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Faculty of Technology

Department of Metallurgy and Materials Engineering

Effect of Boride Layers on the Properties of Lamellar, Spheroidal Graphite, and High-chromium Cast Irons

A Thesis Submitted to the Faculty of Technology (Engineering Sciences) in Partial
Fulfillment of the Requirements for the Degree of
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in
Metallurgy and Materials Engineering

by

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les propriétés des fontes lamellaires, à graphite
sphéroïdal et à haute teneur en chrome

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DEDICATION

إلى كل عائلتي الحبيبة

To all my beloved family

ABSTRACT:

Cast iron stands out because to a desired mix of mechanical, industrial, and financial advantages. They are typically used in machinery, including driving shafts, ball mills, pulling devices, tool guides, and parts for the automotive, mining, and farms that are subject to abrasive wear. The surface of the part gradually loses material due to abrasive wear. Iron's wear resistance can be enhanced by several thermal processes and surface techniques, like carburizing, nitriding, and laser processing, each with some limitations and disadvantages. Cast iron can be a suitable material for boronizing. Boriding enables the formation of desirable phases of Fe_xB_y or M_xB_y in the boride layer. This thesis aims to study the use of powder pack boronizing to improve the hardness, wear, and corrosion performance of cast irons for potential applications in mining, mineral processing, agriculture, and automotive. Boriding has been performed to improve the performance of lamellar and spheroidal graphite and high-chromium irons with a more economical process (recycled boriding agent from conventional powders (90% SiC + 5% B_4C + 5% KBF_4)). The boronizing was carried out in a powder-pack boronizing treatment consisting of recycled powder without the addition of new agents at 950 °C for four hours. The structural, mechanical, tribological, and corrosion properties were analyzed using XRD, OM, SEM, EDX, micro-hardness testing, surface profilometry, Daimler-Benz Rockwell-C, pin-on-disk tribo testing, and electrochemical polarization (OCP, EIS, and Tafel). The experimental findings demonstrated that the boride coating is composed of phases of hard nature (MB, M_2B , $M_{23}(C, B)_6$, and iron oxides, M equal to Fe or Fe, Cr). The depth of the boronized coating on the iron surface varied from 44 to 103 μm based on the kind of iron substrates, while the hardness of the boronized layers created varied from 1400 to 2140 $HV_{0.1}$. Adhesion mechanisms were evaluated by SEM. Findings indicated that boronized coating adhered to lamellar and spheroidal graphite more effectively than high-chromium iron. In addition, it was found that boriding provided an important improvement in the coefficient of friction against a WC ball, wear resistance, and corrosion protection against a 3.5% NaCl medium. The wear resistance of boride high chromium iron increased by 84% compared to bare samples.

Keywords: Boriding/Boronizing; Lamellar cast irons; Spheroidal cast irons; High chromium cast irons; Corrosion; Adhesion; Wear; Friction

المستخلص

تتميز مسبوكات الحديد (الصب) بمجموعة مرغوبة فيه من الخواص الميكانيكية وخصائص التصنيع وفوائد التكلفة. يتم استخدامها عادة في الصناعة بما في ذلك أعمدة القيادة وأعمدة الكامات والبكرات وأدلة الماكينة وقطع غيار الآلات الزراعية والتعدين التي تتعرض للتآكل الكاشطة. يفقد سطح المكون المواد تدريجياً بسبب التآكل الكاشطة. يمكن تحسين مقاومة التآكل في الحديد بإجراء العديد من المعالجات الحرارية وتقنيات معالجة السطح، مثل النتردة والكربنة ومعالجة بالليزر ولكل منها بعض القيود والعيوب. الحديد الزهر مادة مناسبة للبورنة (Boriding). تمكن عملية البورنة من تكوين أطوار مرغوبة من Fe_xB_y أو M_xB_y في الطبقة البوريد. تهدف هذه الأطروحة إلى دراسة استخدام بورنة عبوات المسحوق لتحسين صلادة وأداء تآكل الميكانيكي وتآكل الكيمائي الحديد المصبوبات من أجل تطبيقات المحتملة في التعدين ومعالجة المعادن وصناعة السيارات والآلات الزراعية. تم إجراء البورنة لتحسين أداء الحديد المصبوبات الجرافيت الرقائقي والكروي والحديد الزهر عالي الكروم بعملية أكثر اقتصاداً (عامل البورنة المعاد تدويره من المساحيق التقليدية (5% B_4C و 5% KBF_4 و 90% SiC). تم إجراء البورنة بطريقة تعبئة مسحوق تتكون من عامل معاد تدويره دون إضافة مسحوق طازج عند 1223 كلفن (950 درجة مئوية) لمدة 4 ساعات. تم تحليل الخصائص الهيكلية والميكانيكية والتروبولوجية والتآكل الكيمائي باستخدام حيود الأشعة السينية XRD والمجهر الضوئي OM والمجهر الإلكتروني (SEM) والتحليل الكيمائي الدقيق بالأشعة السينية EDX واختبار الصلادة الدقيقة وقياس ملامح السطح والالتصاق بطريقة Daimler-Benz Rockwell-C واختبار tribo على القرص والاستقطاب الكهروكيميائي على التوالي. أظهرت النتائج العملية أن طبقة البوريد تتكون من أطوار ذات طبيعة صلبة (M_2B و $M_{23}(C,B)_6$ و MB) وأكاسيد الحديد، حيث M تساوي Fe أو Fe مع Cr). اعتماداً على التركيب الكيمائي لركائز الحديد، تراوح سمك طبقة البوريد على سطح الحديد من 44 إلى 103 ميكرومتر وتراوح صلادة مركبات البوريد المتكونة من 1200 إلى 1940 بمقياس فيكر (HV0.1). تم تقييم آليات الالتصاق بواسطة المجهر الإلكتروني (SEM). أظهرت النتائج التصاق أفضل للطبقة البوريد على جرافيت الرقائقي والكروي مقارنة بالحديد الزهر عالي الكروم المعالج. إضافة إلى ذلك، وجد أن عملية البوريد قدمت تحسناً مهماً في معامل الاحتكاك ضد كرة كريد التنجستن، ومقاومة التآكل الميكانيكي (البري)، ومقاومة التآكل الكيمائي في محلول كلوريد الصوديوم بنسبة 3.5%. زادت مقاومة تآكل البري لحديد البوريد عالي الكروم بنسبة 84% مقارنة بالعينات العارية.

الكلمات المفتاحية: الحديد الزهر، رقائقي، الحديد الزهر كروي؛ الحديد الزهر عالي الكروم، البوريد، النحر أو البري، التآكل، التصاق، احتكاك؛

RÉSUMÉ :

Les fontes se distinguent par une combinaison de propriétés mécaniques, de caractéristiques de fabrication et d'avantages en termes de coûts. Ils sont généralement utilisés dans l'industrie, y compris les arbres d'entraînement, les arbres à cames, les poulies, les guides de machine et les pièces pour les machines agricoles et minières soumises à une usure abrasive. La surface du composant perd progressivement de la matière en raison de l'usure abrasive. La résistance du fer à l'usure peut être améliorée par divers traitements thermiques et techniques de surface, tels que la cémentation, la nitruration et le traitement au laser, chacun avec certaines limitations et inconvénients. La fonte est un matériau approprié pour le boriding. La circonscription permet la formation de phases souhaitables de $\text{Fe}_x\text{B}_y/\text{M}_x\text{B}_y$ dans la couche borure. L'objectif de cette thèse est d'étudier l'utilisation de la boruration en poudre pour améliorer les performances de dureté, d'usure et de corrosion des pièces moulées en fonte pour des applications potentielles dans les mines, le traitement des minéraux, l'industrie automobile et les machines agricoles. Boruration a été réalisé pour améliorer les performances du graphite lamellaire et sphéroïdal et des fontes à haute teneur en chrome avec un procédé plus économique (agent de boriding recyclé à partir de poudres conventionnelles (5% B_4C , 5% KBF_4 et 90% SiC)). La boruration a été effectué dans un processus de boruration de paquet de poudre composé d'agent recyclé sans ajout de poudre fraîche à 1223 K (950 °C) pendant 4 heures. Les propriétés structurales, mécaniques, tribologiques et de corrosion ont été analysées à l'aide de DRX, MO, MEB, EDX, de tests de microdureté, de profilométrie de surface, de Daimler-Benz Rockwell-C, de tests tribologiques broches sur disque et de polarisation électrochimique (OCP, EIS, Tafel). Les résultats expérimentaux ont montré que la couche borure est constituée de phases de nature dure (MB , M_2B , $\text{M}_{23}(\text{C}, \text{B})_6$, et d'oxydes de fer, M égal à Fe ou Fe, Cr). Selon la composition chimique des substrats de fer, l'épaisseur de la couche de borure à la surface du fer variait de 44 à 103 μm et la dureté des composés de borures formés variait de 1400 à 2140 $\text{HV}_{0,1}$. Les mécanismes d'adhésion ont été évalués par SEM. Les résultats ont montré une meilleure adhérence de la couche pour le graphite lamellaire et sphéroïdal boridé par rapport à la fonte percée à haute teneur en chrome. En outre, il a été constaté que la boruration apportait une amélioration importante du coefficient de frottement contre une bille de WC, de la résistance à l'usure et de la résistance à la corrosion dans une solution de NaCl à 3,5%. La résistance à l'usure du fer boruré à haute teneur en chrome a augmenté d'environ 84 % par rapport aux échantillons nus.

Mots-clés : Boruration ; usure, fontes lamellaires sphéroïdales ; Ferirones à haute teneur en chrome ; Corrosion ; Adhérence ; Friction

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SYMBOLS AND ABBREVIATION

A	Working electrode area (cm ²).
AISI	American Iron and Steel Institute
CI	Cast iron
CPE	Constant phase element
CR	Corrosion rate (mpy)
d	Density of working electrode (gr/cm ³)
E _{corr}	Potential of corrosion (V)
EDX	Energy Dispersive X-ray Spectroscopy
EW	Equivalent weight of working electrode (g/mol)
F	Normal load (N)
Hi-Cr	High chromium
HV	Vickers hardness
HV0.1	Vickers hardness performed with a load of 100 gf
i _{corr}	Corrosion current density (A/cm ²)
K	Specific wear rate (mm ³ /N.m),
L	Thickness of wear track (mm)
LG	Lammelar graphite
OCP	Open circuit potential (V)
OS	Optical spectroscopy
Q	Constant phase element
Q _c	Constant phase element of the boride layer
r	The WC ball radius (mm).
R	the wear scar radius (mm)
R	The resistance
RBP	Recycled Boriding Powder
R _{ct}	Resistor of the iron substrate
R _p	Polarization resistance (Ω)
R _{po}	Resistor of the boride coating
C _s	The substrate capacity
R _s	The NaCl solution resistance
S	Sliding distance (m),
SEM	Scanning Electron Microscopy
SG	Spheroidal graphite
V	Wear volume loss (mm ³),
XRD	X-ray Diffraction
β _a	Tafel constant for anode, volts/ current decade
β _c	Tafel constant for cathode, volts/ current decade

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CHAPTER 1

1. INTRODUCTION

1.0 Abstract :

More over 10 billion DM, or almost 1% of the gross domestic product, was lost to wear and abrasion in 1975. In the United States, corrosion is estimated to cost between \$9 billion and \$90 billion annually, according to an estimate by the National Institute of Standards and Technology (formerly the National Bureau of Standards). Therefore, it becomes appropriate that wear prevention measures are being implemented more frequently over the world. EKabor boriding agents have demonstrated their value in industrial use for several years in the fight against wear, and it is safe to state that boriding is already one of the traditional techniques of surface hardening [1].

The goal of this study is to use boriding to improve the hardness, wear, and corrosion resistance of cast irons made of high-chromium (Hi-Cr), spheroidal graphite, and lamellar graphite (LG). A recycled agent from commercial 5% B₄C, 5% KBF₄, and 90% SiC agents is used as the boriding powder, and the processes are done at 950°C for 4 hours.

Cast irons (CIs) are an important part of the industrialized world, with rising growth in world consumption. They have wide applications because of their high machinability, mechanical properties, castability, and cost-effectiveness. However, CI's performance and reliability are limited in severe service environments such as coastal, earthmoving, and mining due to poor wear resistance.

1.1 Background

Corrosion, wear, and fatigue entail the material component under consideration interacting chemically and/or mechanically with environmental loads. As a result, a material component's surface region's qualities often play a significant role in a material's performance and service life [2]. Cast iron surface wear and corrosion prevention and

reduction by coatings and surface treatments [3, 4]. Modern engineering places great emphasis on combining a hard exterior with a soft interior, as it withstands extreme loads and fatigue, a necessary property in products such as rolling contact drives and bearings. The boriding method is one method used to enhance surface quality [5].

Cast iron has the benefits of being relatively inexpensive overall, having unique economic qualities and metallurgical properties for the engineer, and being manufactured in second-largest quantities after steel. It is an eutectic polyelement alloy composed primarily of Fe, (2.4–4 wt%) carbon, and (0.8–3.2 wt%) silicon [6, 7]. Additional alloys are sometimes added to cast iron to provide a certain unique characteristic [8, 9]. It is classified as gray iron, white iron, or mottled iron depending on the various forms of precipitated carbon: graphite bearing or graphite-free (carbide) and macro-fracture. Gray (flake graphite) or lamellar graphite (LG), spheroidal graphite (SG), and vermicular graphite iron are the shapes of graphite in gray solidified cast iron. Between white and gray iron lies mottled iron. If solidification followed the metastable equilibrium diagram (Fe-Fe₃C/M_xC_y), white or white alloy iron would result, such as high chromium (Hi-Cr) iron [6, 7].

Gray iron or lamellar graphite iron is a type of cast iron having a graphitic microstructure. Because graphite is present, the fracture that results has a gray color, hence its name [10]. It is the most typical cast iron and the most often used cast material in terms of weight [11]. It is utilized for housings like internal combustion engine cylinder blocks, pump housings, valve bodies, electrical boxes, and decorative castings where the rigidity of the component is more important than its tensile strength. Due to its high heat conductivity and specific thermal capacity, gray iron is often used to manufacture cast-iron cookware and brake discs [3]. Gray iron is a popular engineering alloy because of its low

cost and machinability, as the graphite lubricates the cut and spreads the chips. Because the graphite flakes self-lubricate, it also possesses good galling and wear resistance. Gray iron's great damping ability is partly a result of the graphite since it absorbs energy and transforms it into heat [3].

When cast iron solidifies, graphite flakes are produced. The microcomponent of grey iron is a result of silicon alloying that promotes the development of graphite and slow solidification rates. It typically has moderate strength and low ductility, but also has good vibration dampening qualities and high heat conductivity [3].

Spheroidal graphite cast irons form graphite nodules when they solidify. The spheroidal graphite-iron microcomponent is formed because of slow solidification rates and magnesium or cerium alloys that promote the formation of spherical graphite. It typically exhibits high ductility and strength. Spherical graphite iron was first discovered in the 1940s. It is also named ductile iron or nodular iron [3].

High chromium iron forms eutectic carbide upon solidification. The iron metallography has fast solidification rates and an alloying element that promotes the formation of eutectic carbides. It typically has low ductility, high hardness, and high wear resistance in comparison to gray irons [3].

Wear is a major cause of material degradation. Types of wear include abrasive wear, adhesive wear, surface fatigue, corrosive wear, erosive wear, and fretting wear. During wear, surface and near-surface materials are removed or sideways displaced from their original positions due to contact with other solids, flowing liquids, flowing gases, or a mixture of these.

Corrosion is the gradual degradation of materials through chemical/electro-chemical reactions with their condition. Types include atmospheric corrosion, erosion corrosion, selective corrosion, uniform corrosion, pitting corrosion, fretting corrosion, stress corrosion, and intergranular corrosion.

Boriding is a thermochemical process that forms boron compounds with the base material by diffusing atoms (boron) into the surface of the workpiece. It is used to improve the hardness, wear, and corrosion resistance of these materials in engineered parts for commercial applications requiring these qualities. Boride layers in ferrous alloys can either be a single-phase layer (Fe_2B) or a two-phase layer (FeB and Fe_2B), depending on the boron activity in the boronizing agent and the boronizing conditions.

Due to the fact that cast-iron surface qualities do not meet the performance requirements of mining and automotive machinery, research is needed to enhance the surface characteristics of these parts, especially wear and corrosion resistance. The thesis conducted is evidence of a concept study on the application of boriding to three types of iron to enhance the wear resistance of mining and automotive components.

1.2 Problem Statement of the Research

The objective of this study is to investigate the boriding effect on the characteristics of the surface layers of metallic substrates. The substrates that can be considered are gray cast iron with different morphologies of graphite and high chromium. The boriding process was carried out in a solid mixture consisting of recycled boriding agents from B_4C , KBF_4 , and SiC powders at 950°C for 4 hours of diffusion. A boridized coating typically forms on the surface of the boridized metallic materials. The boride layer may be a two-phase layer of an outer phase of FeB and an inner phase of Fe_2B , or the Fe_2B layer may be a single-

phase. The FeB layer has a larger coefficient of heat expansion, is more brittle and harder, and thus creates a large tensile stress on the surface. Because it is less hard and brittle and creates an exceptionally large compressive stress surface, the Fe₂B phase is preferred in cases of high hardness and low ductility.

This method is of great industrial interest because it composes structures with hardened surface layers of borides so that overall mechanical performance, hardness, wear, and corrosion resistance are enhanced. Depending on conditions of the process, such as temperature and diffusion time, the microstructure is formed principally by a diffusion zone and compound layer.

The boriding processes have many advantages, like increased hardness, wear, and corrosion resistance. It offers materials for the formation of multilayers of boronized layers (FeB+Fe₂B+transition zone). Boride compounds are emerging as promising materials of technological interest due to their favorable characteristics for various tool applications. In addition, these phases are distinguished with high melting temperatures [12]. In contrast to, e.g., nitride cases, boride layer hardness is maintained at elevated temperatures. The essential wear mechanisms of adhesion, tribo-oxidation, abrasion, and surface fatigue are significantly reduced by the combination of the borided layers with high surface hardness and a low surface friction coefficient [1].

For this reason, boronizing is becoming more popular in a variety of industrial uses. In non-oxidizing diluted acids and alkaline mediums, it can greatly strengthen the corrosion and erosion-resistance properties of ferrous materials [1]. Boridized areas are resistant to molten metal attack as well as exhibit good oxidation resistance in excess of 850°C (1550°F). In oxidizing and corrosive situations, the fatigue life and service performance of

borided parts are improved. Several steels and cast irons, including those that can be through-hardened, are compatible with the techniques [13, 14].

Numerous studies on boronizing have demonstrated the superior tribological properties of borided steel compared to carburized or nitrided steels. However, the high cost of the boriding process has severely limited its potential uses. One way to reduce the cost of the boriding process is to use the recycled boronizing agent that is packed around the sample instead of a new agent without affecting the characteristics of the boride layer.

To date, however, there has been little discussion about the boriding of cast iron on its wear and corrosion characteristics. Moreover, no previous study has investigated the boronizing of cast iron using recycled boriding agents.

1.3 The thesis aim

The purpose of the present study is to investigate the effects of a powder-pack employing recycled boronizing powder with no introducing a new agent on the characteristics of the outer layers of cast-iron substrates. How the boronizing treatments improve surface properties such as hardness, adhesion, wear, and corrosion resistance. Gray cast-iron with various graphite morphologies (lamellar and spheroidal) and high chromium are the materials investigated as substrates. The experimental techniques used in this work include optical microscopy, electron metallography, X-ray diffraction, hardness tests, adhesion using Rockwell-C, corrosion tests, and tribological (roughness, friction coefficient, and wear resistance) tests.

1.4 Scope of the thesis

The goal of this research is to look at using powder pack boriding to increase the hardness, wear, and corrosion performance of chosen cast-irons for possible mining, mineral processing, and automotive applications in a more cost-effective way.

[Figure 1.1](#) depicts the fundamental proposal of this thesis. The **first chapter**, as with every research study, is an introduction, and the **second chapter** is an evaluation of the literature. This review looked at cast irons, boriding methods, formed microstructures, corrosion, and wear. For the investigation, LG, SG, and Hi-Cr cast irons were chosen. Powder-pack boriding techniques for cast irons were investigated.

The treated substances were evaluated in **Chapter 3** using optical and electronic microscopy, profilometry, and hardness to identify the borided and non-borided case microstructure, surface roughness, and cross-section micro-hardness. Both borided cast irons and cast irons before boriding were subjected to wear testing. In air conditions, tests were carried out with a ceramic ball (WC)-on-disc device. During the wear test, the coefficient of friction was continually measured. SEM, OM, and profilometry were utilized to measure wear track width and depth, and thus wear rate, as well as other wear track properties such as polishing and debris. The wear behavior was influenced by the characteristics of the boride coating.

The electrochemical corrosion tests were used to measure the corrosion behaviors of untreated and borided casting irons. Three electrodes, the sample as the working electrode, the platinum rod as the counter electrode, and the conventional Ag/AgCl cell as the reference electrode, are placed in a test cell and filled with a corrosive medium (3.5% NaCl). Three techniques were used for testing: open circuit voltage (OCP) (ASTM G106),

electrochemical impedance spectroscopy (EIS), and the Tafel extrapolation technique (ASTM G5). **Chapter 4** (Results and Discussion) is therefore devoted to the characteristics of the lamellar graphite, spheroidal graphite, and austenitized high-chromium (Hi-Cr) substrates. Also, study of microstructure, XRD, hardness, adhesion, friction, wear, and corrosion behaviors of borided and unborided cast irons. The **last chapter** is the conclusions and recommendations.

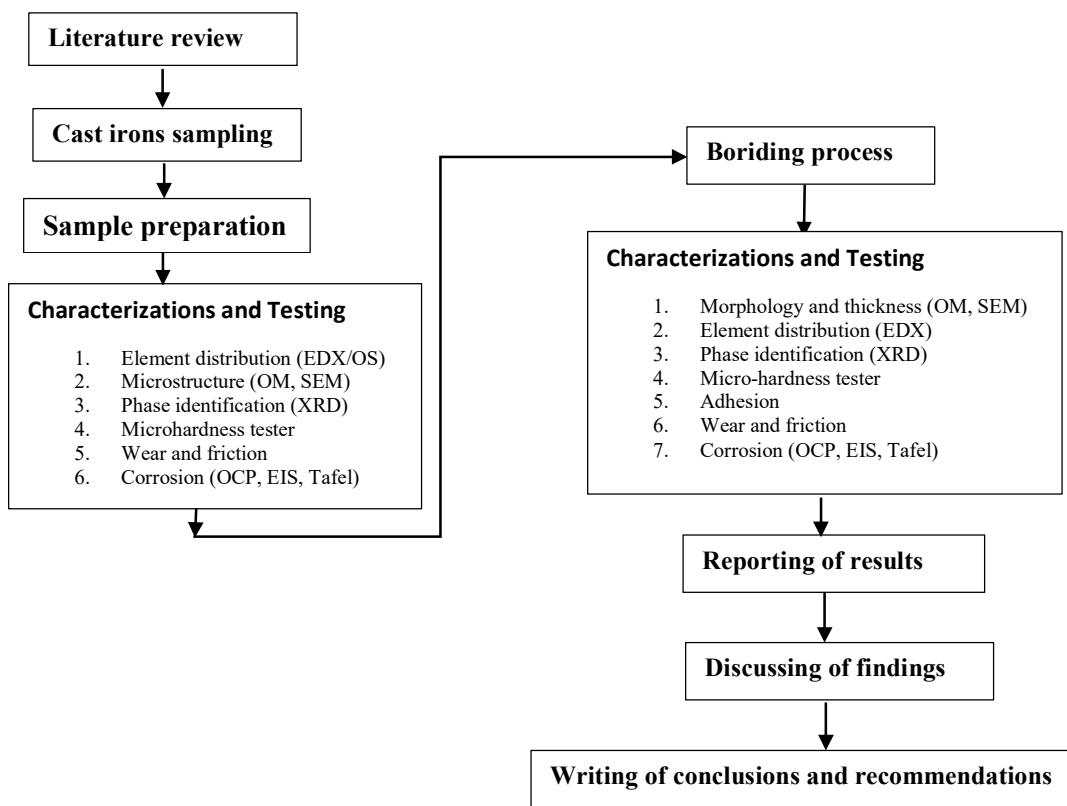


Figure 1.1. An overview of the research study.

CHAPTER 2

2. LITERATURE (BIBLIOGRAPHIC) REVIEW

For this reason, the important types, uses, heat treatment, wear and corrosion behavior of cast iron are reviewed and discussed in this chapter. In addition, surface hardening methods, boriding processes, the wear and corrosion behavior of boronized cast iron are reviewed and discussed.

2.1 Cast Irons

In the modern world there is a greater tendency to develop tools that help us in the exploitation of nature. However, these materials have a finite lifespan due to failures that they will inevitably suffer at some point. These can have short lifetimes due to mechanical failures such as mechanical fatigue or chemically induced failures such as oxidation and corrosion. But, for many applications, metallic materials are chosen by comparing their chemical, mechanical and physical qualities with the design requirements [15, 16].

Casting materials are iron-based casting metals with 2 to 5 percent carbon that pour and fill molds extremely fast, exhibit vibration dampening capabilities, and exhibit corrosion resistance. The melting temperature and solidifying interval are both low (1150–1250 °C) for compositions that are almost eutectic. Less material shrinkage results from the dissociation of carbon into graphite, which increases volume. Cast iron is now utilized in pipes, machinery, the casting industry, and car components, including heads and blocks of cylinders and transmission boxes. It has a wide range of engineering services [17].

2.1.1 Lamellar cast iron

Grey iron cast, composed of 2.5–5% C and 0.8–3% Si, is the most often used material in the production of machinery. The most common type of carbon to be found in its microstructure is graphite flakes. The fundamental structure may include ferritic, ferritic-pearlitic, or pearlitic, depending on how much carbon is liberated. The characteristics of gray cast iron, thus termed owing to the gray hue on the broken appear, rely on the quantity, distribution, and geometrical shape of graphite. The inclusion of graphite within the microscopic structure weakens the material by reducing the size of the efficient section and causing a notch effect. The elongation at rupture is less than 1%, and the deformation ability is small. Yet, the compressive strength of iron is approximately three to four times greater than its strength to tensile [18]. Due to cracks may develop at the tips of the large flakes of gray cast iron because of internal tensions during hardening, heat treatment is not done to those flakes. Hardening is not necessary, nevertheless, for applications when compressive pressures are efficient, such as the slipways of tool equipment. Lammellar graphite in a pearlitic matrix makes up the microscope image (Figure 2.1).

