High Temperature Characterization of Electroless Tribological Coatings

M.Tech. Thesis

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **High Temperature Characterization of Electroless Tribological Coatings** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF MECHANICAL ENGINEERING, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2021 to June 2023 under the supervision of Dr. Satyajit Chatterjee, Associate Professor, Department of Mechanical Engineering, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date
AMAN KUMAR

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

02.06.2023

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AMAN KUMAR has successfully given his M.Tech. Oral Examination held on **26th MAY 2023.**

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With Regards

Aman Kumar

Dedicated

To

My Sister

Abstract

The aim of this M.Tech project is to develop a lubricative coating via an electroless method that can withstand its properties at higher temperatures. Wear and scratching reduce the lifespan of the components significantly. Coating applied on the substrate improves the service life. Electroless plating can create nickel-based protective coatings with excellent mechanical and tribological properties. Among the different compositions explored over the years, borohydride reduced electroless nickel coatings have shown a lot of promise in a variety of technological applications. Hardness, wear resistance, corrosion resistance, and other physical qualities of binary Ni-B electroless coatings are improved by adding tungsten (W) to the matrix. Hexagonal-boron nitride (hBN) is a solid lubricant that can sustain lubricity at extremely high temperatures. Our research focuses on the use of hBN in Ni-B based electroless tribological coatings. When Ni-B-W-hBN is heat treated, it shows a considerable improvement in sliding wear and scratch resistance when compared to other coatings.

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Chapter 1 Introduction and Literature Survey

1.1 Introduction

The purpose of this chapter is to introduce various engineering applications at higher temperature. Several applications of coatings at higher temperatures in tribological situations have also been discussed along with their deposition methods. Literature survey and problem definition along with the project objective and the work plan are presented after that.

1.2 Engineering applications at high temperatures

Engineering applications at high temperatures involve the study and application of materials, lubrication, and surface coatings that can withstand and perform well, under extreme thermal conditions. Tribology is the science and engineering of interacting surfaces in relative motion, including friction, wear, and lubrication. High-temperature tribology finds applications in various fields, such as aerospace, energy generation, automotive, and manufacturing processes [1,2,3]. Here are some examples of engineering applications at high temperatures in tribological situations:

1. **Gas Turbines:** Gas turbines used in power generation and aircraft propulsion operate at high temperatures. These systems require robust materials for components like turbine blades, shafts, and bearings, which can withstand high temperatures, resist wear, and exhibit low friction under high-speed conditions.

2. **High-Temperature Bearings:** where bearings are exposed to high temperatures, such as in steel mills, glass manufacturing, or oven conveyors, specialized bearing materials and lubricants capable of operating at elevated temperatures are employed. Ceramic or self-lubricating materials with high-temperature stability are used to minimize wear and reduce friction.

3. **Automotive Engines:** Internal combustion engines generate substantial heat, and components such as pistons, piston rings, cylinder liners, and valves are subjected to high temperatures and sliding contact. Coatings, like thermal barrier coatings (TBCs), are applied to these components to protect them from excessive heat and minimize wear and friction.

4. **High-Temperature Seals:** Sealing systems used in high-temperature environments, such as gas and steam turbines, require materials that can maintain their integrity under extreme temperatures while providing effective sealing. Materials like graphite, ceramics, and specialized elastomers are used in high-temperature seals to ensure proper functioning and prevent leakage.

5. **Metal Forming:** In metal forming processes like hot forging and extrusion, materials are processed at elevated temperatures. The selection of die materials and lubricants is crucial to ensure reduced friction, prevent wear, and maintain dimensional accuracy. Advanced coatings and solid lubricants are often used to enhance tribological performance in these applications.

6. **High-Temperature Cutting and Machining:** Cutting tools that are used in high-temperature machining applications, such as turning, milling, or drilling of super-alloys, need to withstand the extreme temperatures generated during the process. Coatings with high-temperature resistance, such as titanium nitride (TiN) or diamond-like carbon (DLC), are applied to cutting tools to enhancetheir wear resistance and lower the friction.

7. **High-Temperature Sliding Contacts:** Various industrial processes involve sliding contacts at high temperatures, such as conveyors, kilns, and furnaces. Lubricants and solid lubricant coatings, such as molybdenum disulfide (MoS_2) or graphite, are used to lower friction, prevent seizure, and protect the contacting surfaces.

In all these applications, extensive research and development are conducted to design and optimize materials, lubricants, and coatings that can withstand high temperatures, exhibit excellent tribological properties, and ensure reliable operation under extreme conditions.

1.3 Application of coatings

Coatings have a broad range of applications across various industries and sectors.These are just a few examples of the diverse applications of coatings. Coatings play an important role in improving the functionality, durability, and aesthetics of various products and surfaces in numerous industries[4,5,6,7,8].

Here are some common applications of coatings:

1. **Protective Coatings:** One of the primary uses of coatings is to provide protection to surfaces from corrosion, wear and tear, chemicals, UV radiation, and other environmental factors. Protective coatings are commonly used in various industries such as automobile, aerospace, construction, and marine.
2. **Decorative Coatings:** Coatings are often applied to enhance the appearance and aesthetics of surfaces. Decorative coatings are used in industries such as architecture, interior design, furniture, and consumer products.
3. **Thermal Barrier Coatings:** These coatings are designed to provide thermal insulation to surfaces, protecting them from high temperatures and reducing heat transfer. They are used in applications such as gas turbines, aerospace engines, and exhaust systems.
4. **Conductive Coatings:** Coatings with conductive properties are used to provide electrical conductivity or electromagnetic shielding to

surfaces. They find applications in electronics, telecommunications, automotive components, and aerospace industries.

5. **Lubricant Coatings:** Coatings can be fabricated with lubricating properties with a view to minimize friction and wear between the moving parts. They are used in various mechanical systems, such as engines, bearings, gears, and cutting tools.

1.4 Coatings for high temperature lubrication applications

When it comes to high-temperature lubrication, there are several types of coatings that can be used to improve the performance and service life of lubricated components. These coatings are designed to withstand elevated temperatures and provide effective lubrication in demanding environments. Here are some commonly used coatings for high-temperature lubrication:

Table 1: List of coatings with their working temperature range, lubricious phase and the deposition method.

Coatings	Method of coating	Lubricant Phases	Operational range	Ref
CrN-Ag coating	Magnetron sputtering	Ag	600°C	[9]
CrN /Mo_2N multilayer	Magnetron sputtering	Due to oxidation of MoO_3	400-600°C	[10]
Yttria-stabilized zirconia (YSZ) nanocomposite coatings	Magnetron sputtering and pulsed laser hybrid mode	Ag	700°C	[11]
TiN Coating	Magnetron sputtering	Magneli phases of Ti oxides	700°C	[12]
VN coating	Magnetron sputtering	Magneli phases of vanadium oxides	700°C	[13]
In625-Cr_2O_3-Ag coatings	Cold spraying	Ag	1000°C	[14]
Cu-Mo coating	Ion beam deposited	Oxide phases $CuMoO_4$ and MoO_3	530°C	[15]
aromatic thermosetting polyester (ATSP) coating	electrostatic spray deposition (ESD)	PTFE	300°C	[16]
nano-Cu/h-BN/Ni60	Laser cladding	hBN	600	[17]

1.5 Solid lubricants for high temperature applications

Solid lubricants are materials that reduce friction and provide lubrication in applications where liquid lubricants may not be suitable, such as high-temperature environments. These lubricants can withstand elevated temperatures and offer improved lubrication properties in extreme conditions. Here are some commonly used solid lubricants for high-temperature applications[18,19,20].

1. **Graphite:** Graphite is a widely used solid lubricant due to its excellent lubricating properties at high temperatures. It forms a self-lubricating film on surfaces, reducing friction and wear. Graphite can handle temperatures up to approximately 800°C (1472°F).

2. **Molybdenum Disulfide (MoS_2):** MoS_2 is another popular solid lubricant for high-temperature applications. It provides a low-friction coating and offers good lubrication properties even under extreme pressures and temperatures up to approximately 400°C (752°F).

3. **Tungsten Disulfide (WS_2):**Like MoS_2, WS_2 is a solid lubricant which forms a low-friction film on surfaces. It has exceptional lubrication properties at high temperatures and can withstand temperatures up to approximately 500°C (932°F).

4. **PTFE (Polytetrafluoroethylene):** PTFE, commonly known as Teflon, is a versatile solid lubricant with excellent chemical resistance and low friction properties. It can be used in high-temperature applications up to approximately 260°C (500°F).

5. **Hexagonal Boron Nitride (hBN):**hBN is a lubricious ceramic material that offers good lubrication and high-temperature stability. It can withstand temperatures up to approximately 900°C (1652°F) and provides low friction in various applications.

It's important to note that while solid lubricants can withstand high temperatures, their performance may vary depending on the specific application, load, speed, and other factors.

1.5.1 Decomposition of solid lubricants

Decomposition of solid lubricants refers to the breakdown or chemical transformation of these materials under certain conditions, leading to changes in their lubricating properties. The decomposition of solid lubricants can occur due to several factors, including high temperatures, mechanical stresses, chemical reactions, or environmental conditions. Different types of solid lubricants may decompose in distinct ways, depending on their composition and properties. Here are some common examples.

Table 2: Solid lubricants and their working temperature range

Solid Lubricants	**Working Temperature Range**	**Ref.**
Graphite	500°C	[17]
Molybdenum Disulfide (MoS_2)	300 °C	[21]
Tungsten Disulfide (WS_2)	540°C	[22]
Hexagonal Boron Nitride (hBN)	1000°C	[23]

Hexagonal boron nitride (hBN) is indeed known for its exceptional thermal stability and its ability to withstand high temperatures. hBN is a two-dimensional material composed of alternating boron and nitrogen atoms arranged in a hexagonal lattice structure, similar to grapheme [24]. One of the remarkable properties of hBN is its high thermal conductivity. It has been found to have a thermal conductivity comparable to that of grapheme, making it an excellent heat conductor. This property allows hBN to efficiently dissipate heat, making it suitable for various high-temperature applications[25].

hBN can withstand temperatures well above 1000 degrees Celsius without undergoing significant degradation. It remains stable and retains its structural integrity at such elevated temperatures, making it an ideal material for use in extreme thermal environments[26].

