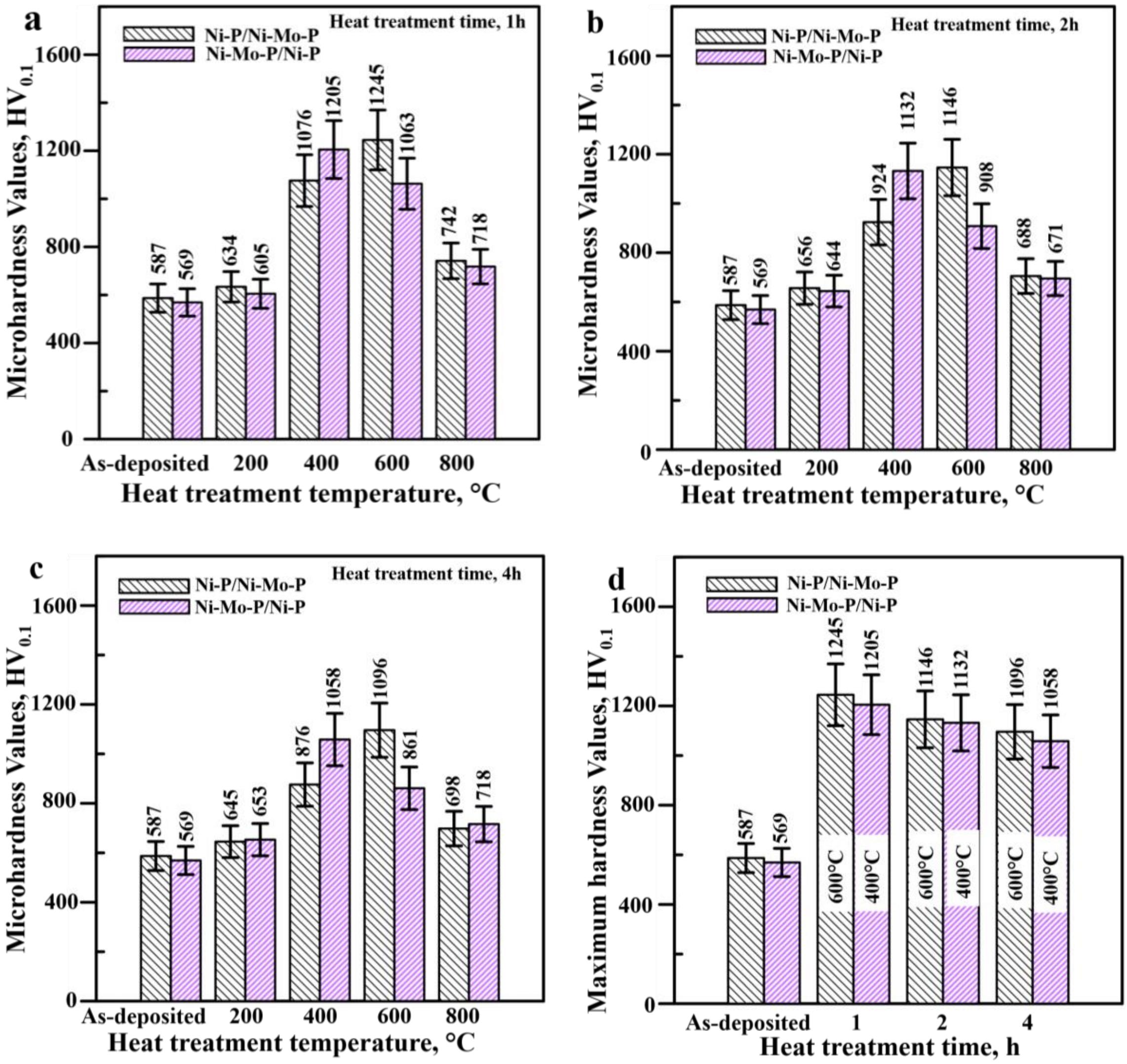

Figure 6.7 *Microhardness plots for (a) 1h, (b) 2h, (c) 4h duration, and (d) maximum microhardness plot*

The microhardness value increases with increasing heat treatment temperature because of the formation of new crystalline phases like Ni, Ni_3P, and Ni-Mo as seen in Figure 6.5 and 6.6. It is found that Ni-P/Ni-Mo-P coating displays rising microhardness with the raise in heat treatment temperature around 600°C beyond which it declines, regardless of the period of heat treatment. Because of the formation of Ni, Ni-Mo and Ni_3P phases, the highest microhardness is found at 600°C temperature for 1h time period. The microhardness value has improved by about 120% as compared to the as-plated conditions. It is also noticed that microhardness is decreased marginally with increased duration of heat treatment (2h and 4h) due to grain coarsening. At 800°C temperature with prolonged treatment period, the microhardness value drastically falls caused by the formation of NiO.

The microhardness value of the as-deposited Ni-Mo-P/Ni-P coating is found to be 569 $HV_{0.1}$. At 200°C heat treatment temperature, microhardness rarely varies due to insignificant microstructural change. There is no phase change observed at this heat treatment temperature as discussed in the previous section. At 400°C heat treatment temperature for 1h of the time period, the maximum microhardness value is obtained due to the creation of hard Ni_3P phase. The microhardness value is improved by around 112 % from the as-plated state due to the Ni_3P precipitation. Due to grain coarsening, the microhardness value decreases after 400°C heat treatment temperature. The microhardness of Ni-Mo-P/Ni-P coating starts to decline after 400°C and continues to do so until 800°C for all heat treatment durations. The reduction in microhardness of the coated sample may be attributed majorly to the grain coarsening phenomenon as mentioned before which will result in softer crystals with reduced hardness. Moreover, at high temperatures (600°C or 800°C), the microhardness value is also affected by the formation of higher amount of oxide phases. In the current experiment, the microhardness of the Ni-P/Ni-Mo-P coating is superior to the Ni-Mo-P/Ni-P coating in all aspects.

6.2.4 Friction performance

The COF plot of duplex electroless nickel coatings under the heat treatment conditions is illustrated in Figure 6.8. In duplex electroless Ni-P/Ni-Mo-P coating, the COF is found to be around 0.39 in as-deposited condition. This is quite low considering the nodular nature of the coating surface. Nodular surface on the coating results in smaller area of contact which in turn results in lower COF provided the material properties of the contacting pairs remain constant.

The COF is found to decrease by increasing heat treatment temperature. The lowest COF is observed at 400°C heat treatment temperature for 1h duration. It is generally seen when all other factors remaining constant, friction rises due to longer contact times. Hardness decreases the actual interaction area of the interface, which manifests as a reduction in friction. The microhardness of the coating is increased by increasing the heat treatment temperature, as a result of the formation of several hard phases that has been discussed in the previous sections. As a result, it is seen in the current instance, the COF value should be lower for heat-treated coating than as-plated. At 400°C heat treatment temperature for 1h, the COF is decreased by around 71% compared to the as-plated coatings. It is found that duplex Ni-

P/Ni-Mo-P coating displays reducing COF with the rise in heat treatment temperature up to around 400°C.

At high heat treatment temperatures (600°C or 800°C), the COF is higher compared to 400°C temperature (refer to Figure 6.8a-c). This may be partly explained by the fact that at these heat treatment conditions nodules get flattened increasing the contact area. However, the COF remains lower than that of the as-plated coating because of the development of the crystalline structure. It is also noticed that the minimum COF value has been found at a heat treatment temperature of 200°C for 2h and 4h duration. In fact, the same underlying factors that affected COF for duplex Ni-P/Ni-Mo-P coating are also responsible for the corresponding COF variations in duplex Ni-Mo-P/Ni-P coating. Figure 6.9 displays the COF vs. time plots which appeared to be stable. A few variations are noticed for duplex Ni-Mo-P/Ni-P coating.

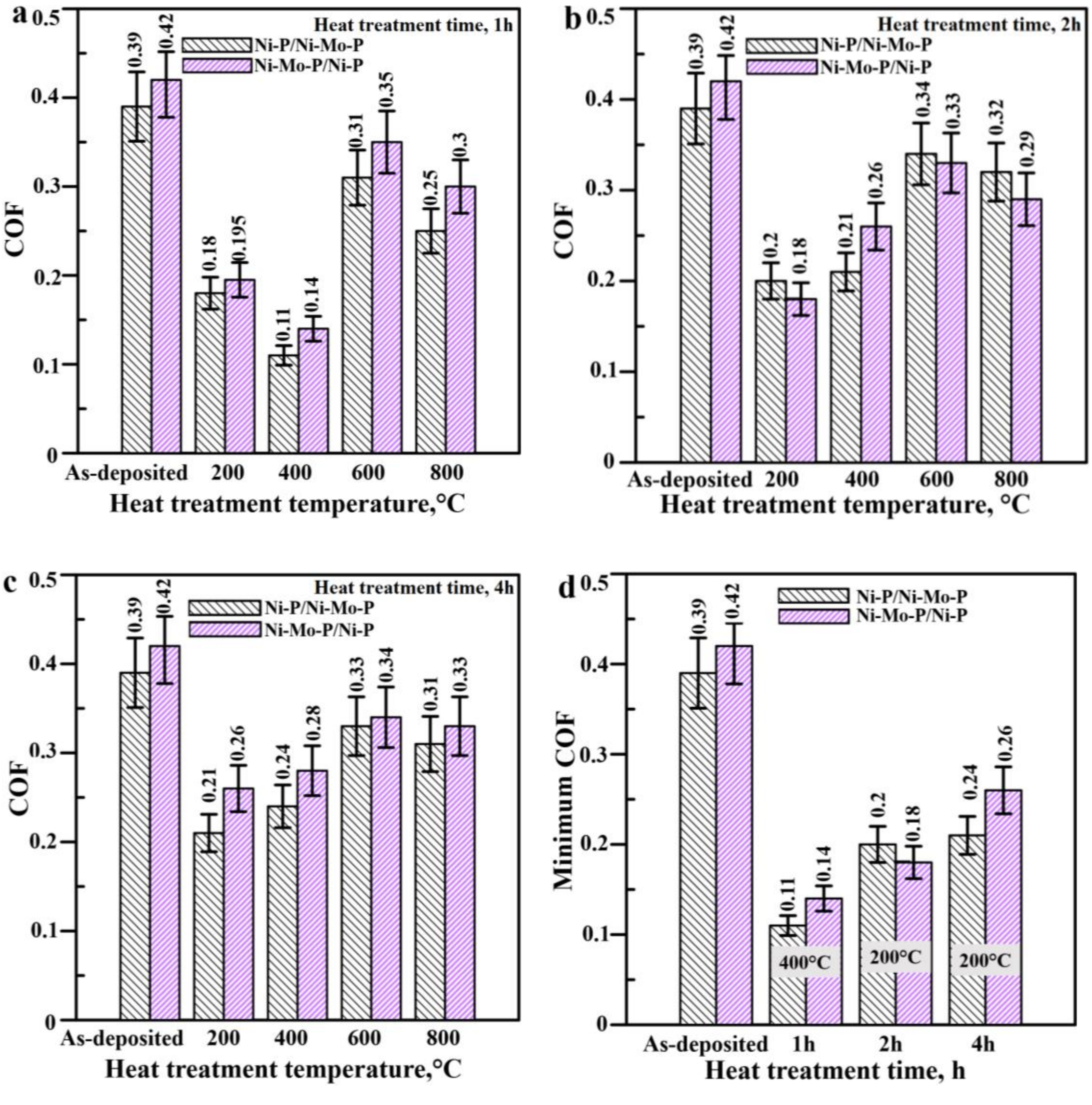

Figure 6.8 *COF plots for various heat treatment temperatures (a) 1h; (b) 2h; (c) 4h; and (d) minimum COF plot*

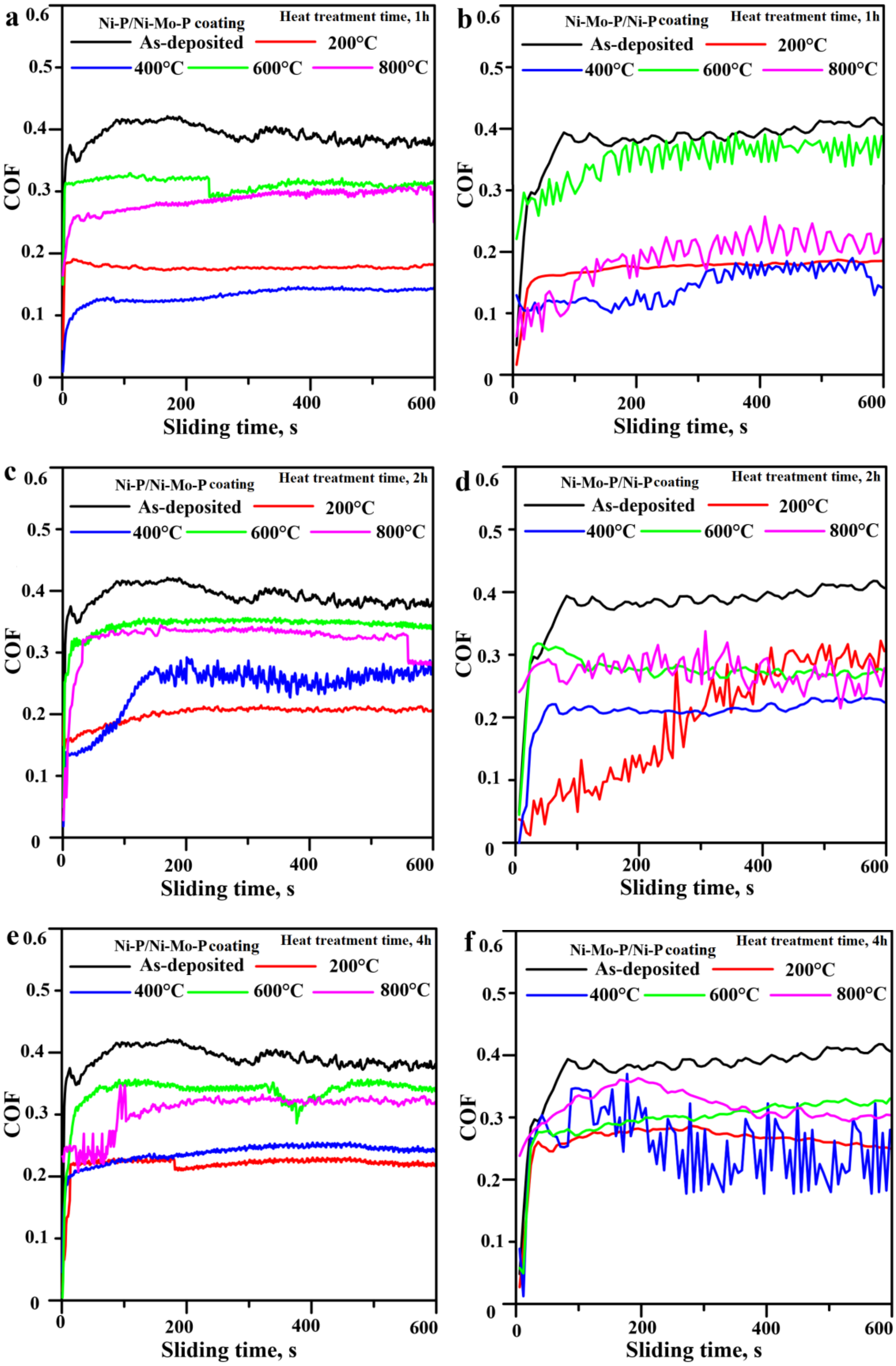

Figure 6.9 *COF vs. sliding duration of (a) Ni-P/Ni-Mo-P coating 1h, (b) Ni-Mo-P/Ni-P coating, 1h, (c) Ni-P/Ni-Mo-P coating, 2h, (d) Ni-Mo-P/Ni-P coating, 2h, (e) Ni-P/Ni-Mo-P coating, 4h and (f) Ni-Mo-P/Ni-P coating, 4h*

The minimum COF value is obtained for duplex Ni-P/Ni-Mo-P coating among all the as-deposited and heat treatment conditions.

6.2.5 Wear performance

6.2.5.1 Wear behaviour

Figure 6.10 displays the wear rate of duplex coating under different heat treatment conditions. For duplex coatings, a significant microstructural change has been observed after heat treatment. As a result, the coating's wear characteristics are influenced by heat treatment temperature and time duration. As-deposited Ni-P/Ni-Mo-P coating shows an approximate 21.56×10^{-5} $mm^3.N^{-1}.m^{-1}$ wear rate under the current combinations of sliding speed and applied

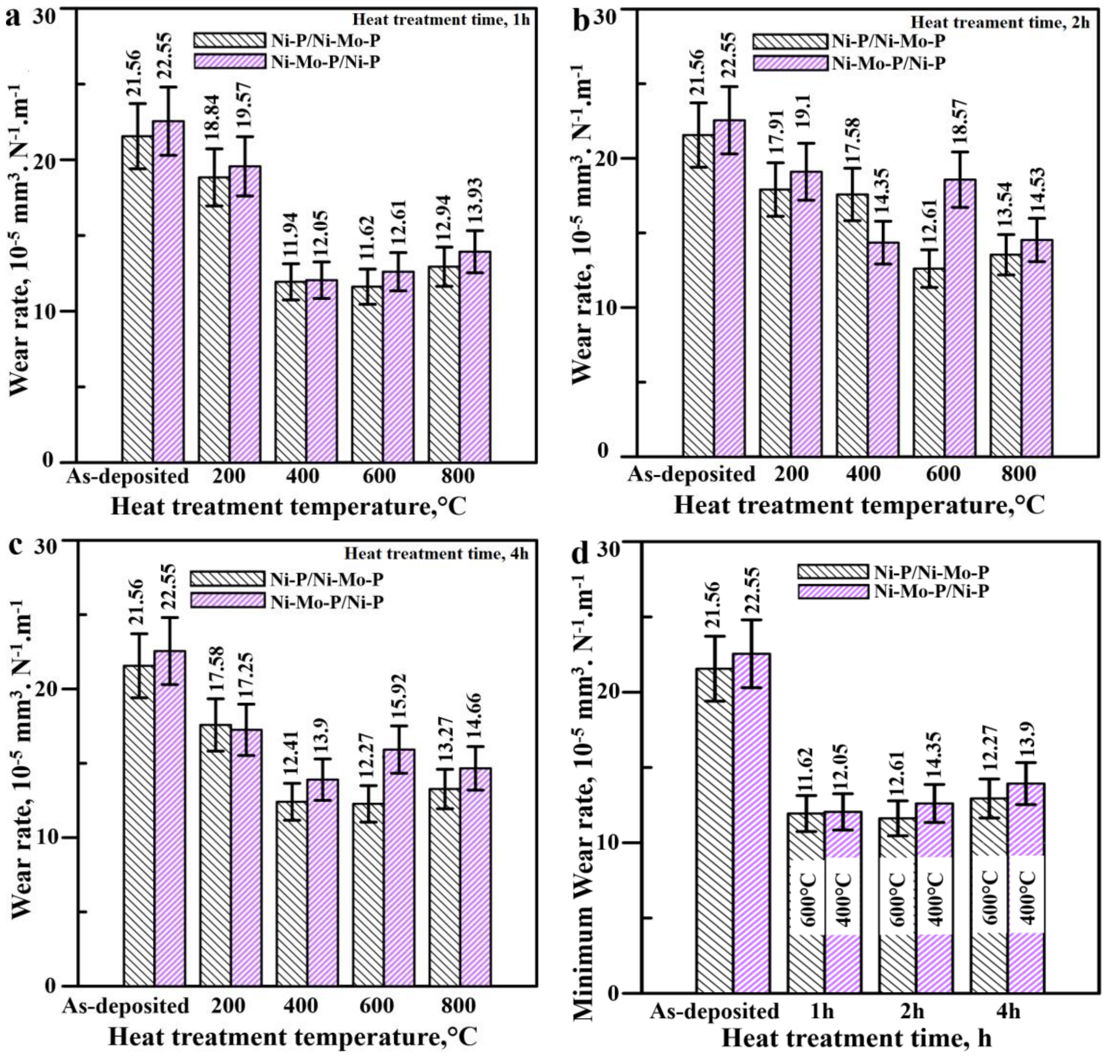

Figure 6.10 *Wear rate for various heat treatment temperatures (a) 1h; (b) 2 h; (c) 4h duration; and (d) minimum wear rate*

load. The wear resistance is improved with rise in heat treatment temperature up to around 600°C temperature because of the development of new crystalline Ni_3P and Ni-Mo phases. Due to the extremely low solubility of iron in the hard Ni_3P and Ni-Mo phases that result from heat treatment, the counterface material presents an almost incompatible surface for these phases, which lowers the wear rate. Additionally, the coatings' microhardness significantly increases after heat treatment. The lowest wear rate is found at 600°C temperature for 1h time period due to the prominence of Ni_3P and Ni-Mo phases. The wear rate is reduced by around 46% at 600°C for 1h compared to the that of as-deposited state. At 800°C heat treatment temperature, wear resistance is decreased as compared to 600°C temperature due to the formation of the NiO phase.

When heat treatment time is increased to 2h or 4h, the wear rate marginally differs from that of 1h duration. It is very interesting to note that the wear resistance of 4h heat treated sample is better than 2h duration in all aspects. Also, at high heat treatment temperature (at 800°C with 1-4h duration), the wear resistance increases more than as-plated coating due to precipitation of hard Ni-Mo and Ni_3P phase at lower diffraction angle.

For duplex Ni-Mo-P/Ni-P coating, the as-deposited coating wear rate is 22.55×10^{-5} $mm^3.N^{-1}.m^{-1}$. This wear resistance is increased with rising heat treatment temperature up to 400°C for different time periods (1-4h), beyond which it declines. At 400°C heat treatment temperature and for 1h duration, a hard crystalline Ni_3P phase is observed as reported in previous sections. It may be the main reason for reducing the wear rate. At this heat treatment conditions, Ni-Mo-P/Ni-P coating achieved the lowest wear rate, almost 46% of that of as-plated coating. At high temperatures (800°C or 600°C) for 1h treatment period, wear resistance of Ni-Mo-P/Ni-P coating decreases because of the creation of oxides (NiO).

Similar wear behaviour is observed for 2h and 4h heat treatment durations. Duplex Ni-P/Ni-Mo-P coating has better wear resistance than Ni-Mo-P/Ni-P coating in all aspects both in as-deposited and heat treatment conditions. This might be explained by the highest microhardness of Ni-P/Ni-Mo-P coating, which makes it more resistant to wear.

6.2.5.2 Wear mechanism

The wear mechanism of duplex electroless Ni-P/Ni-Mo-P coating is shown in its as-deposited state in Figure 6.11a. Ploughing is seen on the worn morphology of the as-deposited coating along the sliding direction. Ploughing marks which is represented by ellipse demonstrates

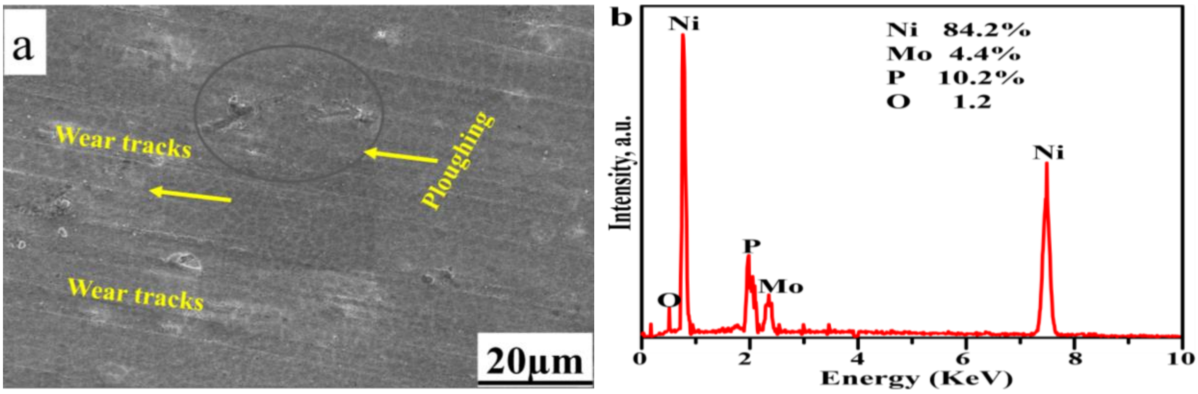

Figure 6.11 *(a) The worn surface image of as-deposited Ni-P/Ni-Mo-P coating and (b) EDX plot.*

where abrasive wear has occurred. Some sporadic grooves can be seen virtually perpendicular to the wear tracks, indicating damage caused by an external force. The trapped hard particles between the sliding surfaces may also contribute to ploughing marks. In as-deposited samples, worn surface has been observed through EDX analysis as seen in Figure 6.11b. The tribological behaviour of Ni-P/Ni-Mo-P coating displays abrasive wear in the form of micro grooves and furrows. The abrasive wear is influenced by microstructure, hardness, roughness, and grain size of the coating.

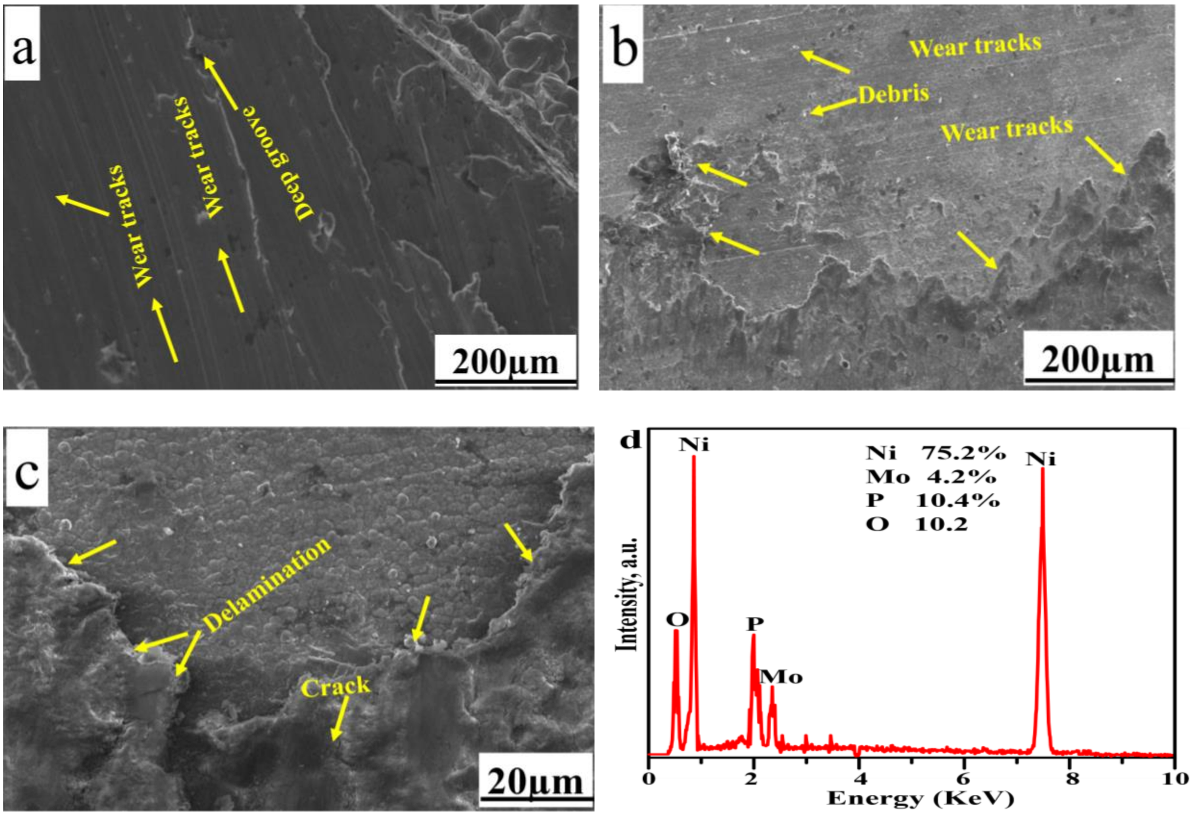

Figure 6.12 *(a) Ni-P/Ni-Mo-P coating worn image at 400°C, 1h (b) at 400°C,4h (c) at 600°C, 2h and (d) EDX at 600°C, 2h*

At 400°C, for 1h duration, few micro-cracks, have been observed on the worn surface as shown in Figure 6.12a. Few plastic deformations are also observed on the surface. At 400°C, 4h duration, the samples experienced more wear debris which is produced due to the sliding wear. Also, wear delamination has been seen on the top surface of the sample as shown in Figure 6.12b. At 600°C heat treatment temperature for 2h duration (Figure 6.12c), sample clearly shows that a significant quantity of material has been sheared off from the contact area as wear debris. In contrast, wear tracks are clearly apparent in other areas of the worn region owing to the crack formation and plastic deformation. The EDX analysis of the surface of sample heat treated at 600°C for 2h period is shown in Figure 6.12d. Oxygen has been detected on the rubbed surface.

At high temperatures, few plastic deformations are observed due to abrasion. For sample heat treated at 800°C temperature for 4h time duration, the SEM image and EDX analysis are displayed in Figure 6.13. At high temperatures, wear debris, micro-ploughing, micro-cutting, cracks, and other features appear to be present on the rubbed surface. At 800°C, 4h time period, more oxygen is detected i.e., above 14% (Figure 6.13b). Therefore, both the abrasive and adhesive wear mechanism seem to govern the wear behaviour of the coated surface.

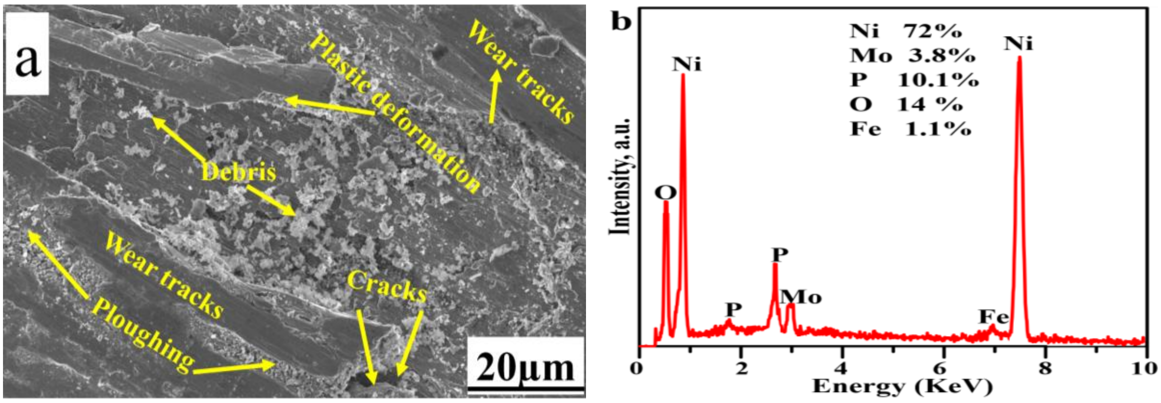

Figure 6.13 *(a) Ni-P/Ni-Mo-P coating worn image of heat treatment at 800°C, 4 h and (b) EDX plot.*

Figures 6.14, 6.15 and 6.16 display the mechanism of wear tested samples of duplex Ni-Mo-P/Ni-P coating. The as-deposited coating (Figure 6.14a) exhibits abrasion marks along the sliding direction. There are a few cracks visible on the rubbed surface, but they appear to be extremely little, and should not cause too much concern. In addition, there is a lot of compacted worn debris that seems to be nearly fused to the coated surface. The sample displaying oxidation at the sliding interface also contains a minor amount of oxygen as shown in Figure 6.14b. Abrasive wear is present at 400°C for 1h heat-treated sample as shown in

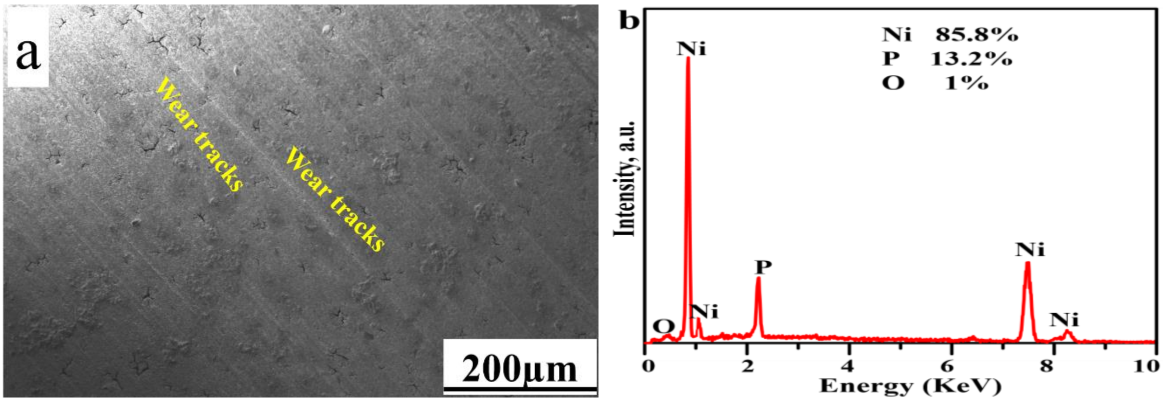

Figure 6.14 *(a) The worn surface image of as-deposited Ni-Mo-P/Ni-P coating and (b) EDX plot.*

Figure 6.15a. Also, the wear tracks are visible on the worn surface. A few pieces of wear debris are dispersed on the worn surface. This debris appears to be welded to the surface. On the worn surface, pits and prows can be seen. However, the surface of Ni-Mo-P/Ni-P coating that has been heated to 400°C for 4h exhibits crack as shown in Figure 6.15b. At 600°C for 2h duration, the worn surface displays more wear debris that has been welded on to the surface of the coating (Figure 6.15c). EDX result shows the presence of oxygen at 11.2% (Figure 6.15d) which indicates high oxidation on the coating surface.

