Microstructure Evolution and Properties of Boronized Low Alloy Steels and Subsequent DLC/CrN Coating

Ph.D. Thesis

By

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DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2021

Microstructure Evolution and Properties of Boronized Low Alloy Steels and Subsequent DLC/CrN Coating

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

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ADITYA KUMAR LITORIA



DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **MICROSTRUCTURE EVOLUTION AND PROPERTIES OF BORONIZED LOW ALLOY STEELS AND SUBSEQUENT DLC/CrN COATING** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2017 to April 2021 under the supervision of **Dr. SANTOSH S. HOSMANI**, Associate Professor, Department of Metallurgy Engineering and Materials Science, IIT Indore.

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

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

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21/09/2021

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ABSTRACT

The present study was focused on establishing an in-depth understanding of the pack-boronizing (a thermo-chemical heat treatment) behaviour of industrially employed low alloy steels (AISI EN41B and AISI 4140). Optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), electron probe microanalysis (EPMA), glow discharge optical emission spectroscopy (GDOES), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, nanoindentation, 2D surface-profilometer, and tribometer were used to investigate the specimens. Microstructure evolution in the boronized layer was studied in the present work. The critical role of alloying elements present in the steel was explored in terms of their migration behaviour during the growth of the boride front and, consequently, in understanding their role in the formation of boride, matrix, and transition region within the boronized layer. Boride morphology and the migration of alloying elements (during the development of a boronized layer) caused a variation in composition and fraction of phases from the surface to the core. Such variation affected the localised mechanical properties of the boronized layer. Maximum hardness of about 1800 HV_{0.1} was found in the nearsurface region of the boronized steel. Alloying elements such as Cr, Ni, Mo, and Mn revealed some solubility in the iron-boride. However, C, Al, and Si were entirely rejected by the boride's growing front. Al and Si were accumulated in the matrix and transition zone. The migration kinetics of Cr, Mn, Mo, and C was found to be almost equivalent to the rate of boride growth. However, Ni, Al, and Si were migrated at a slower rate. Boronizing treatment enhanced the low alloy steels' performance against wear and oxidation. Formation of oxide scale containing Fe₂O₃, Cr₂O₃, and B₂O₃ was revealed when the boride surface was exposed to atmospheric conditions. Contrary, Fe₃BO₆, Fe₃BO₅, Fe₂BO₄, and FeBO₃ were the resulting compounds in the oxide scale during high-temperature oxidation. Among

the investigated wear parameters, the maximum and minimum wearresistance of the boronized surface was ~46 and ~8 times the wear resistance of the non-boronized surface under the dry sliding conditions, respectively. Boronized layer helped in enhancing the load-bearing capacity of the steel; however, a very low coefficient of friction (CoF) was challenging under dry sliding. The observed CoF of the boronized surface was about 0.45-0.68. Synthesis of multilayer architecture by producing a DLC/CrN layer over the boronized surface effectively enhanced the tribological performance of the steel. Considerably low CoF (0.07-0.09) during dry sliding wear was achieved due to the deposition of DLC/CrN coating.

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NOMENCLATURE AND ACRONYMS

У	Boride layer thickness
t	Time of boronizing treatment.
D	Diffusivity
W_{sp}	Wear rate
ΔV	Volume loss
Р	Applied load
L	Sliding distance
$\mathbf{V}_{\mathbf{s}}$	Sliding speed
WTW	Wear track width
DLC	Diamond-like carbon
B-DLC	Boronized + DLC
AB	As boronized
CrN	Chromium nitride
$c_B^{i,j}$ $c_m^{i,j}$ f_B	Concentrations of alloying element i at depth j in the boride phase Concentrations of alloying element i at depth j in the matrix phase Fraction of boride phase
f_m	Fraction of matrix phase
MK_i	Migration kinetics of the alloying
	element 'i',
Н	Hardness
Ε	Elastic modulus
m	Strain-rate sensitivity
V , b ³	Activation volume
Ė	Strain rate
h	Creep displacement
А	Projected area of the indent.
Δm	Mass-change
R _a	Average surface roughness

Introduction

Chapter 1

With the annual production of around 1864 million tonnes in 2020, steel holds a key position as the most potential material for the world's manufacturing industries. Steel has wide applications in various industries such as metal production and processing, transportation, mechanical equipment, infrastructure, domestic appliances, automobile, electrical equipment etc. Hence, steel production and consumption play a crucial role in driving the world's economy.