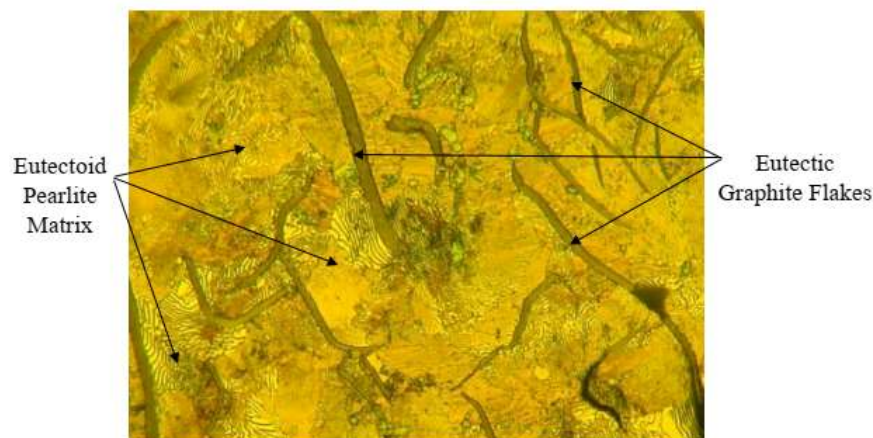


Figure 2.1. Light microscope image of gray iron after etching with Nital and 200X.

2.1.2 Spheroidal graphite iron

The cast iron family was given new life after the 1948 discovery of spheroidal graphite (SG) or ductile iron. As a cost-effective alternative for complex, powerful iron products, SG has achieved wide acceptance for combining the castability of grey iron with the toughness of steel. SG iron typically contains about 3.5–3.9% carbon and 1.8–2.8% silicon [19, 20]. The casting's size and the intended mechanical qualities influence the composition choice. Graphite does not precipitate as flakes as it does in grey iron but rather takes the shape of nodules or spherical in SG iron. Spher formation is influenced by the C and Si content but is not governed by it; rather, it results from the purity of the alloy and the inclusion of spheroidizing elements. However, (1) the Si and C content and (2) the cooling conditions control the quantity of graphite contained in the metallic phases [21]. Micro-image of SG-Si nodular cast iron and pearlitic-ferritic matrix, dark gray graphite nodules covered with a white ferritic phase in a SG iron matrix are referred to as "bull's eyes", nital etch, as shown in [Figure 2.2](#) [19, 22].

SG iron is utilized as a component of structure in a number of machineries for the mining and automotive sectors because of its superior mechanical qualities, including its resistance to fracture and separating, protection against abrasive wear, and impact resistance [20, 23]. These qualities are frequently produced by altering the microstructure to provide the proper combination of properties at a cheaper cost of manufacture [24]. As a result, steel and ductile iron are gradually competing for the same uses, like those needing balls and shells for grinding for use in ball mills for mineral processing and cement grinders [24-27]. Heat treatment is the primary method used to alter the surface's microscopic structure and bring about improvements to these characteristics.

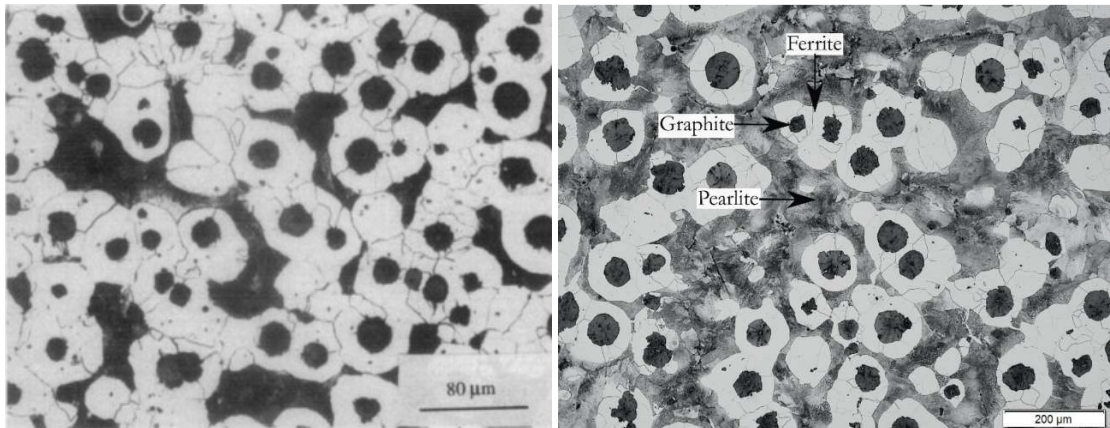


Figure 2.2. Optical microscope images of pearlitic-ferritic spherical graphite irons, etching by nital [19, 22].

2.1.3 High-chromium iron

White irons with high chromium content (Hi-Cr) are iron alloys with different concentrations of manganese, molybdenum, nickel, and copper, as well as 11-30% Cr and 1.8-3.6% C [28]. Chromium is present in all iron with high alloying metals to stabilize the carbide, hinder graphite development upon solidification, and produce chromium carbides, which are harder than iron carbides. In most cases, they also contain molybdenum, nickel, copper, or mixtures of those metals to avoid pearlite production in the structure [29].

ASTM A532-10 is the generally used standard approach for classifying this type of cast iron alloy (2014). The elemental composition, thermal removal rate within solidification, and cooling rate following solidification all influence the white iron microcomponent [30]. Typically, a eutectic compound and an austenitic dendrite form the chromium-rich cast ((Cr, Fe) carbide) at solidification end. During additional cooling, the eutectic compound's carbides do not change [31]. On the other hand, austenite, which is high in carbon-chromium and obtained from both dendrites and eutectics, is easily quenched and exhibits a high martensite start temperature (M_s) and finish temperature (M_f) throughout the metamorphism. Both the elemental content of the cast iron and the cooling

rate in the mold affect the changes that occur during cooling [30, 32, 33]. In their working form, Hi-Cr usually has a high volume fraction of carbides (10–30%) and a metallic matrix composed of varying proportions of austenite, secondary carbides, and martensite, depending on the heat treatment date. The mining and cement industries utilize materials with high carbide fractions because they offer greater hardness and, generally, greater wear resistance. Additionally, this iron is a strong cost competitor compared to other manufactured parts because it can produce complex parts (owing to the casting process)[30, 34, 35].

Figure 2.3 shows the microscopic characteristics of untreated chromium-rich casting (C = 4.52%, Cr =35%, Si = 0.4%, Mn =2.86%, P =0.06%, S = 0.012%) following glycerine etching using: 3 parts of glycerin + 2 parts of HCl acid + 1 part of HNO₃ acid by volume. Its etchant is widely employed for illustrating the microscopic structure of cast iron with high chromium content [36].

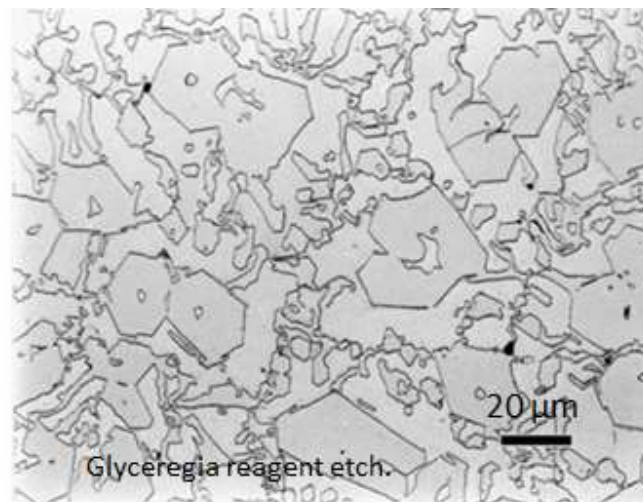


Figure 2.3. (Fe, Cr) carbides in high-chromium iron [36].

Due to noticeable work hardening during service, despite being partially soft, as-cast austenitic iron may perform excellently in several uses requiring wear due to abrasion. Irons with a completely austenitic matrix exhibit the highest resistance to crack propagation

[30]. The highest degree of peeling under repeated impact is provided by martensitic irons that have been properly tempered for reducing residual austenite. Pearlitic, morphologies of matrix are often undesirable due to their moderate toughness and modest abrasion resistance. When alloying is inadequate to prevent pearlite formation, it will always exist. Therefore, desired microstructure can be obtained by heat treatment.

2.1.3.1 Heat treatment

The ability to alter the exterior behavior and qualities of metallic materials and their alloys by making major changes to their microstructure is one of the most important applications of heat treatments [37, 38]. When it's required the parts be machined prior destabilization, Hi-Cr white cast iron alloys are annealed. This process creates a ductile matrix that solidifies with as much ferrite as possible, providing ideal machining conditions. A process known as austenite disintegration into ferrite and carbides occurs at temperatures between 700 and 750 °C [39]. It takes roughly 6 hours to achieve a complete transition of austenite into ferrite [40].

Destabilization is also done when less residual austenite needs to be present, which results in more martensite and increased hardness, as well as improved wear resistance. With a longer soaking period, this procedure is comparable to quenching steel. Because an outcome of the austenite instability, secondary carbides precipitate, raises M_s and M_f while lowering the volume of austenite remaining in the material [38, 39, 41].

The kind and characteristics (size, morphology, distribution, and orientation) of carbides have proven to affect the wear resistance, not only as regards the microstructure of the matrix but also with regard to its properties [42]. Growing the proportion of eutectic carbide in the alloy can increase wear resistance, although it decreases fracture toughness [43]. Therefore, it is better to keep the interior with high durability and then raise the surface resistance by surface treatment.

2.2 Wear mechanisms

During relative movement, a number of wear mechanisms can take place. Some of these mechanisms include adhesive wear, abrasive wear, erosive wear, delamination wear, fretting wear, fatigue wear, and corrosive or oxidative wear. The most frequent wear mechanisms for materials include adhesion, abrasion, fatigue, and corrosion or oxidative wear [44-46].

2.2.1 Adhesive wear

When two clean layers of metal are loaded and forced to move past each other, adhesive wear happens. The local pressure at the defects rises to an incredibly high level under normal pressure and often exceeds the value of the material's yield point. Plastic deformation begins to take place at the asperities once the true region in contact has expanded enough to meet the imposed load. Strong short-range forces begin to work as a result, so powerful adhesive connections may form directly at the point of contact. When there is relative motion, the connecting joints are sheared. The term "adhesive" refers specifically to the formation of strong metallic contacts between the asperities on the outer layers of the contacting materials. Sliding wear, which develops when one solid moves over another, is an illustration of this. Galling wear is a serious type of adhesive wear. When ridges and scratches appear in the direction of sliding, this is known as scoring or scuffing [45, 46].

2.2.2 Abrasive wear

When a hard, rough layer slides over something less hard, abrasive wear results. Sometimes hard particles trapped at the interface exert abrasive pressure on the surfaces they come into touch with, causing abrasive wear. Although both metallic and nonmetallic

particles have the potential to induce abrasive wear in materials, nonmetallic particles are more frequently to blame. Dynamic interactions among the surroundings and the surfaces of the mated substances are crucial throughout the wear process. When a solid particle is put onto the surface of a substance whose hardness is equivalent to or lower than the loading particle's hardness, this type of wear takes place [45, 46].

2.2.3 Corrosive wear

Surfaces develop reaction products at the bumps when in contact with a corrosive condition. Sliding interactions result in fractures and/or attrition, which wears down the reaction products. In actuality, corrosive effects or impacts occur when two surfaces of a substance lose reaction products through physical contact. Both corrosion and friction are therefore necessary for corrosive wear [44, 47].

2.2.4 Surface fatigue

Surface fatigue effect to materials that are subjected to cyclic loading. Ball bearings and gears, for instance, frequently experience fatigue wear as a result of the cyclic stresses present during their applications [44].

2.2.5 Wear mechanisms containing graphite

Graphite-containing cast iron wear mechanisms may experience failure during wear testing, causing the graphite to get damaged and detach from the wear path. Graphite crumbs function as a dry lubricant by minimizing friction and wear. One of the primary wear processes in the absence of a liquid lubricant has been identified as oxidative wear. The oxidation layer quickly rips during the sliding process as a result of its extreme brittleness. Additionally, some high-hardness oxidative abrasion remnants, such as Fe_2O_3 and FeO , can rip or even scrape the base material [48, 49].

2.2.6 Wear resistance of LG iron

Grey iron's most typical microstructure is composed of graphite lamellar in a pearlite base, sometimes with trace amount of ferrite. Gray iron's ductility and tensile strength are reduced to some extent due to the graphite flakes' interconnection, but the alloys still have good compressive strength as well as strong resistance to wear [50-52].

The excellent wear resistance of gray iron while dry sliding under low stress situations is due to the formation of a graphite coating on the contact surface. It is commonly accepted that a pearlitic matrix structure and an A-type graphite lammelar give the optimum resistance to wear for gray iron in motor cylinder bore uses [53, 54]. However, austempered grey iron has more resistant to wear than untreated gray iron in dry as well as wet environments [55].

2.2.7 Wear resistance of SG iron

Many investigators have evaluated the wear resistance of various SG iron types [56, 57]. By integrating the microstructural and mechanical characteristics, Sandikoglu and Gecu [58] conducted a thorough analysis of wear tests to investigate the impact of aluminum amount on the wear characteristics of SG irons.

In their study of the impact of nodule count (NC) on the sliding wear behavior of a ferritic-pearlitic spheroidal graphite iron (SG), Abedi et al. [59] discovered that at less applied loads, samples that have greater NCs wear more slowly than those that have minimal NCs, while at higher applied loads, wear resistance decreases as NCs increase. Sahin et al. [60] investigated the effects of martensite volume ratio (MVR) and tempering duration upon the abrasive wear of ferritic SG iron. The findings indicated that when MVR rose, ductility reduced and weight loss resistant and strength increased.

A novel technique was developed by Podgornik et al. [61] that increased the resistance to wear of SG iron while maintaining other qualities by local reinforcing with inserts. Conclusions of this experiment demonstrated that local surface reinforcing might greatly improve the tribological qualities of SG. Tricky transmission zone hems on the inserts were created by the development of carbides; this zone subsequently supported the load and increased the SG's wear resistance. It kept the friction minimal while doing so.

Using dry sliding wear settings, Du et al.'s research [62] discovered that the friction coefficient of ductile iron was around one-third that of typical LGCr15, a finding attributed to the presence of uniformly dispersed nodule graphite in SG iron.

2.2.8 Wear resistance of Hi-Cr iron

Advanced white cast iron research has encountered issues with toughness and tensile strength. According to Gasan and Erturk, the primary factors affecting the hardness and wear performance of Hi-Cr iron included the morphologies of secondary carbides, the crystallographic characteristics of the phases, as well as the proper proportion of martensite, austenite, and carbides [63]. One way to improve the toughness and resistance to wear of the Hi-Cr iron alloys is to convert the eutectic carbides in their structure to finer along with more spherical carbides. The alloying introduction of certain elements, like silicon and boron, which separate from the matrix or carbide in the interphase phase, additionally altered the microscopic makeup of eutectic carbide [39].

But Çöl et al.[64] showed that the toughness properties decrease with increasing boron amount. This case adds to the hardness as well as wear resistance of the material as the carbide content increases with the increase in boron. In this work (Çöl et al.), the

impacts of boron on the microstructural, mechanical characteristics, and wear resistance of Hi-Cr with various boron amounts were studied.

2.3 Corrosion

Natural corrosion transforms a polished metal into a more stable oxide. Metals frequently slowly degrade by interacting chemically or electrochemically with their surroundings. Corrosion is the term for the process by which environmental elements, such as moisture, acids, etc., attack a metal. There are various types of corrosion, including intergranular corrosion, stress corrosion, erosion corrosion, selective corrosion, and uniform corrosion. when a metal reacts with an additional substance, including oxygen, hydrogen, an electrical current, or even dirt and bacteria.

2.3.1 Corrosion resistance of LG iron

Seikh et al. [65] revealed that the austempered conditions showed better corrosion resistance when comparing the corrosion behavior of copper-added untreated and austempered lammelar graphite iron (ALG). They explained this to the presence of austenite that was left in the ALG microscopic structure.

2.3.2 Corrosion resistance of SG iron

Jeong and Kim [66] reported that spheroidal graphite cast iron showed typical graphitic corrosion in a 3% NaCl solution. The corrosion behavior of Si-Mo spheroidal graphite (SG) castings has been reported by Palumbo et al. [21] after various dive times in a 3.5% by weight NaCl medium by means of electro-chemical tests. According to the findings, Si-Mo SG's corrosion resistance was reduced. The findings revealed galvanic corrosion between the more noble carbide phases and the iron base in the SG samples evaluated. The SEM study revealed that as the ferrite phase dissolved, the pearlite phase

was exposed and accumulated on the SG surface, resulting in strong corrosion acceleration. The increased pearlite/carbide levels might be the cause of the higher corrosion rates seen in the specimens with thicker cast walls.

2.3.3 Corrosion resistance of Hi-Cr iron

Investigators [67-70] observed that Hi-Cr iron corrosion happened in the martensite or eutectic austenite. On the contrary, studies done by other investigators [71-73] reported that corrosion develops on carbides in contrast to austenite or martensite matrixes. Tsai et al. [74] performed corrosion studies on sintered 100% Cr_{23}C_6 using 0.1N NaOH in the temperature range of 275-325 °C. It was found that chromium carbides did dissolve. It can be concluded from these studies that the corrosion of either matrix or carbides occurs in an alkaline solution.

2.4 Summary

Finally, many cast iron castings used in industry have problems with abrasive wear [75]. In the abrasive process, part of the material surface is going to be lost, causing volume loss, and both the hard body along with the softer layer may fracture or become distorted. This scraping wear causes a slow loss of material on the component's surface. It must be done to fix or replace worn components in order to increase the affected machine's production productivity.

There are several techniques to raise the iron components' surface hardness, which will also increase the wear- and corrosion-resistance of the parts and reduce breakdown and maintenance costs. In order to promote the utilization of cast irons in engineering uses, numerous studies on the surface hardening of cast irons have been conducted in recent years.

There are many techniques for enhancing cast iron's resistance to abrasion. This includes mechanical procedures [75-77] and thermochemical treatments e.g., nitriding, carburizing, and boriding [78, 79]. They also comprise alloying, chilling, heating, and cooling utilizing induction, flame, laser, and electron beam methods. In contrast to coatings made by other thermochemical techniques (such nitriding or carburizing), boronizing coatings developed on medium- and low-alloyed steels have a finger-form characteristic.

One key benefit is that the constituent phases of boride layers have high melting temperatures and exceptionally elevated hardness values in the range of 1300 – 5,000 HV. If these cast irons are borided by the boriding process, their hardness, wear, and corrosion properties will improve on surfaces without affecting the toughness of the interior.

2.5 Boriding

2.5.1 Introduction

Besides having an elevated melting point and hardness, boron, boron carbide, boron nitride, and transition metal borides also exhibit great electrical conductivity, are resistant to assault from molten metals, and have exceptional wear and corrosion resistance. Thus, it seems like there is a lot of potential for improving the surface qualities of metals and ceramics by using coatings made of these substances [80].

Boronizing, also known as boriding, is a thermochemical treatment that changes the surface of metals like steel, iron, and nickel, as well as cast iron, to make them harder and more resistant to wear. It's similar to other techniques like carburization, nitro-carbization, and nitriding. Basically, it's a treatment where a small element with an atomic radius (like nitrogen or carbon) is injected into the metal to create a hard film. It does this by diffusing

the element through the metal lattice at high temperatures (around 973 to 1273 K) for 1 to 12 hours [81].

When it comes into contact with a solid or gaseous material made of boron, like a powder, paste, or liquid, boriding can happen. Other methods of boriding that have been developed in the last few years include gas and plasma boronizing as well as fluidized bed boronizing [82, 83].

Boriding can be performed using a variety of media. They are: pack, paste, electroless and electrolytic salt baths, plasma, gas, and salt bath [83].

2.5.2 Gaseous boriding

The procedure for gaseous bonding is easy. The principal component in gaseous boriding, diborane (B_2H_6), which is 10 times more toxic than cyanide, is also very expensive and requires complicated equipment.

2.5.3 Liquid or Salt boriding

A two-phase boride layer (FeB next to Fe_2B) forms, and large production is difficult. Most salt bath media are used in Eastern Europe; However, due to their harmful effects on the environment, they are not used as widely in Western Europe, North America, or Japan. Despite significant early development efforts in gas and plasma boriding in the 1980s, the pack boriding process is still the method of choice (circa 2015) [84].

2.5.4 Solid or pack boriding

Little equipment is required (case hardening box furnaces are suitable), boron sources are available, a single-phase boride layer (Fe_2B) is often generated during the brief, low-temperature process [85]. A Fe_2B /substrate structure is better for use in industries over a FeB/Fe_2B system because the physical and mechanical characteristics of the two layers

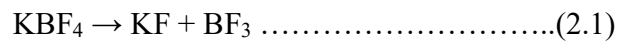
are different. This is due to the fact that the interruption in the stress caused by shear at the interface of FeB and Fe₂B identifies the site of shear damage under specific stress applications [86].

A typical solid agent pack contains 5% B₄C + 90% SiC + 5% KBF₄ (potassium fluoborate) (by weight). Powders for packs are usually milled and agglomerated. This considerably facilitates handling while generating less dust. Since B₄C is the primary source of boron, that breaks down when fluorine is created in the pack, SiC serves as a chemical mixer. The KBF₄ activator's role in the form of flux, which removes exterior oxide coatings that cover treated materials, is the cause of this. Although it is possible to use cryolite (Na₃AlF₆) as an alternative and less expensive activator phase, doing so is less practical because it melts or forms a sticky paste during the bonding step and then becomes cake-like when it re-solidifies (after being cooled to room temperature), making it very hard to remove the treated components.

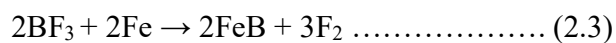
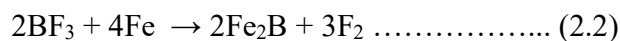
2.5.5 Pack boriding mechanism of boron mass transfer

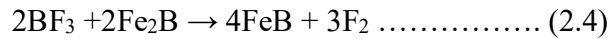
Several probable reactions are proposed as explanations for the process of boron mass being transferred during the pack boriding on steels. **Start** and **development** are the first two phases in boriding, which is typical to most coating establishing methods:

Start: According to Equation 2.1, the KBF₄ activator first starts to break down at a temperature of 700 °C:



Iron borides are produced when the released BF₃ is reduced at the steel surfaces:



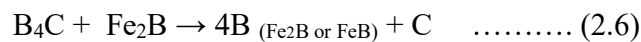


At increasing time and in a parabolic pattern, boron diffuses into steel (from the iron boride layers) [83]. In agreement with Eq. 2.6, was used. Moreover, the gaseous fluorine by-product produced by Equations 2.2 to 2.4 produces additional BF_3 :



The latter BF_3 then takes part in Equations 2.2, 2.3, and 2.4. This iron boride, sometimes referred to as "seed," is needed to maintain the boron layer development going. There is no longer a need for activator (KBF_4) after the "seed" has formed.

Development: When B_4C (found within a boronizing powder) as well as the iron boronized coating over film react, iron boride layer will grow in the way described below:



Once the elementary boron spreads within it, that boron layer gets thicker. The blend for boronizing agents' boron content influences the boride layer's constitution. If the steel's exterior has an elevated boron content (which indicates a high concentration of B_4C in the boriding agent), FeB is going to grow and develop over top of the Fe_2B layer; otherwise, Fe_2B makes up the bulk of the boride coating. Because Fe_2B is the desired layer, SiC has been included to the boronizing mixture to reduce the action of boron near the surface. SiC is referred to as a "diluting" agent as a result [83, 87]. Steel is also borided to increase its ability to withstand dry abrasive wear and to resist mineral acid and molten metal corrosion (especially zinc and aluminum) [80, 88].

2.5.6 Boride layer formation on Material

The formation of the dual-phase structure is seen in [Figure 2.4](#) [89]. Fe_2B nucleation starts initially once the substrate comes into touch with the boron source. Most of the time,

the ratios of Fe and B are not suitable for the prolonged production of the Fe_2B layer. Due to the active boron's tendency to collect in the Fe_2B layer's topmost area, the boron concentration is often lower. This series of events indicates that FeB is often present on the surface of carbon steels that are borided at extreme temperatures and for prolonged periods of time. As a result, the chemical makeup of the substrate, the boron possibility of the boron source, the temperature, and the process duration all affect the thickness as well as the nature of the boride film. So, the form, development, and structure of the phase of the boronized coating are affected by any alloying components found on the base material that may impede the boride diffusing treatment [90].

The layer is not of uniform thickness, as shown in Figure 2.4 [91]. Furthermore, Figure 2.4 shows the fingers-like structure of the boronized coatings.

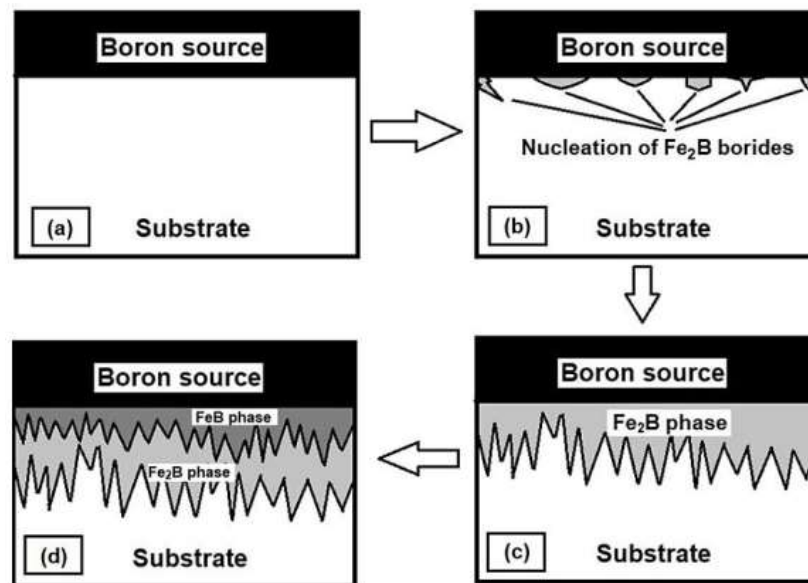


Figure 2.4. Sketch of the formation of an iron boride layer showing the first stage of the process as (a), the second stage, the beginning of the iron boride nucleation as (b), the Fe_2B consolidation of the iron boride phase as (c), and the final stage as (d) the formation of the iron boride FeB phase on the material's surface [89].

In the case of boridized AISI 1018 steels, the sawtooth-shaped structure of FeB and Fe₂B layers and the columnar interface between layer and substrate are illustrated in [Figure 2.5](#).[\[92\]](#).