It's worth noting that while hBN is highly resistant to high temperatures, its properties and behavior can still be influenced by other factors such as the surrounding environment, impurities, and defects. However, in general, hBN demonstrates excellent thermal stability and can sustain high temperatures effectively.

1.5.2 Application of hBN in Tribological Coatings

Hexagonal boron nitride (hBN) is a versatile material that has gained significant attention in various fields, including tribology. Tribological coatings are used to minimize friction, wear, and enhance the durability of surfaces in contact. hBNexhibits excellent lubricating and anti-adhesive properties, making it a promising candidate for tribological coatings. Here are some key applications of hBN in tribological coatings[27,28,29,30].

1. **Solid Lubricant Coatings:**hBN can be used as a solid lubricant in coatings to minimize friction and wear. The lamellar structure of hBN provides excellent lubricating properties, even at high temperatures. It forms a thin film between the mating surfaces, reducing direct contact and minimizing wear.
2. **Protective Coatings:** hBN can be used as a protective coating to reduce wear and corrosion on surfaces. Its strong chemical stability and oxidation resistance make it suitable for protecting surfaces in harsh environments.
3. **Cutting Tool Coatings:** hBN can be used as a coating on cutting tools, such as drills, inserts, and end mills, to enhance their performance and tool life. The low friction and high thermal stability

of hBN coatings help reduce heat generation and tool wear during machining processes.

4. **High-Temperature Applications**: hBN coatings can withstand high temperatures, making them suitable for applications where conventional lubricants fail. They can be used in high-temperature environments, such as aerospace components, turbines, and bearings, to minimize friction and wear.

It's worth considering that the specific application of hBN in tribological coatings may vary depending on the requirements of the particular industry or application. Researchers and engineers continue to explore and develop new techniques to optimize the use of hBN in tribological coatings for various purposes.

These are the few coatings having hBN as solid lubricants.

Table 3: Processes for coating fabrication, coatings having hBN as solid lubricants

Coating	Solid Lubricants	Process of Coating Fabrication	Ref.
Nano -Cu/h-BN/Ni60	hBN	Laser Cladding	[31]
TiB2–TiN–SiC-hBN		Laser Assisted Processing	[32]
Ni-B- hBN		Electro Deposition	[33]
Ni-P- hBN		Electroless Deposition	[34]

1.6 Methods of coatings deposition suitable for tribological situation

In tribological situations, where surfaces are subjected to friction, wear, and corrosion, it is important to apply coatings that can provide enhanced protection and reduce friction. There are several coating deposition methods commonly used in tribological applications. Here are some of the main methods:

1. **Physical Vapor Deposition (PVD):** PVD techniques involve the deposition of a thin film coating by vaporizing a solid material and condensing it onto the substrate surface. Common PVD methods used in tribology include:

    - Sputtering: This method involves bombarding a target material with high-energy ions, causing atoms to be ejected from the target and deposited onto the substrate.

    - Evaporation: It involves heating the target material in a vacuum to generate vapor, which condenses on the substrate surface.

2. **Chemical Vapor Deposition (CVD):** CVD is a process where a thin film is deposited by a chemical reaction of vaporized precursor molecules. These molecules react on the substrate surface to form a solid coating. CVD methods used in tribology include:

    - Plasma-enhanced CVD (PECVD): It involves using plasma to enhance the chemical reactions and promote the deposition of the coating.

    - Low-pressure CVD (LPCVD): It operates at lower pressures and temperatures compared to other CVD methods.

3. **Electroplating:** Electroplating is an electrochemical process that involves depositing a metal coating onto a conductive substrate. The substrate acts as the cathode in an electrolytic cell, and the metal to be plated acts as the anode.

4. **Electroless:** Electroless coating deposition, also known as autocatalytic plating, is a process used to deposit a metal or alloy coating onto a substrate without the need for an external electrical current. Unlike electroplating, which relies on an applied electrical current to drive the deposition process, electroless coating deposition

occurs through a chemical reaction between the substrate surface and a plating solution.

But Electroless coating deposition methods offers several advantages in tribological situation. It enables uniform deposition on complex shapes and internal surfaces, providing excellent coverage even in hard-to-reach areas. It also eliminates the need for an external power source, making it suitable for coating non-conductive materials. Electroless coatings can improve the substrate's corrosion resistance, wear resistance, solderability, and electrical conductivity, among other properties[35].

1.6.1 Eelectroless coating deposition method

Electroless coating, also known as autocatalytic plating, is a method of depositing a thin layer of metal or other material onto a substrate without use of electrical current. Unlike electroplating, which requires an electrical power source to drive the deposition process, electroless coating relies on a chemical reaction to initiate and sustain the coating process [36].

1.6.1.1 The electroless coating process involves several steps:

1. **Surface Preparation:** The substrate, typically made of metal or a non-conductive material like plastic, is thoroughly cleaned and prepared to remove any contaminants or oxide layers. This step ensures good adhesion between the substrate and the coating material.

2. **Activation:** The cleaned substrate is then treated with a chemical activation solution, often containing a strong acid or a metal salt. This step creates a catalytic surface on the substrate that promotes the deposition of the coating material.

3. **Coating Deposition:** The activated substrate is dipped in an electroless plating bath, which contains a solution of metal ions or other desired coating material. The plating bath also contains a reducing agent, usually a chemical such as formaldehyde or sodium

hypophosphite. The reducing agent reacts with the metal ions and initiates a redox reaction, causing the metal to get deposited on the substrate. The coating material forms a uniform layer on the entire surface, including recesses and complex geometries, due to the autocatalytic nature of the process.

4. **Post-treatment:** After the desired thickness of the coating has been achieved, the substrate is typically rinsed and subjected to post-treatment processes, such as rinsing in deionized water and drying. Additional steps like heat treatment or surface finishing may be performed to enhance the properties of the coating or improve its adhesion to the substrate.

1.6.1.2 Industrial Application of electroless coating

Electroless coating, also known as autocatalytic coating, is a plating process that deposits a thin layer of metal onto a substrate without the need for an external electrical power source. This method offers several advantages over traditional electroplating, such as uniform coating thickness, the ability to coat complex shapes, and improved corrosion resistance. Electroless coating finds numerous industrial applications across various sectors. Here are some common examples[37].

1. **Electronics and Electrical Components:** Electroless coatings are widely used in the electronics industry for applications, such as printed circuit boards (PCBs), connectors, and contacts. The coatings provide protection against corrosion, improve solderability, and enhance electrical conductivity.

2. **Automotive Industry:** Electroless coatings are used extensively in the automotive sector for various purposes. They are applied to components, such as fuel injectors, pistons, cylinders, and brake calipers to improve wear resistance, reduce friction, and prevent corrosion.

3. **Aerospace and Defense:** Electroless coatings play a crucial role in aerospace anddefense applications. They are used for coating components like turbine blades, engine parts, aircraft landing gear, and firearms. The coatings provide protection against wear, extend c component life, and enhance performance.
4. **Oil and Gas Industry:** Electroless coatings are utilized in the oil and gas industry to protect equipment and components from corrosion, particularly in harsh environments. Coatings are applied to valves, pipes, fittings, and other critical infrastructure to improve their durability and resistance to chemical exposure.
5. **Chemical Processing:** Electroless coatings find application in chemical processing plants where components encounter corrosive chemicals. Coatings applied to equipment such as tanks, reactors, and heat exchangers provide chemical resistance and prevent degradation.

These are just a few examples of the industrial applications of electroless coating. The versatility and unique properties of electroless coatings make them suitable for a wide range of industries where protection against corrosion, wear resistance, and improved performance are essential.

1.6.1.3 Some common types of electroless coatings:

1. **Electroless Nickel (EN):** Electroless nickel coatings provide outstanding corrosion resistance, wear resistance, and solderability. They are commonly used to enhance the durability and functionality of various components in industries such as automotive, aerospace, electronics, and oil and gas[38].

2. **Electroless Copper (ECu):** Electroless copper coatings are primarily used in the electronics industry for printed circuit boards (PCBs). They help create conductive pathways and provide a protective layer for the underlying substrate[39].

3. **Electroless Gold (EG):** Electroless gold coatings offer excellent corrosion resistance, electrical conductivity, and solderability. They are commonly used in electronics, telecommunications, and semiconductor industries for contacts, connectors, and plating on various substrates[40].

4. **Electroless Silver (EAg):** Electroless silver coatings provide high electrical conductivity and exceptional solderability. They find applications in electronics, telecommunications, and RF/microwave industries for their excellent electrical performance and thermal stability [41].

5. **Electroless Cobalt (ECo):** Electroless cobalt coatings provide excellent wear resistance and high-temperature oxidation resistance. They are used in applications such as gas turbine engines, cutting tools, and wear-resistant surfaces [42].

These are just a few examples of electroless coatings. There are also specialized electroless coatings available for specific applications, such as electroless alloys, composite coatings, and other customized formulations. The choice of electroless coating depends on the desired properties, substrate material, and the intended application.

1.7 Choice between electroplating and electroless plating

Electroplating and electroless plating are two different processes used to deposit a layer of metal onto a substrate. The choice between electroplating and electroless plating depends on the specific requirements of the application.Electroplating involves the use of an electric current to deposit a metal coating onto a substrate. It requires a conductive substrate and involves immersing the substrate in an electrolyte solution containing metal ions. When a current is applied, the metal ions are reduced and deposited onto the substrate. Electroplating is commonly used in a broad range of applications, including improving the appearance, corrosion resistance, and wear resistance of a substrate [43].

On the other hand, electroless plating does not require the use of electric current. It is an autocatalytic process in which a metal layer is deposited onto a substrate through a chemical reaction. The reaction occurs between the substrate and a reducing agent in a solution containing metal ions. Electroless plating is often used for substrates that are non-conductive or have complex shapes where it is difficult to apply an electric current [36].

1.7.1 Few coatings require electroplating deposition method only.
Iron (Fe) and aluminum (Al), the reason they are primarily electroplated rather than electroless plated is due to their inherent properties and the feasibility of the plating processes.

Iron (Fe)is a conductive metal, and electroplating is a well-established and efficient method for depositing iron onto various substrates. Electroplated iron coatings provide excellent corrosion resistance and are commonly used in applications such as automotive parts, machinery components, and decorative finishes [44].