Steels are categorised into various grades based on varying carbon percentage and the types of alloying elements with varying concentrations. Different applications demand different properties of steels. Low alloy steels find foremost applications in automotive and aerospace components, pipes, railway components, and offshore/onshore structural engineering bodies. Industrial components experience deterioration and, sometimes, failure based on the type of application, service conditions, and material properties. However, the engineering components respond efficiently against failure (caused by wear, oxidation, corrosion, etc.) if the microstructure of their surface is customised or the layers of suitable materials are deposited [1-7]. In this regard, the alloy design can be an option. However, an alloy's economic design that can fulfil the bulk and surface requirements of components is challenging. On the other hand, surface engineering (modification of existing surface and coating of suitable material) of a low-cost material is viable. Boronizing, nitriding, carburising, carbo-nitriding, nitro-carburising, etc., are widely used thermo-chemical methods in industries to enhance steels' surface properties.

The current study focuses on scrutinizing the performance of low alloy steel after boronizing/boriding. Boronizing has emerged as one of the promising surface modification routes to produce hardened surfaces of alloys. It enhances surface properties and makes it withstand surface degradation phenomena such as wear, corrosion, and oxidation [8-10].

Surface alloying of steel with boron forms hard iron-borides (like FeB and Fe₂B). Pack-method of boronizing treatment involves the boron source (generally, B₄C), activator (like KBF₄), and diluent (mostly, SiC or Al₂O₃). Steels are typically boronized at elevated temperatures (800–1100°C). During the boronizing treatment, boron-halide gases and trapped oxygen in the pack-mixture react with the boron source, generating a boron-rich atmosphere [7, 11]. Such atmosphere introduces boron into a steel surface and forms boronized layer. Iron-based alloys can show the formation of a single-phase or dual-phase boride layer (i.e., Fe₂B or FeB + Fe₂B), depending on the boronizing process parameters like composition of pack-mixture, temperature, and time [7, 11-12]. The combined effect of alloying elements on the steels' boronized layer's microstructure and properties is complex and least expounded.

A considerable improvement in the surface layer's quality is possible by combining the boronizing treatment with suitable coatings. Primarily, hard, or soft coatings are principally used to overcome wear and frictionrelated issues. The majority of carbides, nitrides, borides, and oxide-based coatings fall under hard coatings. Along with these, different carbon-based coatings (e.g., diamond, low hydrogenated diamond-like carbon (DLC), etc.) also falls under this category. Soft coatings include polymers, sulphates of alkaline earth metals, halides, and soft metals, etc. Generally, a very low value of CoF is the prominent outcome of carbon-based coatings [13-18]. Therefore, the effect of DLC/CrN multilayer coating on the boronized low alloy steel's tribological behaviour is also investigated in the current work.
1.1 Motivation

Typically, the boronizing of iron-based alloys leads to the formation of iron-boride phases in the surface layer. The alloy chemistry has a significant influence on the boronizing behaviour. The microstructure of boronized layer, especially the morphology of borides, is dependent on the concentration of alloying elements [19-24]. High-alloy steels (like stainlesssteel) shows a smooth iron-boride/substrate interface [25, 26]. However, the plain-carbon and low-alloy steels reveal the saw-tooth morphology of ironborides [7, 11]. High-carbon high-alloy steels (e.g., AISI D2) and mediumcarbon medium-alloy steels (e.g., AISI H13) show a relatively less irregular boundary (as compared to low alloy steels) between the Fe₂B layer and the substrate (i.e., less saw-tooth appearance of Fe₂B); however, the FeB layer still shows the saw-tooth morphology [27, 28]. Different elements can have different solubility and migration kinetics in the iron-boride phase and its surrounding regions. The composition and migration behaviour of alloying elements during the layer growth can affect the morphology of borides and the boride/matrix interface nature.