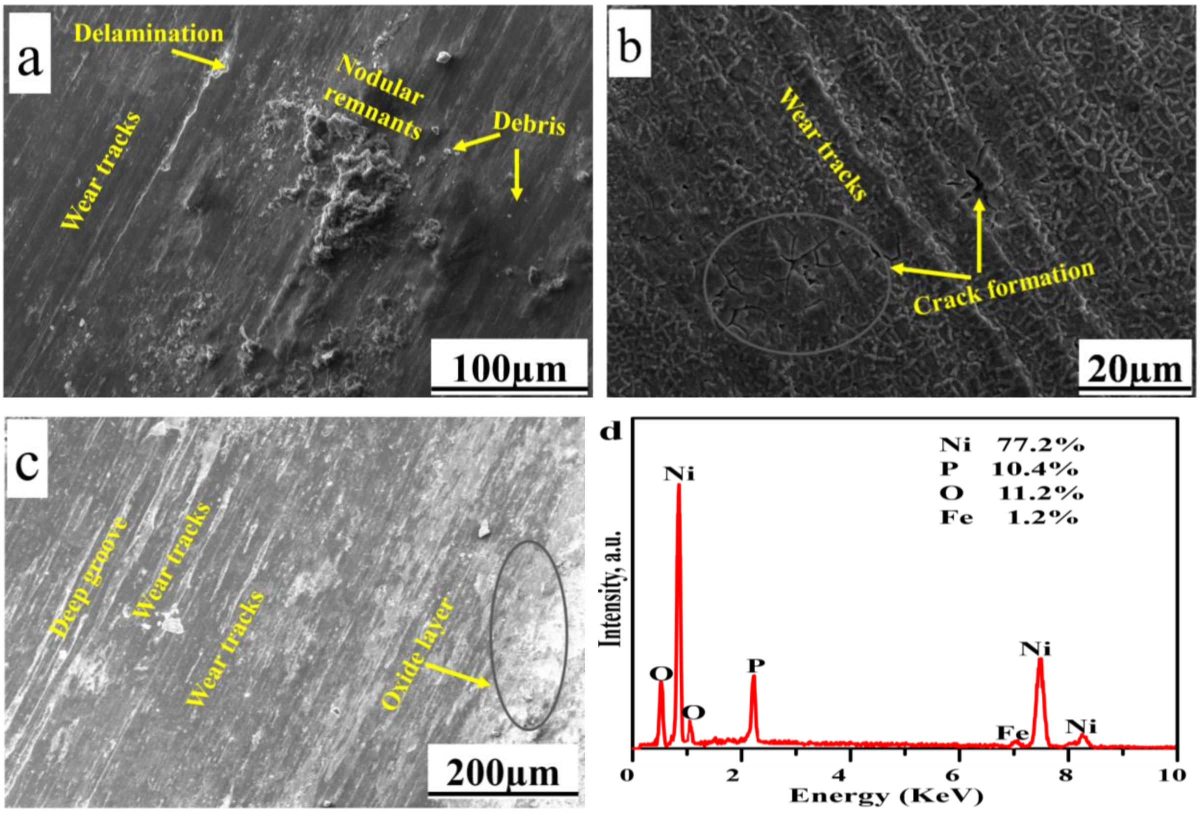

Figure 6.15 *(a) Ni-Mo-P/Ni-P coating worn image at 400°C, 1h (b) at 400°C,4h (c) at 600°C, 2h and (d) EDX plot at 600°C, 2h*

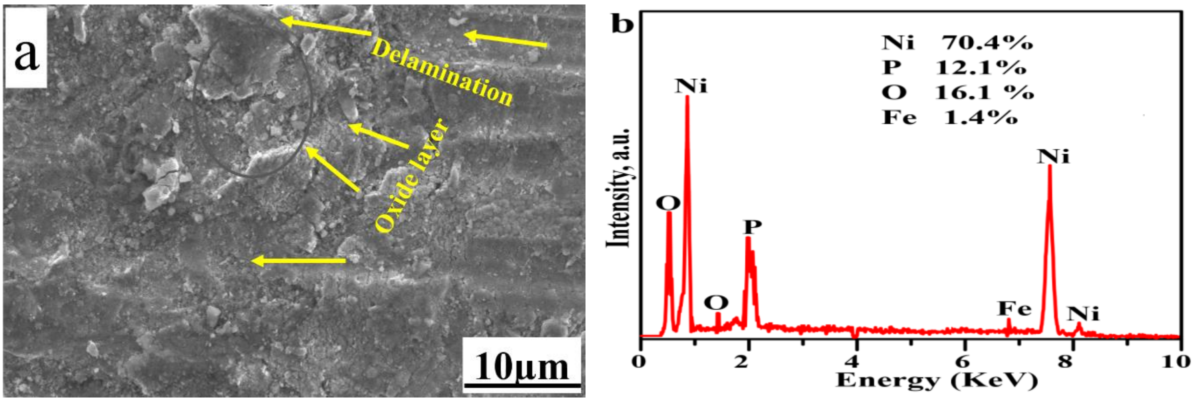

Figure 6.16 *(a) Ni-Mo-P/Ni-P coating worn image of heat treatment at 800°C, 4h and (b) EDX plot*

At 800°C for 4h, a portion of the coating layer appears to have separated, exposing the coating interlayer in addition to wear tracks (refer Figure 6.16a). The sample's wear behaviour is highly influenced by the oxide layer that has been developed on the sample's surface. The EDX results seen on the surface after test contains 16.1% oxygen (Figure 6.16b). Thus, it can be concluded that both duplex coatings experience similar kinds of wear mechanisms.

6.2.6 Corrosion performance

Figure 6.17 shows the potentiodynamic polarisation curves for each of the coatings. The plots display a suitable Tafel area with clearly defined anodic and cathodic parts. According to the PDP results, after heat treatment, the corrosion potential shifts to the positive zone. The results of corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are computed using the Tafel extrapolation technique. The E_{corr} and i_{corr} data are displayed in Table 6.1. It shows that as-plated coatings have the lowest levels of corrosion resistance. This is interesting considering the currently as-plated coating have an amorphous structure. But heat treatment causes the coating to crystallize, which could aid corrosive media to penetrate the coating by passing through the grain boundaries. This unusual behaviour could be explained by the fact that the coating gets denser and more compact after heat treatment. Some researchers have also reported similar kind of observations **(Rabizadeh et al., 2010)**. Additionally, because the present coating is a duplex coating system, heat treatment might be able to provide excellent adhesion between the two deposited layers.

Another interesting finding is that the corrosion potential shifts from negative to positive direction with increasing heat treatment temperature, particularly during 4h treatment

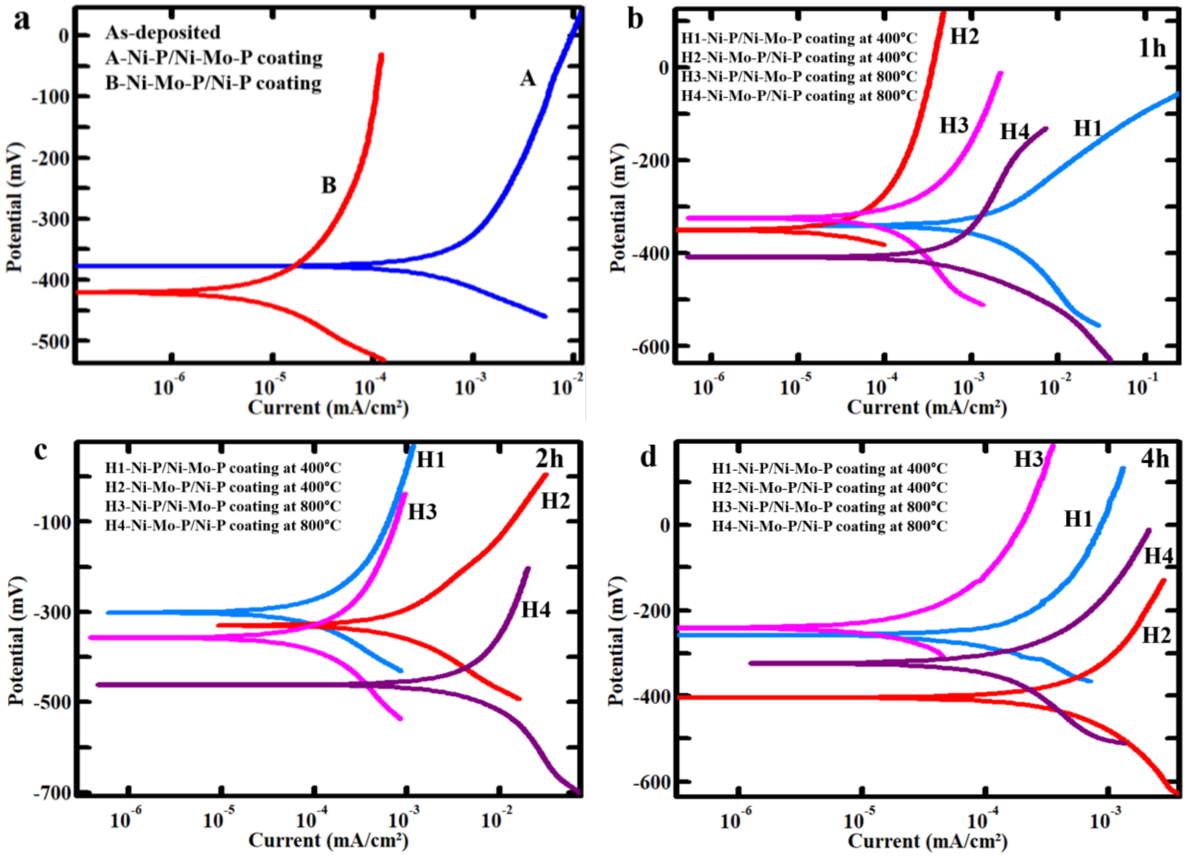

Figure 6.17 *Polarization plots for: (a) as-deposited condition; (b) heat-treated samples 1h duration; (c) heat-treated samples 2h duration; (d) heat-treated samples 4h duration*

cycle (Figure 6.17d). At the high heat treatment temperature, grain coarsening takes place. Duplex Ni-P/Ni-Mo-P coating showed more positive E_{corr} values compared to Ni-Mo-P/Ni-P coating both in as-deposited and heat treatment conditions. This increase in E_{corr} value showed that the duplex Ni-P/Ni-Mo-P coating had a lower corrosion rate. Secondly, compared to duplex electroless Ni-Mo-P/Ni-P coating, the i_{corr} values of Ni-P/Ni-Mo-P coating are much lower. This demonstrated that the duplex coatings with Ni-Mo-P as the exterior layer had a favourable effect on reducing the rate of corrosion in the active corrosion region **(Vitry et al., 2012).**

The corrosion resistance increases with increasing heat treatment temperature. Additionally, no passivation of the coatings could be seen in the anodic curves; instead, there is merely an increase in slope. At 800°C heat treatment temperature for 4h duration, Ni-P/Ni-Mo-P coating exhibited the highest corrosion resistance. Overall, the plots show that duplex Ni-P/Ni-Mo-P coating has greater corrosion resistance than Ni-Mo-P/Ni-P coating in all aspects (Figures 6.17a to 6.17d). From the PDP curve, the best corrosion performance of Ni-

P/Ni-Mo-P coating has been observed at 800°C temperature for a 4h time duration. This kind of trend is also obtained for Ni-Mo-P/Ni-P coating.

Figures 6.18a-d shows the Nyquist plots for the current coating, and Figure 6.18e shows an illustration of the equivalent circuit used. A single semicircle is visible on the plots for the samples subjected to heat treatment. This shows that the corrosion process experienced by the current coatings has a fixed time constant. Additionally, the semicircles differ in size but are essentially identical in shape. This means that all the samples must have encountered the same basic process during corrosion. R_{ct} and C_{dl} values almost exactly mirror the results of the PDP test. Heat-treated samples exhibit higher R_{ct} and lower C_{dl} values in comparison to the as-plated coating. The sample heat-treated at 800°C for 4h had the highest R_{ct} value. According to the results, there may be a little amount of porosity in the coating before heat treatment, which becomes minimized post heat treatment. The fact that the C_{dl} values fall as the heat treatment temperature rises is evidence in favour of this observation. Moreover, nodular morphology is prone to retaining corrosive media as well as pit nucleation **(Toloei et al., 2013)**. But on flattening of the nodules at higher heat treatment temperatures, the surface becomes smoother and it forms a strong passive film which presents fewer sites

Table 6.1 Corrosion data obtained from Tafel extrapolation and Nyquist plots

Samples	**E_{corr} (mV)**	**i_{corr} (mA/cm^2) ×10^{-5}**	**R_{ct} (ohm.cm^2) ×10^5**	**C_{dl} (10^{-6}F)**
As-deposited Ni-P/Ni-Mo-P coating	-378	23.49	2.63	4.95
As-deposited Ni-Mo-P/Ni-P coating	-421	0.88	1.74	8.03
Ni-P/Ni-Mo-P coating, at 400°C 1h	-340	7.67	5.5	3.53
Ni-Mo-P/Ni-P coating, at 400°C 1h	-351	1.654	2.71	9.42
Ni-P/Ni-Mo-P coating, at 800°C 1h	-324	3.39	2.48	1.06
Ni-Mo-P/Ni-P coating, at 800°C 1h	-409	20.55	1.18	9.07
Ni-P/Ni-Mo-P coating, at 400°C 2h	-302	1.68	2.94	0.88
Ni-Mo-P/Ni-P coating, at 400°C 2h	-330	33.28	1.43	5.04
Ni-P/Ni-Mo-P coating, at 800°C 2h	-357	2.56	1.14	1.76
Ni-Mo-P/Ni-P coating, at 800°C 2h	-463	51.47	1.48	4.35
Ni-P/Ni-Mo-P coating, at 400°C 4h	-257	5.78	13.6	4.61
Ni-Mo-P/Ni-P coating, at 400°C 4h	-403	20.13	4.56	1.41
Ni-P/Ni-Mo-P coating, at 800°C 4h	-241	1.08	20.8	0.75
Ni-Mo-P/Ni-P coating, at 800°C 4h	-323	3.66	6.32	2.71

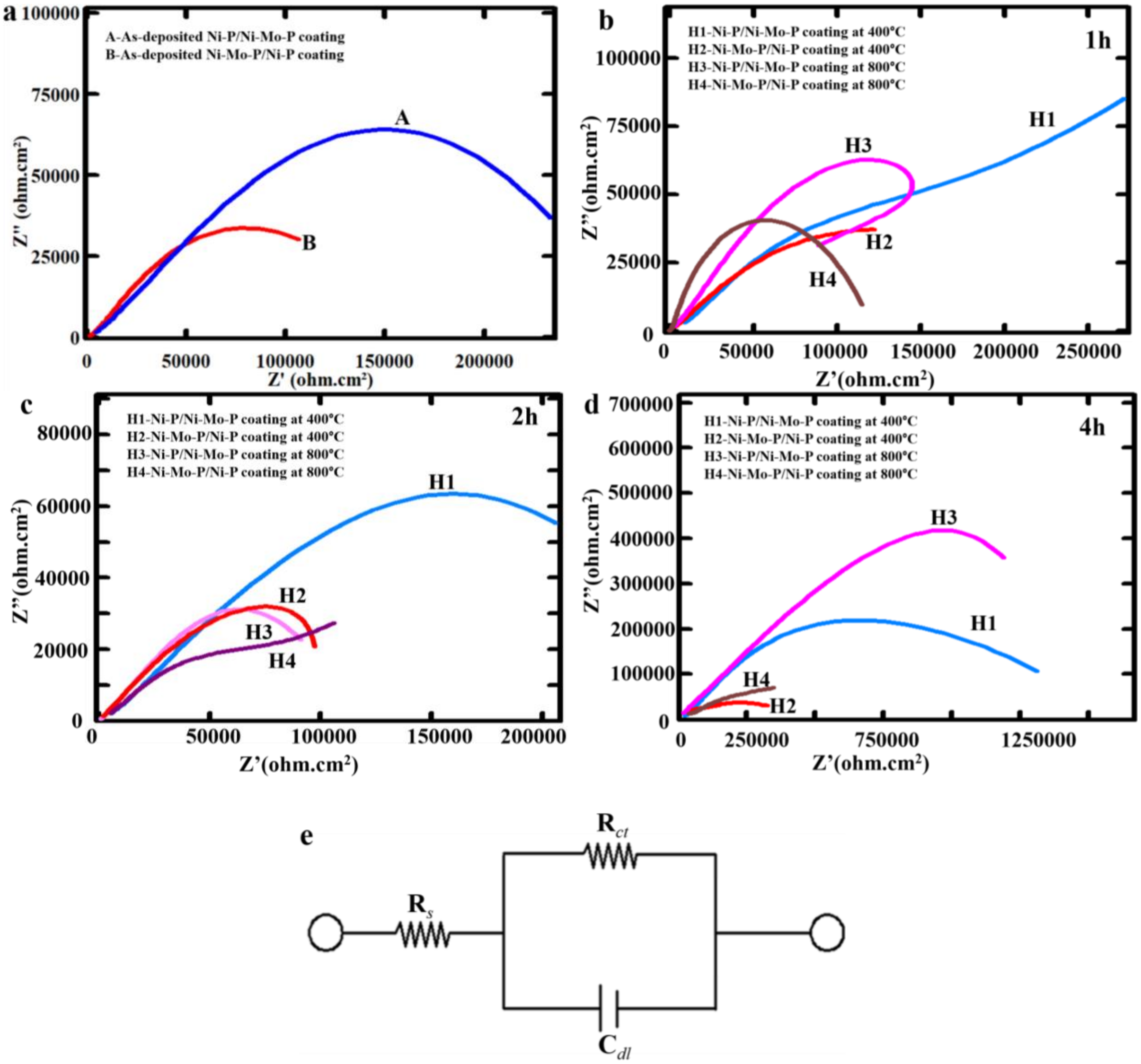

Figure 6.18 *Nyquist plots for (a) as-deposited condition; (b) heat-treated samples 1h duration; (c) heat treated samples 2h duration; (d) heat-treated samples 4h duration and (e) equivalent circuit diagram*

for pit nucleation. Thus, as seen from the results of the corrosion test, the samples heated at 800°C in general show higher corrosion resistance than other samples. The corrosion resistance is higher for Ni-P/Ni-Mo-P coating compared to Ni-Mo-P/Ni-P coating for both as-plated and heat-treated conditions. As heat treatment temperature and time are increased, rate of corrosion decreases. The minimum corrosion rate is obtained for high temperatures and with 4h time duration. According to PDP and EIS tests, Ni-P/Ni-Mo-P coating is the preferable choice for various applications requiring protection against corrosion.

6.3 Closure

The present chapter deals with the effect of heat treatment on the microstructural characteristics of the duplex electroless Ni-P/Ni-Mo-P coatings are investigated using SEM, EDX, and XRD. The effect of heat treatment temperature and its time duration on the hardness, friction, and wear behaviour of both coatings are evaluated and compared. The corrosion behaviour of the coatings is also assessed with the help of electrochemical techniques, viz. PDP and EIS. Heat treatment is found to have a significant influence on the corrosion behaviour of duplex coatings. Overall, the duplex coating with Ni-Mo-P as the outer layer displays better results in both as-deposited and heat-treated conditions.

Chapter 7

Comparison of Duplex Electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P and Ni-P/Ni-Mo-P Coatings

Outline of the chapter: *7.1 Introduction, 7.2 Result and Discussion, 7.2.1 Microstructure characterization and composition analysis, 7.2.2 Phase structure, 7.2.3 Microhardness study, 7.2.4 Friction performance, 7.2.5 Wear performance, 7.2.5.1 Wear behaviour, 7.2.5.2 Wear mechanism, 7.2.6 Corrosion performance, 7.2.7 Performance comparison with single layer coatings, 7.3 Closure*

7.1 Introduction

As already mentioned, duplex electroless nickel coating is suitable for industrial applications due to its combined properties of two coatings in a duplex system that can lead to the development of numerous novel applications both today and in the future. The current chapter compares the mechanical, tribological, and corrosion performance of the duplex electroless coatings: Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P which have been previously discussed. The coatings are characterized by SEM, EDX, and XRD techniques. This chapter compares with wear and friction characteristics of duplex coatings in a dry environment. Also, the corrosion performance is evaluated by the PDP test.

7.2 Result and Discussion

7.2.1 Microstructure characterization and composition analysis

Figures 7.1, 7.2, and 7.3 provide SEM images of the as-deposited and heat treatment duplex electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P coatings, respectively. In their initial, as-deposited state, all three types of duplex coatings exhibit a nodular morphology. These nodules are distributed quite uniformly across the coated surface, and no visible pores are observed in the as-deposited condition, giving the surface a compact appearance. The coating microstructure, which has an impact on their surface characteristics, is influenced by the phosphorous content and the heat treatment temperature **(Biswas et al., 2021)**. In duplex electroless Ni-P/Ni-W-P coating, the nodule size falls within the range of 5 to 10 micrometers

(Figure 7.1a). Duplex electroless Ni-P/Ni-Cu-P coating, on the other hand, has larger nodules, estimated to be between 10 and 15 micrometers (see Figure 7.2a). The size of these nodules in duplex electroless Ni-P/Ni-Mo-P coating is relatively smaller (as seen in Figure 7.3a). Nodular deposition in a coating is influenced by the deposit's growth and nucleation rate. Bath components and deposition conditions affect the nucleation rate. Moreover, the duplex plating appears damage-free across the entire surface in as-deposited state. The size of the nodule increases with heat treatment (refer to Figure 7.1b-f, 7.2b-f, and 7.3b-f) for all the duplex coatings. The microstructure (Figure 7.1) also quite evidently shows the increase in

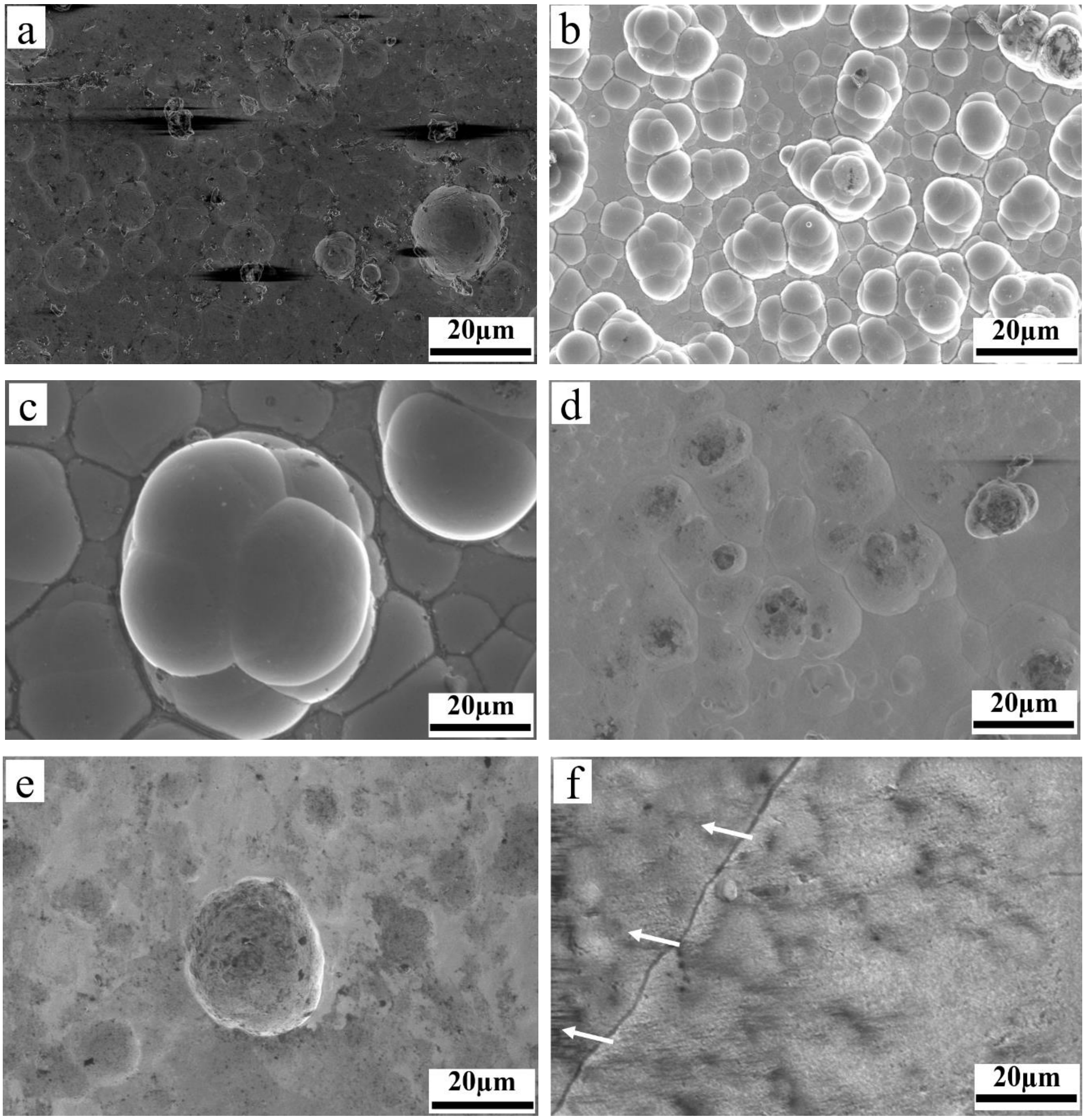

Figure 7.1 *SEM microstructure of Ni-P/Ni-W-P coating(a) as-deposited coating (b) at 400°C for 2h duration (c) at 400°C for 4h duration (d) at 600°C for 1h duration (e) at 800°C for 1h duration (f) at 800°C for 4h duration*

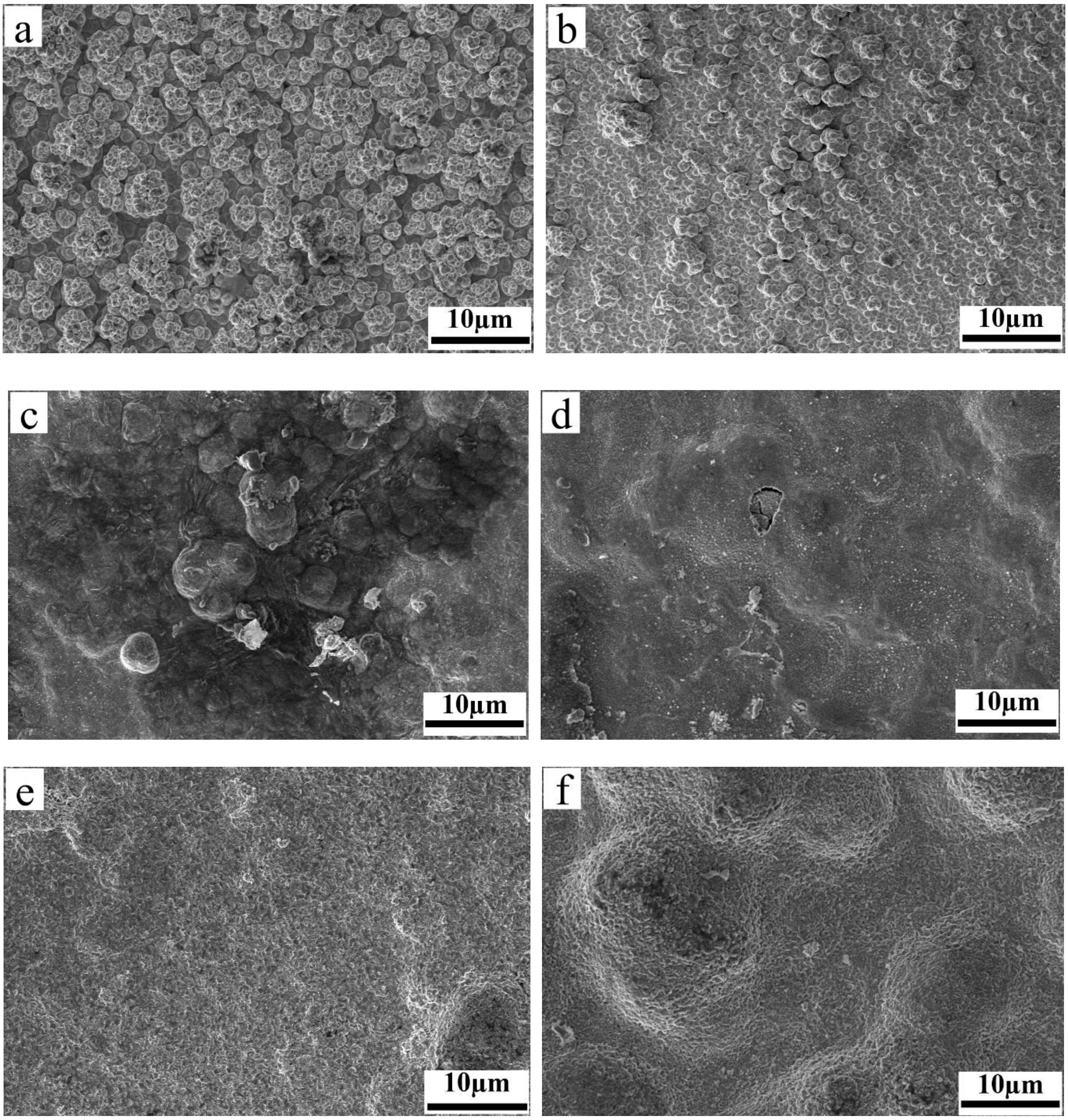

***Figure 7.2** SEM images of Ni-P/Ni-Cu-P coating (a) as-deposited coating (b) at 400°C for 2h duration (c) at 400°C for 4h duration (d) at 600°C for 1h duration (e) at 800°C for 1h duration (f) at 800°C for 4h duration*

the size of the nodules with longer duration of heat treatment. The nodules become more compact and generate a denser structure when heated to 400°C for 2h, as shown in Figures 7.1b, 7.2b, and 7.3b. When exposed to a temperature of 400°C for a duration of 4h, the nodules become larger and more pronounced, as demonstrated in Figures 7.1c,7.2c, and 7.3c. At greater heat treatment temperatures, the wavy surface becomes flatter.

The nodules appear to flatten (refer to Figure 7.1d-f, 7.2d-f, and 7.3d-f), after being heat treated to 600°C and above. The flatness is more prominent at 800°C for 4h duration because of the release of the accumulated thermal stress, as shown in Figures 7.1f, 7.2f, and 7.3f. Furthermore, for duplex electroless Ni-P/Ni-W-P coating, surface cracks have developed, which have been highlighted by white arrows. However, for duplex electroless Ni-P/Ni-Cu-P and Ni-P/Ni-Mo-P coating, no such cracks are visible. Additionally, there are a few black patches on the coated surface, and these dark spots become more pronounced at higher heat treatment temperatures. These dark spots may indicate the occurrence of oxides on the coated surface.