Aluminum (Al), on the other hand, has a strong affinity for oxygen, which forms a protective oxide layer on its surface. This oxide layer makes it challenging to initiate the electroless plating process since the reducing agents used in electroless plating may have difficulty breaking through the oxide layer to deposit the metal onto the substrate. Therefore, electroplating is the preferred method for depositing a layer of aluminum onto a substrate[45].

In summary, while electroplating requires a conductive substrate, it is the preferred method for depositing iron and aluminum due to their properties and the effectiveness of the electroplating process. Electroless plating, although suitable for certain substrates, may not be as feasible or efficient for these metals.

1.8 Reduction Potential

Reduction potential, also known as redox potential or electrode potential, is the measure of the tendency of a chemical species to gain electrons and undergo reduction. It quantifies the ability of a species to be reduced or to act as an oxidizing agent. Reduction potential is typically measured in volts (V) and is relative to a reference electrode [46, 47, 48, 49].

The reduction potential is a fundamental concept in electrochemistry and is used to determine the feasibility and direction of redox reactions. It provides information about the thermodynamic favorability of a reaction and helps predict the flow of electrons in an electrochemical cell.

The reduction potential of a half-reaction is represented by the symbol E°, where the superscript "°" indicates standard conditions. Standard conditions refer to a temperature of 25 degrees Celsius (298 K), a pressure of 1 atmosphere, and concentrations of 1 mole per liter for all species involved in the half-reaction.

The reduction potential of a half-reaction can be positive, negative, or zero. A positive reduction potential indicates that the species has a greater tendency to be reduced and acts as an oxidizing agent. A negative reduction potential indicates a greater tendency to be oxidized and acts as a reducing agent. A reduction potential of zero means that the species is in equilibrium with its oxidized and reduced forms.

Reduction potentials can be experimentally determined using a variety of methods, such as electrochemical cells and potentiometric measurements. These values are often tabulated and used as reference values for comparing the reactivity of different species in redox reactions.

It's important to note that reduction potentials are specific to the conditions in which they are measured, including temperature, pressure, and concentrations of species.

1.9 Tribology

Tribology is the scientific study of interacting surfaces in relative motion, particularly with respect to friction, wear, and lubrication. It encompasses the understanding and control of friction, lubrication, and wear between two or more surfaces in contact. The word "tribology" is taken from the Greek word "tribos," meaning rubbing or sliding[50,51].

Tribology plays a crucial role in various fields, including engineering, materials science, mechanical design, and manufacturing. It is employed to enhance the performance, efficiency, reliability, and lifespan of mechanical systems and components. By studying tribological phenomena, engineers and scientists can develop methods to reduce friction, minimize wear, and optimize lubrication techniques [52].

1.9.1 Properties important to become successful tribological coatings

To become a successful tribological coating, several properties are important to consider. Tribological coatings are designed to reduce friction, wear, and corrosion in various applications. Here are some key properties that contribute to the success of tribological coatings[53,54,55,56].

1. **Low Friction:** A successful tribological coating should exhibit low friction characteristics to minimize energy losses and wear between mating surfaces. Low friction coatings can reduce the amount of force required for movement and improve the overall efficiency of mechanical systems.
2. **High Hardness:** Coatings with high hardness can provide excellent resistance to wear and abrasion. They can withstand contact with rough surfaces, particles, and repeated sliding or rolling motions without significant degradation. Hard coatings ensure prolonged service life and enhance the durability of components.
3. **Low Wear Rate:** A successful tribological coating should have a low wear rate to minimize material loss and prolong the lifespan

of the coated surfaces. Coatings with high wear resistance can withstand the mechanical stresses and frictional forces encountered during operation.

4. **Corrosion Resistance:** Tribological coatings may be exposed to harsh environments, including moisture, chemicals, and extreme temperatures. It is important for the coating to provide effective corrosion resistance to protect the underlying substrate material. Corrosion resistance can prevent surface degradation, maintain performance, and extend the component's lifespan.
5. **Compatibility with Lubricants:** Some tribological coatings work in conjunction with lubricants to further minimize friction and wear. It is crucial for the coating to be compatible with the lubricant used in the specific application. Compatibility ensures optimal lubricant retention and distribution, enhancing the overall effectiveness of the coating.
6. **Thermal Stability:** Coatings may be subjected to high temperatures during operation, especially in applications involving high-speed or high-load conditions. The coating should exhibit good thermal stability to withstand these elevated temperatures without degradation or loss of functionality.

1.10 Electroless coatings in tribological application

Electroless coatings play a important role in tribological applications by providing enhanced wear resistance, reduced friction, and improved surface properties. Tribology refers to the science and study of friction, wear, and lubrication of interacting surfaces in relative motion. Electroless coatings are applied through an autocatalytic process, where a metal or alloy is deposited onto a substrate without the need for an external power source.

Here are some ways in which electroless coatings are utilized in tribological situations [57, 58, 59, and 60].

1. **Wear resistance:** Electroless coatings can significantly enhance the wear resistance of surfaces in tribological systems. These coatings, typically composed of metals such as nickel, cobalt, or their alloys, provide a hard and durable protective layer that can withstand frictional forces and prevent excessive wear of the substrate material.
2. **Friction reduction:** Electroless coatings can reduce friction between interacting surfaces, leading to decreased energy losses and improved efficiency. These coatings can possess self-lubricating properties, enabling them to act as solid lubricants or provide a low-friction interface between two moving components.
3. **Corrosion protection:** Tribological systems often encounter corrosive environments, which can degrade the performance and durability of components. Electroless coatings, such as nickel-phosphorus (Ni-P) or nickel-boron (Ni-B), can act as a barrier against corrosion, protecting the substrate material from chemical attack and reducing the risk of surface degradation.
4. **Surface finish and smoothness:** Electroless coatings can improve the surface finish and smoothness of components, leading to reduced friction and wear. These coatings can fill in surface defects, micro-asperities, or irregularities, resulting in a more uniform and polished surface that promotes better contact and reduces localized stresses.
5. **Thermal stability:** Some electroless coatings, such as nickel-phosphorus, exhibit excellent thermal stability and can withstand high operating temperatures. This property is particularly beneficial in tribological systems that involve high-speed operations or elevated temperatures.

1.10.1 Popularly used electroless tribological coatings

Electroless tribological coatings are widely used to minimize friction and wear in various industrial applications. Several compositions are popularly used for such coatings. Here are some common examples:

1. **Nickel-Phosphorus (Ni-P) Coatings**: Nickel-phosphorus is one of the most widely used compositions for electroless coatings. The phosphorus content can vary to achieve different properties, such as low friction and high hardness. Ni-P coatings provide excellent corrosion resistance and wear resistance, making them acceptable for applications in the automotive, aerospace, and chemical industries [61].

2. **Nickel-Boron (Ni-B) Coatings:** Nickel-Boron coatings are another popular choice for electroless tribological coatings. These coatings offer low friction, good wear resistance, and excellent hardness. They are often used in applications where lubrication is challenging or impractical, such as high-temperature environments or in contact with aggressive chemicals [62].

3. **Chromium (Cr) Coatings:** Chromium coatings are commonly used for their excellent corrosion resistance and wear properties. Electroless chromium coatings provide a hard and smooth surface that reduces friction and wear. These coatings are often applied as a barrier layer or for decorative purposes in industries such as automotive, plumbing, and electronics [63].

1.10.2 Evolution of nickel coatings in the context of tribological properties

Nickel coatings and nickel boron electroless coatings have evolved over time to meet specific requirements and address various challenges in different industries. Here's an overview of their evolution:

Nickel Coating:

1. **Traditional Nickel Plating:** Nickel coatings have been used for decades to provide corrosion resistance, wear resistance, and aesthetic appeal. Traditional nickel plating involves the electroplating process, where a conductive substrate is immersed in a bath containing a nickel salt solution. An electric current is applied to deposit a layer of pure nickel onto the substrate [64].
2. **Electroless Nickel Plating:** Electroless nickel plating, also known as autocatalytic plating, emerged as an improvement over traditional nickel plating. In this process, nickel is deposited onto the substrate through a chemical reaction without the need for an electric current. This method allows for more uniform and controlled deposition, enabling the coating of complex shapes and internal surfaces [65].

Nickel Boron Electroless Coating:

1. **Introduction of Boron:** Boron is a compound added to nickel coatings to enhance their properties. Nickel boron coatings provide improved hardness, wear resistance, and reduced friction compared to traditional nickel coatings. The addition of boron helps to create a uniform, amorphous structure that contributes to the coating's unique characteristics [65].
2. **Amorphous Nickel Boron:** Initially, the nickel boron coatings were primarily amorphous, lacking a defined crystalline structure. These coatings offered excellent hardness, wear resistance, and corrosion protection. They found applications in areas such as automotive, aerospace, and firearms[65].

Ni-B (nickel-boron) and Ni-P (nickel-phosphorus) are both electroless coating processes used to deposit a layer of nickel onto a substrate. However, they have different properties and applications. Here's a comparison between Ni-B and Ni-P electroless coatings [66].

1. **Hardness:** Ni-B coatings generally offer higher hardness compared to Ni-P coatings. The presence of boron in Ni-B coatings improves their wear resistance and hardness, making them suitable for applications where hardness is critical.
2. **Corrosion resistance:** Ni-P coatings typically provide better corrosion resistance compared to Ni-B coatings. The phosphorus content in Ni-P coatings enhances their corrosion resistance properties, making them suitable for applications where protection against corrosion is essential.
3. **Lubricity:** Ni-B coatings exhibit excellent self-lubricating properties due to the presence of boron, which reduces friction and wear. This characteristic makes Ni-B coatings well-suited for applications involving sliding or moving parts.
4. **Magnetic properties:** Ni-P coatings are generally non-magnetic, while Ni-B coatings can have magnetic properties depending on the boron content. This difference is essential for applications where magnetism needs to be considered.

In summary, Ni-B coatings offer superior hardness and lubricity, making them suitable for wear-resistant and low-friction applications. On the other hand, Ni-P coatings provide better corrosion resistance and are often used to protect against corrosion in various industries. The choice between Ni-B and Ni-P coatings depends on the specific requirements of the application, such as hardness, corrosion resistance, lubricity, and magnetic properties.

Several scientific reports published over the years suggest Ni-B based coatings to be superior among all alloy compositions of electroless Nickel-based coatings owing to certain favorable mechanical and tribological properties those made them effective in various engineering applications [66]. These properties improve further on incorporation of several alloying elements, namely tungsten and molybdenum [67, 68, 69].