Most archival literature has focused on binary Fe-based alloys. However, the alloying elements' combined effect on steels' boronized layer is complex and least expounded. Medium-carbon low-alloy steels like 34CrAlMo5-10 (EN41B) have a wide range of applications in the automotive, chemical, oil and gas, and pharmaceutical industries. EN41B steel is primarily used for nitriding. However, boronizing of this steel can give substantially higher surface hardness than the nitrided surface. Therefore, boronizing treatment can widen the applications of EN41B steel, especially for severe conditions of wear. This steel contains various alloying elements like C, Cr, Mn, Mo, Ni, Si, and Al. Understanding the effect of boron, multiple alloying elements, and processing parameters on the microstructure development and distribution kinetics of alloying elements during the layer growth is one of the critical challenges. In the case of low alloy steels like EN41B, saw-tooth morphology of boride and the migration of alloying elements (during the process) cause a change in the composition and fraction of phases with an increase in depth from surface to core. Microstructural variation (with depth), localised mechanical behaviour, and oxidation resistance of the surface (containing a varying proportion of boride and boride-free matrix regions) can affect the tribological characteristics of boronized steels. Therefore, the effect of boronizing on different properties is essential to study.

Duplex surface treatments with variable multi-layer architecture enhance load-bearing capacity together with an improved wear resistance of the material. This approach also protects the material surface from undesirable cracking and delamination [14, 29]. A set of combinations gathering variable surface engineering techniques together under a particular condition can be efficiently applied for various contacting surface applications. Boronizing treatment producing hard boride top surface and DLC being harder along with very low CoF attaining popularity for wide range of applications [14, 30-31].

1.2 Objectives

The current study's principal objective is to understand the packboronizing behaviour of the low alloy steels (34CrAlMo5-10/EN41B and AISI 4140). These steels contain multiple alloying elements. Understanding the effect of boron, multiple alloying elements, and processing parameters on the microstructure development and distribution kinetics of alloying elements during the layer growth is one of the critical challenges. In this regard, the effect of alloying elements on the growth behaviour of ironboride and the corresponding migration behaviour of alloying elements are investigated. The investigated low alloy steels show saw-tooth morphology of boride. During the formation of such boride columns, the migration of alloying elements causes a change in the composition and fraction of phases with an increase in depth from surface to core. Such variation (with depth) can affect the localised mechanical behaviour, oxidation resistance, and tribological characteristics of boronized steels. Therefore, the boride layer's performance is evaluated in terms of its response to oxidation, nanoindentation, and wear. Boronizing treatment produces hard surface. However, such a surface has high CoF. Therefore, effect of DLC/CrN multilayer coating on tribological behaviour of the boronized steel is also studied. Specific objectives of the current study are as follows:

- To investigate the effect of pack-boronizing on alloying elements' migration behaviour and the accompanying mechanism of microstructure development in low alloy steel
- 2) To examine the response of the boronized layer to wear, nanoindentation, and oxidation.
- To develop a multilayer architecture with a boride layer using an advanced coating like DLC and evaluate its tribological response in low alloy steel.

1.3 Thesis Structure

This thesis includes seven chapters describing the microstructure and properties of the boronized low alloy steels (34CrAlMo5-10/EN41B and AISI 4140).

Chapter 1 is the introductory chapter, which describes the background, motivation, and goals of the current work.

Chapter 2 presents a comprehensive literature review on different aspects of boronizing, which led to the foundation of the current thesis. The literature study includes the basics of the boronizing process, an overview of other boronizing techniques, mechanism on pack-boriding, factors affecting boronizing, and the role of prior/subsequent surface treatment in boronizing.

Chapter 3 describes the experimental methodologies associated with the specimen preparation, boronizing treatment, and characterization techniques used in the present work. The experimental strategy of this work is also summarised in the form of a flowchart.

Chapter 4 evaluates the outcomes of pack-boronizing of low alloy steel (EN41B). Migration behaviour of alloying elements is mathematically interpreted and experimentally understood using advanced characterization techniques like GDOES, EPMA. Based on the results, microstructure evaluation during boronizing is systematically explained.