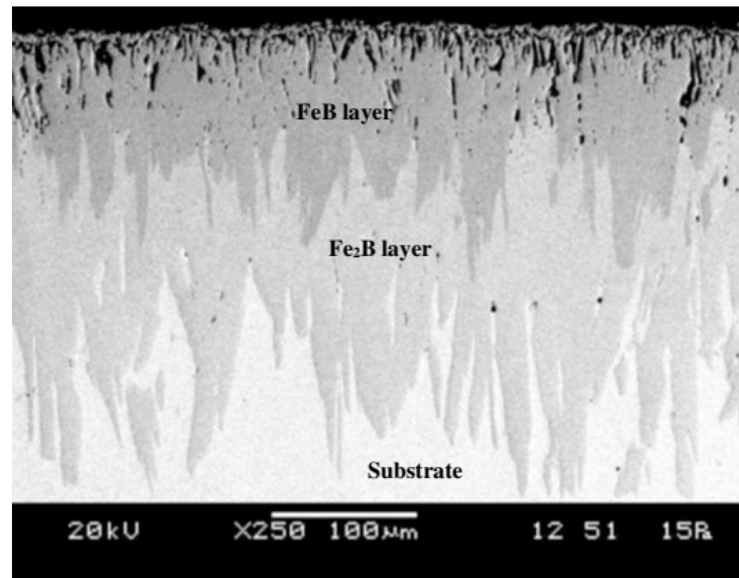


Figure 2.5. A cross-section SEM image of low-carbon steel boronizing at 1000 °C for 6 hours [\[92\]](#).

[Figure 2.6](#) illustrates the smooth microscopic structure of the FeB /Fe₂B coatings forming on the surface of the AISI M2 boridized steel [\[93\]](#).

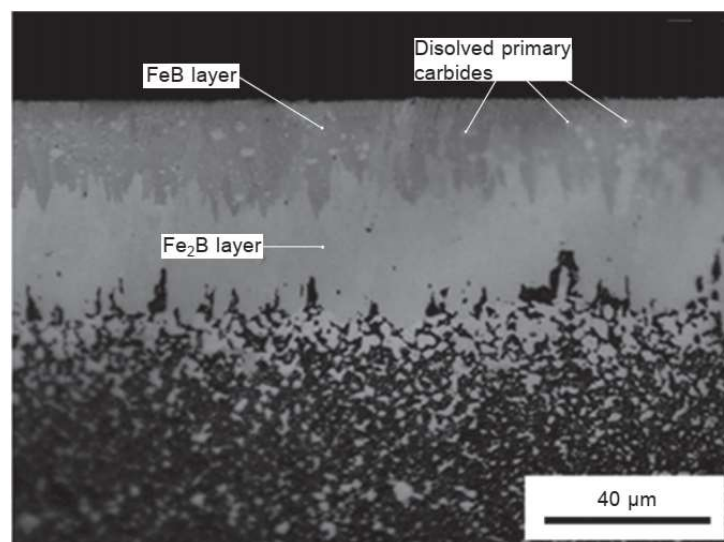


Figure 2.6. High-Alloy M2 boronizing at 1223 K - 6 hours [\[93\]](#).

Figure 2.7 illustrates the cracks in the FeB / Fe₂B layer on the AISI H 13 steel [82].

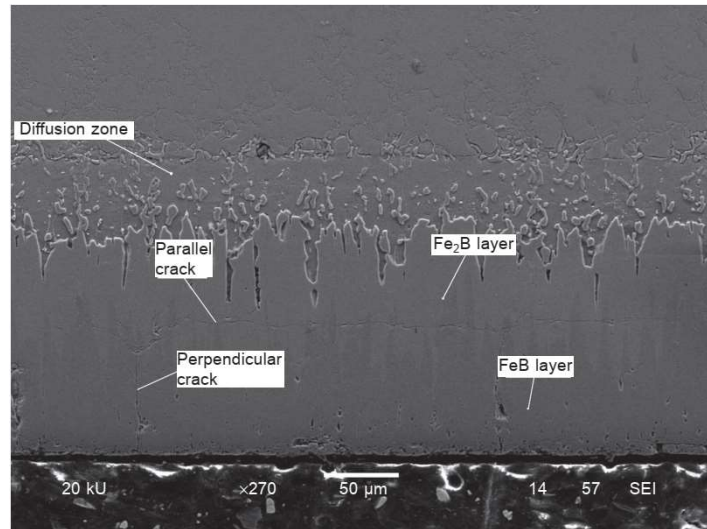


Figure 2.7 shows cracks that appear at the FeB/Fe₂B interface made by AISI H-13 [82].

Figures 2.8 shows the basic structure and the boride layer of cast iron [5]. The microscopic image of boridized high Cr iron is shown in Figure 2.9. The etched surface is formed on the high chrome iron by the boridization process at a temperature of 950 °C over a period of 8 hours. The surface is compact and smooth, and there is no transition zone [94].

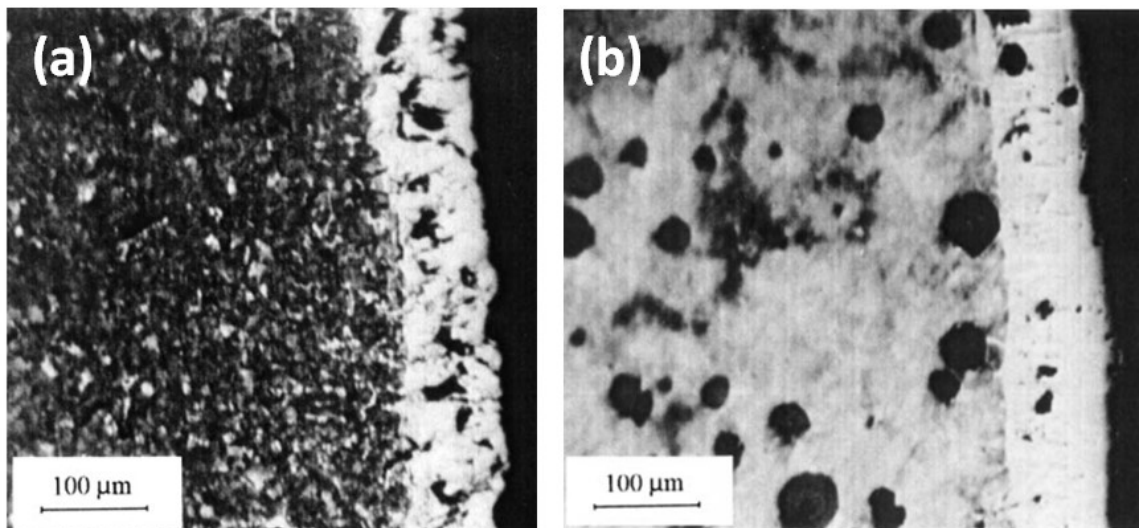


Figure 2.8. Cross-sectional view on the (a) lammellar; (b) spheroidal graphite iron boridized at 950 °C for 4 hours.

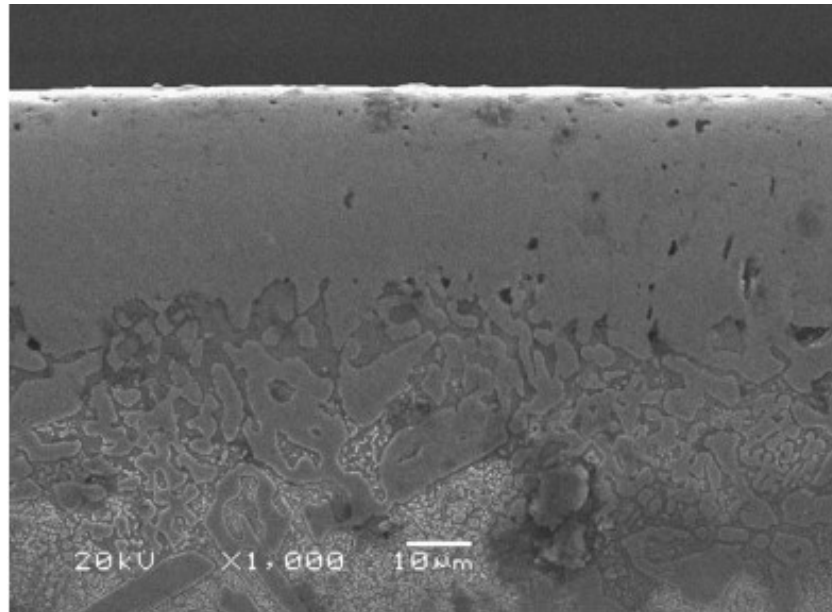


Figure 2.9. High chromium cast with a boride layer that is boridized at a temperature of 950 °C for a period of 8 hours [94].

2.5.7 Features of the boronized coating

The distinct finger-like shape of the boronized coating may be seen in all forms of steel, including low alloy, pure iron, and low-carbon steel. The depth of the boronized film decreases with an increase in the alloying components as well as carbon percentage of the base steel. Moreover, the finger-like form is replaced with the interface's smoothness. With a handful of cobalt, manganese, and nickel that slow down the penetration of boron in the base material [80], elements that alloy can enhance the proportion of FeB content. For instance, alloying components are what create the thin, flat interface of the boride layer's nearly complete FeB component in borided stainless steel.

2.5.8 The advantages of boriding:

1. Between 1450 and 5000 HV, boridized surfaces have extraordinarily high hardness estimates as well as their constituent phases have high melting temperatures.
2. The borided layer's high surface hardness and low surface friction (Friction Coefficient) significantly reduces the main wear mechanisms (Adhesion, Tribo-Oxidation, Abrasion, Surface Fatigue) [1].
3. In contrast to, say, nitride cases, the boride layer's hardness can be maintained at greater temperatures.
4. Several steels, including those that can be through-hardened, are compatibles with boriding technique.
5. Boriding is increasingly employed for this benefit in many industrial applications because it may significantly increase resistance to corrosion and/or erosion in non-oxidizing dilute acids and alkali mediums [1].
6. Borided layer has a high degree of resistance to corrosion by molten metals and a moderate degree of resistance to oxidation (up to 1123 K or 1550°F).
7. In oxidizing and corrosive situations, the fatigue life and service performance of borided parts are improved.
8. Boriding improves low-alloy steel's corrosion resistance to corrosive mediums like sulphur, phosphoric and hydrochloric acid. Borided austenite stainless steels have superior HCl acid resistance. [95].

2.5.9 Boriding vs. Nitriding

To enhance mechanical qualities and resistance to wear, thermochemical diffusion procedures like boriding and nitriding are used. As the name suggests, boriding uses boron, and nitriding uses nitrogen. While boriding can increase the hardness of the material up to 2600 HV, nitriding can only reach 950 HV for certain steel grades. Nitriding is most effective in nitriding steels while boriding is also applied to nickel containing steel grades, nickel super alloys and cobalt super alloys. Boriding and nitriding are not coatings but diffusion treatments. As a result, both treatments are much more durable and can better protect the material. They will not peel or chip like some coatings do.

2.5.10 Boride layer on cast irons

Due to a requirement to improve pure metals as well as alloyed metals in order to improve wear characteristics, corrosion, and high-temperature features, the qualities of boron-borided materials have been intensively investigated.

The Kinetics of Gray Cast Iron (Class 30) have been studied and found that it has an activation energy of 175 KJ/mol, which is pretty high [96]. Cakir & Akcay also found that the mechanical efficiency of Grey Cast Iron cylinder liners was increased by about 6% when borided [97]. Sahin et al. [18] and Meric et al. [5] studied grey iron, nodular iron, and compacted graphite iron. They compared coating hardness, abrasive wear, and coating thickness.

Sen et al.'s [98] study of the borided ductile iron revealed that boride layer was composed of layers of FeB and Fe₂B borides and that globular graphite and Si-rich ferrite

were present on the layer interface. The layer's thickness ranged from 114 to 185 μm , its hardness ranged from 1160 to 1440 HV, and its fracture toughness ranged from 2.19 to 4.47 $\text{MPa}\cdot\text{m}^{0.5}$ [99]. Moreover, a single Fe_2B was seen, the thickness was thinner, and graphite was not observed on the layer interface as the concentration of copper increased [100]. Besides that, the kinetics of borided SG iron were investigated [101, 102]. Toktaş and Korkmaz [103] found that in unalloyed ductile iron, the boronizing process led to higher rates of increased surface hardness and under the same boronizing conditions, alloyed iron creates layers of boride that are thicker. The fracture toughness rose for the two kinds of cast iron based on the boronizing period at 900 °C and reduced at 950 °C.

Investigations on high-chrome iron (Cr12Mn2V2) revealed the characteristics: Fe_2B , FeB , and CrB were created; thickness ranged from 8 to 33 μm ; fracture toughness was 2.85 to 4.18 $\text{MPa m}^{0.5}$; and wear resistance as relative ranged from 1.58 to 13.70 [94].

2.6 Summary

However, due to their rapid expansion, these industries must modify the components they use to satisfy their more demanding operating environments. They also need to be protected against performance deterioration if they're going to achieve and keep up high effectiveness and great function. Through surface modification treatments, it is becoming more important to improve surface properties like corrosion resistance, wear resistance, and fatigue strength [104]. Gas and salt nitriding, carburizing, and nitrocarburizing processes were used to achieve this goal, strengthening the regions that high-frequency heat from induction and heating using laser were unable to reach.

Unfortunately, these procedures have resulted in serious environmental pollution problems and the production of brittle nitrides. Despite being widely used, the surface layer properties of the recently developed plasma ion nitriding suffer as a result of the exposed graphite on the cast iron's surface [105, 106].

The topography evolution after nitriding is significantly influenced by graphite on surfaces, with a Sq rise of 0.13-0.53 μm for grey iron and 0.09-0.31 μm for ductile iron [105]. Baranowska [106] noted that after nitriding lamellar graphite iron, a sharp decrease in surface quality is observed, and the Ra increases by 10 times. Iron boride layers are inferior to nitrided or carburized steel surfaces; they lack the toughness needed to meet the demands imposed by the high contact loads in tough bearing and gear applications [107].

A surface treatment is being tested as a solution to this problem. An example of such a treatment is a boriding surface treatment that combines the processes of in-pack boriding. Currently, a lot of attention is paid to this topic. Field tests on boronized components show a service life that is many times longer in aggressive environments compared to other thermal processes like carburization, nitriding, nitro-carburization, and neutral hardening [85]. Due to the properties of borided samples: (1) abrasive or adhesive has been proven to extend service life by more than 25%. (2) It also has great resistance to high temperature wear, up to 650°C, and oxidation up to 1000°C. (3) Plus, it increases corrosion resistance by 200%, (4) fatigue strength by 25%, and ultimate and yield strength by 10-20% [81, 88, 107].

Moreover, the key wear processes of adhesion, tribo-oxidation, scraping, and surface fatigue are all significantly reduced by the boriding layer's mix of excellent surface

hardness with a small surface friction coefficient. Due to this characteristic, steels that are simpler to machine but nevertheless possess wear resistance and anti-galling capabilities can be used in place of the base metal in molds, superior to those of the original material [1, 92, 108].

Graphite or carbide, which plays the cathode in cast iron, accelerates the anode dissolution of nearby iron, leaving just the graphite structure of the network as a result of the issue with graphite corroding [66, 109] and high-chrome iron corroding in the austenite or martensite matrix [67-70]. However, other researchers' experiments [71-73] revealed that corrosion develops more often upon carbides than on the matrix (austenite or martensite matrix). These observations lead to the conclusion that both the matrix and the carbides corrode. However, it has not been studied thoroughly enough to address this issue.

After all, it will be more cost-effective to use a material with lower wear resistance and replace it more frequently. Service life can often take precedence over profitability, for example, when downtime is very common.

In order to enhance the performance of cast irons, this study examined the viability of applying surface treatment (such as inexpensive chemical boriding) to ferrous materials. Advanced methods and analyses were applied, including as adhesion, wear, and corrosion testing, microhardness measures, SEM, and XRD.

CHAPTER 3

3. EXPERIMENTAL

In order to achieve the research aims, this chapter details the substances and testing techniques utilized or created in this study.

3.1 Materials

3.1.1 Cast irons (substrates)

In this work, we chose cast irons made of lammelar graphite (LG), sheriodal graphite (SG), and high-chrome (Hi-Cr) that are commonly applied in minerals processing, mining, cement, and car engine pices. The chemical content of these cast irons was analyzed by spectrometry and shown in [Table 3.1](#) [110].

Table 3.1. Shows the total weight of chemicals in the chosen cast irons.

Iron	C	Si	Cr	Mn	Mo	Co	Cu	Ni	Al	Mg	S	P	Fe
LG	3.42	1.97	0.15	0.34	0.027	0.008	0.22	0.083	0.001	0.001	0.128	0.128	Bal.
SG	3.58	2.69	0.021	0.07	-	-	0.049	-	0.02	0.05	0.013	0.017	Bal.
Hi-Cr	2.31	0.87	12.7	0.77	0.02	0.012	0.137	0.27	0.002	0.008	0.033	0.073	Bal.

3.1.1.1 Lamellar Graphite cast iron

The LG substrate is approximately equivalent to ASTM A48. Micrographs revealed iron phosphate and graphite flakes embedded in a matrix of pearlite (see [Figure 4.1b](#)), with a mean hardness of 288 HV_{0.1}.

3.1.1.2 Spheroidal graphite cast iron

For SG iron class 60-40-15 (ASTM A536), the area ratio in metallography image is 90% ferrite and 10% pearlite, as shown in [Figure 4.2](#). The tensile strength is 441 MPa; the yield strength is 312 MPa; the surface hardness is 176 HV_{0.1}.

3.1.1.3 high-chrome iron

Hi-Cr substrate is very similar to class A, type A, according to ASTM A 532. It was first annealed at a temperature of 1000 °C for 3 hours, then cooled in the furnace. The Hi-Cr micrograph shows it's made up of M₇C₃, ferrite and a pearlite matrix with some fine dispersed carbides, as illustrated in [Figure 4.3](#). The matrix has a micro hardness of 331 HV_{0.1}.

3.1.2 Stainless Steel Grade 304L

Steel 304L is a go-to material for boriding boxes and cases due to it's easy to come by, cost-effective, and has great machining and weldability. Plus, it's super stable at high temperatures, and it's got lots of other great features like corrosion and oxidation resistance. The chemical composition of SS 304L is provided in [Table 3.2](#).

Table 3.2. The chemical content of SS 304L

Material	C	Si	Mn	Cr	Mo	Co	Ni	Cu	Al	Mg	P	S	Fe
SS 304L	0.036	0.38	1.82	18.5	0.087	0.069	9.75	0.109	0.004	0.01	0.036	0.014	68.97

3.1.3 Boriding agent

Recycled boronizing powder (RBP) was created as a boronizing powder in solid packaging that is made from the agent (5%B₄C+ 5%KBF₄+ 90%SiC) after a single application at a temperature of 1000 °C for a period of 8 hours.

Chemical evaluation of RBP was done with energy-dispersive X-ray assessment (EDX), along with its average overall makeup was 34.57% C, 50.95% Si, 8.48% O, 4.97% F, and 1.04%K, yet the newly formed B₄C (~B_{0.5}C) parts (BC₂) were having a chemical composition of 22.5% B; subsequently, the %B in the recycled powder is 1.11 (5% x 22.5) [110], as shown in [Figure 3.1](#).

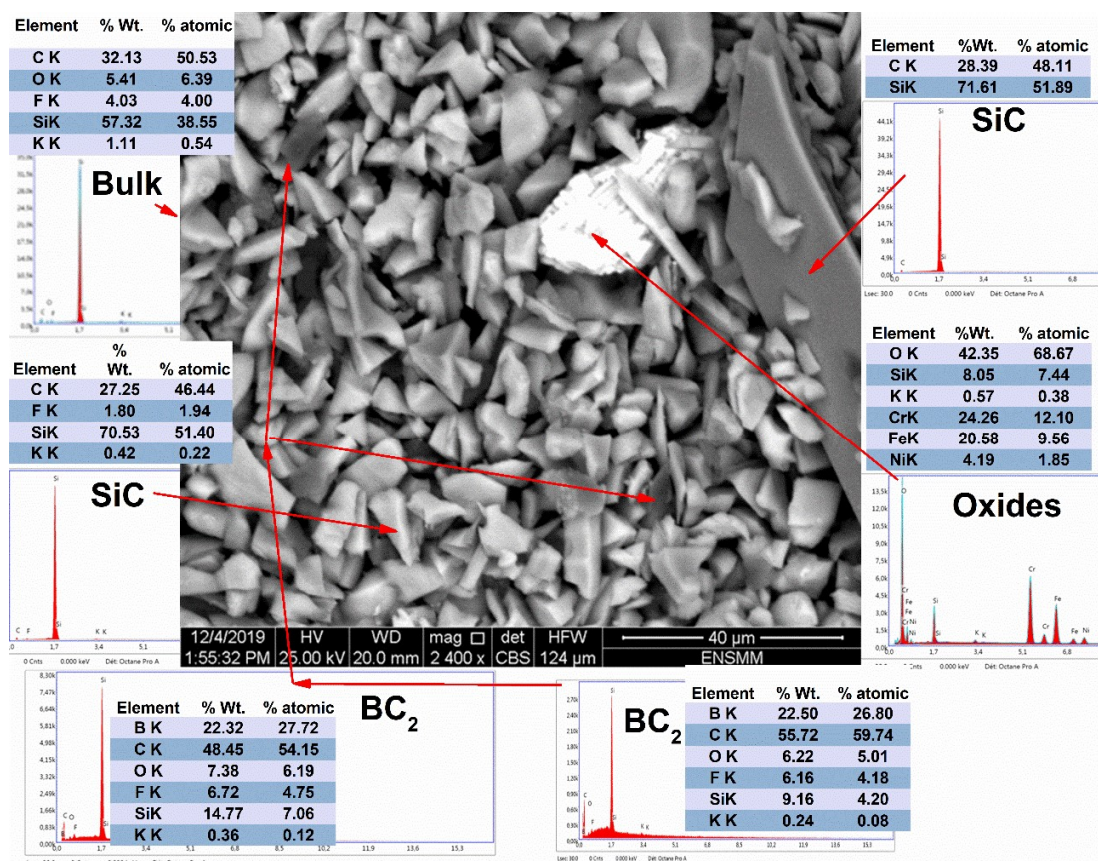


Figure 3.1. SEM microstructure and EDX analysis of recycled boriding agent.

3.2 Methodology

3.2.1 Preparation and Boriding process

The cast iron substrates were borided using the powder pack boriding treatment. By coating the substrate surface in the powdered boriding environment then being heated it at a temperature of 950 °C for a period of four hours in a furnace. Prior to boriding, these specimens were polished to P1200 SiC paper, washed with an ultrasonic instrument in alcohol for 7 minutes, and dried. The specimens were enclosed in a stainless steel case, sealed cylindrical box that also contained RBP powder. The case was placed in a resistance furnace, not an inert gas furnace. After the procedure was finished, the container was taken out of the furnace and allowed to gradually cool to room temperature.

3.2.2 Adhesion test

The adherence of the coated layer can be evaluated using the interfacial micro-indentation fracture toughness examination, the scratch assessment, and the Rockwell-C indentation testing. For coating/substrate mechanisms, the Rockwell-C adherence evaluation is employed as a quick, trustworthy, economical, and destructive quality analysis. It damages the layers close to the indentation's edge [82, 111].

During the present investigation, Rockwell-C marks featuring an approximate tip radius of 200 µm and a force of 150 kg (1471N) were used to assess the adhesion of borided cast alloys. Every specimen underwent four indentations, and it was assessed using SEM.

The VDI specification 3198 calls for the popular Rockwell C indentation assessment as a destructive quality testing for coated materials [112, 113]. The basic concept is illustrated in the upper right section of [Figure 3.2](#).

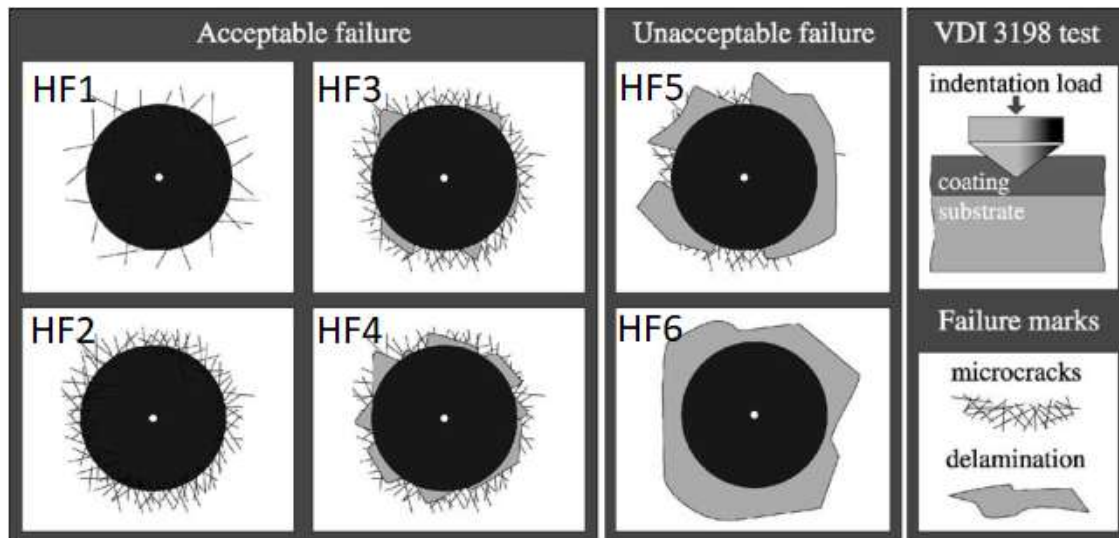


Figure 3.2. The basic concept of the VDI 3198 testing.

3.2.3 Tribology test

For wear tests, lamellar graphite and Hi-Cr rods were used to make specimens measuring 26-12 x 7 mm, whereas spherical graphite cast iron block specimens measuring 10x10x10 mm were used. WC balls about a 6 mm diameter were used as the pin in the CSM devices tribometer ball-on-disk tester to conduct the wear testing under dry sliding situations is presented in [Figure 2.3](#).

Wear testing was conducted on non-borided and borided cast iron specimens with no prior polishing as well as on borided specimens which were polished before being tested. Polishing of the borided SG specimens was carried out with SiC emery paper P4000-grit size for 10-15 seconds only. A load transducer was used to continuously monitor the friction load. The same tribology test parameters were used for all specimens: 30.18 min sliding time, 100 m sliding distance, sliding speed 5.5 cm/s, normal force 10 N, room temperature, relative humidity around 40%.



Figure 3.3. Photograph of tribology experiment device.