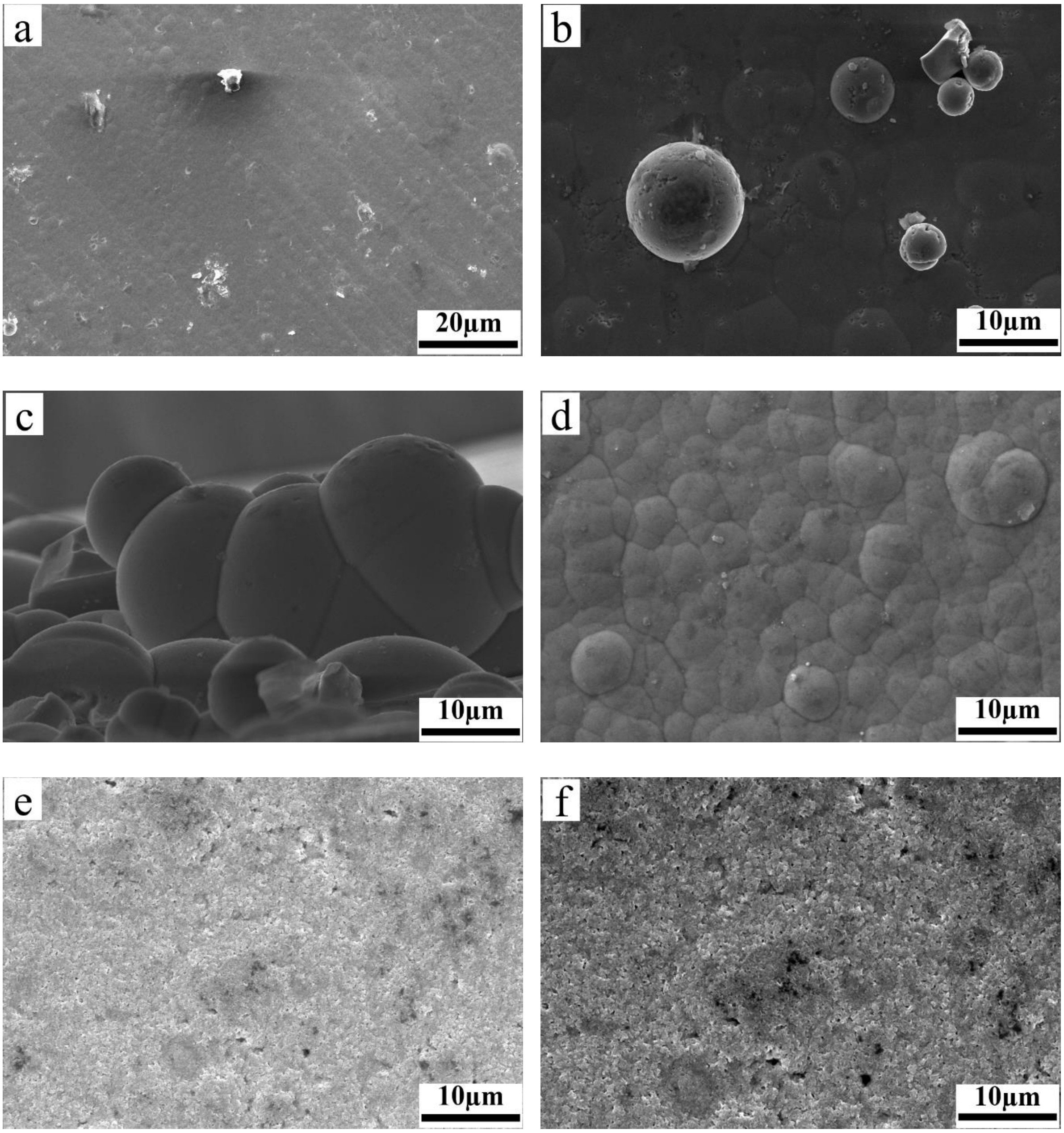

Figure 7.3 *SEM microstructure of Ni-P/Ni-Mo-P coating (a) as-deposited coating (b) at 400°C for 2h duration (c) at 400°C for 4h duration (d) at 600°C for 1h duration (e) at 800°C for 1h duration (f) at 800°C for 4h duration*

In general, when subjected to elevated temperatures and exposed to different time intervals in the current duplex coatings, the process of oxide formation remains quite consistent. The primary reason for these oxide formations is the entrapped air within the furnace. Furthermore, a coarse microstructure is observed in all three coating systems. An analysis of cross-cut SEM images reveals that the coating thickness measures approximately 38 to 40 µm in all instances of the duplex coatings.

The EDX analyzer was involved in evaluating the elemental composition of the duplex platings. Table 7.1 displays the EDX data of the duplex coatings in the as-deposited state. The amount of phosphorous in each coating categorizes them as having a high phosphorous content. As reported in the literature, higher phosphorus content is directly linked to amorphous nature of the coating **(Luo et al.,1997)**. A compositional analysis of as-deposited duplex Ni-P/Ni-W-P coating through EDX revealed that the top surface consists of 87.8% Ni, 3.2% W, and 9% P by mass fraction. According to earlier research by **Luo et al. (1997)**, as phosphorus (P) concentrations rose, the electroless nickel deposit's internal stress decreased.

Moreover, the internal stress of the low phosphorus coating is tensile in nature, while that of the high phosphorus coating is either compressive or neutral. An excessively compressed deposit may blister, distort, or become detached from the substrate. Thus, an appropriate phosphorous concentration can result in decreased internal stress. It also improves the bonding between the substrate and coating. According to the literature **(Balaraju and Rajam, 2009)**, the addition of an intermediate (Cu) element to electroless nickel coating may have an impact on its structure, tending to crystallize it. As a result, duplex electroless Ni-P/Ni-Cu-P coating may have a combination of amorphous and microcrystalline structure. **Hu et al. (2013),** had a similar observation as well. Duplex electroless Ni-P/Ni-Mo-P coating in the current investigation is expected to have amorphous structure based on the phosphorus percentage (> 9% of P), as shown in Table 7.1. **Liu and Liu (2017),** also reported similar observations.

Table 7.1 EDX data of the as-deposited samples

Duplex Coatings	Element in wt.%				
	Ni	P	W	Cu	Mo
Duplex Ni-P/Ni-W-P coating	87.8	9.0	3.2	-	-
Duplex Ni-P/Ni-Cu-P coating	78.0	11.6	-	10.4	-
Duplex Ni-P/Ni-Mo-P coating	83.0	12.2	-	-	4.8

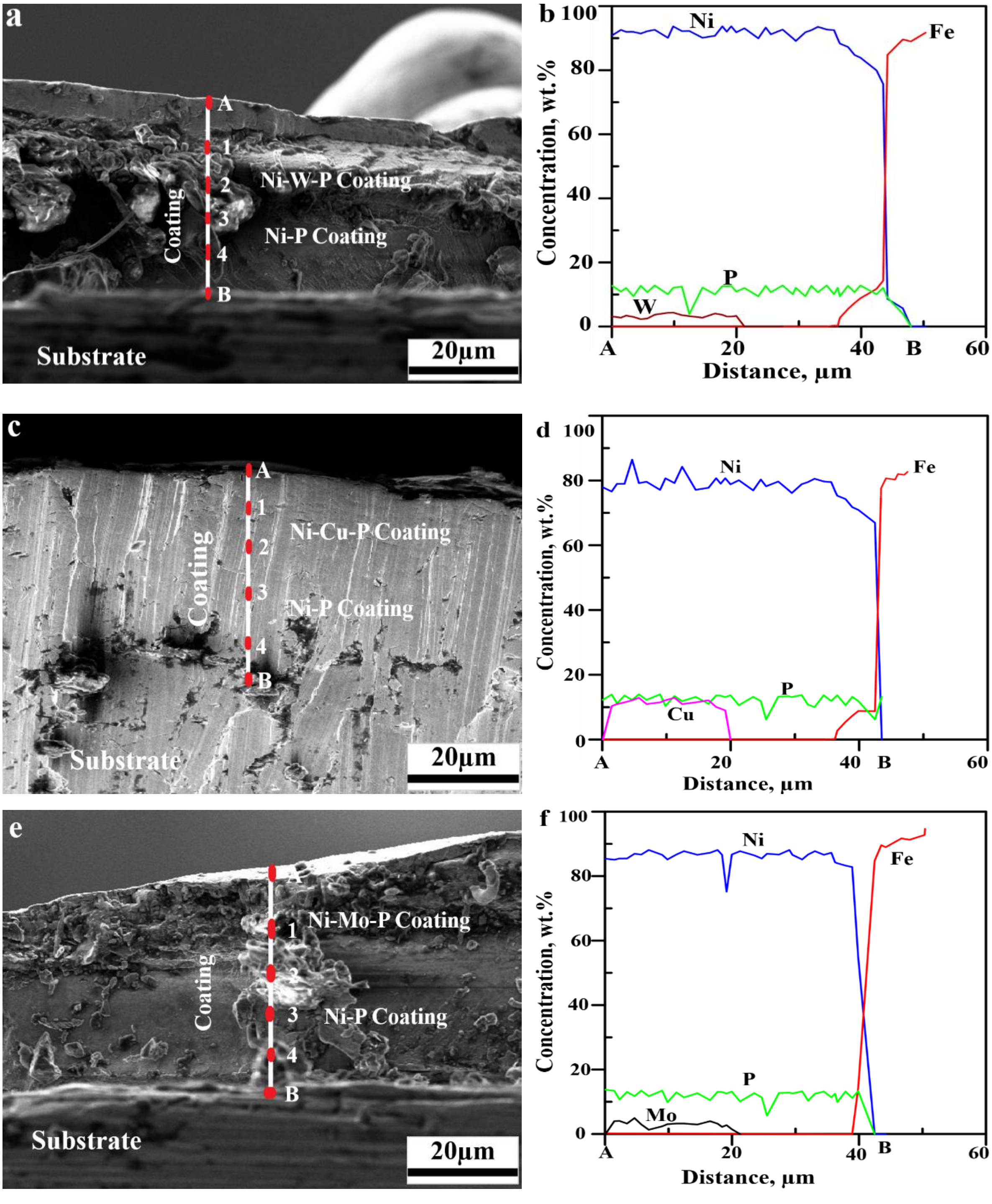

Figure 7.4 *Cross-cut SEM image and line EDX of (a, b) Ni-P/Ni-W-P coating, (c, d) Ni-P/Ni-Cu-P coating, and (e, f) Ni-P/Ni-Mo-P coating*

In order to obtain a more comprehensive understanding of the variations in coating composition at different depths, EDX analysis was performed along the cross-section of the coating, as shown in Figure 7.4. The results confirm the successful deposition of the duplex coatings. This conclusion is primarily drawn from the significant variations in the weight percentages of tungsten, copper, and molybdenum noticed close to the interface of the deposited layers within each respective duplex coating. This suggests a transition from Ni-P to Ni-W-P, Ni-Mo-P, or Ni-Cu-P layers, and vice versa. Moreover, in each instance, the thickness of both deposited layers is nearly identical. Notably, the top and bottom layers of the coating exhibit outstanding adhesion and compatibility, with no noticeable boundary between them. The cross-section analysis of the coating indicates the absence of pores or other defects.

7.2.2 Phase structure

Figure 7.5 illustrates the XRD analysis of duplex plating both before and after heat treatment. In the case of as-deposited duplex electroless Ni-P/Ni-W-P coating, the XRD plot primarily reveals the amorphous structure characteristic of high phosphorus electroless nickel deposits, depicted by a single broad peak within a 2Θ range of 35–55°. However, heat treatment has a substantial impact on the microstructure of duplex electroless Ni-P/Ni-W-P coating deposits. When subjected to temperatures of 400°C or higher, the diffraction profile of the samples undergoes significant changes, exhibiting multiple peaks representing various phases involving nickel, phosphorus, tungsten, and even oxygen. At 400°C, the coatings transform into the primary compounds, namely, Ni_3P and WP phases. Ni_3P is a very hard crystalline phase and plays a crucial role in enhancing microhardness and wear resistance in the duplex plating. In addition to these phases, nickel and WP phases are also detected, alongside other phases. No metastable phases are observed for nickel and phosphorus.

As the heat treatment temperature and time duration increase, the peaks in the XRD patterns become sharper, which can be attributed to enhanced grain growth and the relaxation of surface strain **(Zhao and Zhang, 2008)**. The formation of NiO is detected at 600°C and 800°C heat treatment temperature, indicating the development of oxide layers. The presence of NiO can be seen as dark spots on the coating's top surface. Interestingly, the coated samples exhibit reduced friction and wear rates and show an improvement in corrosion performance. These changes may be attributed to the development of oxide phases at higher heat treatment temperature during a 4h cycle.

Figure 7.5b presents the XRD patterns for duplex electroless Ni-P/Ni-Cu-P coating in both the as-deposited and heat treatment conditions. The as-deposited duplex coating initially exhibits an amorphous structure, but crystalline peaks emerge after heating. At 400°C heat treatment temperature for 2h duration, the primary crystalline phases of Ni_3P, NiCu, and

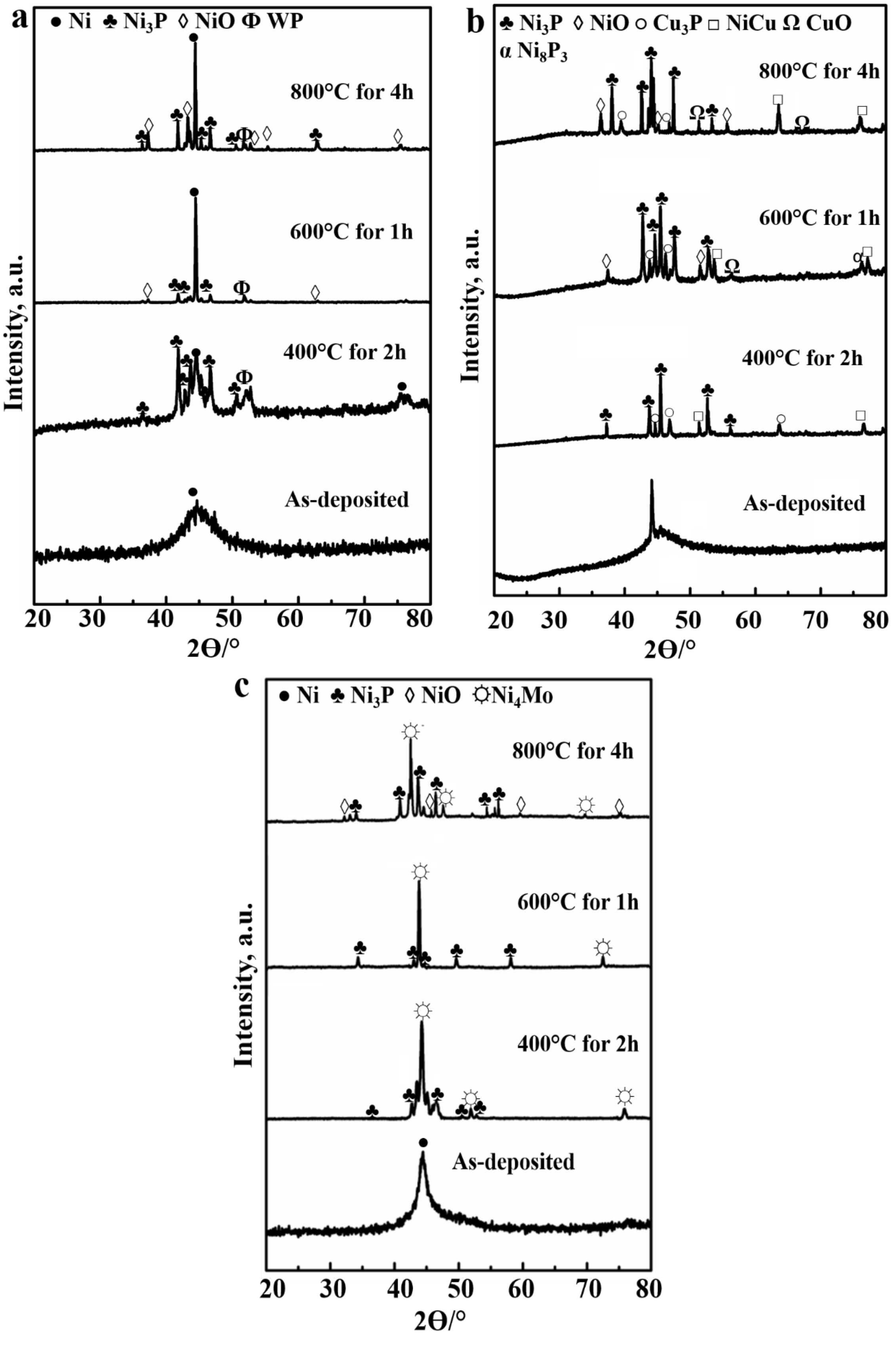

Figure 7.5 *XRD plots of duplex coatings: (a) Ni-P/Ni-W-P (b) Ni-P/Ni-Cu-P (c) Ni-P/Ni-Mo-P*

Cu_3P become apparent. This is attributed to the increased diffusivity of copper **(Sahoo and Roy, 2017)**. Additionally, a CuO phase forms at temperatures of 600°C and 800°C. Some NiO are also observed at these elevated temperatures and longer heating durations. Furthermore, a small amount of the hard and brittle Cu_3P and Ni_3P phases can be detected. The confined air of the furnace is the main cause of these oxide formations. At high temperatures, a metastable Ni_8P_3 phase is formed for the duplex Ni-P/Ni-Cu-P coating. For duplex Ni-P/Ni-Mo-P coating, the diffraction plot is displayed in Figure 7.5c. The as-deposited coating displays a more pronounced peak at a 2θ angle of 45°.

Duplex Ni-P/Ni-Mo-P coating appears to be a combination of amorphous and crystalline phases, likely due to the incorporation of molybdenum into the Ni-P matrix, which increases the degree of crystallinity **(Hong and Qian, 2018; Koiwa et al., 1988)**. However, a noticeable shift in the peaks in the XRD plot is observed when the heat treatment temperature reaches 400°C or higher, resulting in multiple peaks associated with different phases involving nickel, molybdenum, phosphorus, and even oxygen. At 400°C heat treatment temperature for a 2h period, the main phases precipitated in the coating are Ni, Ni_3P, and Ni-Mo phases, such as Ni_4Mo. As indicated by the diffraction patterns (Figure 7.5c), heating the samples to 400°C results in Ni-Mo as the predominant phase in the coating, with traces of Ni_3P. Upon heating the samples to 600°C for 1h, the diffraction peaks become more pronounced, indicating crystallization of the coating. However, at higher temperatures (800°C), a few NiO phases are observed, along with Ni-Mo, Ni, and Ni_3P phases. The emergence of new crystalline phases may potentially enhance microhardness. In the as-deposited state, all the coatings exhibit either an amorphous structure or a combination of microcrystalline and amorphous phases. At 400°C heat treatment temperature, both duplex electroless Ni-P/Ni-W-P and Ni-P/Ni-Cu-P coating transition into a fully crystalline phase. However, in the case of duplex electroless Ni-P/Ni-Cu-P coating, some metastable phases are observed at 600°C heat treatment temperature viz. Ni_8P_3. Such compound however, isn’t detected at higher temperatures. This may be due to the inherently unstable nature of the compound which always tends to transform into stable compounds and hence is difficult to detect with consistency.

Consequently, it can be concluded that the thermal stability of duplex Ni-P/Ni-Mo-P coating is higher than that of the other duplex coatings. No oxide phases are observed when it is heat-treated at 600°C, and no metastable phases are detected at these temperatures. For all the coatings, at a high heat treatment temperature of 800°C and prolonged heating duration, dark NiO spots appear on the coated surface.

7.2.3 Microhardness study

Figure 7.6 displays the microhardness measurements for the duplex electroless coatings in both as-deposited and heat treatment conditions. In its as-deposited state, duplex electroless Ni-P/Ni-W-P coating exhibits the highest microhardness compared to all other as-deposited samples. Duplex electroless Ni-P/Ni-Cu-P and Ni-P/Ni-Mo-P coating show relatively similar microhardness behaviour in their as-deposited states, with not much difference between them. The microhardness of the platings is noticeably impacted by the heat treatment. The smallest change in microhardness is detected at heat treatment temperature of 200°C, likely owing to fewer microstructural alterations. Notably, for duplex electroless Ni-P/Ni-W-P coating, when subjected to heat treatment cycle of 400°C for 1h, the microhardness nearly doubles compared to its as-deposited microhardness, as indicated in Figure 7.6a. The present microhardness data highlights the significant impact of the development of crystalline phases, particularly the Ni_3P phase, on the microhardness of the coatings. For duplex electroless Ni-P/Ni-Cu-P coating, at 400°C and a 1h heat treatment period, it exhibits the highest microhardness because of the development of brittle and hard phases like Ni_3P and Cu_3P. Duplex Ni-P/Ni-Mo-P coating, on the other hand, attains maximum microhardness at 600°C for 1h, mainly because of the prominent growth of the Ni-Mo and Ni_3P phases.

In comparison to their as-deposited states, duplex electroless Ni-P/Ni-W-P coating demonstrates a remarkable 112% increase in microhardness at 400°C for a 1h cycle. The crystalline Ni_3P, Cu_3P, and Ni-Mo hard phases are obtained from the XRD analysis (refer to Figure 7.5). Above these phases is the key factor to increased microhardness values. The microhardness values for both duplex electroless Ni-P/Ni-W-P and Ni-P/Ni-Cu-P coating decline above 400°C in the heat treatment temperature range, primarily due to grain coarsening. However, duplex electroless Ni-P/Ni-Mo-P coating's microhardness decreases by approximately 40% at 800°C for 1h, primarily because of oxide formation compared to 600°C. Nevertheless, the microhardness value remains higher than that of the as-deposited coating.

Upon heat treatment for 2 to 4h, the microhardness of the coatings surpasses that of the as-deposited state, but the values are noticeably lower than those observed for the 1h heat-treated specimens. In the case of a 4h heat-treated sample, it's possible that the formation of Ni_3P phases is reduced, as indicated by the XRD results. Simultaneously, during a 4h heat treatment cycle, there is a greater buildup of thermal stresses, which act as residual stresses and consequently lead to a quicker formation and movement of dislocations. It is evident that, in terms of microhardness, the 1h heat treatment duration appears to be the optimal choice for all the duplex coatings. Among all the cases, duplex Ni-P/Ni-W-P coating exhibits the highest microhardness. Additionally, duplex Ni-P/Ni-Mo-P coating displays higher microhardness than duplex Ni-P/Ni-Cu-P coating owing to the development of hard Ni_3P and Ni-Mo crystalline phases.

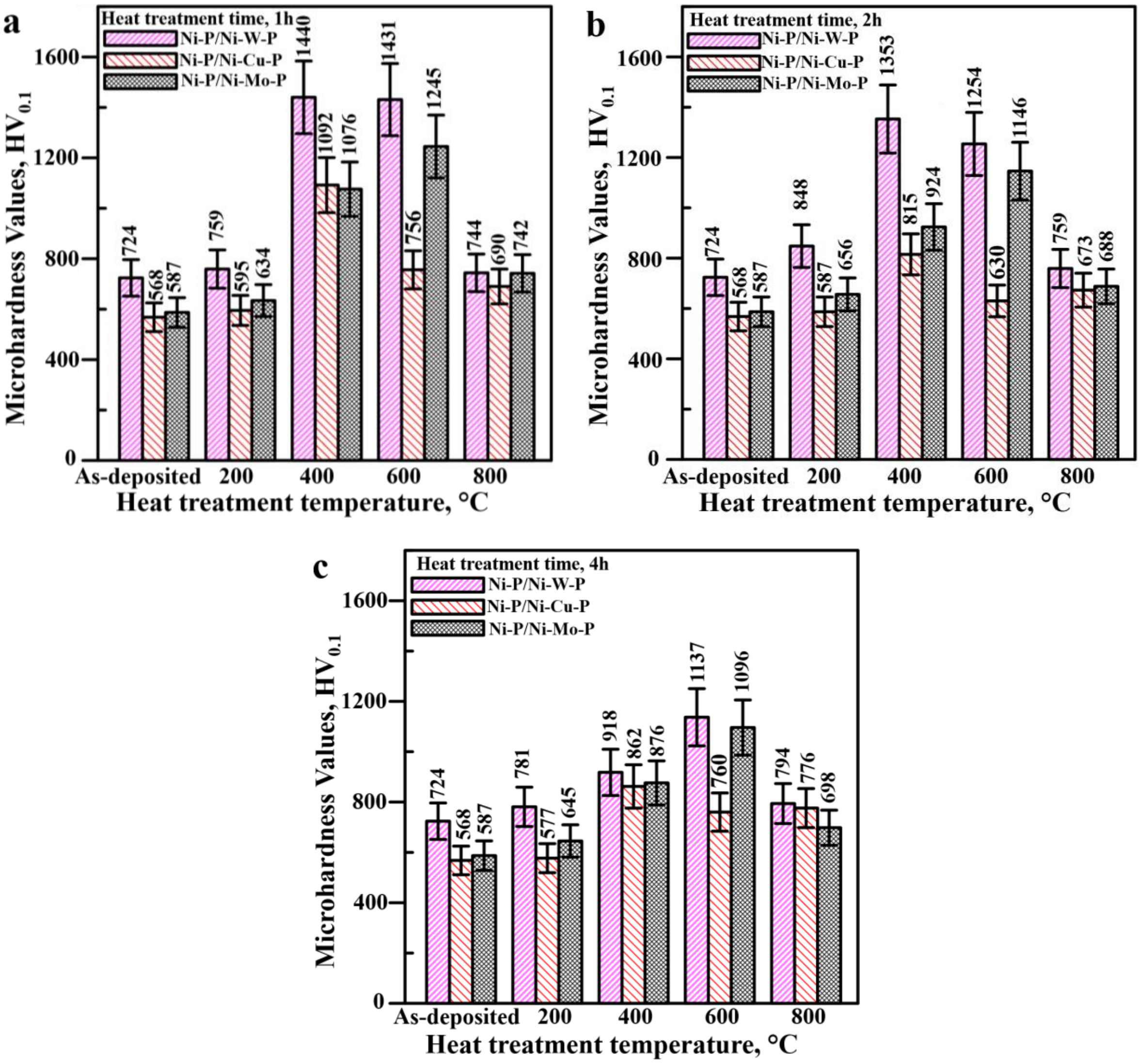

Figure 7.6 *Microhardness results for different heat treatment temperatures; (a) 1h; (b) 2h; and (c) 4h*

7.2.4 Friction Performance

Figure 7.7 illustrates the average COF for the current duplex coatings in both their as-deposited and various heat treatment conditions. After heat treatment, the COF of the coatings decreases, mainly due to the increased microhardness. A harder coating leads to reduced contact area and, consequently, a lower COF. Notably, although the 1h heat treatment at 200°C may not result in maximum microhardness, it does yield the lowest COF among all the present coatings, except for duplex Ni-P/Ni-Mo-P coating (Figure 7.7a). Duplex Ni-P/Ni-W-P coating exhibits a higher COF compared to other duplex coatings, as shown in Figure 7.7. Generally, duplex Ni-P/Ni-Cu-P coating displays a lower COF under heat treatment conditions than other duplex coatings, despite its lower hardness. Therefore, the COF of the coatings may be influenced by various factors, including grain size, the formation of different phases, the presence and distribution of oxide phases, and more. At 400°C for 1h, the lowest COF is observed in duplex Ni-P/Ni-Mo-P coating among all duplex systems. At temperatures of 600 or 800°C, duplex electroless Ni-P/Ni-W-P and Ni-P/Ni-Mo-P coating experience an increase in COF due to the development of Ni_3P phases **(Sahoo and Roy, 2017)**. Meanwhile, in duplex Ni-P/Ni-Cu-P coating, the COF decreases at 600 or 800°C for a 1h duration because of the creation of oxide phases like CuO and NiO, which provide a low-shear layer.

For 2h heat treatment cycles, the highest COF is recorded for duplex Ni-P/Ni-W-P coating at 400°C. In duplex electroless Ni-P/Ni-Mo-P coating, the lowest COF is observed at 200°C heat treatment temperature, likely because of the smaller grain size. It's worth noting that lower grain size has been reported to correlate with a lower COF, as also mentioned by **Biswas et al. 2017**. At 600 or 800°C heat treatment temperature for duplex Ni-P/Ni-Mo-P coating, the COF values increase due to the development of Ni_3P and Ni_4Mo phases.

For duplex electroless Ni-P/Ni-Cu-P coating, there is a slight decrease in COF values at 600°C heat treatment temperature for a 4h duration cycle. This phenomenon could be attributed to increased oxidation, which results in the formation of a surface layer with weak shear strength. Across all cases, elevated heat treatment temperatures lead to an increase in COF due to the development of the Ni_3P phase. However, it is important to note that the formation of other phases, such as oxides on the coated surface, also plays a role in affecting the COF of the duplex systems.

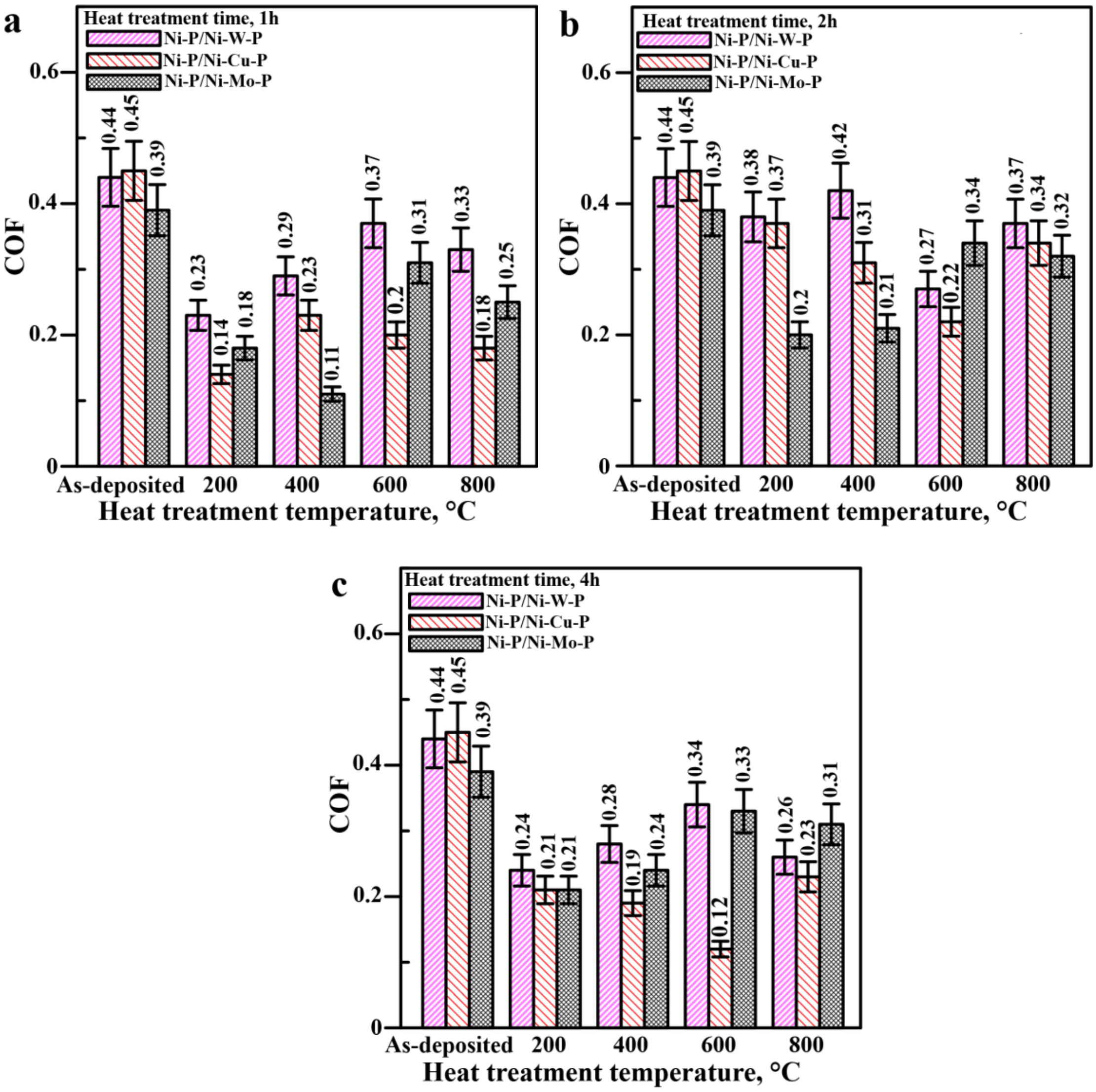

Figure 7.7 *COF plots for various heat treatment temperatures (a) 1h; (b) 2h; and (c) 4h*

7.2.5 Wear performance

7.2.5.1 Wear behaviour

Figure 7.8 exhibits the wear rate of the existing coatings both in as-deposited and heat treatment states. The minimum wear rate is observed for duplex electroless Ni-P/Ni-W-P coating in as-deposited condition. The reason behind this is that the top Ni-W-P layer is harder than Ni-Cu-P or Ni-Mo-P. This is as a result of the fact that Ni-P matrix is strengthened by the addition of tungsten. It has been noticed that after heat treatment, the resistance to wear of the current duplex coatings increases. At 400°C and 1h heat treatment, the samples exhibit the best wear resistance, as expected, with a 48% reduction in wear rate compared to the as-deposited coating. The microhardness of the coating is raised after heat treatment as harder Ni_3P phases precipitate (refer to Figure 7.5). The duplex coatings achieve complete crystallization after being heated to 400°C due to development of the optimal grain size and the right quantity of Ni_3P precipitation. For a 1h heat treatment cycle, the lowest wear resistance is found in duplex electroless Ni-P/Ni-Cu-P coating in all cases due to the formation of a smaller quantity of Ni_3P phases. On the other hand, at 600°C for 1h, duplex electroless Ni-P/Ni-Mo-P coating exhibits the highest wear resistance due to the formation of Ni-Mo and Ni_3P phases. At these temperatures, the said coating obtained its maximum hardness, which is seen in the previous section.

