

**T.R.
SAKARYA UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**DEVELOPMENT OF HIGH TEMPERATURE TRIBOLOGICAL
FEATURES OF ELECTROLESS NiB AND NiB/Al₂O₃
NANOCOMPOSITE COATINGS**

PhD THESIS

Şeyma ŞİMŞEK

Nanoscience and Nanoengineering Department

OCTOBER 2025

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Thesis Supervisor: Prof. Dr. Hatem AKBULUT

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The thesis work titled “**Development of High Temperature Tribological Features of Electroless NiB and NiB/Al₂O₃ Nanocomposite Coatings**” prepared by Şeyma ŞİMŞEK was accepted by the following jury on 03/10/2025 by unanimously of votes as a PhD THESIS in Sakarya University Graduate School of Natural and Applied Sciences, Nanoscience and Nanoengineering department.

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(03/10/2025)

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Şeyma ŞİMŞEK



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ABBREVIATIONS

CMC	: Critical Micelle Concentration
COF	: Coefficient of Friction
CTAB	: Cetyltrimethylammonium Bromide
EDA	: Ethylenediamine
EDS	: Energy Dispersive X-ray Spectroscopy
FWHM	: Full Width at Half Maximum
HT	: High Temperature
HV	: Vickers Hardness
ICP	: Inductively Coupled Plasma
IEP	: Isoelectric Point
ISO	: International Organization for Standardization
MS	: Mass Spectrometry
Ra	: Arithmetical Mean Roughness
Rq	: Root Mean Square Roughness
RT	: Room Temperature
Rt	: Total Height of Roughness
Rz	: Ten Point Mean Roughness
SDS	: Sodium Dodecyl Sulfate
SEM	: Scanning Electron Microscopy
XRD	: X-ray Diffraction



SYMBOLS

μ	: Coefficient of Friction
d	: Coating Thickness [μm]
F	: Applied Normal Load [N]
HV	: Vickers Hardness
L	: Sliding Distance [m]
ρ	: Density [g/cm^3]
Ra	: Arithmetic Mean Roughness [μm]
Rt	: Total Roughness Height [μm]
T	: Temperature [$^{\circ}\text{C}$]
t	: Time [s]
W	: Wear Volume [mm^3]
ε	: Strain
ζ	: Zeta Potential
σ	: Stress [MPa]



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DEVELOPMENT OF HIGH TEMPERATURE TRIBOLOGICAL FEATURES OF ELECTROLESS NiB AND NiB/Al₂O₃ NANOCOMPOSITE COATINGS

SUMMARY

This study examines the microstructural, mechanical, and tribological performance of electroless NiB and NiB-Al₂O₃ coatings applied to mild steel (St-37) substrates. In this dissertation, the electroless NiB and NiB-Al₂O₃ coatings were deposited onto the steel substrates to produce homogeneous microstructures using the electroless deposition method. The effects of electroless deposition parameters on the microstructure and the friction behaviours of the coatings were investigated in detail. A temperature-controlled wear testing setup was employed to evaluate their high-temperature tribological behavior. The investigation specifically explored the influence of Al₂O₃ nanoparticle concentration, the configuration of the wear test, and the testing temperature on the dominant wear mechanisms of the coatings. Tribological testing was carried out to assess the performance of the coatings under varying thermal conditions. The tests were conducted at four distinct temperatures: 25 °C (room temperature), 200 °C, 400 °C, and 600 °C to evaluate the influence of elevated temperatures on the friction and wear characteristics of the coatings. A ball-on-disk configuration was utilized for providing controlled and consistent test conditions. During the experiments, a constant applied load of 3 N was applied to simulate realistic contact pressures typically encountered in practical applications. By systematically increasing the temperature, the study aimed to observe and analyze how thermal effects, and changes in material properties, impacted the tribological behavior of the coatings. The results provided valuable insights into the coatings' ability to maintain wear resistance and frictional performance across a wide range of operating temperatures.

The experimental findings revealed that the electroless NiB-Al₂O₃ nanocomposite coatings consistently demonstrated a lower wear rate across all tested temperatures compared to the electroless NiB coatings without Al₂O₃ reinforcement. This enhanced wear resistance was attributed to the incorporation of Al₂O₃ nanoparticles, which significantly improved the coatings' ability to withstand wear under varying tribological conditions. Detailed characterization of the microstructures of the coatings, worn surfaces, and wear mechanisms was carried out using advanced analytical techniques, including Scanning Electron Microscopy (SEM) for observing surface morphology, Energy Dispersive X-ray Spectroscopy (EDS) for elemental analysis, X-ray Diffraction (XRD) and Raman Spectroscopy for chemical and structural identification. These techniques provided a comprehensive understanding of the tribological behavior of the coatings and the role of Al₂O₃ in improving their performance under high-temperature conditions.



AKIMSIZ NiB VE NiB/Al₂O₃ NANOKOMPOZİT KAPLAMALARIN YÜKSEK SICAKLIK TRIBOLOJİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ

ÖZET

Bu tez çalışmasında, yumuşak çelik (St-37) yüzeyler üzerine uygulanan akımsız NiB ve NiB-Al₂O₃ kaplamaların mikroyapısal, mekanik ve tribolojik özellikleri ayrıntılı olarak incelenmiştir. Çalışmada üretim yöntemi olarak akımsız kaplama tekniği kullanılmıştır. Bu yöntem, dış akım kaynağına ihtiyaç duymadan metal iyonlarının indirgenmesini sağlayarak çelik altlık üzerinde homojen ve yoğun bir kaplama tabakası oluşturmuştur. Homojen mikroyapılar, kaplamaların mekanik dayanıklılığı ve tribolojik performansı üzerinde doğrudan etkili olduğundan, kaplama parametrelerinin mikroyapı üzerindeki etkileri kapsamlı biçimde değerlendirilmiştir.

İlk aşamada akımsız NiB kaplamalar belirlenen banyo bileşimi ve işlem parametreleri esas alınarak hazırlanmıştır. Ardından, bu kaplamaların mekanik ve tribolojik performansını iyileştirmek amacıyla kaplama banyosuna Al₂O₃ nano-seramik partikülleri takviye edilmiştir. Al₂O₃ yüksek sertliği, kimyasal kararlılığı, düşük maliyeti ve NiB matrisiyle güçlü ara yüzey bağı oluşturma kabiliyeti sayesinde tercih edilmiştir. Bu seramik katkı, nikel matrisin aşınma direncini ve yüzey stabilitesini artırarak daha dayanıklı bir kaplama yapısının oluşmasına katkı sağlamıştır.

Al₂O₃ ilavesinin mikroyapı üzerindeki etkileri detaylı biçimde analiz edilmiştir. NiB kaplamaya Al₂O₃ partiküllerinin eklenmesiyle hem mikrosertlik hem de aşınma direnci açısından belirgin iyileşmeler sağlanmıştır. Böylece yüksek sıcaklık koşullarında uzun ömürlü, mekanik açıdan güçlü ve tribolojik olarak kararlı kaplamalar üretilmiştir. Kaplamaların performansı, mekanik testler ve tribolojik analizler aracılığıyla değerlendirilmiş, Al₂O₃ katkısının NiB kaplamaların dayanım ve aşınma direncini önemli ölçüde artırdığı ortaya konmuştur.

Kaplamaların tribolojik davranışları, özellikle sıcaklık değişiminin sürtünme ve aşınma özellikleri üzerindeki etkisini belirlemek amacıyla sistematik olarak incelenmiştir. Deneyler, 25 °C (oda sıcaklığı), 200 °C, 400 °C ve 600 °C sıcaklıklarında gerçekleştirilmiştir. Tüm testlerde bilye-disk (ball-on-disk) konfigürasyonu kullanılmış ve 3 N sabit yük altında sürtünme-aşınma davranışı gözlemlenmiştir. Bu testler sayesinde Al₂O₃ konsantrasyonu ve sıcaklık artışının kaplamaların baskın aşınma mekanizmaları üzerindeki etkileri net biçimde belirlenmiştir.

DeneySEL bulgular, akımsız NiB-Al₂O₃ nanokompozit kaplamaların test edilen tüm sıcaklıklarda Al₂O₃ içermeyen NiB kaplamalara kıyasla daha düşük aşınma oranına sahip olduğunu göstermiştir. Farklı tribolojik koşullar altında, Al₂O₃ partikülleri kaplamanın aşınmaya karşı direncini artırarak yüzey stabilitesini güçlendirmiştir.

Kaplamaların mikroyapısal özellikleri, aşınma yüzeyleri ve aşınma mekanizmaları ileri karakterizasyon teknikleriyle ayrıntılı biçimde incelenmiştir. Kullanılan başlıca analiz yöntemleri şunlardır:

Taramalı Elektron Mikroskobu (SEM): Yüzey morfolojisi, kaplama kalınlığı, mikroyapısal homojenlik ve aşınma izleri incelenmiş; mikro çatlaklar, porozite yapıları ve Al_2O_3 partiküllerinin dağılım özellikleri değerlendirilmiştir. Aşınma sonrası yüzey analizleri, sıcaklıkla değişen aşınma mekanizmalarının belirlenmesinde kullanılmıştır.

Enerji Dağılımlı X-Işını Spektroskopisi (EDS): Kaplamaların elementel bileşimini ve Al_2O_3 partiküllerinin dağılımını belirlemek amacıyla kullanılmıştır. EDS sonuçları, Ni, B ve Al elementlerinin homojen dağıldığını ve yüksek sıcaklıklarda yüzey oksidasyonunun belirgin biçimde arttığını göstermiştir. Tribokimyasal değişimler ve oksit tabakalarının bileşimi de bu yöntemle analiz edilmiştir.

X-Işını Difraksiyonu (XRD): Kaplamaların kristal yapısı, faz bileşimi ve amorf karakteri değerlendirilmiştir. NiB kaplamaların genellikle amorf yapıya sahip olduğu, Al_2O_3 katkısı ile belirli kristal fazların ortaya çıktığı ve ısı işlem sonrası Ni_3B , Ni_2B ve NiO fazlarının olduğu gözlenmiştir. Bu dönüşümler, kaplamanın mekanik kararlılığıyla doğrudan ilişkilendirilmiştir.

Raman Spektroskopisi: Kaplamaların kimyasal bileşimi ve aşınma sonrası yüzeyde oluşan oksit fazları belirlenmiştir. Raman analizleri, yüksek sıcaklıklarda NiO ve Al_2O_3 'un karakteristik bantlarını doğrulamış ve kaplama yüzeyinde oluşan tribokimyasal oksit tabakasının varlığını desteklemiştir. Bu oksit tabakalarının, sürtünme sırasında yüzey koruması sağladığı ve aşınma oranını azalttığı belirlenmiştir.

Bu ileri analiz teknikleri sayesinde, akımsız NiB ve NiB- Al_2O_3 nanokompozit kaplamaların mikroyapısal özellikleri, aşınma mekanizmaları ve tribolojik davranışları ayrıntılı biçimde ortaya konmuştur. Analiz sonuçları, Al_2O_3 katkısının kaplama performansını çok yönlü olarak iyileştirdiğini göstermektedir.

Elde edilen veriler, Al_2O_3 nanopartiküllerinin kaplama matrisine homojen biçimde dağıldığını ve yapısal bütünlüğü güçlendirerek mekanik dayanımı artırdığını ortaya koymuştur. Bu homojen dağılım, aşınma direncini artırmanın yanı sıra yüzeyin daha düzgün morfolojiye sahip olmasını sağlamış, mikro çatlak oluşumunu da minimize etmiştir. Al_2O_3 'un yüksek elastik modülü, yük aktarımını dengeli hâle getirerek matris deformasyonunu azaltmış, böylece hem düşük hem de yüksek sıcaklıklarda kaplamanın fonksiyonel kararlılığını sürdürmesine katkıda bulunmuştur.

Yüksek sıcaklıklarda yapılan tribolojik testler, Al_2O_3 katkısının oksidatif aşınmayı geciktirdiğini ve sürtünme sırasında koruyucu bir bariyer etkisi oluşturduğunu göstermiştir. Kaplama yüzeyinde oluşan bu oksit film, tribo-kimyasal kararlılığı artırarak malzeme kaybını azaltmıştır. Ayrıca, Al_2O_3 parçacıkları sürtünme sırasında üçüncü-cisim tanecikleri gibi davranarak temas yüzeyinde yük dağılımını homojenleştirmiş, lokal sıcaklık artışlarını sınırlamıştır.

Aşınma mekanizmaları incelendiğinde, düşük sıcaklıklarda hafif plastik deformasyon ve adeziv aşınma türleri baskınken, sıcaklık yükseldikçe oksidatif aşınma ve abrazyon mekanizmalarının öne çıktığı belirlenmiştir. Bununla birlikte, Al_2O_3 nanopartikülleri kaplama matrisinde sert ve dayanıklı bir yapı oluşturarak 600 °C'ye kadar aşınma oranının düşük kalmasını sağlamıştır. Bu bulgu, Al_2O_3 'un ısı kararlılığı ve NiB matrisiyle güçlü ara yüzey bağı sayesinde yüksek sıcaklıkta bile etkinliğini koruduğunu göstermektedir.

Sonuç olarak, NiB- Al_2O_3 nanokompozit kaplamalar 25-600 °C aralığında yüksek aşınma direnci, kararlı sürtünme davranışı ve yapısal bütünlük sergilemiştir. Bu özellikleri sayesinde, sert krom kaplamalara çevre dostu ve performans açısından

üstün bir alternatif oluşturduğu ortaya konmuştur. Özellikle yüksek sıcaklıklarda yüzey stabilitesini koruyabilmesi, bu tür kaplamaları otomotiv, havacılık, kalıp ve kesici takım endüstrisi gibi yüksek ısı yüküne maruz kalan uygulamalar için son derece uygun hâle getirmektedir.

Elde edilen sonuçlar, Al_2O_3 katkılı akımsız NiB kaplamaların hem mekanik hem de tribolojik performans açısından klasik sert krom kaplamalara kıyasla önemli avantajlar sunduğunu göstermiştir. Bu çalışma, NiB-bazlı nanokompozit sistemlerin yüksek sıcaklık tribolojisinde kullanım potansiyelini ortaya koyarak yüzey mühendisliği alanına önemli bir katkı sağlamaktadır.





1. INTRODUCTION

1.1. Overview

Surface engineering is a multidisciplinary field focused on modifying and enhancing the surface properties of materials to improve their performance in specific engineering applications. It plays a critical role in extending the operational lifespan, mechanical integrity, and efficiency of components used across various high-demand industries, including power generation, transportation, material processing, aerospace, and automotive sectors. As these industries increasingly use components exposed to severe loads and elevated temperatures, surface engineering has become a critical factor for performance and durability [1–3].

A wide range of surface modification techniques, such as laser processing, physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, and electroless coating, have been developed to tailor material surfaces according to specific functional requirements [4–14]. Among these techniques, electroless coatings have attracted considerable attention for their ability to increase surface hardness and wear resistance while improving service performance under demanding tribological conditions [15–19].

Electroless deposition offers several distinctive advantages over conventional coating techniques. These include uniform coating thickness, compatibility with complex geometries, cost-effective processing, and the ability to operate without external electrical input. Owing to these features, electroless coatings are particularly well-suited for tribological applications, where surface consistency and performance under severe contact conditions are essential [20–24]. While these attributes make electroless coatings attractive, demanding tribo-environments require capabilities beyond those of unreinforced coatings. Such limitations have driven the development of modified coating architectures that integrate reinforcing phases into the electroless matrix. Incorporation of hard ceramic nanoparticles into the electroless matrix significantly enhances the coating's mechanical strength and tribological performance, resulting in a high-performance nanocomposite structure. Therefore, the development and

optimization of advanced electroless nanocomposite coatings is a vital research area aimed at addressing the tribological challenges encountered in extreme service conditions. These coatings have the potential to significantly enhance the durability, efficiency, and reliability of critical components operating in technologically demanding environments, thereby contributing to both academic advancement and industrial innovation [25–27].

1.2. Motivation

In recent decades, the rapid growth of global energy consumption has highlighted the urgent need for efficiency improvements across industrial systems. A considerable portion of this demand is irreversibly dissipated through tribological effects, namely friction and wear, occurring at the interfaces of moving components [28]. According to global assessments, tribological losses represent a major source of both energy dissipation and mechanical degradation. It has been reported that friction alone accounts for nearly one-third of worldwide primary energy use, while wear is responsible for up to 80% of machine component failures. The combined impact of these phenomena results in substantial economic costs, estimated to correspond to approximately 2-7% of the gross domestic product (GDP) in many countries [28]. Complementing these estimates, Holmberg and Erdemir [29] conducted a detailed global analysis and reported that approximately 23% of the world's total primary energy consumption is directly or indirectly related to tribological contacts, including energy losses caused by friction. Their study also predicted that up to 40% of these losses could potentially be reduced through advancements in tribological technologies. Consequently, the effective control of friction and wear has become a major scientific and technological priority, as it offers a direct route to lowering global energy consumption, improving the operational reliability of mechanical systems, and supporting sustainable industrial development [30,31].

These global tribological challenges are directly reflected in the operational requirements of modern engineering systems. The increasing demands placed on modern machinery for enhanced efficiency, reliability, and performance have intensified the need for surface engineering solutions that can withstand extreme operating conditions. Components used in aerospace, automotive, energy generation, and manufacturing industries are often exposed to high loads, elevated temperatures,

and severe environments, leading to severe frictional and wear challenges. In such demanding applications, traditional materials and conventional surface treatments are frequently inadequate in terms of long-term durability [26,27,32].

To address these limitations, advanced surface modification technologies have been introduced. Wear-resistant coatings have become essential technological solutions for enhancing surface hardness and minimizing friction, thereby offering effective protection against tribological degradation in demanding service conditions. [16,27]. Electroless coatings, in particular, offer a unique advantage due to their ability to form uniform, conformal layers even on complex geometries, without the need for external current sources. Their effectiveness in improving tribological performance at both ambient and elevated temperatures makes them highly attractive for use in aerospace propulsion systems, automotive engines, chemical and electrical industries [27,33].

Although wear-resistant coatings have proven effective under many conditions, their behavior under elevated temperatures is not yet fully clarified, especially in the case of electroless nanocomposite systems. Despite considerable progress in the field of tribology, a comprehensive understanding of the tribological behavior of electroless nanocomposite coatings at high temperatures remains incomplete. Specifically, the effects of temperature on the frictional characteristics, wear mechanisms, and structural stability of these coatings are not yet fully elucidated. Therefore, this study aims to bridge this knowledge gap by systematically investigating the tribological performance of electroless NiB-Al₂O₃ nanocomposite coatings under varying temperature and load conditions, providing insights that are critical for the development of durable coating systems for high-performance applications.

1.3. Objectives of the Study

Building upon the motivation outlined in the previous section, this study aims to address the critical challenges associated with the tribological performance of materials under elevated temperature conditions. Specifically, it seeks to provide new insights into the wear behaviors of electroless NiB-Al₂O₃ nanocomposite coatings at both room temperature and high temperatures. By systematically analyzing the influence of temperature, load, and microstructural characteristics on friction and wear resistance, the research contributes to the development of advanced coating systems

capable of meeting the stringent demands of high-performance engineering applications.

The specific objectives of the present study are outlined as follows:

- To investigate the effect of deposition parameters on the microstructure of electroless NiB and NiB-Al₂O₃ coatings.
- To evaluate the mechanical properties of electroless NiB and NiB-Al₂O₃ coatings under various environmental conditions.
- To analyze the tribological behavior of the coatings at different temperatures and loading conditions.
- To systematically examine the influence of elevated temperature on the frictional behavior, wear mechanisms, and key material properties of the coatings, including hardness, toughness, and adhesion strength.
- To provide insights into electroless deposition processes, coating optimization strategies, and the wear behavior of coatings at both room and high temperatures.

Ultimately, this research aims to support the development of durable, efficient, and thermally stable coating systems for critical applications in aerospace, automotive, and energy sectors. By advancing the understanding of how electroless nanocomposite coatings perform under varying thermal and mechanical loads, the study contributes both to the academic literature in high-temperature tribology and to the practical engineering efforts focused on improving the reliability and service life of mechanical components operating under extreme conditions.

1.4. Organization of the Thesis

This dissertation is structured into seven chapters, each designed to progressively build the scientific context, experimental design, and analytical depth of the study on electroless NiB and NiB-Al₂O₃ nanocomposite coatings.

Chapter 1 introduces the background and scope of the study, with emphasis on surface engineering and tribology as the foundational concepts. The electroless coating method is briefly explained, including its relevance to modern tribological challenges. The motivation behind the research, the identified knowledge gaps in high-temperature

tribological coatings, and the specific objectives pursued in this study are outlined in detail.

Chapter 2 presents a comprehensive literature review on electroless Ni-B coatings. This chapter explains the fundamental deposition mechanisms, the chemical roles of nickel sources, reducing agents, complexing agents, and stabilizers. The influence of deposition parameters such as temperature, pH, and agitation on the structural and mechanical properties of the coatings is also reviewed. The formation mechanism of NiB layers is described alongside schematic illustrations.

Chapter 3 continues with an in-depth review of electroless composite coatings, particularly NiB-Al₂O₃ nanocomposites. The rationale for Al₂O₃ nanoparticle reinforcement is discussed, including its effect on hardness, wear resistance, and load-bearing capability. This chapter also explains the role of anionic surfactants in stabilizing particle dispersion and preventing agglomeration. Mechanisms of co-deposition, nanoparticle interaction with the matrix, and zeta potential (ζ) effects are addressed in detail.

Chapter 4 provides a theoretical and literature-based exploration of tribology, covering the fundamental mechanisms of wear, frictional behavior, and lubrication. Particular attention is given to high-temperature tribology, with discussions on matrix softening, oxide film formation, reinforcement detachment, and material transfer phenomena. The interaction between coated surfaces and their counterfaces is emphasized, highlighting third-body abrasion and tribochemical reactions. This chapter contextualizes how temperature and stress influence wear modes and surface degradation.

Chapter 5 details the experimental methodology used throughout the study. The preparation of electroless NiB and NiB-Al₂O₃ coatings on low-carbon steel substrates is described, including bath composition, coating procedures, and surfactant incorporation. Heat treatment conditions are reported where applicable. Characterization methods include scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy, profilometry, nanohardness testing, and high-temperature tribological testing using a ball-on-disk configuration. The configuration and properties of the alumina

counterface are also specified, as it plays a crucial role in interpreting material transfer and tribofilm formation.

Chapter 6 presents and discusses the experimental results. The chapter begins with the analysis of surface morphology, phase composition, and mechanical behavior of the coatings before and after heat treatment. This is followed by a systematic evaluation of tribological performance at four temperatures: 25 °C, 200 °C, 400 °C, and 600 °C. The evolution of the coefficient of friction, wear rate, and oxide formation is analyzed in correlation with temperature-dependent structural changes. SEM and EDS analyses of worn tracks and corresponding counterface surfaces are integrated to clarify material transfer mechanisms, oxide layer development, and particle detachment behavior. A comparative analysis between unreinforced and reinforced coatings is conducted to identify the most thermally stable and wear-resistant configuration.

Chapter 7 concludes the thesis by summarizing the main findings, highlighting the contributions of this work to the field of high-temperature tribology and electroless nanocomposite coatings. The chapter also offers insights into the practical implications of the results and provides recommendations for future research, including advanced reinforcement strategies, multilayer coating designs, and further exploration of counterface-coating interactions under thermal cycling. Figure 1.1 presents the flowchart illustrating the organization of the dissertation.

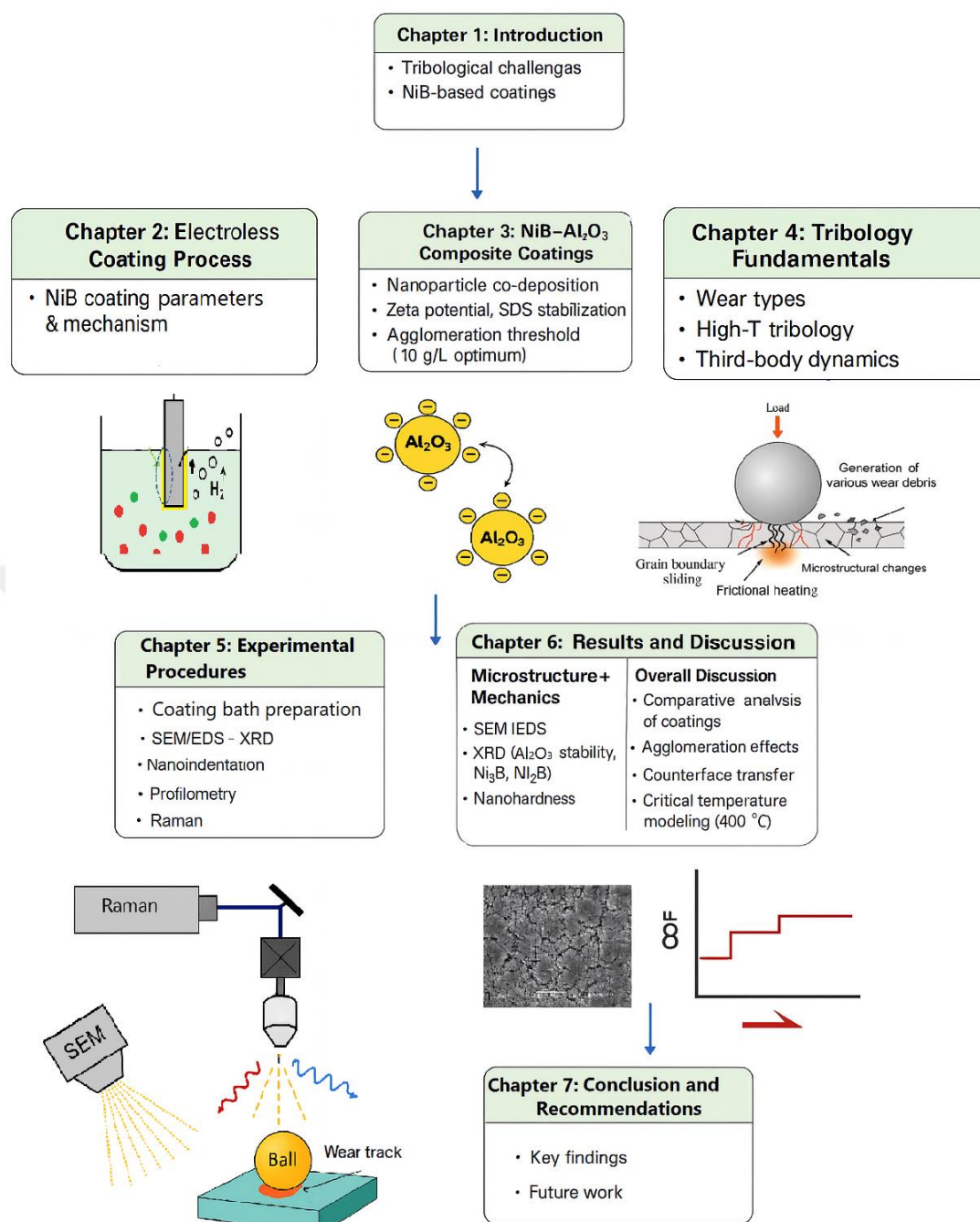


Figure 1.1. The flowchart illustrating the organization of the thesis.



2. ELECTROLESS COATING PROCESS

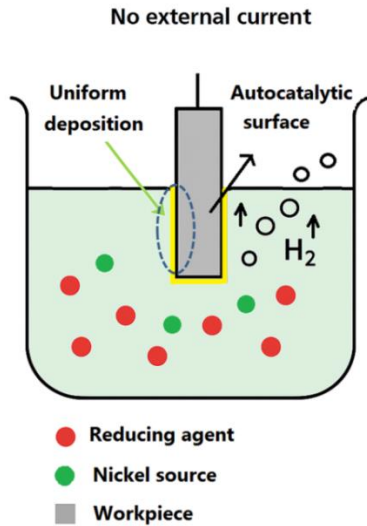
2.1. Electroless Coating

Electroless deposition, also known as electroless coating, is an auto-catalytic process that enables the deposition of metals such as nickel, copper, cobalt, gold, and their alloys onto various substrates without needing any external electrical potential [23,25,34]. The absence of external electrical power simplifies the process, reducing operational complexity and cost. This process relies on the reduction of metal ions or metal complexes to their metallic state, producing a uniform and adherent coating. With its relatively low operating temperature, typically below 100 °C, this technique has become an essential tool for surface metallization, offering precision, versatility, and efficiency in applications ranging from electronics to complex engineering components [23,35,36].

Electroless deposition is an electrochemical process that relies on redox reactions occurring within the electrolyte [11]. The key distinction between electroless and electroplating lies in the source of electrons for reduction: electroless plating utilizes a chemical reducing agent, whereas electroplating depends on an external electrical source. Unlike electroplating, electroless plating is characterized by the selective reduction of metal ions exclusively on the surface of a catalytic substrate immersed in the plating bath [23]. Once the initial metallic layer is deposited, the reaction becomes autocatalytic, meaning that the deposited metal itself acts as a catalyst, promoting further reduction and ensuring continuous growth. As a result, electroless plating achieves highly uniform and conformal coatings, independent of current distribution effects (Figure 2.1). Moreover, since the transfer of electrons does not involve the substrate's atoms, the deposition process occurs without consuming the base material [23]. Thanks to this unique mechanism, electroless plating is considered an efficient and reliable technique for achieving high-quality coatings in advanced surface engineering applications. Compared to conventional deposition techniques, electroless plating offers several advantages, such as cost-effectiveness, uniform thickness even on complex geometries, the ability to coat non-conductive surfaces, and excellent control over coating composition and structure. These features make electroless

plating particularly attractive for applications demanding superior wear resistance and mechanical durability [23] [27].

Electroless Plating



Electroplating

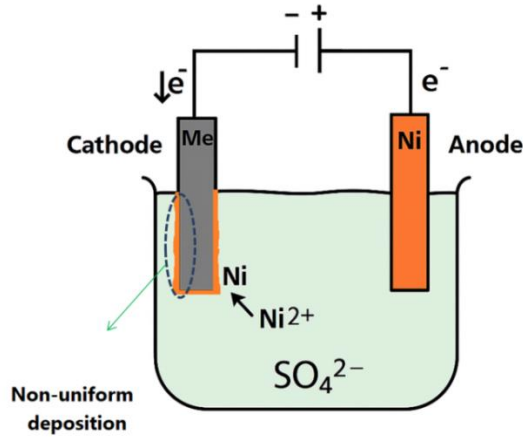


Figure 2.1. Schematic illustration of electroless plating versus electroplating.

2.2. Electroless Ni Coating

Electroless Nickel (Ni) deposition is a chemical process for depositing a nickel alloy onto a substrate from an aqueous solution. This technique involves the reduction of nickel ions in a solution through a chemical reaction, without the need for an external electrical current [37]. In electroless Ni coating, the choice of reducing agent plays a critical role in determining the composition and properties of the Ni alloy coating. Depending on the type of reducing agent used in the coating process, either NiP (Nickel-Phosphorus) or NiB (Nickel-Boron) coatings are obtained [24,34,35,38,39].

NiP coatings are widely recognized for their high corrosion resistance and excellent solderability, making them suitable for applications in corrosive environments [39–41]. On the other hand, NiB-based coatings exhibit outstanding tribological properties, along with high hardness, which makes them ideal for applications requiring superior mechanical and tribological performance. Additionally, electroless NiB-based coatings are gaining attention in high-technology industries due to their exceptional performance characteristics [27,42–44]. This study explores the details of the electroless NiB-based plating process to enhance and better understand its potential for delivering highly effective coatings in demanding applications requiring prolonged durability and smooth performance.

2.3. General Properties of Electroless Nickel-Boron (NiB) Coating

Electroless nickel-boron coating exhibits a unique and characteristic morphology. The morphology of electroless nickel-boron (NiB) coatings is strongly influenced by the deposition process, exhibiting distinctive structural features. Cross-sectional observation indicates a columnar structure resulting from deposit growth. The surface morphology of NiB coating typically exhibits a cauliflower-like structure, which directly results from the coating's nucleation and growth mechanism [22,27,45].

2.3.1. Formation mechanism of NiB coating

The microstructure of electroless nickel-boron coatings typically exhibits multiple columnar layers, with the prominence of these columns diminishing as the distance from the substrate increases. In the early stages of electroless Ni-B coating growth, the microstructural evolution is predominantly governed by the formation of densely packed columnar grains extending perpendicular to the substrate surface [16]. This vertical orientation results from the high initial concentration of reactive species near the substrate, which promotes rapid nucleation and subsequent upward crystal growth. As the deposition proceeds, a progressive depletion of ions in the vicinity of the growing layer leads to the development of a diffusion-limited zone [46]. This shift in local chemical gradients reduces the vertical growth rate and alters the deposition mode, giving rise to a surface morphology characterized by rounded, nodular features. These nodules form as lateral growth becomes more pronounced but spatially restricted by adjacent grains. Thus, the overall coating structure transitions from a well-defined columnar structure towards a more disordered nodular top layer [16,46]. This evolution in growth morphology is schematically illustrated in Figure 2.2., which depicts the initial nucleation and subsequent vertical columnar development during the electroless NiB deposition process.

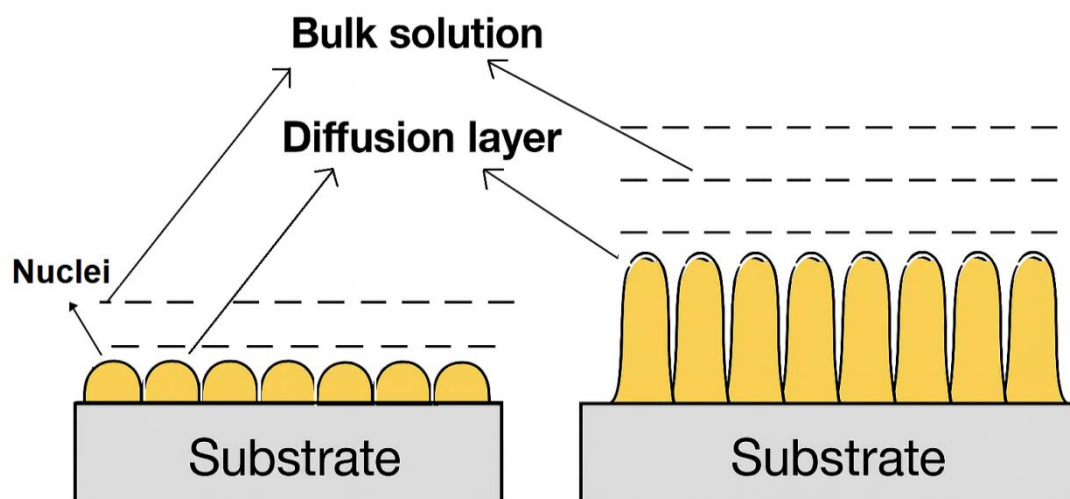


Figure 2.2. Schematic illustration of the nucleation and vertical columnar growth mechanism (adapted from [46]).

2.3.2. Fundamental components of electroless NiB coating

Electroless deposition baths consist of multiple chemical components, each playing a vital role in the functionality of the bath. A detailed understanding of the coating parameters is indispensable for the precise application and refinement of the process. The significance of each component in the coating bath is explained detail below.

2.3.2.1. Nickel sources

In electroless deposition processes, the nickel source plays a critical role as the primary metal ion provider, enabling the formation of a metallic nickel layer on the substrate. Typically, nickel salts such as nickel sulfate (NiSO_4), nickel chloride (NiCl_2), or nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$) are used due to their high solubility and ability to release nickel ions efficiently in aqueous solutions. These nickel ions undergo reduction through the action of a reducing agent resulting in the deposition of metallic nickel [23,27,45,47]. The selection of the nickel source significantly influences the deposition rate, coating uniformity, and overall process efficiency. A carefully chosen nickel source ensures a consistent supply of metal ions, facilitating uniform coatings while maintaining the autocatalytic nature of the electroless process.

2.3.2.2. Reducing agents

Reducing agents are fundamental in the electroless deposition process, as they facilitate the reduction of metal ions to their metallic state, enabling the deposition of the metal on the substrate [48]. In the case of nickel electroless deposition, common reducing agents include sodium borohydride (NaBH_4), and dimethylamine borane

(DMAB), each offering distinct advantages depending on the specific application and process requirements [23,27,48]. These agents donate electrons to the nickel ions in the plating bath, reducing them to metallic nickel while themselves undergoing oxidation. The choice of reducing agent impacts various factors such as the deposition rate, the purity of the metallic layer, and the smoothness of the deposited film. Furthermore, the concentration of the reducing agent is the critical parameter that controls the efficiency of the reduction reaction and the overall quality of the coating. A well-optimized reducing agent ensures consistent and uniform deposition while maintaining the stability of the electroless plating solution throughout the process [23].

2.3.2.3. Complexing agents

Complexing agents, also known as ligands, are essential in the electroless deposition process as they stabilize metal ions in the solution and prevent untimely precipitation. In electroless nickel plating, complexing agents such as ethylenediamine (EDA) and citrate are commonly used to form stable complexes with nickel ions [27,49–51]. These complexes ensure that the nickel ions remain in a soluble and reactive state, enabling continuous and uniform deposition onto the substrate. By replacing water molecules bound to metal ions, complexing agents regulate the concentration of free metal ions, improve the solubility of metal salts, and prevent undesired precipitation [37].

Complexing agents also buffer the solution to maintain a stable pH and influence the deposition rate and quality of the metallic layer. The strength of the complexing agent, the molar ratio between the metal and the complexing agent are critical factors that determine the stability and performance of the plating bath. A well-balanced complexing agent ensures that nickel ions are efficiently available for reduction while preventing side reactions or the formation of undesired deposits. This careful control over the plating process ensures the desired characteristics of the final coating, such as uniformity, adhesion, and overall quality [16].

2.3.2.4. Stabilizer

A stabilizing agent is a crucial component in the electroless NiB coating process, as it prevents the spontaneous decomposition of the plating solution and ensures a uniform, high-quality deposit. The primary function of the stabilizer is to regulate the reduction reaction of nickel ions, ensuring their deposition occurs exclusively on the substrate surface rather than within the bulk solution [52]. Without a stabilizer, nickel ions could

be reduced uncontrollably in the solution, leading to the formation of nickel particles in the bulk. This would cause the plating bath to become unstable and prevent the formation of a uniform coating on the substrate surface [53]. Additionally, the nickel particles formed in the solution could weaken the adhesion of the coating and reduce its quality. Common stabilizing agents include lead, thallium metal ions, organic compounds (e.g., thiourea) or sulfur-containing compounds to moderate the reaction rate. The concentration of the stabilizer must be carefully optimized, as excessive amounts can inhibit the plating process, while insufficient amounts may result in bath decomposition [37,53].

2.3.3. Reaction mechanisms of electroless NiB coating

The electroless deposition of NiB coatings is governed by a series of coordinated chemical reactions, primarily involving a sequence of complexation, redox, and co-deposition steps, each of which is critical for achieving a uniform NiB alloy layer. A simplified overview of the mechanism is illustrated in Figure 2.3.

2.3.3.1. Nickel ion dissolution and complexation

The deposition process begins with the introduction of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) into the bath, which serves as the primary nickel source. Upon dissolution, Ni^{2+} ions are released into the aqueous solution. However, due to the alkaline nature of the plating bath, these free Ni^{2+} ions have a high tendency to precipitate as nickel hydroxide ($\text{Ni}(\text{OH})_2$), which would disrupt bath stability and deposition uniformity. To prevent this, a chelating agent such as ethylenediamine (EDA) is added to the solution. EDA forms stable coordination complexes with Ni^{2+} ions, producing $[\text{Ni}(\text{EDA})]_3^{2+}$ species that remain soluble and available for reduction [16]. This stabilization ensures a controlled and sustained supply of reducible nickel species throughout the deposition process, as shown in Step 1 of Figure 2.3.

2.3.3.2. Electron supply via reducing agent

Sodium borohydride (NaBH_4), used as the chemical reducing agent, undergoes hydrolysis in the alkaline medium. This reaction liberates hydrogen gas and generates free electrons, which are then utilized for the subsequent reduction of nickel complexes. The redox reactions involved in this step also lead to the formation of intermediate borate species and elemental boron [16]. The sequence of electron

generation is detailed in Step 2 and Step 3 of Figure 2.3, where BH_4^- acts as the electron donor, enabling the reduction of $[\text{Ni}(\text{EDA})]_3^{2+}$ to metallic nickel.

2.3.3.3. Co-deposition of nickel and boron

Simultaneously with nickel reduction, elemental boron generated during the hydrolysis of NaBH_4 is incorporated into the growing film. This co-deposition results in the formation of a continuous NiB alloy layer on the substrate surface [16,46]. These boron atoms are co-deposited alongside nickel, forming a continuous NiB alloy structure. The simultaneous presence of both nickel and boron in the deposited structure is emphasized in Step 4 of Figure 2.3, where co-deposition occurs at the substrate-solution interface.