The tribology property was evaluated by determining the wear rate according to Equation 3.4. In all cases, 2-3 experiments were carried out to ensure reproducibility. Wear track widths were determined using a light microscope, and the wear regions were measured by scanning electronic metallography as well as an optical 3D profilometer (model CT100).

$$K1 = \frac{V}{FS} = \frac{2 \pi R \left(r^2 \arcsin\left(\frac{w}{2r}\right) - \left(\frac{wL}{4}\right)(4r^2 - w^2)^{0.5} \right)}{FS} \quad \dots\dots\dots (3.1)$$

Another method to calculate wear rate, the wear track pictures were evaluated in the 3-D profilometer apparatus following the wear testing. The amount of volume loss and particular wear rate measurements were computed using the calculations following after taking an average of the track profile regions determined by a minimum of 3 separate spots in the track picture using the 3-D Profilometer program, as shown in Figure 3.4.

$$V = L A \quad \dots\dots\dots (3.2)$$

$$K2 = \frac{V}{FS} \quad \dots\dots\dots (3.3)$$

Where w represents the wear track width (mm); R represents the radius of the wear scar (mm); and r represents the radius of the WC sphere (mm); K_1 or K_2 represents the particular wear rate ($\text{mm}^3/\text{N m}$); V represents the wear loss of volume (mm^3) by ASTM G99-95a; L represents the length of the track (mm); A represents the average wear track cross-section area (mm^2); F represents the usual force (N); S represents the sliding distance (mm).

$$\text{The final specific wear rate} = (k_1 + k_2) / 2 \dots\dots\dots(3.4)$$

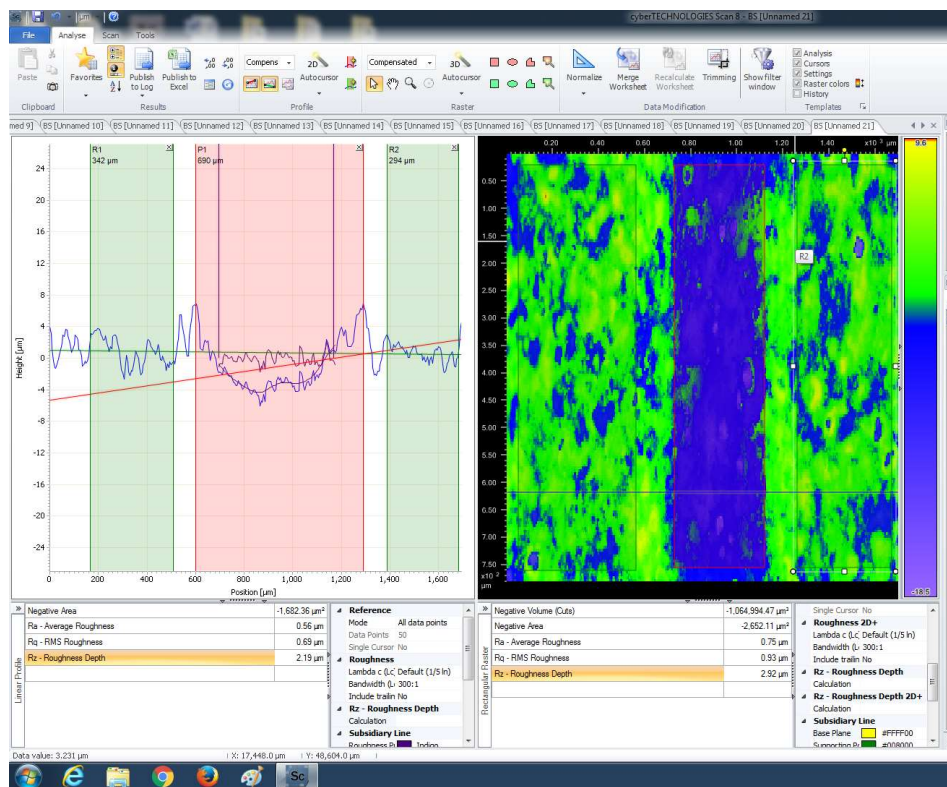


Figure 3.4. Using 3D profilometry computer programs, determine the cross-sectional dimension of the wear track pattern.

3.2.4 Corrosion test

The 1x1 cm² or more or less square samples intended for electrochemical characterization are connected to a conductive copper cables covered in a resin covering, leaving only about a 1 cm² sample (working) section free (Figure 3.5).

The corrosion examination was carried out using a Gamry REF600P-42075 potentiostat (Figure 3.6), an open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and the polarization method (Tafel). 3.5 weight percent of sodium chloride (NaCl) was used for OCP, EIS, and Tafel tests in a typical three-electrode cell during room temperature. The reference and counter electrodes were a platinum grid and an Ag/AgCl (3 M KCl) electrode. The functioning electrode was made from the specimens.

In the first step, an OCP was used for 3600 seconds. In the second step, EIS tests were done at a wide frequency range between 100,000 Hz and 0.01 Hz with a sinusoidal voltage of 5 mV. In the third step, the potential was increased by ± 0.25 V in comparison to the open circuit's potential at a speed of 0.5 mV/s in the Tafel curve. The corrosion rates of the specimens are determined by applying Eq. 3.5:

$$\text{Corrosion rate (mpy)} = 0.13 \times I_{\text{corr}} \times (\text{E.W.}) / D \dots\dots\dots (3.5)$$

I_{corr} represents the corrosion current density ($\mu\text{A}/\text{cm}^2$), E.W. represents the working electrode's equivalent weight, D represents the working electrode's density (gr/cm^3), and A represents the working electrode area (cm^2).

Gamry Echem Analyst edition 7.8.1 was used to evaluate the OCP, EIS, and Tafel graph information that was acquired for each of the test specimens utilizing the Gamry Framework edition 7.8.1.

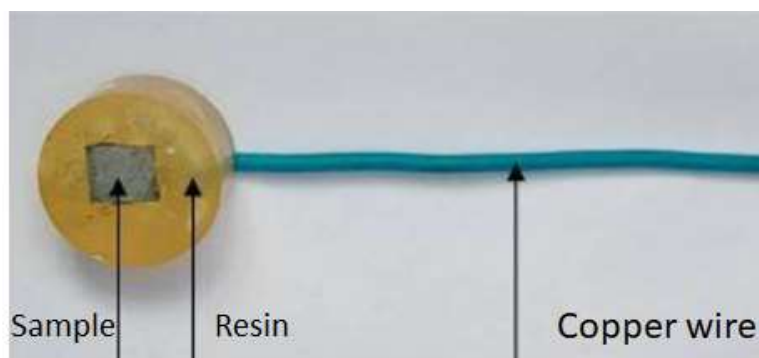


Figure 3.5. Diagram of the embedded sample depicting the working electrode.



Figure 3.6. Potentiostat-Galvanostat Gamry Reference 600+ is used for electrochemical testing.

3.3 Identification Methods

The cast iron, borided, and corroded specimens as well as the specimens after wear and adhesion tests were all analyzed using various identification methods. There is a list of software and equipment needed for these procedures.

Optical emission spectrometry was used to identify the chemical content of the substrate samples as well as the stainless steel box.

Using an Optical and a Quanta 250 scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) analysis, the polished samples were examined for boride coating thicknesses and structure after being cross-sectioned and resin-embedded according with conventional metallographic preparation.

EDX was used to determine the distribution of elements of alloying in the cross-sectioned boride layer (from the surface to matrix) as well as top surfaces before and after corrosion testing.

The specimens were subjected to X-ray Diffraction (XRD) examinations using a diffractometer (Bruker D8 Advance Model) with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and 2θ was ranged from 20° to 90° .

The specimens—untreated and borided—were produced by cutting, grinding and polishing by $3 \text{ }\mu\text{m}$ alumina paste as finish and acetone cleaning. After that, the samples were etched for 10 seconds using a 2 to 3% Nital liquid. At various magnifications, the microstructures were examined using a Nikon Eclipse Lvison optical microscope (OM) coupled with a Nikon DS-Fi2 camera.

Using a Vickers indentation (INNOVATEST-412D20130601) with 100 or 200 g loads for a max. retention period of 15 s, the cross-sections of boronized cast irons and untreated cast iron substrates were subjected to micro-hardness evaluations.

In order to evaluate the roughness, topography, track area, and 3D photographs, an optical profilometer (model CT100) was used.

CHAPTER 4

4. RESULTS AND DISCUSSION

Surface treatments, which alter the microscopic structure and chemical nature of the material, are frequently used to adjust the material's qualities so that they fulfill the important mechanical, wear, corrosion resistance, and heat demands of the goal usage.

Cast irons are composites made of metal matrix that have a number of distinctive properties that make them valuable in a wide range of applications in a variety of sectors, including the cement, mining, cars, and mining industries. The mining and automotive industries both rely heavily on machinery, and routine maintenance is necessary to maintain safety requirements and replace worn-out parts. Repairing the component damage will drastically lower the cost of replacing the component. If these cast irons are borided, their hardness, wear, and corrosion properties will improve. As shown by the following results.

This is why this chapter is devoted to the characteristics of cast iron, including lamellar and spherical graphite and austenitized high-chromium (Hi-Cr). This chapter also covers microstructure, XRD, hardness, adhesion, friction, corrosion, and wear behaviors of boriding and non-boriding cast irons.

4.1 Characterization of cast iron substrates

Cast iron is utilized in a variety of industries, including mining, mineral extraction, cement production, and automotive engine components, and it has contributed significantly to the evolution of the human civilization. For the boriding process in this work, various cast irons, including pearlitic-ferritic lamellar (LG) and ferritic spherical graphite (SG), as well as austenitized high-chrome (Hi-Cr), were chosen.

4.1.1 Lamellar graphite (LG) cast iron

The microscopic structure of lamellar graphite (LG) is pearlitic, with most free carbon forming flakes, as shown in [Figure 4.1](#). The LCI examined in this study was found to have a carbon content of approximately 4.35 wt%, indicating a composition that is close to that of eutectics. This phrase is used to predict if a cast iron concentration will solidify in a hyper- or hypo-eutectic option, depending on whether solidification will start above or below the eutectic concentration (4.3% C) on the phase diagram of iron-carbon [114].

Initially, the flake-shaped graphite in [Figure 4.1\(a\)](#) was randomly spread over the entire non-etched surface. The ASTM (A247-67) specification for flake-shaped graphite distribution of type A and V (starlike graphite) may be confirmed, and the matrix's hardness was determined to be 258-331 HV0.1 (~24-34 HRC). Compared to nodular graphite cast iron, this LCI has lower tensile strength and hardness yet superior castability, heat conductivity, and properties of vibration dampening. In particular, graphite's high surface area ratio as well as a type A lamellar-formed graphite dispersion have been linked to its optimum vibration dampening capacity [115, 116].

In [Figure 4.1\(b\)](#), which also displays the characteristic flake-shaped graphite and pearlite, speckled white regions represent a phosphide eutectic (or Steadite) of LCI following etching. The dimensions, volume, and distribution of lamellar-formed graphite have an impact on the mechanical and physical characteristics of LCI [117]. Instead of a higher area ratio, longer lamellar-formed graphite or its stronger continuity are associated with greater vibration dampening capacity [118]. Due to α -Fe and Fe_3C are arranged in a different plane, the pearlite matrix exhibits comparatively high strength and hardness as a eutectoid transformation product [36, 115, 116].

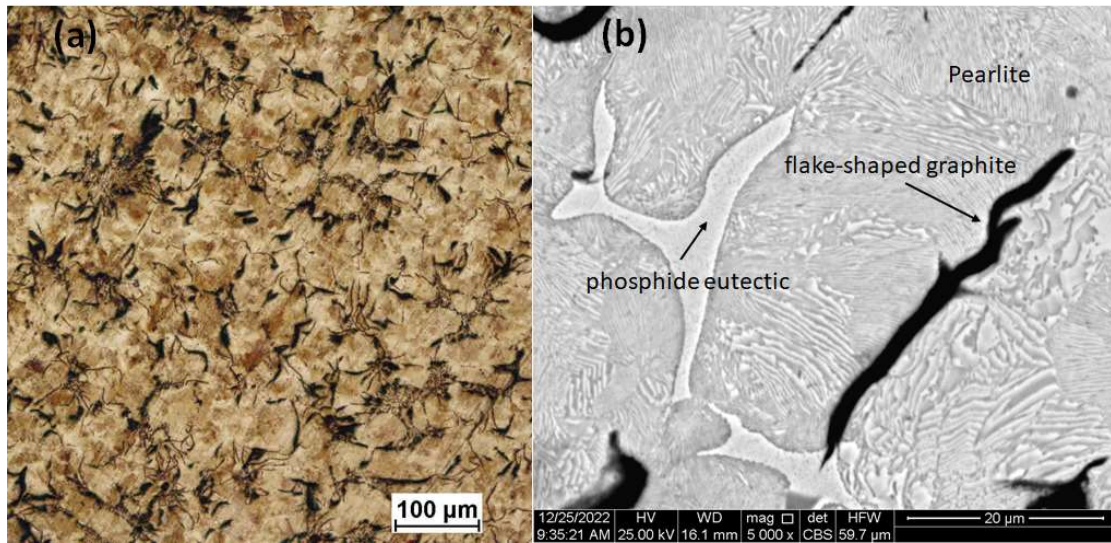


Figure 4.1. Microstructures of the original lamellar graphite cast; (a) OM; (b) SEM.

Steadite is only created when casting LCI with 0.06% or greater phosphorus, and its chemical composition is 10.2% P and 89.8% Fe [36, 119]. In our study, the LCI utilized had an approximate phosphorus content of 0.137% (Table 3.1), the steadite or iron phosphide (white component) of a cellular phosphide structure is recognized on the surface due to the frequently occurs surrounding the eutectic cell plus dendrite if the percentage of phosphorus exceeds 0.4% or higher. By using EDX analysis to determine that the iron phosphide in the LG contained 7.41% phosphorus, it is the presence of the steadite that contributes to this increase in LCI hardness and improves wear resistance, the hard eutectic phosphide may be the reason for this.

The phosphide eutectic has a microhardness of 486 HV [119]. But a high phosphorus content reduces the mechanical characteristics of LCI because iron phosphide becomes cracked and forms at borders of grains., including its impact and tensile strength [119, 120]. Although the LCI in this study has the appropriate P content, the locally generated brittle steadite can act as an area that preferentially generates pitting damage

during wear attack [121]. The XRD patterns (Figure 4.4 a) confirmed the existence of α -Fe as well as cementite (Fe_3C) on the matrix and Fe_4P in the as-cast structure of the LGCI sample.

4.1.2 Spheroidal graphite (SG) iron

Spheroidal graphite (SG) iron in the as-cast state, class 60-40-15 (ASTM A536). Figure 4.2 displays the OM images of SG in its original state. Graphite spheroid that has 0.0287 mm mean diameter was consistently dispersed throughout the matrix. Graphite spheroids were projected to account for around 15.3% of the total volume (Figure 4.2(a)). The as-cast SG iron's OM picture revealed that the matrix was 90% ferrite and 10% pearlite. 312 MPa, 441MPa, and 176 HV0.1, respectively, are the yield strength, tensile strength, and hardness of the sample. XRD patterns (Figure 4.4 b) confirmed the presence of ferrite (α -Fe) in the as-cast structure of the SGCI sample.

In many applications, forged steel and cast as well as malleable iron are successfully replaced by the family of spheroidal graphite cast irons (SGCIs), which span a broad array of mechanical characteristics (for example, gears, wheels, and crankshafts in automobiles and trucks, and more) [122].

Ferritic SGCIs have the same tensile strengths as low-carbon steel and exhibit good ductility. Although hardness and wear resistance are decreased, machinability is improved with a ferritic matrix. More mechanical strength is provided by pearlitic matrix, although machinability is decreased [20, 123, 124].

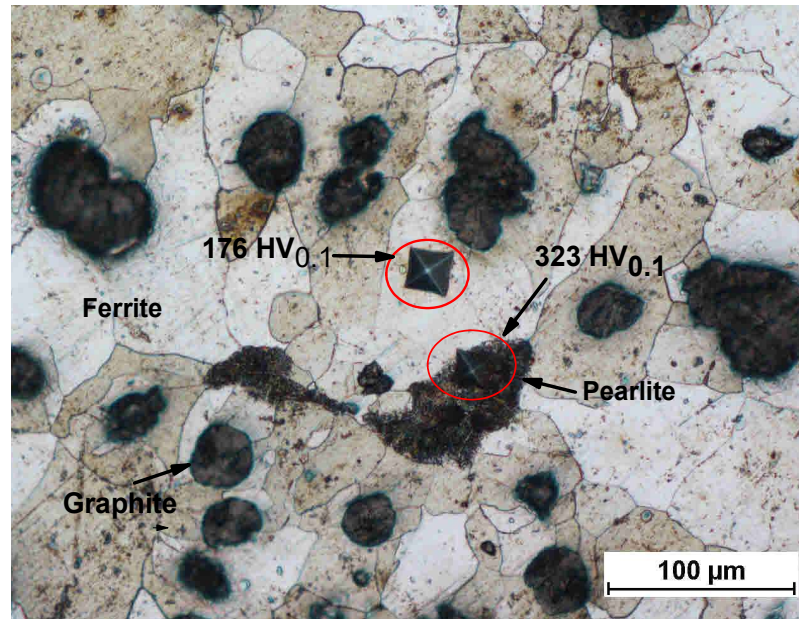


Figure 4.2. OM images of the as-cast spheroidal graphite iron with hardness test.

4.1.3 high-chromium iron

Untreat high-chromium iron is very close to ASTM A 532 (Class II, type A). It was annealed for 3 hours at a temperature of 1,000 °C before cooling in a furnace. The as-annealed Hi-Cr is shown in a series of OM and SEM images in [Figure 4.3](#).

In [Figure 4.3a](#), dark pearlite dendrites are connected to white areas of fine scattered secondary carbides. The hard, eutectic carbide, M_7C_3 , is embedded in a tight cluster. You can see that the microstructure is also divided into rods and plate-shaped carbides, as shown in [Figure 4.3b](#). The martensite presence at the matrix/carbide interface ([Figure 4.3 \(d\)](#)). Moreover, the pearlite dendrites have a few light gray spots, like maybe martensite, or carbide, and some traces of austenite (See the [figures 4.3](#) for more details).

X-ray diffraction peaks ([Figure 4.4\(c\)](#)) were obtained for analysis to determine the existence of phases in the Hi-Cr. According to typical lists of peaks for different phases as

well as the data from the analysis of Bedolla-Jacuinde et al. [125, 126], peaks for various phases are determined using 2-theta values and d-indicators.

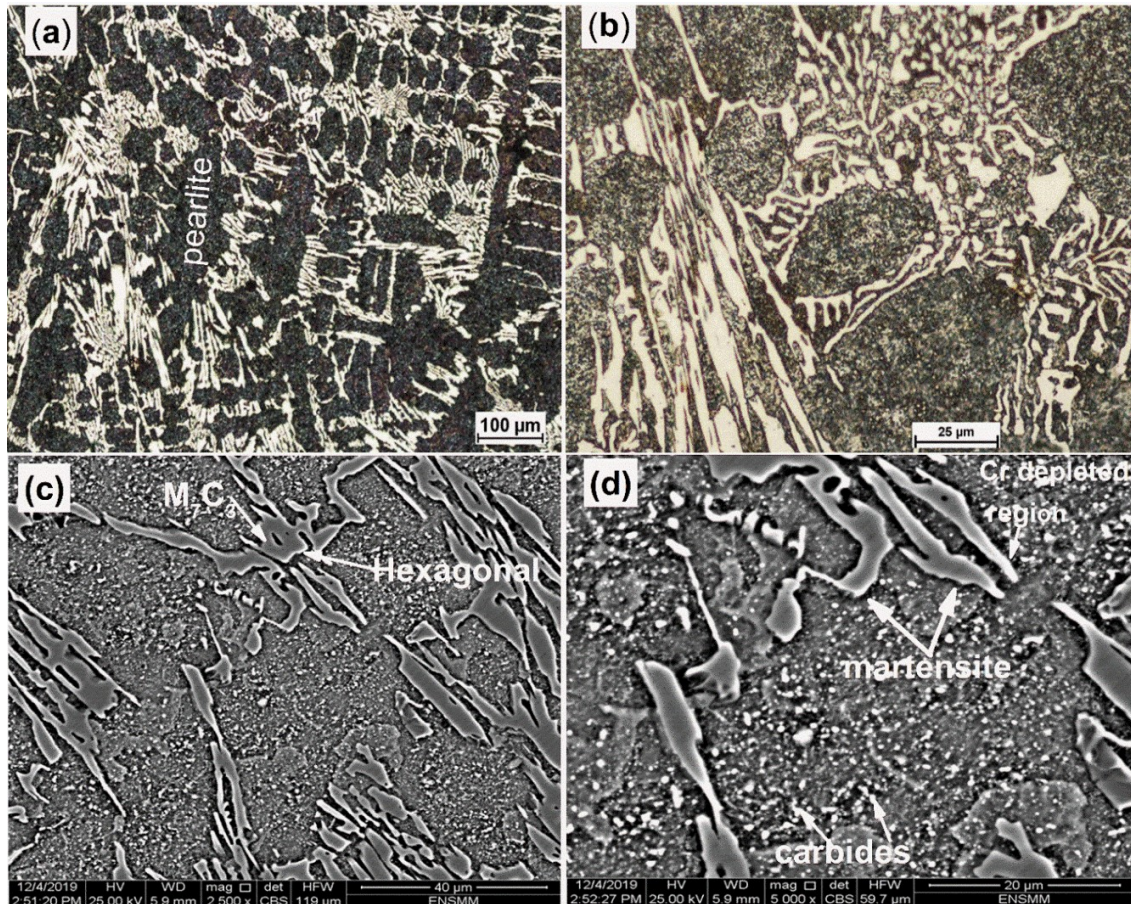


Figure 4.3. Images of the as-annealed Hi-Cr iron: OM (a-b); SEM (c-d).

Pearlite is mainly made up of Cr-ferrite, so the peak of $44.83^\circ(2\theta)$ and the micro-hardness measured at 330–434 HV0.1 (~34–44 HRC) clearly indicate the pearlite is found in Hi-Cr samples in the dendrite-shaped, and also the presence of secondary carbides. On the other hand, the XRD peak also has little austenite left in it ($2\theta = 43.28/49.97^\circ$), and the few Martensite is clearly represented by $2\theta = 44.80/65.17/82.37^\circ$. Austenite is likely to turn into martensite due to the local loss of carbon and chrome from the matrix/carbide interface. A more detailed view of [Figure 4.3 \(d\)](#) shows black martensitic films surrounding eutectic carbides.

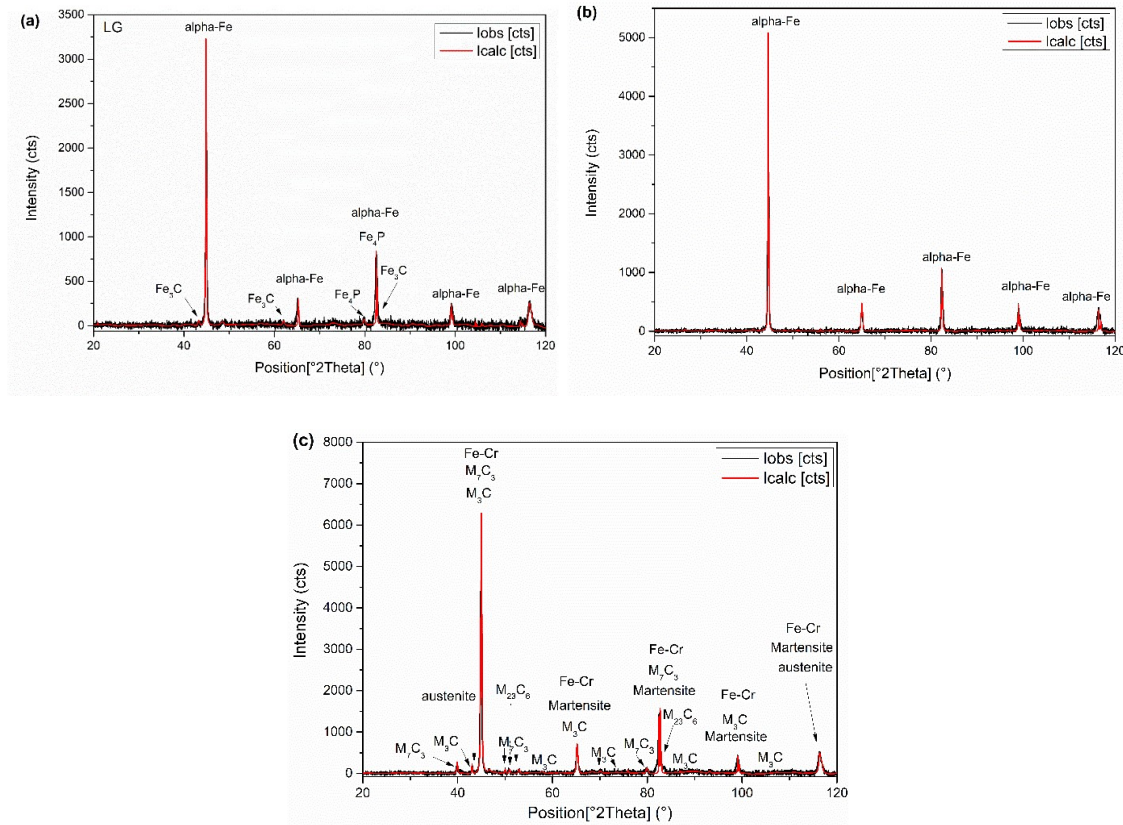


Figure 4.4. XRD patterns of the cast iron samples before the boriding treatment: (a) LG;(b) SG; (c) Hi-Cr cast irons.

Primary austenite generally first solidifies in the hypoeutectic Hi-CrCI solidification path, followed by the eutectic reaction that transforms liquid into austenite plus M_7C_3 [7]. The composition and cooling rate will determine this; austenite transforms into pearlite (and/or martensite, bainite) at room temperature. Since austenite is stabilized by Ni, Mn, Mo, and Cu as well as is cooled rapidly, austenite retention is also possible. As a result, two microcomponents (matrix (eutectic cells plus primary dendrites) and M_7C_3) make up the bulk of the final microstructure.

According to Tabrett et al. [127], austenitic dendrites start to form when these alloys start to solidify. The final liquid to solidify undergoes a eutectic reaction that causes a

eutectic mixture of M_7C_3 and austenite to develop. As the high amount of carbon as well as alloying elements, which causes M_s temperature to fall below zero, the austenitic component persists in its metastable state at room temperature. The following factors provide an explanation for the presence of martensite: Carbide-forming elements like Cr have been removed from the surrounding base, allowing of the eutectic carbide to form. As a result, the austenitic matrix's M_s temperature increases close to the carbides. As a result, martensite is noticeable in the as-cast alloy's microstructure at room temperature.

Karantzalis et al.[39] also demonstrated that the primary austenitic dendrites and a eutectic mixture of M_7C_3 plates and austenite made up the original high-chrome iron structure. Carbide particles have been surrounded with a martensite film as a result of the matrix area's loss of Cr. Si content increases have the reverse effect by promoting the production of pearlite [128].

It is widely known that resistance to wear depends on base microcomponant as well as kind of carbide and attributes (morphology, size, orientation, and distribution) [129]. Resistance to wear could be enhaced with increasing additional eutectic carbide in the alloy, but the alloy's fracture toughness falls as a result. Generally, wear resistance goes up as the material gets harder, while fracture toughness goes down as it gets stronger. Thus, you should expect the characteristics of a material to change depending on how hard it is [35]. Therefore, diffusion of boron in a Hi-Cr iron surface is limited because boron solubility in ferrite or austenite is very low; more diffusion would cause the formation of borides of iron or chromium [130]. Because they are harder and more thermally stable than carbides, borides have the potential to be strong surface wear resistant phases [131].