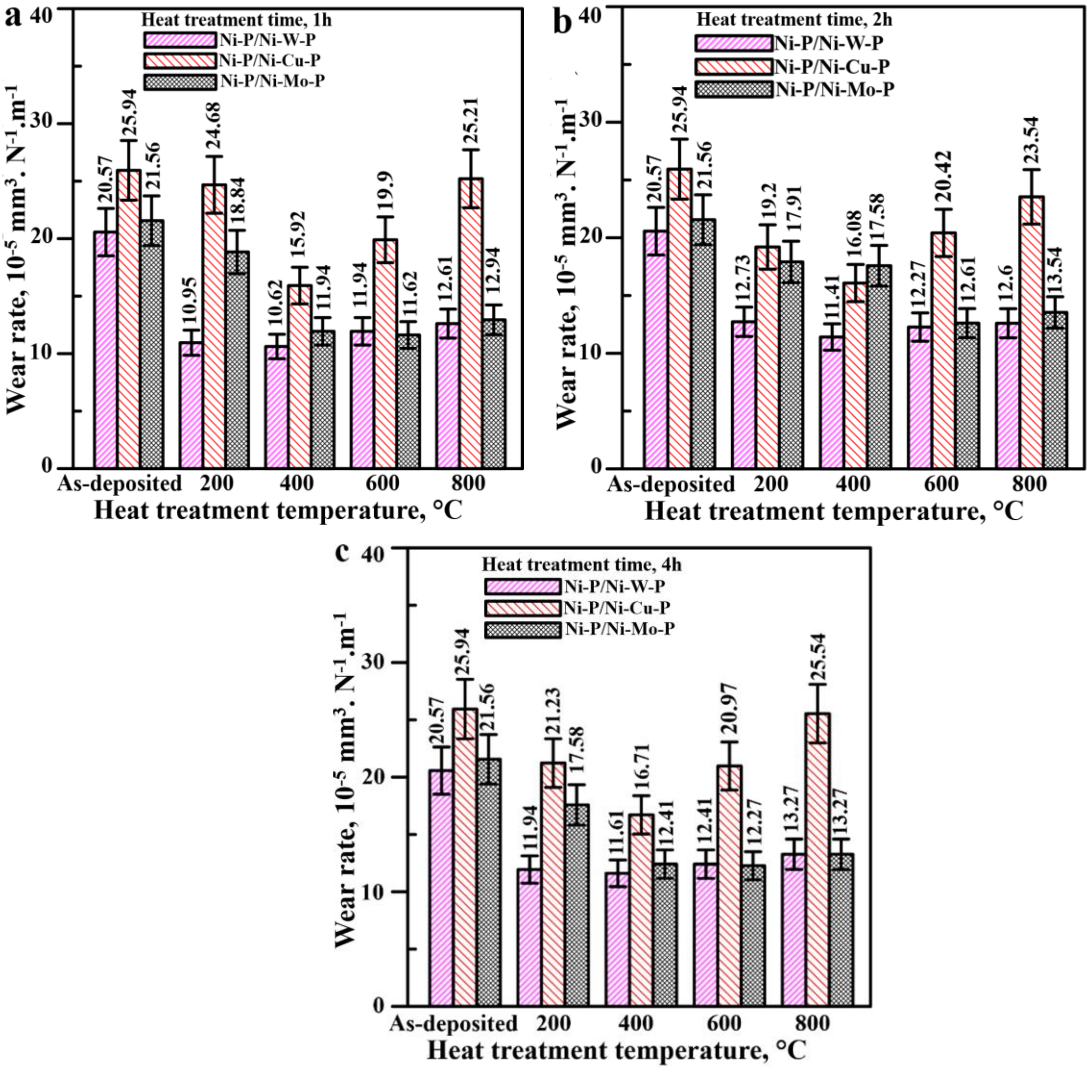

Figure 7.8 *Wear rate for various heat treatment temperatures (a) 1h; (b) 2h; and (c) 4h*

The wear rate rises with heat treatment temperature above 400°C possibly due to various factors, including oxide formation, grain coarsening, and elemental interdiffusion. At 600°C heat treatment temperature, duplex electroless Ni-P/Ni-W-P coating experiences a reduction in wear resistance by approximately 12% compared to a coating heat-treated at

400°C, mainly because of oxide formation. At 600 or 800°C, wear resistance declines from the 400°C level due to the development of the softer oxide phase. However, the wear resistance remains higher than in the as-deposited coatings, thanks to the existence of the Ni_3P phase. Additionally, it doesn't seem that extending the heat treatment duration will significantly improve wear resistance of the coating.

Similar trends are observed when the coatings are heat-treated for 2 and 4h, respectively. Among the three types of duplex electroless coatings, duplex Ni-P/Ni-W-P coating consistently demonstrates the best wear resistance, likely due to its maximum microhardness in all heat treatment cycles. Additionally, wear resistance tends to decrease with higher heat treatment temperature and longer durations.

7.2.5.2 Wear mechanism

The SEM images depicting the surface morphology of duplex electroless Ni-P/Ni-W-P coating in Figure 7.9, both in its as-deposited and heat treatment states following tribological testing, provide valuable insights into the processes and mechanisms of wear. These images reveal the presence of noticeable ploughing marks and deep grooves on the worn surface,

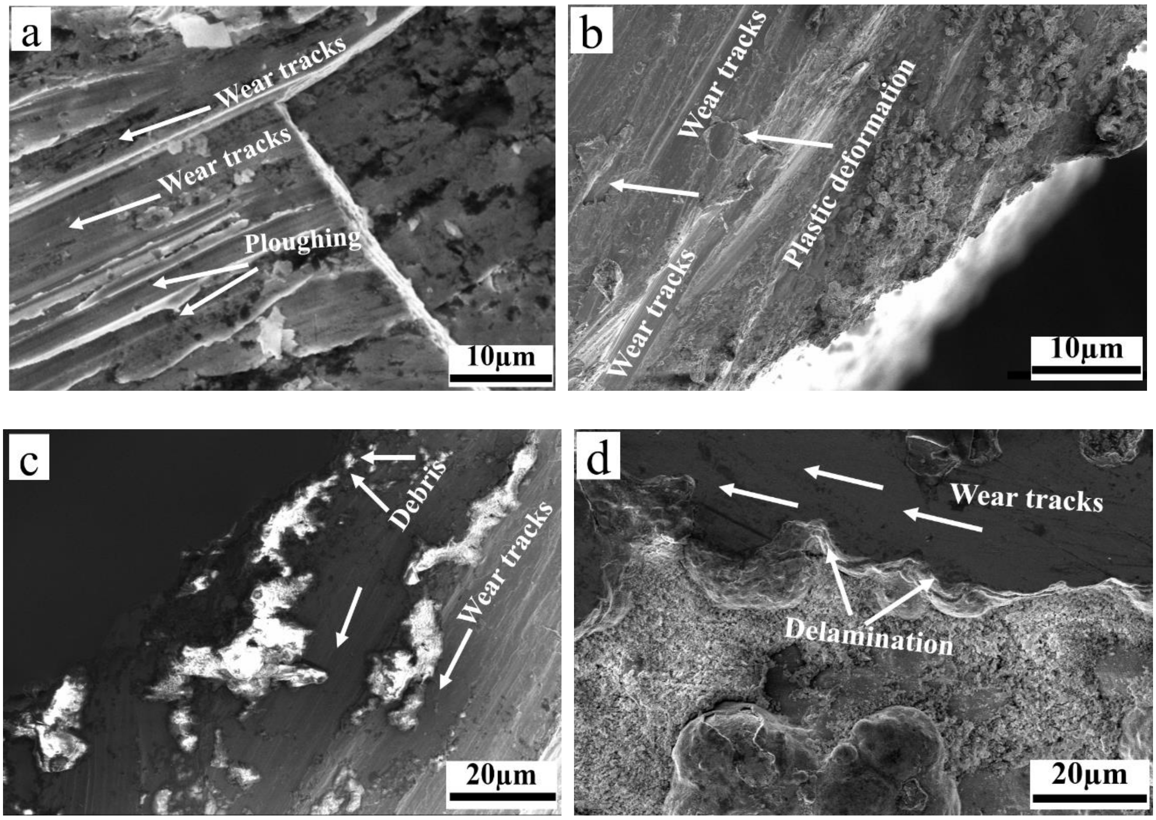

Figure 7.9 *The SEM image of Ni-P/Ni-W-P coating after tribological test (a) as-deposited coating (b) at 400°C for 1h, (c) at 400°C for 4h, (d) at 800°C for 4h.*

primarily aligned with the direction of sliding (as seen in Figure 7.9a). It indicates that the wear mechanism is primarily abrasive in nature. Additionally, there are signs of adhesive wear characterized by pits and prows on the surface. Abrasive wear is also observed in the sample subjected to heat treatment at 400°C for 1h (as seen in Figure 7.9b), where noticeable wear tracks are evident. At this temperature, some remnants of nodules and plastic deformation are also present. Under the conditions of 400°C and a 4h heat treatment cycle, the coating exhibits minimal wear debris along the wear tracks (refer to Figure 7.9c). These wear debris particles seem to be pressed by both the sample and the counter face, suggesting the likelihood of encountering two-body abrasion.

Upon subjecting the coatings to a heat treatment temperature of 800°C for 4h, Figure 7.9d reveals significant damage on the worn surface. A chunk of the coated layer seems to have delaminated, exposing the sublayer of the coating along with wear tracks. This strongly suggests that during the heat treatment, oxidation forms a brittle layer on the coated surface. This oxidation layer renders the coating surface susceptible to flaking and delamination when subjected to contact pressure. It's evident that the top oxide layer lacks the necessary adhesive strength compared to the inner layer.

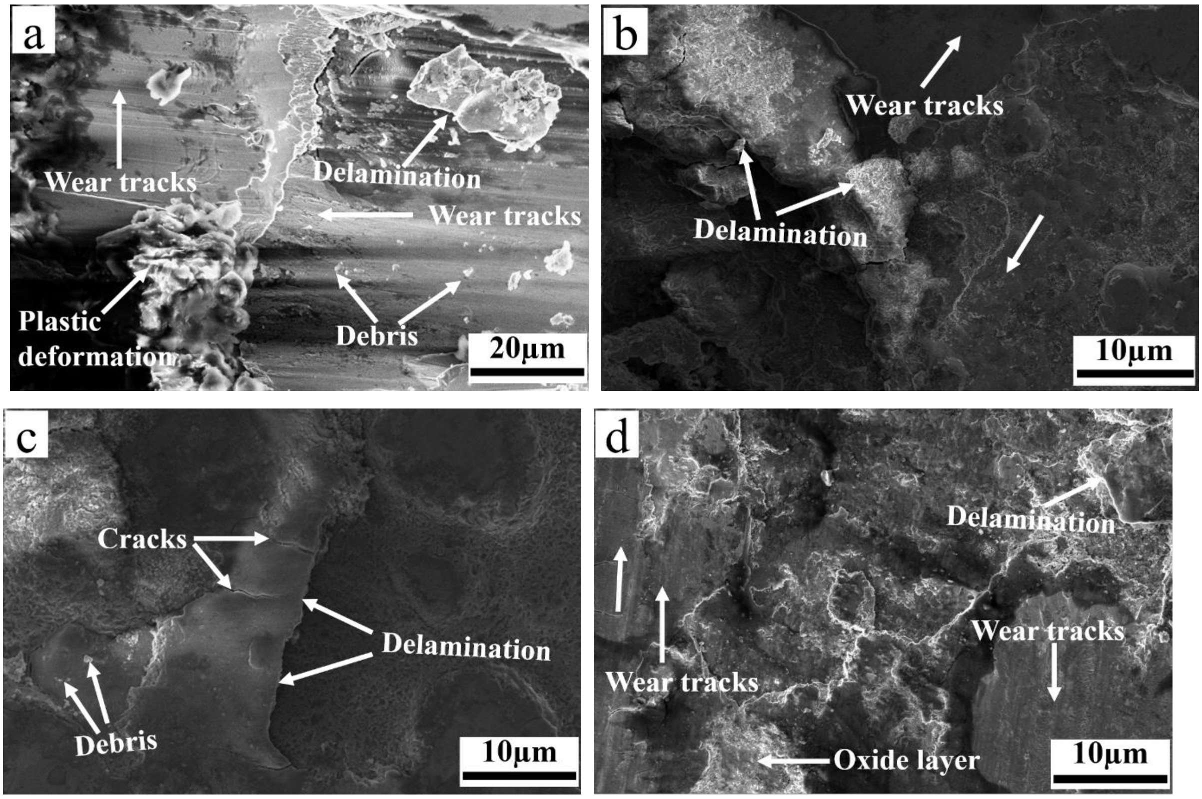

Figure 7.10 *Worn surface SEM image of Ni-P/Ni-Cu-P coating after tribological test (a) as-deposited coating (b) at 400°C for 1h, (c) at 400°C for 4h, (d) at 800°C for 4h.*

Figure 7.10 displays the duplex electroless Ni-P/Ni-Cu-P coating wear behaviour in both its as-deposited and heat treatment conditions. Abrasive wear has occurred, as can be inferred from the coating's surface characteristics, which include tiny longitudinal grooves. The formation of these grooves is owing to ploughing and micro-cutting effects. Additionally, there are some partially irregular pits, which are indicative of adhesive wear. Figure 7.10a shows wear debris in the as-deposited coating. These traits indicate the occurrence of adhesive wear both in as-deposited and heat treatment coatings. In this type of wear, the contacting material undergoes plastic deformation and adheres to the surface.

Abrasion marks are also visible in the sliding direction in the sample treated at 400°C, 1h (refer to Figure 7.10b). In addition to the presence of abrasive marks, some portions of the coating have spalled or detached. Moreover, a small amount of wear debris is visible on the surfaces tested at 400°C for 4h, as depicted in Figure 7.10c. On the worn-out surface of the coating, there are some flank-like features formed during sliding. At a higher heat treatment temperature of 800°C for 4h, the tested surface exhibits severe damage in the form of spallation, delamination, cracking, and other issues, as can be seen in Figure 7.10d.

Figure 7.11 illustrates the wear mechanisms of duplex electroless Ni-P/Ni-Mo-P coating in both its as-deposited and heat-treated conditions. On the damaged surface of the as-deposited coating, ploughing is evident. Additionally, there are some scratching marks seen on the tested surface. It's worth noting that the smoothness and high microhardness of the counterface surface can lead to the trapping of hard particles between the contacting surfaces, contributing to the ploughing action. The tribological performance of the coating suggests the occurrence of abrasive wear, manifested in the form of microgrooves and furrows. This abrasive wear is influenced by various factors such as the microstructure, hardness, roughness, and grain size of the deposited layer. In the worn region, wear tracks become apparent due to the combined effects of ploughing and plastic deformation (Figure 7.11b).

Under heat treatment at 400°C for 4h, it appears that the wear debris becomes welded to the worn surface due to the contact pressure. Moreover, delamination is observed on the top surface of the sample (as shown in Figure 7.11c). At high temperatures (specifically, at 800°C for 4h), a few instances of plastic deformation are noticed as a result of abrasion, as depicted in Figure 7.11d. In fact, at elevated temperatures, various wear-related features, such as wear debris, micro ploughing, micro cutting, and cracks, appear on the rubbed surface. Consequently, it can be concluded that both abrasive and adhesive wear mechanisms are at play on the worn surface, showcasing the complex interplay of factors in the tribological behaviour of duplex electroless Ni-P/Ni-Mo-P coating.

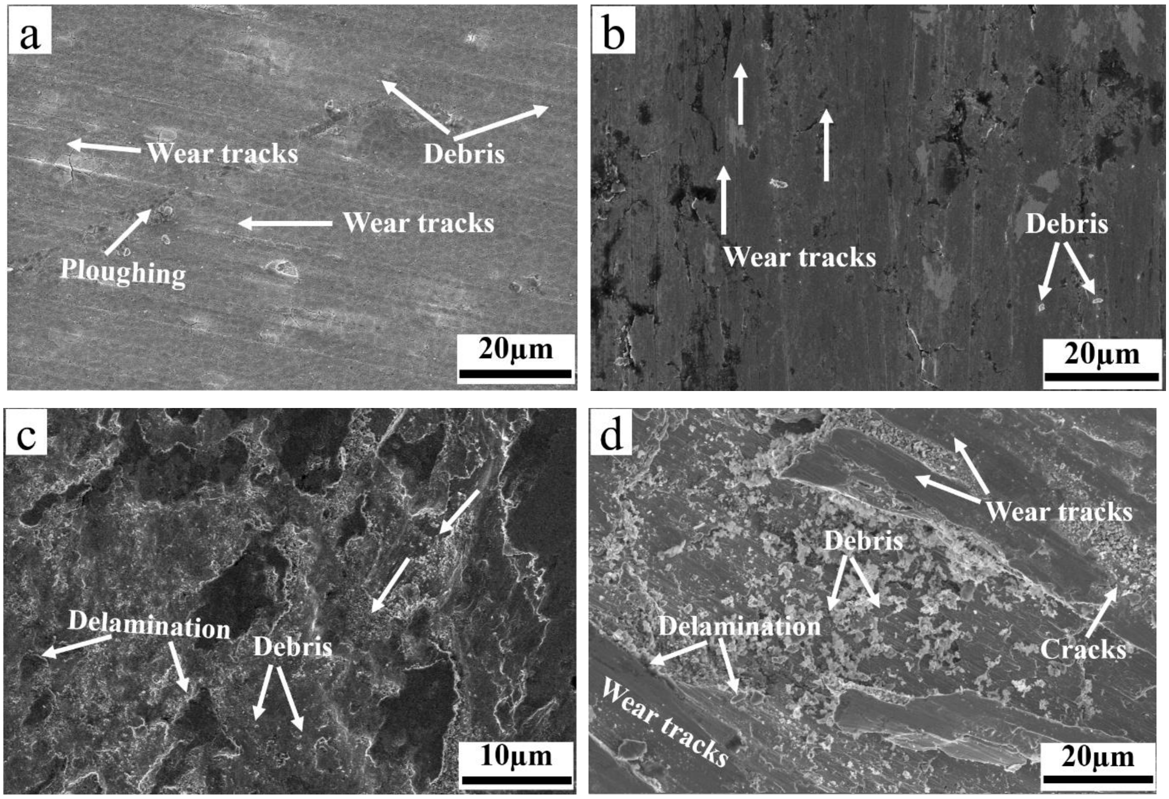

Figure 7.11 *Worn surface of SEM image for Ni-P/Ni-Mo-P coating after tribological test of (a) as-deposited coating (b) at 400°C for 1h, (c) at 400°C for 4h, (d) at 800°C for 4h.*

7.2.6 Corrosion performance

The PDP curves for each coating are depicted in Figure 7.12. These plots exhibit well-defined Tafel regions, clearly indicating both anodic and cathodic segments. Corrosion current densities (i_{corr}) and corrosion potentials (E_{corr}) have been determined using the Tafel extrapolation technique. The results are presented in Figure 7.13 and Figure 7.14, respectively.

In the case of duplex electroless Ni-P/Ni-W-P coating, the lowest level of corrosion resistance is observed in the as-deposited coatings. In its as-deposited state, this coating possesses an amorphous structure. However, when subjected to heat treatment, the coating becomes more crystalline, while also becoming denser and more compact. This observation aligns with findings reported by other researchers **(Rabizadeh et al., 2010)**. Notably, heat treatment appears to promote excellent adherence between the two layers of the deposit, contributing to enhanced corrosion resistance. An intriguing discovery is that, especially for a

1h heat treatment cycle, the E_{corr} shifts from a negative direction to a positive direction with increasing heat treatment temperature (as illustrated in Figure 7.12b). For duplex electroless Ni-P/Ni-W-P coating, the lowest level of corrosion resistance is obtained in as-deposited coatings. This coating has an amorphous structure in the as-deposited state. Heat treatment causes the coating to become more crystalline, but at the same time more compact and denser. Other researchers have also reported this kind of observation **(Rabizadeh et al., 2010)**. A fantastic adherence between the two layers of deposit may also be achieved with the aid of heat treatment which may contribute to the higher corrosion resistance. Another intriguing finding is that, particularly for a 1h heat treatment cycle, the E_{corr} shifts from a negative direction to a positive direction with increasing heat treatment temperature (Figure 7.12b).

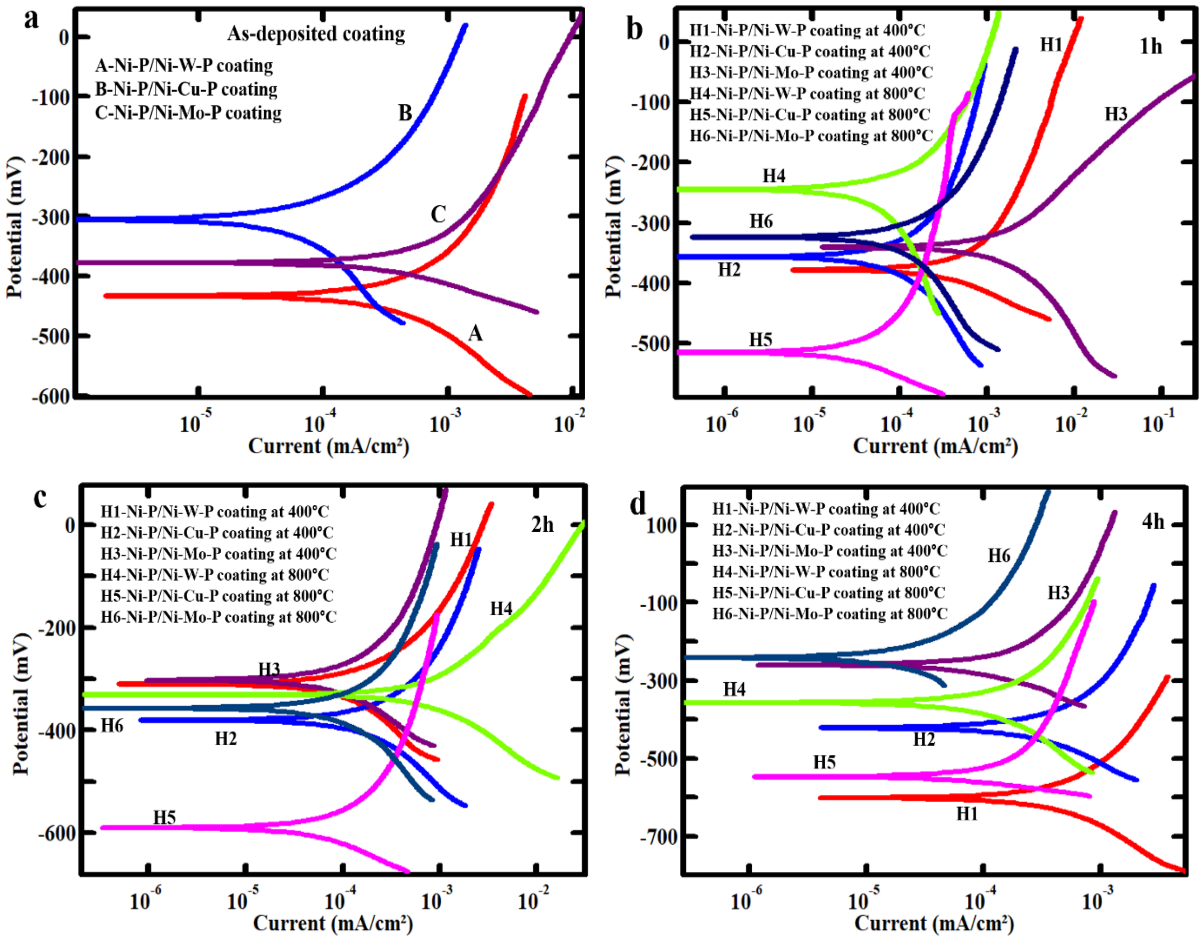

***Figure 7.12** Polarization plots for: (a) as-deposited condition; (b) heat-treated samples 1h duration; (c) heat-treated samples 2h duration; (d) heat-treated samples 4h duration*

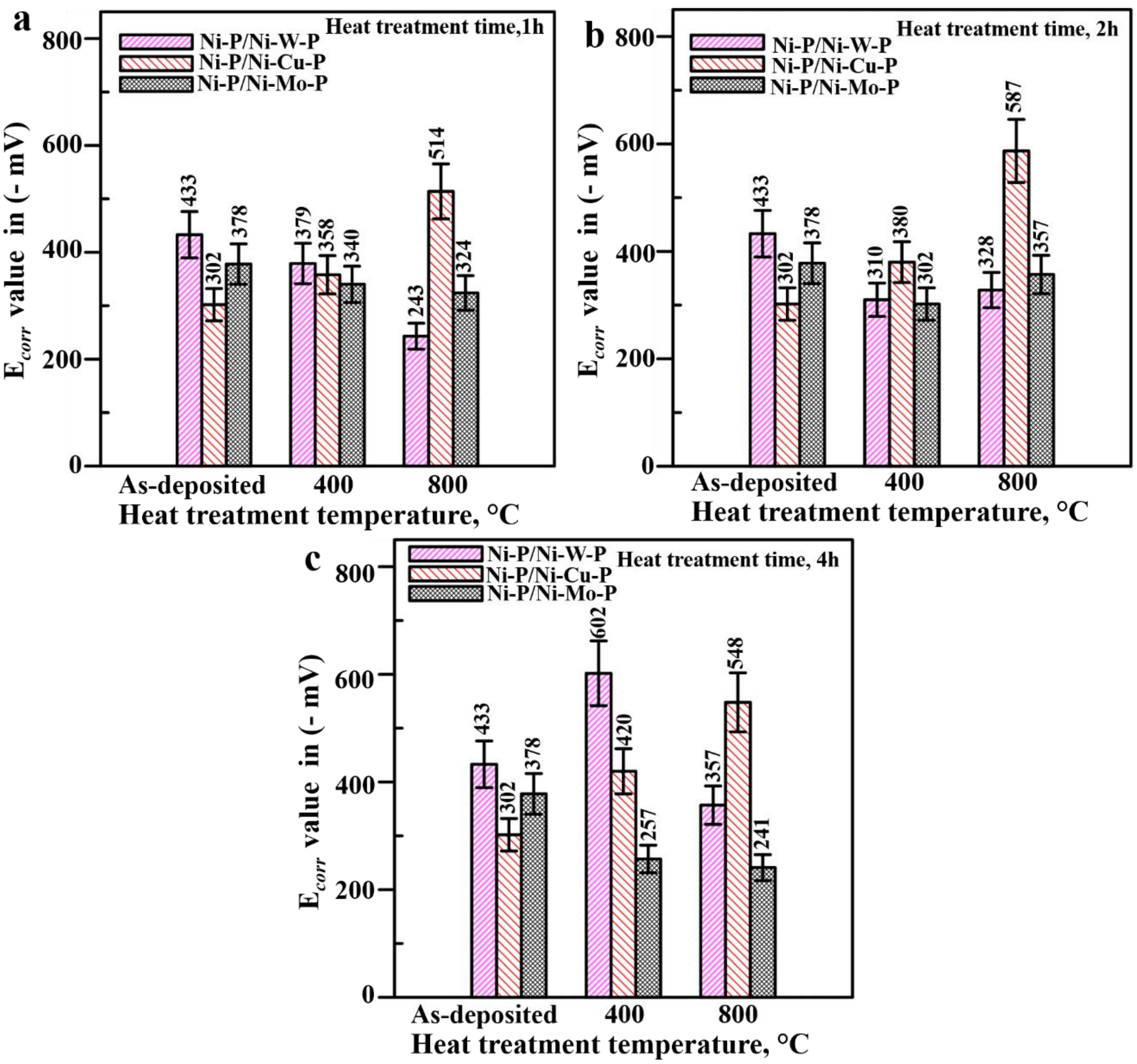

Figure 7.13 *Corrosion potential result from Tafel extrapolation plot with various time duration (a) 1h, (b) 2h, and (c) 4h duration*

It is evident that the post- heat treatment coating exhibits improved corrosion resistance compared to the as-deposited coating, particularly for 2h heat treatment periods. However, an exception to this trend is noted in the case of duplex electroless Ni-P/Ni-Mo-P coating subjected to a 4h heat treatment cycle at 400°C, where the coated samples demonstrate lower resistance to corrosion due to grain coarsening. In the case of duplex electroless Ni-P/Ni-Cu-P coating, the results from PDP tests indicate a general shift of the corrosion potential towards the negative zone following heat treatment. This shift suggests a reduction in corrosion resistance after heat treatment, which is reasonable because the amorphous nature of as-deposited coatings crystallizes after heat treatment forming grain boundaries that are more susceptible to attack by corrosive media **(Chen et al., 2019).**

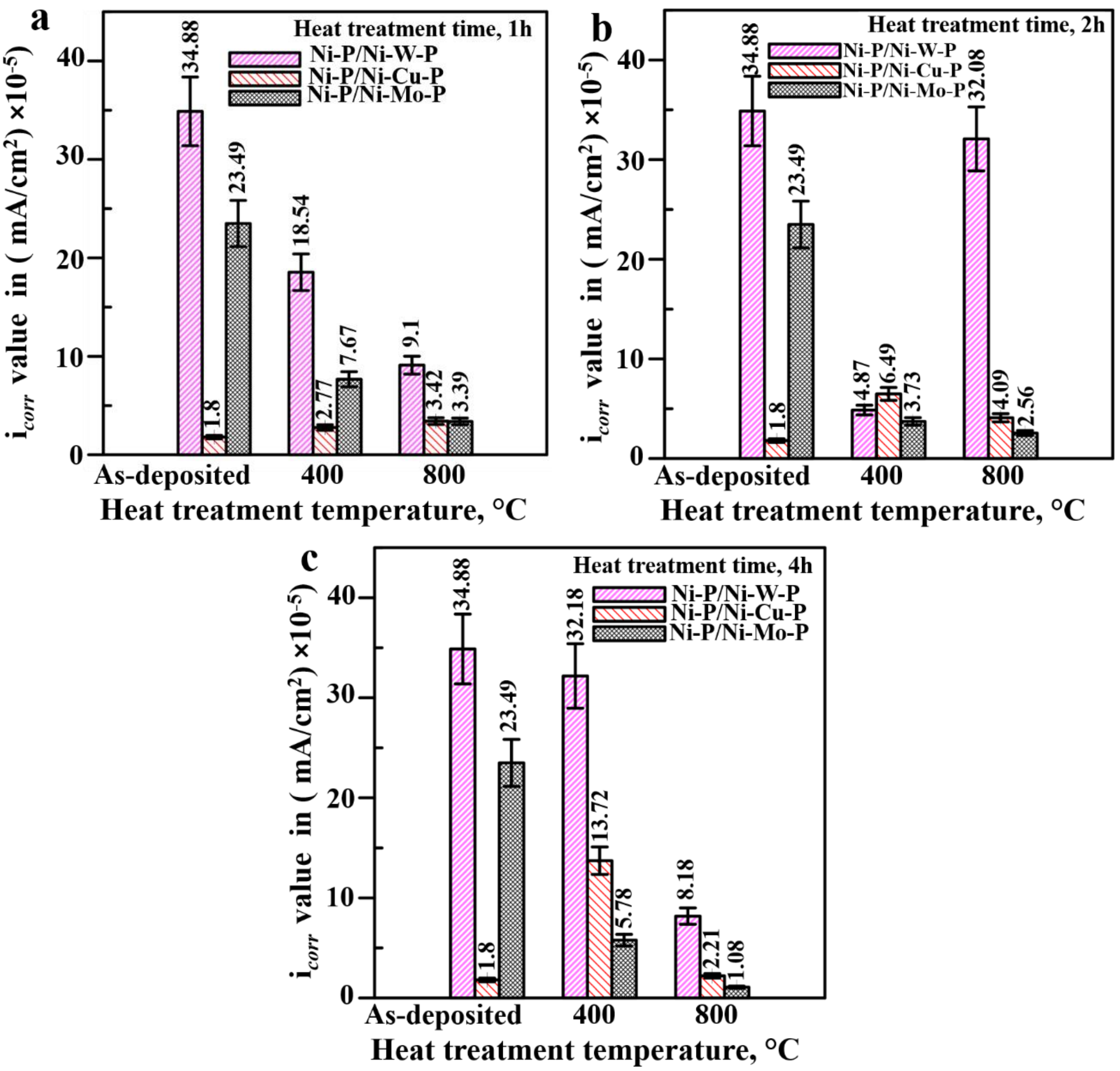

Figure 7.14 *Corrosion current result from Tafel extrapolation plot with various time duration (a) 1h, (b) 2h and (c) 4h duration*

Conversely, for duplex electroless Ni-P/Ni-Mo-P coating, the corrosion potential shifts to the positive zone after heat treatment, as indicated by the PDP results. This results in increased corrosion resistance compared to the as-deposited coating for all heat treatment cycles. The highest level of corrosion resistance is achieved at a high temperature (800°C) and a 4h heat treatment cycle. Now, electroless nickel coatings with higher P content display reduced active anodic metal dissolution due to the formation of passive phosphate film. Moreover, the formation of various phosphide phases after heat treatment have co-valent bonds between nickel and phosphorous atoms which alters the structural as well as electronic properties of the deposits thus making them passive to attack by corrosive media resisting bulk metal dissolution.