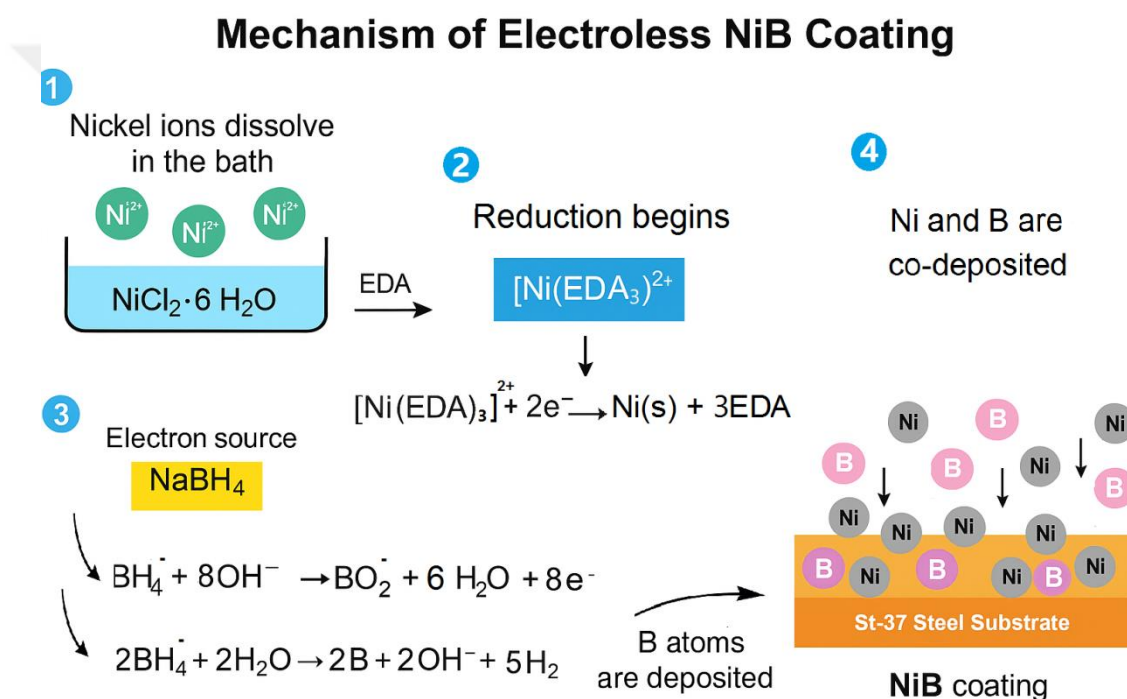


Figure 2.3. Schematic illustration of the electroless NiB coating mechanism, showing sequential steps including nickel ion complexation with EDA, electron donation from NaBH_4 , nickel reduction, and co-deposition of Ni and B atoms on the steel substrate.

2.3.4. Factors affecting the reaction mechanism of electroless NiB coating

The reaction kinetics and elemental composition of electroless NiB coatings are significantly influenced by various parameters, particularly the bath chemistry and reduction conditions. Precise control over these factors is essential to tailor the coating's mechanical strength, tribological performance, and chemical stability [54].

2.3.4.1. Influence of temperature

Bath temperature is a crucial factor that determines the reaction rate. The optimal temperature of approximately 90 °C facilitates the reduction of Ni^{2+} ions, ensuring efficient plating. It also enhances coating uniformity, and balances boron distribution within the coating, thereby optimizing hardness and tribological properties [16]. Excessively high temperatures compromise the chemical stability of the plating bath. This condition promotes the decomposition of the reducing agent and the onset of uncontrolled precipitation, which may cause non-uniform and porous deposits with impaired mechanical performance. Therefore, maintaining the bath temperature close to 90 °C is essential to ensure consistent and high-quality electroless NiB coatings [16,55].

2.3.4.2. Influence of pH level

The pH level of the electroless plating bath plays a pivotal role in controlling the overall efficiency and outcome of the deposition process. It governs the ionization behavior of chemical species and influences the equilibrium dynamics within the solution, thereby affecting both the plating rate and the microstructural quality of the deposited layer. As a direct indicator of the bath's acidity or alkalinity, pH significantly alters the solubility of metal ions and the reactivity of reducing agents. In particular, when sodium borohydride (NaBH_4) is used as the reducing agent, maintaining a highly alkaline pH is essential. When the pH is maintained within this optimal range, it ensures the stable progression of reduction reactions between metal ions and reducing agents, promoting uniform layer growth and controlled thickness [11].

2.3.4.3. Effect of reducing agent concentration

The composition of the plating bath, particularly the ratio of NaBH_4 to Ni^{2+} ions, plays a crucial role in determining the mechanical and tribological properties of the coating. An optimal concentration of the reducing agent ensures uniform deposition, improving hardness, wear resistance, and adhesion of the coating [16,27,37]. Insufficient NaBH_4 levels may lead to incomplete reduction of Ni^{2+} ions, resulting in lower deposition rates. On the other hand, excessive NaBH_4 concentrations can cause uncontrolled hydrogen evolution, leading to porosity and reduced coating density. Therefore, maintaining a well-balanced reducing agent concentration is essential for achieving a high-quality, durable coating with enhanced mechanical performance [16,37].

2.3.4.4. Influence of complexing agent concentration

Complexing agents are essential for stabilizing nickel ions in the solution, preventing their precipitation, and ensuring a controlled and efficient deposition process [21,48]. These agents function by chelating nickel ions and impurities, thereby inhibiting undesired precipitation and promoting the formation of smooth, uniform coatings. The concentration of complexing agents must be carefully optimized. Insufficient amounts can lead to nickel precipitation, resulting in coating defects, while excessive concentrations may reduce the plating rate and affect the coating's composition. Ethylenediamine (EDA), a commonly used complexing agent, plays a critical role in stabilizing nickel ions and preventing undesired precipitation [21].

2.3.4.5. Effect of stabilizer concentration

In electroless plating, the stabilizer plays a critical role in controlling the deposition process by inhibiting excessive or uncontrolled reactions [11]. In our study, lead nitrate ($\text{Pb}(\text{NO}_3)_2$) was used as the stabilizer to regulate bath stability and deposition kinetics [27]. By blocking a significant number of catalytically active sites, the stabilizer directly influences the deposition rate. Under otherwise constant conditions, an increase in stabilizer concentration leads to a reduction in deposition rate due to its suppressive effect on nickel ion reduction. However, in the absence of a stabilizer, the plating bath may become unstable, leading to spontaneous decomposition or poor coating quality. Therefore, stabilizers are typically added in very small quantities to achieve a balance between deposition control and bath stability, ensuring a uniform and high-quality coating [11,16].

2.3.4.5. Influence of agitation

Agitation is a critical factor in achieving a uniform electroless NiB coating, as it ensures that the plating solution remains homogenous throughout the deposition process [11,27]. By continuously stirring the solution, agitation helps to minimize concentration gradients of nickel ions and reducing agents. Without proper agitation, these gradients can lead to uneven deposition and variations in coating thickness. Moreover, effective agitation facilitates the removal of hydrogen gases generated during the reaction, preventing defects such as pitting or poor adhesion. This steady movement also helps in maintaining a consistent bath temperature, further contributing to the controlled nucleation and growth of the NiB layer [11,16].

2.4. Applications of Electroless NiB-based Coatings

Electroless NiB coatings have emerged as a versatile and highly effective surface engineering solution, widely adopted across numerous industries due to their exceptional properties. They are extensively utilized in industries such as automotive, aerospace, chemical processing, and medical devices. Table 2.1 provides a comprehensive overview of the diverse applications of electroless Ni-B coatings, categorizing them by industry and listing key components and typical coating thicknesses.

Table 2.1. Application of electroless NiB-based coatings [11,22,27,35,37,56,57].

Application	Components
Automotive	Fuel injectors, piston rings, cylinder liners, crankshafts, camshafts, gears, turbocharger components, exhaust systems, brake components, and transmission parts.
Aircraft/Aerospace	Turbine blades, landing gear components, hydraulic system parts, engine mounts, compressor components, and structural components.
Electrical	Motor shafts, rotor components, electrical connectors, and switchgear components.
Material Handling	Hydraulic cylinders, conveyor systems, gears, and rollers.
Military	Firearm components, radar systems, and military vehicle parts.
Mining	Hydraulic systems, conveyor components, and mining equipment exposed to abrasive environments.
Moulds & Dies	Plastic injection moulds, die-casting moulds, and extrusion dies.
Railroad	Diesel engine components, brake systems, and railcar hardware.
Textiles	Guides, and weaving machine components.

3. ELECTROLESS NiB-BASED COMPOSITE COATINGS

3.1. Limitations of Electroless NiB Coatings in Demanding Applications

Although electroless NiB coatings are widely used due to their ease of deposition and corrosion protection capabilities, they often fail to meet the performance requirements of more demanding engineering applications. In particular, their tribomechanical response under elevated temperatures, cyclic loads, and prolonged sliding conditions remains insufficient [16,27]. NiB coatings tend to exhibit moderate hardness and limited wear resistance when exposed to such harsh environments, which restricts their use in critical components subjected to high mechanical and thermal stress [11,34]. The underlying causes of this performance gap stem from the amorphous or semi-crystalline nature of the NiB matrix, which lacks the microstructural complexity needed to resist plastic deformation, microcracking, and surface degradation over time. Moreover, under thermal cycling and dynamic contact conditions, these coatings are prone to structural relaxation, surface fatigue, and friction-induced wear, ultimately compromising their reliability and service life [16,27].

To overcome these limitations, recent research has focused on tailoring the microstructure of NiB coatings by incorporating ceramic nanoparticles into the matrix [27]. NiB-based nanocomposite coatings are engineered to enhance mechanical performance through multiple reinforcement mechanisms, including grain refinement, dislocation blocking, and load-bearing effects [58]. In general, materials with finer grain structures exhibit higher hardness compared to those with coarser grains, consistent with the Hall-Petch relationship [59]. This behavior arises because a higher density of grain boundaries acts as barriers to dislocation motion, thereby strengthening the material. In electroless coatings, the incorporation of hard particles further contributes to hardness enhancement. This improvement is primarily attributed to the quantity and distribution of particles embedded in the matrix rather than the inherent hardness of the particles themselves [27].

3.2. Development of Electroless NiB nanocomposite coatings

Various hard ceramic particles have been incorporated into NiB coatings to enhance their hardness and wear resistance, demonstrating the effectiveness of particle reinforcement in improving tribomechanical performance [60]. Georgiza et al. [61] reported that the incorporation of SiC nanoparticles into electroless NiB coatings significantly enhanced their microhardness. This improvement was primarily associated with microstructural modifications induced by the presence of the nanoparticles. Similarly, Niksefat et al. [60] reported that the incorporation of TiO₂ nanoparticles into NiB coatings improved the hardness of the deposits by dispersion strengthening and grain refinement. Moreover, Ekmekci et al. [62] examined the influence of various ceramic reinforcements on the hardness of electroless NiB coatings. A comparison of the microhardness values of NiB and NiB-nanocomposite coatings is illustrated in Figure 3.1. Their results indicated that the incorporation of all types of nanoparticles enhanced the hardness of the deposits, with Al₂O₃ providing the most pronounced improvement, whereas TiO₂ yielded the lowest values. This difference was attributed to the superior compressive strength and higher elastic modulus of Al₂O₃ compared to the other reinforcements.

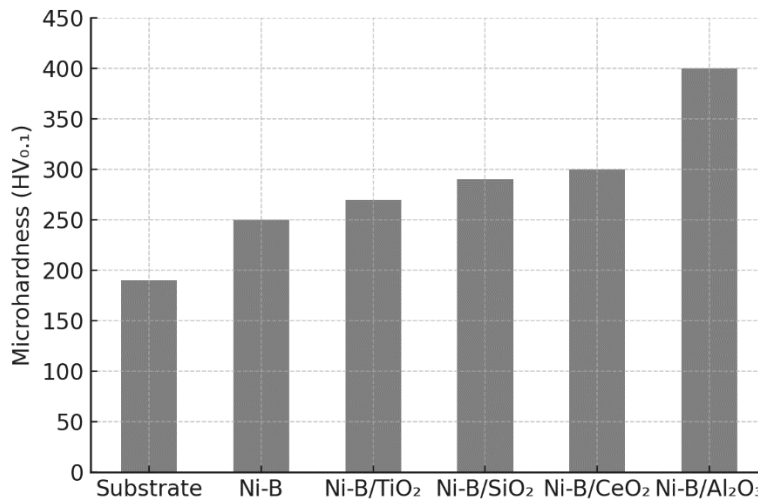


Figure 3.1. Comparison of microhardness values among NiB and NiB-nanocomposite coatings (adapted from [62]).

3.3. Role of Al₂O₃ in Electroless NiB Nanocomposite Coating

Among the wide variety of ceramic reinforcements explored for electroless NiB nanocomposite coatings, Al₂O₃ has attracted particular attention due to its unique combination of mechanical and chemical properties. Its high elastic modulus and

compressive strength make it especially effective in enhancing coating hardness and load-bearing capacity, while its chemical inertness ensures stability in the alkaline plating bath and during service in harsh environments [63,64]. Furthermore, Al_2O_3 exhibits excellent thermal stability, which is crucial for maintaining coating integrity under elevated temperatures and thermal cycling conditions. In tribological applications, the incorporation of Al_2O_3 has been consistently reported to reduce wear rates and improve long-term performance compared to other reinforcements. These attributes collectively justify the choice of Al_2O_3 as the primary reinforcement in the present study, aiming to achieve a balanced improvement in hardness, wear resistance, and high-temperature stability [65,66].

In electroless NiB coatings, the incorporation of Al_2O_3 nanoparticles plays a crucial role in tailoring microstructural evolution. Their presence limits grain growth, provides additional nucleation sites, and hinders localized plastic deformation. As a result, the coating is reinforced through multiple mechanisms, including load transfer, particle-matrix interlocking, and crack deflection. Goral [67] has shown that introducing Al_2O_3 into Ni-based systems promotes grain refinement, modifies crystallographic texture, and enhances surface uniformity, thereby improving structural stability. In this context, the addition of Al_2O_3 to NiB coatings strengthens the matrix by impeding dislocation motion and deflecting crack propagation. These effects contribute directly to an increase in hardness and enhance the overall mechanical reliability of the coating. Moreover, the intrinsic thermal stability and chemical inertness of Al_2O_3 make it particularly beneficial under elevated temperature and oxidative environments, where it contributes to preserving coating integrity and maintaining tribological performance [31].

While the reinforcing role of Al_2O_3 in NiB coatings has been extensively reported in the literature, the consistency and reliability of the resulting properties are largely dictated by the manner in which these ceramic particles are incorporated into the growing matrix during deposition. Achieving a uniform and well-anchored dispersion of nanoparticles is particularly important, as it directly influences the mechanical integrity and wear performance of the final coating. Therefore, a detailed understanding of the particle entrapment mechanism is essential for optimizing deposition parameters and achieving reproducible coating behavior. The following

section presents the underlying mechanism of Al_2O_3 incorporation, offering a process-level framework for interpreting the evolution of nanocomposite microstructure.

3.4. Mechanism of Electroless NiB- Al_2O_3 Nanocomposite Coating

The incorporation of Al_2O_3 nanoparticles into electroless NiB coatings follows a sequential process, which is divided into three successive stages, as illustrated in Figure 3.2. The initial stage of electroless NiB- Al_2O_3 composite coating formation involves the simultaneous autocatalytic reduction of nickel ions and the physical interaction of Al_2O_3 nanoparticles with the growing surface. As the Ni^{2+} ions are reduced by the chemical reducing agent of NaBH_4 , a thin amorphous NiB layer begins to nucleate on the activated substrate. This newly forming matrix provides a dynamic surface for the subsequent capture of dispersed Al_2O_3 particles [48]. Concurrently, Al_2O_3 particles dispersed in the plating bath are transported toward the substrate surface by convection and Brownian motion. Upon approaching the substrate, these particles experience weak physical adsorption, primarily governed by van der Waals forces and electrostatic interactions, resulting in temporary adherence to the growing layer [68]. The magnitude and direction of this interaction are strongly influenced by the surface charge of both the particles and the substrate, which are in turn affected by the bath pH and the presence of dispersing agents [68].

In the second stage, as the autocatalytic reduction of nickel ions proceeds, the incipient NiB matrix gradually encapsulates the loosely adsorbed Al_2O_3 particles. This results in mechanical entrapment. As the electroless deposition continues, the weakly adsorbed Al_2O_3 particles become permanently embedded into the growing NiB matrix, resulting in a uniform composite layer with distributed ceramic reinforcement [48]. This marks stage 3, where the final embedded structure is developed. The degree of incorporation depends on several factors including particle size, zeta potential, concentration, and hydrodynamic conditions such as agitation or substrate rotation. A well-stabilized suspension and uniform particle distribution are critical to avoid agglomeration and to ensure homogeneous particle embedding [48]. The effectiveness of this incorporation mechanism underlies the enhanced hardness, wear resistance, and thermal stability observed in NiB- Al_2O_3 nanocomposite coatings.

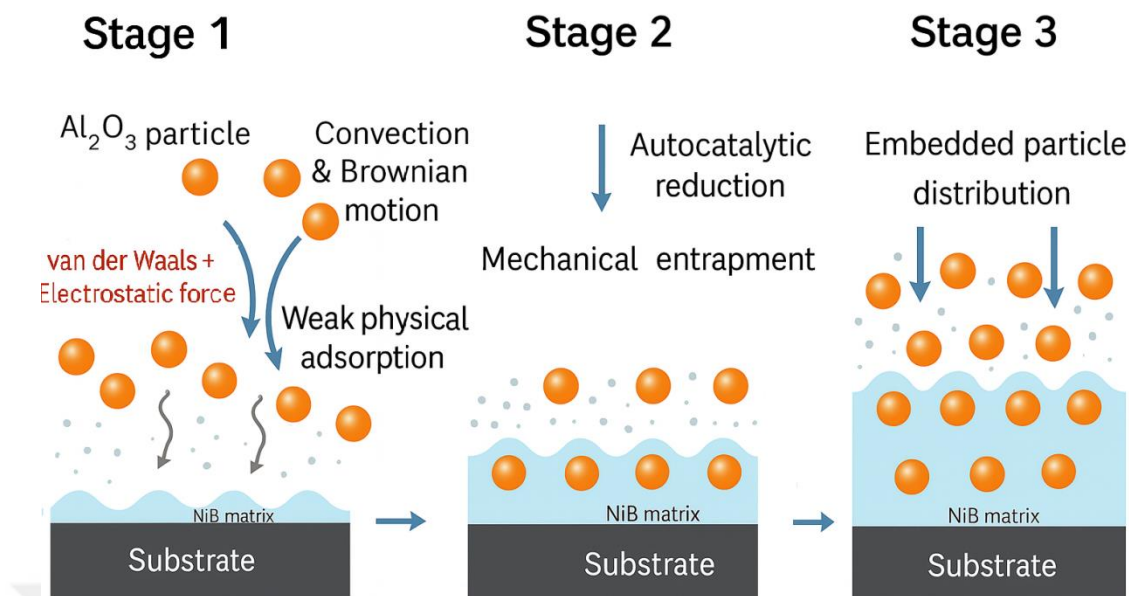


Figure 3.2. Schematic representation of the particle incorporation mechanism in electroless NiB-Al₂O₃ nanocomposite coatings.

3.5. Particle Stabilization Mechanisms in Electroless NiB-Al₂O₃ Baths

The successful co-deposition of Al₂O₃ nanoparticles into electroless NiB coatings depends strongly on the ability to maintain a stable and well-dispersed suspension throughout the plating process. Nanoparticles, due to their high surface energy, tend to agglomerate in aqueous environments, especially under high-ionic-strength conditions such as those found in chemical plating baths. Uncontrolled aggregation leads to inhomogeneous incorporation, porosity, and roughness, severely compromising coating quality and performance [69,70].

One of the most effective approaches to prevent particle agglomeration and maintain a stable suspension within electroless plating baths is the use of surfactants. These amphiphilic molecules facilitate dispersion by introducing repulsive forces that counteract van der Waals attractions and particle-particle collisions. Depending on their molecular structure and charge characteristics, surfactants can stabilize suspensions via electrostatic interactions (by enhancing surface charge repulsion), steric hindrance (by forming physical barriers), or a combination of both, referred to as electrosteric stabilization [68].

However, the effectiveness of a particular surfactant is not fixed but rather highly sensitive to the surrounding physicochemical environment. Among the various bath parameters, pH plays a dominant role, as it directly affects the ionization state of both

the nanoparticle surface and the functional groups of the surfactant. Consequently, a surfactant that is effective under acidic conditions may exhibit poor performance in alkaline environments, or vice versa [70]. Thus, the selection and optimization of surfactants should be carried out with careful consideration of the solution pH, as it plays a critical role in governing the particle-surfactant interaction mechanisms.

3.5.1. pH-dependent surface charge behavior of Al₂O₃ nanoparticles

Aluminum oxide (Al₂O₃) is an amphoteric ceramic whose surface charge is highly sensitive to the pH of the surrounding environment. This behavior arises from the protonation and deprotonation reactions of surface hydroxyl (-OH) groups, which modulate the electrostatic character of the particle surface. The critical point at which the net surface charge is zero is known as the isoelectric point (IEP), which typically lies between pH 8 and 9 for Al₂O₃. Below this point, protonation predominates, leading to positively charged surface sites (Al-OH₂⁺) [71]. Conversely, under alkaline conditions, deprotonation occurs, resulting in negatively charged sites (Al-O⁻). This behavior is summarized in Table 3.2.

Table 3.1. Surface charge behavior of Al₂O₃ nanoparticles as a function of pH.

pH Range	Surface Group	Surface Charge
pH < ~7-8	Al-OH ₂ ⁺	Positively charged (cationic)
pH ≈ 8-9	Al-OH	Near neutral (IEP zone)
pH > 9	Al-O ⁻	Negatively charged (anionic)

This pH-dependent surface behavior critically influences how Al₂O₃ nanoparticles interact with different types of surfactants. Ji et al. [68] highlighted that the stabilization efficiency of surfactants is highly contingent upon the interplay between the solution pH and the point of zero charge (PZC) of Al₂O₃ nanoparticles. Their findings revealed that under acidic conditions (pH < PZC), where Al₂O₃ surfaces are positively charged, anionic surfactants can effectively enhance colloidal stability through electrostatic attraction. In contrast, at alkaline pH values (pH > PZC), the application of cationic surfactants may lead to charge neutralization or even overcompensation, resulting in a diminished zeta potential and increased risk of particle agglomeration [68,71,72].

3.5.2. Surfactant selection for electroless NiB-Al₂O₃ electroless coatings

The ionic nature of the surfactant plays a decisive role in nanoparticle dispersion, suspension stability, and coating quality in electroless NiB-Al₂O₃ systems. Surfactants

are generally classified into three types based on their charge: nonionic, cationic, and anionic [70]. Among the wide variety of surfactants available, Tween 60, CTAB, and SDS were selected for detailed comparison because they are among the most frequently reported in the literature for nanoparticle stabilization in aqueous systems [70,73,74].

The critical micelle concentration (CMC) is a key physicochemical parameter of surfactants. It is defined as the minimum concentration at which surfactant molecules spontaneously aggregate to form micelles in solution, marking the transition from monomeric to aggregated states. A lower CMC indicates higher surface activity at lower concentrations, whereas a higher CMC suggests that larger amounts of surfactant are required to achieve micelle formation [68,70,75]. To illustrate the structural and physicochemical differences among the selected surfactants, Table 3.2 summarizes their basic parameters.

Table 3.2. Structural and physicochemical parameters of representative surfactants [70,71].

Property	CTAB	SDS	Tween 60
Surfactant type	Cationic	Anionic	Nonionic
CMC value	9.2×10^{-4} mol/L	8.2×10^{-3} mol/L	2.8×10^{-2} mol/L
Chemical formula	$C_{19}H_{42}BrN$	$NaC_{12}H_{25}SO_4$	$C_{64}H_{126}O_{26}$
Molecular weight	364.46 g/mol	288.38 g/mol	1310.0 g/mol

While CTAB exhibits the lowest CMC and therefore the highest surface activity at low concentrations, its cationic nature makes it incompatible with highly alkaline plating baths. At $pH > 9$, where Al_2O_3 particles are negatively charged, CTAB molecules are electrostatically attracted to the particle surface. This interaction compresses the electrical double layer and reduces the magnitude of the zeta potential, ultimately promoting agglomeration and sedimentation [70]. On the other hand, Tween 60, with the highest CMC, stabilizes nanoparticles only through steric hindrance and therefore provides limited long-term dispersion stability [70]. In contrast, SDS is an anionic surfactant with a sulfate head group and a hydrophobic tail. Under high-pH conditions, it reinforces the negative surface charge of Al_2O_3 particles and enhances their mutual repulsion. Additionally, its intermediate CMC value allows efficient micelle formation at moderate concentrations, enabling dual-mode stabilization [76]. For these reasons, SDS was selected as the optimal dispersant for the present electroless NiB- Al_2O_3 coating system.

3.5.3. Role of sodium dodecyl sulfate (SDS) in NiB-Al₂O₃ electroless coatings

In this study, Sodium dodecyl sulfate (SDS) was chosen as the surfactant due to its anionic nature, which plays a crucial role in stabilizing Al₂O₃ nanoparticles within the plating bath [77]. SDS molecules dissociate in aqueous solution into sodium cations (Na⁺) and dodecyl sulfate anions (C₁₂H₂₅OSO₃⁻). SDS is an anionic surfactant widely used in colloidal and coating systems due to its strong amphiphilic character. The molecule consists of a negatively charged sulfate head group, which is highly hydrophilic, and a long hydrocarbon chain that forms the hydrophobic tail. This dual structure enables SDS to significantly reduce surface tension, promote wetting, and stabilize dispersions of nanoparticles by providing electrostatic repulsion between particles [75]. In electroless coating processes, SDS plays a crucial role in controlling nanoparticle dispersion, preventing agglomeration, and enhancing the uniformity and quality of the deposited layers. Figure 3.3 depicts the amphiphilic nature of SDS, clearly distinguishing between its hydrophilic head group and hydrophobic alkyl tail, both of which are essential to its surfactant behavior.

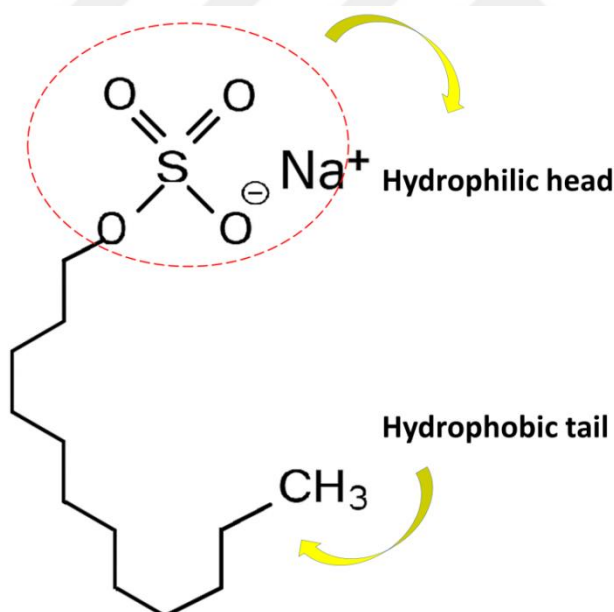


Figure 3.3. Molecular structure of Sodium Dodecyl Sulfate (SDS) showing hydrophilic head and hydrophobic tail.

In the present study, the electroless NiB bath operates at a strongly alkaline pH of approximately 13. Under these conditions, the surface of Al₂O₃ nanoparticles is predominantly negatively charged, resulting in considerable electrostatic repulsion between particles, as shown in Figure 3.2. This repulsion aids in preventing agglomeration, which is essential for maintaining a uniform suspension. However, due

to the elevated ionic strength and the chemically complex environment of the plating solution, electrostatic repulsion alone may not suffice to ensure long-term colloidal stability. To further enhance the dispersion stability, an anionic surfactant, sodium dodecyl sulfate (SDS), was introduced into the bath [76]. SDS molecules, composed of a hydrophilic $-\text{OSO}_3^-$ head and a hydrophobic alkyl tail, contribute to dispersion stability through two complementary mechanisms:

Electrostatic stabilization: At high pH, both the Al_2O_3 surface and the SDS anions are negatively charged, which limits direct electrostatic adsorption. Although direct electrostatic adsorption of SDS molecules onto the negatively charged Al_2O_3 surface is limited at high pH, SDS still exerts a profound influence on the electrical double layer structure. The dissociated sulfate anions ($-\text{OSO}_3^-$) from SDS remain free in solution and enrich the diffuse layer surrounding the particles. This increased anionic concentration extends the diffuse layer and enhances the negative zeta potential measured at the slipping plane [76]. Ultimately, the stabilization effect is achieved not through surface adsorption but through the modification of the surrounding ionic environment. SDS strengthens interparticle repulsion by increasing the electrostatic barrier, even in the absence of direct binding. Consequently, this enhanced electrostatic repulsion between particles improves colloidal stability and prevents aggregation.

Steric stabilization: The hydrophobic tails of SDS molecules form a dynamic shielding layer around the nanoparticles. Even without strong surface binding, these molecular brushes act as physical barriers when particles approach each other, providing steric hindrance that reduces the likelihood of particle agglomeration [76]. These dual mechanisms, electrostatic and steric stabilization, work synergistically to ensure the long-term stability of Al_2O_3 nanoparticles within the highly alkaline electroless plating bath. As a result, homogeneous particle dispersion is maintained throughout the process, enabling the formation of uniform and defect-free NiB- Al_2O_3 nanocomposite coatings with enhanced microstructural integrity. Figure 3.4 schematically illustrates this dual stabilization mechanism, highlighting the role of SDS in preventing particle agglomeration through combined electrostatic and steric effects.

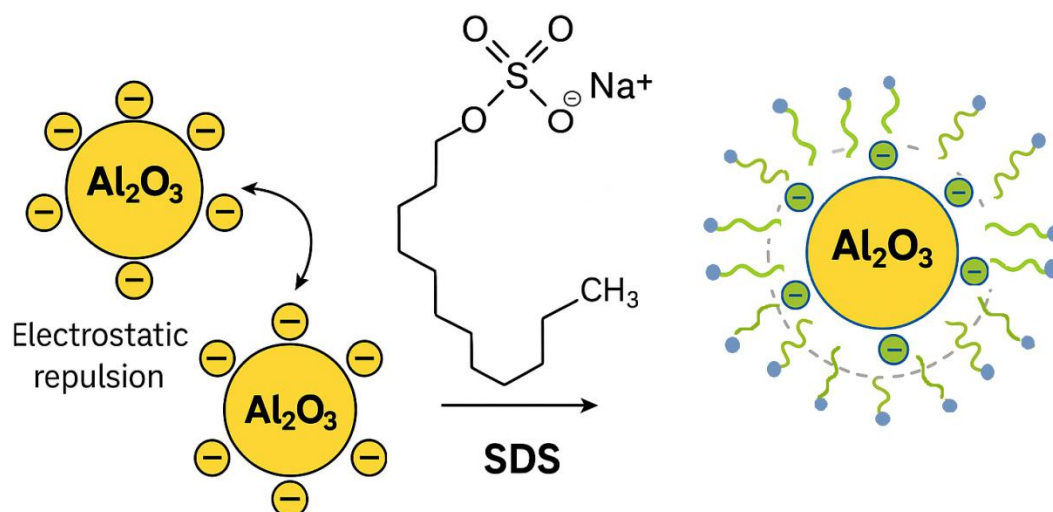


Figure 3.4. Dual stabilization of Al_2O_3 nanoparticles by SDS under high pH. Dissociated sulfate anions (blue) increase the zeta potential via enrichment of the ionic environment, while hydrophobic SDS tails (green) form steric barriers, preventing particle agglomeration.

4. TRIBOLOGY OF COATINGS

This chapter establishes the mechanism-oriented framework needed to interpret the friction and wear responses of electroless NiB and NiB-Al₂O₃ coatings tested at 25 °C, 200 °C, 400 °C, and 600 °C. It sets out the conceptual background, defines the measurements and metrics used throughout the thesis, and formulates the study-specific hypotheses that guide the analysis in later chapters. The chapter is organized along four axes: (i) essential tribology concepts and metrics, (ii) tribochemical and thermo-mechanical processes at elevated temperatures, (iii) the role of the counterface (alumina ball) and third-body dynamics, and (iv) mechanism hypotheses specific to this work.

4.1. Wear Mechanisms in Tribology

Tribology is the study of friction, wear, and lubrication in interacting surfaces under relative motion. It plays a crucial role in engineering, affecting the efficiency, durability, and maintenance of mechanical systems [28,78]. The behavior of contacting surfaces is influenced by various factors, including material properties, surface roughness, environmental conditions, and operating parameters such as load and speed. A comprehensive understanding of tribology enables engineers to develop advanced materials, and implement surface modifications that enhance wear resistance and reduce energy losses. By effectively managing friction and minimizing wear, tribological advancements contribute to improved performance, extended service life, and reduced operational costs in a wide range of applications [79,80].

One of the most critical aspects of tribology is wear, a progressive material loss phenomenon that occurs due to relative motion between contacting surfaces. It plays a significant role in determining the lifespan, efficiency, and reliability of mechanical components in various industries, including aerospace, automotive, biomedical, and manufacturing [28]. Wear mechanisms can be highly complex, involving mechanical, thermal, and chemical interactions. A fundamental understanding of wear mechanisms is essential for designing wear-resistant materials and optimizing tribological performance.

4.1.1. Adhesive wear

Adhesive wear arises from the formation and subsequent rupture of micro-junctions at real contact areas, particularly when protective films are absent or discontinuous. Under such conditions, direct metal-to-metal contact may occur, promoting strong atomic or molecular interactions between the mating surfaces [80]. Once these bonded junctions form, they are subjected to localized shear stresses under sliding, which eventually causes them to fracture. This process results in intermittent material transfer, where fragments detach from one surface and adhere to the other, contributing to the formation of thin transfer films [81]. As sliding progresses, failed junctions may accumulate on the counterface as smeared material, producing patchy layers that vary in thickness depending on local contact dynamics. These transfer films can grow, smear along the wear track, or be periodically removed due to mechanical disruption or poor adhesion [82–84]. Figure 4.1 schematically illustrates this mechanism, emphasizing micro-junction formation, shear-induced fracture, and material transfer under insufficient film coverage.

The occurrence of adhesive wear in systems similar to the present study is often supported by multiple tribological signatures. For instance, COF profiles recorded during dry sliding at low temperatures typically exhibit low average values punctuated by short, irregular fluctuations, which are indicative of transient junction formation and rupture. These intermittent stick-slip events are consistent with localized bonding between the coating and the counterface, followed by abrupt detachment. In terms of surface morphology, adhesive contributions are commonly identified through patchy and smeared regions on the wear track floor, often lacking well-defined cutting traces [85]. These smeared areas differ significantly from the aligned grooves characteristic of abrasive wear, and instead appear as scattered metallic patches and film-like residues. The morphology and composition of these transfer films typically support the presence of adhesive wear mechanisms in the early stages of sliding, before thermally activated processes such as oxidation or particle detachment dominate the interfacial behavior [86,87].

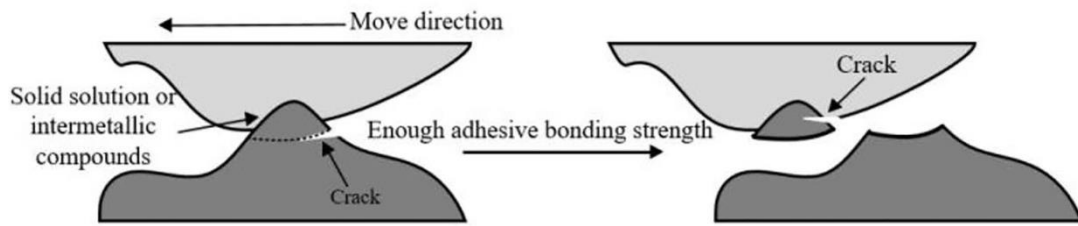


Figure 4.1. Schematic illustration of the adhesive wear mechanism involving crack formation and material transfer due to strong interfacial bonding [80].

4.1.2. Abrasive wear

Abrasive wear emerges when a harder material or abrasive particles interact with a softer surface, leading to material removal through mechanical action. Unlike adhesive wear, which arises due to molecular bonding between contacting surfaces, abrasive wear is primarily mechanical and results from the plowing or cutting action of hard asperities or particles [86,87]. The severity of abrasive wear depends on multiple factors, including the relative hardness of the materials, contact pressure, abrasive particle characteristics, and environmental conditions. Abrasive wear can be categorized into two primary types: two-body abrasion and three-body abrasion.

4.1.2.1. Two-body abrasion

Abrasive wear occurs when a harder asperity or surface directly plows into a softer surface, cutting or deforming it through mechanical interaction. In this type of wear, the harder material acts like a cutting tool, progressively removing material from the softer surface [86]. The extent of wear depends on the hardness difference between the two materials, the contact pressure, and the relative motion between the surfaces, as depicted in Figure 4.2. Abrasive wear is promoted by factors such as high local hardness contrast, inadequate surface film coverage, and the presence of sharp features or hard inclusions on the counterface. In two-body abrasion, the harder surface directly plows into and wears down the softer material, generating wear debris in the form of fine particles. If these debris particles are not efficiently removed from the contact zone, they may accumulate between the sliding surfaces and begin to act as third-body abrasives [86,88].

The severity of two-body abrasion can be significantly influenced by the presence and distribution of hard reinforcement particles within a composite matrix. When ceramic reinforcements such as Al_2O_3 remain well-anchored in the coating, they can inhibit plastic deformation, reduce penetration depth of the counterface asperities, and

promote load distribution. These effects serve to suppress abrasive plowing and contribute to improved wear resistance. However, the effectiveness of reinforcement depends on the integrity of the particle-matrix interface. At elevated temperatures or under prolonged sliding, thermal softening or interfacial fatigue may weaken this bonding, increasing the risk of particle detachment. Once dislodged, formerly protective particles can transform into mobile third-body abrasives, initiating a shift from two-body to three-body wear mechanisms. This transition is often accompanied by increased wear volume, localized surface damage, and a decrease in frictional stability. One of the underlying causes of this transition is thermal softening, which denotes the temperature-induced reduction in mechanical strength or hardness of a material, particularly in metallic matrices. As the operating temperature increases, the metallic phase becomes more susceptible to plastic deformation and less effective at anchoring the ceramic particles. Consequently, thermal softening facilitates the detachment of reinforcement particles, undermines load-bearing capability, and accelerates the wear process through a shift towards less controlled third-body interactions.

In contrast, under moderate temperature conditions where thermal degradation is limited, the dominant wear mode remains two-body abrasion. In many hard coating systems, this occurs when the matrix retains its structural rigidity, and reinforcement particles remain well-anchored. In such cases, material removal typically occurs through micro-cutting and plowing by either hard counterface asperities or embedded ceramic particles acting as micro-cutters. The extent of such abrasion depends on particle morphology, load conditions, and the mechanical stability of the composite structure.

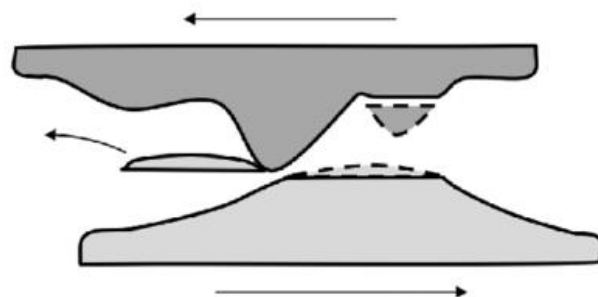


Figure 4.2. Schematic representation of two-body abrasive wear mechanism [80].

4.1.2.2. Three-body abrasion

Three-body abrasion takes place when unattached hard particles lodge between sliding or rolling surfaces, leading to additional wear. Unlike two-body abrasion, where one surface directly wears down the other, three-body abrasion involves freely moving particles that act as a grinding medium between the surfaces [88,89]. These particles may originate from external sources, such as environmental dust or sand, or from wear debris generated by the interacting surfaces themselves, as seen in Figure 4.3.

In tribological systems containing particulate-reinforced coatings, three-body abrasion may arise as a secondary wear mechanism when hard reinforcement particles become detached from the matrix and trapped between the sliding surfaces. This phenomenon tends to become more pronounced at elevated temperatures, where thermal softening and interfacial stresses increase the likelihood of particle pull-out. Detached particles that once acted as reinforcing agents may circulate within the contact zone and function as mobile abrasives, potentially intensifying wear [87,88].

Compared to two-body abrasion, which is driven by rigid asperities or firmly anchored particles, three-body abrasion typically results in irregular, shallow grooves and smeared regions due to the rolling or dragging motion of loose debris. Such features are often accompanied by embedded fines and fragmented particle islands within the wear track, particularly in systems with high reinforcement content or insufficient particle-matrix bonding [86].

Additionally, the transition from two-body to three-body regimes may be reflected in the frictional behavior, with milder COF fluctuations arising from dynamic third-body interactions rather than severe plowing. Thus, the wear resistance provided by ceramic particles depends not only on their intrinsic hardness but also on their mechanical retention within the matrix. Failure of particle-matrix anchorage can facilitate a shift toward less stable, debris-driven abrasion modes.

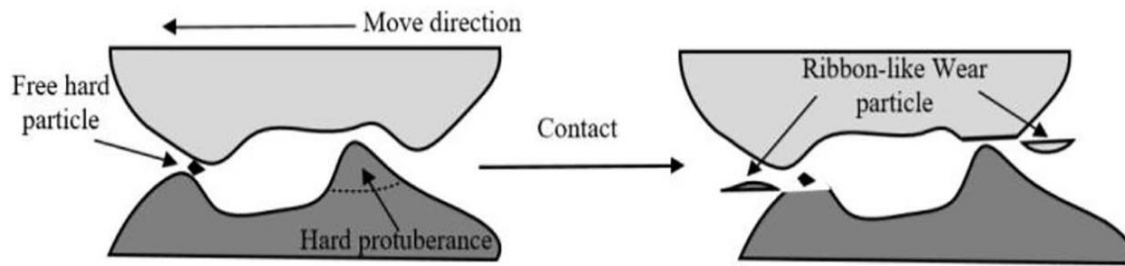


Figure 4.3. Schematic illustration of three-body abrasive wear mechanism, where a free hard particle entrapped between the surfaces generates ribbon-like wear debris through repeated contact and plowing [80].