1.11 Summary of Literature Survey

- Electroless Ternary Ni-B-W alloy coating shows better hardness, oxidation resistance and tribological properties over binary Ni-B alloy deposit.
- The addition of reinforcing phases such as harder ceramics or solid lubricants in electroless alloy coatings shows superior mechanical and tribological properties.
- From the extensive literature survey Ni-B-W coating is the most superior matrix and its properties can be further enhanced by reinforcing with the suitable and desirable particle.
- To achieve further up gradation, in this study, incorporation of hBN in Ni-B-W has been attempted.
- Such study with this novel composition **Ni-B-W-hBN** has not been yet reported.

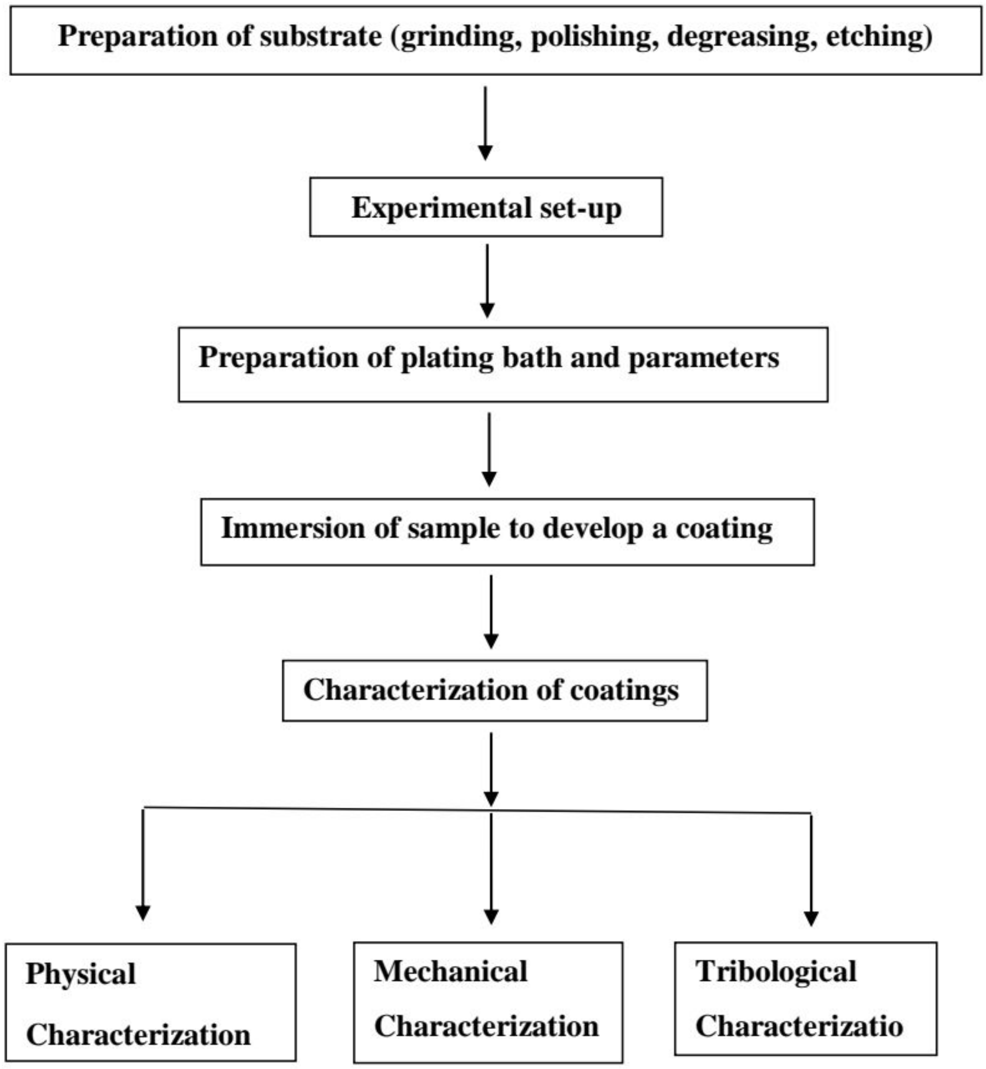
1.12 Objective

To check the efficacy of hBN as solid lubricant at high temperatures by incorporating it in tribological coatings deposited through electroless deposition methods.

1.12.1 Minor Objectives

1. To select and fabricate electroless tribological coatings on steel substrates.
2. To develop a methodology to incorporate hBN in this coating.
3. Thorough characterization of coatings at normal and high temperatures to check improvements in mechanical and tribological properties.

1.13 Work Plan



Chapter 2 Experimental Details

2.1 Introduction

An overview of engineering application of coatings at high temperature has already been presented and a suitable coating deposition method for triblogical situation has also been discussed. Literature survey and novelty of project and the objective of the project is also already discussed. Detailed description of the development of coatings and the experimental details of all the characterization methods, such as SEM analysis, XRD analysis, Micro-hardness analysis, Scratch test analysis, Sliding wear test analysis, are going to be presented next.

2.2 Development of Coatings

2.2.1 Substrate Preparation

The experiments were performed on an AISI 1025 steel specimen sectioned into 25*25*5 mm^3 dimensions. The substrate is further polished with 80 grade SiC paper for 20 minutes, 10 minutes with 220,400,600 grade SiC papers, and 7 minutes with 800,1000,1200 grade SiC papers. On one of the sides, notches were cut to hold the substrate in place while deposition takes place. The sample is degreased using an ultra-sonification process with acetone for 15 minutes. Followed by ultra-sonification the specimens are dipped in a 10 percent NaOH solution for 15 minutes at a temperature of 50–60 degrees Celsius. The sample surfaces are activated by immersing them for 15–20 seconds in a 37 percent hydrochloric acid solution. After each phase of the pre-treatment process, the sample is given an intermediate rinse in deionized water for a few seconds. Now the sample is catalytically active without the presence of oxides grease etc, and is ready for the coating deposition.

2.2.2 Preparation of Electroless Bath

Electroless plating bath contain Nickel Chloride which provided Ni^{+2} ions for Ni deposition, sodium borohydride ($NaBH_4$) as a reducing agent, ethylenediamine (NH_2–CH_2–CH_2–NH_2) as a complexing agent to make complex with excess Ni^{+2} ions and control the reaction, lead nitrate ($Pb(NO_3)_2$) as a stabilizer by producing the Pb^{+2} ions and lead ions gets adsorbed on the activated surface of the substrate and reduces the number of nucleation sites and thus prevents the decomposition of the bath. Sodium tungstate is added to provide tungsten to the coating and an alloy coating of Ni-B-W is developed.

In order to develop a composite coating of hBN in the Ni-B-W matrix, after 20 minutes of a pre-coat of Ni-B-W on the substrate hBN particles of size 1micron are added to the electroless plating bath. The temperature of the bath was maintained at 90±2°C throughout the deposition process, any increase from this range leads to decomposition of the bath and decrease from this range will not make the coating deposition. NaOH was added to maintain the pH of the bath at 13. The bath composition is presented in the table below.

Table 4: Bath Composition of Sodium Borohydride reduced electroless Ni Bath

Constituents	Concentration
Nickel Chloride	20 g/l
Sodium Hydroxide	40 g/l
Sodium Borohydride	0.8 g/l
Sodium Tungstate	25 g/l
Ethylenediamine	59 g/l
Lead Nitrate	0.0175 g/l
hBN particles	1 g/l

2.2.3Synthesis of Electroless Ni-Bbased Coatings

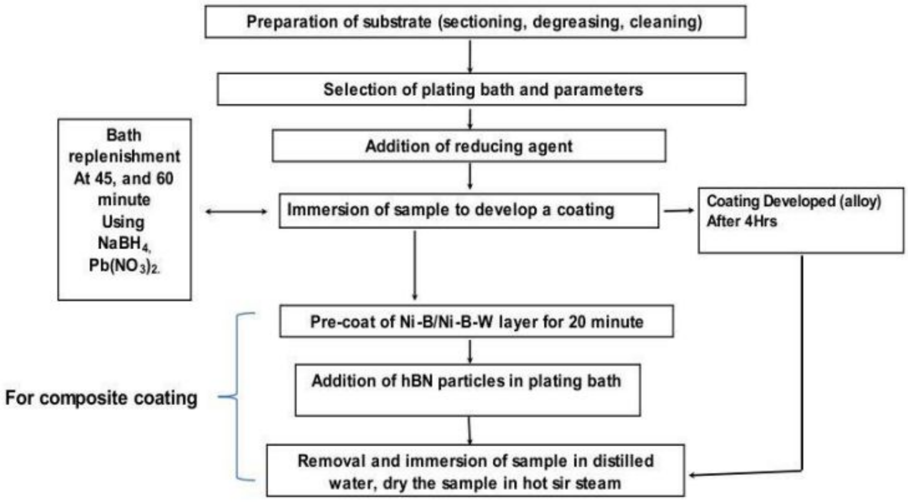


Figure 1 Flow Chart of the Electroless Deposition

Electroless nickel-boron coatings are made by the electroless plating method. In this type of coating, there is no need for an external power source as in electrolysis, the heating of the electroless bath provides energy for deposition. Metal salts present in the bath are the source of metal ions in the bath. Reducing agent reduces the metal ions on the substrate surface. In the initial stage, Ni atoms get attached to the active sites of the substrate and there will be the formation of large nuclei on the surface. With time the growth of the crystallites in the lateral direction gets confined by the neighboring crystallites due to mutual contact. Thus, during deposition, the crystallites grow faster in the vertical direction than that in the horizontal direction till a stage is reached where lateral growth is being hindered, only vertical growth takes place. This leads to the generation of a typical cauliflower-like surface and an alloy coating will be developed on the substrate. If hBN particles are added to the bath after the pre-coat of Ni-B, Ni-B-W, they will get reinforced in the Ni-B-W matrix and a composite coating will be developed.

2.2.4 Sectioning

After the deposition, the substrate is taken out from the bath and submerged into 50^{o}C DM water for pre-treatment, and further cleaned by ultra-sonication with acetone. An increase in weight of the sample is observed after coating and the sample is now sectioned into smaller pieces for the purpose of heat treatment, observing the coating thickness and various tests.