In summary, among the three types of duplex coatings, duplex Ni-P/Ni-Cu-P coating demonstrates the highest corrosion resistance in its as-deposited state. However, duplex Ni-P/Ni-Mo-P coating exhibits better corrosion performance under heat-treated conditions than the other duplex coating systems. Additionally, duplex Ni-P/Ni-W-P coating performs better at higher temperatures for 1h and 2h cycles. This information is based on the data presented in Figure 7.13 and Figure 7.14.

7.2.7 Performance comparison with single layer coatings

A comprehensive assessment of the current study necessitates a comparison between the performance of the duplex coatings and their individual constituent coatings. Table 7.2 presents a comparison of the wear rate and microhardness of both the duplex and single-layer coatings, while Table 7.3 offers a comparison of the corrosion results. The corrosion currents presented in Figure 7.14 for smaples heat treated at 400°C for 1h duration, corresponds to that presented in Table 7.3. In the case of duplex Ni-P/Ni-W-P coating, the microhardness is notably higher than that of Ni-P coatings but slightly lower than Ni-W-P coatings, both in the as-deposited and heat treatment conditions. Notably, duplex Ni-P/Ni-W-P coating exhibits superior wear resistance, which is further enhanced by heat treatment.

This can be attributed to the solid solution-strengthening effect that tungsten imparts to the Ni-P matrix, as previously mentioned. In terms of corrosion performance, the single-layer coating Ni-P outperforms duplex electroless Ni-P/Ni-W-P coating, as evidenced by the lower corrosion potential values listed in Table 7.3. However, when compared to binary Ni-W-P coatings, the duplex coatings perform reasonably well. This comparison clearly indicates that duplex coatings amalgamate the advantages of each of their constituent layers,

Table 7.2 Comparison of microhardness and wear results for single layer and duplex coatings

Coating Type	**Microhardness ($HV_{0.1}$)**		**Wear rate (10^{-5} $mm^3.N^{-1}.m^{-1}$)**	
	As-deposited	Heat treated at 400°C,1h	As-deposited	Heat treated at 400°C,1h
Single layer Ni-P	585	1082	25.32	14.52
Single layer Ni-W-P	735	1435	18.46	7.53
Single layer Ni-Cu-P	556	622	26.18	16.73
Single layer Ni-Mo-P	541	655	22.4	12.38
Duplex Ni-P/Ni-W-P	724	1440	20.57	10.62
Duplex Ni-P/Ni-Cu-P	568	1092	25.94	15.92
Duplex Ni-P/Ni-Mo-P	587	1072	21.56	11.94

allowing them to strike a balance between corrosion resistance and wear resistance. The results highlight that duplex coatings offer a promising combination of properties, making them a valuable option that capitalizes on the strengths of their individual components to provide a well-rounded solution for both corrosion and wear resistance.

Likewise, in the case of duplex Ni-P/Ni-Cu-P coating, the microhardness values are noticeably lower than those of Ni-P coating but higher than those of Ni-Cu-P coating in the as-deposited state. However, in heat-treated conditions, the microhardness exceeds that of both individual coatings, as shown in Table 7.2. The current duplex coatings exhibit superior wear performance compared to Ni-Cu-P single-layer coatings, but their wear resistance is somewhat lower than that of Ni-P single-layer coatings. This relationship between microhardness and wear rate is evident in Table 7.2.

These observations suggest that the duplex coatings, in heat-treated conditions, manage to enhance their microhardness to a level that surpasses the constituent single-layer coatings. However, their wear resistance, as indicated by the wear rate, remains slightly lower than that of the single-layer Ni-P coatings but significantly better than that of Ni-Cu-P single-layer coatings. This underscores the interplay between microhardness and wear resistance in duplex electroless Ni-P/Ni-Cu-P coating. However, the current duplex coating outperforms both the single-layer coating in terms of corrosion performance (refer to Table 7.3).

Table 7.3 Comparison of corrosion performance for single layer and duplex coatings

Coating Type	**As-deposited**		**Heat treated at 400°C,1h**	
	E_{corr} (mV)	i_{corr} (mA/cm^2) ×10^{-5}	E_{corr} (mV)	i_{corr} (mA/cm^2) ×10^{-5}
Single layer Ni-P	-386	32.08	-346	2.052
Single layer Ni-W-P	-452	24.35	-403	7.53
Single layer Ni-Cu-P	-356	22.08	-380	19.02
Single layer Ni-Mo-P	-655	9.07	-514	3.42
Duplex Ni-P/Ni-W-P	-433	34.88	-379	18.54
Duplex Ni-P/Ni-Cu-P	-302	1.83	-358	2.77
Duplex Ni-P/Ni-Mo-P	-378	23.49	-340	7.67

For duplex electroless Ni-P/Ni-Mo-P coating, the microhardness is notably higher than both the single-layer Ni-Mo-P and Ni-P coatings, both in the as-deposited and heat treatment conditions. The wear performance of duplex electroless Ni-P/Ni-Mo-P coating is superior to that of the individual Ni-Mo-P and Ni-P coatings. Additionally, the duplex coating outperforms the two separate single-layer coatings in terms of corrosion performance, as indicated in Table 7.3.

Summing up it can be said that in terms of microhardness, duplex electroless Ni-P/Ni-W-P coating achieves the highest microhardness values in both as-deposited and heat treatment conditions among all the duplex coating systems. Furthermore, the wear behaviour of duplex electroless Ni-P/Ni-W-P coating is superior to that of the other duplex systems. However, in terms of corrosion performance, duplex electroless Ni-P/Ni-Cu-P coating outperforms all duplex and single-layer coatings in the as-deposited state. On the other hand, in most of the heat treatment conditions, duplex electroless Ni-P/Ni-Mo-P coating exhibits better corrosion performance than other duplex and single-layer coatings. This demonstrates the versatility of duplex coating systems, as they can be tailored to suit specific requirements and conditions.

7.3 Closure

The current chapter focuses on a comparative study of the mechanical, tribological, and corrosion behaviour of duplex electroless Ni-P/Ni-Cu-P, Ni-P/Ni-W-P, and Ni-P/Ni-Mo-P coatings. Tribological, corrosion, and microhardness studies are carried out on both the heat-treated and as-deposited samples. All the duplex coatings initially exhibit an amorphous structure in the as-deposited state, but they undergo a transformation into a crystalline microstructure upon exposure to heat treatment at or above 400°C. Duplex electroless Ni-P/Ni-W-P coating exhibits the highest microhardness and wear resistance. This is due to the presence of W in the Ni-P matrix resulting in its strengthening. The wear mechanisms seen in all the coatings involve combined (abrasive and adhesive) mechanisms. However, factors viz. size of grains, the occurrence of precipitated phases, and the presence of oxide films play a significant role in influencing hardness and wear behaviour. Duplex electroless Ni-P/Ni-Cu-P coating exhibits the highest corrosion resistance, while duplex Ni-P/Ni-Mo-P coating also shows moderate performance in the heat-treated state.

Chapter 8

Duplex Electrodeposited Ni-P/Ni-W-P Coatings

Outline of the chapter: *8.1 Introduction, 8.2 Results and Discussion, 8.2.1 Microstructure characterization and composition analysis, 8.2.2 Phase structure, 8.2.3 Microhardness study, 8.2.4 Friction performance, 8.2.5 Wear performance, 8.2.5.1 Wear behaviour, 8.2.5.2 Wear mechanism, 8.2.6 Corrosion performance, 8.3 Comparison between duplex electroless and electrodeposited Ni-P/Ni-W-P coating, 8.4 Closure*

8.1 Introduction

The present chapter focuses on investigating duplex electrodeposited Ni-P/Ni-W-P coatings, where Ni-W-P serves as an outer layer and Ni-P as an inner layer, and vice versa. Duplex electrodeposited Ni-P/Ni-W-P coatings is developed in-house over steel substrates as discussed in chapter 3. The phase structure and composition of the coatings is examined through appropriate microstructural analyses. The microhardness, friction, and wear behaviour is assessed comprehensively. Furthermore, the corrosion resistance of the coatings is evaluated using PDP and EIS techniques, and compared to that of duplex electroless coatings. To carry out a comprehensive analysis, one set of coating is developed with Ni-W-P as the outer layer (denoted as Ni-P/Ni-W-P) and another set with Ni-P as the outer layer (denoted as Ni-W-P/Ni-P).

8.2 Results and Discussion

8.2.1 Microstructure characterization and composition analysis

SEM analysis is conducted to examine the microstructure of coatings and confirm proper deposition. Figures 8.1 and 8.2 illustrate the surface morphology of both duplex electrodeposited Ni-P/Ni-W-P and Ni-W-P/Ni-P coatings under both as-deposited and heat-treated conditions. The as-deposited coating in case of both exhibits a nodular morphology.

In the as-deposited condition, both the duplex electrodeposited coatings exhibit very fine and tiny nodules, typically of the order of a few micrometres, as seen in Figures 8.1a and 8.2a. The rapid deposition process restricts ion diffusion in the plating bath, resulting in minimal diffusion before deposition onto the surface. Consequently, both coatings display

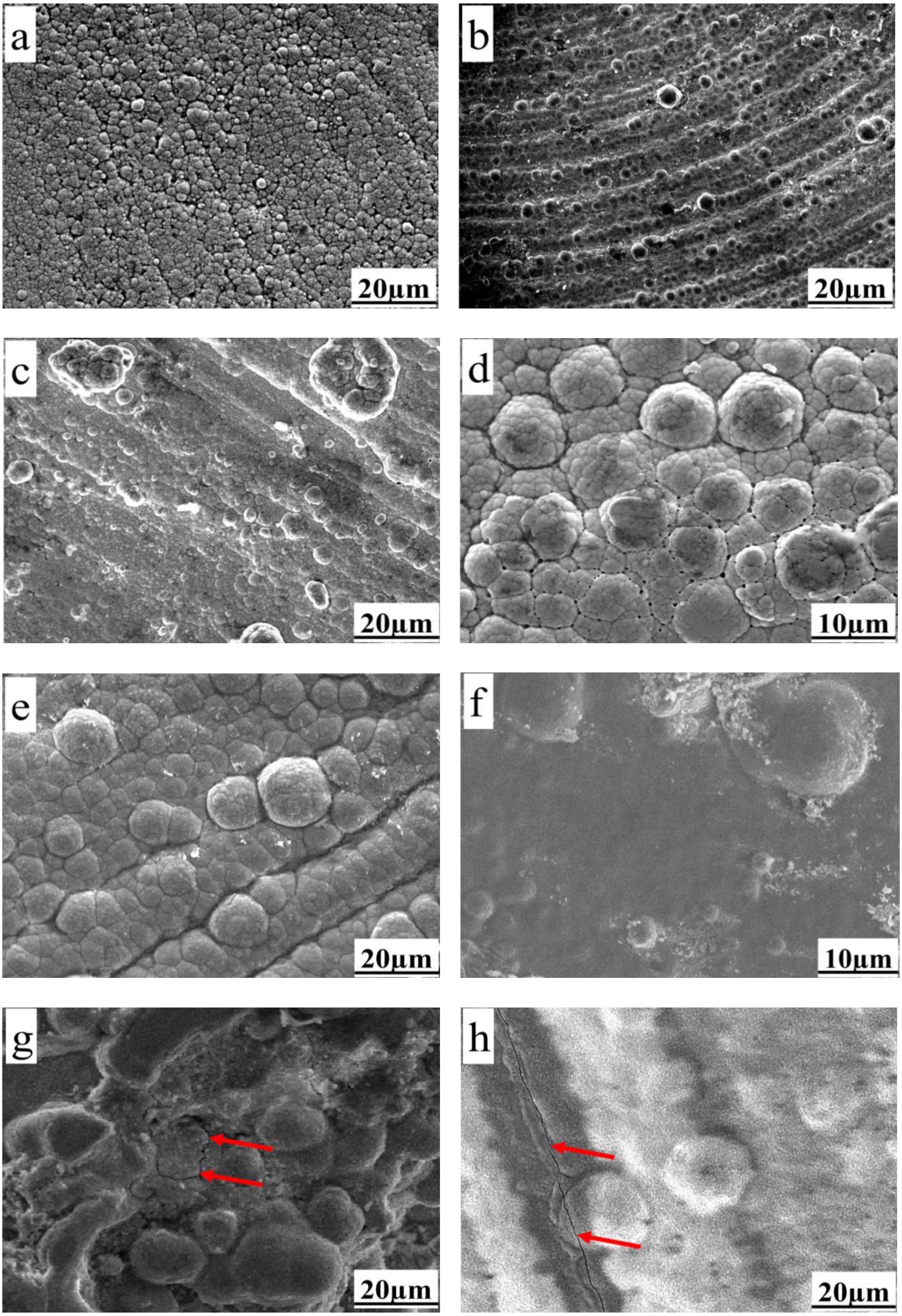

Figure 8.1 *SEM images of Ni-P/Ni-W-P coating at (a) as-deposited coating (b) at 400°C, 1h, (c) at 400°C, 2h, (d) at 400°C, 4h, (e) at 600°C, 1h (f) at 600°C, 4h, (g) at 800°C, 1h (h) at 800°C, 4h*

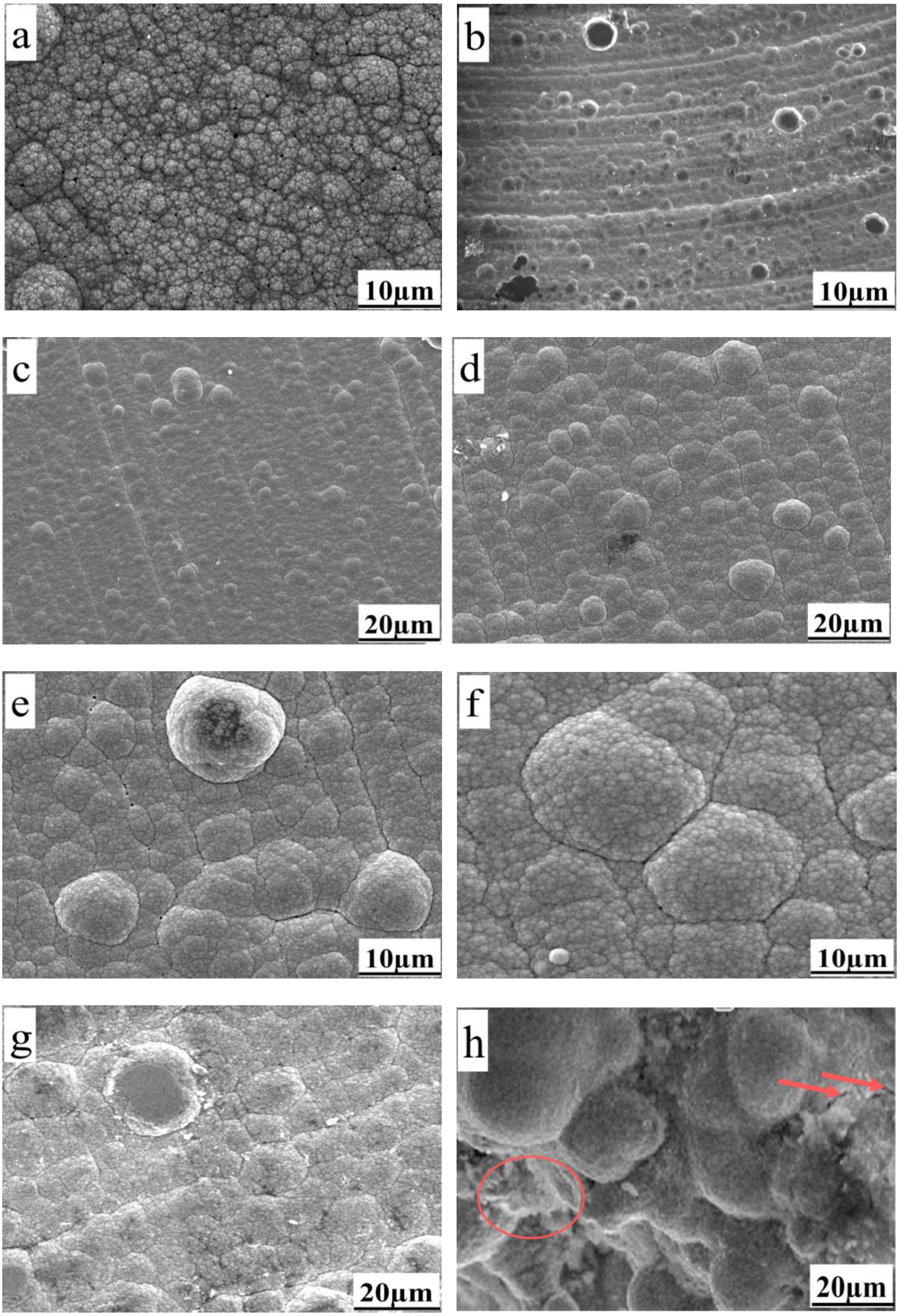

Figure 8.2 *SEM images of Ni-W-P/Ni-P coating at (a) as-deposited coating (b) at 400°C, 1h, (c) at 400°C, 2h, (d) at 400°C, 4h, (e) at 600°C, 1h (f) at 600°C, 4h, (g) at 800°C, 1h (h) at 800°C, 4h*

low porosity, with voids or pores between grains being rare. The deposition process is uniform as the coating is deposited under controlled conditions. Heat treatment can influence the microstructure and properties of the coating, as depicted in Figures 8.1b-h and 8.2b-h. Heat treatment at 400°C for 1-4 hrs reduces porosity and increases grain size in both the coatings (Figures 8.1b-d and 8.2b-d). This increase in compactness enhances wear resistance and microhardness.

At higher heat treatment temperatures (800°C or 600°C) and longer durations, grain growth occurs due to increased energy facilitating atom diffusion and rearrangement (Figures 8.1e-h and 8.2e-h). This grain growth can enhance mechanical and tribological properties. However, at 800°C for 1 and 4 hrs, cracks develop on the surfaces of Ni-P/Ni-W-P coating, as indicated by red arrows in Figures 8.1g and 4h, respectively. These cracks suggest significant thermal stress in the coating or substrate. Similarly, cracks develop in Ni-W-P/Ni-P coating at 800°C for a 4h duration (Figure 8.2h).

In both the coatings, during the heat treatment process, at 600°C or 800°C, the coated material may react with the surrounding atmosphere. This reaction can lead to the development of an oxide layer on the coating. The oxides can have a darker appearance compared to the original coating colour, making them visible as dark spots on the surface (Figure 8.1g-h and Figure 8.2h).

Figure 8.3 displays the SEM image of the coatings and the EDX spectrum, including the percentage composition of elements in their as-plated state. Both coatings belong to the high phosphorous category, with the duplex coating having a phosphorus content exceeding 8 wt%, indicating an amorphous phase structure **(Keong and Sha 2002)**. The surface of Ni-W-P/Ni-P coating consists of 87.1 wt% Ni and 12.9 wt% P, indicating a single layer Ni-P plating on the top surface of the coating. Similar observations have been reported by other researchers (**Biswas et al., 2017).**

In case of Ni-P/Ni-W-P coating, W is additionally present as constituent along with Ni and P, indicating that the outer layer of the duplex coating is a Ni-W-P layer. As for Ni-P/Ni-W-P coating, the composition of the top surface as a Ni-W-P is obtained at 83.4 wt% of Ni, 6.5wt% of W, and 10.1wt% of P respectively. This composition is more or less similar to the Ni-W-P coating obtained through electroless method as discussed in chapter 4.

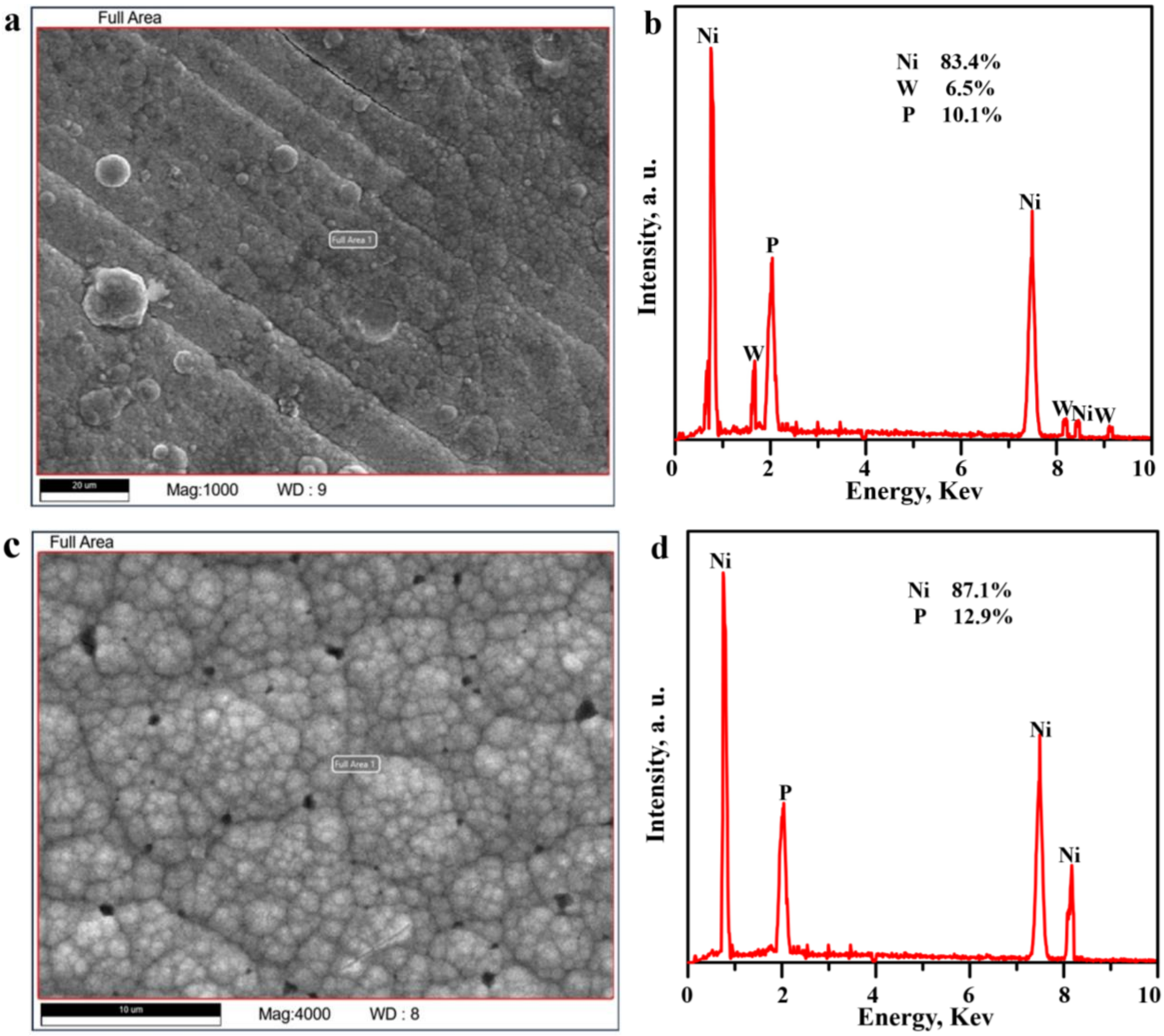

Figure 8.3 *SEM image and EDX plot of Ni-P/Ni-W-P coating (a, b) and Ni-W-P/Ni-P coating (c, d)*

The cross-section analysis using line EDX provides insights into the element distribution within the coating, as illustrated in Figure 8.4. This data facilitates the determination of transition points between different layers of Ni-P/Ni-W-P coating, such as the boundary between the Ni-P layer and the Ni-W-P layer, or vice versa. Additionally, the technique offers information regarding coating uniformity, adherence, and the presence of defects. Both Ni-P/Ni-W-P and Ni-W-P/Ni-P coating are successfully deposited onto the mild steel substrate. This is primarily inferred from the noticeable change in tungsten (W) wt% observed near the interface of the outer and inner layers (approximately 22 μm depth), indicating a transition in composition from the Ni-P layer to the Ni-W-P layer, or vice versa. Each layer of the coating exhibits nearly identical thickness, with the total coating thickness measuring around 45 μm.

The deposition process demonstrates consistency, resulting in a uniform coating. The top and bottom layers exhibit excellent adhesion and compatibility. Moreover, the cross-section analysis of the coating reveals no pores or other defects, indicating a high-quality deposition process. Given the absence of defects and the successful deposition of the duplex coating with uniform layers, the coating is anticipated to demonstrate outstanding wear and corrosion resistance.

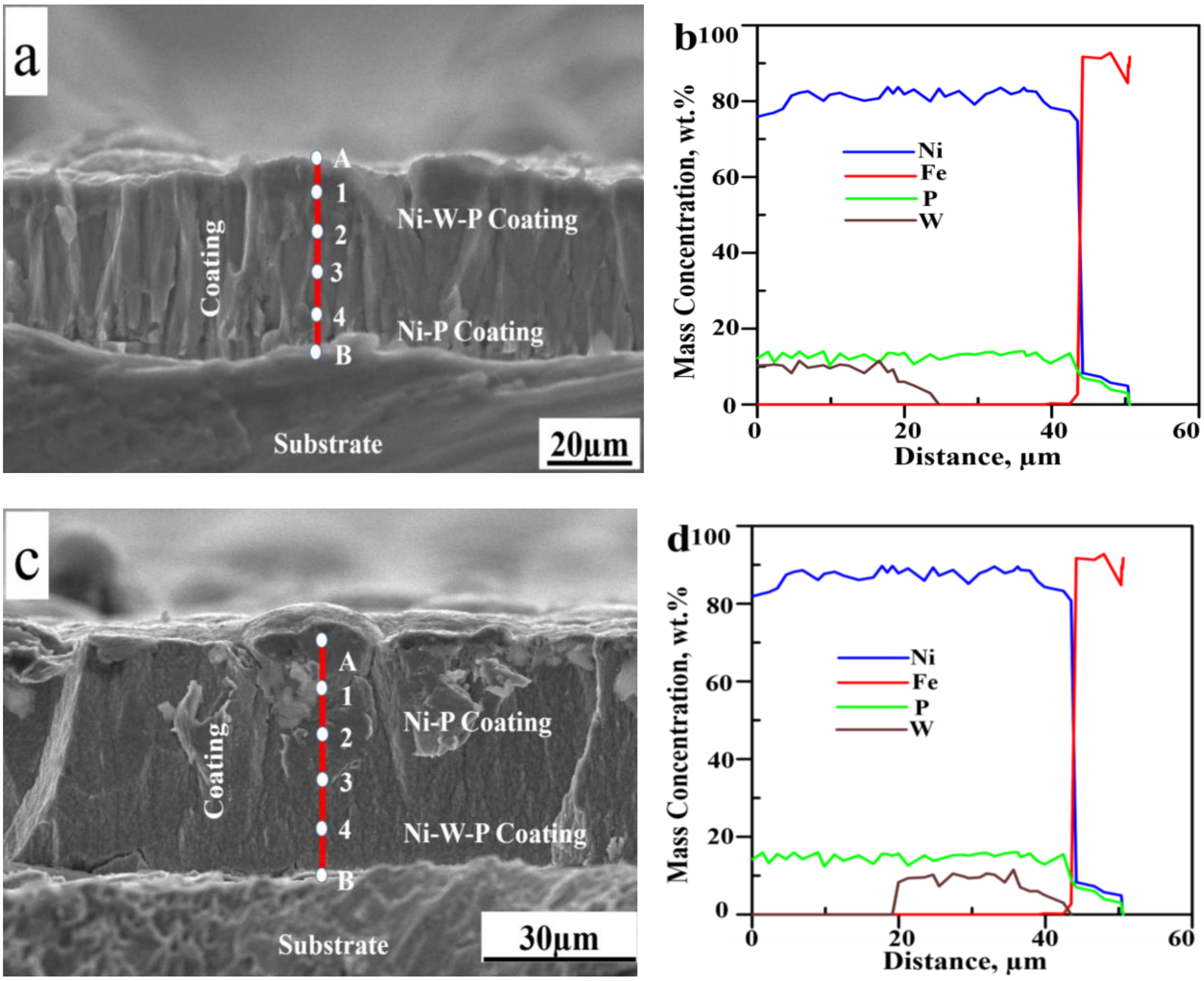

Figure 8.4 *Cross-section of the coating including line EDX result of Ni-P/Ni-W-P (a, b) and Ni-W-P/Ni-P (c, d)*

8.2.2 Phase structure

The XRD results for Ni-P/Ni-W-P and Ni-W-P/Ni-P coating are presented in Figures 8.5 and 8.6, respectively, under both as-deposited and heat treatment conditions. The as-deposited coatings exhibit an amorphous phase nature, characterized by broad, diffused peaks in the

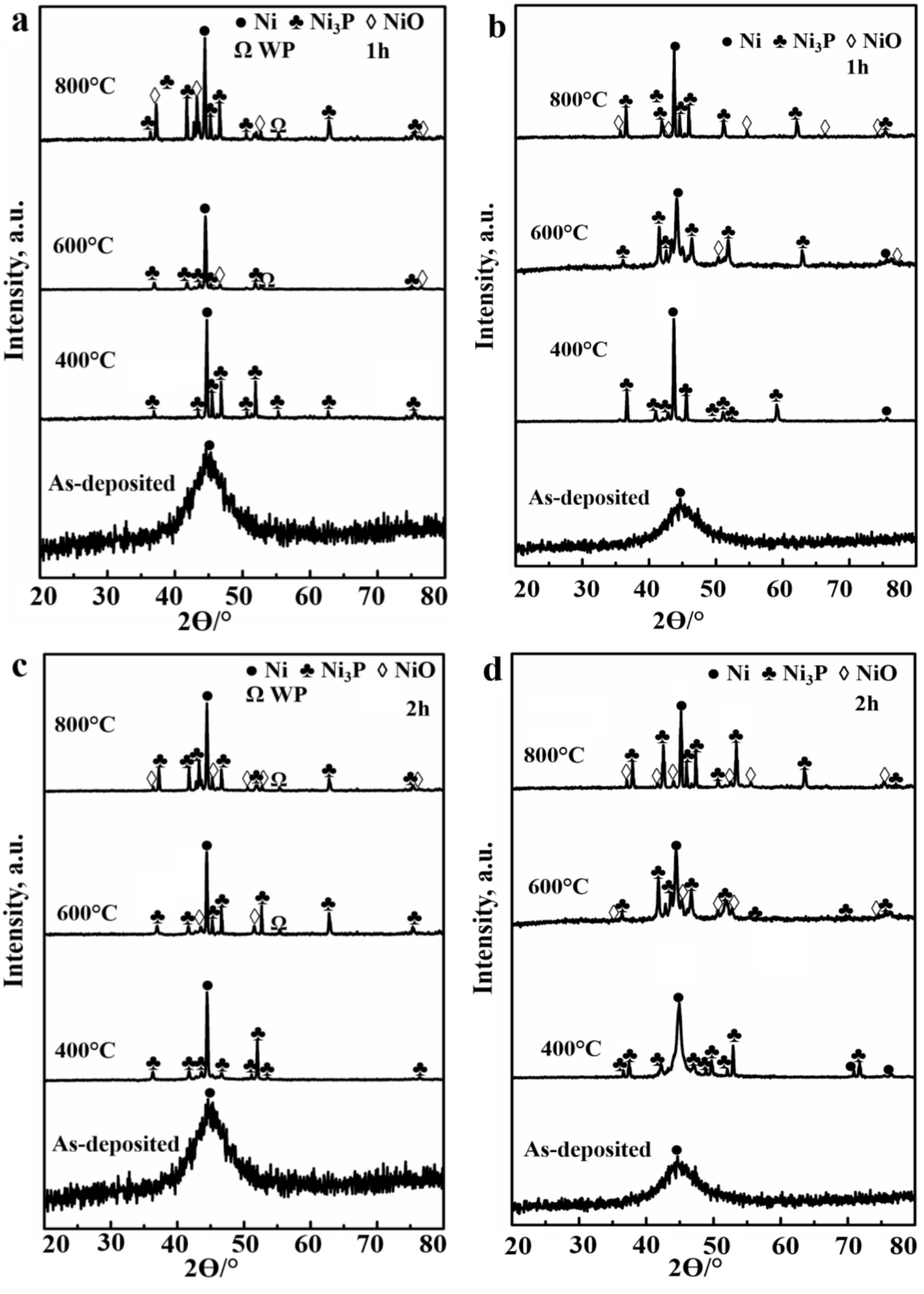

Figure 8.5 *XRD plots of duplex electrodeposited: (a) Ni-P/Ni-W-P coating for 1h duration, (b) Ni-W-P/Ni-P coating for 1h duration, (c) Ni-P/Ni-W-P coating for 2h duration and (d) Ni-W-P/Ni-P coating for 2h duration*

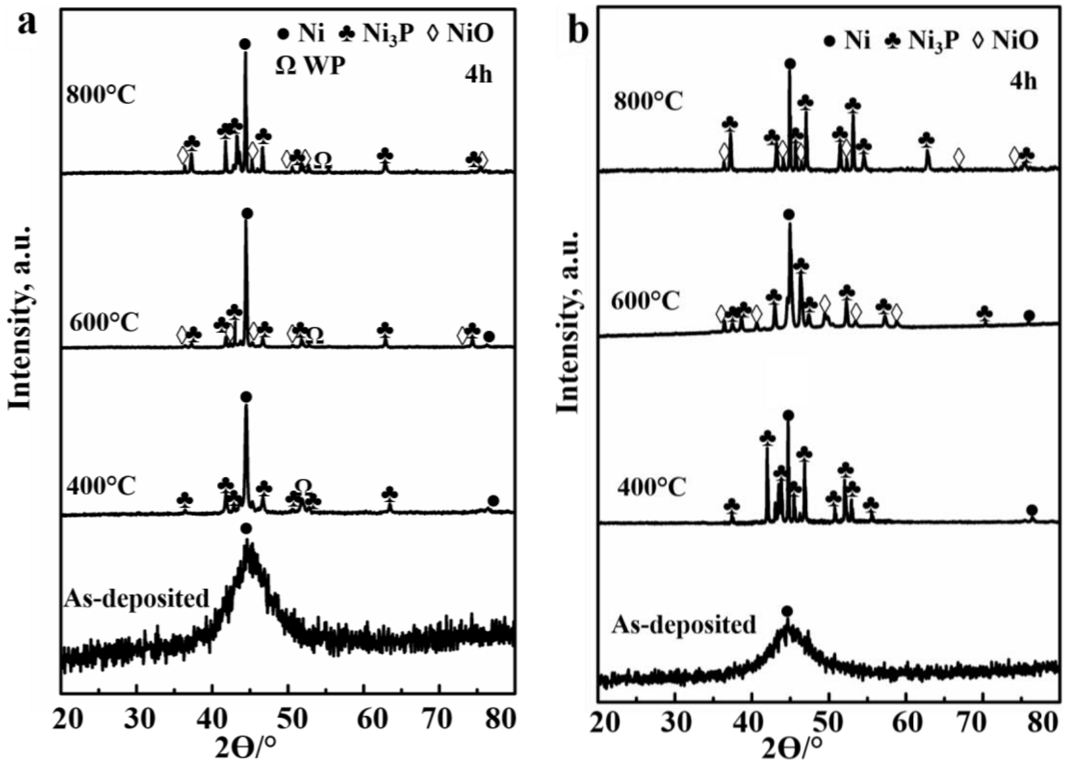

Figure 8.6 *XRD plots of: (a) Ni-P/Ni-W-P coating for 4h duration, (b) Ni-W-P/Ni-P coating for 4h duration*

XRD pattern, unlike crystalline coatings which display sharp, well-defined peaks. Notably, the as-plated Ni-P/Ni-W-P coating shows a sharper peak compared to Ni-W-P/Ni-P coating, particularly at the 45° diffraction angle.