4.1.3. Erosive wear

Erosive wear is a distinct form of material degradation that arises from the repeated impact of high-velocity solid particles striking a surface. Unlike abrasive or adhesive wear, erosive wear is primarily governed by the dynamic interaction between the incoming particles and the target material, rather than continuous surface contact or sliding. During erosion, hard particles collide with the surface at various angles, leading to localized plastic deformation, microcutting, or crack initiation depending on the impact conditions and material response [80,87,90]. This complex interaction between impacting particles and the surface is schematically illustrated in Figure 4.4, where both plastic deformation and brittle fracture zones are shown as a result of repeated high-energy impacts.

Several key parameters influence the severity and mechanism of erosive wear. Among them, the impact angle plays a critical role [86]. Ductile materials tend to exhibit the highest erosion rates at relatively shallow impact angles, approximately 20° , where localized plastic deformation governs the response around impact zones. At normal incidence (90°), however, these materials typically show improved erosion resistance due to the reduced effectiveness of plowing mechanisms. In contrast, brittle materials behave oppositely: they are more susceptible to severe surface damage at 90° impact angles, primarily due to crack initiation and propagation. Nevertheless, they demonstrate greater erosion resistance at lower impact angles, where the likelihood of crack formation is significantly reduced [86]. Additionally, the impact velocity of the particles significantly affects the kinetic energy transferred during each collision, thus directly influencing the erosion rate, often following a power-law relationship. The hardness and toughness of both the target material and the erodent particles are also

crucial. Harder particles are more likely to penetrate or fracture the surface, while softer target materials may undergo plastic flow or embedment [80,90].

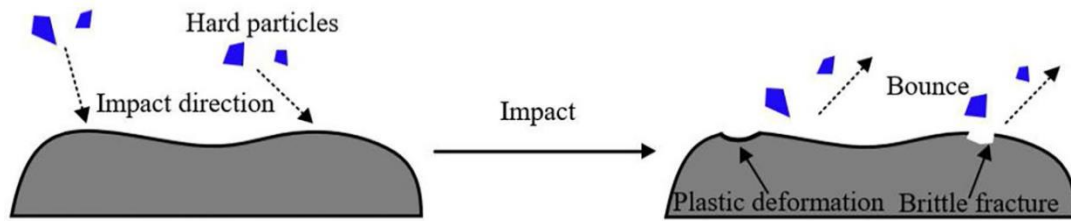


Figure 4.4. Schematic illustration of the erosive wear mechanism caused by hard particle impacts [80].

4.1.4. Fatigue wear

Fatigue wear is a degradation mechanism driven by the accumulation of subsurface damage under cyclic loading conditions. Unlike abrasive or adhesive wear, which primarily affect the surface layer, fatigue wear originates beneath the surface due to repeated mechanical or thermal stresses [86]. This mechanism involves the progressive nucleation and propagation of microcracks, which eventually coalesce and lead to surface spallation or delamination. The failure typically occurs along planes of maximum shear stress, often oriented parallel to the surface, and results in the detachment of flake-like debris [86]. The severity of fatigue wear is influenced by factors such as material ductility, hardness gradients, cyclic strain amplitude, and possibly thermal expansion mismatches. These damage features and their progression are schematically represented in Figure 4.5, which highlights the typical subsurface crack evolution associated with fatigue wear under cyclic loading [91–93] [80].

In high-temperature tribological systems, fatigue wear may become increasingly relevant due to thermal expansion mismatches between contacting materials, which generate additional interfacial stresses during sliding. These mismatches can be exacerbated by matrix softening and repetitive thermal cycling, ultimately leading to subsurface crack initiation and fatigue-related surface damage. The resulting features may include step-like surface morphologies, flake detachment, and crack mouths, often observed in systems operating under extreme thermomechanical conditions and coexisting with other mechanisms such as three-body abrasion or oxidative wear [94–96].

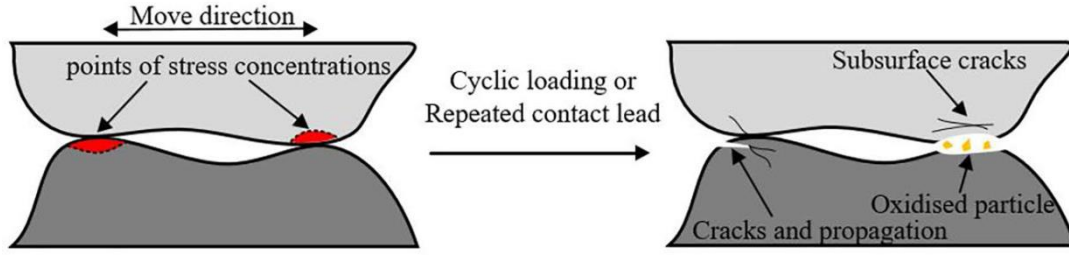


Figure 4.5. Schematic illustration of fatigue wear mechanism, showing crack initiation at stress concentration zones followed by subsurface crack propagation and formation of oxidized wear particles under cyclic loading [80].

4.2. Coefficient of Friction (COF) Behavior and Regime-Based Analysis

The time-dependent coefficient of friction, denoted as $\mu(t)$, typically exhibits three distinct stages during ball-on-disk tribological tests: an initial run-in period, a subsequent steady-state regime, and a breakdown or mild decrease. These regimes reflect the evolution of contact conditions, material transfer, and tribolayer stability under varying mechanical and thermal loads [97]. To quantitatively evaluate the frictional behavior during the stable regime, the average coefficient of friction ($\bar{\mu}$) was calculated over a predefined steady-state time window $[t_1, t_2]$, excluding short-term transients or sharp frictional spikes associated with tribofilm failure or sudden debris interaction. The average COF was defined using equation 4.1:

$$\bar{\mu} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \mu(t) dt \quad (4.1)$$

where:

$\mu(t)$ is the instantaneous friction coefficient as a function of time,

t_1 and t_2 define the bounds of the steady-state regime.

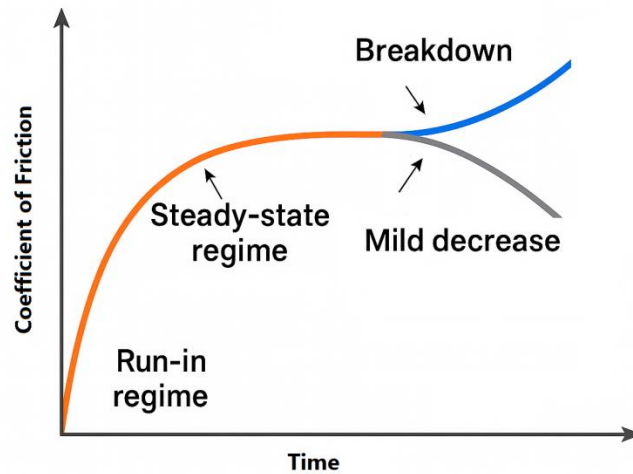


Figure 4.6. Schematic representation of the typical COF evolution during ball-on-disk tribotests, highlighting three major regimes: (i) the run-in period with asperity adaptation, (ii) the steady-state regime with stabilized tribofilm formation, and (iii) two terminal outcomes: (a) a breakdown regime caused by tribolayer failure, or (b) a mild decrease regime driven by surface smoothing and thermal softening.

The coefficient of friction generally evolves in a regime-based manner throughout the sliding duration, particularly under controlled tribotesting conditions. As illustrated schematically in Figure 4.6, the frictional response typically progresses through three main regimes: (i) an initial run-in stage, (ii) a steady-state phase with relatively stable COF behavior, and (iii) a terminal regime characterized by either a sudden increase or a mild decline in friction.

During the run-in regime, asperities from both contacting surfaces undergo mechanical adaptation. This stage is typically marked by an initial rise in COF due to microcutting, plowing, or unstable third-body interactions. As the surfaces conform and initial tribofilms begin to develop, the system transitions into a more stable condition. The steady-state regime reflects a dynamic balance between tribofilm formation, debris removal, and interfacial accommodation [97]. If a continuous third-body layer or lubricating tribofilm forms successfully, the COF may stabilize with only minor fluctuations, indicating long-term frictional equilibrium. The nature and duration of the steady-state regime can vary significantly depending on material composition, surface properties, reinforcement type, and temperature. In some systems, well-retained reinforcement particles such as Al_2O_3 may contribute to improved load-sharing and reduced interfacial stress, indirectly promoting tribofilm stability and COF uniformity [98,99].

Beyond this regime, two distinct outcomes may occur. In the breakdown regime, tribological stability becomes unsustainable due to mechanisms such as tribofilm rupture, surface delamination, or oxide fragmentation. This stage is often manifested by chaotic COF fluctuations or a sudden increase in friction. Alternatively, a mild decrease in COF may be observed due to mechanisms such as progressive tribofilm densification, matrix softening, or tribological compaction of asperities. These effects may enhance conformity between sliding partners and reduce interfacial shear stress. In composite coatings, especially those with effective reinforcement retention, such gradual decreases may occur without aggressive third-body abrasion [97].

4.3. Wear Rate and Archard-Based Approach

The wear rate (W) is a critical parameter used to quantify material degradation in tribological systems. It serves as a measure of mechanical durability and provides a robust basis for comparing different coatings, materials, contact conditions, and test environments. In order to standardize this evaluation, the Archard equation [87,97] remains one of the most widely adopted analytical models, particularly for dry sliding conditions involving adhesive and abrasive wear mechanisms. The Archard wear equation is expressed as equation 4.2:

$$W = \frac{K \cdot L \cdot S}{H} \quad (4.2)$$

It is more commonly rearranged as the volumetric wear rate per unit load and sliding distance, as shown in equation 4.3:

$$\text{Wear rate} = \frac{V}{L \cdot S} \quad (4.3)$$

where:

W is the specific wear rate (mm³/N.m),

V is the wear volume (mm³),

L is the normal load (N),

S is the sliding distance (m),

H is the hardness of the softer surface (Pa),

K is the dimensionless wear coefficient.

This formulation assumes that wear is linearly proportional to both the applied load and the sliding distance, and inversely proportional to the hardness of the material. While originally developed for metallic sliding pairs, the model remains valid for tribological systems involving coatings, multilayer systems, and nanocomposites, especially when used comparatively [87].

In the present study, the wear rate values were interpreted based on the Archard model to establish a consistent and comparable framework across different coating compositions and test conditions. This approach offers a simplified view of wear, focusing on the effects of load, distance, and the hardness of the surface. Even though more complex effects, such as tribochemical film formation, oxidation, or third-body abrasion, become influential at elevated temperatures, the Archard model still offers a useful reference point for comparative analysis and aligning current findings with trends reported in the literature [87,100,101].

4.4. Role of Counterface and Third-Body Dynamics in Tribological Interactions

In a tribological contact, the counterface plays a critical role in shaping interfacial interactions, influencing both friction and wear mechanisms [102]. Under certain conditions, such as elevated temperature or mechanical stress, its function may shift from passive contact to active participation in tribochemical reactions, material transfer, and third-body dynamics [103].

The spherical Al_2O_3 ball serving as the counterface in the tribological system provides interfacial stability through its chemical inertness, high hardness, and thermal stability, enabling the formation of distinct surface interactions [104]. It may become actively involved in third-body dynamics under high-temperature or high-load conditions, thereby influencing friction and wear behavior. In such cases, the Al_2O_3 counterface can engage in micro-contact interactions that contribute to the generation of fine debris. These fragments, along with reinforcement particles released from the coating, may accumulate between the sliding surfaces to form a dynamic third-body layer. Depending on their size, morphology, and mobility, this intermediate layer may facilitate smoother sliding by promoting energy dissipation, or it may contribute to

material loss through abrasive interactions, depending on how it evolves within the contact zone [105].

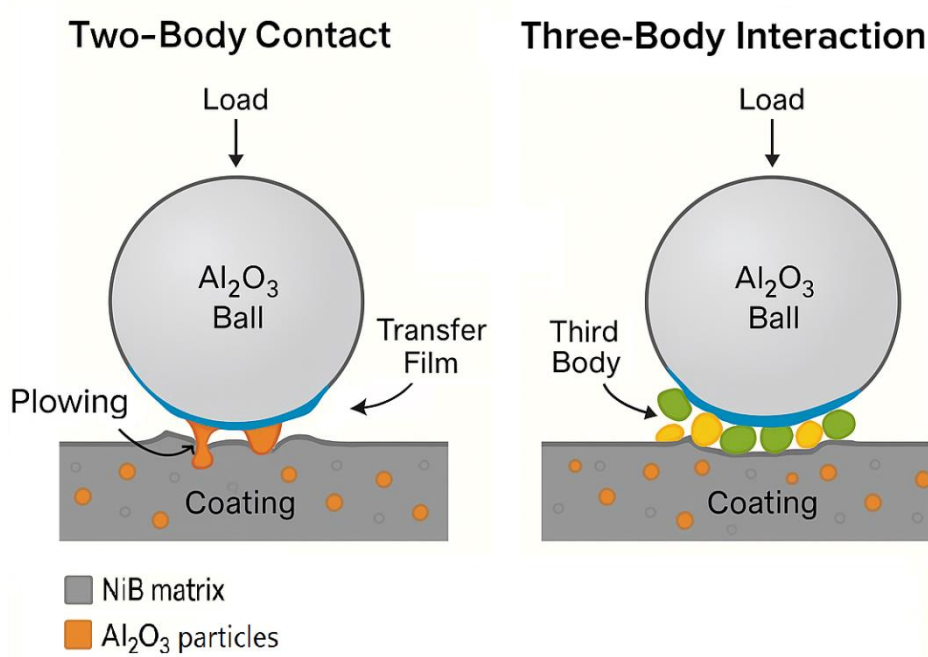


Figure 4.7. Schematic representation of two-body and three-body interactions.

As illustrated in Figure 4.7, tribological interactions in NiB and NiB- Al_2O_3 coated systems can be broadly categorized into two-body and three-body contact regimes, each presenting distinct wear responses and frictional behavior. In two-body contact, direct asperity interactions between the alumina ball and the coating dominate the sliding interface. Detached fragments or hard asperities embedded within the matrix become anchored between the surfaces, inducing a plowing mechanism [106]. This results in deeper penetration into the wear track, producing pronounced grooves and higher R_t values. Consequently, the coefficient of friction curve exhibits short, high-frequency fluctuations due to intermittent adhesion and rupture events at the contact junctions, a behavior commonly associated with adhesive wear. These fluctuations reflect mechanical instabilities, where micro-junction formation and rupture cycles introduce sharp force variations [106].

In contrast, the three-body interaction regime is governed by mobile third-body particles (e.g., loose Al_2O_3 or debris), which roll or drag between the contacting surfaces. These particles act as dynamic load-bearing elements that dissipate energy more uniformly across the contact zone. In the rolling/dragging mode, the wear tracks tend to be shallower and more laterally distributed, as particles reduce vertical

penetration while still causing lateral displacement [107]. As a result, the COF profile becomes more stable, exhibiting lower amplitude oscillations and smoother transitions. This indicates a more controlled frictional response, where tribo-film mediation and particle mobility reduce mechanical shocks at the interface. In some cases, third-body interactions may result in lower and more stable friction profiles, especially when the particles facilitate energy dissipation. However, abrasive or immobilized third-body particles may lead to erratic COF behavior [106]. Nevertheless, it is important to recognize that third-body effects are not universally beneficial. While such layers may reduce friction under certain conditions, particles with angular morphology or limited mobility may instead promote abrasive wear, potentially resulting in increased surface damage rather than enhanced tribological performance.

Supporting this interpretation, SEM-EDS analyses of the alumina counterface revealed localized material transfer, particularly Ni-rich patches, suggesting that the ball surface was partially active in tribofilm formation. This finding challenges the conventional assumption of a passive counterface and underscores its role as an active participant in third-body dynamics, especially at elevated temperatures where material softening and oxidation facilitate adhesion. Therefore, the evolution from two-body to three-body regimes alters the wear morphology while also significantly reshapes the frictional signature of the system, shifting from a mechanically unstable, adhesive-driven plowing mode to a more stabilized third-body-mediated tribological condition [106].

4.5. Surface Roughness Parameters of Worn Tracks and Tribological Interpretation

The surface topography of worn tracks reflects the cumulative outcome of interfacial interactions, including direct asperity contact, third-body effects, and material transfer [38,108]. To characterize this complexity, four key roughness parameters (R_a , R_q , R_z , and R_t) are employed in this thesis to establish quantitative relationships between track morphology and tribological behavior. Surface roughness metrics used in this study are defined as follows. R_a is the arithmetic mean of the absolute deviations from the mean line and provides an overall measure of surface roughness. R_q , the root-mean-square roughness, gives greater weight to outliers than R_a and therefore becomes more sensitive to occasional sharp peaks or deep valleys. R_z is the ten-point height, defined

as the difference between the average height of the five highest peaks and the average depth of the five deepest valleys. It reflects the peak-valley characteristics that govern load carrying and debris accommodation. R_t is the total height of the profile, i.e., the vertical distance between the single highest peak and the single deepest valley observed over the entire evaluation length, making it particularly sensitive to isolated defects [109]. In this work, R_a and R_q are primarily used to quantify the average topography, which is especially relevant to conformity and adhesive tendencies. In contrast, R_z and R_t describe the functional extremes, where peaks control load transfer and valleys govern debris storage. These metrics are particularly useful for correlating worn-surface morphology with transitions between different wear mechanisms. Formally, these parameters are expressed by equations 4.4 through 4.7:

$$R_a = \frac{1}{L} \int_0^L |z(x)| dx \quad (4.4)$$

$$R_q = \sqrt{\frac{1}{L} \int_0^L z^2(x) dx} \quad (4.5)$$

$$R_z = \bar{z}_{5 \text{ peaks}} - \bar{z}_{5 \text{ valleys}} \quad (4.6)$$

$$R_t = \max(z) - \min(z) \quad (4.7)$$

where $z(x)$ denotes the leveled surface profile, and L represents the evaluation length. Figure 4.8 schematically illustrates the principal roughness parameters and emphasizes how each metric captures a distinct functional aspect of worn-surface morphology, thereby linking roughness characterization to tribological performance. The black curve represents the measured surface profile after sliding, while the dashed orange line corresponds to the mean line, which serves as the baseline for roughness evaluation. The schematic illustrates how the mean line provides the reference for calculating R_a and R_q , which describe the average deviation of the profile and are relevant to surface conformity and adhesive behavior. The banded regions defined by the five highest peaks and five deepest valleys (not explicitly drawn but conceptually included) correspond to R_z , capturing the combined role of asperity summits in load

transfer and valleys in accommodating wear debris. In the Figure 4.8, the highest asperity (red triangle) and the deepest valley (blue triangle) are highlighted, together defining the total height parameter $R_t \approx 1.23 \mu\text{m}$. This value corresponds to the extreme vertical distance across the profile and reflects the presence of a pronounced asperity-valley pair, which is highly sensitive to localized defects or severe plastic deformation.

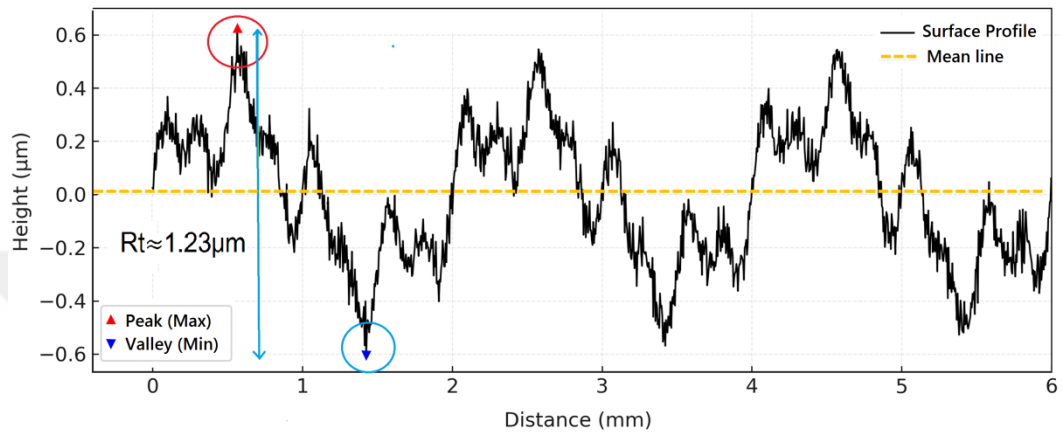


Figure 4.8. Schematic illustration of a worn-track roughness profile with reference to the mean line and principal roughness parameters.

From a tribological perspective, such a schematic is essential because it visualizes how individual roughness parameters highlight distinct functional aspects of surface morphology. R_a and R_q represent the average roughness relevant to adhesion and conformity, whereas R_z and R_t capture the extremes that control peak-peak contact stresses and debris storage capacity [110]. The balance between these metrics provides valuable insights into the evolution of wear regimes: high R_t values suggest asperity fracture or deep groove formation, while moderate R_z values may indicate stable debris accommodation.

4.6. High-Temperature Tribology

High-temperature tribology refers to the study of friction, wear, and lubrication processes in materials and systems operating under elevated thermal conditions, typically above 200°C , where conventional tribological behavior begins to change significantly [78,111]. At such temperatures, both the physical and chemical properties of materials undergo substantial changes, and the resulting surface interactions become increasingly complex. A variety of temperature-induced effects, including oxidation,

softening, and surface transformations, can significantly influence friction and wear behavior. These changes may activate wear mechanisms that are either absent or negligible under ambient conditions, making high-temperature environments particularly challenging for tribological systems [111].

To better understand how elevated temperatures influence surface performance, it is essential to examine the key mechanisms that drive tribological behavior under such extreme conditions. Several interrelated mechanisms influence tribological behavior at high temperatures, as illustrated in Figure 4.9. As the temperature rises, materials may experience softening, which reduces their hardness and load-bearing capacity. This makes them more prone to plastic deformation and adhesive wear. In parallel, thermal activation of atomic diffusion can lead to grain boundary sliding, phase instability, and surface microstructural changes. Additionally, thermally induced stresses may trigger crack initiation and propagation beneath the contact surface, further accelerating material degradation. These factors contribute to increased wear rates, unstable friction behavior, and the generation of wear debris [111].

A more fundamental tribo-mechanical framework can be used to explain these frictional changes. According to the classical model proposed by Bowden and Tabor, the coefficient of friction (μ) is directly proportional to the shear strength (τ) and inversely proportional to the contact pressure (p). At elevated temperatures, matrix softening leads to an increase in real contact area and a corresponding reduction in contact pressure. Simultaneously, the presence of brittle oxide films may increase shear strength due to interlocking and ploughing effects. Collectively, these interrelated mechanisms explain the observed increase in the coefficient of friction (μ) with increasing temperature, as shown in equation 4.8.

$$\mu = \frac{\tau}{p} \quad (4.8)$$

In addition to mechanical effects, chemical and tribochemical processes become increasingly significant at elevated temperatures [111]. Many metallic surfaces react with atmospheric oxygen to form oxide layers. These films can act as protective barriers when they are thermodynamically stable, strongly adherent, and capable of self-repair. However, some oxides are brittle and prone to cracking or delamination during sliding, which leads to oxidative wear. The repeated formation and breakdown

of such layers alters surface topography and may cause instabilities in the coefficient of friction [79].

Therefore, a detailed understanding of the mechanical, thermal, and chemical mechanisms that dominate at high temperatures is vital for the design of reliable tribosystems [112]. Importantly, tribological performance is influenced by the intrinsic properties of materials as well as by system-level factors such as contact geometry, counterface characteristics, and environmental conditions. A comprehensive evaluation of these interdependencies is essential for developing surface treatments and protective coatings that can retain structural integrity and ensure frictional stability under severe thermal stress [29,79]. Consequently, developing engineering materials that retain dimensional stability and tribological efficiency across a wide temperature range remains a central pursuit in high-temperature tribology research.

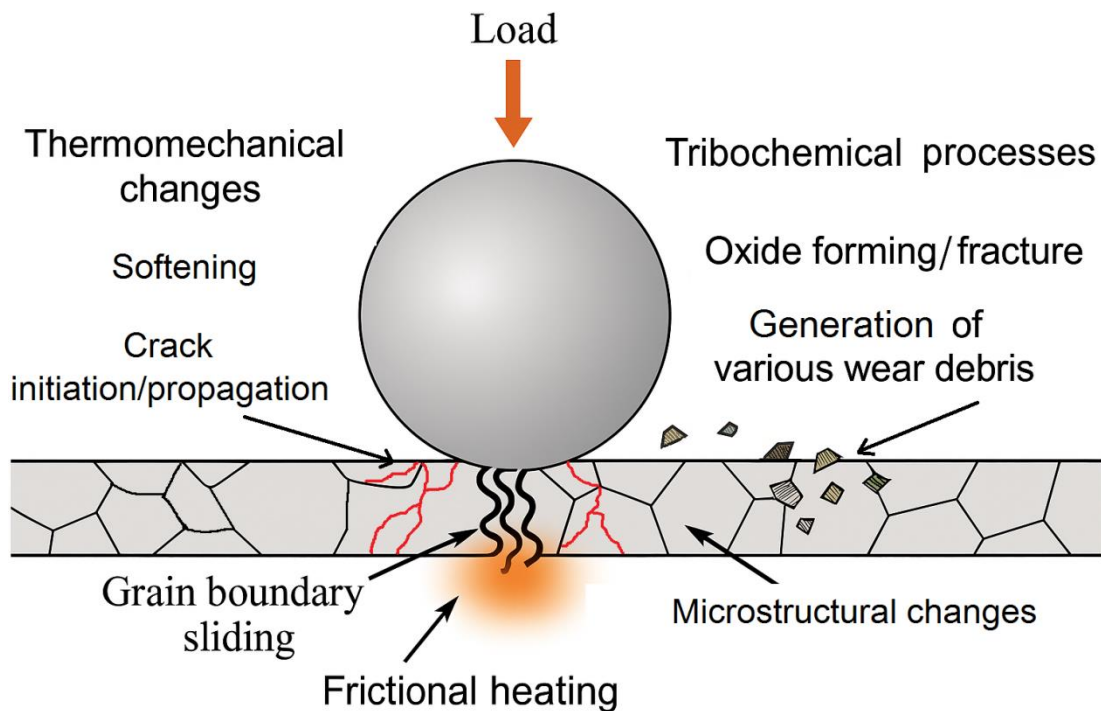


Figure 4.9. Schematic representation of dominant mechanisms in high-temperature tribology.

4.7. High-Temperature Tribology Applications

The practical significance of high-temperature tribological behavior becomes increasingly critical in modern engineering systems, where components are routinely exposed to severe thermal and mechanical conditions. The field of high-temperature tribology has gained increasing importance in recent years due to the growing demand

for components that can sustain mechanical integrity and tribological performance under thermally severe conditions. Unlike conventional systems that operate within narrow temperature bands, modern applications such as jet engine bearings, rolling-element bearings, turbocharger rotors, and thrust assemblies require surfaces that can maintain functional reliability across a broad thermal spectrum [78,113]. These components are subjected to elevated operating temperatures and experience rapid thermal fluctuations, thermal cycling, and complex stress states that intensify wear processes and accelerate material degradation. These high-temperature operating conditions introduce complex tribological challenges, as summarized schematically in Figure 4.10.

Many critical components used in aerospace propulsion systems, automotive engines, and energy conversion devices routinely operate within the 200 °C to 600 °C temperature range, where cyclic contact, oxidative environments, and thermally driven phase transformations play a major role in determining surface performance. In high-temperature environments, processes such as oxide layer formation, matrix softening, reinforcement debonding, and subsurface crack propagation may act as dominant damage mechanisms, either individually or in combination. These factors collectively compromise the wear resistance and functional lifespan of tribological interfaces [78].

Such a changing perspective demands a holistic understanding of how coatings behave across temperature variations, including the transitional evolution of wear mechanisms that cannot be captured through single-point evaluation. This thesis is aligned with this approach. Instead of limiting evaluation to a fixed temperature, the tribological behavior of electroless NiB and NiB-Al₂O₃ nanocomposite coatings is examined across a comprehensive temperature range from 25 °C to 600 °C, thereby uncovering the underlying transformations in wear mechanisms and failure modes. By addressing how tribological responses evolve as thermal activation increases, this research contributes to the development of surface technologies that offer both high performance and thermal adaptability, which are critical requirements for next-generation mechanical systems operating under thermal extremes.

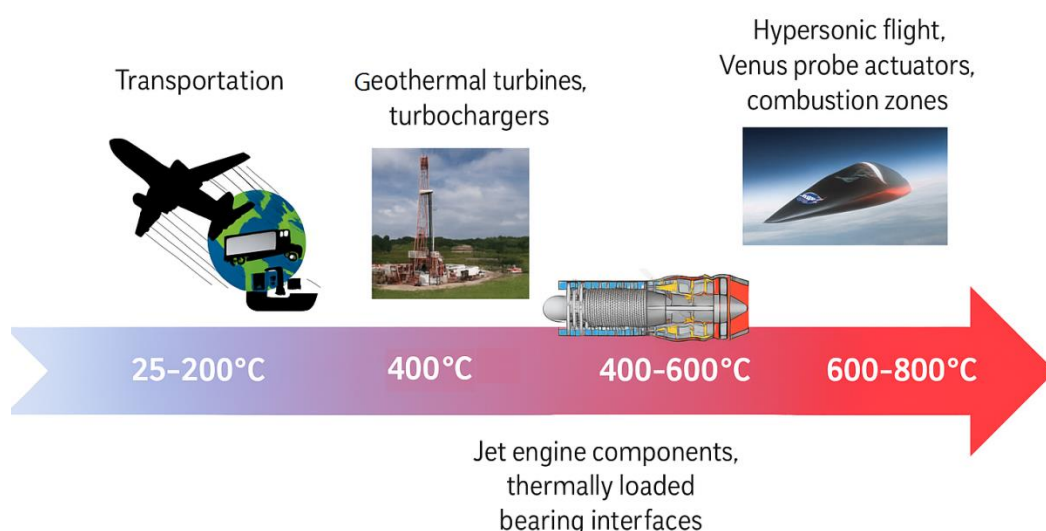


Figure 4.10. Representative high-temperature tribological applications (adapted from [114]).

Note: The shaded region (25-600 °C) highlights the practical temperature window explored in this study. Temperatures above 600 °C were excluded due to the severe oxidation, and interfacial degradation, which compromise the integrity of NiB-based coatings.

Given the increasing relevance of high-temperature tribology across advanced engineering applications, it becomes essential to understand how Ni-based coatings behave under thermal stress and evolving wear conditions. In particular, NiB and NiB- Al_2O_3 systems offer a promising balance of hardness, wear resistance, and structural stability within the moderate-to-high temperature range explored in this study (25-600 °C). The following section critically reviews the literature on Ni-based coatings, with emphasis on their performance across different thermal regimes and the underlying tribological mechanisms they exhibit.

4.8. Literature Review on Ni-Based Coatings in High Temperature Tribology

Table 4.4 presents a comparative overview of recent studies on NiB, NiB- Al_2O_3 and other Ni-based composite coatings, focusing on their tribological performance across various temperature regimes. While room-temperature (RT) behavior has been widely reported, only a limited number of studies extend their investigations to elevated temperatures, and even fewer provide mechanistic insights under dry sliding conditions.

Among the few studies that do consider temperature, most are restricted to moderate temperatures and tend to report performance metrics such as coefficient of friction or hardness changes, without delving into the underlying wear mechanisms. The lack of

systematic evaluation across a broad temperature range is particularly evident in NiB-Al₂O₃ systems, highlighting a key gap in the current literature. Pal et al. [115] examined the NiB system up to 400 °C and observed a slight reduction in COF attributed to oxide formation. However, their analysis lacked morphological or chemical evidence to confirm tribofilm composition or wear mode transitions. Mukhopadhyay et al. [116] extended the temperature range to 500 °C for NiB and its Mo/W-doped variants and reported improved performance above 300 °C, which they linked to the formation of lubricious oxide layers, yet without detailed investigation of debris morphology or counterface effects. While the works of Zellele et al. [117], Li et al. [63], and Cooke et al. [118] on Ni-Al₂O₃ composites provide valuable insights at ambient conditions, they do not account for thermally induced changes such as tribochemical transformations or oxide stability reflecting an overlooked aspect of high temperature tribology of NiB-Al₂O₃ coatings.

Since very few studies address the high-temperature behavior of NiB-Al₂O₃ coatings, especially under dry sliding and extended temperature ranges, Table 4.1. also includes RT-only studies and related Ni-based systems to provide contextual benchmarks. This inclusive comparison underscores the novelty of the present work, which offers a detailed wear mechanism mapping from RT to 600 °C, covering oxide layer evolution, matrix softening, debris morphology, and counterface interactions.

Table 4.1. Summary of selected studies on the tribological behavior of NiB, NiB-Al₂O₃ and other Ni-based composite coatings under various thermal conditions.

References	Coating System	Temperature	Key Findings
Arias et al. [119]	NiB	RT	RT tribology, no temperature effects.
Zhao et al. [120]	NiB	RT	Wear resistance and hardness studied, no thermal evaluation.
Pal et al. [115]	NiB	100-400 °C	Moderate COF drop at high T, oxide formation inferred.

Table 4.1. (More) Summary of selected studies on the tribological behavior of NiB, NiB-Al₂O₃ and other Ni-based composite coatings under various thermal conditions.

References	Coating System	Temperature	Key Findings
Mukhopadhyay et al. [116]	NiB, NiB-Mo, NiB-W	RT-500 °C	Tribological performance improved above 300 °C due to oxide-based film formation.
Zellele et al. [117]	Ni-Al ₂ O ₃	RT	Hardness and RT wear resistance, high-T not studied.
Raghavendra et al. [121]	Ni-Al ₂ O ₃	RT	Electrodeposited coating, only RT behavior reported.
Li et al. [63]	NiB-Al ₂ O ₃	RT	Electroless nanocomposite, no high-T wear study.
Gao et al. [122]	Ni-Al ₂ O ₃	RT	Mechanical and tribological study at RT.
Cooke et al. [118]	Ni-Al ₂ O ₃	RT	RT wear testing, hardness vs. particle content.
Huang et al. [123]	Ni-SiC	RT-200 °C	Slight COF reduction at 200 °C, comparable Ni-based matrix.
Li et al. [124]	NiP-MoS ₂	RT-500 °C	NiO film formation improved high-T performance.
Zhu et al. [125]	Ni-based superalloy	RT-750 °C	Oxide layer evolution at high T (NiO, Cr ₂ O ₃ , spinels).
Liu et al. [126]	Ni-rich alloy	RT-600 °C	Oxidative wear, matrix softening, tribofilm breakdown above 400 °C.
This work [27]	NiB and NiB-Al ₂ O ₃	RT-600 °C	Comprehensive investigation of wear behavior from RT to 600 °C revealed the evolution of distinct tribological mechanisms, and coating-counterface interactions in both NiB and NiB-Al ₂ O ₃ systems.

Previous studies have typically focused on narrow temperature intervals, often confined to room temperature or moderate conditions, and have largely overlooked the fundamental mechanisms governing wear behavior under thermal stress. Even in cases where elevated temperatures were explored, most of the research emphasized bulk metrics, such as coefficient of friction and hardness, without delving into the

temperature-dependent evolution of wear mechanisms, including oxidation kinetics, matrix softening, third-body dynamics, or tribochemical film transformations.

To the best of the author's knowledge, there is no comprehensive study investigating the tribological behavior of electroless NiB-Al₂O₃ composite coatings at elevated temperatures. This thesis directly addresses that gap by providing a temperature-dependent tribological framework for both monolithic NiB and Al₂O₃-reinforced composite coatings, supported by extensive microstructural and surface chemical analyses. The present work offers a comprehensive evaluation that spans the full range from room temperature to 600 °C. By correlating surface morphology, debris characteristics, and counterface interactions across this thermal spectrum, this thesis contributes a mechanism-oriented framework that surpasses existing studies both in scope and analytical depth. This novel approach lays the groundwork for understanding how electroless NiB-based systems respond to complex thermomechanical conditions, and this represents an essential step toward the development of wear-resistant coatings for high-temperature applications.

5. EXPERIMENTAL PROCEDURES

This chapter provides a comprehensive description of the experimental procedures and methodologies employed in the preparation, deposition, and characterization of electroless NiB and NiB-Al₂O₃ composite coatings. To achieve consistent coating quality and reliable performance, each experimental step must be carefully controlled and precisely carried out. Therefore, particular attention was paid to critical parameters including experimental design, substrate preparation, deposition process, characterization techniques, and tribological tests of the coatings.

5.1. Experimental Design and Coating Codes

To systematically investigate the influence of Al₂O₃ particle concentration on the structural, mechanical, and tribological properties of electroless NiB-based coatings, a series of five distinct coating compositions were developed. In each case, a controlled amount of Al₂O₃ nanoparticles was introduced into the plating bath, while all other bath parameters were maintained constant in order to isolate the effect of the ceramic reinforcement phase. This experimental design facilitates a direct comparison of coating performance as a function of Al₂O₃ content, providing insights into the role of particle dispersion and its interaction with the NiB matrix. In this study, the code C0 refers to the pure NiB coating, while C1 to C4 correspond to NiB- Al₂O₃ composite coatings containing 2.5 g/L, 5 g/L, 10 g/L, and 20 g/L of Al₂O₃ nanoparticles, respectively, as detailed in Table 5.1.

Table 5.1. Composition and deposition conditions of electroless NiB and NiB-Al₂O₃ coatings with varying Al₂O₃ content.

Coating Code	Ni Source (g/L)	Reducing Agent (g/L)	Complexing Agent (mL/L)	Stabilizer (g/L)	Al ₂ O ₃ (g/L)	pH	Deposition Time (min)	Bath T (°C)
C0	20	1	90	0.016	0	13	60	90
C1	20	1	90	0.016	2.5	13	60	90
C2	20	1	90	0.016	5	13	60	90
C3	20	1	90	0.016	10	13	60	90
C4	20	1	90	0.016	20	13	60	90

Note: C0: NiB; C1-C4: NiB-Al₂O₃ with 2.5, 5, 10, and 20 g/L Al₂O₃, respectively.

5.2. Substrate Preparation

Mild steel substrates with dimensions of 25 mm × 30 mm × 5 mm were chosen for the electroless deposition of NiB and NiB-Al₂O₃ nanocomposite coatings. Achieving strong coating adhesion and consistent quality demands a thoroughly cleaned and well-prepared surface. Consequently, substrate preparation was performed systematically in two main stages: solvent cleaning and surface activation.

5.2.1. Solvent cleaning

In the first stage, the mild steel substrates were placed in a container filled with acetone and subjected to ultrasonic cleaning for 10 minutes. The ultrasonic action dislodges and removes organic contaminants such as oil, grease, and residual lubricants from the substrate surface. Following this step, the substrates were immediately rinsed with ethanol to eliminate any remaining acetone or additional impurities [22,48].

5.2.2. Surface activation

After solvent cleaning, the substrates underwent an acid activation treatment to further enhance adhesion of the subsequent coating. The substrates were immersed in a freshly prepared 10% hydrochloric acid (HCl) solution for 2-3 minutes, which effectively removes surface oxides, rust, or other corrosion products [22,48]. Immediately afterwards, they were thoroughly rinsed with distilled water to wash away any residual acid. Finally, the substrates were dried in a laboratory oven at 60 °C for 15-20 minutes to ensure complete moisture removal and minimize the risk of oxidation before coating deposition. By carefully implementing these preparation steps, the substrates were rendered clean, active, and free of contaminants. This, in turn, significantly improved the uniformity, adhesion strength, and overall performance of the electroless NiB and NiB-Al₂O₃ coatings.

5.3. Preparation of Electroless NiB Coating Bath

For the electroless deposition of NiB, a carefully formulated chemical bath was used. Each component contributes to a stable plating environment, ensuring efficient nickel reduction and consistent deposition on the mild steel substrates. The deposition parameters for the electroless NiB coating bath, along with their respective roles, are summarized in Table 5.2.

Table 5.2. The deposition parameters for the electroless NiB coating bath.