4.1.4 Summary

Lamellar Graphite cast iron has a pearlite microstructure, which means most graphite is made up of flakes. XRD patterns showed the presence of Alpha-Fe and Fe_3C , as well as Fe_4P . Even though the LCI used in this study has the right P amount, the locally formed, brittle steadite might be the area that gets pitting damage the most during wear.

The XRD patterns showed that ferrite (Alpha-Fe) was present in the matrix of the SG iron. The OM picture showed that 90% of the iron was ferrite, and 10% was pearlite. Ferritic SGCI's have tensile strengths comparable to low-carbon steels and exhibit good ductility. Although hardness and wear resistance decrease, machinability is improved with a ferritic matrix. Therefore, improving the surface properties of LG and SG irons has been the main goal for many years.

High-Cr iron shows eutectic carbides ($(\text{Fe}, \text{Cr})_7\text{C}_3$) and dendrites of pearlite with secondary carbides; XRD peaks confirmed the presence of ferrite, M_7C_3 , martensite, and negligible retention of the austenite.

Cast iron is a popular material used in a lot of different industries. It requires high wear resistance. This study looked at how boriding affects the micro-structural, mechanical, wear and corrosion characteristics of cast iron.

4.2 Boriding process of cast irons

Due to its cheap cost of hard coating processing, powder-pack boronizing was utilized specifically in this work on LG, SG, and Hi-Cr irons as a surface thermochemical process to boost hardness and wear resistance on the cast iron specimens. Iron components' corrosion resistance can also be improved via boriding.

4.2.1 Effect of cast iron type on boride layer thickness and nature

Figures 4.1 to 4.3 depict the microstructure of the polished and etched surfaces of unborided cast irons, while Figure 4.5 displays OM and SEM images of specimens that have been boronized at 950 °C for four hours.

Figure 4.5 illustrates how the surface layers of borided specimens differ from unborided specimens as a result of the phases contained. Only the Fe₂B phase is present in the boride layer on borided LG, as can be seen in Figure 4.5a. On borided SG, it was easy to see how different FeB and Fe₂B layers developed in Figure 4.5b. Only the lighter Fe₂B phase is present in the layer under the outer layer, which only contains the darker FeB phase. Additionally, it was found that the sawtooth-like shape reported by various researchers [100, 132] represented both boride layers. The saw-tooth shape boronized coatings, according to Türkmen [133], exhibit excellent bonding between the base material and the boronized coating.

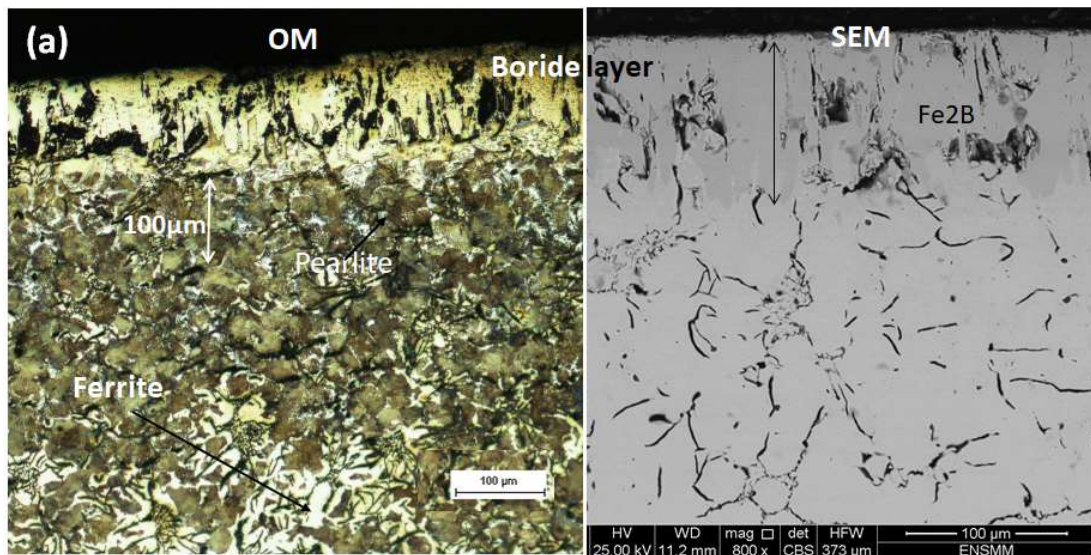
The boronized layers of LG and SG exhibit saw tooth-form shape. It's because the movement of borons depends on the direction of the crystals in the borate layers, which are anisotropic. The layer thickness of boronized cast iron has changed as a result of the alteration of the chemical makeup and the structure of the cast iron. In Figure 4.5b, cracks appear close to the interface between two different layers (FeB/Fe₂B) because of the large difference in properties between the two layers.

As shown in Figure 4.5, the average boronized coating depths for LG, SG and Hi-Cr were 109 ± 10 , 94 ± 13 and 45 ± 8 micrometers, respectively. However, unlike the boride coating that is generated on the surface of borided LG or borided SG, the boride coating that is formed on the top of the Hi-Cr samples has a distinct microstructure shape. The

contact between the substrate and boronized coatings are smooth in borided Hi-Cr specimens [134], as opposed to LG and SG in which a saw-tooth-like structures were seen. The difference results from the addition of chromium to the Hi-Cr, which raised the boronized coating's hardness [135]. Inducing the development of the FeB layer in ferrous metals, the components of the alloy act as a barrier to diffusion for the boron atoms, raising the boron content at the sample's surface.

4.2.1.1 Summary

It can be concluded saw tooth-form layer of development on the LG and SG, is less intense for Hi-Cr because of the chromium is really high on the surface of the substrate. It stops the diffusion of boron by reacting right away to make interstitial compounds made of CrB or Cr₂B in addition to FeB and Fe₂B. In addition, the average thickness of the boronized layer for LG, SG and Hi-Cr were 109, 94, and 45 micrometers, respectively.



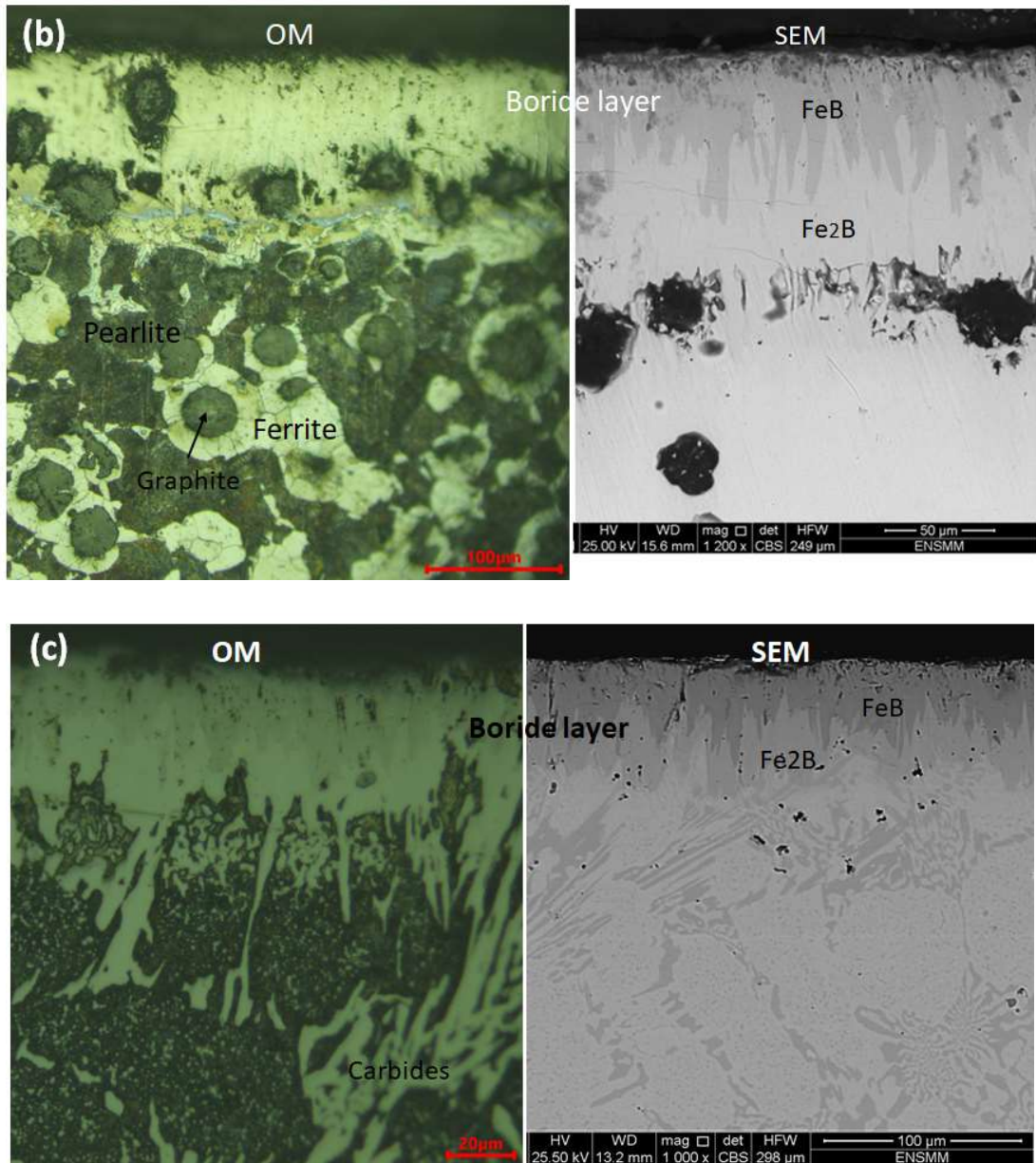


Figure 4.5. Micrographs of borided specimens: (a) boronized LG; (b) boronized SG; (c) boronized Hi-Cr.

4.2.2 SEM surface topography and EDX analysis of boride layer

Figure 4.6 depicts the cast iron's SEM microstructure and EDX analysis following the boriding treatment. Cast iron top compositional differences (average atomic number difference) are typically detectable by backscattering electron detection. The three cast iron

surfaces under both conditions have radically different microstructure images. The microstructure modifications that took place during boriding are what caused this disparity.

Figures 4.6(a) and 4.6(c) illustrate the boronized coating topography on the LG and the Hi-Cr. The layers were homogenous, without cracks, and included tiny particles, as can be observed. While larger particles and open graphite are observed in the layer on SG (Figure 4.6 b).

Figure 4.6 also illustrates the EDX analysis of boride casting irons. The EDX peaks of the boron produced on the boronized surface could be seen clearly, as could the peaks of C, Fe, Cr and O. This indicates that FeB, CrB, Cr₂B, Fe₂B, FeM₂₃(C, B)₆ as well as oxides, were formed on the surface. Furthermore, the presence of boron at 9% in borided LG is evidence of the presence of Fe₂B. Additionally, noted were the creation of boride phases, the homogeneity of the borons spread on the surfaces, as well as distribution of phase consistency. Both enhance the homogeneity of the three cast-iron surfaces, thus improving the mechanical and hardness as well as other boriding properties.

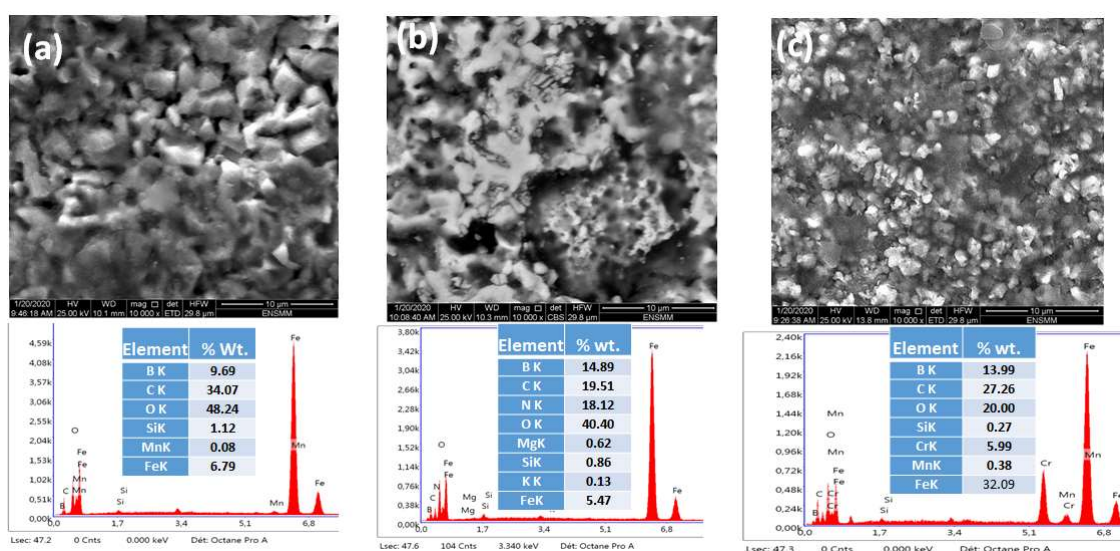


Figure 4.6. Surface images by SEM, backscattering electrons, and EDX, on the boronized specimens: (a) LG, (b) SG, and (c) Hi-Cr irons.

4.2.3 XRD analysis of borided samples

Because of their small size and great mobility, boron atoms are able to penetrate ferrous alloys to create the intermetallics FeB and Fe₂B. Depending on the boriding media and chemical content of the base materials, diffusion can be expected to result in the to form of Fe₂B or FeB boride layers in addition to Fe₂B [86, 134, 136].

Figures 4.4 and 4.7, respectively, demonstrate the XRD characteristics produced for unborided and borided specimens of cast irons. Figure 4.7 illustrates the presence of FeB and Fe₂B phases in the coating of borided SG. The Fe₂B layer makes up the majority of the coating for the borided LG. Many studies on borided LG and SG irons produced similar results [100, 101, 137-139]. It is probable that carbon has a detrimental impact on the diffusion of boron atoms, which might account for the change in chemical formula under various circumstances. Since the carbon cannot dissolve in the iron boronized coating, a diffusion region will be created by pushing it from the surface to the base. It may form FeM₃ (C, B) phase in addition to /or FeM₂₃ (C, B)₆ [18, 135].

Unlike what was observed for LG and SG, the XRD patterns (Figure 4.7(c)) obtained for Hi-Cr that has been borided shows the existence of other borides. Chromium, the main alloying component in Hi-Cr, interacted with boron to create additional borides such CrB and Cr₂B. The boride layer's structure and characteristics can be changed by chromium. Because chromium is soluble in the Fe₂B phase, it displaces iron to create (Fe, Cr) B and (Fe, Cr)₂B on the surface. The boride layer's depth is reduced as a result of Cr diffusion, while the boride layer/substrate interface becomes smoother [134, 140]. Chromium facilitates the creation of the FeB phase on top of the Fe₂B phase.

4.2.3.1 Summary

It can be concluded that XRD peaks on the coated boronized irons revealed that the layers are composed of Fe_2B , FeB , CrB , Cr_2B , Fe or $\text{M}_{23}(\text{C}, \text{B})_6$ and iron oxides depend on the iron type. The coatings are created by a chemical equilibrium between Fe or Cr molecules in the substrate and boron molecules dispersed by a boriding agent. Hi-Cr samples are sufficiently active for the formation of CrB or Cr_2B .

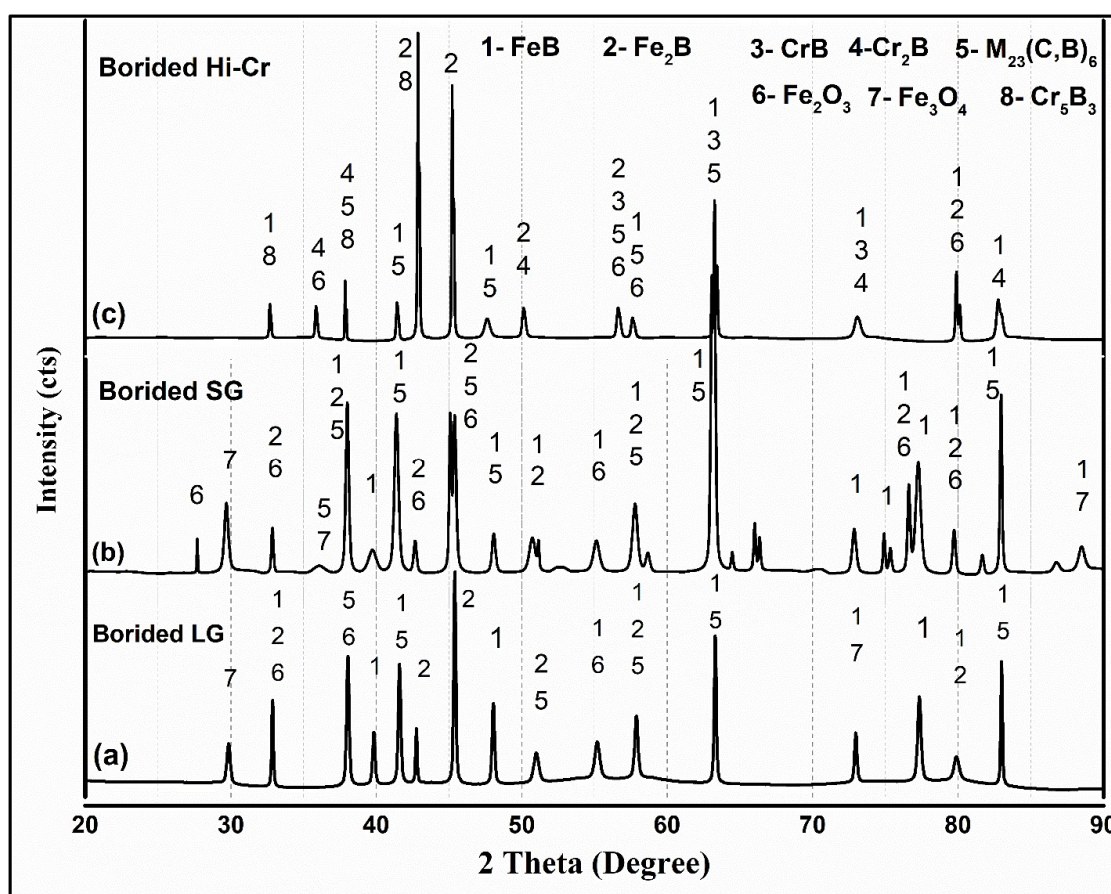


Figure 4.7. XRD peaks on the boronized cast iron specimens: (a) LG; (b) SG; (c) Hi-Cr.

4.2.4 Morphological Assessment of Surfaces

Optical profilometry was employed to determine the roughness of the surface of the cast iron specimens prior to and post-boriding process, as illustrated in [Figure 4.8](#) and [Figure](#)

4.9, respectively, as outlined in Chapter 3. The absolute average in relation to the base length is called the arithmetic mean roughness, or Ra. The Ra value, or the average difference between peaks and valleys, represents the average surface roughness over the entire gauge length for the sake of simplicity. Surface roughness is typically assessed using this measurement. On the other hand, the Ra values of unborided iron samples are $0.05\text{ }\mu\text{m}$ (see Table 4.1), whereas the Ra value of an SG that has been borided (Figure 4.8) is about $0.9\text{ }\mu\text{m}$ (Figure 4.9). Notice that the roughness of the surface of the cast specimens increased due to the boriding process. In addition, according to Sahin [18], boroiding the cast irons results in an increase in the roughness of the polished samples.

Roughness, porosity, and graphite spheres are open to the surface, and they also play an important part in determining the friction coefficient. It has a high degree of roughness and a high degree of porosity or surface morphology/topography, which increase the coefficient of friction [141, 142].

Post-boriding, the surface of the iron specimen developed Fe_xB_y or $(\text{Fe}, \text{Cr})_x\text{B}_y$ particles in various orientations, which is what caused the rise in roughness that was observed [143]. According to Şahin, the boriding process had a considerable impact on the materials' surface roughness (the surface roughness decreased for rough surfaces while increasing for smooth surfaces). The threshold roughness value relied on the nature of the substrate material and the boronizing conditions [144]. The iron surface can become distorted as a result of the volume change brought on by the creation of the boride layer, which may not be consistent throughout the surface. But after using P4000 grit abrasives to grind the borided SG, a reduction was seen; Figure 4.9 depicts the resulting surface topography. This effect can be related to the volume shift that occurs when iron reacts with

boron to form iron boride [134], which causes the particles to form in various orientations and fill in the surface creeks left by grinding.

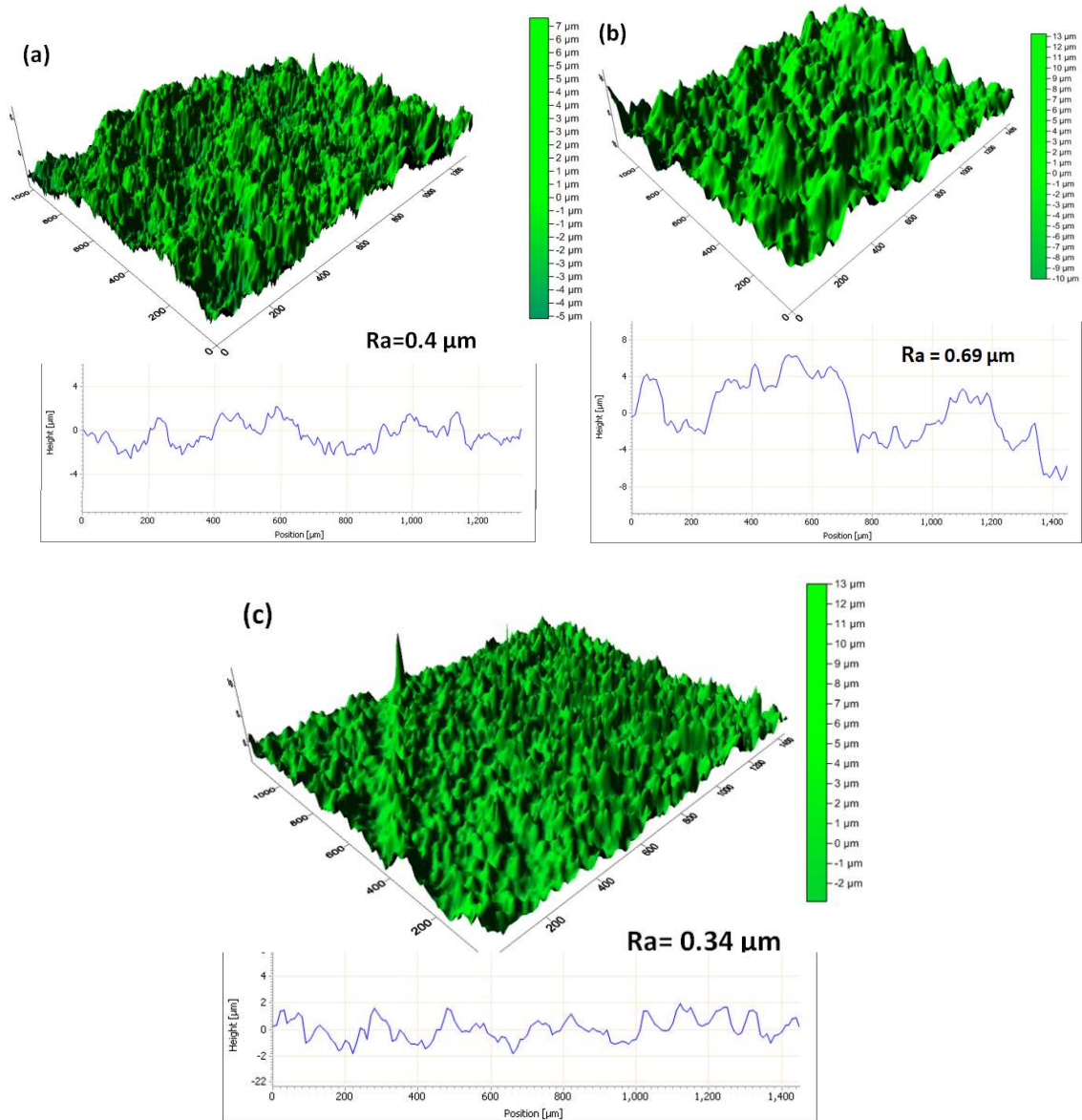


Figure 4.8. 3D Surface topography evolution of samples: (a) borided LG;(b) borided SG; (c) borided Hi-Cr.

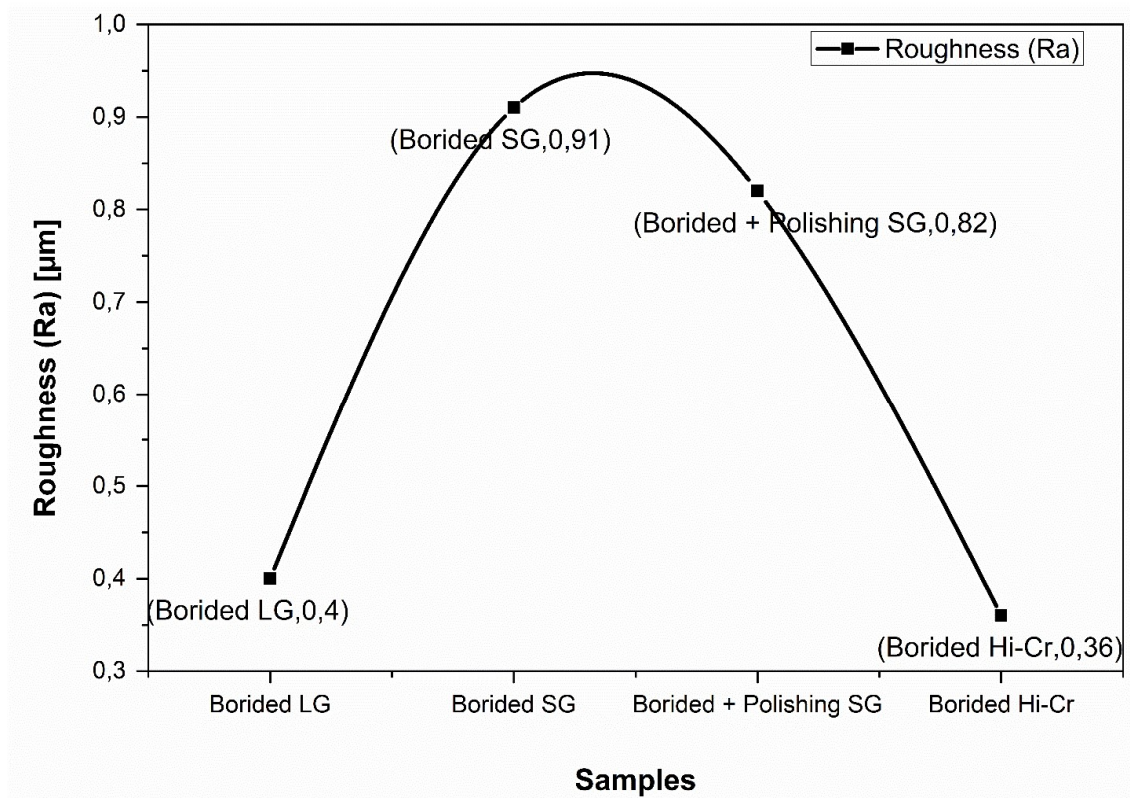


Figure 4.9. Surface roughness of boronized cast irons.