For both coatings, at a heat treatment temperature of 200°C across all cycles, there is minimal difference in the phase structure as compared to as-deposited condition. However, at heat treatment temperatures of 400°C and above, significant changes occur in the XRD profiles of the samples, with multiple peaks indicating various phases including Ni, P, W, and even O.

In the case of Ni-P/Ni-W-P coating, at 400°C for 1h, the highest peak is observed at 45° for Ni, indicating the presence of the Ni_3P phase, which is crystallized and highly durable. This phase contributes to increased microhardness and reduced wear rate, as observed in previous chapters. Precipitation of Ni_3P and Ni phases is evident at this temperature. At 600°C for 1h, a few NiO phases emerge alongside Ni_3P, Ni, and WP phases. The formation of oxides and distinct diffraction peaks become more pronounced at 800°C, indicating crystallization of Ni-P/Ni-W-P coating. The oxide phase significantly impacts tribological and corrosion performance. Additionally, at this temperature, Ni_3P phase is observed at multiple planes alongside the WP phase.

At temperatures of 400°C and above, the coating exhibits numerous crystalline peaks, predominantly Ni_3P phases found in the (141), (112), (322), and (321) planes. Notably, at 400°C for a duration of 2h, the Ni-W-P outer layer coating prominently displays the WP phase alongside the Ni_3P phase (refer to Figure 8.5c). As the temperature increases further, nickel oxide emerges as a new component of Ni-P/Ni-W-P coating, with the existing Ni, Ni_3P, and WP phases becoming more concentrated. This trend is particularly evident at 800°C, with durations of 2h and 4h. The primary source of these oxide phases is the trapped air within the furnace. The development of additional crystalline phases contributes to the enhancement of the material's microhardness.

The precipitation of Ni_3P and Ni phases is observed for Ni-W-P/Ni-P coating at 400°C temperature, as depicted in Figures 8.5b, d, and Figure 8.6b. Additionally, at 600 or 800°C temperatures for 1h duration, the NiO phase emerges alongside the Ni_3P and Ni phases. Similar observations are noted for 2h and 4h heat treatment cycles.

8.2.3 Microhardness study

The microhardness values of Ni-P/Ni-W-P and Ni-W-P/Ni-P coating are presented under both as-deposited and heat treatment conditions in Figure 8.7. In the as-deposited state, the microhardness of Ni-P/Ni-W-P coating measures 637 $HV_{0.1}$. Following heat treatment at 200°C, Ni-P/Ni-W-P coating experiences improved microhardness attributed to minor microstructural changes. Heat treatment leads to the precipitation of tungsten in the coating, forming hard tungsten particles. These particles are uniformly dispersed throughout the coating, contributing to an overall increase in microhardness. At 400°C for 1h heat treatment cycle, the highest microhardness value is achieved due to the development of hard crystalline Ni_3P phase. Compared to the as-deposited coating, the microhardness value is enhanced by approximately 62% at this temperature. However, beyond 400°C for 1h heat treatment cycle, a slight decline in microhardness is observed due to the formation of a few oxide phases.

At high heat treatment temperatures, the coating's microhardness surpasses that of the as-deposited conditions. At temperatures of 600°C or 800°C, the presence of a few Ni_3P phases (as indicated in Figure 8.7a) is the primary factor contributing to the improved microhardness.

Remarkably, for a 2h heat treatment cycle, the microhardness value demonstrates an increasing trend with rising temperature up to 600°C. Compared to the as-deposited coating, the microhardness value increases by nearly 89% after 2h heat treatment at 600°C. However,

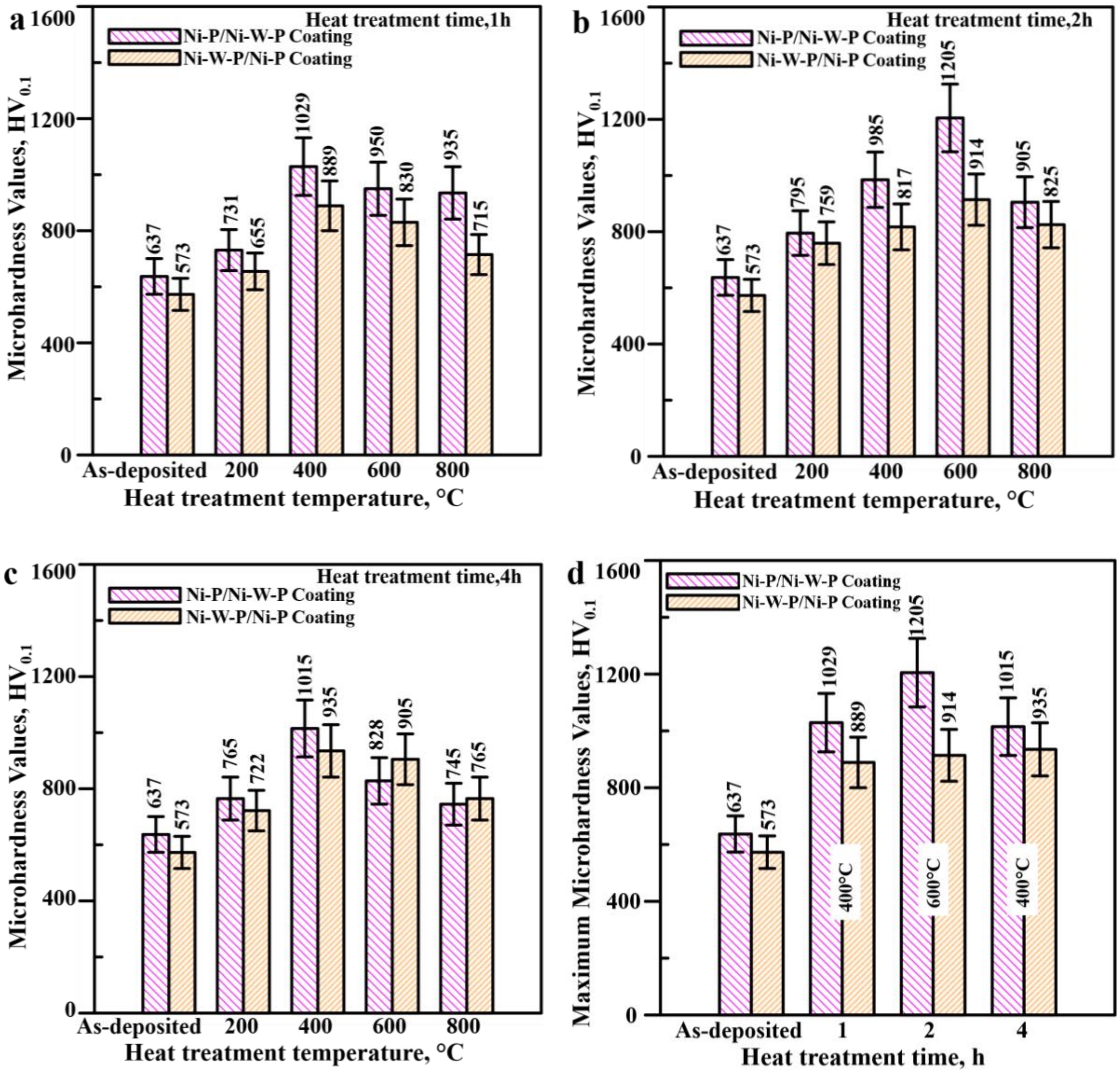

***Figure 8.7** Microhardness plots for (a) 1h, (b) 2h, (c) 4h duration, and (d) maximum microhardness plot*

beyond 600°C, the microhardness experiences a drastic decline due to oxide formation. Notably, at 600°C for a 2h duration, the highest microhardness is observed across all heat treatment cycles (refer to Figure 8.7d).

When the heat treatment duration extends to 4h, the microhardness follows a similar trend as observed in the 1h heat treatment cycle. In both cases, the microhardness increases up to 400°C and then decreases. Initially, during heat treatment, the metal dissolves its alloying elements into a solid solution, rendering it softer. However, with prolonged heat treatment duration, the metal begins to precipitate out the alloying elements, forming new phases. These new phases are harder than the solid solution, leading to an increase in microhardness. Nonetheless, if the heat treatment duration is excessively long, the new phases may grow too large, resulting in the metal becoming softer again. Primarily, in the 4h heat treatment cycle for Ni-P/Ni-W-P coating, the microhardness value tends to decrease compared to the 1h and 2h heat treatment cycles. This reduction in microhardness may be attributed to the excessive growth of new phases and formation of oxides during prolonged heat treatment duration.

The microhardness of as-plated Ni-W-P/Ni-P coating is measured at 573 $HV_{0.1}$. The similarity in hardness trend change with heat treatment temperature between the two coatings suggests that identical factors influence the hardness of both the coatings. These factors include coating composition and heat treatment temperature. Primarily, the microhardness of Ni-P/Ni-W-P coating tends to be higher than that of Ni-W-P/Ni-P coating due to the presence of tungsten on the top surface. Tungsten is known for its exceptional hardness and also aids in preventing the diffusion of alloying elements within the coating. This prevents the formation of soft phases, contributing to the overall hardness of the coating.

8.2.4 Friction performance

Figure 8.8 illustrates the COF of Ni-P/Ni-W-P and Ni-W-P/Ni-P coating at various heat treatment conditions. In the as-deposited condition, the COF of Ni-P/Ni-W-P coating is measured at 0.41, while Ni-W-P/Ni-P coating exhibits a COF of 0.26. The COF of the coating is influenced by several parameters, including coating thickness, tungsten content, and surface roughness. Notably, the COF of Ni-P/Ni-W-P coating consistently exceeds that of Ni-W-P/Ni-P coating, regardless of heat treatment temperature or duration. This can be attributed to the higher tungsten concentration in Ni-P/Ni-W-P coating compared to Ni-W-P/Ni-P coating. Moreover, the COF tends to increase with rising heat treatment temperature for both types of electrodeposited coatings, particularly for 1h and 2h heat treatment cycles. The development of the Ni_3P phase during the heat treatment process is identified as the primary factor contributing to the increased COF. Phase transition is not initiated at lower temperatures (below 400°C).

Indeed, Ni-P/Ni-W-P coating initiates the precipitation of the phosphide phase at 400°C, with significant grain development occurring at higher temperatures. The precipitation of the Ni_3P phase notably enhances the microhardness of the coating, resulting in an increased resistive force against dislocation motion and consequently elevating the COF. Moreover, an increase in phosphorus content in the coating promotes phosphide precipitation, further contributing to the rise in COF.

In a 4h heat treatment cycle, the COF decreases at 800°C for both types of plating due to the development of the NiO phase. The lowest COF is observed at 800°C for a 4h cycle (refer to Figure 8.8d). Additionally, the plots of COF versus time, as depicted in Figure 8.9 appear to be stable. For Ni-W-P/Ni-P coating, the minimum COF value is consistently observed under all as-deposited and heat-treated conditions, except at temperatures of 400°C and 600°C for 4h duration.

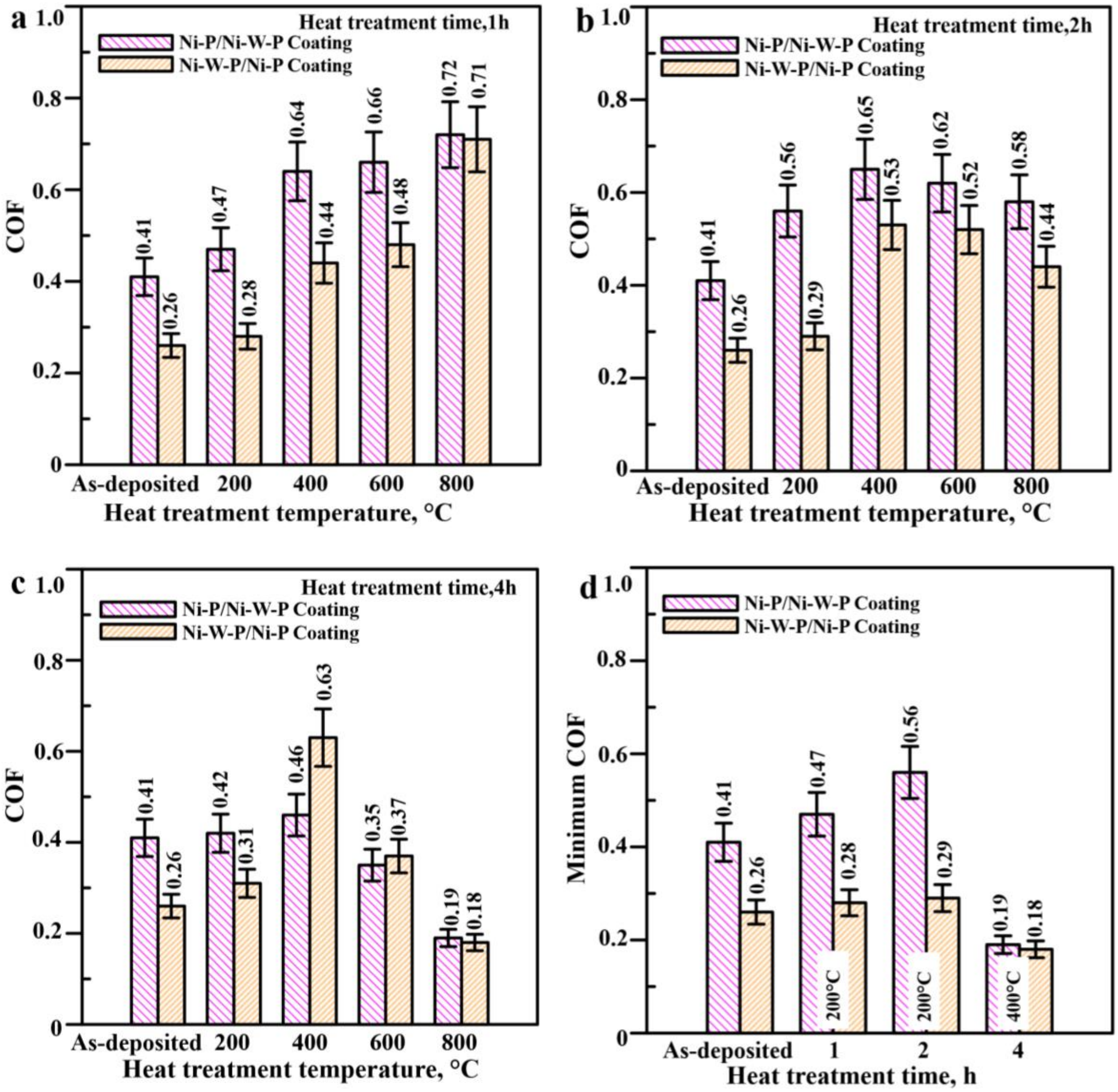

Figure 8.8 *COF plots for various heat treatment temperatures (a) 1h; (b) 2 h; (c) 4h; and (d) minimum COF plot*

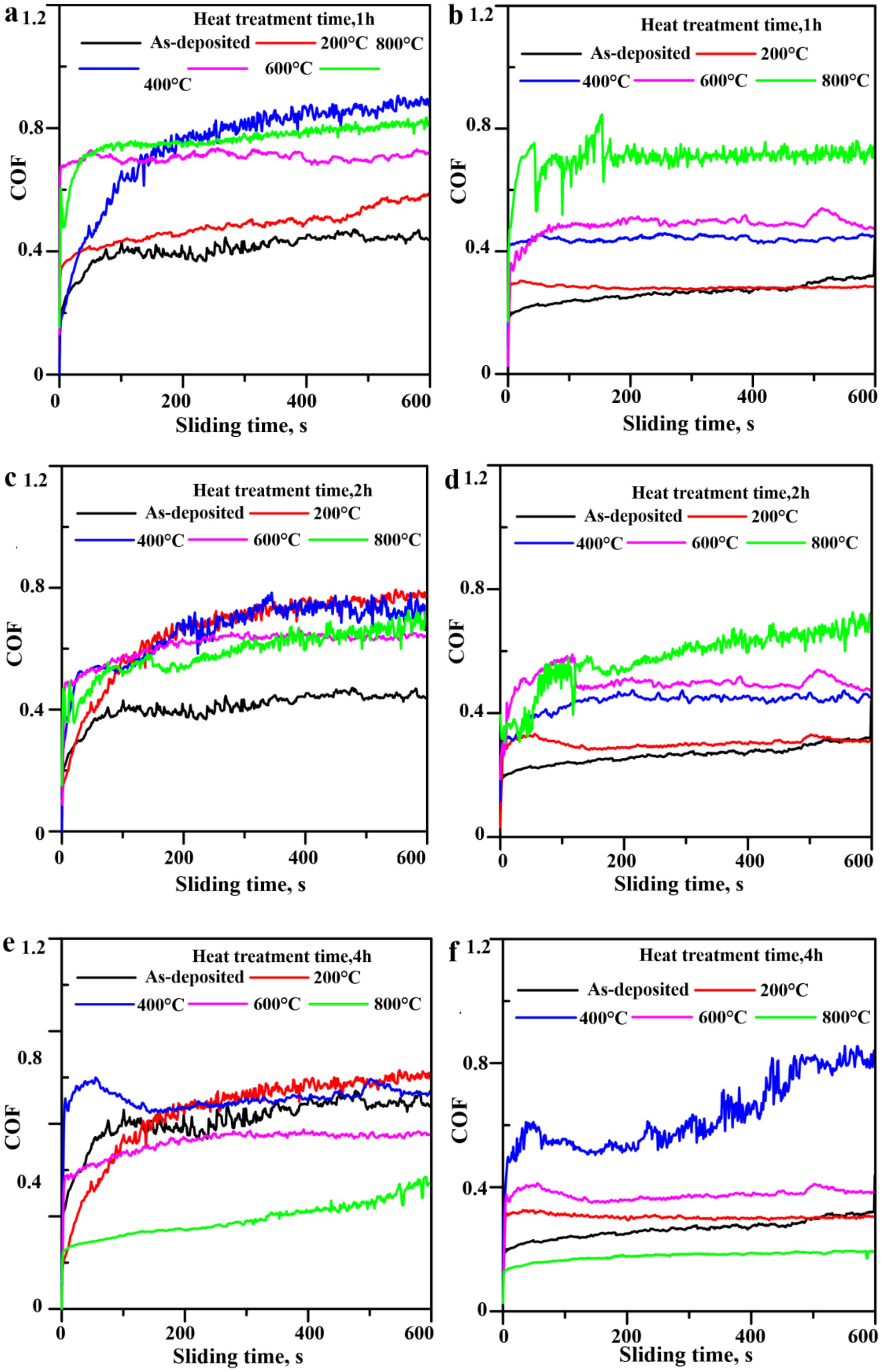

Figure 8.9 *COF vs. sliding duration of electrodeposited coating (a) Ni-P/Ni-W-P, 1h, (b) Ni-W-P/Ni-P, 1h, (c) Ni-P/Ni-W-P, 2h, (d) Ni-W-P/Ni-P, 2h, (e) Ni-P/Ni-W-P, 4h, and (f) Ni-W-P/Ni-P, 4h*

8.2.5 Wear performance

8.2.5.1 Wear behaviour

The wear rates of electrodeposited duplex Ni-P/Ni-W-P and Ni-W-P/Ni-P coatings are depicted in Figure 8.10 across different heat treatment temperatures and durations. Multiple factors, including deposition parameters, coating composition, and wear conditions, influence the wear rate of the duplex electrodeposited coating. Generally, the wear rate of Ni-P/Ni-W-P coating, in both as-deposited and heat-treated states, is lower than that of Ni-W-P/Ni-P coatings due to its higher microhardness, rendering it more resistant to wear. Specifically, in the as-deposited state, the wear rate of Ni-W-P/Ni-P coating measures approximately 22.45×10^{-5} $mm^3.N^{-1}.m^{-1}$.

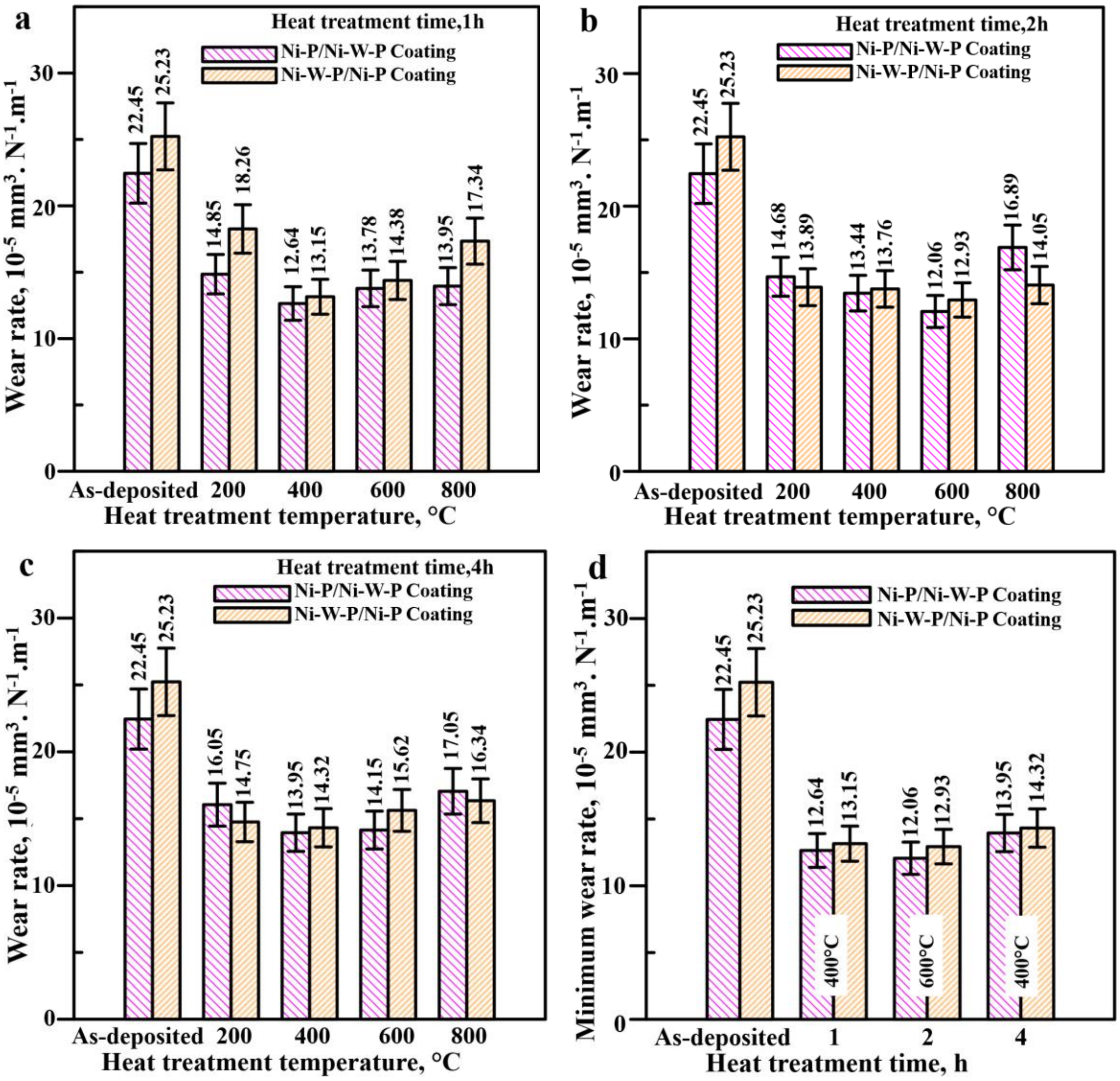

Figure 8.10 *Wear rate for various heat treatment temperatures (a) 1h; (b) 2h; (c) 4h duration; and (d) minimum wear rate*

The wear rate of the duplex electrolytic coating decreases with increasing heat treatment temperature up to 400°C, except for a 2h duration. Beyond 400°C, the wear rate increases; however, it remains lower than that of the as-deposition condition. This is because, precipitation of Ni_3P phases in the coating occurs due to heat treatment, enhancing the coating's resistance to wear. The Ni_3P phase is known for its hardness, contributing significantly to the protective properties of the coating against wear. Optimal heat treatment temperatures for both electrolytic duplex Ni-P/Ni-W-P and Ni-W-P/Ni-P coatings are observed at 400°C, except for the 2h duration, where the lowest wear rate is found at 600°C.

Comparing specific conditions, at 400°C for a 1h duration, the wear rate of the duplex coating is reduced by approximately 44% for Ni-P/Ni-W-P coating and around 48% for Ni-W-P/Ni-P coating. Similarly, at 600°C for 2h duration, the wear rate decreases by approximately 46% for Ni-P/Ni-W-P coating and 49% for Ni-W-P/Ni-P coating compared to their respective as-deposited states. However, at 800°C, the wear rate increases due to the development of the NiO phase. Nevertheless, even at 800°C, the wear rate remains lower than that of the as-deposited coating in all cases. The presence of the oxide phase may significantly influence wear resistance. Duplex Ni-P/Ni-W-P coating exhibits higher microhardness compared to Ni-W-P/Ni-P coating, rendering it more resistant to plastic deformation and wear. Furthermore, a longer heat treatment time, such as in a 4h cycle, leads to increased grain size in the coating, making it soft and prone to wear. The formation of the NiO phase, which is soft and porous, contributes to increased wear.

8.2.5.2 Wear mechanism

In Figure 8.11a, the worn surface of Ni-P/Ni-W-P coating in its as-deposited condition is illustrated. The surface of the coating reveals a few micro-cracks aligned in the sliding direction (indicated by the white arrow). The presence of longitudinal cracks suggests abrasive wear, a phenomenon occurring when sharp features of a harder counterface penetrate the softer coating. Some worn debris is observed adhered at the sliding interface, while a few pits indicate potential adhesive wear mechanisms. The abrasive wear resistance of a coating is influenced by various factors including grain size, microstructure, surface roughness, and hardness. The EDX results corroborate the presence of oxygen in the coating that may have come due to oxidation at the sliding interface during tribological testing. This is supported by the data in Figure 8.11b, indicating an oxygen concentration of 1.6% in the worn sample.

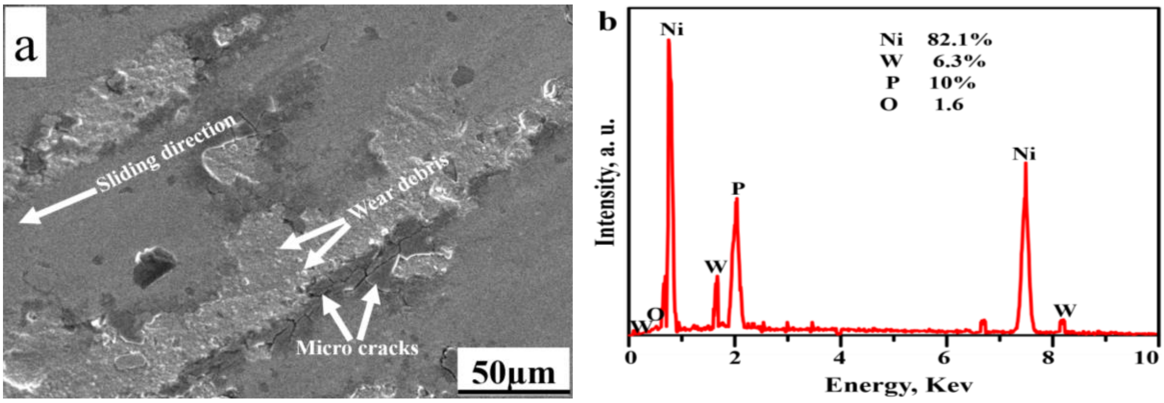

Figure. 8.11 (a) The worn surface image of as-deposited electrolytic duplex Ni-P/Ni-W-P coating and (b) EDX plot.