Chemical	Concentration	Role/Description
Nickel chloride hexahydrate (NiCl ₂ .6H ₂ O)	20 g/L	Primary nickel source. Nickel ions (Ni ²⁺) are reduced to metallic nickel, forming the base of the NiB coating [22].
Sodium borohydride (NaBH ₄)	1 g/L	Reducing agent. Generates hydride ions in alkaline medium, reducing Ni ²⁺ to Ni and enabling boron incorporation [22].
Sodium hydroxide (NaOH)	90 g/L	pH regulator. Maintains an alkaline environment crucial for stable and efficient electroless deposition [127].
Lead nitrate (Pb(NO ₃) ₂)	0.016 g/L	Stabilizer. Trace lead ions help control reaction kinetics, preventing excessive hydrogen evolution and ensuring uniform deposition [127,128].
Ethylenediamine	90 mL/L	Complexing agent. Complexes with nickel ions, keeping them in solution and preventing undesired precipitation [127,129]

The preparation of the electroless plating bath was carried out in a stepwise manner to ensure proper dissolution of the chemicals and bath stability. Firstly, nickel chloride hexahydrate (NiCl₂.6H₂O) was completely dissolved in distilled water under continuous stirring. Subsequently, ethylenediamine was introduced into the bath to form a stable nickel complex, preventing premature nickel precipitation. Once the nickel complex was formed, sodium hydroxide (NaOH) was gradually added to the bath to adjust the pH to 13, ensuring an optimal alkaline environment for the deposition process. After reaching the desired pH, lead nitrate (Pb(NO₃)₂) was incorporated as a stabilizer to regulate the reduction reaction and prevent undesired side reactions. Then, the substrates were placed into the bath to initiate the deposition process. Finally, sodium borohydride (NaBH₄) was carefully added as the reducing agent, initiating the electroless deposition process. Due to its high reactivity, NaBH₄ was added slowly under vigorous stirring to prevent excessive hydrogen evolution and ensure uniform nickel-boron deposition. The plating process was conducted at 90 °C for 60 minutes under constant stirring (300 rpm) to maintain bath homogeneity and promote uniform coating formation on the mild steel substrates. A step-by-step representation of the

plating bath preparation process is provided in Figure 5.1, summarizing the sequential addition of components and bath conditions.

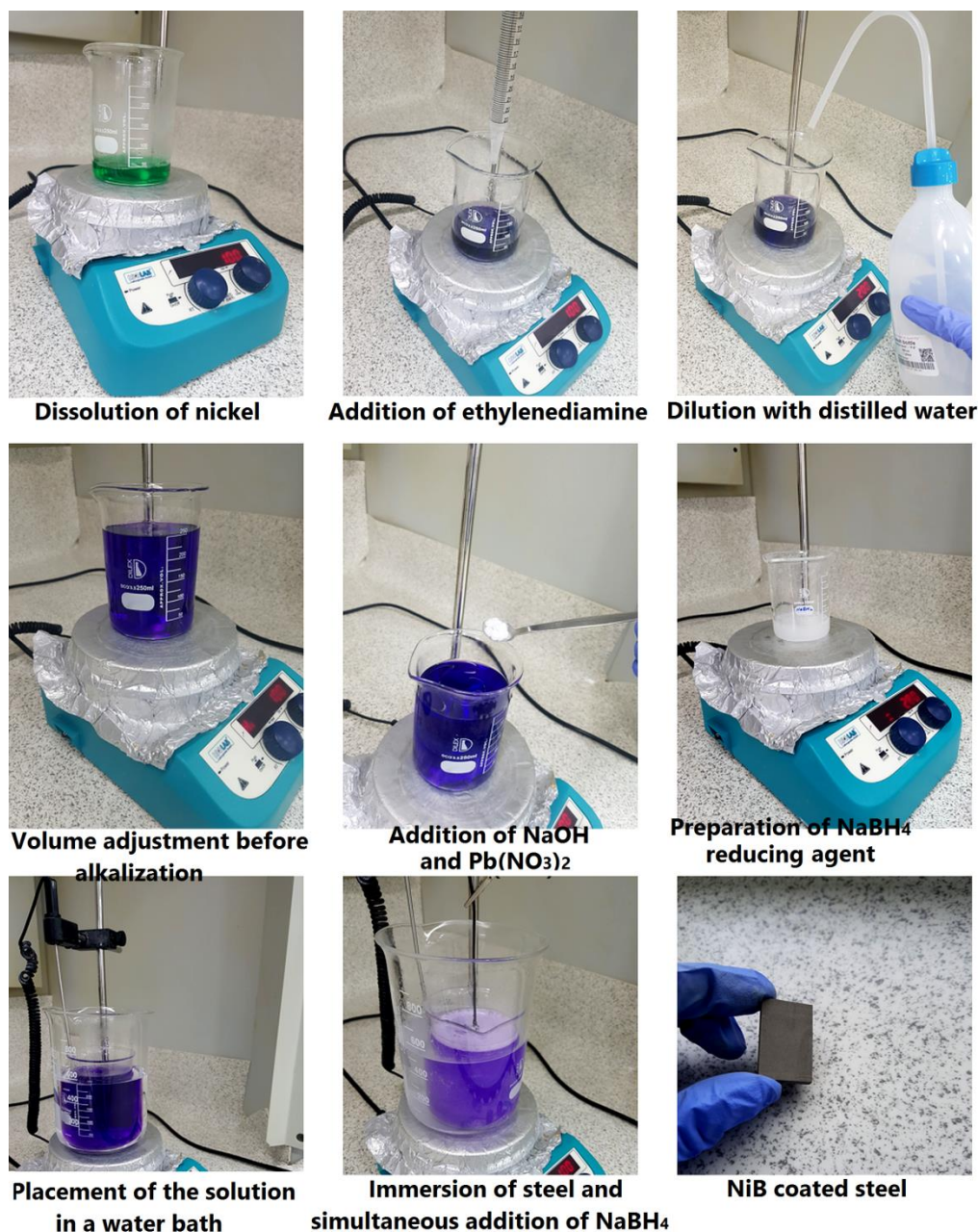


Figure 5.1. Stepwise preparation of the electroless NiB plating bath.

5.4. Preparation of Electroless NiB- Al_2O_3 Nanocomposite Coating Bath

The preparation of the electroless plating bath for NiB- Al_2O_3 nanocomposite coatings followed a procedure similar to that of the electroless NiB bath, ensuring proper dissolution of chemicals and overall bath stability. As schematically illustrated in Fig. 5.1, the sequence of steps was identical to the NiB bath, with the only distinction being the incorporation of Al_2O_3 nanoparticles.

To achieve a stable and homogeneous distribution, Al_2O_3 nanoparticles were ultrasonically agitated for 30 minutes in the presence of sodium dodecyl sulfate (SDS) as a surfactant. The combined action of SDS and ultrasonication prevented agglomeration by providing both electrostatic and mechanical stabilization, thereby ensuring long-term suspension stability. Finally, the Al_2O_3 nanoparticles were added at concentrations of 2.5 g/L, 5 g/L, 10 g/L, and 20 g/L before the addition of NaBH_4 , which initiated the reduction process and subsequent codeposition with the NiB matrix.

5.5. Zeta Potential Measurement

Zeta potential measurements were carried out to evaluate the dispersion behavior of Al_2O_3 nanoparticles in the electroless plating environment. To simulate the actual conditions of the coating bath, synthetic suspensions were prepared by dispersing Al_2O_3 nanoparticles into aqueous solutions containing nickel ions and SDS at varying particle concentrations (2.5-20 g/L). The pH of each solution was adjusted to 13 using NaOH to reflect the alkaline nature of the electroless bath during deposition. Importantly, NaBH_4 which is the reducing agent responsible for initiating the electroless reaction, was deliberately excluded from the mixture to avoid spontaneous hydrogen evolution, particle motion artifacts, and bath instability during measurement. The suspensions were ultrasonicated for 30 minutes to ensure homogeneous dispersion prior to analysis. Each measurement was performed in triplicate, and the reported values represent the average $\pm$ standard deviation.

After ultrasonication, the well-dispersed Al_2O_3 nanoparticle suspension was gradually added to the electroless NiB bath under continuous mechanical stirring. The stirring was maintained at a constant rate (300 rpm) to prevent the settling of nanoparticles and to ensure their even distribution throughout the bath. Then, the cleaned and activated substrates were immersed in the electroless bath for 60 minutes. Finally, NaBH_4 was slowly added as the reducing agent under vigorous stirring to ensure uniform deposition and minimize hydrogen gas evolution. The electroless nanocomposite deposition process was conducted at 90 °C for 60 minutes under constant stirring. During this period, the bath was continuously stirred to maintain homogeneity and ensure uniform coating thickness. After the deposition, the coated substrates were rinsed with distilled water and dried in an oven at 60 °C. This careful preparation and

dispersion process ensured that the Al_2O_3 nanoparticles were uniformly embedded within the NiB matrix during the electroless deposition, leading to the formation of a homogeneous nanocomposite coating with enhanced mechanical and tribological properties.

5.6. Heat Treatment of the Coatings

To enhance the mechanical and tribological properties of the electroless NiB- Al_2O_3 nanocomposite coatings, heat treatment was applied to the as-plated samples. The coatings were heat treated at 400 °C for 2 hours in a controlled atmosphere furnace to ensure consistent thermal conditions and minimize oxidation or contamination [130]. The heating rate was maintained at a consistent value (10 °C/min) to avoid thermal shock and ensure uniform temperature distribution throughout the samples. After the heat treatment, the samples were allowed to cool gradually inside the furnace down to room temperature to prevent microcrack formation due to thermal stresses. This controlled slow cooling process was critical to prevent the development of thermal shock, which can occur due to rapid temperature changes. Sudden cooling can generate high internal stresses within the coating and between the coating and the substrate due to differences in thermal expansion coefficients. These stresses may lead to the formation of microcracks, which compromise the coating's mechanical integrity and reduce its wear resistance. Therefore, careful thermal management during the cooling phase was essential to maintain the structural stability and performance of the coatings.

The primary aim of the heat treatment was to induce structural changes in the NiB matrix by promoting the transformation from an initially amorphous or nanocrystalline state to a more crystalline structure. As-deposited electroless NiB coatings are often amorphous due to the rapid deposition process, which does not allow sufficient time for atoms to arrange into a well-ordered lattice. As temperature increases, the atoms gain mobility and rearrange themselves into a more thermodynamically stable crystalline structure. In particular, the formation of Ni_3B intermetallic phases during annealing contributes to a significant increase in coating hardness and thermal stability. This crystallization process leads to grain growth and phase transformations that improve the hardness and the wear resistance of the coating [130]. Furthermore, heat treatment enhances the bonding between the ceramic Al_2O_3 nanoparticles and the NiB matrix by relieving internal stresses and promoting better particle distribution.

These microstructural improvements result in a coating with superior mechanical integrity and enhanced performance under tribological conditions. Overall, heat treatment is a critical step in optimizing the structural and functional characteristics of electroless NiB-based nanocomposite coatings, especially for applications demanding high surface durability and reliability.

5.7. Nanohardness Measurements of the Coatings

Nanohardness measurements were performed using an Anton Paar NHT³ nanoindenter equipped with a Berkovich diamond tip, following the instrumented indentation technique. Each specimen was placed on a flat, stable support to minimize vibration and ensure accurate depth sensing. A maximum load of 50 mN was applied at a constant loading and unloading rate of 100 mN/min, and the peak load was held for 10 seconds to minimize creep effects.

The hardness values were calculated according to the Oliver-Pharr method, which analyzes the unloading segment of the load-displacement curve to determine the contact stiffness and projected contact area [131]. To account for local heterogeneities in the coatings, five indentations were performed on different regions of each sample surface. This number of indentations was chosen to balance measurement reliability and test efficiency, in accordance with common practice in nanoindentation studies of thin coatings. The reported values represent the average nanohardness, and the standard deviation is provided to indicate measurement consistency and reproducibility.

5.8. Surface and Cross-sectional Characterization of the Coatings

A Scanning Electron Microscope (SEM, Quanta FEG 450) was employed to investigate both the surface morphology and the cross-sectional microstructure of the as-deposited coatings. These analyses were performed prior to tribological testing to assess the microstructural integrity, coating quality, and uniformity of the deposition process. Sample preparation involved sectioning representative coated specimens, mounting them in bakelite using a hot-press mounting technique, and sequential polishing with progressively finer abrasives to obtain a smooth and artifact-free cross-sectional surface. Imaging was conducted in both secondary electron (SE) and backscattered electron (BSE) modes under an accelerating voltage typically ranging

from 10 to 20 kV. SE mode provided detailed topographical information, while BSE mode was utilized to enhance compositional contrast, aiding in the identification of nanoparticle distribution, matrix homogeneity, and interface features. Top-view SEM images enabled evaluation of the surface texture and dispersion state of Al_2O_3 nanoparticles, whereas cross-sectional images were critical for verifying coating thickness consistency and adhesion quality across the substrate.

5.9. Xrd Analysis of the Coatings

X-ray diffraction (XRD) was used to identify the crystalline phases within the coatings and to detect any phase transformations resulting from heat treatment. Diffraction data were collected on a Rigaku D/MAX 2000 X-ray Diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The scanning was performed over a 2θ range of 20° to 70° at a rate of $2^\circ/\text{min}$. Any observed diffraction peaks were compared with standard reference patterns to determine phase compositions. Where relevant, approximate crystallite sizes were determined by using line-broadening methods, providing insights into the degree of crystallinity and the influence of heat treatment on microstructural evolution.

By integrating the results obtained from SEM, ICP-MS, and XRD analyses, a comprehensive overview of the coatings' morphology, chemical composition, and crystal structure was achieved. These complementary datasets confirmed the integrity of the coating-substrate interface, validated the chemical makeup, and elucidated the influence of thermal treatment on phase transformations.

5.10. Tribological Testing of the Coatings with High Temperature Tribometer

The tribological performance of heat-treated electroless NiB and NiB- Al_2O_3 coatings was systematically evaluated under dry sliding conditions using an Anton Paar TRB³ high-temperature tribometer configured in a ball-on-disk arrangement, as illustrated in Figure 5.2. The ball-on-disk setup was specifically selected to evaluate the tribological performance of the coatings by enabling comparison of sliding wear results as a function of varying coating parameters. Additionally, this test configuration was preferred to minimize the running-in period, which is particularly critical for electroless coatings having limited thickness [115]. The ball-on-disk setup also provides precise control over critical testing parameters such as load, sliding speed, and temperature, thereby allowing the simulation of severe tribological conditions

similar to those encountered in real-world applications where lubrication is often impractical or undesired.

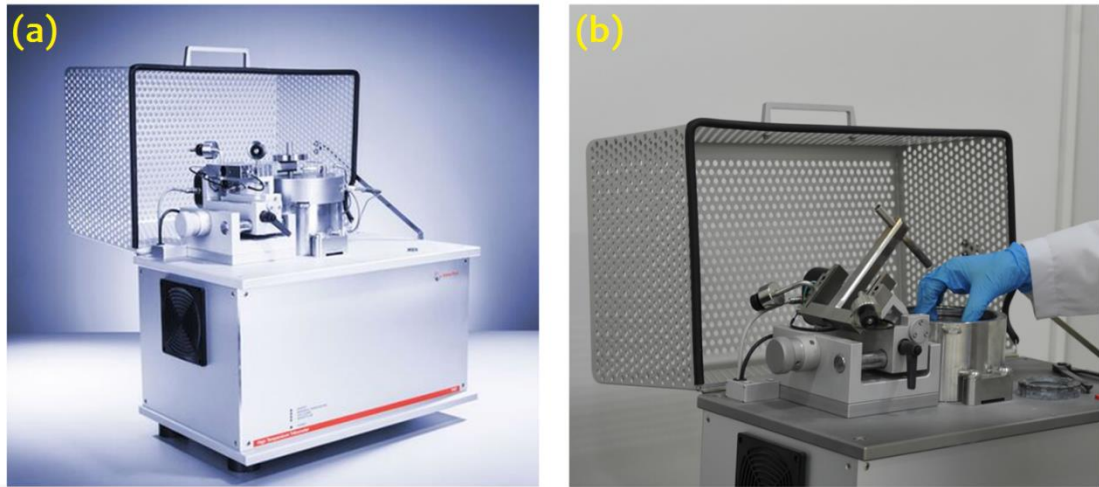


Figure 5.2. General view of the Anton Paar TRB³ high-temperature tribometer: (a) promotional image from Anton Paar GmbH [132]; (b) experimental setup used in this work.

The applied load was set at 3 N, specifically chosen to minimize substrate effects during tribological testing, particularly at elevated temperatures. At higher loads, deformation or damage could penetrate through the coating into the underlying substrate, compromising the validity of coating-specific wear measurements. This load was selected to minimize substrate influence while ensuring measurable wear depth. By selecting 3 N, the tests ensured that the wear depth remained primarily within the coating layer itself, thereby enabling an accurate and reliable evaluation of the intrinsic tribological behavior and durability of the NiB and NiB-Al₂O₃ coatings.

The sliding speed was fixed at 20 cm/s, and each test was carried out to a total sliding distance of 400 m. This distance was selected to ensure sufficient wear progression for reliable measurement while remaining within the thickness limits of the electroless coatings. These parameters were kept constant across all samples to enable direct comparison of their wear performance.

An alumina (Al₂O₃) ball with a diameter of 6 mm was carefully selected as the counter material for tribological testing due to its excellent mechanical and thermal properties. Alumina is well-known for its high hardness and excellent oxidation resistance, enabling it to retain its chemical and structural stability even at elevated testing temperatures [115]. Furthermore, the high thermal stability of alumina ensures consistent tribological behavior across the entire temperature range of testing from

room temperature to 600 °C, thus providing reliable and reproducible wear data. The detailed parameters used in the tribological testing are presented in Table 5.3.

Table 5.3. Tribological testing parameters for electroless NiB and NiB-Al₂O₃ coatings.

Applied Load	3 N
Sliding Speed	20 cm/s
Sliding Distance	400 m
Counter Material	Alumina (Al ₂ O ₃) ball with a diameter of 6 mm
Test Temperatures	25 °C, 200 °C, 400 °C, and 600 °C

5.10.1. Ball-on-disk tribometer configuration

The tribological tests were carried out using the internal configuration of a high-temperature tribometer, as illustrated in Figure 5.3. In this configuration, the electroless NiB and NiB-Al₂O₃ coated samples were mounted onto a heated rotating disk stage located inside the enclosed test chamber. A 6 mm diameter alumina (Al₂O₃) ball was employed as the counter body and was positioned in direct contact with the coated surface. The ball-on-disk contact takes place within a heated test chamber, where the disk is placed on a temperature-controlled stage and the alumina ball is loaded vertically via an external arm throughout the test.

As shown in the schematic on the right side of Figure 5.3, the disk underwent rotational motion beneath the fixed ball, generating a circular wear track under dry sliding conditions. This configuration ensured a well-defined contact geometry and allowed for consistent control of tribological parameters, including sliding speed, applied load, and temperature. All tests were performed at a constant sliding speed of 20 cm/s and a total sliding distance of 400 m. The temperature within the chamber was precisely adjusted to 25 °C, 200 °C, 400 °C, and 600 °C for separate test sets, in order to investigate the coatings' behavior under varying thermal conditions. Moreover, each coating was tested multiple times to confirm the repeatability of the results. This test configuration, combined with carefully selected parameters allowed for a detailed evaluation of the coatings' wear resistance and frictional response, while minimizing substrate effects to ensure that the measured tribological performance represented the coating material itself.

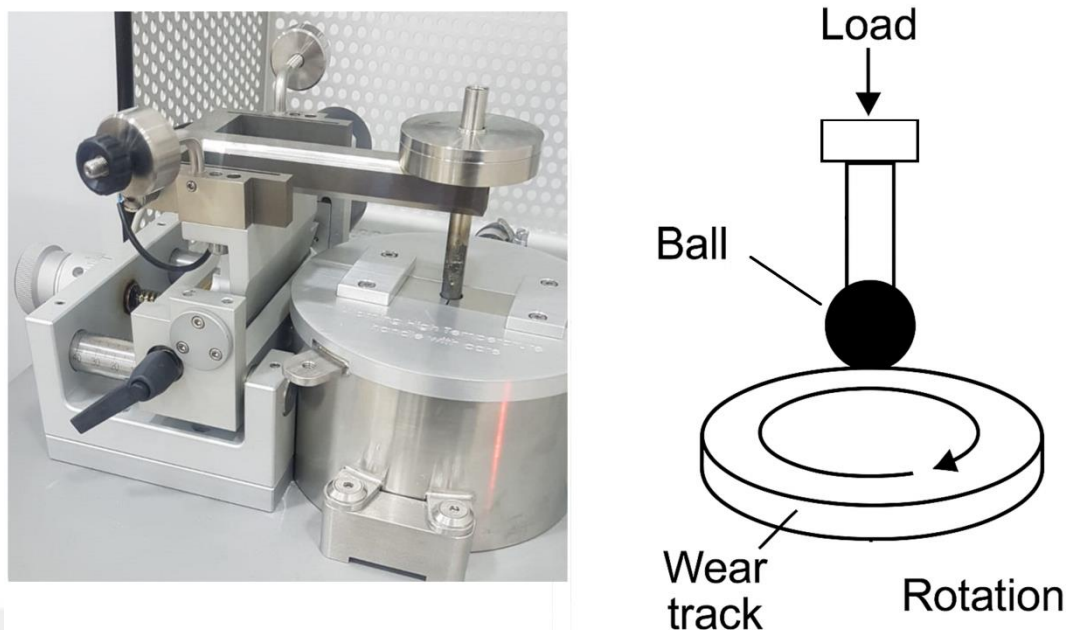


Figure 5.3. Internal test configuration of the high-temperature tribometer and schematic representation of the ball-on-disk contact geometry.

5.10.2. Post-wear SEM analysis of the wear tracks

Following the high-temperature tribological tests, the worn surfaces of the coatings were thoroughly examined using Scanning Electron Microscopy (SEM) to investigate wear morphology and to identify dominant wear mechanisms. SEM was selected as a primary post-wear characterization tool due to its ability to resolve fine-scale features such as micro-grooves, ploughing marks, delamination zones, fatigue cracks, and localized particle detachment, all of which are critical for understanding material degradation under thermal and mechanical stress.

In each test condition (25 °C, 200 °C, 400 °C, and 600 °C), representative wear tracks were imaged at multiple magnifications using both secondary electron (SE) and backscattered electron (BSE) modes. SE imaging enabled the visualization of surface topography and debris morphology, while BSE mode provided compositional contrast, facilitating the identification of oxidation zones, tribofilm residues, or counterface material transfer. Particular attention was paid to morphological features such as oxide layer formation at elevated temperatures, crack initiation and propagation, and third-body particle accumulation.

These SEM observations provided critical insights into the evolution of wear mechanisms as a function of test temperature. Characteristic degradation features including groove formation, oxide debris accumulation, and crack development were

systematically evaluated to distinguish between abrasion, delamination, and oxidation-dominated wear modes. The morphological data served as a foundation for the temperature-dependent wear mechanism interpretations presented in Chapter 6.

5.11. Roughness Measurements of the Wear Tracks

To quantitatively assess the wear track geometry and compare surface degradation among the coatings, 2D profilometric measurements were performed using a stylus surface profilometer (KLA Tencor P-6). The line profiles provided detailed cross-sectional information such as wear track depth, width, and residual roughness features resulting from sliding contact. All roughness values are reported after standardized filtering and within a defined measurement window. In order to minimize filter edge effects and avoid bias from edge pile-up, the ridge regions at both ends of the wear track profiles were excluded from the analysis. Roughness parameters, including Ra, Rq, Rz and Rt, were evaluated in the central region of the track in accordance with the definitions specified in ISO 4287 and the evaluation length guidelines outlined in ISO 4288. Roughness parameters were computed on the filtered roughness profiles using a Gaussian cutoff filter, as specified by ISO 16610 with a cut-off wavelength $\lambda_c = 0.8$ mm, in order to separate the actual roughness component from the overall form and long-wavelength waviness.

5.12. Raman Spectroscopic Characterization

Raman spectroscopy (Kaiser RXN1) was employed to characterize the chemical phases present on the coatings after sliding tests conducted at room temperature, 200 °C, 400 °C, and 600 °C. Measurements were performed directly on the worn tracks, without any additional surface preparation, in order to preserve tribologically induced features. This technique provided critical insights into tribo-oxidation processes and the possible formation of boron-containing tribofilms. Phase identification was particularly valuable for revealing the temperature-dependent onset of oxide formation and chemical transformations within the coatings. The information obtained from these analyses contributed to a comprehensive understanding of the wear mechanisms and their correlation with temperature-dependent tribological performance.

5.13. Process Flow of Electroless Coating and Testing

To provide a clear and concise overview of the experimental procedures followed in this study, a schematic illustration is presented in Figure 5.4. The flowchart summarizes the key stages involved in the preparation, deposition, and evaluation of electroless NiB-Al₂O₃ nanocomposite coatings. The process begins with substrate cleaning (Figure 5.4a), which involves sequential acetone degreasing, acid activation using hydrochloric acid (HCl), and rinsing with distilled water to ensure a contaminant-free and active surface. This is followed by the preparation of the electroless plating bath (Figure 5.4b), in which nickel chloride hexahydrate (NiCl₂·6H₂O) is dissolved and combined with EDA, NaOH, and Pb(NO₃)₂ to form a stable deposition medium. For composite coatings, Al₂O₃ nanoparticles are first ultrasonicated in the presence of SDS to ensure proper dispersion and then added to the bath prior to the introduction of the reducing agent NaBH₄ (Figure 5.4c). The deposition is carried out at 90 °C for 60 minutes with continuous stirring, resulting in the formation of uniform NiB-Al₂O₃ nanocomposite coatings on the steel substrates (Figure 5.4d). Following the deposition, all coated samples undergo heat treatment at 400 °C for 2 hours to improve their structural and tribological properties. Finally, the wear performance of the coatings is assessed using ball-on-disk tribological tests conducted at various temperatures (Figure 5.4e). The same process was applied to pure NiB coatings (C0), excluding the Al₂O₃ dispersion and ultrasonication step. This allowed for direct comparison between monolithic and composite coatings under identical deposition and testing conditions.

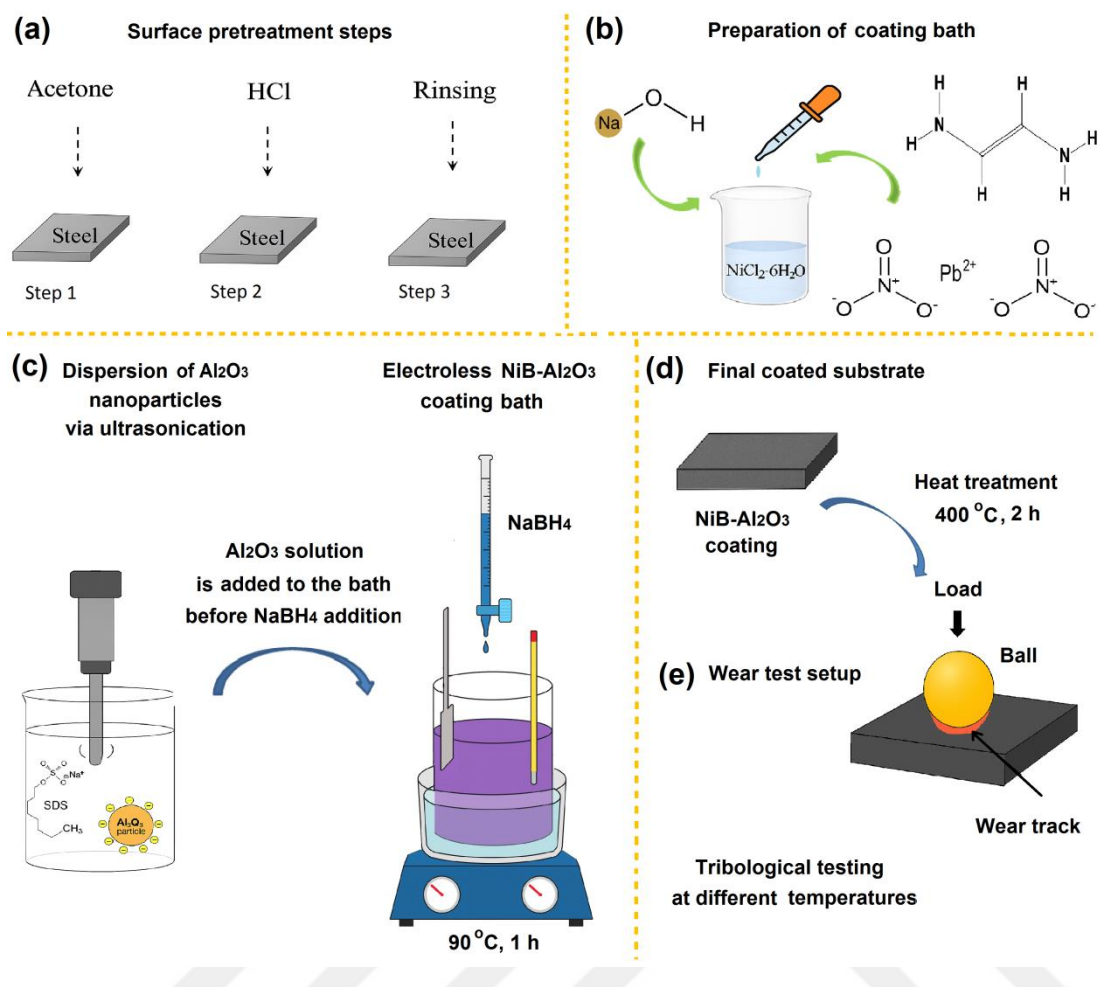


Figure 5.4. Schematic illustration of the experimental procedure followed for the fabrication of electroless NiB-Al₂O₃ nanocomposite coatings and subsequent tribological testing: (a) Substrate cleaning, (b) Preparation of the coating bath, (c) Ultrasonic dispersion of Al₂O₃ nanoparticles with SDS, (d) Final coated substrate after 60 min deposition at 90 °C, (e) Ball-on-disk tribological testing at various temperatures to evaluate wear performance.

Note: The same coating procedure was applied to pure NiB samples, excluding the Al₂O₃ dispersion step.

6. RESULTS AND DISCUSSION

This chapter presents a comprehensive evaluation of the experimental results obtained from the electroless deposition of NiB and NiB-Al₂O₃ nanocomposite coatings on mild steel substrates. Following the methodology detailed in the previous chapters, the influence of Al₂O₃ nanoparticle incorporation on the structural and morphological characteristics of the coatings was systematically investigated. Scanning electron microscopy (SEM) was employed to examine the surface and cross-sectional morphologies, allowing for the assessment of coating uniformity, porosity, and nanoparticle distribution within the NiB matrix. Additionally, the elemental composition of the coatings was determined through inductively coupled plasma mass spectrometry (ICP-MS), with particular emphasis on boron and aluminum content as indicators of the coating chemistry. The impact of varying Al₂O₃ concentrations in the electroless bath was studied to identify the optimal conditions for particle incorporation without compromising coating integrity. The study particularly focused on how the amount of Al₂O₃ particles added to the bath affects the uniformity of the coating structure, since higher concentrations can cause particle agglomeration and negatively influence bath stability. Overall, this chapter aims to interpret the observed results and provide insights into the mechanisms governing nanocomposite formation, adhesion behavior, and the role of ceramic reinforcement in enhancing coating performance.

6.1. Microstructural and Morphological Characterization of Electroless NiB and NiB-Al₂O₃ Nanocomposite Coatings

This section presents a comprehensive microstructural and morphological evaluation of electroless NiB and NiB-Al₂O₃ nanocomposite coatings. Surface and cross-sectional SEM analyses were performed to investigate the effects of Al₂O₃ nanoparticle incorporation on the coating texture, integrity, and internal dispersion. The evolution of nodular morphology, coating thickness, and particle agglomeration behavior was systematically assessed across different Al₂O₃ concentrations. Additionally, chemical composition analysis via ICP-MS was conducted to determine

the influence of ceramic inclusion on boron content. To further understand particle dispersion behavior during deposition, zeta potential measurements were performed using a simulated plating bath. These characterizations provide an integrated understanding of how Al_2O_3 content affects the nucleation, growth, and structural refinement of electroless NiB-based coatings.

6.1.1. Surface morphological characterization of NiB coatings

Electroless NiB coatings are known to exhibit a characteristic cauliflower-like surface structure, which is frequently reported in the literature as a typical morphological feature of electroless NiB deposits produced via autocatalytic chemical reduction [130,133,134]. This morphology is composed of aggregated nodules, which originate from initial nucleation events occurring on the activated substrate surface, followed by radial outward growth and subsequent aggregation.

To better understand this morphological development, it is essential to consider the underlying deposition mechanism. In electroless NiB coatings, nickel ions (Ni^{2+}) in the plating bath are chemically reduced by borohydride ions (BH_4^-) to form elemental nickel atoms. These atoms preferentially deposit onto catalytically active sites on the substrate, forming nanoscale clusters known as nuclei. These nuclei act as catalytic centers for subsequent reduction reactions, promoting autocatalytic growth. Once a sufficient number of stable nuclei are formed, additional nickel atoms deposit continuously onto these sites, leading to radial outward growth. As growth progresses, the nodules gradually coalesce, ultimately forming the characteristic cauliflower-like morphology (Figure 6.1a) [16]. The final surface texture is determined by the density and distribution of nucleation centers, as well as the rate and directionality of growth during deposition. This nucleation-dominated and radially outward growth mechanism also explains the columnar-to-nodular transition observed in the cross-sectional morphology (Figure 6.1b), where directional grain growth near the substrate gradually evolves into cauliflower-like nodules toward the surface.

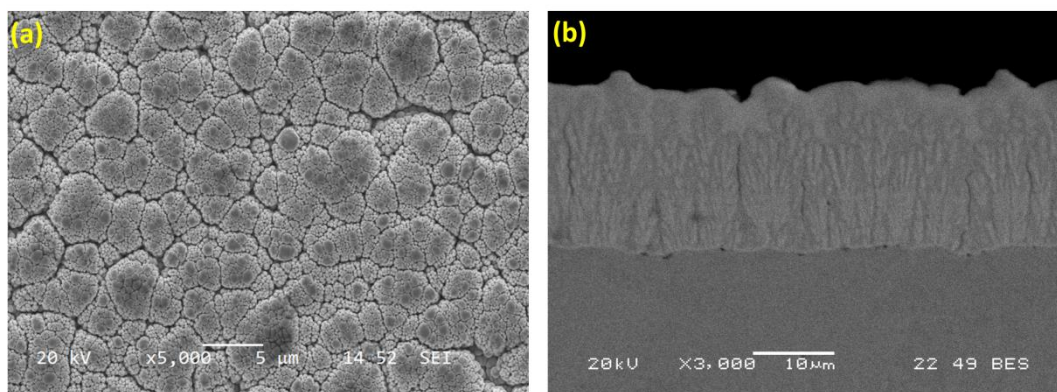


Figure 6.1. SEM micrographs of the electroless NiB coating (C0): (a) surface morphology showing cauliflower-like structure (reproduced from the author's previous publication [27]), and (b) cross-sectional view revealing a continuous coating-substrate interface, obtained within the scope of this thesis.

As seen in Figure 6.1, the NiB coating exhibits a characteristic cauliflower-like morphology composed of compact and uniformly distributed nodules. The boundaries between adjacent nodules are clearly defined, and the inter-nodular gaps are minimal, reflecting the typical nucleation and growth behavior associated with electroless NiB deposition. This morphology results in a continuous coating with a well-defined surface texture, representing the characteristic structural signature of electroless NiB deposits.

6.1.2. Surface morphological characterization of NiB-Al₂O₃ nanocomposite coatings

To assess the effect of ceramic reinforcement on coating morphology, the surface characteristics of NiB-Al₂O₃ coatings were systematically examined and compared with the pure NiB structure. NiB-Al₂O₃ coatings exhibit a more fragmented and fine-grained surface morphology, when compared to NiB coating. The nodules appear smaller and more densely packed, with less distinct boundaries between them. This refined structure suggests an increased nucleation density during deposition. The incorporation of Al₂O₃ nanoparticles likely provides additional heterogeneous nucleation sites, leading to more frequent initiation points on the substrate surface. In addition to promoting nucleation, these particles also influence the subsequent growth behavior. As a result, the surface exhibits a finer grain structure with a more heterogeneous nodular distribution. While radial outward growth from nucleation sites continues during deposition, the presence of Al₂O₃ nanoparticles disrupts lateral

growth and merging between adjacent nodules. This interruption moderately limits lateral coalescence, resulting in a refined and more finely divided surface morphology. In order to further elucidate the impact of Al_2O_3 addition on the coating structure, surface morphologies of the NiB- Al_2O_3 composite coatings were examined using scanning electron microscopy (SEM). By analyzing coatings produced with varying Al_2O_3 concentrations, insights into particle distribution, surface uniformity, and the tendency for nanoparticle agglomeration were obtained. This morphological evaluation, depicted in Figure 6.2, provides complementary evidence to the chemical findings and helps to better understand the structural implications of Al_2O_3 incorporation.

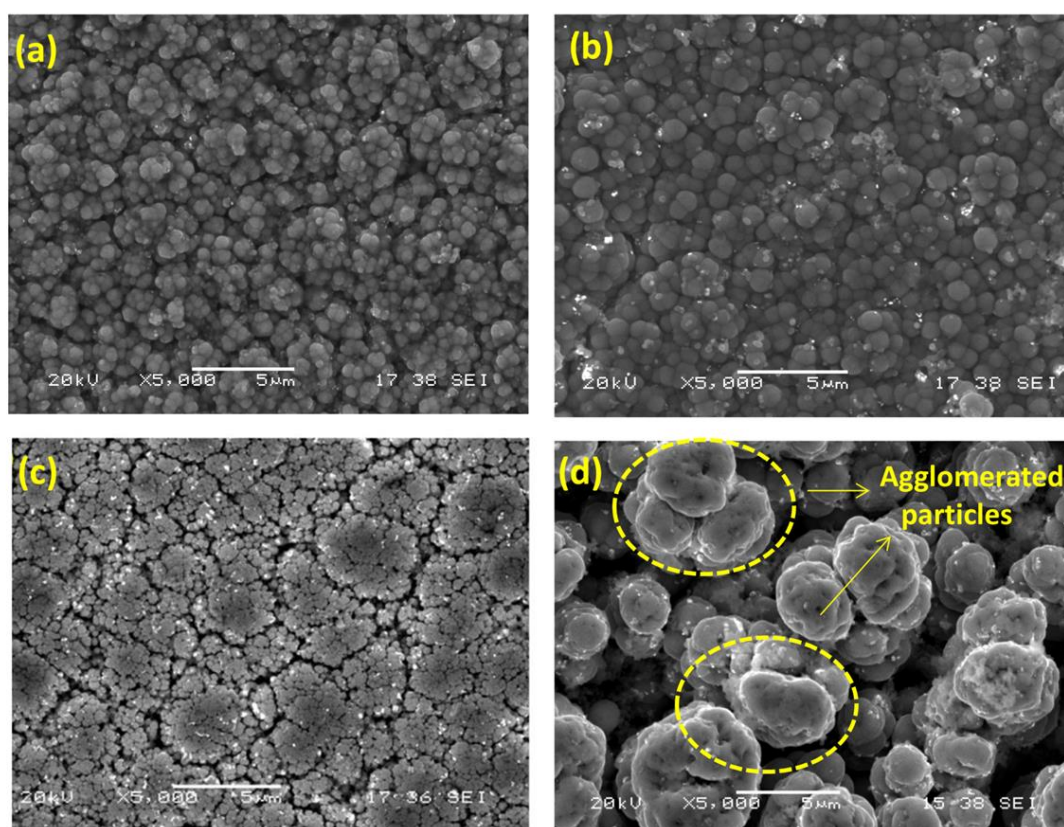


Figure 6.2. SEM surface images of electroless NiB- Al_2O_3 composite coatings prepared with varying Al_2O_3 concentrations: (a) 2.5 g/L, (b) 5 g/L, (c) 10 g/L (optimum), and (d) 20 g/L.

Figure 6.2a displays the surface morphology of the NiB- Al_2O_3 composite coating fabricated with 2.5 g/L Al_2O_3 , representing the lowest reinforcement level among the studied samples. The image reveals a nodular structure that is continuous yet relatively coarse and morphologically inconsistent. The ceramic content at this concentration is insufficient to effectively promote heterogeneous nucleation during deposition,

resulting in a limited number of nucleation sites and consequently larger and more irregular nodules. This microstructure suggests that the Al_2O_3 nanoparticles are only partially co-deposited and are not uniformly distributed throughout the matrix. As a result, the coating lacks structural compactness and exhibits a comparatively loose surface topology. Although major agglomeration or porosity is not observed, the overall surface homogeneity and density remain suboptimal. These findings indicate that 2.5 g/L Al_2O_3 does not provide adequate particle-matrix interaction or microstructural refinement, leading to an under-reinforced condition that falls short of the desired mechanical and morphological performance.

Figure 6.2b presents the surface morphology of the NiB- Al_2O_3 composite coating produced with 5 g/L Al_2O_3 , representing an intermediate reinforcement level. Compared to the 2.5 g/L sample, this coating exhibits a relatively more refined and coherent surface texture. While the nodular structure remains pronounced, certain regions display slightly reduced nodular size and increased packing density. These localized morphological adjustments suggest the initial influence of Al_2O_3 nanoparticles in promoting heterogeneous nucleation during deposition. At this concentration, the Al_2O_3 nanoparticles begin to actively participate in the deposition process, providing additional nucleation sites and thereby contributing to localized refinement of the nodular microstructure. However, full structural homogenization has not yet been achieved, as minor irregularities and occasional textural discontinuities are still evident across the surface. These observations suggest that while the ceramic content at 5 g/L enhances coating compactness to a certain extent, it remains below the optimal level required for complete microstructural refinement.

Figure 6.2c illustrates the surface morphology of the NiB- Al_2O_3 composite coating with 10 g/L Al_2O_3 (C3), which corresponds to the optimal reinforcement condition. The surface SEM image reveals a well-developed microstructure characterized by compactness, continuity, and morphological uniformity. At this concentration, Al_2O_3 nanoparticles are clearly embedded within the NiB matrix and exhibit a uniform spatial distribution across the surface. The absence of visible agglomerates confirms the effective dispersion of Al_2O_3 nanoparticles in the plating solution and their uniform co-deposition with the metallic matrix. This optimal dispersion contributes significantly to the surface integrity by minimizing structural defects, leading to a dense and cohesive morphology. This refined microstructure results from the role of

Al_2O_3 nanoparticles in promoting heterogeneous nucleation, which increases nucleation site density and leads to finer, closely packed nodules with a continuous texture.