4.2.5 Influence of boronizing on the microhardness

Vickers method was used to measure the micro-hardness of the layers of boride with a weight of 100 g. The mean value was used as the hardness.

Figure 4.10 shows the hardness profiles of samples boronized at 950 °C for 4 hrs. There were variations in the microhardness plot. The microhardness diagram showed differences due to the sawtooth shape, graphite inclusions, and the different phases of the boronized coating (like FeB and Fe₂B/CrB and Cr₂B). The hardness obtained for the borided specimens depends on the cast iron kind (chemical content and structure). In general, it increased with the presence of alloy elements such as Cr. Borided Hi-Cr showed

the highest hardness [135], about 2148 ± 334 HV0.1, while borided LG showed the lowest hardness. The unborided LG hardnesses are about 311 HV, whereas that of the borided specimen ranges from about 1475 ± 535 HV.

In borided SG, [Figure 4.10](#) clearly shows the decrease in transition zone hardness compared to the SG core. A Si-rich part formed between sawtooth boronized coatings and diffusion parts. In common irons, ferrite is formed due to a high Si amount; also, a fairly soft-ferrite area appears below the boronized coating in comparison to the iron-base hardness. A very hard and brittle layer of boronized iron penetrates the softer intermediate layer and is severely failed as the surface pressure rises. Sen et al. [145] and Fichtl [1] suggested that this state was called the silicon-rich and carbon-rich ferrite impact. Casteletti et al. [108] found that silicon reduced the resistant to wear of boronized coatings and that the silicon content in conventional steels did not need to exceed 0.8%.

Furthermore, as shown in [Figure 4.10](#), the borided samples are harder than the unborided ones. The hardness goes up 4.7-6.5-fold because of the FeB phase, Fe₂B phase, CrB phase, and Cr₂B phase.

4.2.5.1 Summary

It can be concluded that the degree of hardness of the surface-forming boronized properties on casts LG, SG, and Hi-Cr ranged from 940 to 2010 HV0.1, 1377 to 2399 HV_{0.1}, and 1814 to 2482 HV0.1, respectively, while the hardnesses of unborided casts LG, SG, and Hi-Cr were 311 HV0.1, 176 HV0.1, and 311 HV0.05, respectively. The boride layer obtained using recycled agents has shown a high superficial hardness that will enhance wear resistance.

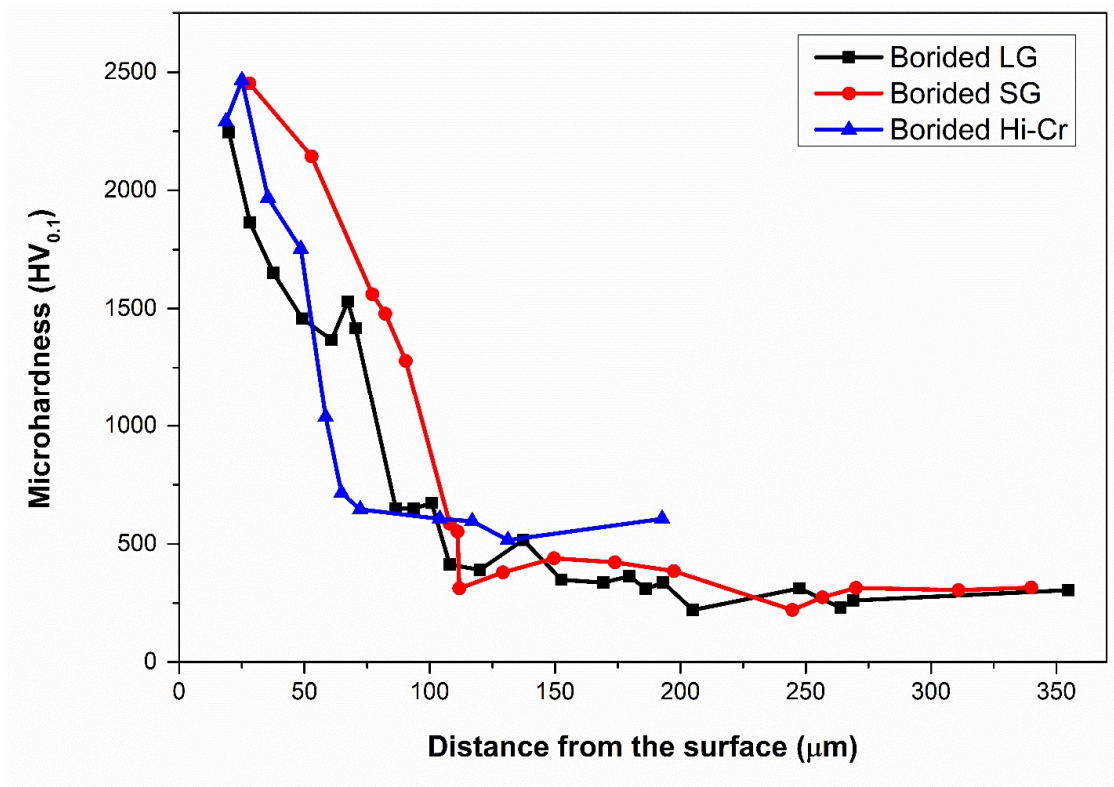


Figure 4.10. The hardness features of the borides produced on the cast irons.

4.2.6 Rockwell-C adhesion

Among the most of the crucial characteristics of industrial uses, coatings is adhesion to the substrate because it greatly affects their suitability for especially for parts subject to tribological stress [146]. The Rockwell-C method was used to test the boride coatings' adherence and deformation surface characteristics.

Figure 3.2 illustrates the comparison between HF1 to HF6 adherence quality labels and the damage to the boronized coating. Summary, adequate adhesion is determined by the HF1-HF4 score, while inadequate adhesion is indicated by HF5 and HF6 [111, 147-155].

See [Figure 4.11](#) for SEM features of the craters on the cast irons surface. The samples that were borided (LG and SG) revealed no signs of cracks or peeling ([Figures 4.11 a and b](#)). In the adhesion strength quality chart [112], these samples are HF1-HF3, which is acceptable [113]. However, in spite of the existence of brittle and hard CrB and FeB compounds on the iron surface, the borided Hi-Cr samples ([Figure 4.11\(c\)](#)) displayed circumferential fractures and incomplete peeling near the periphery of depression holes. HF4 and HF5 have an impact on how well the boronized coating adheres. As demonstrated by [Figure 4.11\(c\)](#), the CrB phase exhibited a negative impact on the surface boride layer's adhesion, causing it to delaminate and develop large fractures as a result of the indented action.

Taktak [156] studied the adhesion experiment using Rockwell-C on boronized 440C steel. Because of the existence of hard and brittle FeB and CrB phases on the steel surface, he noticed radial fractures and a part spalling along the perimeter of impression pits after the examination. This result demonstrated that, in accordance with the adhesion strength quality maps, the boronized layers' adherence to the 440C steel is inadequate. The overall findings show that our technique produces a strong and adhesion single Fe₂B layer on LG surfaces. So, it's clear that the Fe₂B and saw tooth shape of the layer helps make the borided system stronger.

4.2.6.1 Summary

The adhesion strength of the LG and SG boronized coatings is satisfactory, but, radial cracks and partial flakes were observed at the edges of the impression craters, because of the hard and fragile (FeB & CrB) phases and the flat morphology of the borided Hi-Cr surface which decreases the strength quality.

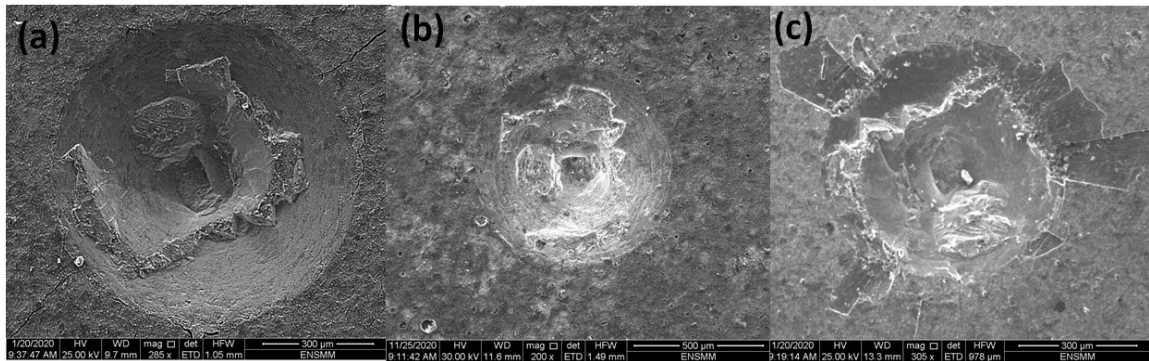


Figure 4.11. SEM images of impression effect on boronized specimens: (a) borided LG, (b) borided SG, (c) borided Hi-Cr.

4.2.7 Friction and wear characteristic of borided cast irons

The friction and wear characteristics of metal samples are now being improved by scientists and engineers with the best possible technology. Coating is one technique for lowering the friction coefficient of these samples. When used on different metals, diamond-like carbon is an effective coating that lowers the friction coefficient below 0.1. The second way to enhance the tribological properties of materials is to introduce appropriate boron diffusion within the material surfaces to form borides.

4.2.7.1 Friction coefficient

The evolution of the coefficient of friction (COF) was studied in the tribological reaction of surface-borided specimens. The COFs were recorded continuously during the wear test. More than three tests were performed for each material/boriding combination. The boride coating conditions, top roughness and graphite/carbide parameter all have an impact on the COF.

Figure 4.12 shows COF curves that were taken while the cast iron substrates were being tested for wear, boronized specimens, and polished boride SG under dry conditions

against a WC ball with a 10 N load at ambient temperature. The COFs and roughness of the samples are compared in Table 4.1.

The borided LG has the lowest friction coefficient of about 0.028 for less than 40 m sliding, as shown in Figure 12(a). While, the COF of non-borided SG consistently has a value below 0.13, suggesting that graphite is lubricating the environment. After the boriding process, the COF strength steadily climbed to 0.53 as debris with hard components collected in the worn track. However, the COF of borided SG after polishing reduced about 0.095 and decreased by 27% compared to the non-borided sample at 30 m sliding.

In Figure 4.12(c), there are a number of spikes that represent non-boronized Hi-Cr with some elevated COF quantities. Sharp fluctuations that produce wear behaviour and high COF may be to blame for this [157]. Table 4.1 and Figure 12(c) illustrate this: the friction coefficient of borided Hi-Cr was more stable and decreased by 37% when compared to the non-borided sample.

Table 4.1. Roughness (Ra) and quantities for the friction coefficient acquired from a wear experiment.

Specimens	Treatment	Roughness (Ra) [μm]	Coefficient of friction (μ) at 30 m	Coefficient of friction (μ) at 100 m
LGCI	Unborided	0.05	0.4	0.41 - 0.60
	Borided	0.40	0.012	0.10 - 0.55
SGCI	Unborided	0.05	0.13	0.13 - 0.22
	Borided	0.91	0.4	0.33 - 0.70
	Borided + Polishing	0.82	0.095	0.20 - 0.53
Hi-Cr CI	Unborided	0.05	0.85	0.75 - 1.23
	Borided	0.36	0.48	0.40 - 0.91

*COFs are determined by dividing the mean values for each test by the difference between the maximum and the steady state values.

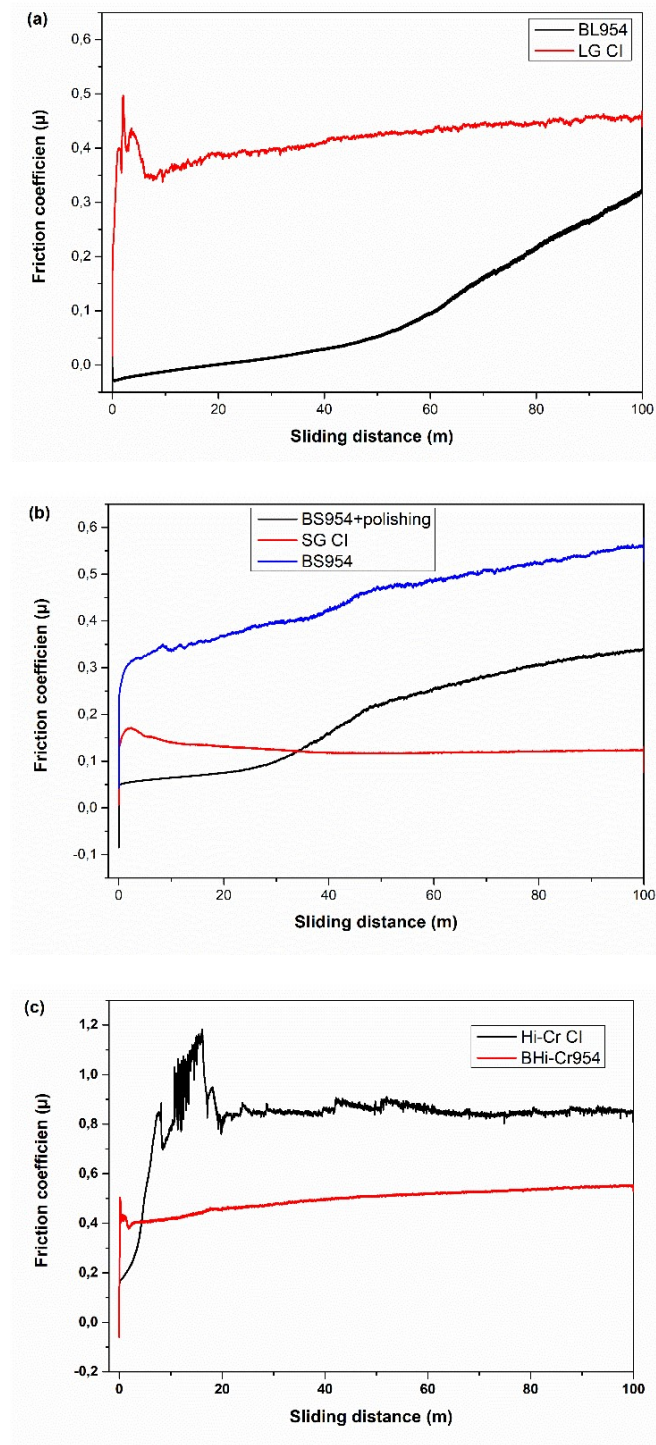


Figure 4.12: Curves of friction coefficient versus sliding distance for irons that have been borided and unborided: (a) LG, (b) SG, and (c) Hi-Cr irons.

The change in COF of the cast iron substrates and borided samples is related to phase type (graphite, carbide, FeB, and Fe₂B), hardness, and roughness of the specimen layers, [Figure 4.12](#) illustrates this phenomenon.

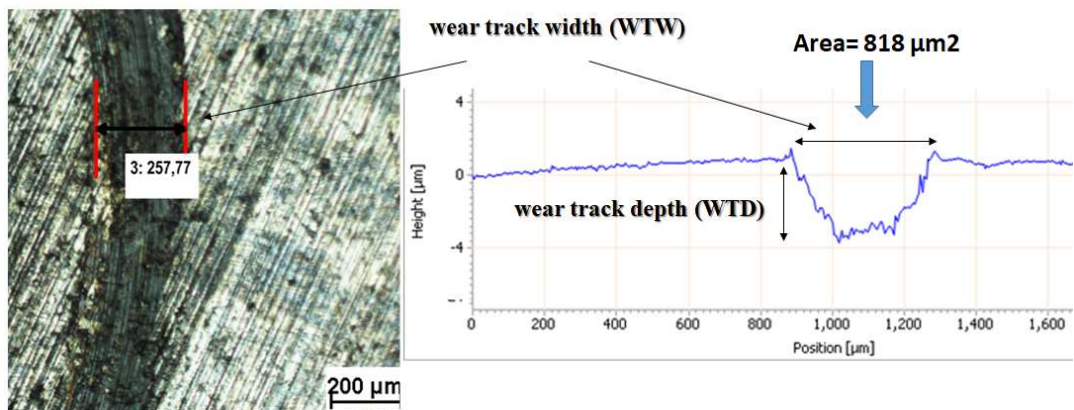
The samples' coefficient of friction decreases with increasing sample hardness. This is due to the fact that there were fewer actual contact areas between the hardened boride sample and the WC sphere in the wear test [158]. Furthermore, because the borides are so hard, the friction coefficient is also stable; the COF has changed, probably depends on the amount of Fe₂B, the hardness of the diffusion zone, and thermal conductivity; FeB has a lower thermal conductivity than Fe₂B. Based on Kulka et al. [159], the thermal conductivities (w/cm.k.) of FeB and Fe₂B are 0.12 and 0.301, respectively. And as shown, the higher hardness of borided Hi-Cr also contributes to a friction system that is stable; the COF actually barely varies for sliding distance.

4.2.7.2. Quantification of the wear track's width, depth, and area

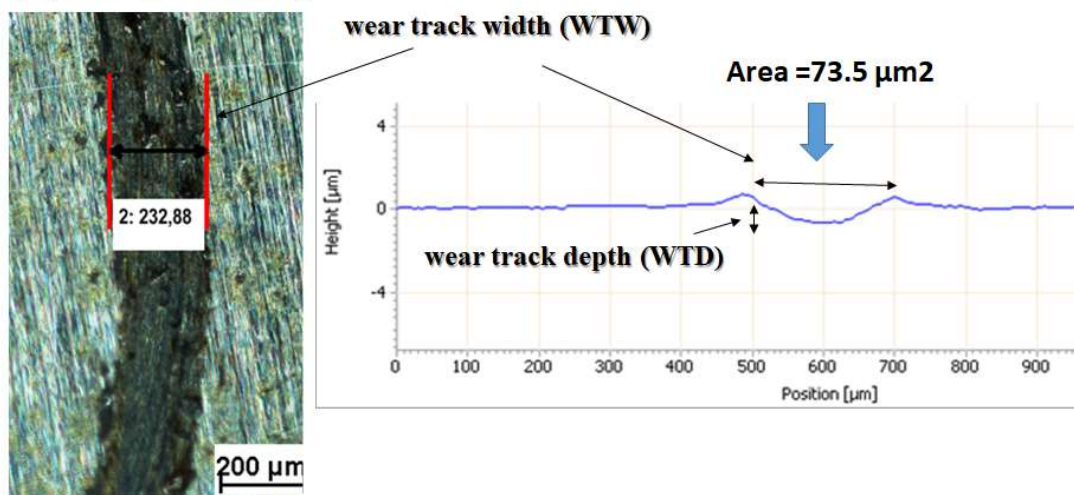
The boride surface is typically blamed for the great tribological characteristics of borided components. One of the easiest things to do, however, and also one of the most effective ways to describe the improvement in wear resistance brought on by the boriding processes is to measure the wear track's parameters.

[Figures 4.13 and 4.14](#) show the wear track width (WTW), wear track depth (WTD), and wear track cross-sectional area (WTA) as they were assessed using a mix of OM, SEM, 3-D profilometer, and picture analysis systems. [Figure 4.13](#) show wear track of unborided cast irons, while [Figure 4.14](#) show wear track of borided cast irons.

(a) LG before boriding



(b) SG before boriding



(c) Hi-Cr before boriding

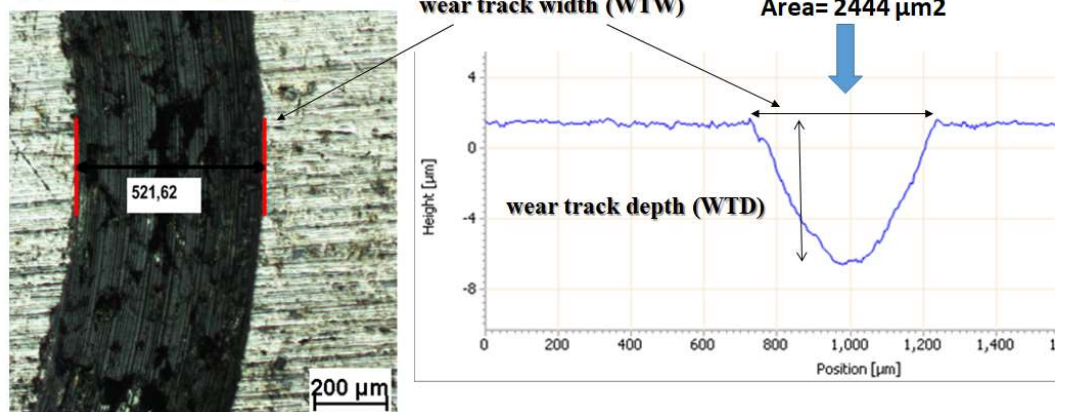
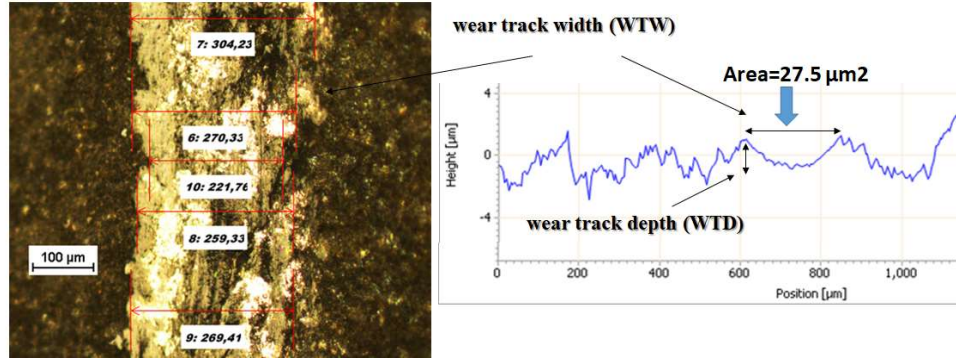
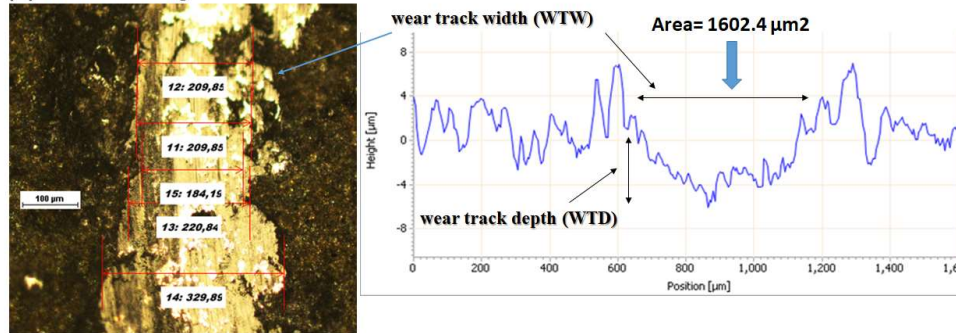


Figure 4.13. The width, depth, and area of the wear track of unborided cast irons: (a) LG, (b) SG, and (c) Hi-Cr samples.

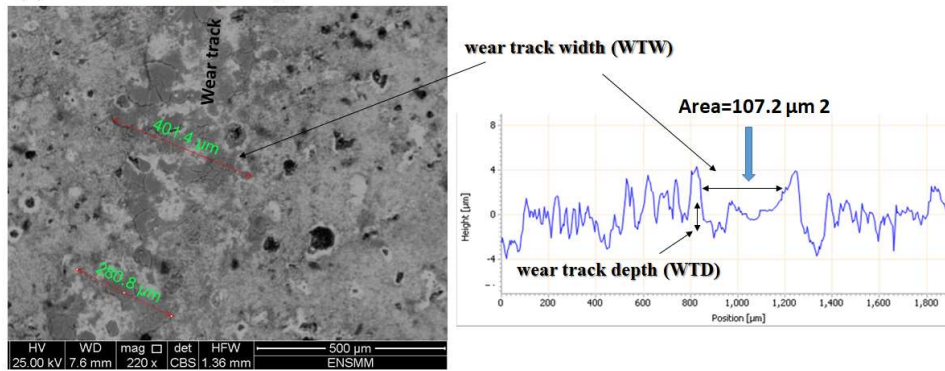
(a) LG after boriding



(b) SG after boriding



(c) Polished SG after boriding



(d) Hi-Cr after boriding

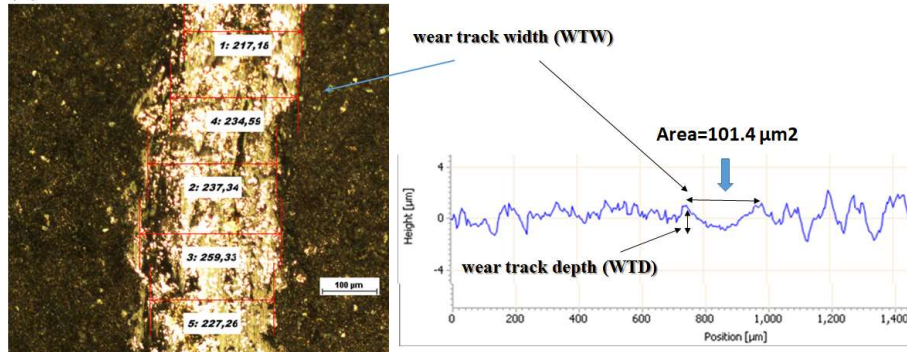


Figure 4.14. The width, depth, and area of the wear track of boronized samples: (a) borided LG; (b) borided SG; (c) polished borided SG; (d) borided Hi-Cr.

4.2.7.3 SEM observations of wear tracks

Characterization of the wear worn surfaces, worn track morphology, and debris were studied using scanning electron microscopy (SEM). Figures 4.15–16 show SEM views of worn tracks of unborided and borided cast irons.

Figure 4.15 for unborided cast irons show that the worn track width decreases in $\text{Hi-Cr} > \text{LG} > \text{SG}$. Figure 4.16 of borided cast irons shows that the worn track width decreases in borided $\text{SG} > \text{borided LG} > \text{borided Hi-Cr}$.

The widths of wear tracks changed with changes in cast type during wear tests. Despite being nearly smooth, the worn tracks had a few small failure modes on their surface. According to LG and Hi-Cr (Figures 15a and c), the oxidative wear mode was the main type of wear that was seen. This led to delamination, which was the main type of wear that was seen in their samples. Although new cavities did not form in SG, a few did form at the graphite particles.

In Figure 16(a–d), the oxidative wear caused local spalling. This is the case for all borided cast samples. In addition, Figure 16(b) clearly demonstrates pits or indentations brought on by surface wear, as found by Sezgin and Hayat [160]. Microcracks appeared on the surface as the oxide layer delaminated (Figures 15(a) and 16 (a)). Compared to Hi-Cr iron, the delaminated contact area for boronized Hi-Cr was very small. According to Sezgin and Hayat [160], most high-manganese steel experienced the abrasive oxidative wear mechanism. High-manganese steel showed wear scoring and delamination in the sliding direction under each wear loading. Some cracks are observed in the oxide surface.