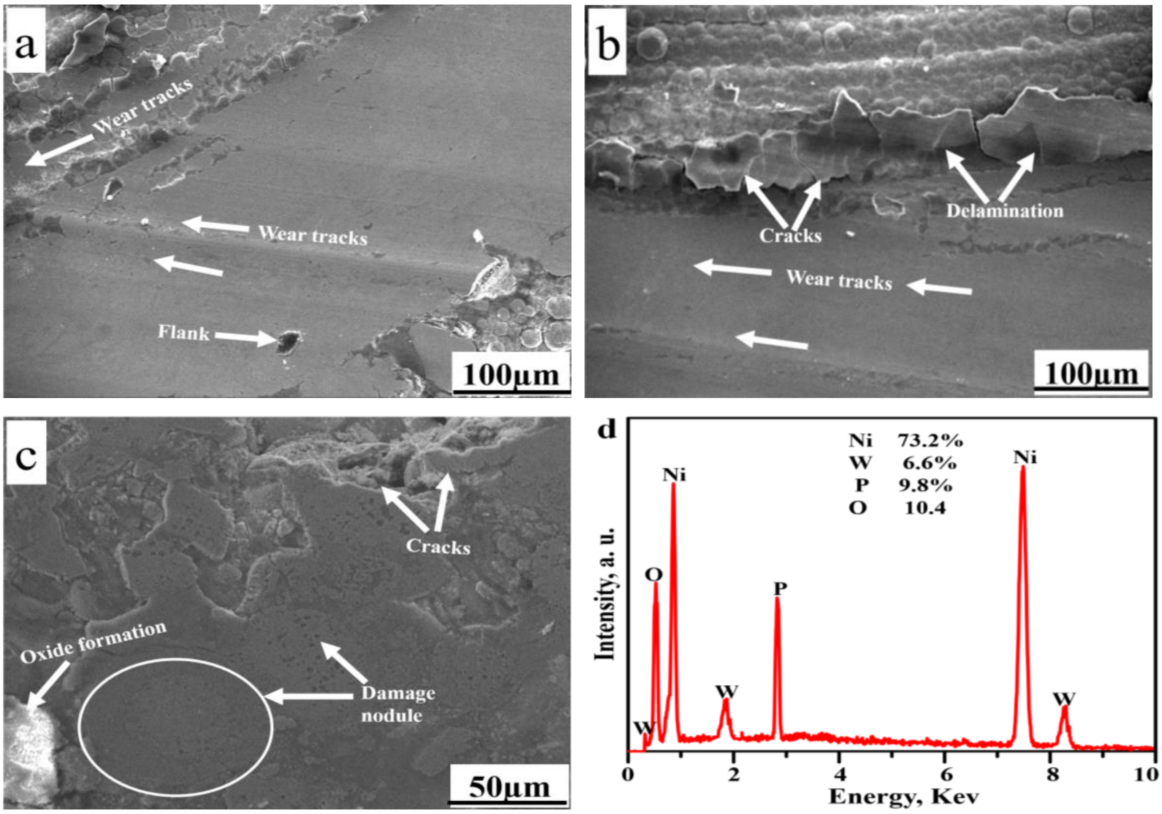

Figure 8.12 *(a) Ni-P/Ni-W-P coating worn image at 400°C, 1h (b) at 400°C,4h (c) at 600°C, 2h and (d) EDX at 600°C, 2h*

For sample treated at 400°C, 1h, Figure 8.12a illustrates the presence of a few microcracks and micro-cutting on the worn surface. Additionally, signs of plastic deformation are evident. The samples exhibit wear tracks resulting from sliding wear at this temperature and duration. Furthermore, at 400°C, 4h, Figure 8.12b showcases wear delamination on the top surface of the sample. Wear delamination occurs when a layer of coated material is peeled away from the worn surface. High contact pressure between two surfaces can lead to significant plastic deformation and crack formation, eventually causing material layers to delaminate. Wear tracks align with the sliding direction, where friction and wear are most pronounced. Friction between surfaces abrades material, resulting in the formation of wear tracks that are wider and deeper in the sliding direction due to increased material removal. In Figure 8.12c, the rubbed surface of the coating heated at 600°C for 2h exhibits numerous cracks, indicating significant surface degradation. Additionally, a flattened nodule with fine grooves and patches of exposed material is observed, indicating material loss due to sliding contact. An oxide layer is also visible on the worn surface, suggesting oxidation due to exposure to elevated temperatures. Further confirming oxidation, the EDX spectrum at 600°C for 2h, as shown in Figure 8.12d, reveals the presence of oxygen along with other elements. This presence of oxygen signifies surface oxidation mainly due to heat treatment and partly during sliding.

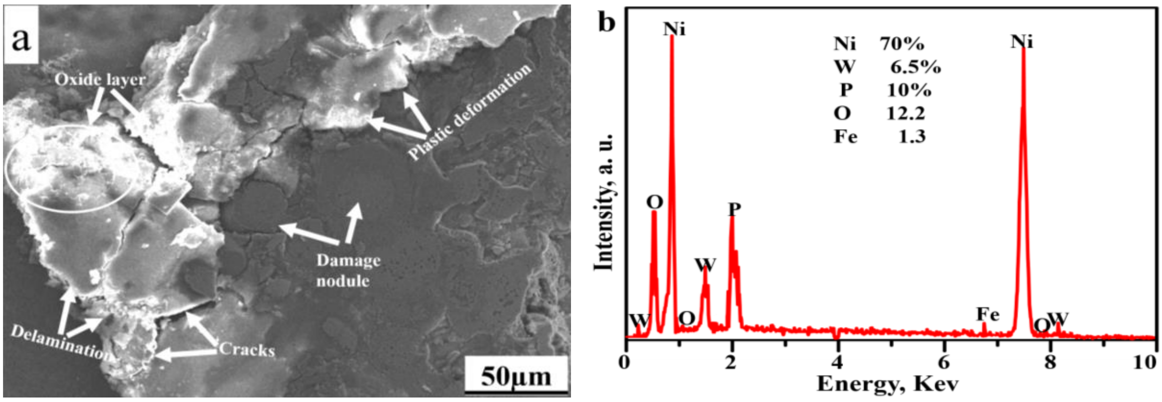

Figure 8.13 *(a) Ni-P/Ni-W-P coating worn image of heat treatment at 800°C, 4h and (b) EDX plot.*

In Figure 8.13, the SEM image and EDX plot depict the rubbing surface of a heat-treated Ni-P/Ni-W-P coating at 800°C for 4h. The image reveals various features including micro-cutting, cracks, plastic deformation, and an oxide layer on the rubbed surface. Additionally, Figure 8.13b from the EDX analysis indicates the presence of an oxide layer and iron on the worn surface. The significant mutual solubility of iron and nickel under testing conditions leads to adhesive wear between the counterface and coating surfaces. Consequently, the wear behaviour of the coated surface suggests a combination of adhesive and abrasive mechanisms.

Figures 8.14 to 8.16 provide insight into the wear mechanism of Ni-W-P/Ni-P coating. In Figure 8.14a, ploughing marks are observed in the sliding direction of the as-deposited coating. Although small cracks are visible on the rubbed surface, they are minor and unlikely to be of significant concern. Additionally, wear tracks show deep grooves. Figure 8.14b reveals the presence of a trace amount of oxygen on the coating, suggesting oxidation at the sliding interface.

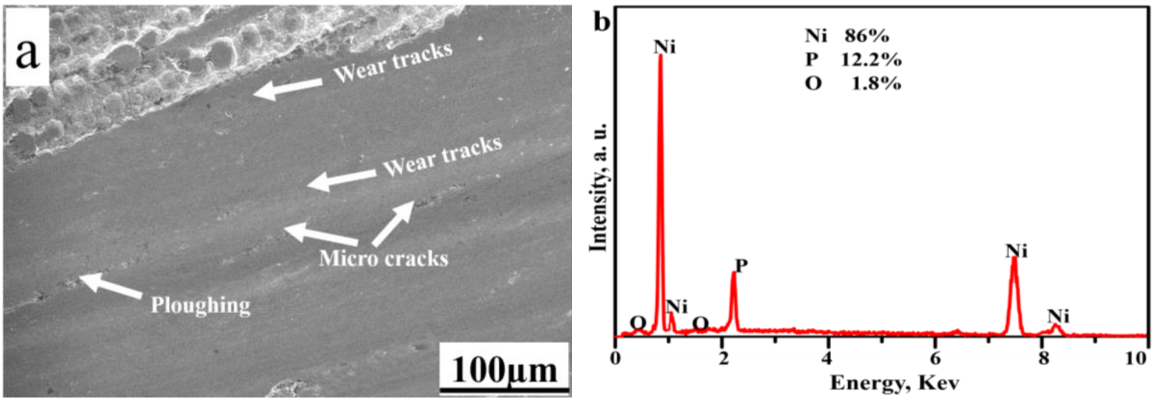

Figure 8.14 *(a) The worn surface image of as-deposited duplex electrolytic Ni-W-P/Ni-P coating and (b) EDX plot*

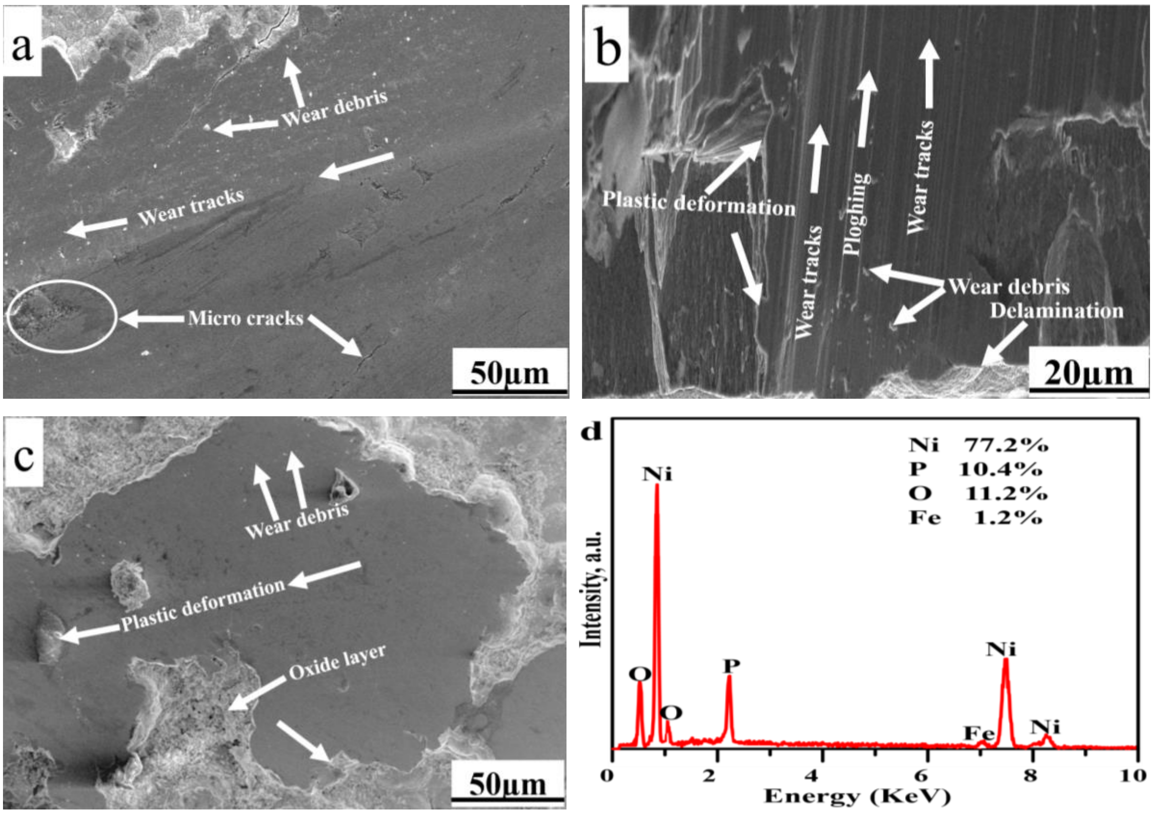

Figure 8.15 *(a) Duplex electrolyte Ni-W-P/Ni-P coating worn image at 400°C, 1h (b) at 400°C,4h (c) at 600°C, 2h and (d) EDX plot at 600°C, 2h*

At 400°C for a duration of 1h, Figure 8.15a reveals the presence of a few microcracks on the worn surface of Ni-W-P/Ni-P coating. Additionally, wear debris appears to be fused to the surface due to contact pressure during sliding, with dispersed wear debris and wear tracks evident. Adhesive and abrasive wear typically generate more dispersed wear debris compared to other types of wear. At 400°C, 4h duration, on the worn surface, a few plastic deformations are also visible (Figure 8.15b). Ploughing can be seen as long, narrow grooves on the worn surface. The grooves are typically parallel to the direction of sliding. The depth of the grooves can vary depending on the severity of the wear. The sample showed greater wear debris, which is a result of sliding wear. The top surface of the sample also exhibits wear delamination (see Figure 8.15b). At heat treatment condition of 600°C, 2h, a significant amount of material is found to be sheared off in the contact area, indicating wear debris formation (Figure 8.15c). An oxide layer and plastic deformation are visible on the worn region. Figure 8.15d indicates the presence of a small amount of oxygen on the sample surface, along with around 1.2% of iron detected at 600°C, 2h heat treatment condition.

Figure 8.16 presents the SEM image at 800°C for 4h, accompanied by the EDX analysis. At elevated temperatures, the rubbed surface exhibits signs of plastic deformation, micro-cutting, cracks, and other related features. Plastic deformation can manifest in various forms such as slip or shearing. Additionally, delamination is observed on the worn surface, indicating the separation of layers from the surface due to the wear process. The elevated temperatures can weaken the material, rendering it more prone to delamination. The substantial presence of oxygen, at 16.1% in the EDX result (refer to Figure 8.16b), indicates significant oxidation on the coated surface. Consequently, both abrasive and adhesive wear mechanisms contribute to the wear behaviour of the coated surface. Thus, it is evident that the wear mechanisms in both duplex coating systems are quite identical.

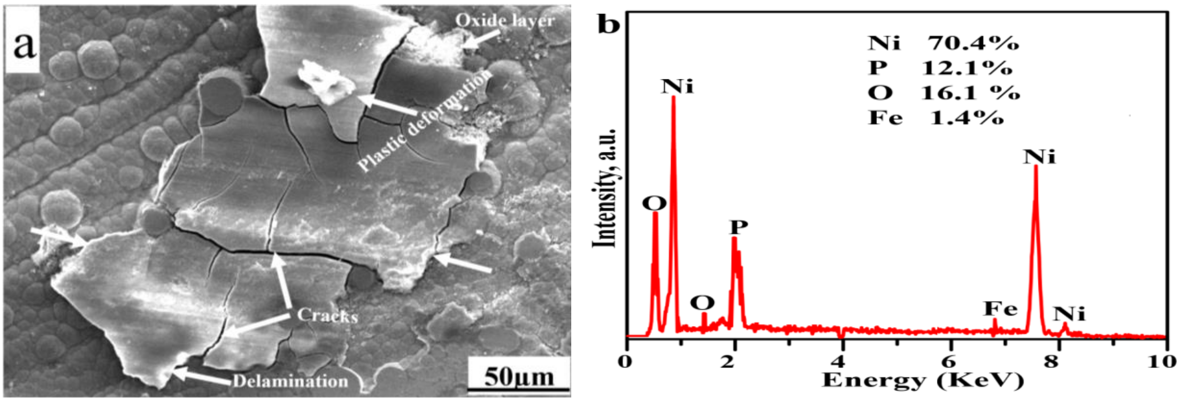

Figure 8.16 *(a) Duplex electrolytic Ni-W-P/Ni-P coating worn image of heat treatment at 800°C, 4h and (b) EDX plot*

8.2.6 Corrosion performance

Figure 8.17 presents the PDP curves for each coating. These plots exhibit a suitable Tafel region with distinct anodic and cathodic sections. Tafel extrapolation and Nyquist plots are utilized to determine the corrosion results, as outlined in Table 8.1. The PDP results for Ni-P/Ni-W-P coating indicate a shift of the corrosion potential towards the negative zone following heat treatment. Corrosion resistance is observed to decrease across all heat treatment cycles compared to the as-deposited coating (refer to Table 8.1). This decline in corrosion resistance can be attributed to the transformation from the amorphous structure of the as-deposited coating to a crystalline structure after heat treatment. The active sites present in the grain boundaries of the crystalline structure render it more susceptible to attack by corrosive media **(Chen et al., 2019).** It is noted that increasing the heat treatment temperature and heating duration for Ni-P/Ni-W-P coating leads to a reduction in the coating's E_{corr} (corrosion potential) value and an increase in its i_{corr} (current density) value. A lower E_{corr} and a higher i_{corr} value typically indicate increased susceptibility to corrosion. This suggests that factors beyond crystallinity may influence corrosion resistance. Passivation is one such factor, wherein a protective layer forms on the surface of the coated material, enhancing its resistance to corrosion. The passivation effect is commonly observed in electrodeposited Ni-W-P coatings. However, heat treatment can diminish this passivation effect, rendering the coatings more prone to corrosion.

Indeed, in Ni-W-P/Ni-P coating, corrosion resistance is enhanced at 400°C for all heat treatment cycles compared to the as-deposited coating. It's plausible that the amorphous structure of the as-deposited coating may crystallize after heat treatment. These crystallized phase structures might facilitate the passage of corrosive media through the coating's grain boundaries. However, the denser and more compact nature of the coating following heat treatment could contribute to this distinctive behaviour. Similar observations have been made for the electroless coatings in the previous chapter. The current duplex coating demonstrates significantly improved adhesion between the two layers during heat treatment. There is decrease in corrosion resistance for sample heat treated at 800°C. This may be due to microstructural heterogeneity because of the formation of oxides and other phases. Variations in composition and structure within the material can create localized differences in corrosion susceptibility, leading to accelerated corrosion in certain regions. Moreover, cracks are formed due to the thermal stresses (refer to Figure 8.1 and Figure 8.2) through which corrosive media may enter and the corrosion resistance may be compromised **(Barman et al.,**

2023). Overall, in as-deposited conditions, Ni-P/Ni-W-P coating outperforms Ni-W-P/Ni-P coating in the PDP test. However, in heat treatment conditions, Ni-W-P/Ni-P coating surpasses Ni-P/Ni-W-P coating across all heat treatment cycles.

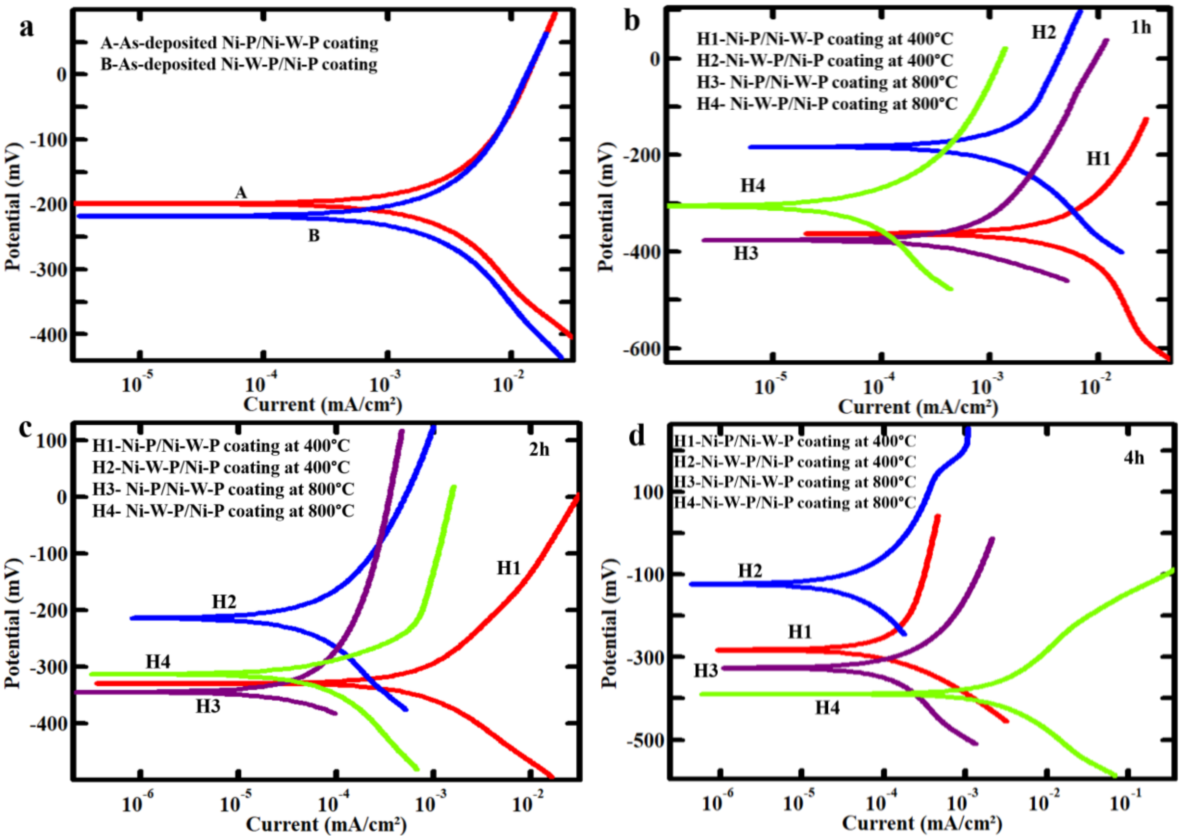

Figure 8.17 *Polarization plots for: (a) as-deposited coating; (b) heat-treated samples 1h duration; (c) heat-treated samples 2h duration; (d) heat-treated samples 4h duration*

Figure 8.18 presents Nyquist plots for both the as-deposited and heat treated duplex electrodeposited nickel coatings. While the shape of the curves is identical, their amplitudes differ. This indicates that the same underlying mechanism governs the corrosion behaviour of all samples, but the extent to which this mechanism is active varies. Similar observations have been reported in previous research **(Banerjee et al., 2022)**.

In the as-deposited state, Ni-P/Ni-W-P coating exhibited higher impedance values compared to Ni-W-P/Ni-P coating, as indicated in Table 8.1. This is further evidenced by Ni-P/Ni-W-P coating displaying a larger diameter in the Nyquist plot, suggesting superior corrosion resistance relative to Ni-W-P/Ni-P coating. Conversely, in heat-treated conditions, Ni-W-P/Ni-P coating demonstrated better performance than Ni-P/Ni-W-P coating, as previously noted. The charge transfer resistance (R_{ct}) value serves as a crucial indicator of corrosion resistance, with lower R_{ct} values corresponding to reduced corrosion resistance. After heat treatment, the R_{ct} value of Ni-P/Ni-W-P coating decreased across all conditions, except at 400°C for 4h (refer to Table 8.1). Consequently, the corrosion resistance of Ni-P/Ni-W-P coating diminished following heat treatment in all instances.

Table 8.1 Corrosion data obtained from Tafel extrapolation and Nyquist plots

Samples	E_{corr} **(mV)**	i_{corr} **(mA/cm^2) ×10^{-5}**	R_{ct} **(ohm. cm^2) ×10^5**	C_{dl} **(10^{-6}F)**
Ni-P/Ni-W-P coating, as-deposited	-198	67.44	0.258	35.71
Ni-W-P/Ni-P coating, as-deposited	-217	65.37	0.190	14.52
Ni-P/Ni-W-P coating, at 400°C 1h	-363	82.82	0.076	13.79
Ni-W-P/Ni-P coating, at 400°C 1h	-182	14.35	0.537	44.07
Ni-P/Ni-W-P coating, at 800°C 1h	-374	68.05	0.085	34.56
Ni-W-P/Ni-P coating, at 800°C 1h	-306	2.16	0.248	22.68
Ni-P/Ni-W-P coating, at 400°C 2h	-329	67.81	0.1725	30.12
Ni-W-P/Ni-P coating, at 400°C 2h	-212	1.883	0.2198	37.29
Ni-P/Ni-W-P coating, at 800°C 2h	-344	76.8	0.1202	60.7
Ni-W-P/Ni-P coating, at 800°C 2h	-313	2.778	0.147	60.05
Ni-P/Ni-W-P coating, at 400°C 4h	-283	4.143	0.482	53.38
Ni-W-P/Ni-P coating, at 400°C 4h	-124	1.843	0.649	20.19
Ni-P/Ni-W-P coating, at 800°C 4h	-324	3.582	0.073	2.256
Ni-W-P/Ni-P coating, at 800°C 4h	-388	101.71	0.058	1.324

In fact, the corrosion resistance of Ni-W-P/Ni-P coating is enhanced at 400°C for heat treatment cycles. However, at higher temperatures, such as 800°C, the corrosion resistance is diminished across all heat treatment cycles. Microstructural analysis reveals oxide formation on the coated surface and the development of microcracks at 800°C. This can be attributed to the increased brittleness of the coating induced by heat treatment. The presence of the oxide layer and microcracks creates pathways for corrosive ions to penetrate to the substrate, thereby reducing corrosion resistance. Nonetheless, corrosion resistance decreases with prolonged heat treatment time at 800°C. This decline may be attributed not only to oxide and fracture formation on the coating surface but also to increased thermal stress under these conditions. Notably, the lowest corrosion resistance is observed at heat treatment cycle of 800°C, 4h among all coated samples.

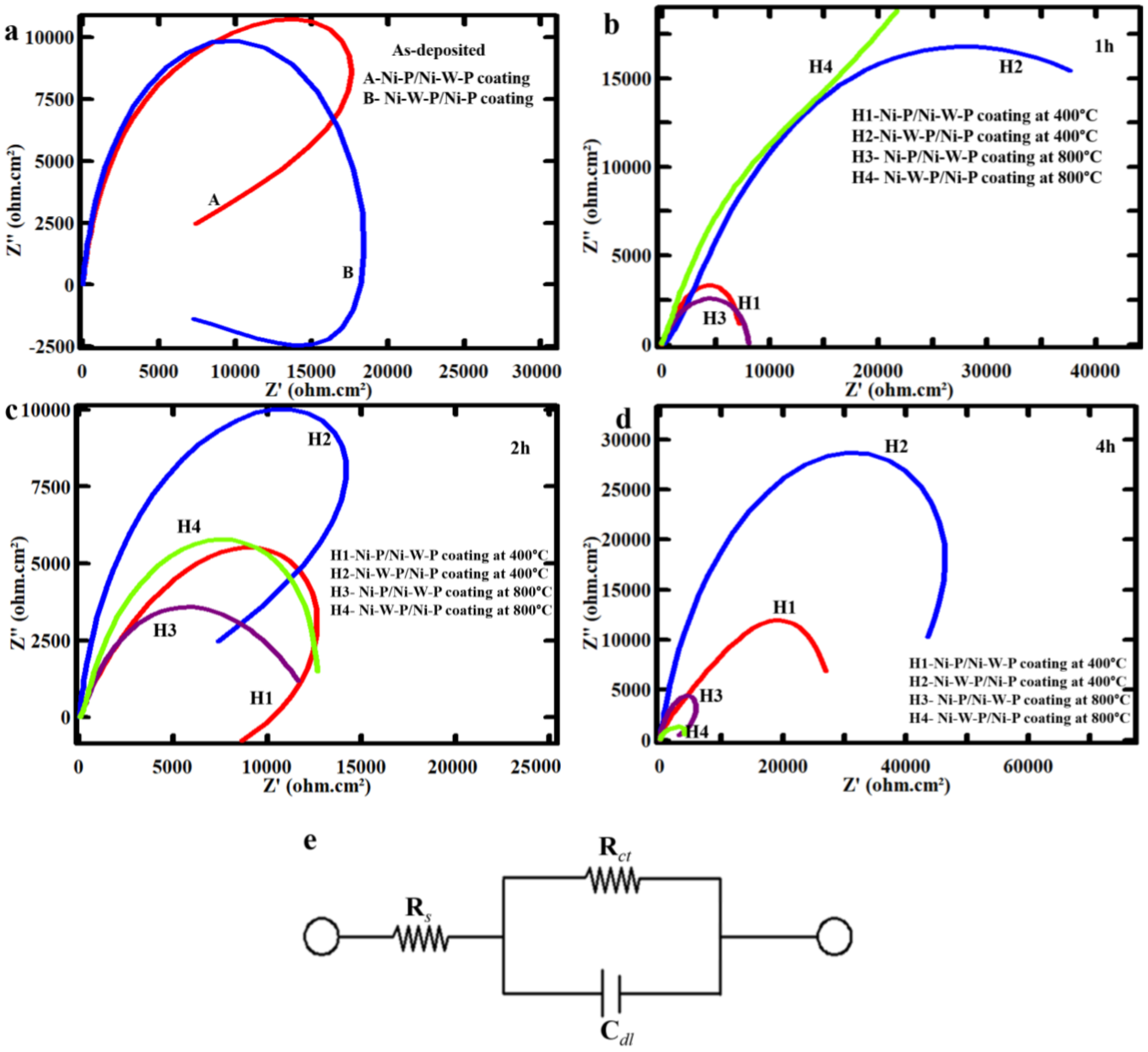

Figure 8.18 *Nyquist plots for (a) as-deposited condition; (b) heat-treated samples 1h duration; (c) heat treated samples 2h duration; (d) heat-treated samples 4h duration and (e) equivalent circuit diagram*

8.3 Comparison between duplex electroless and electrodeposited Ni-P/Ni-W-P coating

Comparing the performance of the current electrodeposited coatings with similar electroless Ni-P/Ni-W-P coatings is crucial for drawing meaningful conclusions from the present study. Table 8.2-8.5 present a concise comparison of microhardness, COF, wear rate, and corrosion performance in a sequential manner.

In terms of microhardness, the duplex electroless coating exhibits higher values than the electrodeposited coating in as-deposited and heat treatment conditions as shown in Table

8.2. This disparity can be attributed to several factors. Firstly, electroless deposition is a self-catalytic process, while electrodeposition requires an external power source. As a result, electroless deposition typically yields a finer grain structure and higher hardness. Moreover, the electroless process tends to be more uniform and less prone to defects compared to electrodeposition, contributing to enhanced hardness. Additionally, the Ni-W-P or Ni-P layer in an electroless coating is generally more homogeneous, as the electroless process is less sensitive to impurities, thereby resulting in higher hardness. In addition to these factors, the microhardness of a duplex coating can also be affected by the thickness of the individual layers, the composition of the layers, and the heat treatment conditions.

Table 8.2 Comparison of microhardness performance for duplex electroless and electrodeposited coatings

Duplex Coating Type	**Microhardness values ($HV_{0.1}$)**			
	As-deposited	Heat Treated (400°C,1h)	Heat Treated (400°C,2h)	Heat Treated (800°C,4h)
Electroless Ni-P/Ni-W-P	724	1440	1353	794
Electroless Ni-W-P/Ni-P	649	980	1189	637
Electrodeposited Ni-P/Ni-W-P	637	1029	985	745
Electrodeposited Ni-W-P/Ni-P	575	889	817	765

Although the COF values of both the deposits lie in the same range, they don't display any typical trend over one another (refer to Table 8.3). COF shows a lower value for higher heat treatment condition (800°C,4h) which may be due to grain coarsening combined with oxide formation which create a surface layer with low shear strength in both the coatings.

Table 8.3 Comparison of friction performance for duplex electroless and electrodeposited coatings

Duplex Coating Type	**Coefficient of friction**			
	As-deposited	Heat Treated (400°C,1h)	Heat Treated (400°C,2h)	Heat Treated (800°C,4h)
Electroless Ni-P/Ni-W-P	0.44	0.29	0.42	0.26
Electroless Ni-W-P/Ni-P	0.53	0.39	0.64	0.37
Electrodeposited Ni-P/Ni-W-P	0.41	0.64	0.65	0.19
Electrodeposited Ni-W-P/Ni-P	0.26	0.44	0.53	0.18

The wear rate analysis indicates that the duplex electroless coating outperforms the electrodeposited coating (refer to Table 8.4). This superiority can be attributed to the electroless deposition process, which yields a more uniform coating with a finer grain size.

The smaller grain size enhances the hardness of the plating, rendering it more resistant to cracking and spalling. Additionally, electroless nickel plating exhibits higher hardness compared to electrodeposited coating (refer to Table 8.2). This increased microhardness is the primary factor contributing to the reduction in wear. Consequently, the duplex electroless coating demonstrates superior wear resistance when compared to the electrodeposited coating.

Table 8.4 Comparison of wear results for duplex electroless and electrodeposited coatings

Duplex Coating Type	**Wear rate (10^{-5} mm^3.N^{-1}.m^{-1})**			
	As-deposited	Heat Treated (400°C,1h)	Heat Treated (400°C,2h)	Heat Treated (800°C,4h)
Electroless Ni-P/Ni-W-P	20.57	10.62	11.41	13.27
Electroless Ni-W-P/Ni-P	22.27	11.71	12.78	14.28
Electrodeposited Ni-P/Ni-W-P	22.45	12.64	13.44	17.05
Electrodeposited Ni-W-P/Ni-P	25.23	13.15	13.76	16.34

The corrosion potential (E_{corr}) value is higher for electrodeposited coatings than electroless coatings especially in as-deposited state as seen from Table 8.5. In fact, the systems with Ni-W-P as the outer layer has a higher E_{corr} value than the ones with Ni-P as the outer layer. This is definitely due to the presence of tungsten which is having excellent corrosion resistance **(Tiana et al., 2021).** For both the coatings, heat treatment appears to significantly influence the corrosion behaviour. Apart from the corrosion potential however, duplex electroless coatings seem to outperform the corresponding duplex electrodeposited coatings as far as the corrosion current density is concerned. Moreover, EIS results also suggest that electroless coating performs better than electrodeposited coating in all the heat treatment conditions considered in the current study (refer to Table 8.5). This may be due to high level of uniformity and homogeneity provided by the electroless process over electrodeposition process. In fact, the electrodeposited coating may contain impurities which may have come from the nickel electrode. These impurities may lead to a reduction in corrosion resistance. Besides, both types of coatings can adhere well to substrates when properly applied. However, electroless coatings tend to offer better adhesion. Moreover, electroless coatings typically exhibit lower porosity compared to electrodeposited coatings. Lower porosity reduces the pathways for corrosive agents to reach the substrate, thereby enhancing corrosion resistance.