As shown in Figure 6.2d, the surface SEM image of the NiB- Al_2O_3 composite coating deposited with 20 g/L Al_2O_3 clearly exhibits significant nanoparticle agglomeration. Instead of a uniform distribution, the Al_2O_3 particles tend to cluster, forming localized aggregates across the coating surface. These agglomerates disrupt the compactness of the NiB matrix and result in a non-homogeneous surface topology. Additionally, the presence of voids and porous regions surrounding the agglomerates indicates poor particle dispersion and diminished packing density. This morphological deterioration can be attributed to the excessive concentration of ceramic particles exceeding the suspension stability threshold, which promotes uncontrolled particle-particle interactions during deposition. Such localized particle clusters may also act as stress concentrators, potentially initiating microcracks under mechanical loading. These surface features are therefore undesirable, as they may compromise the mechanical integrity and wear resistance of the composite coating.

6.1.3. Cross-sectional morphological characterization of NiB- Al_2O_3 nanocomposite coatings

In addition to surface morphology, the internal structure and thickness distribution of the NiB- Al_2O_3 composite coatings were examined through cross-sectional SEM analysis. Figure 6.3 presents the cross-sectional images of coatings prepared with different Al_2O_3 concentrations, providing insight into the dispersion behavior of ceramic particles within the NiB matrix as well as the coating-substrate interface.

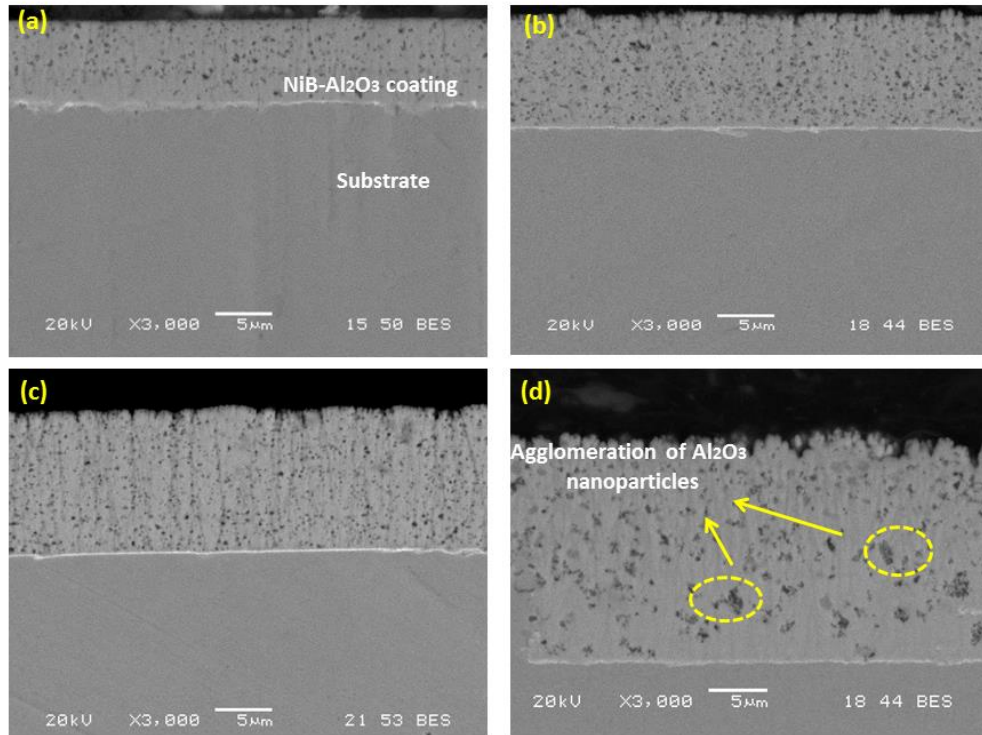


Figure 6.3. Cross-sectional SEM images of NiB-Al₂O₃ composite coatings deposited with different Al₂O₃ concentrations: (a) 2.5 g/L, (b) 5 g/L, (c) 10 g/L, and (d) 20 g/L (reproduced from [27]).

As shown in Figure 6.3a, the cross-sectional SEM image of the coating prepared with 2.5 g/L Al₂O₃ displays a relatively thin and uniform layer with no observable cracks or delamination at the coating-substrate interface, indicating good adhesion. Although the coating appears continuous, the number of embedded Al₂O₃ particles within the NiB matrix is visibly low. The ceramic particles are sparsely distributed, suggesting that the low concentration in the plating bath results in insufficient particle availability for significant incorporation. This limited content restricts the potential reinforcing effect of the ceramic phase, and the microstructure closely resembles that of a pure NiB deposit. Nonetheless, the crack-free interface and compact structure suggest minimal internal stress and a stable deposition process at this concentration.

As illustrated in Figure 6.3b, the cross-sectional SEM image of the coating deposited with 5 g/L Al₂O₃ reveals a relatively uniform structure with a slightly increased coating thickness compared to the 2.5 g/L sample. Similar to the lower concentration, no cracks or interfacial separation are observed at the coating-substrate interface, confirming strong adhesion and low internal stress. In contrast to the limited distribution observed at 2.5 g/L, the Al₂O₃ particles appear more frequently embedded

within the NiB matrix, although their overall density remains moderate. The dispersion of the ceramic phase remains relatively homogeneous, indicating that the suspension stability is still maintained at this level. While the particle incorporation is improved, the microstructure still lacks the level of reinforcement and compactness observed in the optimal formulation. Therefore, 5 g/L Al_2O_3 results in a transitional structure, where the reinforcing effect becomes more noticeable, but not yet fully optimized.

As shown in Figure 6.3c, the cross-sectional SEM image of the NiB- Al_2O_3 composite coating prepared with 10 g/L Al_2O_3 reveals a compact and uniformly structured layer with a clear and continuous interface between the coating and the steel substrate. No visible cracks or delamination are observed at the interface, indicating strong adhesion and low internal stress. At this concentration, the incorporation of Al_2O_3 nanoparticles reaches its optimal level within the NiB matrix. The ceramic particles are well dispersed throughout the coating thickness, without any signs of agglomeration, resulting in a homogenous microstructure. This uniform distribution contributes to the formation of a dense and well-integrated composite layer, enhancing the structural integrity of the coating. The layer thickness also increases slightly compared to lower concentrations, yet remains consistent and defect-free. The observed morphology and phase dispersion clearly support the identification of 10 g/L as the most effective Al_2O_3 concentration for achieving a balanced and reinforced NiB- Al_2O_3 nanocomposite structure.

As presented in Figure 6.3d, the cross-sectional SEM image of the NiB- Al_2O_3 composite coating with 20 g/L Al_2O_3 clearly shows significant microstructural deterioration compared to the lower concentrations. Despite the overall structural degradation, the coating-substrate interface remains continuous and free of cracks, indicating acceptable adhesion. The internal structure of the coating, however, exhibits some irregularities. The most notable feature is the presence of pronounced agglomerates of Al_2O_3 nanoparticles, which disrupt the uniformity of the NiB matrix. These large clusters, highlighted in the image, lead to localized porosity and reduced packing density in the surrounding regions. As the Al_2O_3 concentration exceeds the suspension stability threshold, uncontrolled particle-particle interactions occur during deposition, preventing homogeneous distribution. Consequently, the effective incorporation of Al_2O_3 into the matrix decreases despite the higher nominal concentration. The resulting structure is less compact and morphologically

unbalanced, which may compromise the mechanical performance and reliability of the coating. These observations confirm that 20 g/L surpasses the optimal reinforcement level and leads to detrimental effects in the composite microstructure.

6.1.4. EDS and ICP-MS characterization of NiB and NiB-Al₂O₃ nanocomposite coatings

To complement the morphological findings discussed in Sections 6.1.2 and 6.1.3, the elemental composition of the coatings was further analyzed using EDS and ICP-MS techniques. EDS was primarily utilized to assess the incorporation of Al₂O₃ particles within the NiB matrix, which is essential for understanding the microstructural development and reinforcement mechanism. The corresponding results are presented in Table 6.1. While EDS provides spatially resolved, surface-specific elemental information, it is inherently limited in detecting light elements such as boron due to their low atomic number and weak characteristic X-ray signals. As a result, boron content was accurately quantified using inductively coupled plasma mass spectrometry (ICP-MS). The combined use of both techniques ensures a comprehensive understanding of the elemental composition, capturing both spatial distribution and total content. For this reason, the quantitative results for boron are reported separately in Table 6.2 to complement the EDS findings.

Table 6.1. Surface elemental composition (wt.%) of NiB and NiB-Al₂O₃ coatings obtained from EDS analysis (B was not detected by EDS).

Coating Code	Ni	B	Al	O
C0	100.00 ± 0.50	n.d.	-	-
C1	92.85 ± 0.42	n.d.	3.75 ± 0.18	3.40 ± 0.16
C2	89.25 ± 0.36	n.d.	5.41 ± 0.21	5.34 ± 0.22
C3	87.65 ± 0.33	n.d.	6.02 ± 0.24	6.33 ± 0.25
C4	84.25 ± 0.41	n.d.	7.81 ± 0.29	7.94 ± 0.30

Note: n.d. indicates not detected by EDS.

Table 6.2. Boron content (wt.%) in electroless NiB and NiB-Al₂O₃ coatings determined by ICP-MS analysis.

Coating Code	Al ₂ O ₃ (g/L)	B (wt%)
C0	0	6.54 ± 0.08
C1	2.5	6.35 ± 0.07
C2	5	6.15 ± 0.05
C3	10	5.94 ± 0.06
C4	20	5.70 ± 0.09

As presented in Table 6.1, the incorporation of Al₂O₃ nanoparticles into the NiB matrix was confirmed by EDS analysis, which showed a progressive increase in both aluminum and oxygen content with increasing particle concentration. The presence of these ceramic inclusions both verifies their successful embedding, and plays a crucial role in modifying the microstructure of the coating. This result also indicates that the distribution of Al₂O₃ becomes more pronounced as particle concentration increases, consistent with the morphological changes observed in the SEM images.

During the electroless deposition process, Al₂O₃ nanoparticles influence the local chemical reduction environment by acting as heterogeneous nucleation sites within the plating bath [135]. Their presence disrupts the uniformity of the Ni²⁺ and BH₄⁻ ion distribution near the substrate surface, thereby facilitating localized metal reduction and NiB matrix growth. This interaction enhances the effective surface area available for deposition and promotes the formation of a more compact and uniformly distributed microstructure. SEM images clearly show the uniform dispersion of Al₂O₃ particles across the NiB matrix, supporting the conclusion that a well-integrated composite microstructure was achieved.

Table 6.2 presents the quantitative boron content determined by ICP-MS. The data reveal a gradual decrease in boron content from 6.54 wt% in the pure NiB coating (C0) to 5.70 wt% at the highest Al₂O₃ concentration (C4). This decline can be attributed to several concurrent effects associated with ceramic particle incorporation. This reduction in boron content is attributed to several interacting mechanisms. Firstly, the incorporation of Al₂O₃ nanoparticles into the plating bath leads to a dilution effect, in which the relative concentration of boron within the deposited matrix decreases due to the physical inclusion of inert ceramic particles. Since these nanoparticles occupy a certain volume fraction in the coating, the proportion of active metallic constituents such as Ni and B per unit mass is reduced, resulting in a lower measured boron content. Secondly, these nanoparticles partially block active nucleation sites on the substrate

surface, thereby limiting the number of available locations for boron co-deposition. The presence of Al_2O_3 also alters the reduction kinetics of boron species such as BH_4^- , which further restricts the extent of boron incorporation during the deposition process.

6.1.5. Evaluation of Al_2O_3 nanoparticle dispersion by zeta potential (ζ)

The dispersion quality of Al_2O_3 nanoparticles in the electroless plating bath plays a critical role in determining the uniformity and performance of the resulting nanocomposite coatings. In this study, zeta potential measurements were specifically performed using a simulated electroless plating bath containing Ni^{2+} ions and SDS at pH 13, in order to closely simulate the actual deposition environment. NaBH_4 , the chemical reducing agent typically present in actual baths, was intentionally excluded to prevent undesired reduction reactions and hydrogen gas evolution, which could interfere with the stability measurements. Although SDS-only systems (i.e., SDS + Al_2O_3) typically yield more negative ζ values due to stronger adsorption of sulfate groups in the absence of competing cations, such conditions do not accurately represent the particle behavior during coating formation. Therefore, the aim was to assess how effectively SDS can stabilize Al_2O_3 nanoparticles under the ionic strength and chemical complexity of the plating bath. This approach provides a more realistic understanding of nanoparticle dispersion behavior in the actual deposition process.

In this study, zeta potential measurements were carried out at varying Al_2O_3 concentrations within the SDS-stabilized plating bath to systematically evaluate colloidal stability and interparticle interactions. As an established indicator of surface charge and electrostatic repulsion, zeta potential offers direct insight into the efficiency of nanoparticle stabilization and the conditions that promote homogeneous dispersion during co-deposition [76]. Figure 6.4 illustrates the variation of ζ with increasing Al_2O_3 content, while the corresponding numerical values and stability interpretations are summarized in Table 6.3.

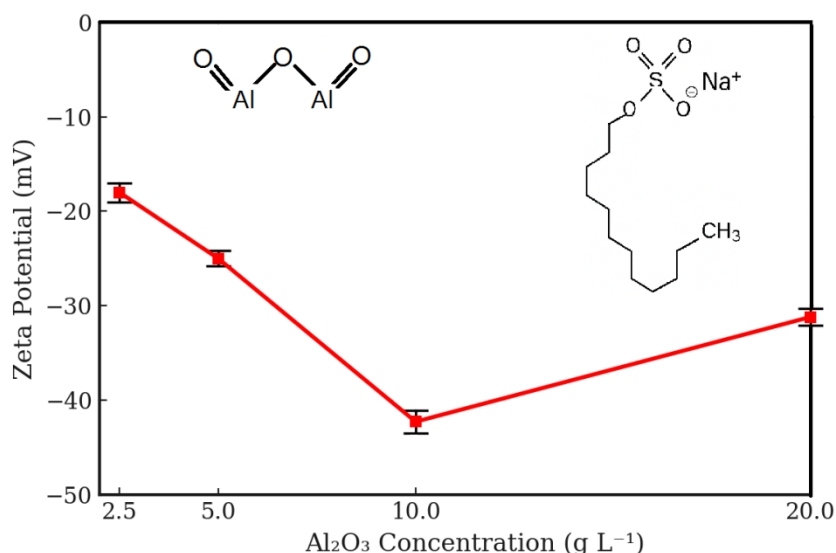


Figure 6. 4. Variation of zeta potential (ζ) with Al_2O_3 concentration in SDS-stabilized plating baths, illustrating the relationship between particle loading and colloidal stability.

Table 6.3. Zeta potential (ζ) values and corresponding colloidal stability interpretations for Al_2O_3 suspensions in SDS-stabilized plating baths.

Al_2O_3 Concentration (g/L)	Zeta Potential (mV)	Stability
2.5	-18.0 ± 1.0	Moderate repulsion, limited stability
5	-25.0 ± 0.8	Improved repulsion and dispersion
10	-42.3 ± 1.2	Optimal electrostatic stabilization
20	-31.2 ± 0.9	Reduced stability due to particle-particle interactions

A progressive increase in the absolute value of ζ is observed as the Al_2O_3 concentration rises from 2.5 g/L to 10 g/L, indicating improved electrostatic repulsion and enhanced dispersion quality. This trend reflects the increasing surface coverage of SDS molecules on the Al_2O_3 particles, leading to a greater net negative charge and stronger interparticle repulsion. The ζ value reaches its most negative point at 10 g/L, suggesting an optimal balance between particle loading and surfactant-mediated stabilization. However, beyond this threshold, at 20 g/L, a noticeable reduction in the absolute ζ value occurs, implying a decline in electrostatic stabilization. This suggests that particle-particle interactions begin to dominate over electrostatic repulsion, thereby reducing dispersion efficiency and promoting agglomeration. These findings are in strong agreement with the microstructural evidence discussed in Sections 6.1.2

and 6.1.3, where significant agglomeration-related deterioration was observed both on the coating surface and within the internal matrix at high Al_2O_3 loadings.

6.1.5. Effect of particle agglomeration beyond the critical reinforcement threshold

The formation and evolution of agglomerates during electroless deposition play a decisive role in determining the uniformity and structural quality of NiB- Al_2O_3 composite coatings. At low and moderate Al_2O_3 concentrations, the nanoparticles remain well-dispersed within the plating bath, promoting a high nucleation density on the substrate surface and leading to a fine-grained, compact morphology. This condition favors homogeneous particle incorporation and uniform growth of the NiB matrix, producing a dense and coherent composite layer, as evidenced by the SEM images of coatings containing up to 10 g/L Al_2O_3 (Figures 6.2c and 6.3c).

As the particle content increases beyond this threshold, the suspension stability is gradually lost due to intensified particle-particle interactions and insufficient surfactant-mediated repulsion. The elevated particle concentration promotes collisions and clustering among Al_2O_3 nanoparticles, resulting in the formation of agglomerates even before deposition. These pre-formed clusters are partially entrapped within the growing NiB matrix, disrupting the compactness and continuity of the coating. The cross-sectional observations of the 20 g/L sample (Figure 6.3d) clearly reveal such structural irregularities, where large Al_2O_3 clusters coexist with voids and porous regions. In these regions, local stress concentrations and weak interfaces are likely to form, acting as potential initiation sites for microcrack propagation under mechanical or thermal loading [106].

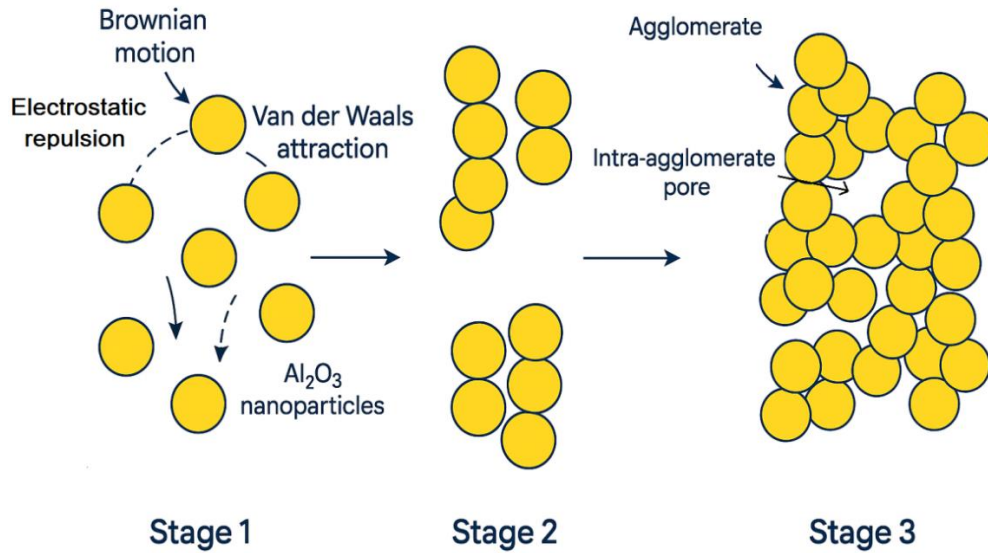


Figure 6.5. Schematic representation of Al_2O_3 nanoparticle agglomeration stages: (Stage 1) well-dispersed nanoparticles, (Stage 2) initial interparticle contact, and (Stage 3) agglomerate formation with intra-agglomerate pores (adapted from [136]).

Note: Agglomeration occurs when the attractive Van der Waals forces overcome electrostatic repulsion, allowing nanoparticles to adhere.

From a physicochemical perspective, several fundamental interactions contribute to agglomeration behavior in colloidal and particulate systems. These include van der Waals attractions, hydrogen bonding between surface hydroxyl groups, and adsorption of foreign species. Among these, van der Waals forces are universal in nature and always exert an attractive effect between similar particles. When the particles come sufficiently close to each other, they act as the primary driving force for agglomeration. This close approach typically corresponds to interparticle separations of only a few nanometers ($\approx 1\text{-}3\text{ nm}$), at which the van der Waals attraction exceeds the repulsive forces such as electrostatic or steric interactions, leading to irreversible particle adhesion. Although other causes can be partially mitigated by optimizing bath chemistry and dispersion stability, the inherent nature of van der Waals (vdW) attraction imposes a physical limit on the maximum achievable dispersion [136]. The magnitude of this attraction can be expressed using the classical Hamaker formulation (equation 6.1).

$$F_{vdw} = -\frac{AR}{6D^2} \quad (6.1)$$

where A is the Hamaker constant describing the dielectric properties of the interacting materials, R is the particle radius, and D represents the surface-to-surface distance between particles. Under typical conditions, when two oxide particles with diameters on the order of $1\text{ }\mu\text{m}$ come into contact, the van der Waals attraction can exceed their gravitational weight by approximately 5-7 orders of magnitude [136]. This quantitative relationship illustrates why particle agglomeration becomes practically irreversible once the interparticle distance decreases to a few nanometers.

6.2. X-ray Diffraction (XRD) Analysis of NiB and NiB-Al₂O₃ Nanocomposite Coatings

X-ray diffraction (XRD) analysis was performed to assess the phase composition and crystallinity of the electroless NiB and NiB-Al₂O₃ nanocomposite coatings. This technique provides critical insight into the structural characteristics of the coatings, including the presence of amorphous regions, crystalline phases, and their transformation behaviors. The results for both as-deposited and heat-treated coatings are interpreted in detail to evaluate the microstructural evolution and the thermal stability of reinforcing ceramic and metallic constituents.

6.2.1. Xrd analysis of as-deposited NiB and NiB-Al₂O₃ nanocomposite coatings

X-ray diffraction (XRD) analysis was conducted to investigate the structural characteristics of the as-deposited electroless NiB and NiB-Al₂O₃ nanocomposite coatings. The diffraction patterns of the coatings are presented in Figure 6.6. Both types of coatings exhibit a broad diffraction peak centered at approximately $2\theta \approx 44.7^\circ$, corresponding to the (111) plane of face-centered cubic (fcc) nickel, along with a weaker and similarly broadened feature near $2\theta \approx 52.4^\circ$, attributed to the (200) plane. The broad and diffuse nature of these peaks indicates that the coatings possess a predominantly amorphous structure [115].

This structural amorphization is primarily attributed to the presence of boron, which plays a critical role in disrupting the long-range atomic order of the NiB matrix [137]. Due to the significant disparity in atomic radii between nickel ($1.24\text{ }\text{\AA}$) and boron ($0.97\text{ }\text{\AA}$), boron atoms can easily occupy the interstitial sites within the nickel matrix. This interstitial placement disrupts the periodic atomic arrangement of the Ni lattice, introducing local lattice strains and inhibiting long-range atomic order. Additionally, the interstitial boron atoms generate significant local stresses that destabilize the lattice

and reduce the driving force for crystal nucleation. This structural distortion hinders the formation of well-defined crystallites, promoting the development of an amorphous structure [137]. This phenomenon is not merely theoretical but also occurs during the electroless deposition process, where nickel and boron atoms co-precipitate onto the substrate and directly form the NiB matrix. The simultaneous presence of boron atoms during atomic assembly prevents the establishment of long-range crystalline order, leading instead to a structurally disordered, amorphous phase.

Moreover, boron's high affinity for nickel may lead to the formation of boron-rich clusters that act as physical barriers to atomic mobility and crystal growth [138]. These effects collectively result in a dense, compact atomic structure with suppressed long-range periodicity, which is directly reflected in the XRD patterns. The characteristic Ni peaks appear broadened and low in intensity, confirming the presence of significant atomic disorder. This is especially pronounced in high-boron NiB coatings, where the diffraction profiles exhibit amorphous-like humps with no distinct crystalline features.

In contrast to the amorphous matrix of pure NiB coatings, the NiB- Al_2O_3 composite coatings include an additional ceramic phase, $\gamma\text{-Al}_2\text{O}_3$, which plays a critical role in defining the microstructural and functional properties of the composite system. Among the polymorphs of alumina, $\gamma\text{-Al}_2\text{O}_3$ is particularly favored for nanocomposite coatings due to its metastable spinel-type structure, high surface area, and good dispersibility in aqueous plating solutions. These characteristics enhance its integration into the electroless matrix and promote stable reinforcement effects without phase degradation during deposition. The XRD patterns of the composite samples exhibit sharp and well-defined peaks corresponding to $\gamma\text{-Al}_2\text{O}_3$, located at approximately 25.44° , 35.26° , 43.46° , 57.59° , and 66.48° , which match the (012), (104), (113), (116), and (214) planes, respectively. These diffraction peaks are consistent with the standard XRD patterns reported in the literature [63,139,140]. The presence of these reflections confirms the successful co-deposition of $\gamma\text{-Al}_2\text{O}_3$ particles into the NiB matrix without degradation during deposition.

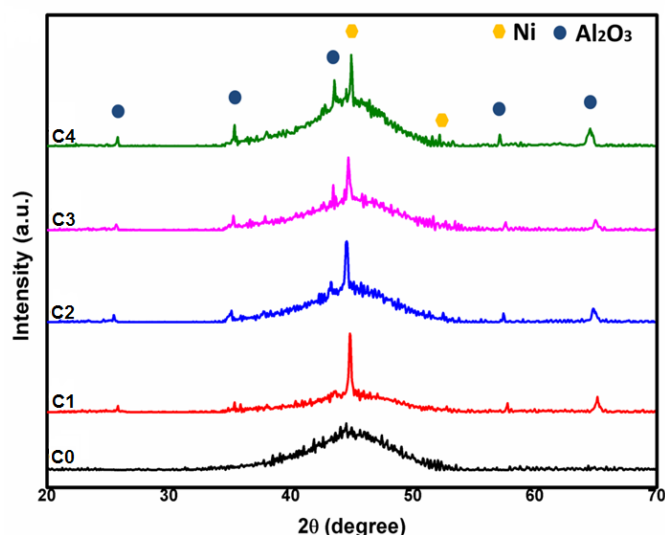


Figure 6.6. XRD patterns of as-deposited electroless NiB and NiB-Al₂O₃ nanocomposite coatings (C0-C4) (reproduced from [27]).

As clearly seen in Figure 6.6, the intensity of γ -Al₂O₃ diffraction peaks increases progressively from C1 to C4, reflecting the successful incorporation of ceramic particles in accordance with their increasing concentration in the plating bath. The appearance of sharp and well-defined reflections confirms that the Al₂O₃ nanoparticles retain their original γ -phase crystalline structure throughout the co-deposition process. Moreover, the consistent peak position and width across all samples indicate that the ceramic phase remains structurally stable and chemically inert, without any detectable degradation or interaction with the surrounding amorphous NiB matrix. To provide a clearer overview of the XRD results, the diffraction data discussed above are compiled in Table 6.4, highlighting the structural characteristics of the as-deposited coatings.

Table 6.4. Major XRD peaks identified in as-deposited NiB and NiB-Al₂O₃ coatings.

Observed 2 θ (°)	Assigned Phase	Miller Indices (hkl)	Phase Type
~44.7°	Ni (amorphous)	(111)	Broad peak - fcc Ni (distorted)
~52.4°	Ni (amorphous)	(200)	Broad peak - fcc Ni (distorted)
~25.44°	γ -Al ₂ O ₃	(012)	Crystalline alumina
~35.26°	γ -Al ₂ O ₃	(104)	Crystalline alumina
~43.46°	γ -Al ₂ O ₃	(113)	Crystalline alumina
~57.59°	γ -Al ₂ O ₃	(116)	Crystalline alumina
~66.48°	γ -Al ₂ O ₃	(214)	Crystalline alumina

Note: Peak positions are approximate and may slightly vary due to instrumental resolution or sample-specific factors.

6.2.2. XRD analysis of heat-treated NiB and NiB-Al₂O₃ coatings

After the heat treatment at 400 °C for 2 hours, the XRD patterns of the NiB and NiB-Al₂O₃ nanocomposite coatings exhibit a significant structural transformation, as shown in Figure 6.7. In the pure NiB coatings, the broad and diffuse peak observed in the as-deposited state disappears and is replaced by sharp diffraction peaks corresponding to crystalline phases. Prominent reflections emerge at approximately 44.7° and 52.4°, attributed to the (111) and (200) planes of face-centered cubic (fcc) nickel, indicating the recrystallization of the previously amorphous NiB matrix into its thermodynamically stable form. In addition to fcc-Ni, new diffraction peaks corresponding to intermetallic nickel boride phases appear after annealing [141]. Specifically, Ni₃B is identified by reflections at approximately 36.6°, 42.6°, and 46.5°, while Ni₂B is confirmed by peaks near 41.2°, 44.3°, and 47.5° [26,63]. These intermetallic phases are formed as boron atoms diffuse out of the disordered matrix and react with nickel during heat treatment. Consequently, the initial amorphous NiB solid solution decomposes into a thermodynamically stable multiphase structure composed of fcc-Ni, Ni₃B, and Ni₂B.

This transformation is closely associated with the role of boron in the system. During deposition, the high boron concentration hinders the nucleation of ordered crystalline phases by increasing the critical free energy required for nucleation. This is due to the additional strain and lattice distortion introduced by boron atoms, which act as barriers to atom migration and lattice rearrangement. As a result, crystallization is suppressed, promoting the formation of an amorphous structure in the as-deposited coatings. However, upon heat treatment, the atomic mobility increases substantially, especially for boron due to its small atomic radius (0.87 Å). This enhanced mobility facilitates boron diffusion and allows for the formation of thermodynamically favorable crystalline phases such as Ni₃B and Ni₂B alongside recrystallized fcc-Ni. This atomic rearrangement leads to the development of nanosized crystalline domains with enhanced structural integrity, underscoring the dual role of boron as both an amorphizer during deposition and a crystallization promoter upon annealing.

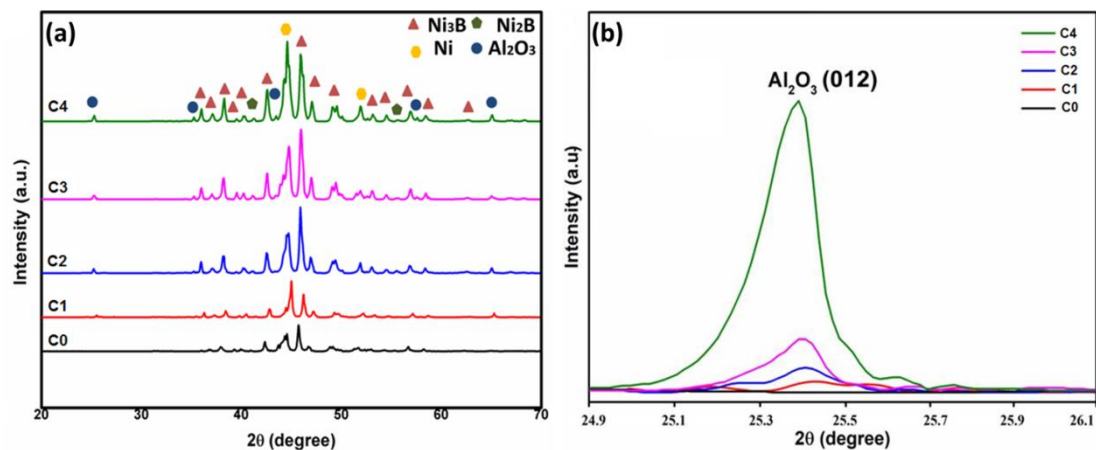


Figure 6.7. XRD patterns of heat-treated NiB and NiB-Al₂O₃ nanocomposite coatings. (a) Full diffraction patterns indicating the emergence of fcc-Ni, Ni₃B, and Ni₂B phases after annealing at 400 °C. (b) Magnified view of the (012) peak of γ-Al₂O₃ at ~25.3°, highlighting the evolution of Al₂O₃-related crystallinity with increasing particle content (reproduced from [27]).

In the case of NiB-Al₂O₃ coatings, the XRD patterns also reveal the presence of distinct γ-Al₂O₃ reflections after heat treatment, which are consistent with those observed in the as-deposited state. These peaks appear at approximately 25.44° (012), 35.26° (104), 43.46° (113), 57.59° (116), and 66.48° (214), confirming that the Al₂O₃ nanoparticles retain their original crystalline γ-phase structure after the heat treatment at 400 °C. This structural stability indicates the thermal inertness of γ-Al₂O₃ within the NiB matrix during annealing. The characteristic diffraction peaks associated with these crystalline phases are summarized in Table 6.5, providing a concise overview of the phase composition and crystallographic features observed in the heat-treated coatings.

Table 6.5. Major XRD peaks identified in heat-treated NiB and NiB-Al₂O₃ coatings.

Observed 2θ (°)	Assigned Phase	Miller Indices (hkl)	Phase Type
~25.44	γ-Al ₂ O ₃	(012)	Crystalline alumina
~35.26	γ-Al ₂ O ₃	(104)	Crystalline alumina
~41.2	Ni ₂ B	(121) / (211)	Intermetallic (nickel boride)
~42.6	Ni ₃ B	(121)	Intermetallic (nickel boride)
~43.46	γ-Al ₂ O ₃	(113)	Crystalline alumina
~44.7	Ni	(111)	Face-centered cubic (fcc) Ni
~46.5	Ni ₃ B	(211)	Intermetallic (nickel boride)
~52.4	Ni	(200)	Face-centered cubic (fcc) Ni
~57.59	γ-Al ₂ O ₃	(116)	Crystalline alumina
~66.48	γ-Al ₂ O ₃	(214)	Crystalline alumina

To provide a clearer understanding of the structural evolution of the γ-Al₂O₃ phase after heat treatment, a magnified view of the (012) diffraction peak is shown in Figure

6.7b. This enlarged region highlights the progressive increase in the intensity of the γ - Al_2O_3 (012) diffraction peak from C1 to C4, reflecting the successful incorporation and retention of Al_2O_3 nanoparticles with rising bath concentrations. While the overall peak positions remain largely consistent across samples, a negligible variation is observed for the C1 coating. In this sample, the γ - Al_2O_3 (012) peak appears broader and less intense compared to higher Al_2O_3 loadings. This behavior is attributed to the very low content of ceramic reinforcement, as also supported by the SEM observations, where only a limited number of Al_2O_3 particles were incorporated. As a result, the XRD signal becomes weaker and more diffuse, resembling the amorphous background of the NiB matrix. This behavior is not the result of any phase transformation but rather an expected response arising from the insufficient crystalline volume, which limits the intensity and sharpness of the diffraction peak. Importantly, the absence of significant peak broadening or asymmetry confirms that the overall crystalline integrity of the γ - Al_2O_3 phase is preserved. These observations confirm that the γ - Al_2O_3 phase retains its crystalline identity and thermal stability after heat treatment at 400 °C, without undergoing any detectable phase transformation or chemical interaction or degradation between the Al_2O_3 particles and the surrounding NiB matrix. In contrast to the NiB matrix, which undergoes amorphous-to-crystalline transformation during heat treatment, the Al_2O_3 nanoparticles maintain their original crystalline identity. This consistent behavior underscores the thermal stability of the γ - Al_2O_3 phase under annealing at 400 °C a temperature significantly below the known transition threshold to α - Al_2O_3 . Thus, no phase transformation is expected, which aligns well with the experimental observations.

6.2.3. Crystallite size evolution of NiB and NiB- Al_2O_3 coatings after heat treatment

The crystallite sizes of the fcc-Ni phase in the NiB and NiB- Al_2O_3 coatings were calculated using the Debye-Scherrer equation, as shown in equation 6.2. This phase typically emerges as the dominant crystalline component. Therefore, determining the crystallite size of this phase provides valuable insight into several key microstructural characteristics. It reflects the overall degree of crystallinity, indicates the extent of grain growth, and correlates with the mechanical behavior of the matrix, particularly hardness and structural integrity. Furthermore, the grain-refining effect of ceramic reinforcements such as Al_2O_3 is often evaluated through their influence on the

crystallite size of the fcc-Ni phase. In this context, the crystallite size of fcc-Ni serves as a direct indicator of the matrix refinement and microstructural stability.

The Scherrer method provides an obtain of coherent diffraction domain sizes, based on the full width at half maximum (FWHM) of the corresponding XRD peaks.

The Scherrer equation is given as:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (6.2)$$

where:

D is the crystallite size (nm),

λ is the wavelength of Cu K α radiation (0.15406 nm),

β is the FWHM in radians,

θ is the Bragg angle.

For all samples, the (111) reflection of fcc-Ni was used for the calculation, as it is the most prominent and clearly distinguishable peak. The calculated crystallite sizes for the heat-treated coatings are summarized in Table 6.6.

Table 6.6. FWHM and Bragg Parameters Corresponding to the Crystallite Sizes of Heat-Treated NiB and NiB-Al₂O₃ Coatings Based on the fcc-Ni (111) Reflection at $2\theta \approx 44.7^\circ$.

Sample	2θ ($^\circ$)	θ ($^\circ$)	FWHM ($^\circ$)	B (rad)	D (nm)
C0	44.7	22.35	0.21	0.00366	41
C1	44.7	22.35	0.226	0.00395	38
C2	44.7	22.35	0.239	0.00416	36
C3	44.7	22.35	0.253	0.00441	34
C4	44.7	22.35	0.245	0.00428	35

Note: The values were derived using the Debye-Scherrer equation, assuming Cu K α radiation ($\lambda = 0.15406$ nm).

Among all the samples, C3 exhibited the smallest crystallite size (~ 34 nm) after heat treatment, which corresponds to the most refined microstructure. The relatively small crystallite size observed in the C3 sample offers several microstructural advantages. In metal matrix systems, reduced crystallite size leads to a higher density of grain boundaries, which contributes to enhanced structural integrity by limiting dislocation activity. Moreover, the homogeneous dispersion of Al₂O₃ nanoparticles in the C3

coating plays a critical role in suppressing grain growth during both deposition and subsequent heat treatment. These well-distributed particles effectively pin grain boundaries and inhibit coalescence, resulting in a more refined and thermally stable microstructure. The increased grain boundary area associated with smaller crystallites is also expected to improve phase stability and resistance to structural degradation under elevated temperatures. The implications of this microstructural refinement on the functional performance of the coatings will be discussed in subsequent sections.

6.3. Evaluation of Nanomechanical Behavior of NiB and NiB-Al₂O₃ Nanocomposite Coatings

Understanding the nanomechanical performance of electroless NiB and NiB-Al₂O₃ nanocomposite coatings is essential for evaluating their reliability under contact-induced stresses, especially in tribological environments where both plastic deformation and elastic recovery play a critical role. In this study, instrumented nanoindentation tests were conducted to quantitatively assess hardness, elastic modulus, and the derived mechanical parameters (H/E and H^3/E^2) across various coating compositions, both in the as-plated and heat-treated conditions. As summarized in Figure 6.8, four complementary perspectives were employed to interpret the mechanical response. The load-depth indentation curves, reflecting the resistance to penetration and plastic deformation are depicted in Figure 6.8(a,b). Figure 6.8c shows the nanohardness evolution with increasing Al₂O₃ content, highlighting reinforcement trends. Finally, Figure 6.8d represents the elastic modulus variation, revealing changes in stiffness with composition and annealing. This multi-faceted approach allows a comprehensive analysis of how amorphous-to-crystalline transitions in pure NiB coatings and ceramic particle incorporation in composite systems synergistically contribute to mechanical performance. The following sections systematically dissect each contribution to elucidate the fundamental strengthening mechanisms and their implications on coating durability.

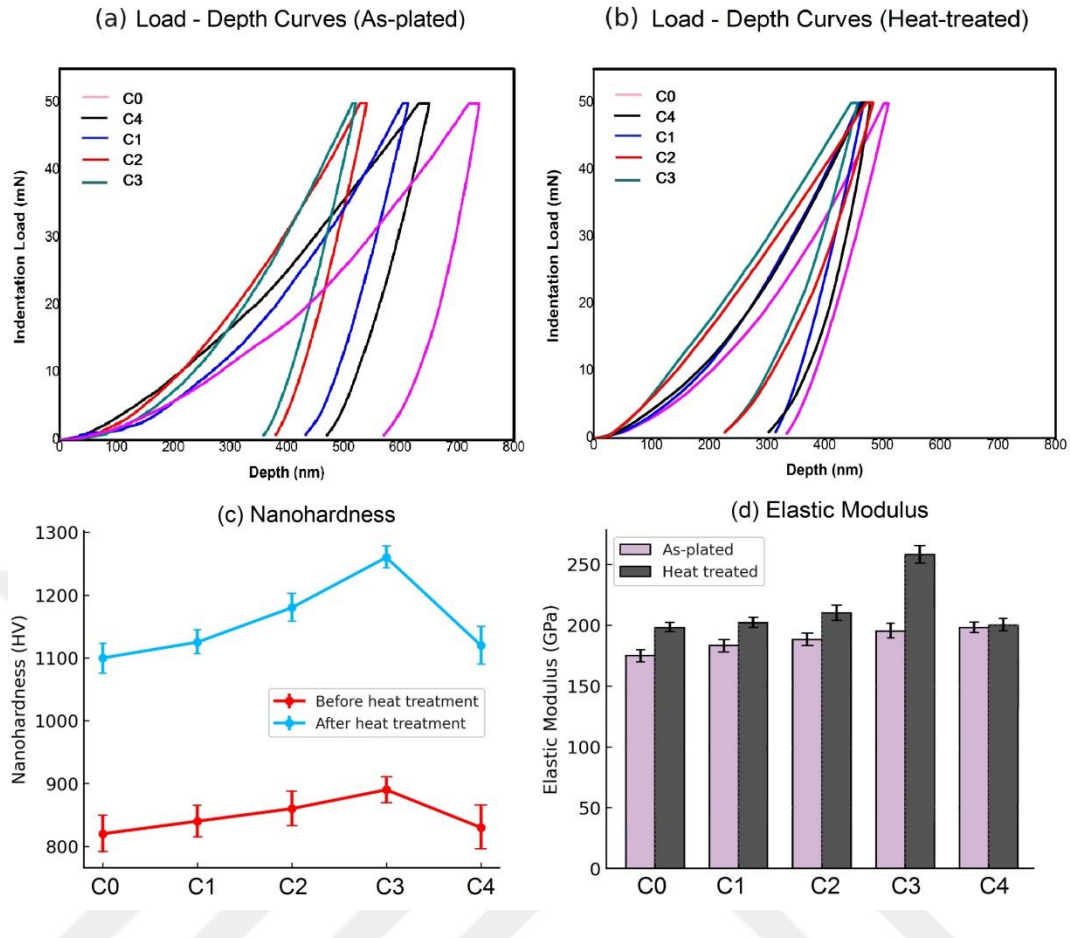


Figure 6.8. Load-depth curves, nanohardness, and elastic modulus of NiB and NiB-Al₂O₃ coatings before and after heat treatment: (a) indentation behavior of as-plated coatings, (b) indentation behavior after heat treatment, (c) nanohardness evolution with Al₂O₃ content, (d) corresponding elastic modulus values. The results highlight the combined influence of particle reinforcement and phase transformation on nanomechanical properties.