2.2.5 Mounting

A small section of the sample is mounted and polished till diamond polishing to impart mirror finish for the purpose of hardness testing and observation of coating thickness.

Figure 2 Hot Mounting Machine

2.2.6 Polishing

After hot mounting, polishing of the sample has been done. In order to, see the thickness of coating or to do hardness on the cross section of the coating.

The mirror finishing of the samples has been done by using selvyt cloth and diamond paste.

Figure 3: Polishing Machine

Samples Prepared

Table 5: Coatings Fabricated

Compositions
Ni-B
Ni-B-W
Ni-B-W-hBN

2.3 Basic Characterization of Coatings

2.3.1 Coating Thickness Analysis

After mounting the coated sample we do measure the coating thickness of the sample to assure the coating health of the coating. And we also analyze the cross section of the coated sample in Scanning Electron Microscopy to insure the adhesion of the coating with the substrate. Scanning Electron Microscopy (SEM) imaging can provide high-resolution images of the coating-sample interface. With the assistance of software, the coating thickness can be measured by analyzing the cross-sectional images of the coating. We can also measure the coating thickness by using optical microscopy.

Figure 4: Optical Microscope

2.3.2Micro-hardnessTest

Vickers micro-hardness test is one of the most commonly used techniques for the measurement of micro-hardness of coated samples. In this technique, indentation is performed by a square-based, highly polished, and pointed pyramidal diamond indenter having a face angle of 136^{o}

Vickers micro-hardness value is typically expressed in kgf/mm^2 without mentioning the unit. Of late, the literature on coating has expressed Vickers micro-hardness in GPa. In the current research work, the cross-sectional hardness of the coatings has been measured by using a Mitutoyo HM-210A micro-hardness tester. An average of at least 10 readings has been reported for a specific coating.

The vivkers Micro-hardness is calculated by using the below equation.

$$HV = \frac{2P \sin {}^{\alpha}/_{2}}{D^2}$$

Where, P is the applied load in kgf, α is the face angle and D is the mean diagonal length of the indentation mark in mm.

Figure 5: Micro Hardness Machine

2.3.3 Microscopy (FESEM) Analysis

To get the further insight into the coating, the samples were observed under FESEM. FESEM offers high magnification and higher quality images than an optical microscope. The samples were thoroughly polished until diamond polishing with SELYVT cloth. The coating cross-section is observed to know the father insight into coatings homogeneity and thickness.

With the increase in sophistication of investigation, instruments having superior depth of focus or spatial resolution are required. So, for the purpose of detailed material characterization Scanning Electron Microscope is used. The resolution of SEM can approach a few nm and it can operate at wide range of magnifications.

2.3.4 X-ray Diffraction (XRD) Analysis

X-ray Diffraction (XRD) is a good technique for identifying and measuring the structural properties of crystalline phases present in materials.The thickness of thin films and multilayer, as well as the atomic configurations in amorphous materials, is calculated using this method. (including at interfaces). Thin-film XRD can precisely determine the existence and composition of phases.

X-ray diffraction Analyses are vital in identifying the phases contained in the coating since the properties of the coating are directly tied to the phases present in it.

Figure 6: X-ray Diffraction machine

2.4 Tribological Characterization

2.4.1 Scratch Test

In scratch testing, a diamond ball indenter of 200µm radius is drawn across the surface of coated samples over a defined distance with a predefined load. the load can be constant or progressively increasing. The constant load tests were performed is given in the table, to see the coatings variation of friction coefficient when exposed to low loads, to check the scratch response of the coating, progressive load scratch test is conducted. Scratch hardness and scratch volume loss are also calculated from the tests performed.

Scratch test has been done on the coated surface of the coating samples in order to find out the critical load of the coatings. Critical load is the load at which coating get flaked off from the substrate. So we do check the health or can say the coating's adherence to the substrate.

In order to find out the scratch hardness and the fracture toughness properties of the coating, a scratch tester (DUCOM, TR-101) with Rockwell C diamond indenter (Blue Star, apex angle: 120o, tip radius: 200μm) is used. Formula used is mentioned below.

$$K_c = F_{eq}/\sqrt{2pA}$$

$$F_{eq} = F_T \qquad \alpha = 0$$

$$= \sqrt{\left(F_T{}^2 + \frac{3}{5}F_V{}^2\right)} \quad \alpha > 0$$

$$\sqrt{2pA} = \left(\sqrt{4d^3(\tan\emptyset/\cos\emptyset}\right) \text{ For conical Tool}$$

$$= \left(\sqrt{2(w + 2d)wd}\right) \text{ For Parallelepiped Tool}$$

K_c - Fracture toughness

F_{eq} - Contributions of both the vertical and the horizontal forces

2 pA - Scratch probe shape function

F_T - Horizontal force

F_V - Vertical force

α - Inclined angle with respect to the vertical axis

d - Penetration depth

Ø - Half-apex angle of conical indenter

w - parallelepiped blade of out-of-plane width

$$\text{Scratch hardness}(H_S) = \frac{8F_N}{\pi D^2}$$

H_s - Scratch hardness

F_N - Normal load

D/2 - Half of scratch width

H - Indentation depth from the top surface of the sample + height of ridge

Ø - Half-apex angle of conical indenter

Figure 7: Constant Load Scratch Tester

2.4.2 Sliding Wear Test

Wear is defined as the loss of material from a surface caused by the action of another surface in contact with it and wear resistance is the ability to resist that loss. In this study, a coating has been developed on the substrate with a view to impart high wear resistance and to decrease the coefficient of friction of the surface. Sliding wear test (reciprocating ball-on-disk type sliding wear test(Ducom CM-9104)) was performed on the samples using a hard spherical (WC with 6mm diameter) counter body in contact under load. Various wear tests were carried out on NiBW and NiBW-hBN samples with different amplitude of reciprocation, and frequency at various loads.

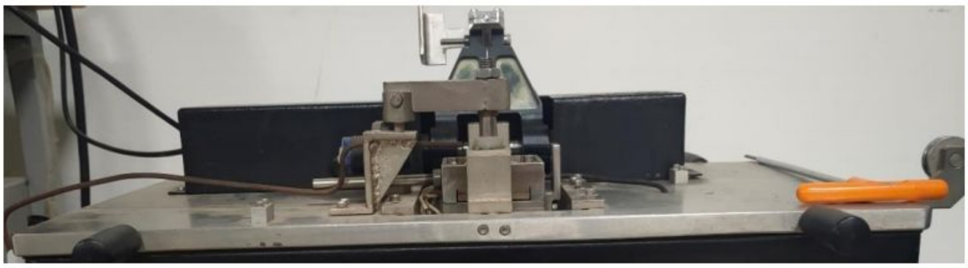


Figure 8: Ball on Disc Tribometer

Chapter 3 Development of Electroless Coatings and Its Basic Characterization

3.1 Introduction

In the previous chapter the experimental details of the coating development along with the experimental details of all the tests going to performed in this project has been discussed. In this chapter the basic characterization of the coatings such as SEM analysis, Micro-hardness analysis, Coating thickness analysis and XRD analysis has been done.

3.2 Experimental Details.

The coatings are fabricated with same procedure as already mentioned in the chapter 2 and Section 2.1. And the detailed experimental details of SEM analysis are discussed in chapter 2 and section 2.2.3. And also the experimental details of Micro-hardness analysis, XRD analysis has already been discussed in chapter 2 and section 2.2.2 and 2.2.4 respectively.

3.3 Results & Discussion

3.3.1 Microscopy (FESEM) Analysis

Top surface morphologies of coatings are presented in Fig. 10 (a-c) at higher magnification. Although Ni-B and Ni-B-W deposits do not show significant difference, the top surface of Ni-B-W-hBN can be seen to have a relatively irregular formation because of many nodular protrusions, possibly as a result of favored deposition at specific sites. The uniformity of deposition of an electroless coating depends on the more activation sites concentrated overthe substrate surface. A very low concentration results in a patchy coating with uneven thickness. A coherent coating made up of microscopic grains is produced by a high concentration of activation sites; this coating often has a fine texture and no obvious defects. The growth initiation of nano-sized alloy or composite globules upon the catalytic sites takes place first horizontally then vertically during the reduction process onto the catalytic surface of the substrate. Here it is important to state that the deposition rate in the horizontal direction is faster than vertical direction, and this makes the coating pore free. After close examination of morphological features of the top surfaces of Ni-B, Ni-B-W, Ni-B-W-hBN coatings under scanning electron micrograph (SEM) reveals a typical cauliflower-like structure, resulting of nucleation and subsequent grain growth in a columnar form (Figure 10 (a-c)).Inside the bath solution, generation of the columnar structure in the deposition process depends on the diffusion layer thickness around the crystallites growing in sites of nucleation on the substrate. The existence of boron retards the crystallization and restricts nucleation of nickel grains during the deposition which subsequently leads to the formation of an amorphous/ crystalline mixed structure. In the initial stage, Ni atoms get attached to the active sites of the substrate and formation of large nuclei on the surface takes place. Crystallites, with time, grow faster in the vertical direction than that in the lateral direction till a stage is reached where lateral growth gets hindered by the adjacent crystallites due to mutual contact and only vertical growth takes place. This develops the cauliflower-like surface, and a coating will be developed on the substrate. As thickness of the coating increases with further deposition, variation in the contribution from amorphous and crystalline structure can also be observed. The presence of hBN particles in the electroless bath during the deposition of Ni-B-W-hBN composite causes generation of a dissimilar top surface morphology, as shown in Figure 10 (c) as compared to that of Ni-B coating in Figure 10 (a-b). An increase in the size of colonies of nodules in case of composite Ni-B-W-hBN coatings can be related to the change in nucleation and growth rate of as-deposited coatings with the addition of hBN particulates in the electroless solution.Scanning electron micrographs of the cross sections of Ni-B-W-hBN composite coatings show well-adhered layer of coatings on steel substrates with no visible gap at the coating-substrate interface (Figure 11). This shows that the steel substrate surface's peaks and troughs have been covered by deeper deposits. As the thickness increased during deposition, the coating's granules combined to create smooth and flat top surfaces[70].