Table 8.5 Comparison of corrosion performance for duplex electroless and electrodeposited coatings

Samples	**Heat treatment condition**	**E_{corr} (mV)**	**i_{corr} (mA/cm^2) ×10^{-5}**	**R_{ct} (ohm. cm^2) ×10^5**	**C_{dl} (10^{-6}F)**
Electroless Ni-P/Ni-W-P coating	As-deposited	-433	34.88	1.108	21.08
Electroless Ni-W-P/Ni-P coating		-537	24.73	1.047	21.45
Electrodeposited Ni-P/Ni-W-P coating		-198	67.44	0.258	35.71
Electrodeposited Ni-W-P/Ni-P coating		-217	65.37	0.190	14.52
Electroless Ni-P/Ni-W-P coating	At 400°C 1h	- 379	18.54	1.415	13.03
Electroless Ni-W-P/Ni-P coating		- 421	13.96	1.607	13.06
Electrodeposited Ni-P/Ni-W-P coating		-363	82.82	0.076	13.79
Electrodeposited Ni-W-P/Ni-P coating		-182	14.35	0.537	44.07
Electroless Ni-P/Ni-W-P coating	At 400°C 2h	-310	4.87	2.44	1.11
Electroless Ni-W-P/Ni-P coating		-381	3.75	1.88	0.106
Electrodeposited Ni-P/Ni-W-P coating		-329	67.81	0.1725	30.12
Electrodeposited Ni-W-P/Ni-P coating		-212	1.883	0.2198	37.29
Electroless Ni-P/Ni-W-P coating	At 800°C 4h	-357	8.18	2.31	1.48
Electroless Ni-W-P/Ni-P coating		-303	1.878	3.03	2.2
Electrodeposited Ni-P/Ni-W-P coating		-324	3.582	0.073	2.256
Electrodeposited Ni-W-P/Ni-P coating		-388	101.71	0.058	1.324

In general, both electrodeposited and electroless duplex coatings possess distinct characteristics. Electrodeposition facilitates the deposition of conductive materials with ease. However, it's worth noting that electrodeposition isn't suitable for nonconductive materials, whereas electroless deposition can accommodate them. Furthermore, the issue of bath decomposition is less prevalent in the electrodeposition process. When comparing coatings with similar thickness and composition, electroless coatings tend to outperform electrolyte coatings in mechanical, corrosion, and tribological performance.

8.4 Closure

The present chapter focuses on investigating duplex electrodeposited Ni-P/Ni-W-P coatings to evaluate the effect of heat treatment conditions on their microhardness, friction, wear, and corrosion resistance. It is observed that heat treatment temperature and duration has had tremendous impact on the microstructure of the coating which manifests in the performance of the coating. Optimal microhardness and lower wear rates are observed at 400°C temperature for 1h duration. However, at 800°C for 4h, duplex electrodeposited coatings display cracks and increased oxide layers, negatively impacting mechanical, tribological, and corrosion properties. The coating performance is also compared with similar duplex coatings developed through electroless methods. It is found that electroless coating displayed higher hardness and lower wear rate than electrodeposited coatings. Corrosion performance assessment reveals that duplex electroless Ni-P/Ni-W-P coatings outperform electrodeposited coatings.

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Chapter 9

Conclusions and Future Scope of Work

Outline of the chapter: *9.1 Conclusions from the Present Work, 9.2 Contribution of the Thesis and New Findings, 9.3 Future Scope of Work*

9.1 Conclusions from the Present Work

In this investigation, diverse duplex electroless nickel coatings were effectively developed on mild steel utilizing the dual bath technique. Furthermore, a duplex electrodeposition Ni-P/Ni-W-P coating was deposited through the electrolytic deposition technique. Comprehensive analyses encompassing microhardness, tribological, and corrosion studies were conducted on both the heat-treated and as-deposited samples. It was observed that both the temperature and duration of heat treatment significantly influenced the properties of the coating, thereby impacting its performance. Based on these findings, the following conclusions can be drawn from the present study:-

- The top and bottom layers exhibit excellent adhesion with no visible separation in the SEM micrographs. The duplex coatings are amorphous in their as-deposited state but transform into a crystalline structure upon heat treatment at or above 400°C. Higher heat treatment temperatures, such as 600°C and 800°C, lead to grain coarsening and oxide formation.

- The microhardness of all duplex electroless coatings increases significantly after heat treatment, peaking at 400°C in most cases. Beyond 400°C and with extended heat treatment, grain coarsening and oxidation reduce the microhardness. Ni-P/Ni-Mo-P coatings achieve optimal microhardness and minimal wear rate at 600°C. Ni-P/Ni-W-P coatings show the highest microhardness and wear resistance due to the strengthening effect of W in the Ni-P matrix. A strong correlation between microhardness and wear resistance is observed across all duplex coatings.

- The duplex coatings exhibit consistent friction behavior. Heat treatment significantly enhances wear resistance due to increased hardness. The wear mechanisms observed are a combination of abrasive and adhesive actions. Beyond hardness, wear behavior is influenced by various factors such as grain size, phase distribution, and the presence of oxide films.

- Corrosion studies reveal that duplex coatings offer substantial protection to mild steel substrates. Heat treatment enhances their corrosion resistance. Among them, Ni-P/Ni-Cu-P coatings demonstrate the highest corrosion resistance, while heat-treated Ni-P/Ni-Mo-P coatings show moderate performance.

- When compared to similar electrodeposited coatings with equivalent phosphorous content, electroless coatings performed better in terms of mechanical, tribological, and corrosion performance.

- The present set of duplex systems clearly outperforms their individual single-layer coatings in both tribological and corrosion performance.

9.2 Contribution of the Thesis and New Findings

This study focuses on evaluating the tribological and corrosion performance of duplex electroless nickel coatings with various ternary combinations. The key findings are as follows:

- **Corrosion Resistance:** Duplex coatings provide significant protection to mild steel substrates. Heat treatment enhances corrosion resistance but deteriorates at higher temperatures (e.g., 800°C) due to microcracks and oxide formation. Among all the coatings, Ni-P/Ni-Cu-P exhibits the best corrosion resistance.
- **Optimal Heat Treatment:** The 400°C, 1-hour heat treatment cycle is optimal, balancing tribological and corrosion properties. Higher temperatures or extended durations lead to oxide formation, degrading coating performance. Electroless coatings outperform similar electrodeposited coatings with equivalent phosphorus content in mechanical, tribological, and corrosion resistance.
- **Superior Duplex Coatings:** Duplex coatings with Ni-W-P, Ni-Cu-P, or Ni-Mo-P as the top layer outperform those with Ni-P as the outer layer. Ni-P/Ni-W-P, with Ni-W-P as the outer layer, demonstrates the best overall performance, making it suitable for applications requiring high tribological and corrosion resistance.

9.3 Future Scope of Work

This study focuses on investigating the mechanical, tribological, and corrosion performance of duplex electroless Ni-P/Ni-W-P, Ni-P/Ni-Cu-P, and Ni-P/Ni-Mo-P coatings. However, there is potential to explore other promising duplex electroless and electrodeposition nickel coatings, including Ni-P/Ni-B, Ni-P/Ni-W-B, Ni-P/Ni-Mo-B, Ni-P/Ni-W-Cu-P, among others, and evaluate their properties. The characterization of coatings in this study utilizes SEM, EDX, and XRD techniques. Future research could enhance the understanding of coating microstructure by employing additional characterization methods such as transmission electron microscopy (TEM), inductive coupled plasma (ICP) among others.

Modifying the composition of duplex electroless and electrodeposition nickel coatings offers avenues to enhance their mechanical, tribological, and corrosion performance. Following corrosion tests, SEM analysis can reveal the corroded surface, providing insights into the coating's behavior. Additionally, EDX analysis proves valuable in assessing corrosion performance by comparing the elemental composition of samples before and after corrosion, thus elucidating the protective efficacy of the coatings.

Quantifying the adhesion between layers can be achieved through scratch tests, providing valuable insights into the tribological behavior of duplex coatings. Such tests help assess the integrity and cohesion of the layers, offering a deeper understanding of their performance under mechanical stress.

Therefore, this field remains ripe for exploration, presenting vast opportunities for the development of multifunctional duplex and multilayer coatings that can effectively meet the diverse needs of industries. Moreover, these innovations hold promise for scalability, paving the way for widespread industrial applications.

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Publications from the Thesis

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PAPER

Tribological and corrosion performance of duplex electrodeposited Ni-P/Ni-W-P coatings

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Abstract

The present research investigates the properties of duplex electrodeposited Ni-P/Ni-W-P coatings consisting of Ni-P and Ni-W-P as inner layers alternately. This study aims to examine how various heat treatment conditions affect the mechanical, tribological, and electrochemical properties of the coatings.The results show that the heat treatment temperature and duration have a profound influence on the coating's microstructure, which significantly affects its overall performance. Optimal microhardness and lower wear rates are observed at 400 °C temperature for 1 h duration. However, at 800 °C for 4 h, duplex electrodeposited coatings display cracks and increased oxide layers, negatively impacting mechanical, tribological, and corrosion properties. The Ni-W-P outer layer coating exhibited higher hardness and a lower wear rate compared to the Ni-P outer layer coatings. However, the assessment of corrosion behavior shows that Ni-P offers increased corrosion resistance, largely due to its ability to form a passive layer, which is further enhanced after heat treatment. When compared to their individual single-layer coatings, the present duplex coatings demonstrate superior overall performance.

1. Introduction

Electrodeposited nickel coating offers a flexible and cost-efficient method to enhance both the functionality and aesthetics of various materials across diverse industrial sectors, including automotive, aerospace, electronics, and medical devices, among others. This method allows for the uniform and rapid creation of different coatings on a large scale without significant expense [1, 2]. Over recent years, numerous electrodeposition techniques have been developed to increase the microhardness, corrosion resistance, and wear resistance of materials. Notably, electrodeposited Ni-P plating has gained significant traction in industries like electronics, automotive, and aerospace due to its excellent microhardness, friction, wear, and corrosion resistance [3]. As-deposited Ni-P coatings exhibit favourable electrochemical, mechanical, tribological, and catalytic properties, along with advantageous magnetic properties, contingent upon their composition and structure [4, 5]. Heat treated Ni-P coatings can achieve hardness levels exceeding those of hard chromium coatings [1]. However, for specialized industrial applications, binary Ni-P coatings may not always suffice. Hence, researchers have turned their attention to electrodeposited ternary alloys, which involve the incorporation of a third metal (such as W, Zn, Sn, Cu, Mo or Co) into the Ni-P electrolytic coating [6–10]. Electroless Ni-W-P coatings exhibit improved mechanical and tribological performance compared to Ni-P coatings, attributed to the presence of tungsten (W).

According to Aleksinas [11], a single type of coating is unable to meet the diverse physical, mechanical, and tribological demands of various applications. In the pursuit of superior combined characteristics, a new duplex coating strategy has been devised, comprising an inner layer optimized for corrosion resistance and an outer layer optimized for wear resistance [9]. The aim is to leverage the synergistic effects of both layers, maximizing their advantages while mitigating their individual drawbacks.This creates a final product with superior characteristics that in turn, opens up new possibilities for innovative applications.Developing a unique duplex

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PAPER

Tribological behavior of autocatalytic Ni-P based duplex coatings

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Keywords: duplex coatings, electroless nickel, friction, microhardness, wear, corrosion

Abstract

The present research evaluates the tribological performance of different Ni-P based duplex autocatalytic coatings (electroless coatings). The study investigates coatings including Ni-P/Ni-W-P, Ni-P/Ni-Mo-P, and Ni-P/Ni-Cu-P, examining various factors such as heat treatment conditions, sample composition, and their influence on the coatings' performance. The phase structure of the coatings is influenced by heat treatment parameters viz. temperature and duration as well as phosphorus content. Notably, at temperatures above 400 °C, all duplex coatings form a robust nickel phosphide phase, enhancing hardness and wear resistance which is almost double of that in as-deposited state in some cases. When subjected to a temperature of 400 °C for duration of 1 h, the Ni-P/Ni-W-P coating displays the highest microhardness (1440 $HV_{0.1}$) and the lowest wear rate ($10.62 \times 10^{-5}. mm^3. N^{-1}. m^{-1}$) among all the duplex coatings. In all three duplex systems, the wear typically involves a combination of abrasive and adhesive mechanisms. Among the as-deposited coatings, the Ni-P/Ni-Cu-P demonstrates higher corrosion potential (E_{corr} −302 mV) and lower corrosion current (i_{corr} 1.83×10^{-5} mA cm^{-2}) which imply superior corrosion resistance compared to the other duplex coatings. In the heat-treated state, the Ni-P/Ni-Mo-P duplex coating generally exhibits better corrosion resistance when compared to the other two types of duplex coatings.

1. Introduction

Autocatalytic nickel (EN) coatings developed by electroless technique coatings find extensive industrial applications such as electronics, textiles, aerospace, and food processing because of their remarkable mechanical and physical properties. These properties encompass high microhardness, resistance to corrosion, low wear rates, and anti-friction characteristics [1]. The EN coating is produced using an autocatalytic process, where a chemical substance already of bath (the reducing agent) causes the reduction of metal ions in the solution, leading to their deposition as a film. This process occurs without the need for an external electric current [2]. A key feature of EN coatings is their uniformity, ensuring that even holes or sharp edges in contact with the solution receive a consistent deposition [3]. EN coatings typically fall into three categories: pure nickel, composites, and alloy coatings. Pure electroless nickel coatings are no longer used due to the risks associated with the use of hydrazine as the reducing agent. Nickel alloy plating, produced from sodium borohydride or sodium hypophosphite-based electroless baths, has become quite popular.

Ni-P deposits exhibit outstanding tribological behavior and mechanical properties, even in corrosive environments [4]. Heat treatment of the coating forms crystalline nickel phosphide phases, contributing to its exceptional hardness [5, 6]. Ni-P plating performs well in terms of wear resistance at high temperatures [7]. The incorporation of elements such as W, Sn, Co, Mo, Fe, or Cu to create quaternary or ternary alloys further enhances their tribological behavior, corrosion resistance, and thermal stability [8–11]. For instance, Ni-Mo-P plating is often stronger and more corrosion-resistant than Ni-P plating [12]. Electroless composite deposits of Ni-P offer better wear resistance compared to binary Ni-P deposits [13]. Electroless Ni-P-ZnO composite coating has enhanced microhardness and corrosion resistance from Ni-P coating. However, with a high

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RESEARCH ARTICLE-MECHANICAL ENGINEERING

Mechanical, Tribological and Corrosion Performances of Autocatalytic Duplex Ni–P/Ni–Mo–P Coating

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Abstract

Duplex Ni–P/Ni–Mo–P coating systems were developed using electroless dual bath technique with Ni–P and Ni–Mo–P as outer layers alternately. The coatings were subjected to heat treatment at temperatures from 200 to 800 °C and for 1–4 h. The effect of heat treatment on the microstructural characteristics of the coatings was investigated using field emission scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction. The influence of heat treatment conditions on microhardness, friction, wear, and corrosion behavior was studied. Heat treatment has a beneficial impact on the coating with the detection of harder crystalline phases. In general, the duplex coating with Ni–Mo–P as the outer layer outperforms the coating where Ni–P was the outer layer. For Ni–Mo–P as the external layer coating, the highest microhardness, and lowest wear rate is obtained when heat treated at 600 °C temperature with an hour duration. This is due to the formation of hard crystalline phases like Ni_3P and Ni–Mo. However, when heat treated at higher temperature of 800 °C with 4 h, Ni–Mo–P exterior layer exhibits cracks and plastic deformation together with few oxide patches. This deteriorated the wear performance of the coating system. The wear mechanism displayed by both coatings indicates the occurrence of both adhesive and abrasive wear. The corrosion performance of the coatings improved upon heat treatment and was enhanced with increasing temperature and duration. Sample (Ni–Mo–P as outer layer) heat treated at 800 °C for 4 h displayed the highest corrosion potential ($E_{corr} = -241$ mV) and also significantly higher charge transfer resistance ($R_{ct} = 20.8\ \Omega\ cm^{-2} \times 10^5$) than others.

Keywords Electroless · Duplex coating · Friction · Wear · Hardness · Corrosion

1 Introduction

Autocatalytic electroless nickel (EN) coatings have gained widespread acceptance since being developed by Brenner and Riddle in the middle of the twentieth century [1]. Electroless Ni–P plating is well known for being extensively used in industry due to its benefits which include improved surface hardness, wear resistance, corrosion resistance its ease of use and inexpensive cost [2]. The properties of the coating are highly influenced by the source of nickel, complexing agent, bath temperature, reducing agent, buffers, pH level, and deposition time. Heat treatment (HT) can further improve the coating's characteristics. The binary Ni–P coating cannot always satisfy the demands of special industrial applications, particularly those requiring multifunctional abilities. As a result, several investigations have focused on the electroless ternary alloy, which is created by co-depositing a third metal like Sn, Mo, Cu, Zn, Co, and W into the Ni–P electroless deposit [3–5].

The properties of Ni–P alloy coating can be improved by the addition of Co, Mo, Cu, Fe, etc. [6–8]. The additional element is chosen based on the chemical and physical characteristics that need to be incorporated into the deposit. Although molybdenum and its alloys have a wide range of applications, electrochemistry makes use of them due to their high catalytic activity [8]. Electroless ternary Ni–Mo–P alloy coatings are frequently stronger and more corrosion resistant than binary electroless Ni–P alloy coatings, and they can also raise the crystallization temperature [9]. According to Aleksinas [10], it has become clear that one type of electroless nickel (EN) coating cannot possibly match all the physical, mechanical, and tribological requirements that

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Evaluation of Microhardness, Wear, and Corrosion Behavior of Duplex Ni-P/Ni-W-P Coatings

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Abstract: Electroless Ni-P/Ni-W-P coatings in the duplex form are deposited on mild steel substrates. These deposits were subjected to heat treatment with different temperatures (200 to 800°C) and for time periods of 1h & 4h. Heat treatment condition has a significant influence on the coating properties. The coatings' microhardness and wear resistance increase significantly when heat is treated up to 400°C temperature. However, there is a degeneration in the microhardness when the coatings are treated beyond 400°C and also for 4h duration. This is due to coarsening of grains together with the formation of oxides, as indicated by the microstructural studies. At a heat treatment temperature of 800°C for 4h, the coating exhibits cracks and tends to delaminate. The wear mechanism encountered during the sliding test under dry conditions and at room temperature is predominantly abrasive. The electrochemical-based corrosion studies indicate that corrosion resistance of the present duplex coatings increases after heat treatment which may be due to the coarsening of grains. Finally, the comparison is made between the performances of the present duplex coatings to the constituent binary coatings. Overall, it is found that upon being subjected to the optimal condition of heat treatment, the duplex coating presents an all-around performance that may be suitable for applications demanding both wear and corrosion resistance. This will lead to their application in bio-tribology-related applications.

Keywords: electroless; deposit; microstructure; heat treatment; friction; tribology.

1. Introduction

The electroless Nickel (EN) deposition procedure is widely practiced, providing several advantages over conventional coating techniques relevant to industries. Brenner and Riddell invented this method of deposition in 1946 [1]. The deposition process eliminates the need for electricity as it is an autocatalytic reduction process. EN coating has obtained popularity because of its uniformity, higher hardness, lower wear rate, and better corrosion resistance. EN coating is now considered an effective surface engineering technique for changing the physicochemical properties of the substrate surface. The coating can be homogeneously deposited on any irregular shape, surface, or geometry. Due to these aspects, Ni-P coatings are suitable for all industries, from food processing to aerospace [2]. Moreover, due to its deposition uniformity and moderate bio-compatibility, EN coatings have been applied to medical devices for protection against corrosion. Some medical components on which EN coatings have been applied include anesthesia delivery components, laryngoscope handles, radiation focus plates, radiation lead, etc. [3].

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Investigation of tribological and corrosion performance of duplex electroless Ni-P/Ni-Cu-P coatings

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ABSTRACT

To improve the hardness, wear, and corrosion resistance of substrate materials, the duplex electroless Ni-P/Ni-Cu-P coatings are developed on mild steel substrates. Two types of coatings are deposited with Ni-Cu-P and Ni-P layers once with Ni-Cu-P as the outer layer and subsequently with Ni-P as the outer layer respectively. Heat treatment is carried out at temperatures between 200 and 800°C. Heat treatment is found to significantly affect the coatings. The hardness is increased by about 43 % after heat treatment whereas friction and wear rate are reduced by about 50 % and 40 % respectively. Heat treatment at 400°C is found to be the best for tribological performance of the coatings. The microstructural tests show the formation of nickel phosphide which are responsible for improved hardness of the coatings after heat treatment. However, heat treatment at higher temperature lead to grain coarsening and oxide formation which affect the tribological performance of the coatings negatively. The coating with Ni-Cu-P as the outer layer shows better corrosion resistance ability due to the presence of copper which promotes the formation of passive layer.

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1. Introduction

In order to protect or change the surface characteristics based on need, coating is one of the widely utilized surface engineering approaches. Electroless nickel (EN) coating is one of the proven methods for improving mechanical, corrosion, and tribological properties of surfaces. Electroless nickel coating on mild steel protects it from corrosion and wear. This coating also improves the surface hardness of steel. Brenner and Riddell were the first to develop this type of coating in 1946 [1]. These coating is very popular because of its splendid hardness, better resistance to corrosion and wear as well as for consistent coating deposition. Electroless nickel coating is one of the best techniques to change the physical and mechanical properties of the surface of substrate materials. Electroless nickel coating can be uniformly deposited on any materials even with irregular shape and size. In this type of coating deposition, no electricity is required due to an autocatalytic reduction process. For these aspects, electroless Ni-P coating is very popular for all types of industries like automobile, electrical, aerospace, food processing industry, etc. [2]. For Ni-(high P) coating, the hardness values are reduced during superfluous annealing due to grain coarsening. Heat treatment of Ni-P coating at 800°C temperature and for an extended period did not provide satisfactory results in terms of tribological and mechanical properties. [3]. Alternatively, the addition of the third elements (like W, Co, Cu, Mn, Mo, etc.) in Ni-P coating provides better tribological and corrosion properties.

Incorporating copper into the coating may result in the enhancement of anti-corrosion qualities, thermal stability, paramagnetic stability as well as aesthetic properties. In comparison to binary Ni-P coatings, the ternary Ni-P-Cu coating achieves an improvement in corrosion resistance. The ternary Ni-Cu-P plating is better than Ni-P alloy plating [4–6]. As part of enhancing the capabilities of deposition, few researchers have developed duplex [7–8], multilayer [9], and graded coatings [10]. Duplex coating or multilayer coating shows the potential to outperform monolayer coatings due to various industrial applications. Duplex electroless nickel coatings often combine two different electroless nickel deposit types to produce a finished product that is superior to any single layer electroless nickel deposition. There are several instances of these coatings being used already in the metal finishing sector like duplex Ni-P/Ni-B, Ni-P/Ni–W-P, and Ni-P/Ni-Mo-P

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Technical report

Duplex electroless Ni-P/Ni-Cu-P coatings: Preparation, evaluation of microhardness, friction, wear, and corrosion performance

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Abstract

The current study focuses on the development of duplex Ni-P/Ni-Cu-P coatings by the electroless deposition method. Coatings are developed on mild steel substrates with Ni-Cu-P as the outer layer and Ni-P as the inner layer and vice versa. The coated samples are heat-treated at temperatures ranging between 200 to 800 °C during 1 and 4 h. Coated samples are characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The effect of heat treatment temperature and its time duration on the hardness, friction and wear behaviour of both coatings are evaluated and compared. This would help in understanding how heat treatment influences the duplex system of coatings and helps in identifying the suitable condition of heat treatment for optimal performance of the coating. It is observed that heat treatment has a positive influence over the coating performance, which is the best when treated under optimal temperature and time duration conditions. The corrosion behaviour of the coatings is also assessed with the help of electrochemical techniques, viz. potentiodynamic polarization and electrochemical impedance spectroscopy. The results show that the duplex coatings can provide substantial protection to the mild steel substrates. Heat treatment is also found to have a significant influence on the corrosion behaviour of duplex coatings.

Keywords

Mild steel; electroless nickel deposits; duplex coatings; heat treatment; physical properties; corrosion

Introduction

Electroless deposited nickel (EN) coating enhances corrosion and wear resistance, leaving a consistent, homogeneous nickel coating for high-precision products [1]. The coating may be applied to ferrous and nonferrous surfaces of any geometry or complicated shape. For these reasons, EN coatings are gaining popularity across various industrial applications. EN coating was originally invented in 1946 by Brenner and Riddell [2]. No electricity is required in this process and the coating happens due to an autocatalytic reduction process [3]. This enables a greater range of industrial

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Duplex electroless Ni-P/Ni-P-W coatings: Effect of heat treatment on tribological and corrosion performance

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ABSTRACT

The current study attempts to investigate the effect of heat treatment on duplex electroless Ni–P/Ni–W-P coatings. Duplex electroless Ni-P/Ni–W-P coatings are produced on mild steel and heat-treated for 2 h at temperatures ranging from 200 to 800 °C. A pin-on-disc arrangement is used to test the friction and wear characteristics of the as deposited and heat-treated coatings. The microstructural aspects are studied, viz. surface morphology, composition and the crystallographic structure. Heat-treatment at 400 °C for a two-hour duration produces the maximum hardness due to the formation of the crystalline nickel phosphide (Ni_3P) phase. The friction and wear performance of the coating seems to be diminishing at higher temperatures due to the formation of oxides and grain coarsening. Corrosion tests on duplex coatings reveal better corrosion resistance for coating with Ni–W-P as the outer layer.

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1. Introduction

Coatings are mostly used to protect the component surface against wear as well as corrosive environment. Electroless nickel (EN) coating is one of the popular deposition methods which yield uniform coating. Electroless Ni–P coatings has found industrial applications in several arenas like, automobile, aerospace, electro-chemical and electronics industries due to its properties viz. high hardness, ductility, high wear, and excellent corrosion resistance [1–6]. EN technique obtains uniform deposition without any special requirement for substrate materials. Electroless Ni-P alloy coating can be subdivided into three categories depending on the weight percent of P in the coating, i.e., low (1 to 5%) medium (5 to 8%), and high (above 9%) [7]. For Ni-(high) P deposition, amorphous microstructure is obtained [8–11]. But hardness of Ni-(high) P coatings is found to reduce during superfluous heat treatment due to the effect of grain coarsening. In fact, heat treatment at 800 °C temperature for a prolonged time duration on electroless Ni-P coating did not provide suitable tribological and mechanical properties [9]. Alternatively, adding a third element to Ni-P coating improves the properties of the coating. The ternary Ni-W-P alloy which includes the transition metal tungsten (W) provides better tribological and mechanical properties than the binary electroless Ni-P coating. Tungsten has a high melting point temperature; in addition of tungsten (W) in Ni-P coatings improved the higher temperature resistance in any type of nickel (Ni)-based deposition. Addition of ternary elements is also found to improve corrosion resistance of Ni-P coating [4–6].

Recently, few researchers have shifted their focus towards multilayer coating which is found to significantly improve physical, mechanical, and tribological properties of monolayer coatings. The electrodeposition technique is a proven methodology for the deposition of duplex, multilayer, and graded coatings. Duplex Ni-P/N-P-W coatings are employed in a variety of industries, including hydraulics, nuclear, machinery, automobile surfaces, computers, aircraft structures, pump parts, and engines, for their higher hardness and high wear and corrosion resistance. By using the double bath technique, duplex or graded electroless nickel coating is possible to prepare through consecutive immersions in the respective EN baths. Duplex Ni-P/Ni-B coating had been prepared and their microhardness, friction–wear, and corrosion resistance evaluation has been performed [8,12]. Ni-P/Ni–W-P coating was successfully plated with a smooth appearance which also provides higher corrosion resistance [13]. Ni-P graded coating has also been successfully prepared and characterized. Both graded and multilayer EN

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Role of heat treatment on the friction and wear behavior of duplex electroless nickel deposits

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ABSTRACT

In the present investigation, duplex electroless Ni-P/Ni-Cu-P and Ni-P/Ni–W-P coatings are deposited on mild steel specimens using the dual bath technique. Both the coatings are developed with Ni-P as the inner layer. The scanning electron microscope (SEM), X-ray diffraction techniques (XRD) and energy dispersive X-ray analysis (EDX) are used to characterize the duplex coatings at pre and post-heat treatment state. Heat treatment is carried out at a temperature range between 200 °C and 800 °C. The surface morphology of the as-deposited coatings is nodular. Grain growth and grain boundaries are clearly visible in heat treated coatings. The EDX of Ni-P/Ni-Cu-P and Ni-P/Ni–W-P coating showed the phosphorus content as 12% and 9% respectively indicating high-P deposits. The copper and tungsten content of the coatings are 10% and 3% respectively. XRD analysis of both the as-deposited coatings indicate amorphous phase while heat-treated ones have crystalline phase structure. The crystalline structure increases the hardness of coating along with its wear resistance. The friction and wear behavior are assessed by a pin on disc tribometer. Overall, it can be seen that Ni-P/Ni–W-P system performs better compared to Ni-P/Ni-Cu-P in terms of friction and wear. However, heat treatment at higher temperature has negative impact on both the coatings as far as the tribological behavior is concerned.

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1. Introduction

Electroless nickel (EN) plating on mild steel substrate is used to protect it from wear and corrosion. This deposition method was first invented by Brenner and Riddell in 1946 [1]. EN coating is very popular due to its low wear rate, high hardness, and anti-corrosion properties. It is an autocatalytic reduction process. Uniform coating can be developed on all types of substrates even with intricate shapes. For these features, monolayer electroless Ni-P coating has found widespread application in various industries like aerospace, construction, automobile parts, electrical parts, surgical parts, etc. [2]. The properties of EN coatings can be highly customized by application of heat treatment as well as incorporation of third elements. In fact, introducing elements viz. Mn, Cu, W, Co, Mo, etc. results in better tribological and anti-corrosion properties in binary EN coatings. Recently, few researchers have devoted attention towards multilayers [3] and duplex [4–7] coatings to improve mechanical, tribological and anti-corrosion properties. Duplex coatings are found to exhibit promising properties which need to be explored further.

The objective of the present investigation is to develop duplex electroless Ni-P/Ni-Cu-P and Ni-P/Ni-W-P coatings. Coated samples will be subjected to a series of heat treatment temperatures (200 °C to 800 °C) for 2-hour duration. The hardness value of coated samples is measured by Vickers microhardness tester. Various characterization approaches for microstructure evaluation would be employed viz. Scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and energy dispersive X-ray analysis (EDX). To evaluate the friction performance and wear behavior of the coating, dry sliding test is conducted on a pin-on-disc tribometer.

2. Experimental details

2.1. Deposition method

Duplex electroless nickel coating is deposited on mild steel substrate. Mild steel is chosen is chosen as the substrate as it is cheap

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Deposition of Duplex and Multilayer Electroless Ni–P/Ni–B Coating and Study of Their Wear Resistance

Palash Biswas, Suman Kalyan Das, and Prasanta Sahoo

1 Introduction

Electroless Nickel coating was initially developed by Brenner and Riddell [1]. Electroless deposition technique doesn't require electricity during deposition process. Electroless deposition method has experienced more popularity for industrial applications due to excellent tribological, electrical, mechanical and physical properties [2]. Producing homogeneous coatings with electroless deposition is possible which also exhibits high-quality adhesion on different substrate materials. Basically, electroless deposition method is carried out by a chemical reduction process. Here, reduction of metal ions occurs through autocatalytic way from aqueous solution containing source of metal ion, a reducing agent, stabilizers and operating in a specific pH value and temperature [3]. Electroless processes allow producing very uniform homogeneous coatings. Properties of the developed coating, deposition rate and structural nature predominantly depend on plating bath conditions and composition. During the deposition period, every parameter plays a specific role for the development of microstructure. Bath load and temperature is an effective parameter for higher deposition rate [4]. Electroless Ni–B-based coatings have better mechanical and tribological performance depending on the coating thickness while Ni–P coating provides the best corrosion resistance [5].

To increase corrosion resistance, alloying element like Zn, Mo, Cu, etc. [6–8] is added to electroless Ni–P and Ni–B deposits. However, researchers have also paid considerable attention to duplex Ni–P/Ni–B coating as well as multilayer coating deposition which combines the best of the mechanical and tribological properties of the individual deposits [9]. Wear rate is very low in the duplex coatings [10]. The present work involves with preparation of duplex Ni–B/Ni–P coating and multilayer

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