Note: The legend in Figures 6.8a and 6.8b is ordered based on the positional arrangement of the load-depth curves in the graph.

6.3.1. Nanomechanical behavior of pure NiB coating

The unreinforced NiB coating (C0) displays the deepest indentation depth, reflecting its relatively lower hardness and weaker load-bearing capability. The as-deposited NiB coating exhibits a relatively broad and deep penetration profile (Figure 6.8a) when compared to all other compositions, indicating limited resistance to plastic deformation. This behavior is consistent with its relatively low nanohardness (~820 HV), as shown in Figure 6.8c. The as-deposited NiB matrix possesses a fully amorphous structure due to rapid atomic deposition and boron-induced crystallization suppression. The incorporation of boron atoms distorts the nickel lattice and prevents long-range atomic ordering, leading to an amorphous morphology that inherently lacks

dislocation motion. As a result, the coating exhibits moderate hardness but limited stiffness and recovery.

After heat treatment, the load-depth curve of the C0 coating exhibits a steeper slope and a reduced maximum penetration depth compared to its as-plated state, indicating the expected increase in hardness and elastic modulus. However, despite this improvement, the absolute performance of C0 remains lower than that of the composite coatings (C1-C3), where alumina reinforcement provides additional strengthening. The hardness of pure NiB coating increases significantly to around 1100 HV after heat treatment. Moreover, elastic modulus increases from ~175 GPa to ~200 GPa, as presented in Figure 6.8d. These enhancements are primarily attributed to the structural transformation from an amorphous phase to crystalline nickel borides, specifically Ni_3B and Ni_2B . These intermetallic compounds improve structural order and mechanical resistance [135]. This behavior clearly demonstrates the dual functional role of boron: it contributes to the formation of an amorphous structure during deposition and, on the other hand, promotes the nucleation of reinforcing crystalline phases upon thermal activation. This structural evolution explains the substantial increase in nanohardness observed after annealing.

6.3.2. Load - depth curves of NiB- Al_2O_3 nanocomposite coatings

In the as-plated state (Figure 6.8a), the incorporation of Al_2O_3 nanoparticles leads to a marked leftward shift in the load-depth curves, indicating reduced indentation depth under identical loading conditions. This behavior is particularly evident in the C3 coating, which displays the shallowest penetration among all samples. This reduction in depth signifies enhanced load-bearing capacity and resistance to plastic deformation, in agreement with the highest nanohardness values observed in Figure 6.8c. The intermediate curves of C1, C2, and C3 demonstrate that the indentation resistance is strongly correlated with the nanoparticle concentration, where excessive reinforcement (C4) causes partial agglomeration and slightly reduces the mechanical integrity compared to the optimal composition (C3). Thus, the load-depth characteristics further confirm the beneficial role of Al_2O_3 incorporation up to a critical threshold.

After the heat treatment, the enhancement in mechanical performance becomes even more pronounced, as shown in Figure 6.8b. The indentation curves of the C1, C2, and C3 coatings exhibit a distinct leftward shift relative to their as-deposited counterparts,

reflecting the combined influence of crystalline boride phase formation within the NiB matrix and the reinforcing action of well-dispersed Al_2O_3 nanoparticles. Among the investigated samples, the C3 coating maintains the shallowest indentation depth following annealing, reaffirming that an Al_2O_3 concentration of 10 g/L represents the optimal reinforcement level. The indentation response of this sample evidences a stiffened, structurally consolidated matrix capable of withstanding deeper penetration and exhibiting improved elastic recovery under load.

In contrast, the C4 coating, with the highest Al_2O_3 content, does not exhibit further improvement despite its elevated ceramic fraction. The excessive particle concentration promotes agglomeration within the NiB matrix, disrupting the uniform microstructural arrangement achieved at lower concentrations. These agglomerated regions generate localized microstructural inhomogeneities, including voids and weakly bonded particle-matrix interfaces, which act as stress concentrators during mechanical loading. Consequently, they facilitate the initiation and propagation of microcracks, leading to a measurable reduction in both nanohardness and elastic modulus compared with the optimally reinforced C3 coating. Although the nominal ceramic content is higher, the effective load transfer and the matrix's ability to constrain plastic deformation are markedly diminished due to the non-uniform stress distribution introduced by particle clustering. This deterioration in mechanical performance underscores the existence of a critical reinforcement threshold, beyond which additional ceramic incorporation ceases to enhance the coating's mechanical properties. Instead, it compromises microstructural coherence, promotes defect formation, and ultimately undermines the mechanical reliability of the composite system.

6.3.3. Nanohardness evolution with Al_2O_3 content

The hardness values of the NiB- Al_2O_3 nanocomposite coatings exhibit a clear dependence on the concentration of Al_2O_3 nanoparticles incorporated into the plating bath. As shown in Figure 6.8c, the nanohardness of the coatings improves with increasing Al_2O_3 content up to an optimal concentration of 10 g/L, beyond which the mechanical benefits diminish due to particle agglomeration and structural heterogeneity. This improvement is primarily attributed to the dispersion strengthening mechanism, whereby hard ceramic nanoparticles serve as effective obstacles to dislocation propagation. The presence of uniformly distributed Al_2O_3

particles limits the movement of dislocations under applied stress, thereby reducing localized plastic deformation and promoting strain hardening within the matrix. A high-quality dispersion of Al_2O_3 nanoparticles is crucial in maximizing this strengthening effect, as poorly dispersed or agglomerated regions can act as weak points within the microstructure, promoting localized deformation instead of restricting it. Similar results have been reported in previous studies on electroless NiB-ceramic composite coatings, where an optimal nanoparticle concentration was found to enhance hardness through effective dispersion strengthening mechanisms [76,135].

In addition to blocking dislocation motion, Al_2O_3 nanoparticles contribute to the mechanical performance by bearing part of the externally applied loads. The rigid ceramic particles, embedded within the NiB matrix, share the mechanical load, reducing the mechanical stress experienced by the metallic matrix itself [106,135]. This load transfer mechanism further enhances the overall mechanical rigidity of the coating. The beneficial synergistic effect of dislocation blocking and load sharing is particularly evident in the C3 sample, where the maximum hardness was achieved, reaching approximately 1260 HV after heat treatment.

6.3.4. Elastic modulus of coatings

Figure 6.8d further supports the mechanical reinforcement by showing a clear upward trend in elastic modulus with Al_2O_3 content. The elastic modulus values reveal a similar trend to hardness, with a consistent increase after heat treatment due to the crystallization of the NiB matrix and the effect of Al_2O_3 addition [76]. The C3 coating exhibits the highest elastic modulus, which can be attributed to the presence of stiff Al_2O_3 nanoparticles acting as load-bearing reinforcements. Notably, the improvement in elastic modulus following heat treatment suggests that the precipitation of Ni_2B and Ni_3B phases enhances the stiffness of the matrix. The combined increase in both hardness and elastic modulus implies that the coatings are capable of sustaining higher loads with reduced elastic strain, a feature that is essential for their long-term tribological performance under elevated temperatures. The as-plated C3 coating has an elastic modulus of ~ 195 GPa, which increases to ~ 260 GPa after annealing, which is the highest among all samples. This demonstrates that Al_2O_3 not only hardens the coating but also significantly stiffens the structure by enhancing its resistance to elastic strain.

6.3.4.1. H/E ratio and elastic strain to failure

In addition to absolute hardness and elastic modulus values, the H/E ratio provides valuable information regarding the elastic strain to failure and the ability of a material to elastically accommodate applied stresses [142]. Higher H/E ratios generally indicate improved toughness and enhanced resistance against crack initiation under cyclic or concentrated loading conditions [39,143]. In the present study, the C3 coating exhibited the highest H/E ratio among all compositions, suggesting that the optimal incorporation of Al₂O₃ nanoparticles not only increases hardness but also improves the elastic accommodation of stresses. This combined effect is advantageous for tribological applications, as coatings with higher H/E ratios exhibit improved resistance to crack initiation and delayed onset of failure under sliding conditions. In contrast, the lowest H/E ratio observed for the unreinforced NiB (C0) coating indicates its relatively limited capacity for elastic deformation, which contributes to higher susceptibility to plastic damage and wear.

6.3.4.2. H³/E² ratio and resistance to plastic deformation

Another critical mechanical performance parameter is the H³/E² ratio, which represents the resistance to plastic deformation and is often correlated with wear resistance. A higher H³/E² value implies that a material can withstand higher contact stresses without undergoing permanent deformation, thereby offering superior durability under tribological loading [143]. In this study, the C3 coating demonstrated the maximum H³/E² ratio, highlighting its ability to resist plastic indentation and correlating well with its superior wear resistance observed in tribological tests. The over-reinforced C4 coating showed a moderate decrease in H³/E² despite having relatively high hardness, which can be explained by nanoparticle agglomeration and the resulting microstructural defects that compromise the effective load distribution. This observation confirms that the optimal Al₂O₃ concentration not only enhances hardness and stiffness but also maximizes the coating's plastic deformation resistance, directly contributing to its superior tribological performance at elevated temperatures.

Overall, the combined evaluation of hardness, elastic modulus, H/E, and H³/E² ratios clearly demonstrates that the mechanical integrity and tribological reliability of electroless NiB-Al₂O₃ nanocomposite coatings are governed not solely by their absolute hardness, but more importantly by the balance between stiffness and plastic accommodation. The C3 coating, with its optimal reinforcement level, achieves the

most favorable balance, thereby ensuring enhanced durability and long-term performance under severe operating conditions.

6.4. Analysis of Tribological Behaviors of Electroless NiB and NiB-Al₂O₃ Nanocomposite Coatings

In this section, the tribological behaviors of the electroless NiB and NiB-Al₂O₃ nanocomposite coatings are comprehensively analyzed under dry sliding conditions, with a focus on key tribological parameters such as the coefficient of friction (COF), wear rate, and wear track morphology. The coatings were tested at four distinct temperatures (25 °C, 200 °C, 400 °C, and 600 °C) to evaluate the combined effects of temperature, Al₂O₃ reinforcement, coating microstructure, and dominant wear mechanisms on overall tribological performance.

6.4.1. Temperature-dependent friction behavior of NiB and NiB-Al₂O₃ coatings

The friction behavior of electroless NiB and NiB-Al₂O₃ nanocomposite coatings is primarily determined by their microstructural characteristics, the distribution of reinforcing particles, and the contact conditions during sliding. In the following sections, the effects of these factors, along with the influence of temperature, on the friction behavior of these coatings are discussed.

6.4.1.1. Friction behavior at 25 °C

At 25 °C, the unreinforced NiB coating (C0) exhibited the lowest initial coefficient of friction (~0.25), likely due to its dense and compact columnar microstructure, which initially reduces the real contact area. However, instead of maintaining this low friction behavior, the COF progressively increased throughout the sliding distance, reaching ~0.55 by the end of the test. This continuous rise suggests that, in the absence of reinforcing Al₂O₃ nanoparticles, the NiB matrix gradually undergoes plastic deformation and surface damage under repeated loading. Moreover, the lack of hard, load-bearing phases limits the formation of stable third-body layers, causing the sliding to occur primarily on the metallic matrix. Consequently, the initial advantage offered by the compact structure cannot be sustained, and the system evolves toward higher friction as sliding proceeds.

On the other hand, the incorporation of Al₂O₃ nanoparticles into the NiB matrix can significantly affect the friction response, resulting in higher COF values. Initially, Al₂O₃ particles act as heterogeneous nucleation sites, refining the grain structure [135].

This refinement can increase the number of contact points and the overall interaction area at the micro-scale, potentially raising the frictional forces during sliding. Additionally, Al_2O_3 particles, being significantly harder than the NiB matrix, can form local stress concentrations at the particle-matrix interface, which increase the coefficient of friction by promoting micro-plowing and localized deformation. This frictional behavior is clearly reflected in the COF profiles shown in Figure 6.9.

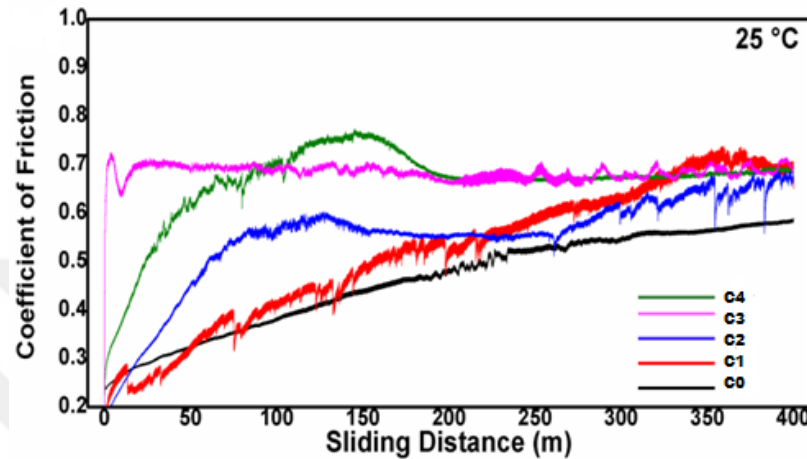


Figure 6.9. Coefficient of friction (COF) graphs of electroless NiB and NiB- Al_2O_3 nanocomposite coatings tested at 25 °C under dry sliding conditions (reproduced from [27]).

As shown in Figure 6.9, in contrast to the unreinforced NiB coating (C0), the Al_2O_3 -reinforced composite coatings (C1-C4) exhibited higher initial friction coefficients but demonstrated more stable behavior in the steady-state regime. Among them, the C3 coating showed the most consistent and stable COF trend after the initial running-in stage, maintaining a nearly constant value around 0.65 throughout the sliding distance. This steady-state behavior suggests that the optimal dispersion of hard Al_2O_3 nanoparticles in the C3 coating facilitates the formation of a protective third-body layer, which helps minimize further surface damage and friction fluctuations. In particular, a more uniform particle distribution enhances load-bearing capacity and minimizes localized stress, promoting stable friction over longer sliding distances. However, the C1 and C2 coatings (with lower Al_2O_3 contents) exhibited moderately fluctuating COF profiles, indicating that partial reinforcement provides some tribological benefits but does not achieve a fully stable sliding regime. Notably, the C4 coating, despite its high Al_2O_3 content, showed an initial sharp COF rise followed by a significant drop and then restabilization. This irregular behavior is primarily

attributed to particle agglomeration, which causes uneven load distribution and promotes localized stress concentrations.

6.4.1.2. Friction behavior at 200 °C

Compared to 25 °C, the tribological behavior of all coatings at 200 °C marks the onset of temperature-induced degradation mechanisms, including matrix softening, partial particle detachment, and early-stage oxide formation. The unreinforced NiB coating (C0), which previously exhibited a gradual increase in COF, and shows pronounced instability and sharp fluctuations throughout the sliding distance, with values ranging between ~0.45 and ~0.6. This behavior suggests that, at elevated temperatures, the NiB matrix becomes increasingly susceptible to localized plastic deformation, which undermines its ability to maintain uniform contact under cyclic loading and ultimately causes repeated breakdown and reformation of weak third-body layers, leading to unstable friction. The reduced mechanical stability facilitates intermittent frictional responses and increases COF variability. The COF curves of all coatings at 200 °C are presented in Figure 6.10, illustrating the distinct frictional responses of both the monolithic and composite coatings.

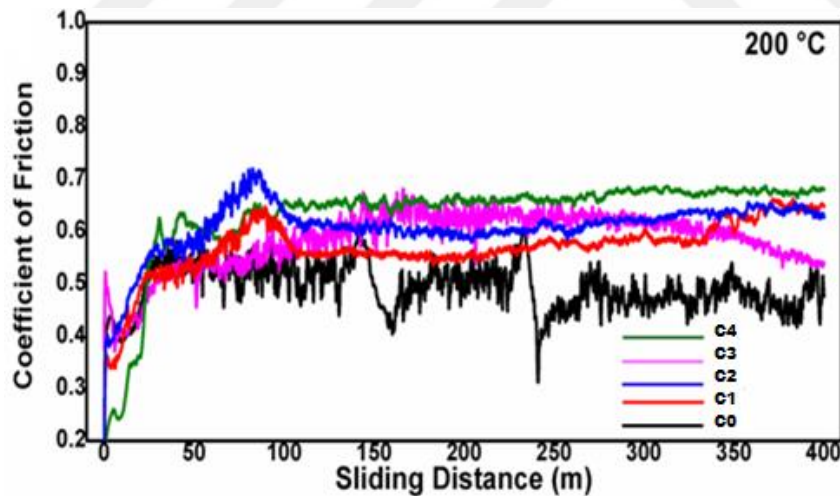


Figure 6.10. Coefficient of friction (COF) graphs of electroless NiB and NiB-Al₂O₃ nanocomposite coatings tested at 200 °C under dry sliding conditions (reproduced from [27]).

As the temperature increases, the NiB matrix gradually loses stiffness, reducing its ability to maintain strong interfacial bonds with the embedded ceramic particles. Although C1 and C2 exhibit only moderate increases in COF (~0.55-0.65), early signs of instability become apparent, including incipient surface roughening and minor third-body interactions. These features are likely associated with partial particle

detachment and oxide fragmentation under shear loading. The C3 sample continues to display the most favorable frictional performance among the reinforced coatings, characterized by smooth COF evolution and low fluctuation amplitude. This stability originates primarily from mechanical load sharing and effective stress distribution provided by the optimally dispersed Al_2O_3 particles, rather than from tribochemical film formation, which remains limited at this stage. The interfacial integrity between the NiB matrix and the reinforcement is largely preserved at 200 °C, preventing excessive debris generation.

In contrast, the C4 coating exhibits a sharp rise in COF during the initial sliding stage, rapidly reaching ~0.65. This increase can be attributed to its high Al_2O_3 content, which enhances interfacial roughness and contact stiffness, thereby elevating friction. Although the COF appears stable during the steady-state regime, this stability is superficial. Agglomerated Al_2O_3 clusters and weak interfacial bonding promote localized stress accumulation and subsurface damage. At 200 °C, the oxide layer remains in an incipient state and lacks mechanical integrity. As sliding proceeds, fragmented oxides and dislodged particles contribute to mild third-body effects; however, their influence is still limited at this temperature. This early-stage behavior in C4 likely represents the precursor to the more pronounced third-body-driven degradation observed at higher temperatures, as discussed in subsequent sections.

6.4.1.3. Friction behavior at 400 °C

At 400 °C, the frictional behavior of all coatings undergoes a pronounced transformation, reflecting intensified thermally induced degradation processes. COF values rise noticeably for every sample, accompanied by larger fluctuation amplitudes and reduced sliding stability. These changes result from the combined influence of matrix softening, tribo-oxidation, and interfacial weakening, all of which progressively dominate the tribological response at this temperature. The overall frictional evolution of the coatings at 400 °C is illustrated in Figure 6.11.

The pure NiB coating (C0) continues to exhibit the lowest COF values (~0.45-0.55) among all samples, maintaining a relatively smooth and stable frictional profile. However, this apparent stability should not be interpreted as superior performance. The absence of ceramic reinforcement limits the load-bearing capacity and accelerates localized plastic deformation within the softened NiB matrix. Consequently, while the friction remains moderate, subsurface fatigue and oxidative wear are likely

accumulating with sliding distance. The lack of a rigid reinforcement network prevents efficient stress distribution, allowing stress concentrations at asperities that promote microcrack initiation and progressive structural degradation beneath the surface.

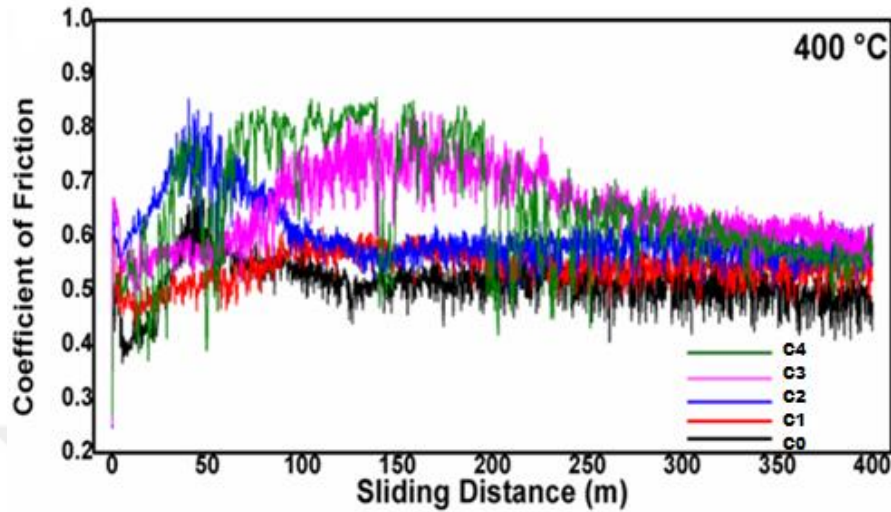


Figure 6.11. Coefficient of friction (COF) graphs of electroless NiB and NiB-Al₂O₃ nanocomposite coatings tested at 400 °C under dry sliding conditions (reproduced from [27]).

Among the composite coatings, frictional divergence becomes more pronounced at 400 °C due to differences in particle distribution, matrix-reinforcement adhesion, and thermally activated degradation kinetics. C1 and C2 exhibit moderately increased COF values (~0.60-0.65) with occasional spikes, indicating localized third-body interactions caused by oxide fragmentation and partial particle-matrix debonding. As the NiB matrix softens further, its ability to retain Al₂O₃ particles weakens, enabling some particles to detach and act as rolling or plowing debris within the contact interface.

The C3 coating displays a distinct and dynamic frictional evolution at 400 °C. During the early sliding stages, COF fluctuates within ~0.65-0.85 due to transient instability associated with surface reorganization, oxide film development, and partial particle detachment. However, toward the steady-state regime, the COF stabilizes near ~0.6, reflecting a partial reformation of a protective tribolayer and effective re-engagement of well-bonded Al₂O₃ particles. This indicates that the C3 coating retains its functional integrity longer than other composites, achieving a temporary frictional balance once the initial surface disruptions subside.

Conversely, the C4 coating exhibits the most unstable and irregular frictional response, with COF oscillating between ~ 0.65 and 0.85 throughout the test. The excessive Al_2O_3 loading promotes agglomeration, forming stiff particle clusters that inhibit accommodation of thermal strains. These clusters act as stress concentrators, triggering interfacial microcracking and particle ejection. The resulting hard debris intensifies third-body abrasion and disrupts the contact interface. Simultaneously, a thick, brittle oxide layer develops and undergoes spallation under cyclic stress, producing fragmented oxide scales that further amplify COF fluctuations and surface instability.

6.4.1.4. Friction behavior at 600 °C

As the temperature reaches 600 °C, all coatings exhibit signs of advanced thermal and mechanical degradation, characterized by intensified oxide formation, matrix instability, and increasingly disruptive third-body interactions. These synergistic effects lead to significant changes in the coefficient of friction (COF) behavior, as shown in Figure 6.12. The unreinforced NiB coating (C0) maintains the lowest and most stable COF (~ 0.60 - 0.65) across the sliding distance. However, this apparent stability likely reflects a friction regime dominated by weak tribo-oxidized films and limited third-body dynamics. The internal degradation mechanisms such as plastic deformation and thermal fatigue may continue to progress insidiously beneath the contact surface, posing long-term durability concerns.

In contrast, the Al_2O_3 -reinforced coatings display more pronounced frictional responses. C1 and C2 show moderately high average COF values with frequent spikes, indicating unstable tribological behavior. These fluctuations are primarily driven by interfacial degradation at the particle-matrix boundary, where thermal stresses and matrix softening promote localized cracking and partial particle detachment. The dislodged Al_2O_3 particles become entrapped within the contact zone, acting as hard third-body abrasives that initiate micro-cutting and surface roughening.

The C3 coating, previously noted for its superior stability at lower temperatures, maintains relatively moderate COF values (~ 0.65 - 0.75) during the initial sliding stages at 600 °C. However, after approximately 300 m of sliding, the amplitude of COF fluctuations increases, indicating the progression of tribo-oxide delamination and intermittent third-body interactions. While initial signs of degradation had already emerged at 400 °C, the behavior at 600 °C reflects a more advanced stage of these

mechanisms, driven by intensified thermal effects and prolonged exposure. Despite this, the relatively uniform particle dispersion and strong matrix-particle bonding in C3 continue to mitigate rapid failure, delaying the full transition to a severe abrasive regime and reinforcing the importance of optimized reinforcement content under elevated thermal conditions.

On the other hand, the C4 coating, containing the highest Al_2O_3 concentration, shows the most unstable COF behavior, fluctuating dramatically between ~ 0.75 and 0.90 . The excessive ceramic content leads to particle agglomeration and weak interfacial cohesion, which in turn causes uneven stress distribution and increased particle detachment. These loose clusters act as aggressive third bodies within the sliding interface, causing severe abrasion and destabilizing the tribolayer. Additionally, the oxide scales formed at 600°C tend to be thicker and mechanically fragile due to thermal expansion mismatch, making them prone to spallation. Their delamination further exposes the substrate, intensifies debris formation, and accelerates wear progression.

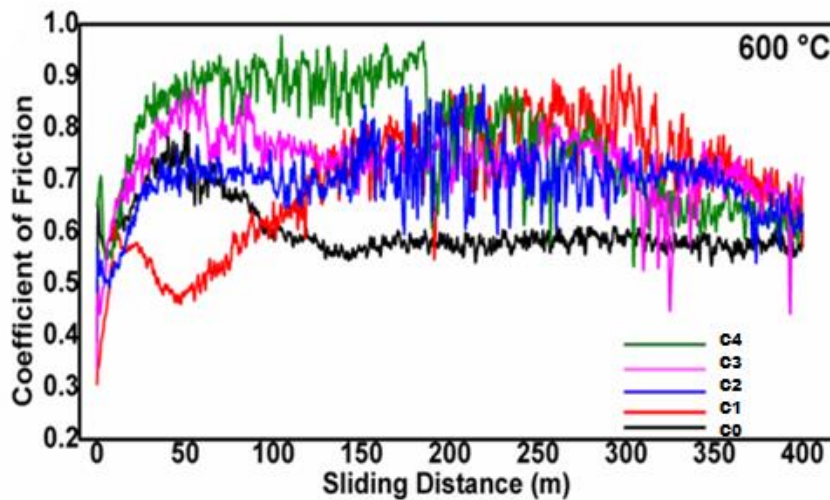


Figure 6.12. Coefficient of friction (COF) graphs of electroless NiB and NiB- Al_2O_3 nanocomposite coatings tested at 600°C under dry sliding conditions (reproduced from ([27])).

6.4.2. Wear rate evaluation of electroless NiB and NiB- Al_2O_3 nanocomposite coatings

The coefficient of friction defines the shear resistance between two contacting surfaces. This resistance is influenced by surface roughness, surface energies, real contact area, and the presence of third-body particles. However, COF is not directly proportional to the volumetric material loss. A surface may exhibit a low friction

coefficient for several reasons: it may be soft and easily deformable, thereby minimizing mechanical interlocking with the counterface; it may be homogeneous and smooth, leading to reduced asperity contacts; or it may lack abrasive third-body particles, which decreases ploughing and cutting effects. Nevertheless, such a surface often lacks sufficient load-bearing capacity, possesses low hardness, and is prone to plastic deformation or flow under load. These shortcomings accelerate crack initiation and propagation, ultimately resulting in severe material loss despite the low COF. This phenomenon was particularly evident in the C0 sample, which exhibited the lowest COF yet suffered the highest volumetric wear loss among all coatings likely due to its limited hardness, poor load-bearing capacity, and increased susceptibility to plastic deformation. Clearly, a low coefficient of friction does not necessarily reflect superior wear performance, as it may stem from mechanically unfavorable factors such as insufficient hardness or structural degradation. When frictional reduction arises primarily from insufficient hardness or limited load-bearing capacity rather than from robust surface engineering, the coating remains vulnerable to accelerated material loss under mechanical stress. Therefore, COF values should be evaluated together with the mechanical properties of the coating to fully understand its tribological behavior.

To overcome the mechanical limitations observed in the unreinforced NiB coating, Al_2O_3 nanoparticles were incorporated into the matrix to enhance its structural integrity and tribological performance. The addition of Al_2O_3 significantly improved the wear resistance, mainly due to the inherent hardness and thermal stability of the ceramic particles, which increased the composite's load-bearing capacity and suppressed localized plastic deformation. Furthermore, their uniform distribution facilitated dispersion strengthening and reduced the real contact area with the counterface by limiting asperity engagement. These improvements collectively reduced the extent of plastic flow and crack propagation under mechanical stress. Similar observations have also been reported in the literature. Raghavendra et al. [121] observed a steady decrease in the wear rate of Ni-based coatings with increasing Al_2O_3 content, attributing this behavior to enhanced structural reinforcement. Likewise, Algailani et al. [144] associated the wear resistance improvement in Ni- Al_2O_3 systems with better hardness and interfacial stability provided by the ceramic phase. These microstructural mechanisms are clearly reflected in the experimental results, as presented in Figure 6.13, where the wear rate decreases systematically with increasing

Al_2O_3 content, confirming the beneficial role of ceramic reinforcement under both ambient and elevated temperatures.

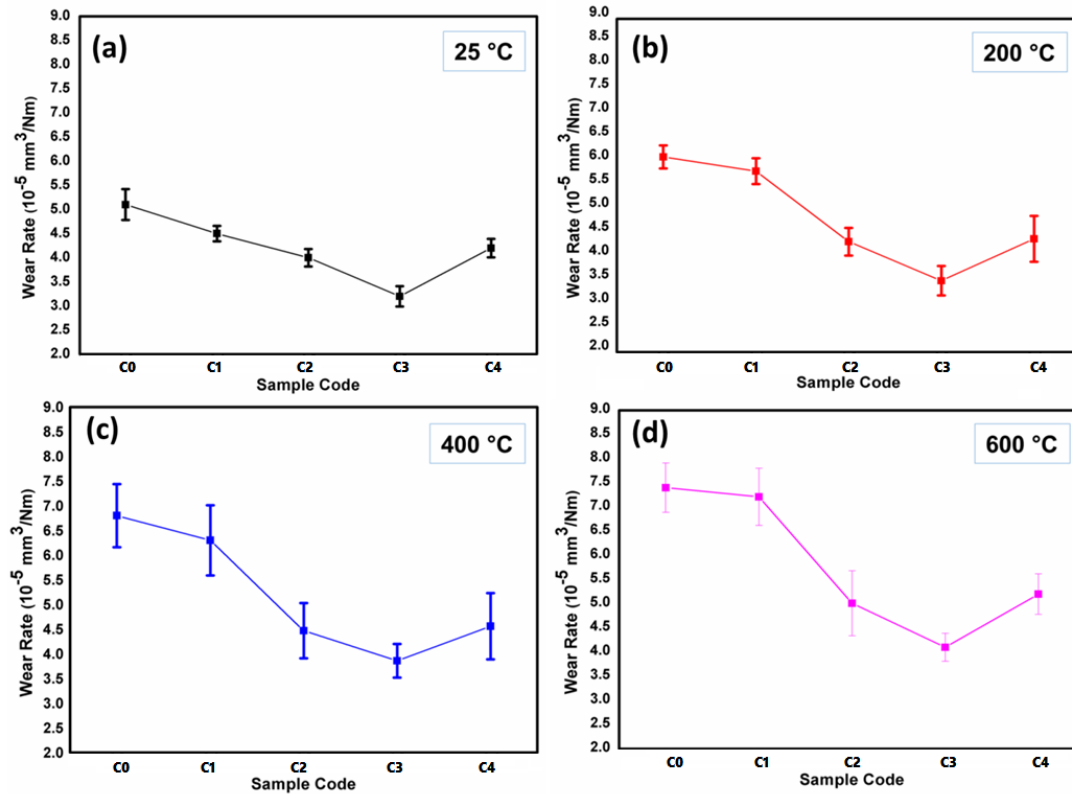


Figure 6.13. Wear rates of electroless NiB and NiB- Al_2O_3 nanocomposite coatings as a function of Al_2O_3 concentration at different test temperatures (a) 25 °C, (b) 200 °C, (c) 400 °C, and (d) 600 °C (reproduced from [27]).

The experimental results illustrated in Figure 6.13 provide a comprehensive basis for evaluating the wear performance of the coatings as a function of Al_2O_3 concentration and operating temperature. The wear resistance of the coatings exhibited a clear dependence on both the Al_2O_3 content and the operating temperature. At room temperature, the unreinforced NiB coating (C0) suffered from the highest wear rate, highlighting its limited ability to withstand mechanical loading in the absence of particulate reinforcement. The addition of Al_2O_3 nanoparticles progressively reduced the wear rate, with the C3 composition of 10 g/L showing the most significant improvement. Moreover, the inclusion of Al_2O_3 nanoparticles enhances the coating's resistance to crack initiation and propagation. These particles act as barriers that impede the movement of dislocations and slow down the growth of microcracks, effectively increasing the coating's toughness and wear resistance. This crack-arresting mechanism is critical in minimizing the risk of severe coating failure under cyclic loading conditions, where repeated stress can otherwise lead to rapid crack growth and

material loss [80]. This suggests that a well-dispersed and optimally concentrated ceramic phase can effectively enhance the mechanical integrity of the matrix, even under mild sliding conditions. However, further increasing the particle content to 20 g/L (C4) led to a partial deterioration in wear resistance, most likely due to agglomeration-induced microstructural inhomogeneity. At higher concentration, excessive particle clustering disrupts the uniform distribution within the matrix, introducing microstructural defects that act as stress concentrators, thereby reducing the overall mechanical stability and increasing the likelihood of localized failure. Additionally, the formation of large agglomerates increases the surface roughness of the coating, leading to an uneven contact surface. This rougher surface is more likely to trap debris and promote three-body abrasive wear, further accelerating material loss. Furthermore, excessive Al_2O_3 loading can reduce the matrix's ability to effectively transfer and distribute mechanical loads, weakening the interfacial bonding between particles and the matrix. This weakened bonding increases the likelihood of particle pull-out during sliding, significantly reducing the overall wear resistance of the coating [106].

As the temperature increased to moderate and high levels, the differences between coatings became more pronounced. Particularly at 200 °C, the NiB matrix began to show signs of thermal softening, making it increasingly susceptible to deformation-driven wear. The C0 coating exhibited a noticeable rise in wear rate, indicating that the unreinforced amorphous structure lacked sufficient thermal robustness. In contrast, the composite coatings, especially C3, benefited from the inclusion of Al_2O_3 nanoparticles, which provided thermally stable reinforcement. The wear rate of C3 was nearly half that of C0, suggesting the activation of crack deflection and particle-assisted load-sharing mechanisms under elevated temperature. This indicates that 200 °C marks the onset of thermally activated degradation in the unreinforced NiB matrix, whereas particle-reinforced systems maintain integrity through structural reinforcement.

At 400 °C, the difference in performance between C3 and the other coatings became more pronounced. The C0 and C1 coatings exhibited a further increase in wear rate, likely due to matrix softening and potential spallation of surface oxides formed during sliding. While C2 maintained intermediate performance, the C3 coating continued to display excellent wear resistance, supported by the uniform dispersion of Al_2O_3

nanoparticles, which acted as crack-arresting sites and thermal stabilizers. Additionally, the formation of adherent tribo-oxide films on the worn surface may have contributed to this enhanced resistance. The wear stability of C3 at this temperature highlights the synergistic effect of optimized ceramic dispersion and oxide-assisted protection.

At the highest test temperature, 600 °C, thermal effects became the dominant factor shaping tribological behavior. The C0 coating showed the most severe wear, confirming the inability of the NiB matrix to withstand extreme thermal and mechanical stresses. Although C1 and C2 showed minor improvement, they remained inferior to C3, which continued to perform exceptionally well. The superior high-temperature behavior of C3 is attributed to the presence of thermally inert Al₂O₃ particles, which retained their reinforcing capability. The stabilization of the tribological interface by oxide layer formation likely played a role in reducing both direct contact and wear progression. The sustained low wear of C3 at 600 °C confirms its suitability for high-temperature applications, where structural integrity and thermal stability are essential.

Interestingly, the C4 coating, despite its higher ceramic content, failed to outperform C3 at any temperature. This is primarily due to nanoparticle agglomeration, which created microstructural inhomogeneities and interfacial voids acting as stress concentrators. Moreover, these agglomerates contributed to surface roughening and third-body abrasion by trapping debris within the contact zone. These results reinforce the importance of achieving an optimal particle concentration beyond which the benefits of reinforcement are undermined by dispersion instability and interfacial weakness.

6.4.3. Temperature-dependent surface and cross-sectional SEM analysis of NiB and NiB-Al₂O₃ nanocomposite coatings after wear testing

This section provides a comprehensive examination of the temperature-dependent wear behavior of electroless NiB and NiB-Al₂O₃ nanocomposite coatings through surface and cross-sectional SEM investigations. By analyzing worn surfaces and subsurface regions at 25 °C, 200 °C, 400 °C, and 600 °C, the aim is to elucidate how thermal exposure and mechanical loading jointly influence the evolution of wear mechanisms. These observations highlight the relationship between microstructural

stability and tribological performance, demonstrating the crucial role of reinforcement particles in enhancing resistance to degradation under elevated temperatures.

6.4.3.1. Wear behavior of electroless NiB coatings at different temperatures

In NiB coatings, a relatively low coefficient of friction was observed at all test temperatures, while the wear rate remained high. The low COF originates substantially from the formation of B-rich tribochemical films on the sliding surface, which reduce the interfacial shear stress against the counterface. Although these films are discontinuous and localized, they still provide a lubricating effect that lowers friction. On the other hand, the relatively low hardness and limited fracture toughness of NiB restrict its load-bearing capacity. As a result, subsurface microcracks, lateral cracks, and progressive delamination evolve under load, causing significant volumetric material loss. Thus, while the COF remains low, the WR is consistently high.

This mechanism is indirectly supported by the post-wear SEM observations in Figure 6.14, which reveal characteristic features associated with subsurface cracking and material loss. The surface morphology appears to retain its characteristic cauliflower-like texture at all temperatures, but this should not be mistaken as a sign of structural integrity. Due to the low hardness and limited fracture toughness, subsurface cracking initiates at an early stage, and the coalescence of these cracks results in delamination and the formation of unsupported voids beneath the surface. Consequently, even when the top-view SEM images suggest that the coating remains largely intact, cross-sectional examinations clearly reveal crack networks and partial material loss.