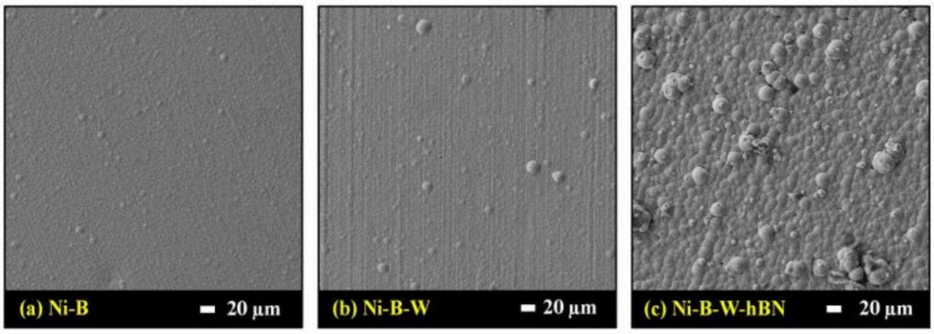


Figure 9: Top surface morphologies of (a) Ni-B, (b) Ni-B-W (c) Ni-B-W/hBN coatings observed under scanning electron microscopes.

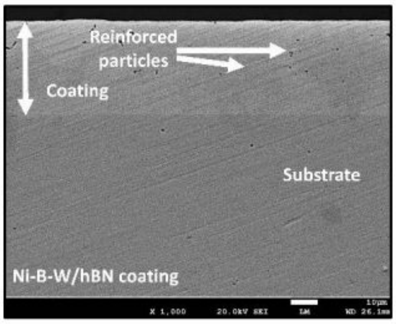


Figure 10: Cross-sectional micrograph of representative of electroless Ni-B-W/hBN composite coatings observed under Scanning electron microscope

3.3.2 Micro-hardness Analysis

Vickers hardness tests were performed 10 times on the coated samples and the results are plotted in the bar graph shown below. the hardness of the heat-treated samples is more than those of the as deposited samples, the hBN reinforced samples shown slight improvement in hardness than the Ni-B-W samples this may be due to formation harder N-B inter-metallic as identified by the XRD data or the change in grain size of the crystals formed due to presence of hBN.

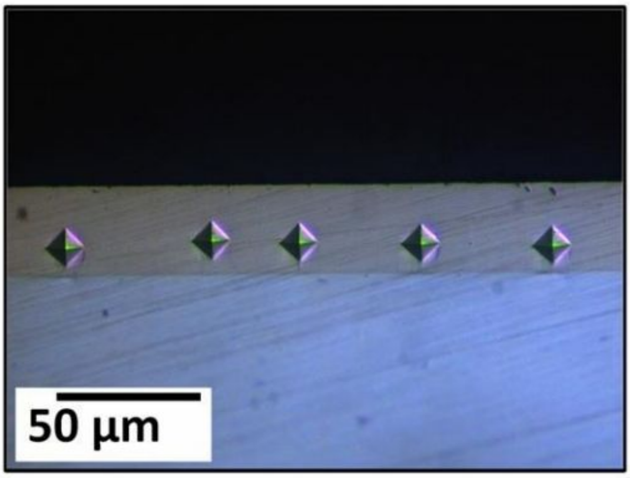


Figure 11: Indentation on the cross section of coatings (Ni-B-W) as representative

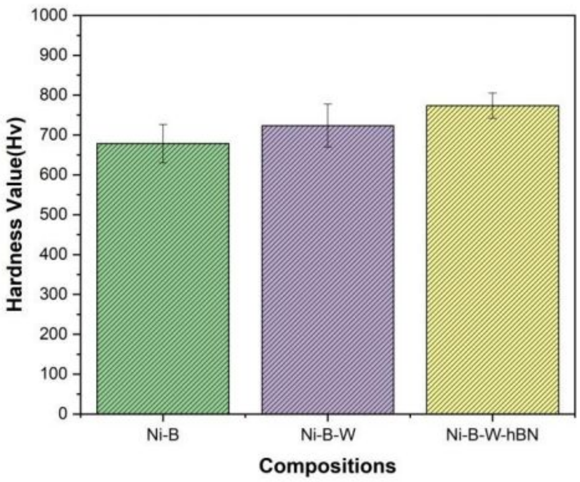


Figure 12: Bar graph comparison of coatings Microhardness.

3.3.3 X-ray Diffraction (XRD) Analysis

To examine the crystal structure and purity of the phases formed in the synthesised electroless coatings in their as-deposited state on low carbon steel (AISI1025) substrates, x-ray diffraction spectra of coatings are used. Figure 14 shows a comparison of XRD spectra of substrate, Ni-B, and Ni-B-W and Ni-B-W-hBN electroless coatings, with the Ni-B coating exhibiting a broad peak representative of Ni (111) reflections at 44.5° 2theta, which is equivalent to the crystalline form of Ni (111).The high boron content of the coating promotes the formation of small crystalline phases of nickel. It is important to note that Ni-B coatings containing tungsten (W) exhibit significant broadening of the Ni (111) peak at the expense of other peaks, demonstrating the coating structure's complete amorphousness. The amorphous nature of the Ni-B-W coatings in their electroless deposited state is confirmed by the presence of only one broad Ni (111) peak in the XRD pattern, which is consistent with the other findings and earlier research.

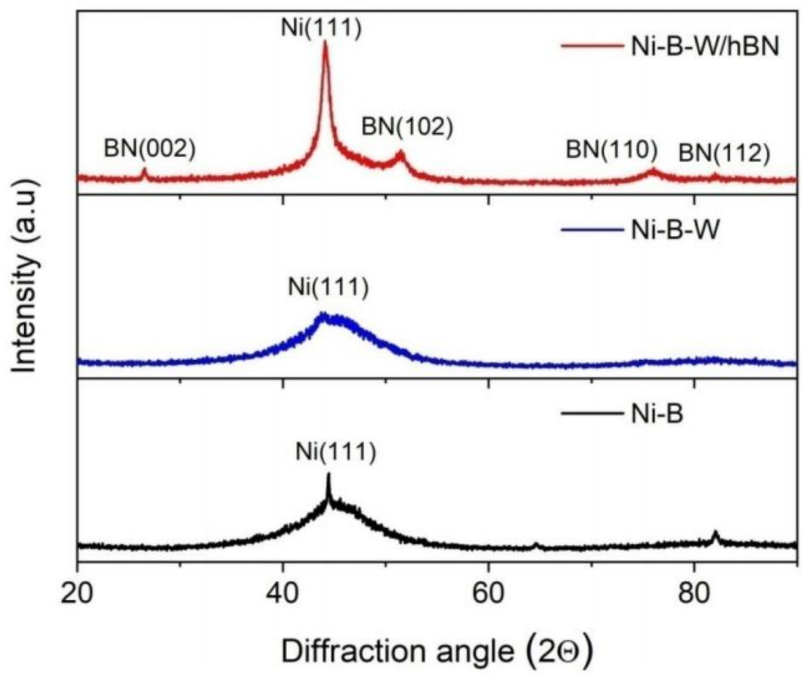


Figure 13: Comparison XRD pattern of theof substrate, Ni-B, and Ni-B-W and Ni-B-W/hBN electroless coatings.

3.4 Summary

Electroless alloy and composite coatings are developed successfully on the AISI 1025 steel specimen. And the incorporation of hBN as solid lubricants in Ni-B-W electroless coating has also been done successfully. Various Micro-structural and physical properties of the coatings have been analyzed thoroughly. Micro-structural analysis of coatings' cross-section and top surface under FESEM confirms the cauliflower structure of the deposition. And it also confirms the different growth rate of electroless alloy and composite coating, and composite coating has bigger nodular formation than the alloy coating. X-ray diffraction analysis confirms the presence of hBN and it also confirms the amorphous nature of the coatings.

Chapter 4 Tribological Characterization of Developed Coatings at Room Temperature

4.1 Introduction

The study presented in the previous chapter establishes the developement of electroless coating compositions such as Ni-B, Ni-B-W and Ni-B-W-hBN. Basic characterization such as SEM analysis, Xrd analysis, microhardness analysis also has been done. Now in this chapter all tribological characterizaton such as scratch test and sliding wear test at room temprature has be done.

4.2 Experimental details

4.2.1 Scratch Tests

Scratch test has been done on the coated surface of the coating samples in order to find out the critical load of the coatings.

Another scratch test has been performed to know the fracture toughness and scratch hardness of the coatings of all compositions. Detailed experimental details of this test has already been discussed in Chapter 2 and section2.4)

Table 6: The parameters of tests are given.

Sr.No	Compositions	Load(N)	Scratch Speed(mm/s)
1	Ni-B	14	1
2	Ni-B	17	1
3	Ni-B	20	1
4	Ni-B	14	3
5	Ni-B	17	3
6	Ni-B	20	3
7	Ni-B	14	5
8	Ni-B	17	5
9	Ni-B	20	5
10	Ni-B-W	14	1
11	Ni-B-W	17	1
12	Ni-B-W	20	1
13	Ni-B-W	14	3
13	Ni-B-W	14	3
14	Ni-B-W	17	3
15	Ni-B-W	20	3
16	Ni-B-W	14	5
17	Ni-B-W	17	5
18	Ni-B-W	20	5
19	Ni-B-W-hBN	14	1
20	Ni-B-W-hBN	17	1
21	Ni-B-W-hBN	20	1
22	Ni-B-W-hBN	14	3
23	Ni-B-W-hBN	17	3
24	Ni-B-W-hBN	20	3
25	Ni-B-W-hBN	14	5
26	Ni-B-W-hBN	17	5

4.2.3 Sliding Wear Test

Sliding wear test (reciprocating ball-on-disk type sliding wear test) was performed on the samples using a hard spherical (Si3N4 with φ6mm diameter) counter body in contact under load.

Table 7: The sliding wear test parameters are as follows

Composition	Load (N)	Frequency (Hz)	Amplitude (mm)	Temperature (°C)
Ni-B	3	5	3	Room temperature
Ni-B-W	3	5	3	Room temperature
Ni-B-W-hBN	3	5	3	Room temperature

4.3 Results and Discussion

4.3.1 Scratch Tests

It has been observed that critical load of electroless Ni-B is good and after addition of alloying element it has increased significantly. And after further addition of composite particle hBN as solid lubricant it further improved the critical load of Ni-B-W-hBN. Thus it improved the mechanical properties of the coating.