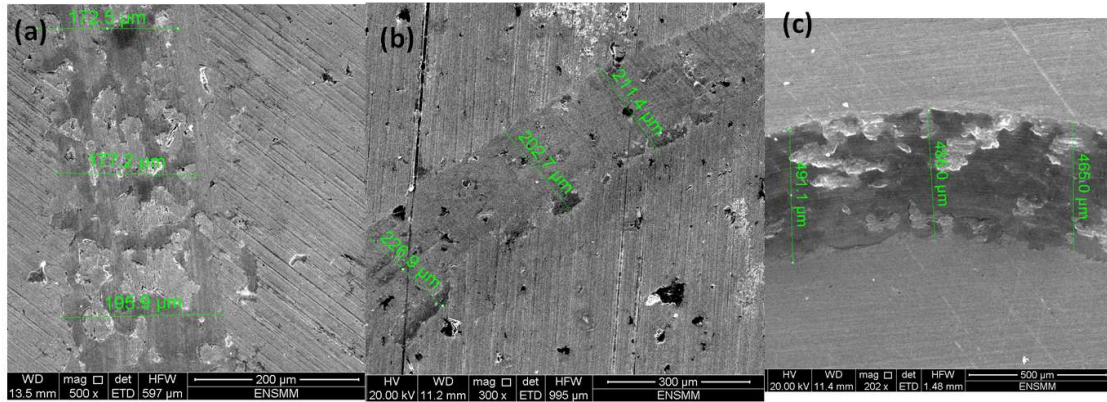


Figure 4.15. SEM observations of the worn track of unborided cast irons: (a) LG; (b) SG; (c) Hi-Cr samples.

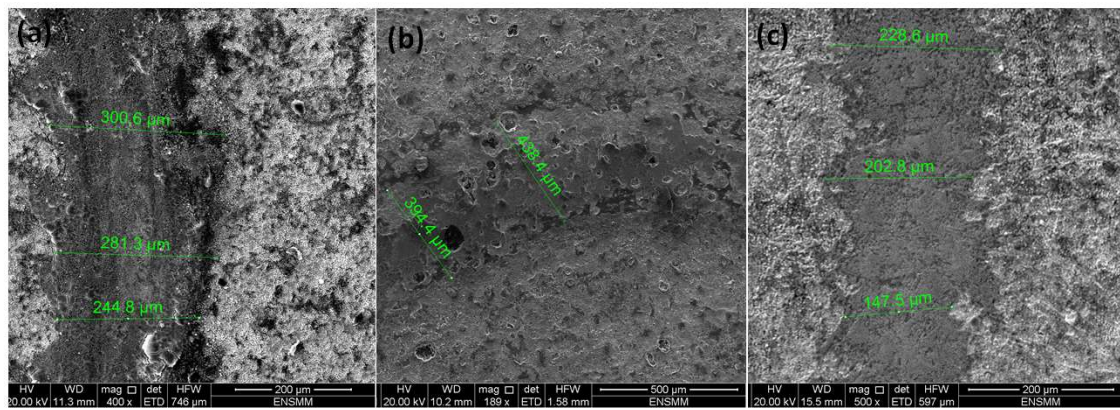


Figure 4.16. SEM observations of the wear track worn of boronized samples: (a) borided LG; (b) borided SG; (c) borided Hi-Cr.

4.2.7.4 3D optical observations of worn surfaces

Figures 4.17- 4.19 show the 3D optical images of worn surfaces of unborided and borided cast irons.

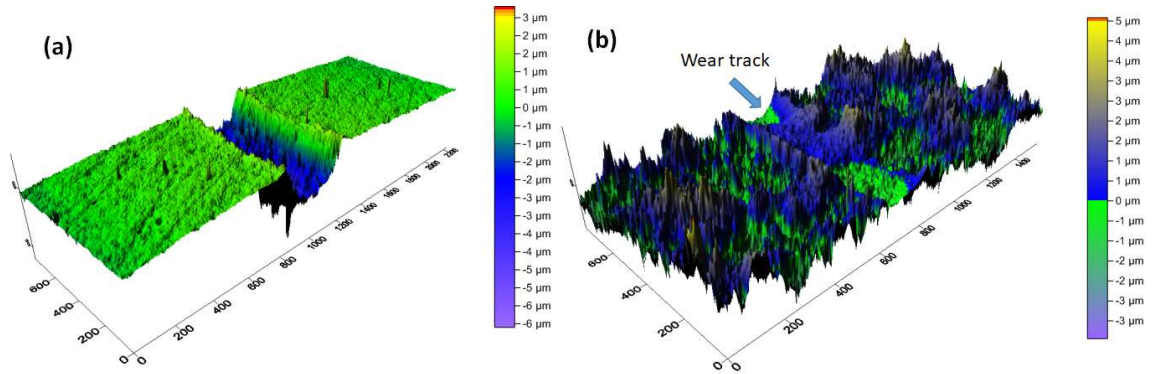


Figure 4.17. The worn surfaces' 3D optical photos: (a) unborided and (b) borided LG irons.

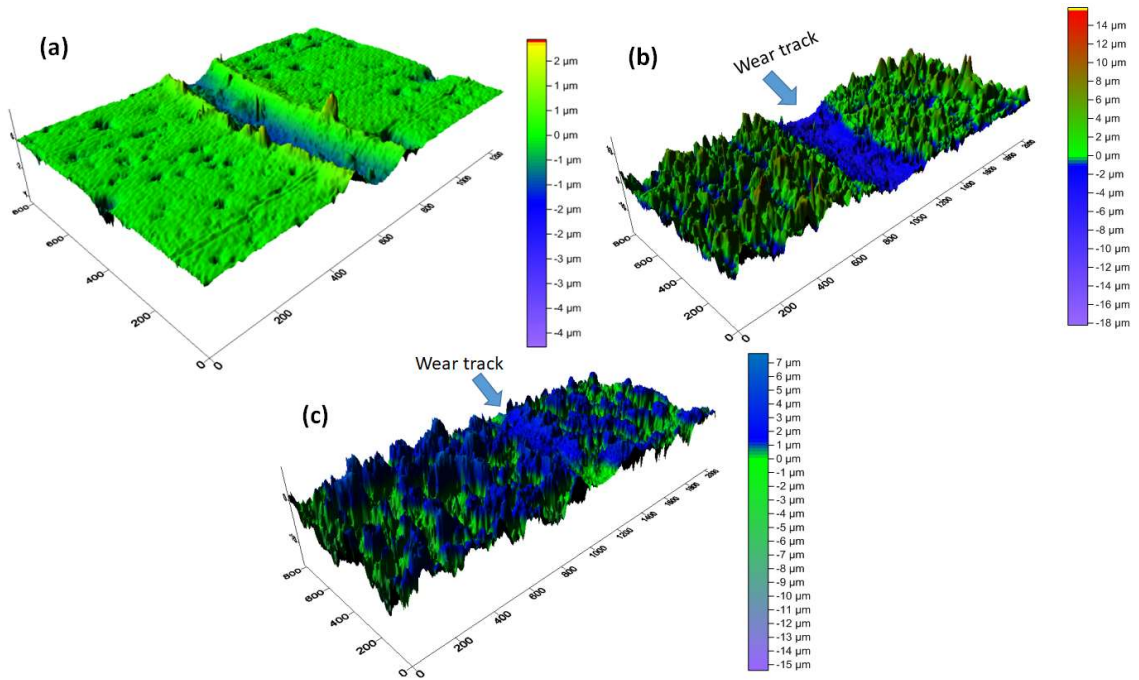


Figure 4.18. The 3D optical images of worn layers: (a) unboronized; (b) boronized SG; (c) polished borided SG irons.

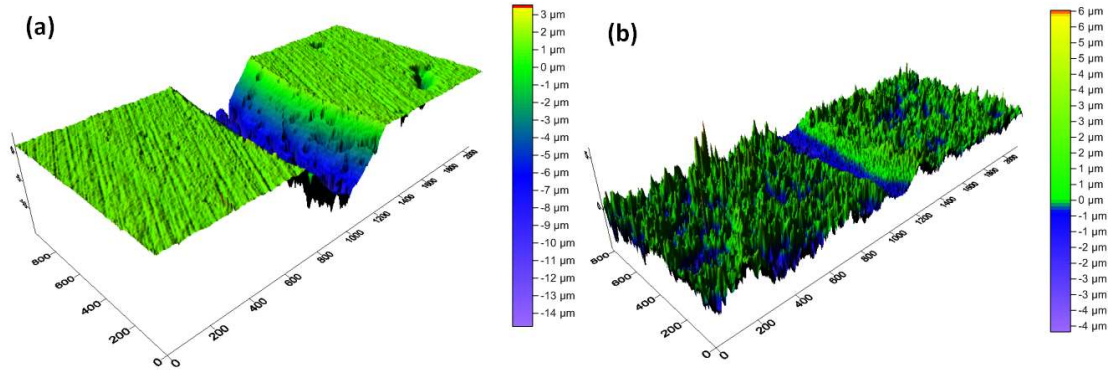


Figure 4.19. The worn surfaces' 3D optical photos: (a) unborided and (b) borided Hi-Cr irons.

It can be observed that the worn volume of borided samples is less than that of unborided ones. This indicates a clear improvement in wear resistance after boriding. It can be quantitatively calculated by the wear rate as follows:

4.2.7.5 Wear rate

The two major formulae utilized to measure wear rate are based either on the thickness of the worn tracks measured using an optical microscope [Eq.3.1] or by the area of the wear tracks calculated using a 3-D profilometer [Eq.3.3] (Figure 3.4), as shown in Chapter 3. The 3D optical images of wear surfaces of unborided and borided cast irons are shown in Figures 4.17- 4.19.

By using SEM and EDS to examine the structural and chemical makeup of wear surfaces, the impacts of the test circumstances on the boride layers' wear process were investigated. The calculated wear rates of the boronized and non-boronized cast irons are shown in Table 4.2. In turn, these data were used to determine the boriding efficiency (k%) calculated from the values obtained for wear rate (k) with Equation (4.1):

$$\text{Boriding efficiency (k\%)} = 100 \times (k_0 - k_i) / k_0 \quad \dots\dots\dots(4.1)$$

where k_0 is the rate of wear in the before of the boride and k_i is the corresponding rate of wear in the boride layer's existence.

Table 4.2. Average wear rate of the borided and unborided cast irons

Sample	Average wear rate $\times 10^{-6} \text{ mm}^3/\text{N.m}$	St.dev. $\times 10^{-6} \text{ mm}^3/\text{N.m}$	Efficiency %
Borided LG	4.76	1.22	71.14
LG	16.48	0.98	
Borided SG	14.68	1.38	-487.00
Polished Borided SG	3.12	1.68	-24.80
SG	2.50	0.10	
Borided Hi-Cr	4.25	0.66	83.38
Hi-Cr	25.55	9.41	

Table 4.2: Comparison of Hi-Cr (borided), the highest wear resistance, and the worst wear resistance when SG (borided). The COF of SG samples exhibited linear behavior; moreover, when contrasted to all the specimens subjected to the identical wear situation, SG samples showed the lowest value. Owing to the rise in carbon content in the SG, this characteristic can be linked to the graphite coating's structure (as a solid lubricant). Previous studies [62, 132, 161] show that graphite layers resist abrasive and adhesion wear, the primary wear mechanisms seen in the testings. Moreover to the graphite shape, the worn resistances are affected by the composition, structure, and hardness of sample as well as, to a large extent, by the working conditions [162].

In comparison to borided LG and Hi-Cr samples, borided SG exhibited a greater rate of wear. The reason for this is that due to the significant the hardness gradation of the layer to the substrate (see [Figure 4.10](#)) and the resulting brittleness of both, The harder the layer,

the more likely it is to break [163]. This finding was in agreement with the volume loss findings, which showed that volume loss for borided Hi-Cr was inversely related to the layer hardness, while for borided SG was directly related compared to the bare samples.

4.2.7.6 EDX microanalysis of worn surfaces

Figure 4.20 shows EDX microanalysis of the worn surfaces of the samples. The boride layer for borided SG peeled off during the wear testing (Figure 4.16(b)). Also, the X-ray microanalysis (EDX) test of it corroborated the absence of boron at the worn surface (Figure 4.20(b)). Conversely, borided LG and borided H-Cr exhibit uniform distributions B and Fe, which suggests the existence of a worn trace of a residual boronized film following wear testing. At the same treatment conditions, the only phase that forms on the LG is Fe_2B (see Figures 4.5(a) and 4.7(a)) because the boriding treatment is mainly based on the chemical composition that has a comparatively low boron potential in this process. Monophasic Fe_2B coatings are believed to be extra abrasive-wear resistant since the Fe_2B phase is more plastic (toughness) than FeB, as previously mentioned [142].

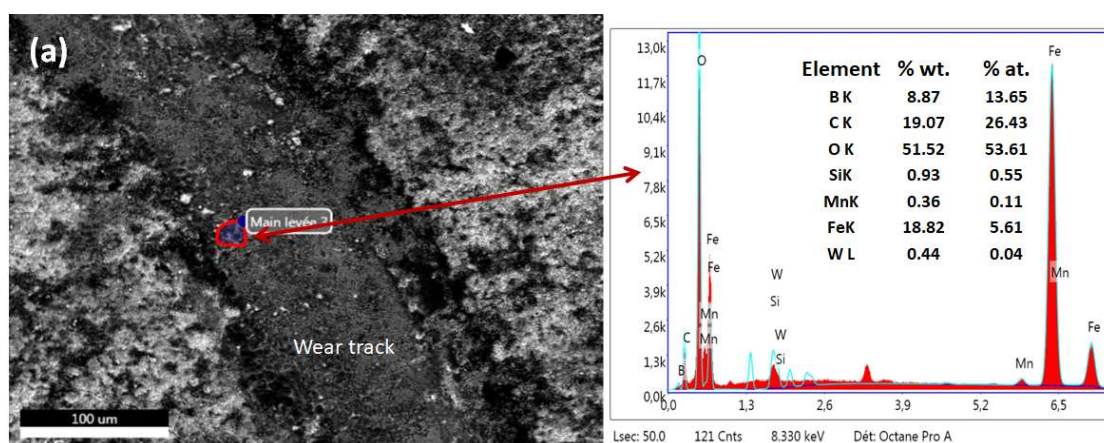
Figure 4.20(c) shows that the amounts of Fe, B, and C decreased clearly on the worn area compared to before wear testing. The presence of a dark zone in the wear track resulted in an increase in O throughout the entire zone. The presence of Fe in the wear track increased significantly, while the presence of Fe decreased significantly in the nonworn zone. Moreover, borided Hi-Cr (Figure 4.12(c)) exhibited stable behavior or a constant value of COF. Which may be attributed to considering that the two layers' (FeB and Fe_2B) thicknesses are essentially equal and the high hardness of diffusion zone is due to the presence of more carbides formed by boron diffusion, the layer becomes more resistant to wear environments as a result of the steady decrease in the hardness differential from the

surface to the substrate. Numerous researches, like Meric et al. [5], Erdoğan [164], and Ramadan et al. [165], indicated that under both low and high temperature circumstances, all boronized specimens showed greater wear resistance than unprocessed base metal.

These results suggest that the borided SG with a biphasic layer (FeB/Fe₂B) is more susceptible to wear than the borided LG with a mainly Fe₂B monophasic layer. A low-boron potential agent, such as recycled boriding agent, can produce monolayer Fe₂B or reduce layered FeB to increase the fracture toughness of the boronized coatings in order to enhance wear resistance.

4.2.7.7 Summary

In this study, cast iron's friction coefficient and wear rate can both be reduced via boriding, with the exception of borided SG. The borided layer's lowest wear rate when dry sliding against a WC ball in an ambient environment is approximately $4.25 \times 10^6 \text{ mm}^3/\text{N.m}$, it barely makes up 1/6 of the raw Hi-Cr cast iron. Abrasive and fatigue wear is the mode of wear for unborided cast iron in dry sliding against WC, whereas adhesive and oxidative wear is the mode of wear for samples treated with boriding.



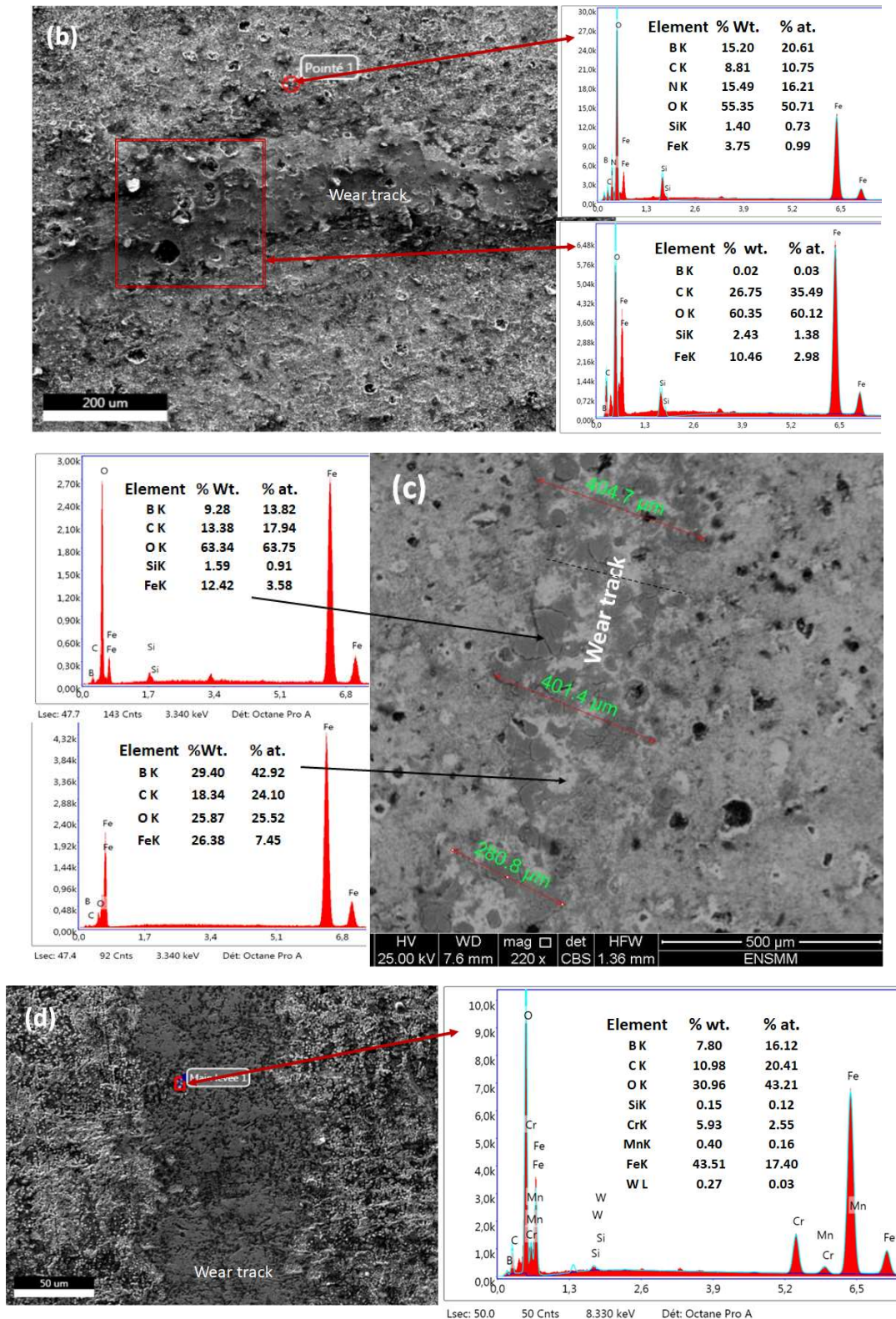
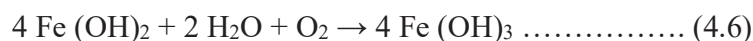
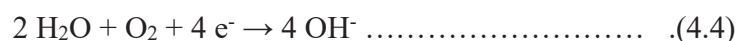


Figure 4.20. Wear track EDX point examination and SEM photos of: (a) borided LG, (b) borided SG, (c) polished borided SG, and (d) borided Hi-Cr cast irons.

4.2.8 Corrosion behavior of borided cast irons

4.2.8.1 Electrochemical properties

Electrochemical investigations in corrosive solutions allow the corrosion properties of hard material coatings to be examined and precise statements to be made about the behavior of the coating system [166, 167]. In addition, corrosion can be caused by ions that are aggressive and can pass through the layers, e.g., Cl ions. These ions penetrate the pores and reach the cast iron substrate. At this point, iron ions are formed, and the iron base dissolves. Ferrous ions penetrate through the coated surface, where OH ions interact with ferrous ions to form rust [168]. The following is the electrochemical procedure:



The corrosion reactions (4.2) and (4.4), which correspond to the reactions of the oxidation/anode and the reduction/cathode, take place simultaneously [169]. The polarization plots (Tafel) and Electrochemical impedance spectroscopy EIS charts (Nyquist) can be applied to assess the influence of the boronized layer on the resistance to corrosion of LG, SG, and Hi-Cr cast iron specimens. By creating a Tafel curve, one can determine the kinetics of corrosion.

4.2.8.2 The polarization curves (Tafel)

Figure 4.21 illustrates the Tafel curves of the specimens that began to corrode. The Tafel constants, corrosion potential (E_{corr}), corrosion current density (I_{corr}), and corrosion rates are calculated applying Gamry programs and are given in Table 4.3. The corrosion potential (E_{corr}) was calculated first while the applied current was zero. The corrosion potential was determined with the Gamry programs from the E at the minimum value of the current density in the Tafel diagram in Figure 4.21. The corrosion current density was determined by fitting the crossing point of the Tafel anodic and cathodic lines to the E_{corr} line and was determined by the programs using the Stern-Geary equation and the anode area, as shown in equation (4.7).

$$R_p = \frac{\Delta E}{\Delta i} = \beta_a * \beta_c \div 2.3 * i_{corr} * (\beta_a + \beta_c) \dots\dots\dots(4.7)$$

Where R_p is the slope at the origin of the polarization resistance curve in ohm-cm²; i_{corr} is the corrosion current density, amperes/cm²; β_a and β_c are the Tafel constants from a Tafel plot, volts/current decade.

Figure 4.21 and Table 4.3 show that the E_{corr} of borided irons was more positive value than that of non-borided samples, indicating that the boride layer is corrosion resistant. While, the borided Hi-Cr presents a more noble direction E_{corr} compared to borided LG and borided SG, this indicates that the durability of the boride layers on LG and SG decreased may be due to corrosion at the boride layer–substrate interface. Since the more positive corrosion potential of the cast irons after the treatment, in sodium chloride medium, means more corrosion resistance from a thermodynamic standpoint. Whereas the corrosion current density (I_{corr}) followed an opposite trend for both boridized SG and boridized Hi-Cr. It was also observed that as the amount of FeB increased, the I_{corr}

increased. Moreover, the I_{corr} for boride Hi-Cr samples is lower than that of boride SG samples. However, the lowest I_{corr} was observed in the boride LG iron.

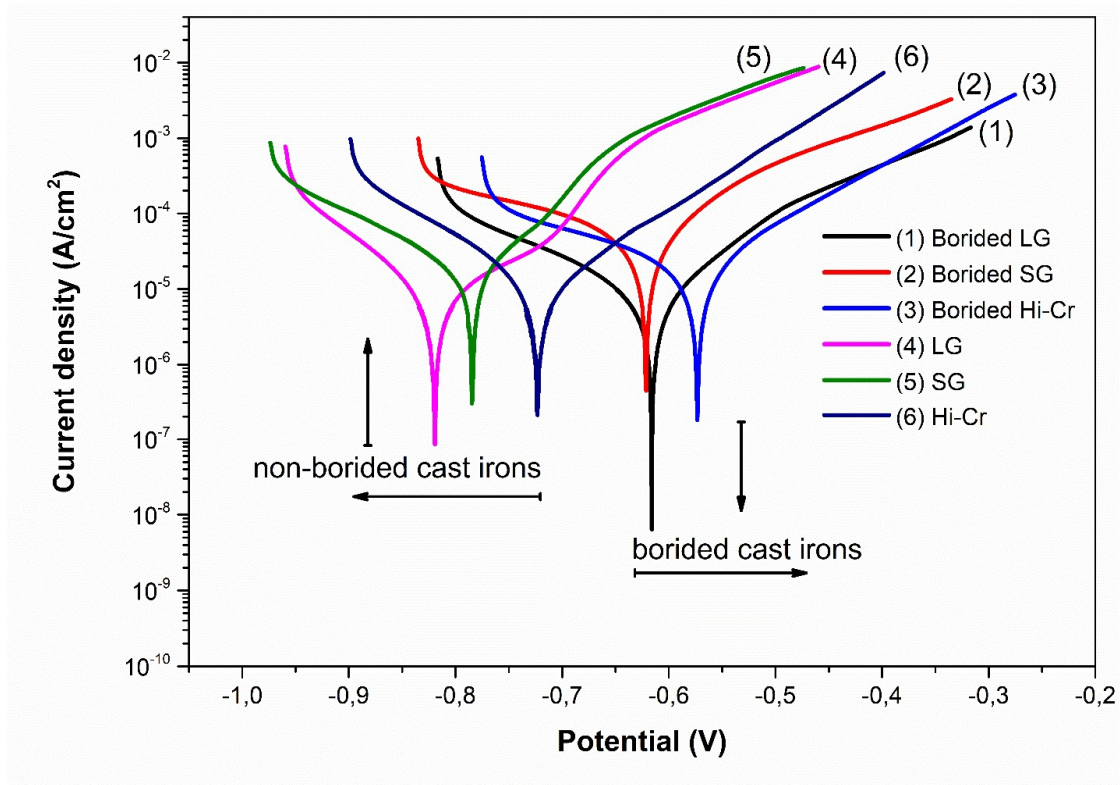


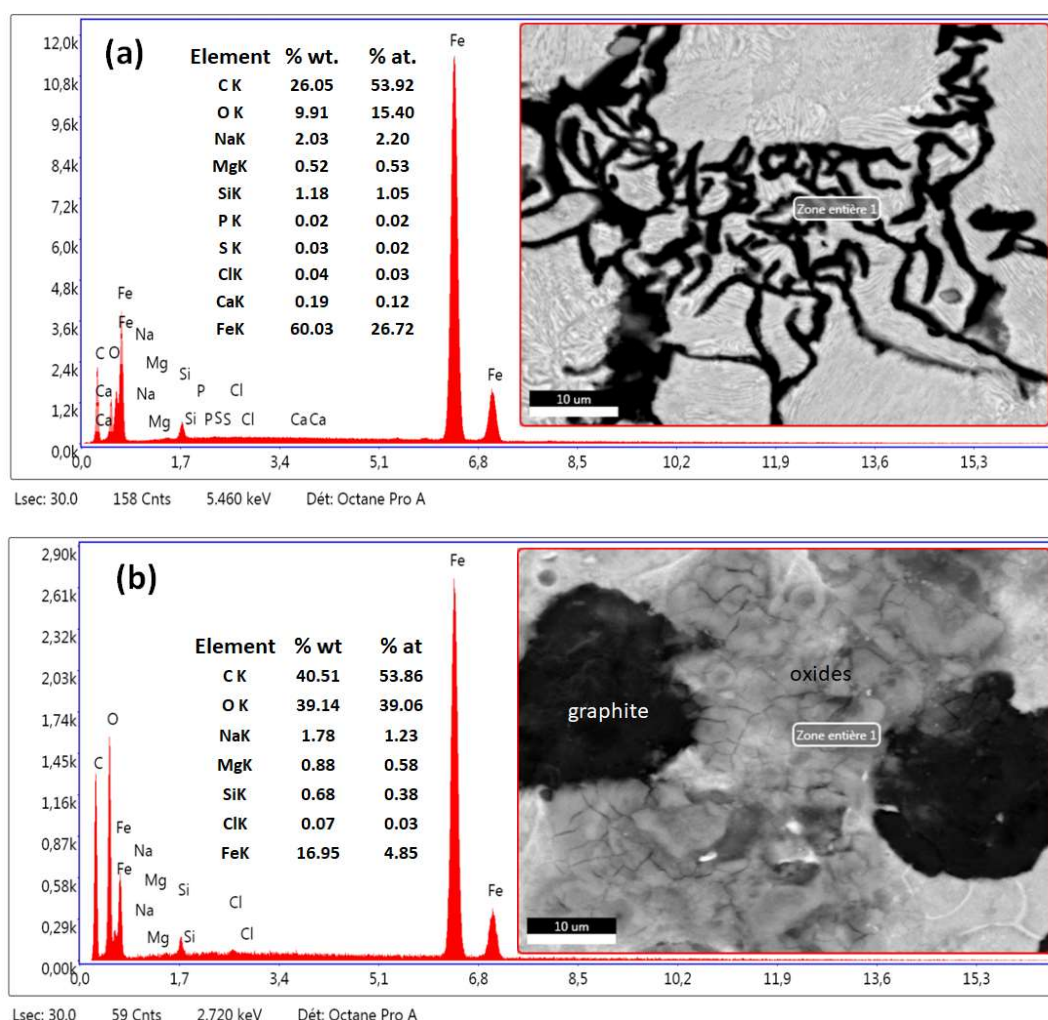
Figure 4.21. Potentiodynamic polarization curves for unborided and borided cast irons in a 3.5 wt.% NaCl media.