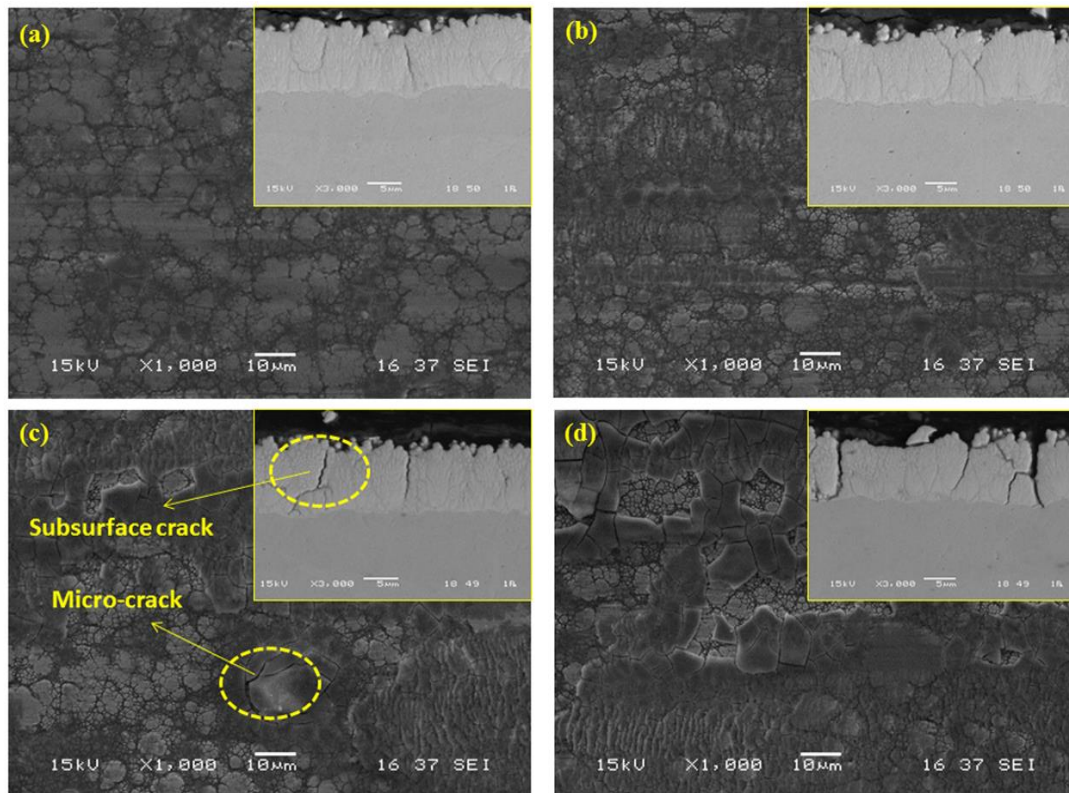


Figure 6.14. SEM images of the worn surfaces and cross-sections of NiB (C0) coatings after wear testing: (a) 25 °C, (b) 200 °C, (c) 400 °C, and (d) 600 °C. Insets show the corresponding cross-sectional views (reproduced from [27]).

At intermediate temperatures (e.g., 200 °C, Figure 6.14b), microcracking becomes more apparent, reflecting thermal softening and increased plastic deformation. With further temperature elevation (400 °C, Figure 6.14c), subsurface cracks extend and merge, while oxidation promotes the embrittlement of wear debris. This accelerates local delamination, although the cauliflower-like texture remains partially visible on the surface. At the highest test temperature (600 °C, Figure 6.14d), the wear mechanism transitions decisively to delamination. Subsurface cracks propagate toward the substrate and coalesce, resulting in large-scale spalling and severe loss of load-bearing capacity. Consequently, while the surface SEM images may suggest that the cauliflower morphology is partly preserved, cross-sectional analysis demonstrates that the load-bearing capacity of NiB coatings rapidly deteriorates under tribological stress, resulting in severe volumetric material loss.

6.4.3.2. Wear behavior of electroless NiB-Al₂O₃ coatings at room temperature

The SEM images of the NiB-Al₂O₃ coatings after room temperature wear testing are presented in Figure 6.15. The worn surface of the C1 sample (Figure 6.15a) exhibits severe delamination, characterized by large cracks and fragmented debris. This is likely due to the excessive strain hardening caused by the high Al₂O₃ content, which leads to localized stress accumulation. The brittle fracture and flake-like detachment indicate that the matrix could not effectively accommodate the strain, resulting in extensive surface damage. The C2 sample (Figure 6.15b) shows a more compact and slightly smoother wear track compared to C1, with fewer large cracks but still noticeable plastic deformation. Fine debris is scattered across the surface, suggesting ongoing surface fatigue and microcrack propagation. The reduced severity of surface damage compared to C1 indicates a better balance between hardness and toughness.

As clearly seen in Figure 6.15c, the surface of the C3 sample appears significantly smoother, with fewer cracks and minimal debris formation. The thin, uniform wear track suggests efficient load distribution and reduced plastic deformation. This indicates that the optimal Al₂O₃ content (10 g/L) provides effective reinforcement, minimizing severe wear and maintaining structural integrity under sliding conditions. The worn surface of the C4 sample reveals a rough, uneven texture with deep grooves and extensive surface cracking. Large particles have likely detached, leaving behind voids and exposed matrix regions. This reflects the negative effects of excessive Al₂O₃ concentration (20 g/L), where particle agglomeration leads to stress concentration and accelerated coating failure, as depicted in Figure 6.15d.

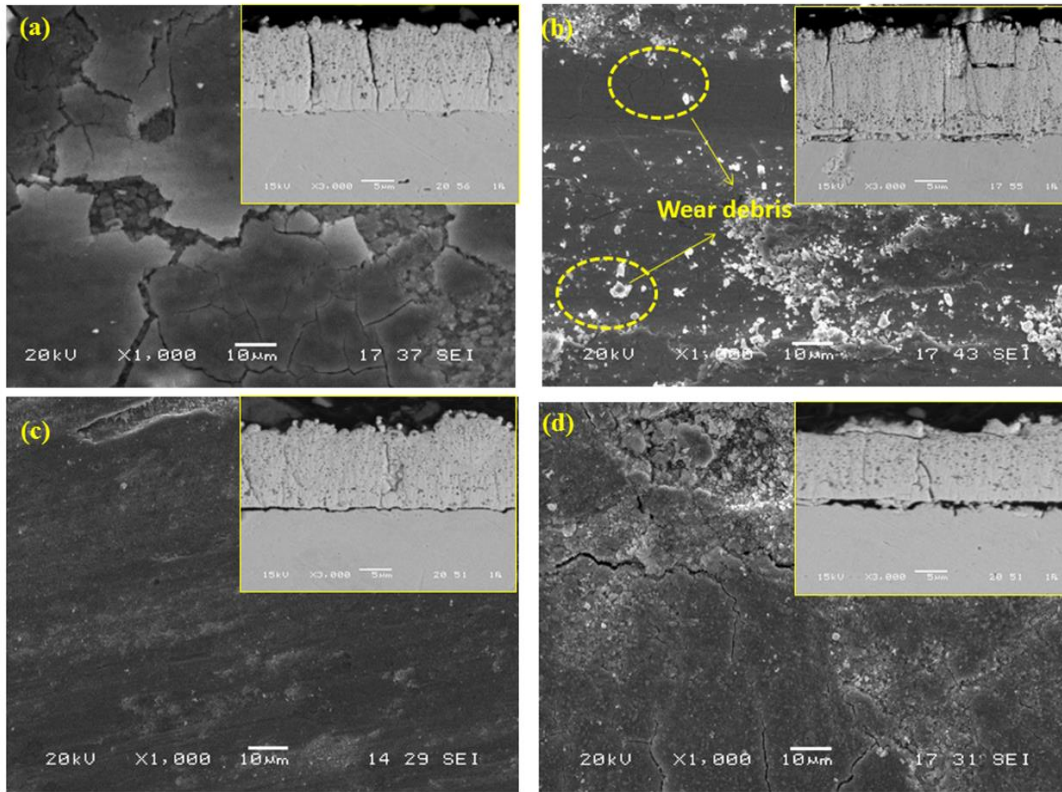


Figure 6.15. SEM images of the worn surfaces and cross-sections of NiB-Al₂O₃ coatings after wear testing at room temperature: (a) C1, (b) C2, (c) C3, and (d) C4. Insets show the corresponding cross-sectional views (reproduced from [27]).

After examining the surface morphologies, a closer inspection of the cross-sectional images provides further insight into the subsurface damage and structural integrity of the NiB-Al₂O₃ coatings under wear conditions. These cross-sectional observations reveal the extent of plastic deformation, microcrack propagation, and particle detachment, reflecting the varying reinforcement effects of Al₂O₃ at different concentrations. The cross-sectional image of the C1 sample shows a severely deformed surface layer with pronounced plastic deformation, indicative of significant strain hardening. The dense and compacted appearance suggests that the high contact stress during sliding caused localized grain flattening. Fine microcracks are also visible, indicating the onset of subsurface fatigue. The cross-sectional view of the C2 sample displays a comparatively smoother surface layer compared to C1. However, microcracks are still present, albeit less dense. The coating shows a more uniform structure with moderate plastic deformation, indicating that the wear mechanisms are less severe compared to C1. Small voids, likely due to Al₂O₃ particle detachment, are sporadically observed.

In the C3 sample, the cross-sectional image exhibits a relatively smooth and intact surface layer with minimal plastic deformation. This indicates enhanced load-bearing capacity, attributed to the optimal concentration of Al_2O_3 (10 g/L). The absence of severe cracking or particle detachment suggests that the reinforcement is well-distributed and effectively integrated into the NiB matrix, and maintaining coating cohesion during sliding. However, the cross-sectional image of the C4 sample shows an irregular surface with signs of coating delamination and localized fracture. The presence of large voids indicates that agglomerated Al_2O_3 particles have detached, leaving behind cavities that compromise the coating's integrity. This suggests that the excessively high concentration of Al_2O_3 (20 g/L) led to poor particle-matrix bonding and structural instability.

6.4.3.3. Wear behavior of electroless NiB- Al_2O_3 coatings at 200 °C

The worn surface of the C1 sample exhibits significant delamination and large, brittle cracks (Figure 6.16a). This indicates poor structural integrity, likely due to insufficient ceramic reinforcement. The low Al_2O_3 concentration provides limited load-bearing support, leading to excessive localized plastic deformation and rapid crack propagation. The fragmented debris scattered across the surface further suggests that the coating lacks sufficient hardness to resist abrasive wear. With a moderate increase in Al_2O_3 content, the C2 sample shows improved wear resistance, evidenced by fewer large cracks and a generally smoother wear track (Figure 6.16b). However, isolated regions still exhibit significant plastic deformation, indicating that the ceramic reinforcement is not yet sufficient to fully stabilize the matrix under sliding conditions. The presence of finer debris suggests reduced but ongoing microcracking and surface fatigue.

The C3 sample, containing the optimal Al_2O_3 concentration, exhibits the most uniform wear track, characterized by a thin, continuous surface layer with minimal cracking (Figure 6.16c). This indicates effective load distribution and reduced plastic flow, reflecting a well-balanced combination of hardness and toughness. The absence of large debris and the presence of only minor surface undulations confirm the superior wear resistance provided by the optimal Al_2O_3 reinforcement. At the highest Al_2O_3 concentration, the C4 sample shows a rough, uneven wear track with extensive surface cracking (Figure 6.16d). The deep grooves and fractured regions indicate that excessive ceramic content has led to particle agglomeration, reducing the coating's

structural coherence. This agglomeration not only weakens the matrix-particle interface but also promotes brittle fracture and localized stress concentration, significantly compromising the wear performance. These morphological observations are clearly illustrated in Figure 6.16, which presents SEM images of the worn surfaces and corresponding cross-sections for each NiB-Al₂O₃ coating tested at 200 °C.

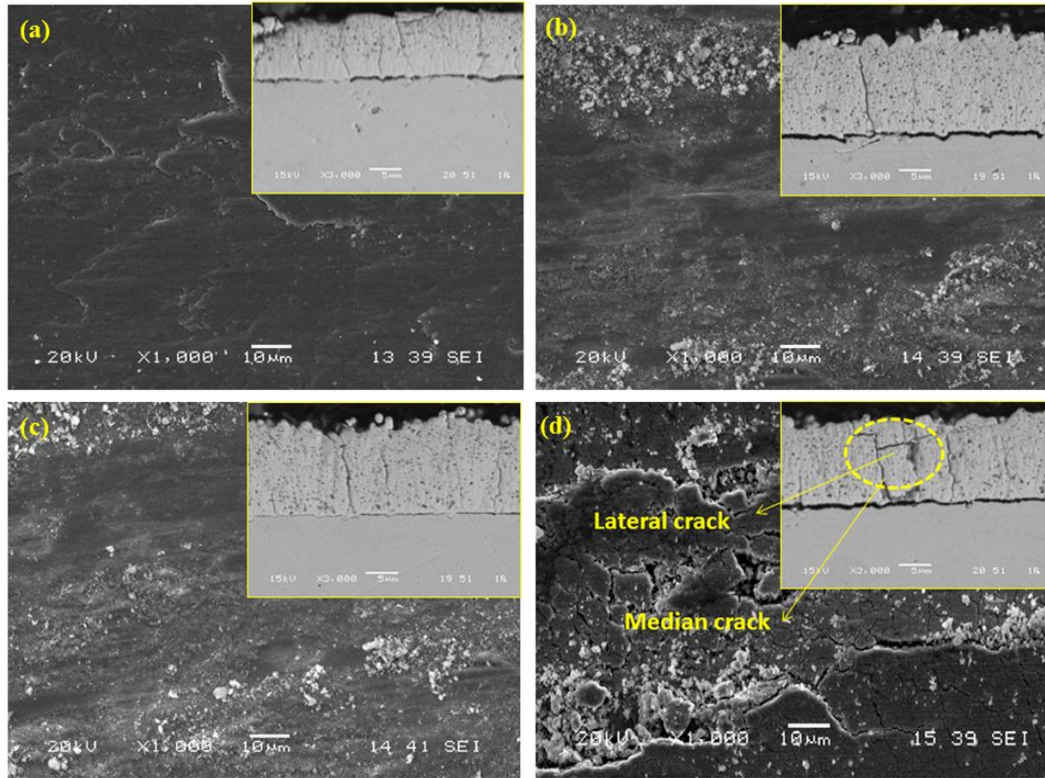


Figure 6.16. SEM images of the worn surfaces and cross-sections of NiB-Al₂O₃ coatings after wear testing at 200 °C: (a) C1, (b) C2, (c) C3, and (d) C4. Insets show the corresponding cross-sectional views (reproduced from [27]).

The cross-sectional view of the C1 sample reveals a relatively thin coating layer with a clearly defined but irregular interface between the coating and the substrate. The lack of significant Al₂O₃ reinforcement results in a less compact microstructure, characterized by voids and microcracks extending into the bulk of the coating. This weak interfacial bonding suggests that the matrix lacks sufficient support, making it prone to rapid delamination and crack propagation under mechanical stress. The C2 sample displays a thicker and more uniformly adhered coating compared to C1, with fewer internal voids. The incorporation of a moderate Al₂O₃ content improves the mechanical interlocking at the coating-substrate interface, enhancing the overall structural integrity. However, the microstructure still exhibits localized microcracking, indicating that the matrix reinforcement remains incomplete, potentially leading to

gradual subsurface crack growth during sliding. In the cross-sectional view of the C3 sample, the coating appears dense and well-bonded to the substrate, with a more refined and compact microstructure. The Al_2O_3 particles are well distributed, acting as effective load-bearing elements that reduce localized plastic deformation. The absence of significant voids or internal cracks highlights the optimal dispersion and phase compatibility at this concentration, which collectively enhance the coating's resistance to subsurface damage. The cross-section of the C4 sample reveals a thicker but more porous coating, with visible agglomerates disrupting the continuity of the structure. This excessive Al_2O_3 loading results in weak particle-matrix bonding and a more brittle overall structure, as evidenced by the presence of microvoids and interfacial gaps. These defects can serve as initiation sites for crack propagation, reducing the coating's durability under repeated loading.

6.4.3.4. Wear behavior of electroless NiB- Al_2O_3 coatings at 400 °C

The morphological changes observed on the worn surfaces and cross-sections of the electroless NiB- Al_2O_3 coatings after wear testing at 400 °C are systematically illustrated in Figure 6.17 and are discussed in detail below for each Al_2O_3 concentration. The worn surface of the C1 sample (Figure 6.17a), with the lowest Al_2O_3 concentration, exhibits severe surface damage characterized by deep grooves, widespread cracks, and extensive plastic deformation. The limited reinforcement effect from the low Al_2O_3 content results in reduced load-bearing capacity, making the coating more prone to localized plastic deformation. The high testing temperature accelerates oxide formation, further weakening the surface. The fragmented debris and crack propagation indicate a brittle failure mode, suggesting poor high-temperature mechanical stability. With a slightly higher Al_2O_3 concentration, the C2 sample (Figure 6.17b) shows reduced but still significant surface damage. The wear track appears less severe than in C1, with fewer wide cracks and a somewhat more uniform wear pattern. However, localized plastic deformation is still evident, indicating that the Al_2O_3 content at this level is insufficient to fully stabilize the matrix against high-temperature wear. Fine debris and microcrack networks are present, reflecting partial improvement in wear resistance but ongoing subsurface fracture.

The C3 sample, as clearly depicted in Figure 6.16c, demonstrates the most balanced wear behavior. The wear track is noticeably smoother, with minimal surface cracking and reduced debris formation. The homogeneous distribution of Al_2O_3 particles

effectively reinforces the matrix, enhancing load-bearing capacity and reducing localized plastic deformation. This combination leads to a more stable surface structure under elevated temperatures, indicating a significant improvement in wear resistance. The C4 sample (Figure 6.17d) containing the highest Al_2O_3 concentration, suffers from particle agglomeration, which undermines the coating's structural integrity. This results in pronounced surface damage, including deep cracks, severe fragmentation, and extensive delamination. The excessive Al_2O_3 content creates stress concentrations and weak particle-matrix interfaces, leading to early-stage degradation. The coating appears brittle, with clear evidence of mechanical instability under thermal and mechanical stress.

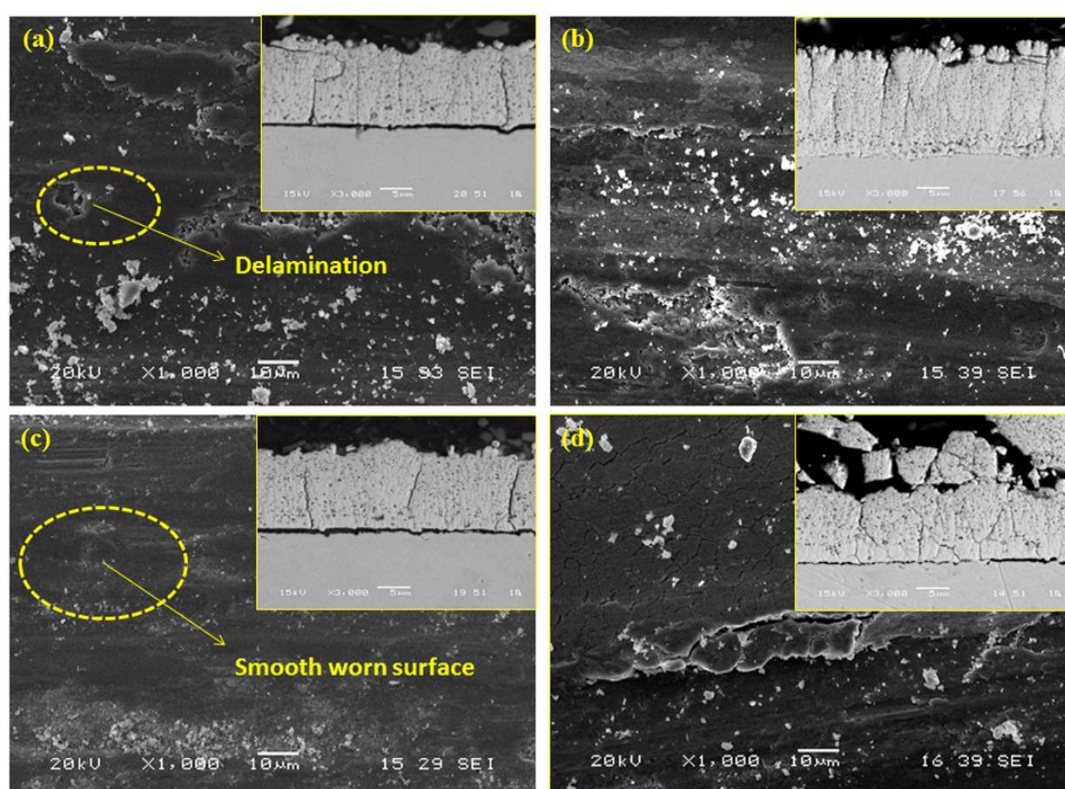


Figure 6.17. SEM images of the worn surfaces and cross-sections of $\text{NiB-Al}_2\text{O}_3$ coatings after wear testing at 400 °C: (a) C1, (b) C2, (c) C3, and (d) C4. Insets show the corresponding cross-sectional views (reproduced from [27]).

The cross-sectional view of the C1 sample reveals significant subsurface damage, including extensive plastic deformation and crack propagation reaching deep into the coating layer. The limited reinforcement effect of the low Al_2O_3 content results in poor load distribution, leading to pronounced microstructural disruption. The high temperature accelerates matrix softening, reducing the overall structural stability. The coating exhibits clear signs of delamination, with uneven interfaces and fragmented

regions, indicating a brittle fracture mode. The C2 sample shows a more compact but still mechanically unstable cross-section compared to C1. The coating displays fewer large cracks but still suffers from localized plastic deformation. The Al_2O_3 particles, while more abundant than in C1, are not uniformly distributed, leading to stress concentrations and microcrack formation at particle-matrix interfaces. This results in partial detachment of the coating from the substrate, suggesting that the reinforcement effect is still insufficient to fully stabilize the microstructure under high-temperature wear.

The cross-sectional image of the C3 sample reveals a well-preserved microstructure with minimal internal cracking and a more uniform particle distribution. The optimal Al_2O_3 concentration effectively reinforces the matrix, enhancing the load-bearing capacity and reducing the extent of plastic deformation. The coating-substrate interface remains intact, with no significant signs of delamination. This indicates that the 10 g/L Al_2O_3 concentration provides the best balance between hardness and toughness, reducing subsurface damage under severe wear conditions. In the C4 sample, excessive Al_2O_3 content leads to agglomeration and poor interfacial bonding, resulting in severe internal damage. The cross-sectional view shows widespread microcracking, particle pull-out, and void formation, reflecting the negative impact of particle clustering. The lack of uniform particle distribution compromises the structural integrity, leading to rapid crack propagation and extensive delamination. This highlights the detrimental effect of excessive ceramic content on the mechanical stability of the coating.

6.4.3.5. Wear behavior of electroless NiB- Al_2O_3 coatings at 600 °C

The SEM image (Figure 6.18) shows a rough and extensively fractured surface with widespread delamination. The formation of deep grooves and fragmented debris suggests severe mechanical degradation. This indicates that the coating could not withstand the combined effects of thermal softening and mechanical stress, leading to substantial surface damage. The brittle nature of the NiB matrix at this temperature, combined with weak particle-matrix adhesion, likely contributed to rapid crack propagation and localized material removal. Compared to C1 (6.18a), the C2 (6.18b) sample exhibits a more compact surface with slightly reduced crack density. However, significant debris and microcracks are still visible, indicating ongoing brittle fracture. The improved load distribution provided by the Al_2O_3 particles likely mitigated the

severity of wear to some extent, but the overall wear resistance remains limited due to reduced matrix toughness at elevated temperatures.

In the C3 sample (6.18c), the worn surface exhibits noticeable signs of plastic flow, indicating localized softening and ductile deformation under elevated thermal and mechanical stress. This flow-like morphology suggests that the optimized Al₂O₃ content provided sufficient reinforcement to delay fracture, although it could not entirely prevent surface instability at 600 °C. The observed degradation at this temperature stems from the effects of thermal softening, third-body abrasion, and material transfer dynamics, all of which intensify beyond the temperature of 400 °C. Among these, the thermal expansion mismatch between the NiB matrix and Al₂O₃ reinforcement plays a critical role. Although such mismatch exists at all temperatures, its adverse effects become particularly pronounced during thermal cycling at 600 °C. With typical thermal expansion coefficients of approximately $13\text{--}15 \times 10^{-6} \text{ K}^{-1}$ for Ni-based alloys and $\sim 8 \times 10^{-6} \text{ K}^{-1}$ for Al₂O₃, localized interfacial stresses are generated, which are further accentuated under high-temperature sliding conditions. These stresses can initiate microcrack formation and promote decohesion around the Al₂O₃ particles. As a result, the structural continuity of the tribofilm is compromised, leading to its fragmentation and the entrainment of third-body debris, as clearly observed at 600 °C.

However, the C4 sample (6.18d) shows a complex mixture of severe cracking and fragmented debris, along with significant surface roughness. The high Al₂O₃ concentration likely caused particle agglomeration, reducing matrix-particle adhesion and leading to brittle fracture under thermal and mechanical stress. This region also displays deep grooves and crack branching, indicating a failure to effectively distribute the applied load.

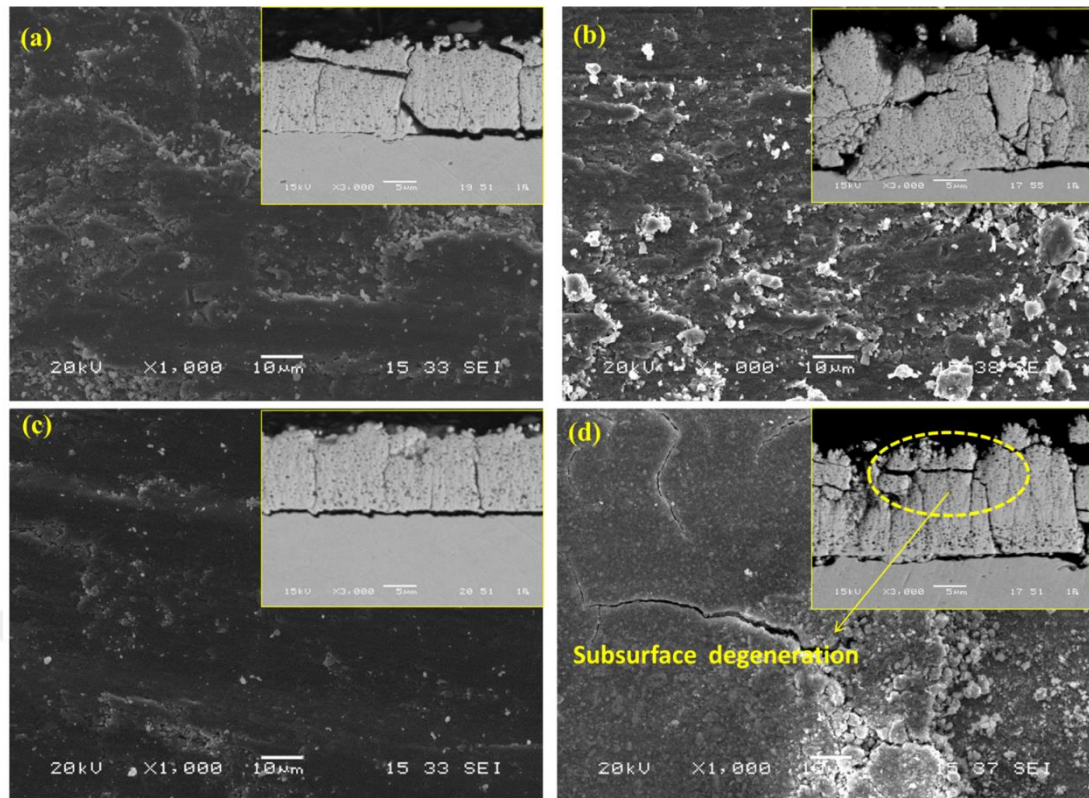


Figure 6.18. SEM images of the worn surfaces and cross-sections of NiB-Al₂O₃ coatings after wear testing at 600 °C: (a) C1, (b) C2, (c) C3, and (d) C4. Insets show the corresponding cross-sectional views (reproduced from [27]).

As seen in Figure 6. 18a, the cross-sectional view reveals that the coating has largely lost its structural integrity. Cracks and detachments are evident in the upper region, while voids and discontinuities are visible across the layer. The low reinforcement content was insufficient to provide thermal and mechanical stability at 600 °C, resulting in pronounced brittleness and degradation. In Figure 6.18b, the cross-sectional morphology of the C2 coating after wear at 600 °C is presented. Compared with C1, the coating exhibits a more compact structure, though surface spallation and irregular morphology remain apparent. The increased Al₂O₃ content reduces crack density to some extent. However, embrittlement of the NiB matrix combined with oxidation-induced weakening still leads to partial breakdown of the coating. In Figure 6.18c, the cross-sectional morphology of the C3 coating after wear at 600 °C is shown. The cross-sectional morphology demonstrates the most stable structure among the coatings. The coating layer remains relatively uniform, and the interface with the substrate is preserved. Surface degradation is limited, and the homogeneous microstructure indicates that the optimal Al₂O₃ content improves load-bearing capability, crack deflection, and oxide layer stabilization, thus enhancing high-

temperature wear resistance. In Figure 6.18d, the cross-sectional view of the C4 coating after wear at 600 °C is illustrated. A pronounced subsurface degeneration zone is evident beneath the worn surface. Excessive Al₂O₃ addition leads to particle agglomeration and weak matrix-particle interfaces, which act as stress concentration sites. These defects promote crack initiation and rapid propagation, causing severe internal damage and large-scale spalling. Consequently, C4 exhibits the poorest structural integrity and the weakest performance at 600 °C.

6.5. Summary of Temperature-Dependent Wear Mechanisms

The comprehensive evaluation of the nanomechanical and tribological behaviors of electroless NiB and NiB-Al₂O₃ nanocomposite coatings reveals a strong interdependence between mechanical reinforcement, thermal stability, and wear resistance. In terms of mechanical characterization, the unreinforced NiB coating exhibited the lowest hardness, elastic modulus, and indicating limited load-bearing capability and a high susceptibility to plastic deformation under contact loading. Although post-deposition heat treatment improved these properties through the formation of Ni₃B and Ni₂B phases, the mechanical performance of pure NiB remained inferior to that of the Al₂O₃-reinforced composites.

The addition of Al₂O₃ nanoparticles into the NiB matrix markedly improved the mechanical behavior up to a critical threshold of 10 g/L (C3 sample). This composition exhibited the highest hardness, and elastic strain resistance due to synergistic mechanisms such as dislocation pinning, effective load sharing, and structural refinement. However, increasing the particle concentration beyond this level (C4 with 20 g/L) led to agglomeration and interfacial weaknesses, which acted as stress concentrators and degraded mechanical integrity. These findings clearly establish the presence of an optimal reinforcement level, beyond which the beneficial effects are counteracted by dispersion instability.

The evolution of tribological performance was found to be intrinsically governed by the underlying nanomechanical characteristics, wherein hardness, and plastic strain resistance collectively dictated the coating's ability to withstand frictional and thermal stresses during sliding. Despite displaying low coefficients of friction, the NiB coating suffered from high wear rates due to its poor structural integrity and inability to sustain mechanical loading, especially under elevated temperatures. In contrast, while the C3

coating exhibited higher COF values than pure NiB, it nevertheless maintained a generally stable friction profile across all test temperatures. Its balanced reinforcement facilitated the formation of a protective third-body tribolayer at the sliding interface, suppressed crack propagation, and enhanced thermal reliability. These effects account for the stable frictional response and significantly reduced wear rates observed across the temperature range, reflecting a more robust tribo-mechanical interface and effective load distribution during sliding.

The tribological stability of the C3 coating was particularly evident up to 400 °C, suggesting that its microstructural integrity remained intact under elevated thermal stress. Uniform nanoparticle dispersion and strong matrix-particle interfaces contributed to a homogeneous contact zone, preventing premature material failure. However, at 600 °C, signs of degradation emerged: plastic flow features, increased surface roughness, and third-body debris circulation became dominant. These transitions marked the onset of thermal softening and localized stress accumulation, signaling a breakdown in the tribo-mechanical interface. Thus, 400 °C can be identified as the thermal reliability threshold for the optimized C3 coating under a 3 N load. Beyond this temperature, the coating begins to lose its structural coherence and wear resistance. Table 6.7 provides a concise summary of the observed surface features and dominant wear mechanisms across all tested temperatures, offering clear insight into how tribological performance evolves with increasing thermal load.

Table 6.7. Temperature-dependent surface state and wear mechanism of the C3 coating.

T (°C)	Surface Morphology	Wear Features	Dominant Mechanism
25	Smooth and continuous wear track, minimal cracks and debris	Uniform surface, limited deformation, no significant transfer film	Mild adhesive interaction, no third-body effect
200	Slightly more defined wear track, fine surface debris	Thin tribolayer likely formed, moderate surface fatigue, localized microcracks	Adhesive wear with minor transfer film formation
400	Stable wear track, homogeneous morphology	Homogeneous particle distribution, enhanced load-bearing	Thermally stable wear regime with suppressed plastic deformation
600	Flow-like morphology, surface roughness and deformation visible	Plastic flow, debris circulation	Mixed mechanism: thermal softening + third-body interaction onset

The findings presented in this chapter clearly establish C3 as the optimal coating composition, achieving the best balance between mechanical strength and tribological

durability. Its ability to maintain stability up to 400 °C under dry sliding conditions makes it a promising candidate for high-temperature tribological applications. Therefore, all subsequent in-depth microstructural and spectroscopic analyses in this study focus exclusively on the C3 sample, serving as a representative model for understanding the wear mechanisms and performance limits of electroless NiB-Al₂O₃ coatings.

6.6. Surface Roughness Evaluation of Worn Tracks Under Varying Temperatures

The evolution of surface roughness across the worn tracks of the optimized NiB-Al₂O₃ composite coating (C3) was systematically investigated at four different temperatures: 25 °C, 200 °C, 400 °C, and 600 °C. The roughness parameters were extracted exclusively from the contact zone, excluding the pile-up regions to better reflect the actual worn surface. While the line profiles presented in Figure 6.19 provide valuable insight into the topographical morphology, it should be noted that stylus profilometry inherently involves disproportionate vertical-to-horizontal magnification, which may visually exaggerate the steepness of surface features. However, this optical effect does not diminish the tribological significance of the peripheral pile-up formations. These elevated edge zones are consistently observed across repeated measurements and are interpreted as genuine outcomes of plastic flow and material displacement during sliding. Therefore, while quantitative roughness metrics (Ra, Rq, Rz, and Rt) were calculated solely from the central contact zone to ensure accuracy and comparability, the presence of peripheral pile-ups remains an important morphological indicator of displacement-dominated wear behavior in composite coatings such as NiB-Al₂O₃. The numerical results are summarized in Table 6.8, and the corresponding line profiles are shown in Figure 6.19.

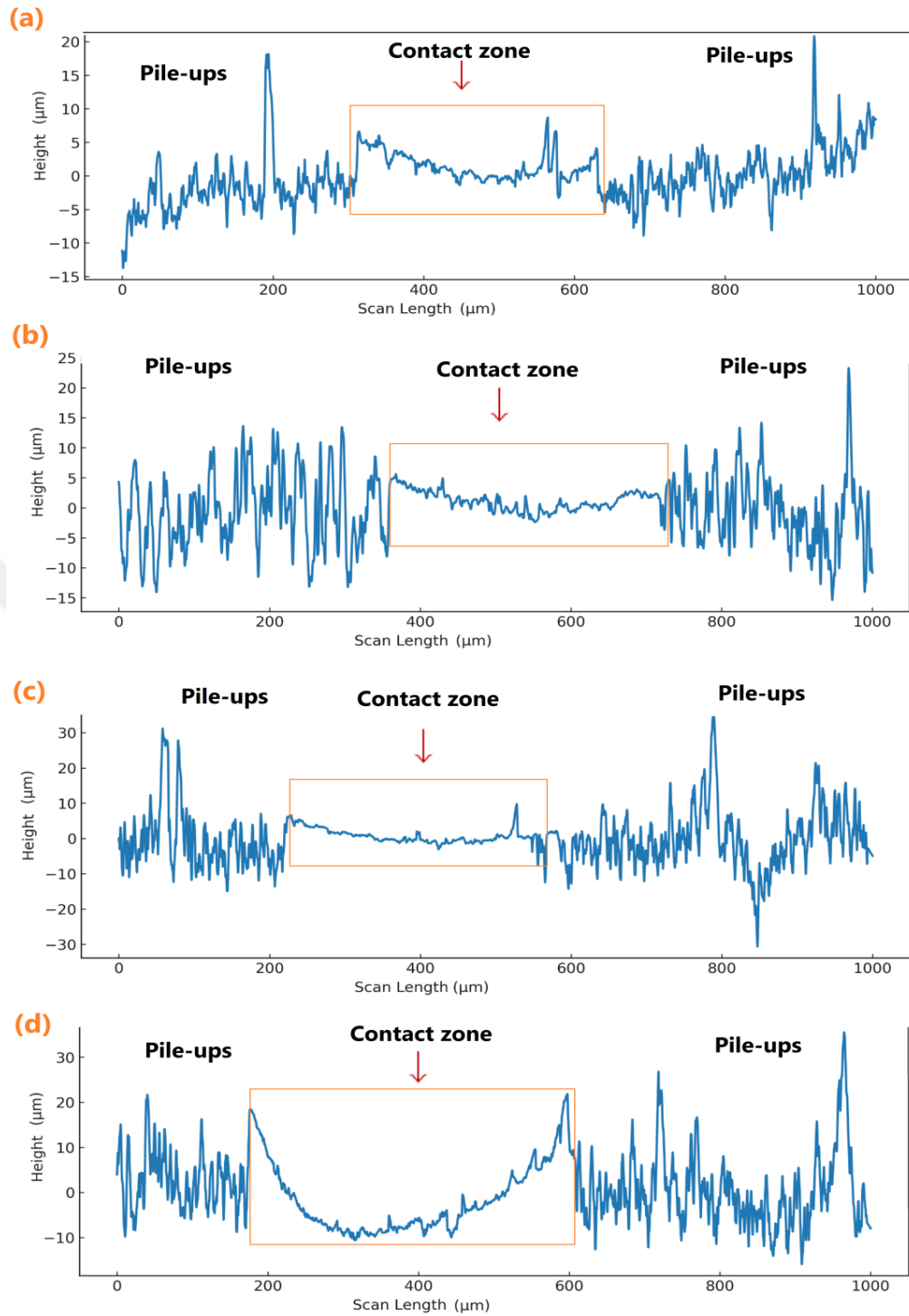


Figure 6.19. Temperature-dependent line profiles across the worn tracks of the NiB- Al_2O_3 coating (C3), (a) 25 °C, (b) 200 °C, (c) 400 °C, and (d) 600 °C. Profiles were Gaussian-filtered (ISO 16610) with cut-off (λ_c) = 0.8 mm. Edge zones showing pile-up were excluded from roughness metrics; the full profiles are shown for completeness.

Table 6.8. Surface roughness parameters of wear track core regions at different temperatures.

Temperature	Ra (μm)	Rq (μm)	Rz (μm)	Rt (μm)
25 °C	1.026	1.128	7.531	9.179
200 °C	1.152	1.350	6.206	8.002
400 °C	1.104	1.304	5.806	9.048
600 °C	3.989	4.627	13.681	19.288

At room temperature, the worn track exhibits a relatively smooth and shallow wear morphology, with a moderate Ra of 1.026 μm . The wear mechanism at this stage is largely governed by plastic ploughing and mild third-body effects due to the embedded Al_2O_3 nanoparticles. The pile-up formations on either side of the contact zone, as seen in the line profile, suggest a displacement-dominated wear regime where material is redistributed laterally rather than removed.

Upon increasing the temperature to 200 °C, only a slight increase in Ra and Rq is observed, indicating limited thermal softening of the matrix. The reduced Rz compared to room temperature may be attributed to the smoother track floor formed under enhanced plasticity, coupled with possible initiation of tribo-oxidation products acting as lubricating phases.

Interestingly, at 400 °C, both Ra and Rq remain similar to those at 200 °C, while Rz and Rt slightly decline. This behavior implies a smoother but more compact worn surface, likely stabilized by the formation of a continuous tribo-oxide layer and increased third-body interactions. The observed morphology suggests effective stress dissipation across the contact zone, with Al_2O_3 particles contributing to load bearing and crack deflection. At this temperature, the C3 coating maintains structural integrity and resists severe surface disruption. However, a significant shift occurs at 600 °C, where all roughness metrics exhibit a dramatic rise, particularly Ra and Rt, indicating the onset of more aggressive wear. The profile reveals a pronounced bowl-shaped wear scar with large vertical variations and deeper material removal. The sharp increase in Rz and Rt reflects the dominance of removal-dominated mechanisms, likely triggered by matrix softening, oxide layer spallation, and possible fatigue cracking under high thermal stress. The formerly beneficial role of Al_2O_3 is diminished as embedded particles become detached and participate in abrasive interactions, further increasing the surface damage.

In summary, the NiB- Al_2O_3 composite coating demonstrates thermally robust wear resistance up to 400 °C, maintaining relatively low and stable roughness values due to

efficient load support by hard ceramic reinforcements and formation of protective tribofilms. The transition to 600 °C, however, marks a critical degradation point where the protective mechanisms are no longer sufficient, resulting in elevated surface roughness and a transition from displacement-dominated to removal-dominated wear behavior. This temperature-dependent transition in wear behavior is schematically illustrated in Figure 6.20, which compares the characteristic surface topographies associated with displacement- and removal-dominated wear regimes.

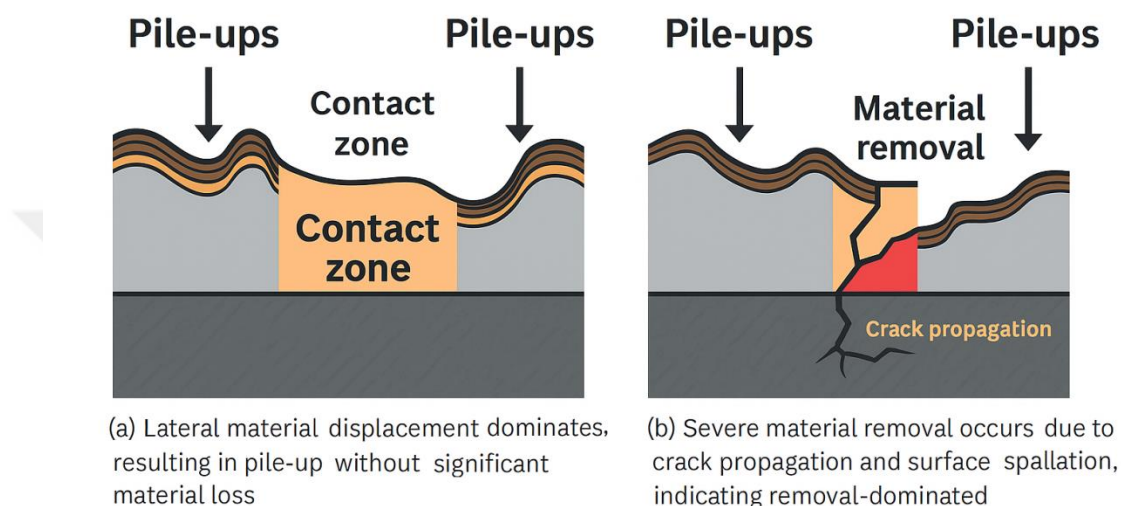


Figure 6.20. Schematic comparison of (a) displacement-dominated, and (b) removal-dominated wear mechanisms illustrating pile-up formation, material removal, and subsurface cracking.