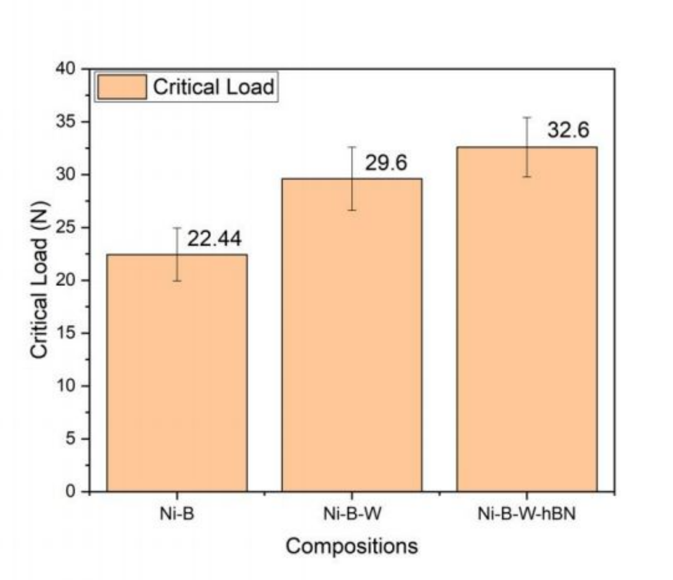


Figure 14: Values of critical load of coatings

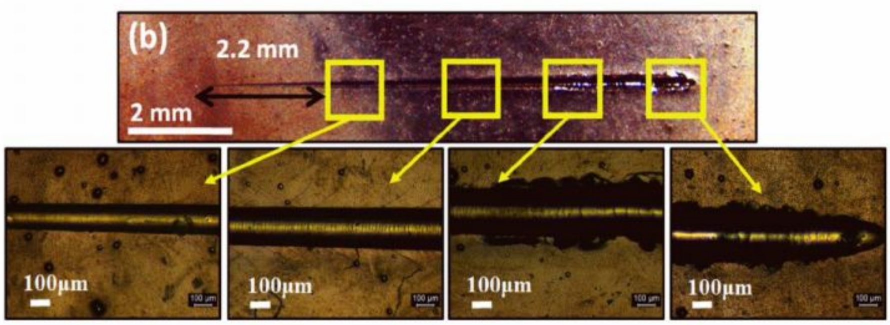
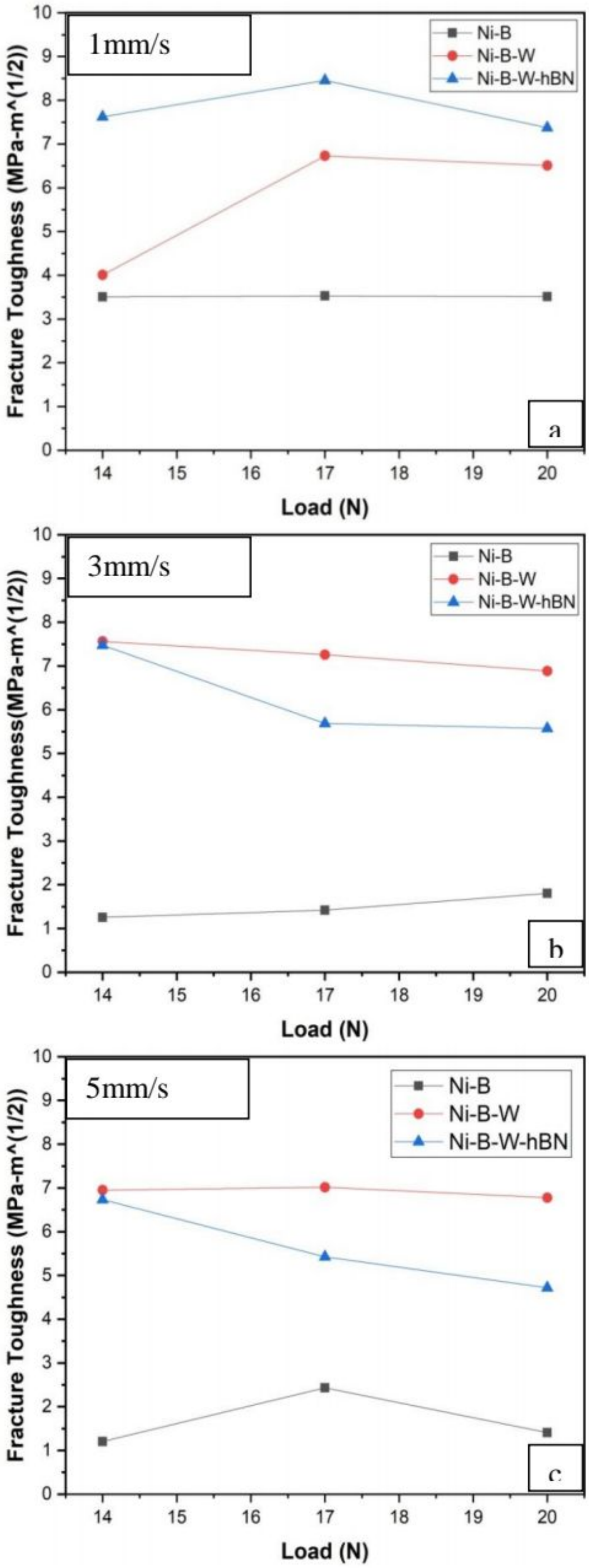


Figure 15: Optical microscopy image of coating Ni-B-W-hBN as representative

Fracture toughness and scratch hardness have been calculated.

Table 8: Fracture toughness and scratch hardness

Compositions	Load(N)	Sratch Speed(mmps)	Fracture toughness	Scratch hardness
Ni-B	14	1	3.579547657	7.368413295
Ni-B	17	1	4.329819219	7.140689628
Ni-B	20	1	4.882801928	7.341175638
Ni-B	14	3	3.480636709	7.660797882
Ni-B	17	3	3.135312809	7.433437697
Ni-B	20	3	3.891602978	7.57354093
Ni-B	14	5	3.250927387	7.852117694
Ni-B	17	5	2.639695861	7.494200011
Ni-B	20	5	3.722084417	7.934482093
Ni-B-W	14	1	5.760120751	7.727646001
Ni-B-W	17	1	5.439914618	7.695779426
Ni-B-W	20	1	5.446554516	7.853891781
Ni-B-W	14	3	3.999022713	8.467713306
Ni-B-W	17	3	4.240949126	7.905218141
Ni-B-W	20	3	4.407198601	7.874374238
Ni-B-W	14	5	3.744656546	8.685021607
Ni-B-W	17	5	3.571659747	7.961234444
Ni-B-W	20	5	4.174001982	7.939674123
Ni-B-W-hBN	14	1	5.275860803	7.711969308
Ni-B-W-hBN	17	1	4.8702715	8.015906332
Ni-B-W-hBN	20	1	5.487977764	8.039824202
Ni-B-W-hBN	14	3	4.284243634	8.702698079
Ni-B-W-hBN	17	3	4.710492079	8.369775956
Ni-B-W-hBN	20	3	4.715382504	8.313627081
Ni-B-W-hBN	14	5	4.344416005	9.708166921
Ni-B-W-hBN	17	5	4.444345515	9.151450819
Ni-B-W-hBN	20	5	4.730569895	9.152485076


1mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Fracture Toughness (MPa-m^(1/2))
Load (N)
a
3mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Fracture Toughness(MPa-m^(1/2))
Load (N)
b
5mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Fracture Toughness (MPa-m^(1/2))
Load (N)
c

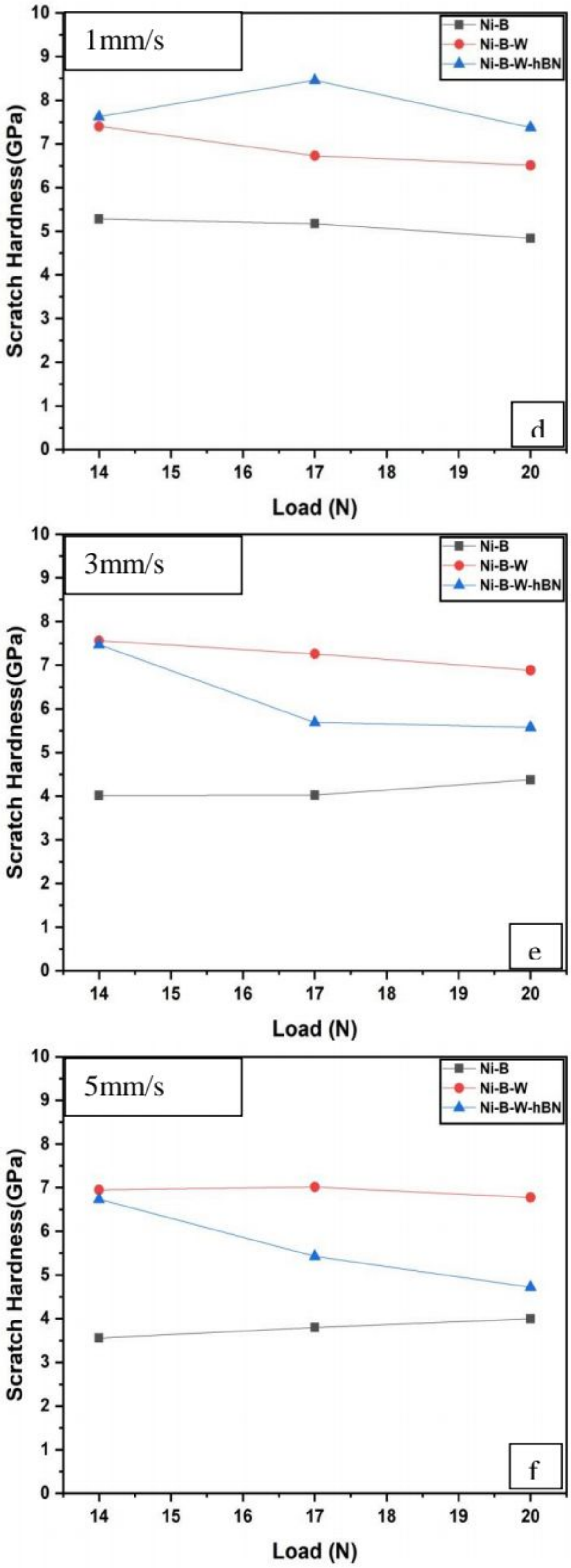

1mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Scratch Hardness(GPa)
Load (N)
d
3mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Scratch Hardness(GPa)
Load (N)
e
5mm/s
Ni-B
Ni-B-W
Ni-B-W-hBN
Scratch Hardness(GPa)
Load (N)
f

Figure 16: Scratch Hardness and Fracture Toughness Comparison

Assessing the suitability of the coatings for actual applications in tribological systems requires a thorough evaluation of scratch characteristics. Microscale scratching behavior of the coatings are studied for the evaluation of scratch hardness and fracture toughness by performing constant load scratches with parameters given in table 7. The width of a scratch is measured to evaluate scratch hardness following a model proposed in previous study. Scratch hardness values of samples obtained at different values of scratch loads (see Table 9) are plotted in Figure 17(a-f). It can be observed that addition of tungsten in Ni–B deposits contributes to improvement in scratch hardness and that improves even further as indenter experiences a lesser displacement to the dynamic deformation upon reinforcement and distribution of hBN particulates in a metal matrix.