Table 4.3. Polarization test results.

Sample	Beta A (V/decade)	Beta C (V/decade)	$E_{\text{corr.}}$ (mV)	$I_{\text{corr.}}$ ($\mu\text{m}/\text{cm}^2$)	Corrosion rate (mpy)
Borided LG	0.092	0.106	-616.0	8.77	4.01
LG	0.304	0.127	-819.0	14.53	6.65
Borided SG	0.118	0.234	-621.0	71.50	32.74
SG	0.139	0.112	-784.0	21.00	9.61
Borided Hi-Cr	0.147	0.270	-573.0	31.90	14.59
Hi-Cr	0.118	0.078	-723.0	11.80	5.41

Surface images of bare and boride cast iron samples after the corrosion tests are shown in Figures 4.22 and 4.23, respectively. Following the corrosion tests, the non-borided surfaces (Figure 4.22) showed corrosion products, suggesting that iron was dissolved and dispersed on the surface throughout the test, resulting in the formation of iron oxides or chromium oxides. It is obvious that there are some pores and open graphite on the boride layer surface of SG samples (Figure 4.23b).

A higher current density, in general, denotes a lower-quality coating with probably more open porosity. A thicker Fe_2B layer of boron material allows corrosive solutions to enter more slowly and inefficiently.



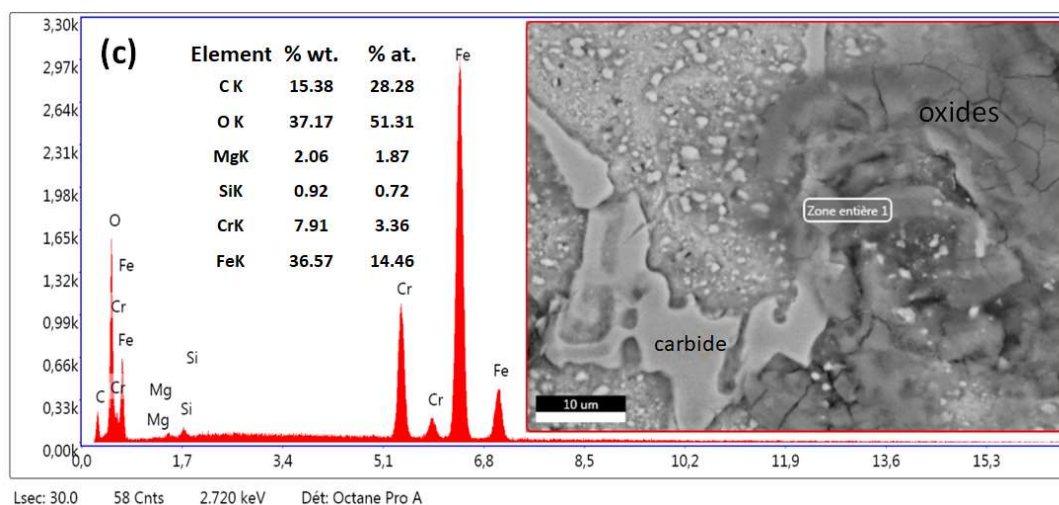
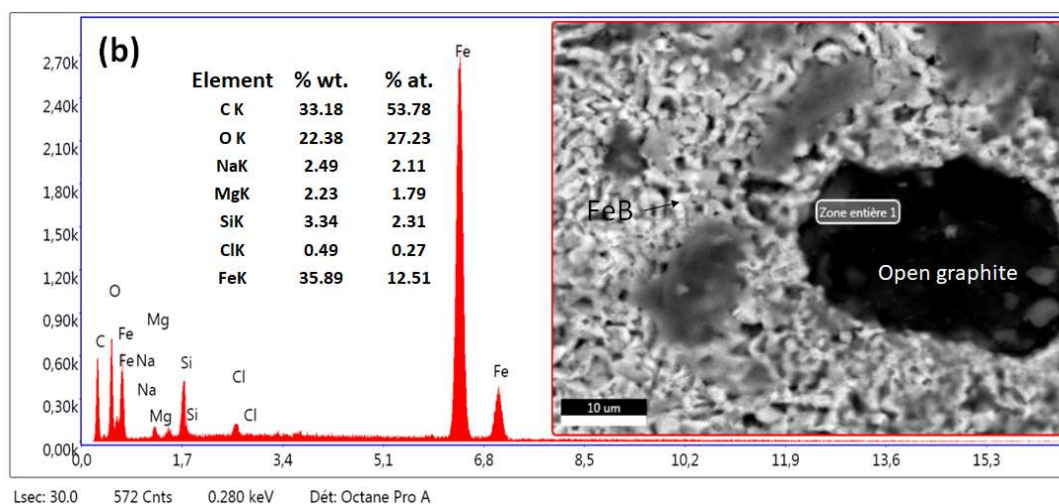
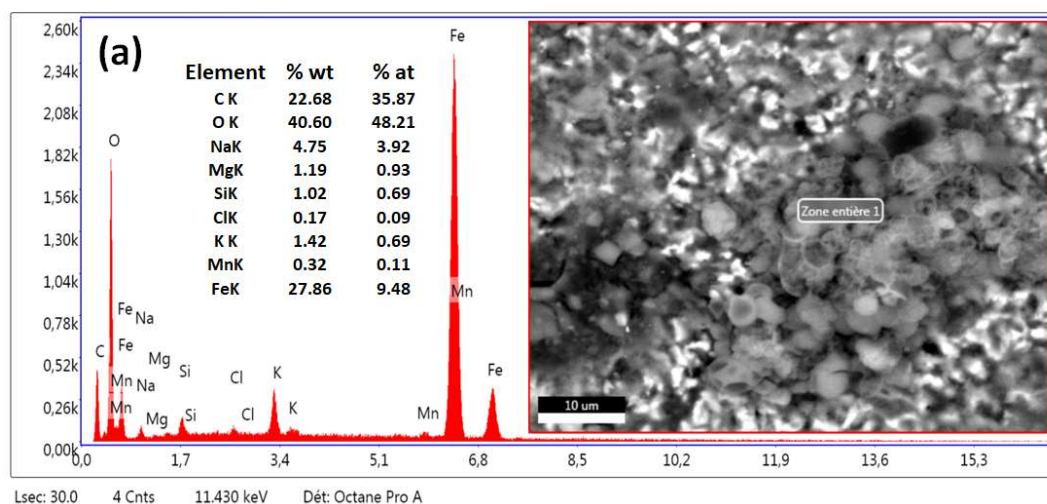


Figure 4. 22. SEM images and EDX examinations of surface of bare cast irons: (a) LG, (b) SG, and (c) Hi-Cr following the corrosion testing.



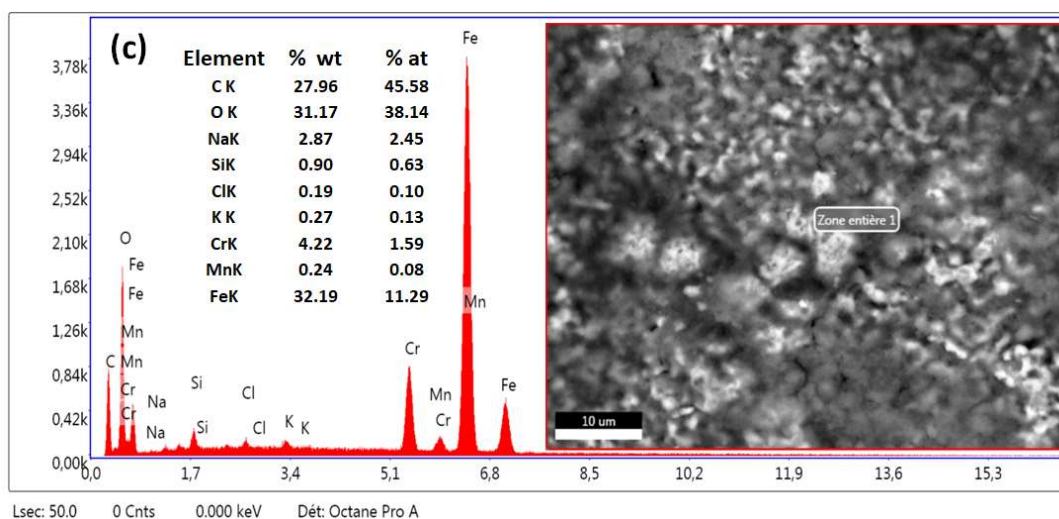


Figure 4.23. SEM images and EDX examinations of surface of boride cast iron samples (a) boronized LG, (b) boronized SG, and (c) boronized Hi-Cr following the corrosion test.

The coating's ability to resist electro-chemical corrosion depends on how much of a different phase is utilized as a boride layer compared to the substrate. Borides, FeB , Fe_2B , and Cr_xB_y are examples of noble phases that have a positive relationship to iron [170]. As a result, they are intact and provide a protective barrier. So, following boriding, more iron boride components accumulate on the surface, increasing the corrosion resistance.

According to [Table 4.3](#), the sample LG iron that underwent boriding had lower charge exchange activity at the interface than the unborided LG, which was reflected in a reduction in the corrosion current, I_{corr} . Otherwise, despite being subjected to the same conditions and processes, boronized SG and boronized Hi-Cr exhibit the largest corrosion current, indicating that they have the least amount of the phase Fe_2B that provides protection them as a result of Cl ions reacting chemically. Furthermore, the increase in the corrosion rate for boride SG is due to the influence of copper content on the kind of boride and underboride layer formed as well as pore formation in the boride layer ([Figure 4.23\(b\)](#)), it resulted in a greater surface size than bronized LG and a boost in roughness. While the

impact of the Cr content on the kind of boride and underboride layer generated can be used to explain the rise in the corrosion rate of boride Hi-Cr. Also, for borided Hi-Cr, Compos et al. [171] suggested that the chromium oxide outer layer that forms on the surface of high Cr steel may be diminished during the development of the borided layer, at least according to thermodynamics. As a result, B_2O_3 rather than Cr_2O_3 is formed, which reduces its corrosion resistance.

The corrosion potential and current on cast irons, which measure the electrochemical behaviour of passive boride layers, are highly dependent on the integrity of the boronized layer. This comprises the quantity and size of voids, the layer's thickness and adhesion, and the diffusion of particles inside pores and the boronized layer. It can suggest using electrochemical impedance spectroscopy to assess this.

4.2.8.3. Layers' impedance spectroscopy experiment

The strong technique of electrochemical impedance spectroscopy (EIS) can be used to examine the corrosion behavior of coated substrates [167, 170]. Nyquist curves collected from boronized and unborided cast irons after 1 hour exposure to the 3.5% NaCl solution are illustrated in [Figure 4.24](#).

[Figure 4.24](#) illustrates the EIS curves obtained during testing of boronized LG, boronized SG, boronized Hi-Cr, and unborided iron specimens, in NaCl solution. The enhanced electrical circuit equivalent obtained for unborided and borided samples is shown in [Figure 4.25](#). This is one way to simulate the chemical action of chloride ions on the iron layer. Concerning the unborided specimen ([Figure 4.25\(a\)](#)), R_s is the resistance of corrosive media, and the layer that is created on the top of the specimen of the during the electrochemical etching process has a resistance of R and a constant phase element of Q ,

possibly iron oxides or chromium oxides. [Figure 4.25\(b\)](#) shows the equivalent circuit for the borided specimens, R_s is the resistance of the medium; Q_c is the constant phase element; R_{po} could represent the boride layer; C_s could represent capacity, and the resistor, R_{ct} could be the substrate.

The findings of X-rays and microstructure of the boronized coatings, which demonstrate the occurrence of a Fe_xB_y or $(Fe, Cr)_x B_y$ component, are compatible with this explanation. It should be emphasized that the suggested circuit complies with advice from other researchers [167, 172].

The R_s , Q_c , n , R_{po} , C_s , and R_{st} qualities of the boronized layer are shown in [Table 4.4](#) along with the molded data using the equivalent circuits (shown in [Figure 4.25](#)) that were used to fit the data. There is evidence that high R - qualities mean better anti-corrosion abilities for the coatings [173]. For borided LG with $1.22 \text{ k}\Omega\text{-cm}^2$ resistance to charge transfer, a higher resistance arises, as shown in [Table 4.4](#). The behavior of the resistance of the boronized coating depends on Fe_2B layer amount, with a lower value for the borided Hi-Cr sample at $154 \text{ }\Omega\text{-cm}^2$, and a value of $408 \text{ }\Omega\text{-cm}^2$ for sample borided SG.

The solution resistance R_s , layer resistance R_{po} , and charge transfer resistance R_{st} are added together to form the polarization resistance R_p . It is important to note that the correlation between the corrosion rate and the polarization resistance R_p is inverse, with a large R_p correlating to a small corrosion rate [174, 175]. Since the same solution was employed, it should come as no surprise that R_s is extremely similar for the samples.

The results show that the sum of the R_{po} and R_{st} values of the samples increases when the amount of Fe_2B increases, though it reduces in borided SG. This is in line with

what [Figure 4.23\(b\)](#) shows, in that the layers of deteriorated boride and open graphite increase their surface area because of the roughness. The deterioration of the specimen surface with increasing roughness could be the cause of the decline in corrosion resistance. The actuality that the R_{ct} value of the boronized LG sample is higher than that of the unboronized specimens shows that significant Fe_2B effectively inhibits corrosion notwithstanding the surface properties.

The testing result produced impedance graphs for unborided and borided samples, and the computer generated impedance plots using the Gamry impedance matching software ([Figure 4.24](#)). The model utilized in all test information produced a fair match.

It is evident in [Figure 4.24](#) that the evaluated impedance graph matches the circuit model depicted in [Figure 4.25](#). Also, the presence of Fe_2B enhances the value of R_{ct} and decreases Q_{dl} , indicating that the exposed area decreases. Furthermore, the creation of a boride coating on the electrode's surface is enabled by a drop in Q_{dl} that could be brought on by a reduction in the local dielectric value and/or a rise in the electrical double layer depth. An increase in Fe_2B causes a decrease in the Q_{dl} of this boride coating. Since the Q_c exponent (n) refers to criteria for the surface heterogeneity, n quantities specify that the cast iron top is increasingly homogenous by boriding because of its coating on the surface of iron and decreasing corrosion ([Table 4.4](#)). This is consistent with what has been observed in terms of topography and roughness value ([Figures 4.8, 4.9](#), and [Table 4.1](#)).

It can be shown from a comparison of the X-ray analysis results for the boronized LG, boronized Hi-Cr, and boronized SG specimens in [Figure 4.7](#) that borided LG contains more Fe_2B phase than borided Hi-Cr and borided SG. Therefore, when compared to borided Hi-Cr and borided SG samples, the higher resistance to corrosion for borided LG was

attributed to higher amount of the Fe_2B structure as well as the better corrosion resistance of the Fe_2B phase. The Fe_2B microstructure efficiently shields the outer layer from the chlorine ion assault that causes steel corrosion, suggest Tavakoli and Mousavi-Khoie [172].

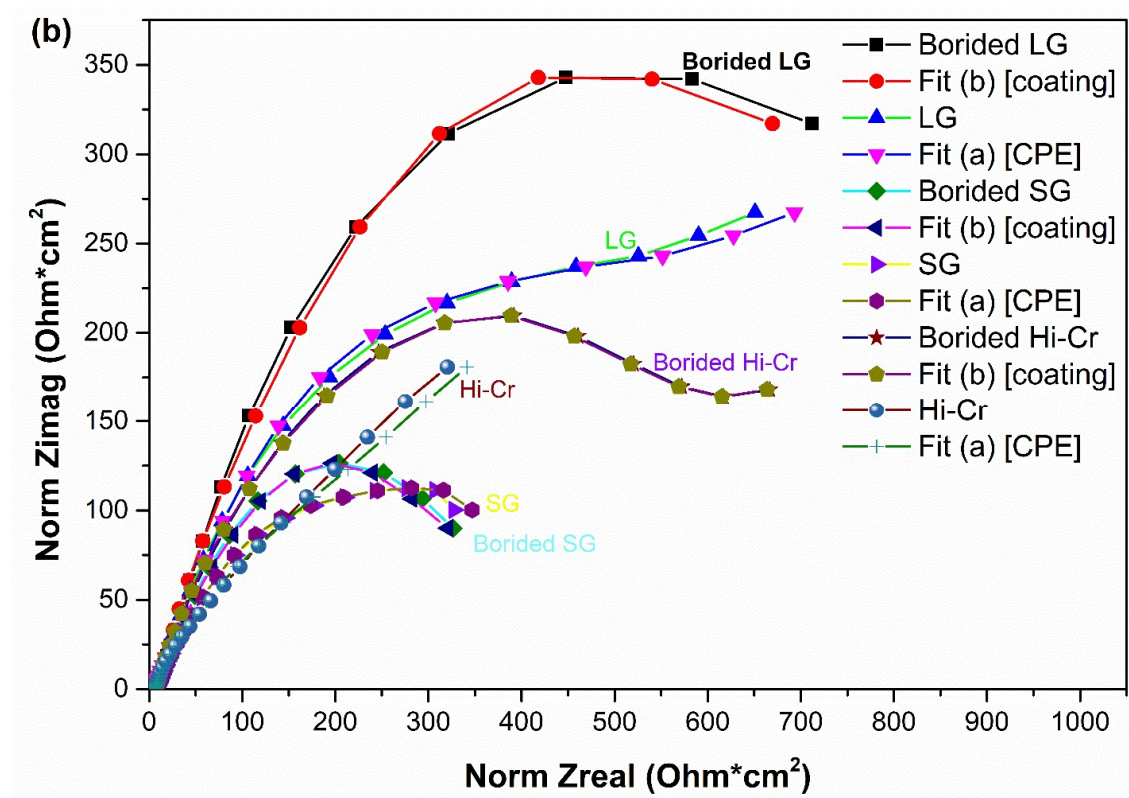
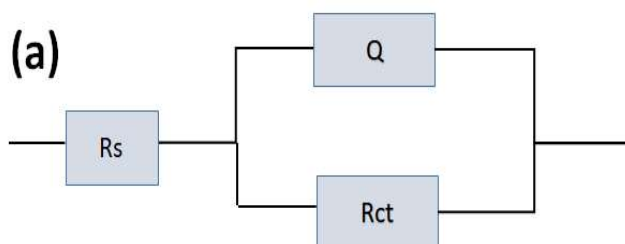


Figure 4.24. The curves of EIS obtained during testing of boronized LG, boronized SG, boronized Hi-Cr, and unborided iron specimens, in NaCl solution.



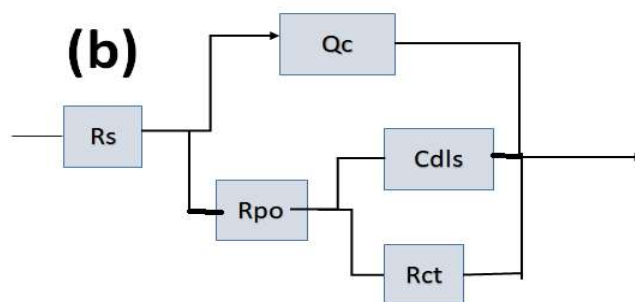


Figure 4.25. Equivalent electrical circuit of (a) cast irons before boriding (CPE) and (b) after boriding of cast irons, in NaCl solution.

Table 4.4. Impedance characteristics of the substrates and boronized cast irons in 3.5 wt.% NaCl liquid.

Specimen	R_s ($\Omega \text{ cm}^2$)	R_{po} ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	$Y_o - Q_c$ (mF/cm^2)	n_c	C_{dls} (mF/cm^2)
Borided LG	5.0 ± 0.05	57.8 ± 4.9	$1,220 \pm 61.2$	17.23	0.637	1.02
LG	5.1 ± 0.05	-	910.0 ± 19.6	-	0.623	4.18
Borided SG	7.1 ± 0.07	52.7 ± 5.8	408.2 ± 17.8	17.92	0.602	1.44
SG	5.5 ± 0.05	-	472.2 ± 11.6	-	0.557	8.08
Borided Hi-Cr	7.01 ± 0.07	719.4 ± 21.2	154.8 ± 96.12	2.02	0.660	158.4
Hi-Cr	4.79 ± 0.05	-	614.9 ± 22.35	-	0.522	19.0

4.2.8.4 Summary

The resistant to corrosion of cast iron is slightly improved by the boronizing treatment, and the resistance to corrosion of the borided samples rises as the amount of Fe_2B increases. These are explained by the reduced porosity of the boride in the hardened layers. The boriding process provides a means of obtaining more positive E_{corr} values. The corrosion outcomes demonstrate that boronizing increases the cast irons' resistance to corrosion by chlorine ions. The findings of the Tafel polarization evaluation and the EIS method generally agree.

CHAPTER 5

5. CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

Cast irons were treated with powder-pack boriding utilizing recycled boriding agent without the addition of new powder to evaluate how it impacted the microstructure, hardness, adhesion, wear, friction, and corrosion behaviors. The following findings can be taken from the study of boriding treatments at 950 °C for 4 hours, done on lamellar, spheroidal graphite, and high-chromium cast irons:

- 1) The Fe₂B of the boride layer is obtained on Lameller graphite cast iron by using a recycled boriding agent.
- 2) A sawtooth-like morphology grown on LG and SG is less intense for Hi-Cr due to the base surface's large chromium conten. The immediate formation of interstitial compounds of CrB or Cr₂B in conjunction with FeB and Fe₂B stops the diffusion of boron.
- 3) Measurements of the boride layers formed revealed that both the micro-structural and chemical makeup significantly affect the boride layer thickness. The borided cast iron borided Hi-Cr had the thinnest layer of $45 \pm 8 \mu\text{m}$, while the lamellar cast iron borided LG had the thickest boride layer of $109 \pm 10 \mu\text{m}$
- 4) The coated borided irons' XRD, OM, SEM, and EDX results showed that, due to the type the of iron, the layers are made of Fe₂B, FeB, CrB, Cr₂B, Fe, or M₂₃ (C, B)₆ and iron oxides.
- 5) Cast iron makes a suitable choice for boriding since the procedure makes it harder. Additionally, cast iron has superior hardness that is obtained after boriding, making it a less expensive material than other ferrous alloys. On Hi-Cr, the boronized coatings of 2148 HV_{0.1} with the highest hardness were produced.
- 6) Although the LG and SG adhesion strengths of boride layers are satisfactory, flaking is caused by hard CrB phases near the indentation's edge, and the flat layer on borided Hi-Cr surfaces lowers the strength.

- 7) The present results showed that boriding lamellar (LG) and high-chromium (Hi-Cr) cast irons helped improve wear resistance by reducing the friction coefficient and wear rate comparison with the non-borided materials. The wear resistance of boride samples increases by about 84% for Hi-Cr iron and 71% for LG iron compared to bare samples.
- 8) A higher wear rate is observed for borided spheroidal cast iron because of the creation of the soft layer under the boronized coating and the inhomogeneous morphology and brittleness of the surface layer.
- 9) Polishing of spheroidal (SG) cast samples after boriding slightly improves tribological characteristic by reducing wear rate.
- 10) In general, the boronizing procedure may offer a noticeable increase in wear resistance.
- 11) The boriding treatment provides a means of obtaining more positive E_{corr} values and slightly improves protection against corrosion in cast iron. That is attributable to the creation of borides in the surface layers. As a result, they could offer longer lifetime protection than cast iron parts that are not borided.
- 12) The boriding results also indicate that the use of a recycled packing boriding agent was effective in producing borided layers that improved the hardness, tribological, and corrosion behaviors of cast iron materials. The best wear and corrosion resistance after boriding were observed for $LG > Hi-Cr > SG$.

5.2 Recommendations

According to the study, the boron layers on LG and Hi-Cr irons with the less brittle FeB phase significantly improved the iron's resistance to corrosion and wear. Thus, it can be applied as a multipurpose coating in oil, gas, mining, mineral processing, cars, and farming applications such as gears, valves, milling, pump shafts, and pit tools, ensuring longer component life.

The following future work is recommended:

1. Conduct experiments with plasma nitriding on the boride layers.

2. Conducting a study on the wear tests for a longer distance and higher temperatures.
3. To fully understand the wear characteristics as well as mechanisms on the unborided and borided samples in wet options, conduct wear tests under lubricated conditions.
4. Perform X-ray diffraction (XRD) or other appropriate instruments to identify the phase formation of corrosion products obtained on the boride coatings.

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