6.7. Temperature-Dependent Raman Spectroscopic Analysis of Worn Surfaces

Raman spectroscopy was employed as a complementary characterization technique to provide deeper insight into the chemical and structural evolution of the coatings after sliding. Raman spectra were acquired from the worn regions of the C3 sample after sliding tests conducted at room temperature, 200 °C, 400 °C, and 600 °C, to provide detailed insight into its tribochemical stability under varying thermal conditions. The analysis revealed the presence of key tribo-induced phases, including NiO, Al₂O₃ particles, and boron-based compounds such as boric acid (B(OH)₃), and B₂O₃ which are typically formed under high contact stress and frictional heating.

6.7.1. Raman analysis of aluminum oxide phases on worn surfaces

Figure 6.21 presents the Raman spectra obtained from the worn surfaces of the C3 coating after tribological testing at different temperatures. Characteristic bands observed near 580, 660, and 790 cm⁻¹ are attributed to the vibrational modes of γ -

Al_2O_3 , consistent with previous reports [145–147]. The more pronounced features at approximately 1390 cm^{-1} and 1585 cm^{-1} are primarily assigned to second-order or combination modes of $\gamma\text{-Al}_2\text{O}_3$ [148]. At $600\text{ }^\circ\text{C}$, the formation of vitreous B_2O_3 may contribute a minor B-O-B overlap near 1390 cm^{-1} ; however, the dominant assignment remains associated with second-order $\gamma\text{-Al}_2\text{O}_3$ scattering. In addition to these peaks, a weak shoulder is also detected around 1800 cm^{-1} , corresponding to high-order combination scattering of $\gamma\text{-Al}_2\text{O}_3$ rather than a distinct fundamental vibration.

This temperature-sensitive behavior arises from the combined effects of thermal and mechanical interactions during sliding. Elevated-temperature wear accelerates the mechanical fragmentation of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles embedded in the NiB matrix, generating smaller fragments with higher surface area and enhanced light-scattering efficiency. Simultaneously, the softening of the NiB matrix facilitates the extrusion and redistribution of alumina particles along the wear track. The increased surface exposure and redistribution of Al_2O_3 particles lead to stronger Raman activity and more pronounced oxide-related features at high temperatures. Overall, the synergistic effects of nanoparticle fragmentation, matrix softening, and temperature-assisted particle redistribution provide a consistent explanation for the intensified $\gamma\text{-Al}_2\text{O}_3$ response observed at elevated test temperatures.

From a tribological perspective, the increased exposure of $\gamma\text{-Al}_2\text{O}_3$ particles at elevated temperatures exerts a dual influence on the sliding interface. When these particles are homogeneously distributed and remain securely embedded within the NiB matrix, they function as load-bearing reinforcements and micro-scale rolling elements. In this state, they reduce direct metal-to-metal contact and limit plastic deformation, thereby contributing to lower wear rates. Conversely, at higher temperatures, excessive accumulation or detachment of Al_2O_3 particles may lead to the formation of loosely bound third-body debris. In such cases, the particles act as abrasive agents that plough through the surface, enhancing friction and promoting wear. Therefore, the intensified $\gamma\text{-Al}_2\text{O}_3$ signals observed in the Raman spectra reflect a higher surface availability of reinforcement particles; however, their ultimate effect on tribological performance depends on their spatial distribution and mechanical integration within the contact interface.

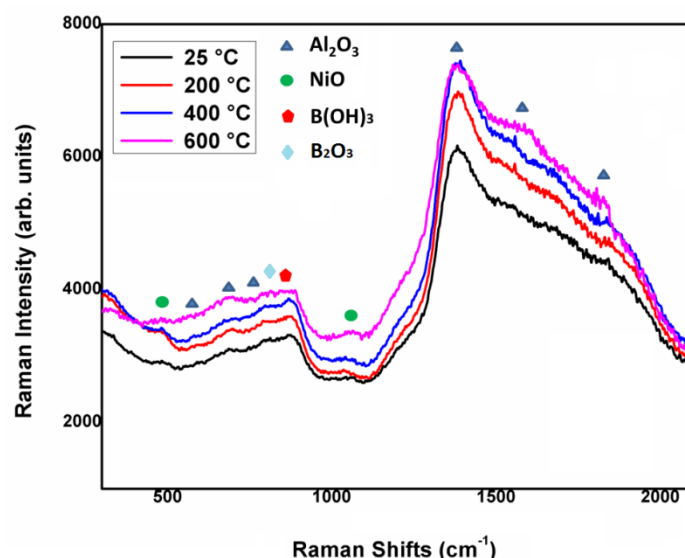


Figure 6.21. Temperature dependent Raman spectra of electroless C3 coating (reproduced from [27]).

6.7.2. Raman analysis of NiO on worn surfaces

In addition to the Al_2O_3 peaks, two characteristic Raman features of nickel oxide (NiO) were identified, with the one-phonon (1P) mode appearing at approximately 480 cm^{-1} and the two-phonon (2P) mode near 1050 cm^{-1} . These positions are consistent with previously reported NiO Raman bands [143,149]. From $25\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$, the 1P peak intensity shows a slight increase while the full width at half maximum (FWHM) remains nearly constant, suggesting the presence of a limited amount of NiO at the surface, with mild oxidation or tribo-oxidation occurring as temperature rises. Between $200\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$, both the intensity and sharpness of the 1P peak increase more noticeably, indicating the formation of a more crystalline and continuous NiO layer. At this stage, a stable and adherent oxide film can act as a protective barrier, reducing direct metal-to-metal contact and potentially improving tribological performance. However, when the temperature increases to $600\text{ }^\circ\text{C}$, the 1P peak reaches its highest intensity but loses some sharpness, implying that while NiO content continues to increase, higher temperatures introduce lattice strain, defect formation, or partial amorphization, which reduce long-range crystalline order. This observation aligns well with previous reports describing oxide fragmentation and deterioration of structural integrity at elevated temperatures [143].

The 2P band exhibits a similar temperature-dependent behaviour, with intensity increasing up to $400\text{ }^\circ\text{C}$ and showing slight broadening at $600\text{ }^\circ\text{C}$. As the 2P band is a second-order overtone of the 1P mode, its enhancement reflects reduced defect density

and longer phonon lifetimes within the crystalline regions of NiO. The concurrent evolution of both 1P and 2P bands indicates that NiO formation is promoted and structurally stabilized up to approximately 400 °C, but undergoes partial loss of crystalline order and increased defect accumulation at higher temperatures. At 400 °C, the oxide layer remains dense and adherent, effectively reducing metal-to-metal contact and enhancing tribological performance. Beyond this threshold, the instability and fragmentation of the oxide layer reduce its protective effect, accelerating surface degradation and leading to a noticeable decline in tribological performance at elevated temperatures.

6.7.3. Raman analysis of boron-based tribofilms on worn surfaces

The Raman spectrum provides clear evidence for the presence of boric acid, $B(OH)_3$, as indicated by the distinct peak observed around 880 cm^{-1} , as shown in Figure 6.21. A similar Raman feature near 880 cm^{-1} was reported by Yamauchi et al., supporting the assignment of this band to the vibrational modes of $B(OH)_3$ [150]. This attribution is further supported by Gilson et al., who identified a corresponding $B(OH)_3$ signal during vapor-phase spectroscopic studies [151]. Boric acid possesses a triclinic layered crystal structure, where the atomic layers are aligned parallel to the basal plane. The structure of boric acid is composed of layers where B, O, and H atoms are strongly bound by covalent bonds within each layer, while the layers are held together only by weak van der Waals forces. The interlayer spacing is approximately 0.318 nm. The layered arrangement of boric acid is illustrated in Figure 6.22.

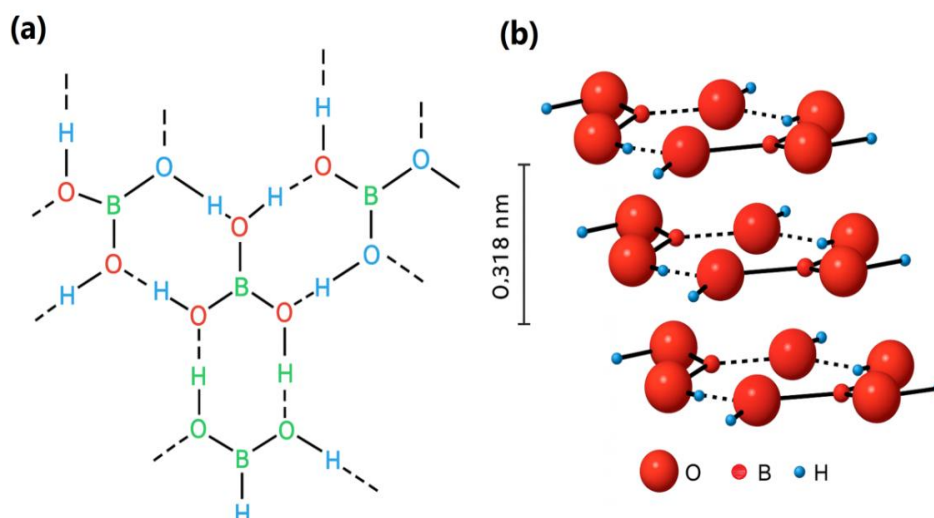


Figure 6.22. The chemical structure of boric acid ($B(OH)_3$). (a) Two-dimensional representation showing covalent B-O bonds and intermolecular hydrogen bonding between adjacent molecules. (b) Three-dimensional layered structure of boric acid (adapted from Larsson et al. [150], based on structural descriptions in Erdemir et al. [152]).

There are many studies in the literature that report the contribution of boric acid to tribological properties [152–154]. According to Zapol et al. [155], the intralayer bonds are nearly three times stronger than the weak van der Waals forces that hold the layers together. Because the interlayer bonding is very weak, the layers can undergo easy shear along the planes, which contributes to their lubricating behavior. Dvorak et al. [154] carried out in situ Raman analyses while testing boric acid coatings under reciprocating sliding against a sapphire counterface. Their results showed that the friction levels stayed low as long as boric acid was present within the contact zone. Sawyer et al. [156] also reported that the continuous addition of boric acid powder to stainless-steel surfaces under dry sliding conditions results in a noticeable reduction in friction. These findings highlight the well-established lubricating role of boric acid in reducing friction. However, while most of the studies in the literature are confined to tribological tests conducted at room temperature, our study addresses this limitation by systematically examining the effect of boron-based tribofilms on wear properties under varying temperature conditions.

A comprehensive evaluation of the lubricating function of boric acid therefore requires an examination of how it behaves under varying thermal conditions. This thermal evolution can be tracked through a sequence of dehydration reactions and corresponding structural transformations. At room temperature and under humid

atmospheric conditions, the B(OH)_3 phase is primarily formed on the surface. With increasing temperature, this phase undergoes stepwise dehydration, first forming metaboric acid (HBO_2) and subsequently tetraboric acid ($\text{H}_2\text{B}_4\text{O}_7$) [150]. These intermediate hydrated oxide phases are generally regarded as transient rather than stable phases. Therefore, it is often difficult to detect them as distinct peaks in Raman analyses. As the temperature increases further, these transient phases gradually disappear, and by around 600 °C the dehydration process is completed, with anhydrous B_2O_3 emerging as the dominant phase. This is confirmed by the appearance of the B_2O_3 peak at $\sim 808\text{ cm}^{-1}$ band observed at 600 °C, as seen in Figure 6.21 [153]. The stepwise dehydration reactions of B(OH)_3 upon heating are given in the Table 6.9.

Table 6.9. Thermal dehydration reactions of boric acid (B(OH)_3) [150–152].

Step	Reaction	Description
1	$\text{B(OH)}_3 \xrightarrow{\Delta} \text{HBO}_2 + \text{H}_2\text{O}$	Initial dehydration, formation of metaboric acid (HBO_2)
2	$4\text{HBO}_2 \xrightarrow{\Delta} \text{H}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$	Condensation of metaboric acid into tetraboric acid
3	$\text{H}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} 2\text{B}_2\text{O}_3 + \text{H}_2\text{O}$	Final step, yielding boron trioxide (B_2O_3)

As a result of these dehydration reactions, the final B_2O_3 product exhibits a vitreous glass-like network composed of interconnected boroxol rings. To better understand how this structural configuration affects its mechanical and tribological behavior, a schematic representation of the B_2O_3 network is shown in Figure 6.23. The boroxol rings (2), which are composed of B-O units, represent the fundamental motifs of the vitreous B_2O_3 structure. These rings are continuously connected to each other through B-O-B bridges, giving rise to a three-dimensional network. This configuration is fundamentally different from layered and easily sheared structures of boric acid (B(OH)_3). In B_2O_3 , there are no weakly bonded planes that could facilitate interlayer sliding; instead, the entire structure is strongly interconnected. Although the B-O-B bond angles (1) possess a certain degree of flexibility (capable of vibration, bending, or stretching), they do not create effective slip planes within the network. [153,157].

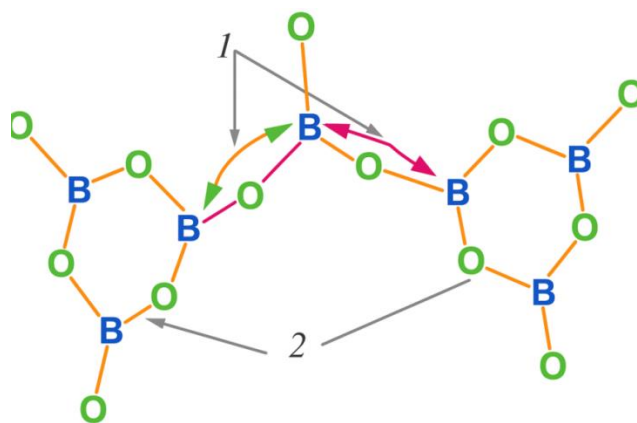


Figure 6.23. Schematic representation of the vitreous B_2O_3 network structure: (1) B-O-B bond angle, (2) boroxol ring (adapted from [157]).

Experimentally, the Raman spectra obtained from the worn surfaces provide clear evidence of this temperature-dependent evolution and its tribological consequences. At 25 °C, the Raman spectrum reveals a clear $B(OH)_3$ signal, which correlates with the relatively low COF and wear rate of the C3 coating. The layered structure of boric acid provides an effective lubricating film that facilitates interlayer shear and reduces friction. At 200 °C, the $B(OH)_3$ signal remains evident, and the coating continues to show improved tribological behavior compared to higher temperatures, confirming that the boric acid layer is still stable and contributes to friction reduction. At 400 °C, the Raman spectrum still exhibits a pronounced $B(OH)_3$ peak, indicating that boric acid tribofilms remain present within the contact zone. Nevertheless, the tribological response remains generally stable, with only slight differences from that at lower temperatures. The COF displays slight fluctuations, and the wear rate shows only a minor increase, indicating that although the lubricating contribution of boric acid tribofilms persists, its influence begins to diminish as oxide phases such as NiO and γ - Al_2O_3 become increasingly important in governing the tribological response. Upon reaching 600 °C, the $B(OH)_3$ -related peak has largely disappeared as dehydration is completed and B_2O_3 becomes the dominant phase, in agreement with the structural analysis. When the temperature increases to around 600 °C, the glassy phase undergoes significant softening, and its viscosity decreases. Under these conditions, the surface can display flow-like morphologies and localized plastic flow, as revealed by the tribological experiments.

6.8. Temperature-Dependent Material Transfer and Counterface Behavior in the NiB-Al₂O₃ Tribological System

Material transfer between contacting surfaces is a critical factor influencing frictional behavior, wear resistance, and long-term surface integrity in tribological systems. This phenomenon becomes increasingly significant at elevated temperatures, where thermally induced softening, oxide formation, and microstructural degradation can accelerate the detachment and migration of material across the sliding interface. Depending on the contact conditions, material transfer typically occurs in two distinct ways. One common mechanism is adhesive wear, where surface fragments detach and become permanently adhered to the opposing surface. Another form involves third-body interaction, in which detached wear debris circulates between the two surfaces and influences the tribological response dynamically. Understanding the relative contribution of these mechanisms under different thermal conditions is essential for interpreting how surface interactions evolve in coating-counterface tribosystems. Therefore, this study investigates the temperature-dependent material transfer behavior between an electroless NiB-Al₂O₃ coating and an alumina counterface. The surface morphology of the alumina balls after sliding tests at 25 °C, 200 °C, 400 °C, and 600 °C was examined using SEM, as shown in Figure 6.24.

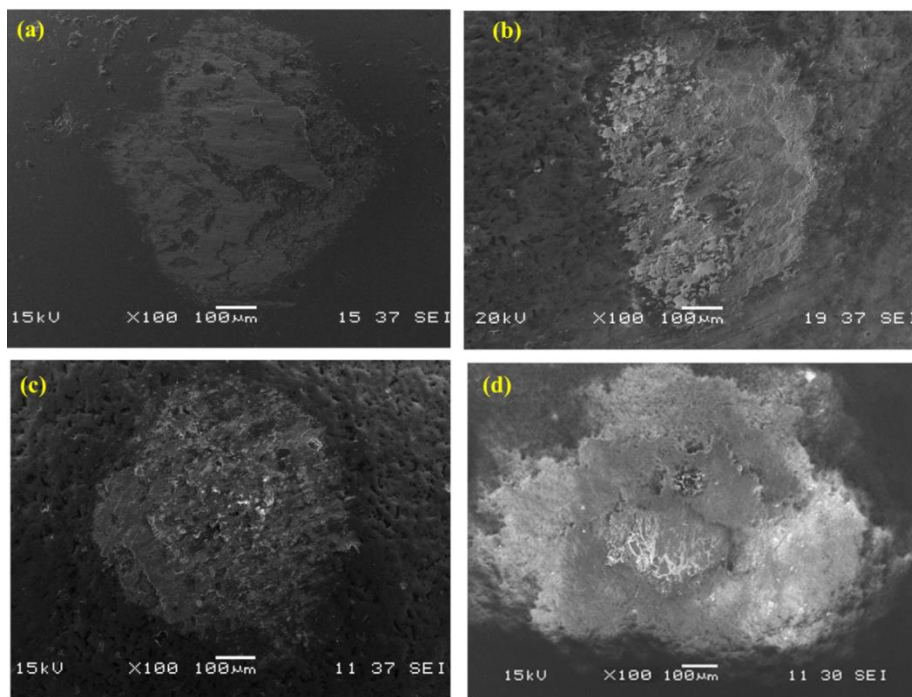


Figure 6.24. SEM images of the worn surfaces of alumina counter balls after sliding against the C3 coating at various temperatures: (a) 25 °C, (b) 200 °C, (c) 400 °C, and (d) 600 °C (reproduced from [27]).

The SEM images in Figure 6.24 reveal temperature-dependent morphological changes on the alumina counterface after sliding against the C3 coating. To complement these observations, energy-dispersive X-ray spectroscopy (EDS) was performed on the worn surfaces of the alumina balls to identify and quantify the transferred material from the coating. The resulting elemental compositions provide insight into the transfer mechanisms and oxidation behavior at different temperatures. The corresponding EDS results are summarized in Table 6.10.

Table 6.10. Temperature-dependent elemental composition (wt.%) obtained from EDS analysis of alumina counterballs, corresponding to the SEM images in Figure 6.24 (reproduced from [27]).

Temperature	Ni	Al	O
C3- 25 °C	9.8 ± 0.8	51.8 ± 3.8	38.4 ± 1.4
C3- 200 °C	7.3 ± 1.2	52.9 ± 2.6	39.8 ± 2.8
C3- 400 °C	3.4 ± 0.3	54.9 ± 1.2	41.7 ± 3.2
C3- 600 °C	1.1 ± 0.2	48.1 ± 4.3	50.8 ± 5.3

Note: These EDS results represent material transferred onto the alumina counterballs after sliding, not the original composition of the NiB-Al₂O₃ coatings. Therefore, the Ni content appears significantly lower compared to the coating itself.

Based on the SEM micrographs and the corresponding EDS results presented above, the material transfer behavior at each temperature is discussed in detail below to elucidate the underlying wear mechanisms and surface interaction behavior.

At 25 °C, the alumina counterface exhibited a smooth and continuous wear track with no visible surface cracking or delamination (Figure 6.24a). The SEM image revealed minimal surface damage, indicating that the tribological interaction remained within the mild wear regime. No significant debris accumulation or transfer film formation was observed, suggesting limited coating-counterface interaction under low thermal and mechanical stress. These findings confirm that, at room temperature, the wear mechanism was primarily governed by elastic contact and weak adhesive interaction, with no evidence of third-body effects or surface film formation.

Complementary EDS analysis supports these morphological observations. A moderate amount of nickel was detected on the worn counterface (9.8 ± 0.8 wt.%), indicating incipient material transfer from the NiB-Al₂O₃ coating, likely due to transient micro-contacts. However, the absence of localized deposition zones suggests that this transfer was minimal and not associated with oxidation or film accumulation. In addition, the aluminum (51.8 ± 3.8 wt.%) and oxygen (38.4 ± 1.4 wt.%) contents remained

consistent with the stoichiometry of pure Al_2O_3 . According to Bharthasaradhi et al. [158], EDS analysis of aluminium oxide nanomaterials synthesized via the co-precipitation method typically reveals ~62 at.% Al and ~38 at.% O, without detectable impurities, which further confirms that the measured oxygen originates from the alumina counterface rather than from tribologically induced oxidation. These combined observations validate that no substantial chemical modification occurred at room temperature and that both the coating and counterface retained their structural integrity.

As the operating temperature increased to 200 °C, noticeable changes began to emerge on the alumina counterface. The wear track on the alumina counterface became more defined compared to the 25 °C condition, with visible signs of fine debris and localized microcracks (Figure 6.24b). These morphological changes indicate the onset of fatigue-related surface deterioration, likely caused by thermal expansion and increased mechanical stress. No continuous transfer film was observed, suggesting that the material exchange between the coating and counterface remained discontinuous and surface-limited. These morphological observations are further corroborated by EDS analysis. The detected Ni content decreased to 7.3 ± 1.2 wt.%, indicating continued but still moderate material transfer from the NiB- Al_2O_3 coating. The aluminum level showed only minor variation compared to 25 °C, consistent with the stable nature of the alumina counterface. The oxygen content slightly increased to 39.8 ± 2.8 wt.%, suggesting the onset of temperature-induced oxidation at the sliding interface. However, no continuous, dense, or homogeneous oxide film was observed in the SEM image, indicating that any oxidation was likely mild, transient, and locally confined. Overall, the tribological behavior at 200 °C reflects a transition zone where adhesive wear and early-stage oxidation begin to contribute, though no dominant tribochemical interaction has yet developed.

As the test temperature reached 400 °C (Figure 6.24c), the wear scar on the alumina counterface exhibited a circular geometry with well-defined contours, suggesting a centralized and symmetric contact pattern during sliding. Compared to lower test temperatures, the wear scar appeared more clearly defined, reflecting increased tribological activity while still avoiding catastrophic damage. Notably, there were no signs of delamination, severe cracking, or substantial oxide accumulation, suggesting that the contact remained mechanically stable. In addition, shallow and irregular pits

were scattered across the surface, which may have resulted from the mechanical impact of detached coating particles or localized tribochemical interactions. These features point to the early onset of third-body effects, where loose debris circulates within the contact interface and induces localized surface abrasion. The overall morphology suggests a moderately altered surface shaped by partial material transfer, incipient oxidation, and contact-induced stresses. Despite these changes, the worn alumina ball retained its structural coherence and did not exhibit signs of deep deterioration. These findings are consistent with the stable wear behavior observed on the C3 coating and indicate that the tribological system remained largely under control at this temperature. Nevertheless, preliminary indicators of oxidative wear and third-body abrasion began to emerge, signaling the approach of the coating's thermal performance threshold. To further support the morphological observations and clarify the underlying mechanisms at 400 °C, EDS analysis was conducted on the worn counterface surface. EDS analysis supported these observations, revealing a further decline in nickel content to 3.4 ± 0.3 wt.%, implying limited but persistent transfer of metallic phases. In contrast, aluminum remained high (54.9 ± 1.2 wt.%), and oxygen content increased slightly to 41.7 ± 3.2 wt.%, suggesting mild surface oxidation. However, the oxidation appeared superficial, as no continuous tribofilm or substantial oxide layer was detected in SEM images.

Upon reaching the maximum test temperature of 600 °C, the tribological interaction between the C3 coating and alumina counterface led to pronounced surface degradation on the ball. The wear scar on the alumina counterface exhibited extensive morphological damage, characterized by the formation of dense and irregular oxide accumulations, particularly in the central region. The contact zone appeared heavily deformed, with a widespread and irregular wear scar displaying a brighter contrast in SEM imaging, as seen in Figure 6.24d. These bright and uneven zones suggest the presence of accumulated oxide-rich phases and thermally altered debris that lacked structural uniformity and coherence. The central region displays morphological features indicative of localized melting and pronounced smearing, driven by combined thermal and mechanical stresses. The disrupted surface topography, marked by smeared textures and local detachment features, reflects the mechanical instability of the oxide films formed at this temperature and their tendency to fragment under load. Moreover, peripheral areas displayed a less pronounced contrast, implying non-

uniform oxidation and asymmetric material transfer. Collectively, these features point to a breakdown in the protective function of the oxide layer, leading to increased susceptibility to wear and loss of surface integrity. The observed morphology aligns with the evidence of oxide layer instability, which contributes to the deterioration of tribological performance and indicates that the thermal durability threshold of the coating system has been exceeded.

As the temperature increased from 25 °C to 600 °C, EDS results showed a progressive decline in nickel content from 9.8 ± 0.8 wt.% to only 1.1 ± 0.2 wt.%. This observation reflects the gradual oxidation of the NiB-Al₂O₃ nanocomposite coating, with partial metallic transfer still evident at intermediate temperatures, as indicated by the presence of 7.3 wt.% Ni at 200 °C and 3.4 wt.% at 400 °C. At 600 °C, although Ni remained detectable in small amounts on the counterface, it likely existed in oxidized form rather than as metallic Ni, due to the formation of a thick, oxygen-rich oxide scale. The detection of residual nickel, combined with the elevated oxygen content (50.8 ± 5.3 wt.%), suggests the formation of a surface NiO layer. Similar behavior was reported by Haugrud [159], who observed that an oxygen-enriched NiO layer forms rapidly on pure nickel surfaces around 600 °C due to the high reactivity between Ni and ambient oxygen. Consistent with this oxidation tendency, the aluminum content (48.1 ± 4.3 wt.%), showed a relative decrease compared to 400 °C, likely due to the partial coverage of the alumina surface by the newly formed NiO layer. These findings indicate that at 600 °C, the surface no longer exhibits a single-phase composition but rather develops into a chemically heterogeneous oxide layer, consisting predominantly of NiO and Al₂O₃ phases enriched in oxygen.

Although the wear track on the C3 coating at 600 °C appeared relatively intact in certain regions, the corresponding alumina counterface exhibited pronounced surface degradation, including widespread oxidation and melting-induced smearing. This apparent discrepancy stems from the thermo-mechanical asymmetry between the compliant, heat-softened composite coating and the rigid alumina ball. At such high temperatures, the coating undergoes significant matrix softening, which enables it to accommodate contact stresses through plastic flow, thereby minimizing brittle fracture or spallation. However, the ceramic counterface, unable to deform plastically, experiences more aggressive surface damage, particularly due to tribo-oxidation and thermally activated wear mechanisms. Furthermore, third-body effects and tribofilm

fragmentation intensify at elevated temperatures. Even if the coating retains some structural continuity, loose debris and unstable oxide fragments can circulate in the contact zone and abrade the ball surface. The reduction in boron-based lubricating film formation at 600 °C, as evidenced by Raman spectra, also diminishes interfacial protection, contributing to the observed counterface degradation.

6.9. Critical-Temperature Modelling of Wear Mechanisms at 400 °C

The temperature of 400 °C was identified as a critical point for evaluating wear mechanisms, as it represents a transitional regime where thermally activated processes begin to dominate the tribological response of the coatings. At this temperature, wear mechanisms become more distinct, enabling the evaluation of how both reinforcement presence and its distribution influence the tribological response. To better understand the coating behavior under these conditions, a schematic model was developed to illustrate the dominant wear mechanisms observed in selected samples. While quantitative parameters such as wear rate and coefficient of friction provide valuable insights, they are insufficient to fully capture the complex material responses occurring at elevated temperatures. Therefore, this modelling approach serves to visually and conceptually differentiate the wear behaviors of unreinforced, optimally reinforced, and over-reinforced coatings (C0, C3, and C4, respectively), with an emphasis on how reinforcement content influences damage evolution. Based on the wear test observations and SEM analyses discussed in the previous sections, the following schematic model, depicted in Figure 6.25, was constructed to illustrate the underlying mechanisms at 400 °C.

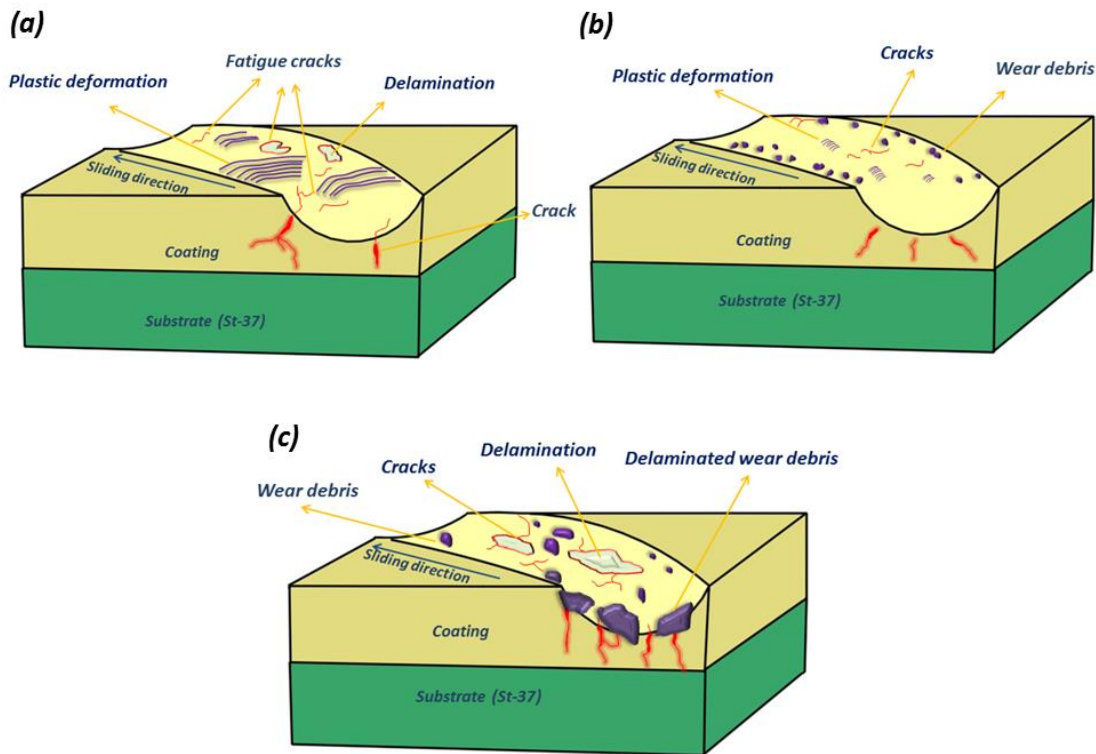


Figure 6.25. Schematic representation of dominant wear mechanisms at 400 °C for (a) unreinforced NiB (C0), (b) optimally reinforced NiB-Al₂O₃ (C3), and (c) over-reinforced NiB-Al₂O₃ (C4) coatings. Each illustration highlights characteristic failure modes such as plastic deformation, crack propagation, and delamination, which evolve differently depending on the reinforcement content and distribution (reproduced from [27]).

As illustrated in Figure 6.25a, the unreinforced NiB coating (C0) exhibits pronounced plastic deformation along the sliding direction. Due to the elevated temperature, surface oxidation takes place, which contributes to surface embrittlement and promotes the initiation of fatigue cracks under cyclic loading. These cracks eventually coalesce, leading to the formation of delamination-type wear debris. Furthermore, the progressive deformation facilitates crack propagation toward the substrate, weakening the structural integrity of the coating. The dominant wear mechanism in this sample is therefore characterized by surface oxidation-induced fatigue and delamination.

In comparison, the C3 sample, shown in Figure 6.25b, reveals a more stable wear response under the same conditions. The worn surface of the coating exhibits extensive plastic deformation. However, this deformation is less detrimental compared to that in the C0 sample. This improvement is attributed to the uniform dispersion of Al₂O₃ nanoparticles, which enhances the load-bearing capability of the coating and inhibits

crack propagation. The reinforcement phase contributes to stress redistribution and crack arrest, resulting in the formation of fine wear debris and localized micro-delamination rather than large-scale material removal. Although the elevated temperature still facilitates some degree of softening and crack formation, the structural support provided by the well-dispersed ceramic phase effectively mitigates deep crack penetration and severe damage.

In contrast, the wear behavior of the C4 sample, depicted in Figure 6.25c, is dominated by extensive delamination, which is significantly more severe than in C3. In this case, the excessive Al_2O_3 content leads to particle agglomeration within the coating matrix. These agglomerated regions act as local stress concentrators and serve as favorable sites for crack nucleation. As the sliding progresses, microcracks form beneath the surface and propagate laterally due to subsurface shear stresses. With the convergence of these cracks, broad subsurface fractures develop, ultimately resulting in the pull-out of large wear particles. This wear pattern reflects a structurally compromised coating in which the excess reinforcement content adversely affects mechanical stability.

These comparative models, developed specifically to explain the wear mechanisms observed at 400 °C, underline the broader importance of optimizing the reinforcement level and achieving uniform particle dispersion in nanocomposite coatings. While moderate reinforcement improves structural stability and suppresses damage propagation, excessive particle loading may lead to undesirable failure modes due to stress concentration around agglomerated regions. Therefore, proper nanocomposite design is essential to balance mechanical integrity and thermal durability under severe tribological conditions. Based on these findings, this thesis highlights the critical role of achieving a well-balanced nanocomposite structure to ensure reliable performance, both at room temperature and under elevated temperature wear conditions.



7. CONCLUSION AND RECOMMENDATIONS

7.1. Summary and Conclusions

This dissertation presented a comprehensive investigation into the temperature-dependent tribological behavior of electroless NiB and NiB-Al₂O₃ nanocomposite coatings.

- The coatings were deposited on low-carbon steel substrates using electroless plating and systematically evaluated in terms of their surface morphology, frictional response, and wear mechanisms under dry sliding conditions at 25 °C, 200 °C, 400 °C, and 600 °C.
- The incorporation of Al₂O₃ particles significantly influenced the structural and tribological characteristics of the coatings, with the 10 g/L Al₂O₃ formulation (C3) exhibiting optimal performance across all test temperatures.
- Compared to the unreinforced NiB coatings, this composite structure demonstrated enhanced hardness, improved load-bearing capacity, and greater thermal stability.
- Friction and wear responses demonstrated that increasing temperature influenced the transition from mechanically-driven wear modes, such as abrasion and adhesion, to thermally-activated processes including oxidation and third-body effects. These transitions were interpreted using SEM, EDS, XRD, and Raman spectroscopy, enabling precise identification of tribofilm composition and material transfer dynamics.
- Importantly, the results emphasize that evaluating tribological coatings for high-temperature applications requires more than testing under fixed thermal conditions and instead requires a comprehensive understanding of how these materials behave under continuously changing temperature and stress environments.

- In this context, the present study positions itself beyond conventional single-point evaluations by tracing and modeling the full mechanism evolution of the same coating system over a broad thermal range.
- The proposed temperature-dependent wear mechanism model reflects this dynamic transformation and provides a conceptual framework for predicting coating behavior in real-world high-temperature applications.
- The C3 coating, in particular, was found to maintain structural and tribological stability even at 400 °C, indicating its applicability within a wide operational window.
- In conclusion, this research contributes not only to the development of high-performance composite coatings but also to the foundational understanding of high-temperature tribology as a field that demands multiscale, multi-mechanism, and multi-temperature insight.

7.2. Contributions to Original Knowledge

This dissertation offers several original contributions to the field of high-temperature tribology and electroless composite coatings, which can be summarized as follows:

- A comprehensive temperature-resolved tribological investigation was carried out on both unreinforced and Al₂O₃-reinforced electroless NiB coatings under dry sliding conditions at four representative temperatures: 25 °C, 200 °C, 400 °C, and 600 °C. Through this investigation, the study elucidated how reinforcement content, thermal exposure, and microstructural evolution collectively govern wear mechanisms, tribofilm development, and material transfer phenomena.
- Among multiple Al₂O₃ concentrations, the 10 g/L formulation was determined to offer the best balance between hardness, surface homogeneity, and frictional stability under both ambient and elevated temperatures.
- By combining temperature-resolved tribological testing with SEM, EDS, XRD, and Raman analysis, the study identified key transitions from low-temperature adhesive wear to high-temperature oxidative and third-body dominated mechanisms, correlating these transitions with morphological and chemical changes in the coating structure.

- Through in-depth SEM-EDS evaluation of the worn alumina counterface, the study revealed how material transfer behavior evolves with temperature, and how surface oxide stability influences tribofilm formation and breakdown.
- Based on experimental findings, a conceptual model was developed to describe the evolution of dominant wear mechanisms in both reinforced and unreinforced coatings as a function of temperature and surface interaction dynamics.
- The findings highlight the potential of electroless NiB-Al₂O₃ coatings to maintain tribological stability under a wide range of thermal conditions, expanding their applicability beyond room-temperature wear protection.
- This dissertation challenges the conventional approach of single-temperature tribological assessment by demonstrating that wear mechanisms evolve substantially across different thermal regimes. It advocates for a holistic, temperature-resolved evaluation framework that captures the dynamic interplay between oxidation, matrix softening, and interfacial failure factors critical for real-world performance.

7.3. Suggestions for Future Works

- This study has shown promising results for Al₂O₃-reinforced NiB coatings. Building upon these findings, future work may explore hybrid reinforcement systems incorporating rare-earth oxides such as yttrium oxide (Y₂O₃). As a chemically stable ceramic with well-known phase-stabilizing capabilities, Y₂O₃ could enhance oxidation resistance and facilitate the formation of coherent tribo-oxidized layers at elevated temperatures. The synergistic combination of Al₂O₃ and Y₂O₃ may yield multifunctional coatings with improved high-temperature durability and tribological stability under thermally demanding service conditions.
- In addition to ceramic-ceramic reinforcement systems, future research may also explore polymer-based self-lubricating strategies. In particular, impregnating Al₂O₃-reinforced NiB coatings with polytetrafluoroethylene (PTFE) could offer significant advantages in reducing friction and mitigating adhesive wear, especially under moderate temperature conditions where PTFE

maintains structural stability. Owing to its low surface energy and excellent chemical inertness, PTFE can form thin transfer films and minimize direct asperity contact. Investigating such PTFE-functionalized surfaces may enhance the tribological performance of the coatings in environments characterized by intermittent lubrication, chemical exposure, or fluid-solid interactions.

- In this dissertation, the tribological behavior was evaluated under dry sliding conditions. Future research is recommended to investigate the performance of the same coatings under lubricated, humid, or oxidative atmospheres in order to simulate more realistic service conditions. These alternative conditions would provide deeper insights into the coatings' environmental robustness and enhance their relevance for practical industrial applications where thermal, oxidative, or fluid-based interactions are prevalent.
- While alumina balls were used as counterfaces in this study, future work could explore how different counterface materials (e.g., steel or Si_3N_4) influence tribofilm chemistry, material transfer tendencies, and interfacial wear mechanisms at elevated temperatures. Such variations could reveal critical dependencies between tribopair combinations and the resulting oxide layer evolution, enabling more tailored coating-counterface designs for specific applications.
- Future work may also include scale-up and application testing. Transitioning the coating from laboratory scale to industry-scale plating baths is essential. Future studies should address challenges in plating larger or more complex parts with $\text{NiB-Al}_2\text{O}_3$ and conduct field tests on actual components (e.g., engine parts, hydraulic cylinders). Such investigations will validate performance in operational environments and allow direct comparison against conventional hard-chrome coatings.
- Another recommended direction is modeling and mechanistic studies. Computational approaches such as finite element analysis or tribological wear modeling could be employed to simulate the high-temperature wear processes of NiB composites. These methods may facilitate the prediction of failure modes, the optimization of coating thickness or composition, and the reduction

of experimental costs. Additionally, advanced microscopic techniques (e.g., TEM for interfacial structure, XPS on wear debris for oxidation state analysis) could provide nanoscale insights into tribofilm formation and oxidation mechanisms, complementing the experimental observations.





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