4.3.3 Sliding Wear Test

Here it has been observed that after adding an alloying element, such as tungsten, values of coefficient of friction reduced. This is because after addition of alloying element it increased the hardness of the coating and that reduce the material removal. Thus coefficient of friction got decreased. And after addition of solid lubricants the coefficient of friction further decreased considerably. Because the hBN particles provides the lubricious phase to the coatings and hence coefficient of friction decreased significantly.

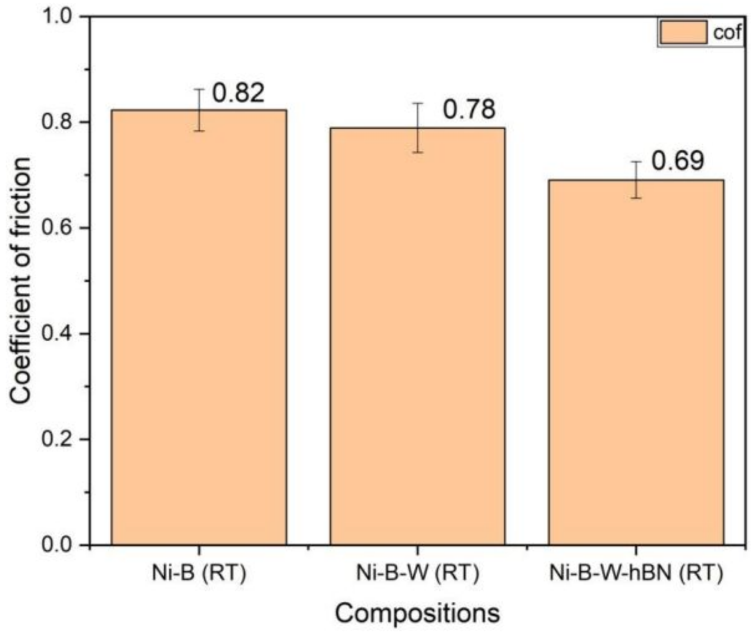


Figure 17: Bar graph comparison of coefficient of friction of the coatings.

4.4 Summary

Mechanical and tribological properties of Ni-B, Ni-B-W, and Ni-B-W-hBN coatings fabricated by electroless deposition method are studied thoroughly. Remarkable improvement in scratch hardness, fracture toughness and wear resistance properties has been noticed in Ni-B-W coating. And further improvement is noticed after the addition of hBN in Ni-B-W coatings. The addition of hBN lead to significant reduction in coefficient of friction.

Chapter 5 Tribological Characterization and Comparison of Developed Coatings at High Temperature

5.1 Introduction

In the previous chapter the tribological characterization of all the developed coatings has been done. And it has been observed that tribological properties at room temperature of Ni-B-W-hBN are much better to the Ni-B-W and Ni-B-W. So now in thischapter, tribological tests will be performed at higher temperatures, in order to check the feasibility of coatings at higher temperature.

5.2 Experimental Details

Sliding wear test (Universal Tribometer) was performed on the samples using a hard spherical (Si3N4 with φ6mm diameter) counter body in contact under load at high temperature.

Table 9: Parameter used for this test is as follows:

Composition	Load (N)	Frequency (Hz)	Amplitude (mm)	Temperature(°C)
Ni-B	3	5	3	450
Ni-B-W	3	5	3	450
Ni-B-W-hBN	3	5	3	450

5.3 Results and Discussion

5.3.1 High temperature tribological characterization

The sliding wear test was performed at high temperature that is at 450°C. It can be identified that in the bar graph, figure 19. The overall coefficient of friction has been reduced. This is becaue of formation of harder phases such as nickel boride (Ni_3B, Ni_2B) at high temperature happened. And it can also be identified that addition of solid lubricants hBN caused significant reduction in the coefficient of friction of the coatings.

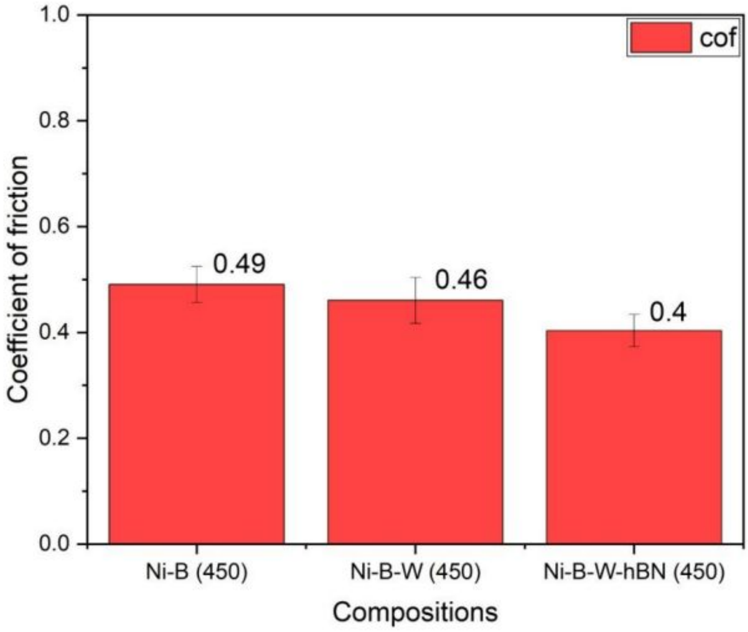


Figure 18: Bar graph comparison of coefficient of friction of the coating.

5.4 Comparison of Coefficient of Friction at Room Temperature and High Temperature

As the sliding wear test was performed at room temperature and at high temperature (450°C) in in-situ at the specific parameter given in the table. And in this section the comparison of coefficient of friction of all the coatings is analyzed. Bar graph of coefficient of friction of coatings is given below in figure 20. Here it can be seen that coefficient of friction of coatings is high in room temperature condition than the high temperature in in-situ condition. This is because the formation of nickel boride (Ni_3B, Ni_2B) occurred at high temperature. And that phase makes the coating harder and it results in a low coefficient of friction. Additionally, coatings containing hBN particles have a significantly lower coefficient of friction.

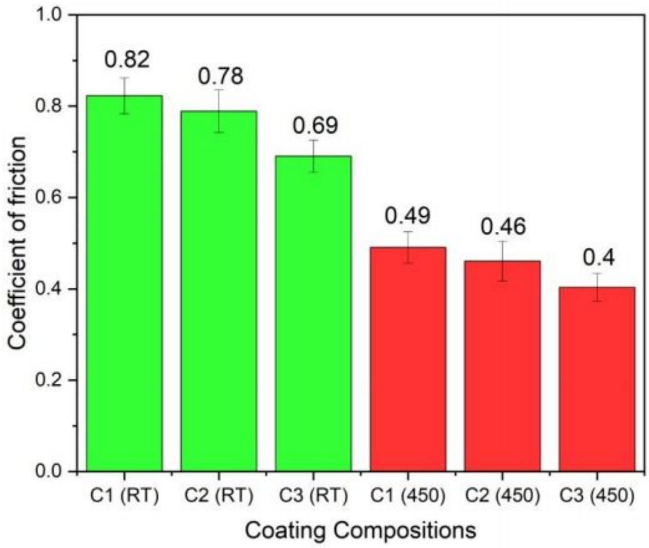


Figure 19: bar graph comparison of coatings at room temperature and at high temperature.

5.5 Summary

The testing of the samples was performed at room temperature and in in-situ high temperature. And the result shows that the in tribological testing resulted to the reduction of coefficient of friction. So it may be due to the formation of nickel boride phases within the crystalline nickel matrix. So as in in-situ condition there may be the formation of nickel boride phases which leads to the reduction in the damages at the wear track and the reduction in the wear debris that resulted in the coefficient of friction.

Samples containing hBN particles within their matrix show the lowest value of coefficient of friction and it is due to the properties of the hBN particle which is having hexagonal structure. Due to the slippage action during the tribological interactions the coefficient of friction value get reduces and even if it is in in-situ condition the similar observation is observed and it proves that the hBN can sustain at 450°C to show better results in terms of coefficient of friction.

Chapter 6 Conclusion and Scope for Future Work

6.1 Introduction

In the previous chapter the suitability of coatings at high temperatures has been checked. Here, in this chapter. A conclusion to the whole project has been drawn and future scopesare discussed.

6.2 Conclusions

- Electroless Ni-B, Ni-B-W, Ni-B-W-hBN composite coatings are successfully deposited on AISI 1020 mild steel substrates.
- Typical cauliflower like structure is observed under FESEM for both the alloys and composite coatings.
- Amorphous structure of the as deposited coatings is confirmed by dome shaped XRD pattern. Coatings when heated at 450^oC that revealed different peaks of Ni_3B, Ni_2B thus confirming its crystalline nature post heat treatment.
- The tribological parameters of the Ni-B-W alloy matrix, such as friction coefficient and wear, are greatly enhanced by the presence of hBN.Ni-B-W-hBN composite coatings that had been heated up outperformed previously deposited coatings in terms of tribology.

6.3 Scope for Future Work

- In-situ high temperature scratch test can be performed to check its effect on the critical load values, hardness and toughness.
- Incorporation of hard phase along with hBN to check possibilities of further improvements in hardness and wear resistance.
- Modification of bath composition, such as complexing agent, stabilizer, surfactant to optimize deposition parameters for better deposition rate and thicker coating.

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