Chapter 5 contains a detailed study of various properties of the boronized EN41B steel. This chapter explains the nanoindentation, oxidation, and wear behaviours of the steel. In this study, specimens are characterised using microscopy, various spectroscopic techniques, nanoindentation, surface profilometer, and tribometer. Nanoindentation has revealed the effect of microstructural inhomogeneity on the localised mechanical behaviour of boronized layer. Room temperature oxidation behaviour of the boronized layer's microstructure is investigated by polishing the surface to different depths and recording the XPS spectra. Oxidation study is also performed at elevated temperatures (200, 550, 850°C). Wear behaviour of the boronized and non-boronized specimens under different loading conditions (20, 40, 60 N) and sliding speeds (0.3 and 0.5 m/s) is also discussed in this chapter.

Chapter 6 is designed to understand the effect of multilayer architecture, combined with the boride layer, on the tribological behaviour of low alloy steel (AISI 4140). In this regard, DLC/CrN multilayer coating is synthesized over the boronized surface.

Chapter 7 contains the overall conclusions of the present thesis and the scope of future work.

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Chapter 2 Literature Survey

2.1 Surface Engineering

Surface engineering is adopted to enhance the service life and performance of engineering components with minimal or no change in the material's bulk properties. Performance and life of many components used in the automotive, chemical, oil and gas, and pharmaceutical industries are primarily governed by the characteristics of surface and sub-surface regions of the materials [1-6]. Since most failures of components are linked with surface deterioration, surface engineering has emerged as a principal tool to overcome material loss. It gives additional characteristics to the surface so that the material become functional and persistent against various adverse conditions like improper loading, mishandling, atmospheric challenges (such as temperature, humidity, friction), etc. [1, 6]. Generally, the performance of surface-treated components is evaluated in terms of various parameters such as [2, 5, 6]: (i) resistance to wear, corrosion, fatigue, and oxidation; (ii) enhanced mechanical, thermal, electrical, and electronic properties; and (iii) reliability and cost-effectiveness of materials and processing routes.

The surface region can be characterised as a multilayer architecture under service condition. The topmost surface is distinguished by its roughness, and the sub-surface region is possible to divide into five distinct zones with different attributes (Figure 2.1) [6]. Based on the type of applications, different processes are popular to transform the surface so that the material gains various combinations of properties [5]. For example, when a component is exposed to a severe wear condition, its surface requires several properties like hardness, toughness, lubricity, oxidation, and corrosion resistance. Machine components at an abandoned stage can be brought into service by treating their surface.

Apart from the positive aspects of surface engineering, inevitable flaws are associated with improper surface modification. Formation of cracks, porosities, and oxides on an engineered surface can lead to material failure. Moreover, the difference in mechanical, physical, and chemical properties of the modified surface and the bulk (core/non-treated) material can weaken their interface, resulting in an inappropriate performance of components [1].

Figure 2.2 summarizes different techniques of surface engineering [1]. Typically, surface engineering methods are categorised as follows: (i) modification of the existing surface of a component and (ii) deposition (coating) of materials on the surface of a component. Surface modification techniques are further classified based on the metallurgical transformations, where surface chemistry may or may not change [1, 2]. In case of surface deformation (e.g., shot peening) and phase transformation (e.g., induction hardening) based processes, surface chemistry does not change. However, surface alloying processes like boronizing, nitriding, carburizing, alter the surface chemistry. Current work focuses on boronizing, which is a thermochemical and diffusion-based processes.



Figure 2.1: Schematic of five zone architecture of sub-surface region under service condition [6].



Figure 2.2: Flow chart corresponding to various surface modification techniques [1].

2.2 Boronizing

Boronizing (also called 'boriding') is one of the prominent surface hardening treatments based on temperature-driven chemical reactions at the metal surface and subsequent controlled diffusion of boron atoms into the substrate [2, 7-13]. Boronizing treatment is gaining popularity due to its feasibility in industrial applications [2, 9, 11]. This treatment is suitable for many ferrous and few non-ferrous alloys [8, 9, 14-23]. Boronizing of alloys can effectively be carried out in the temperature range of 850-1000°C [2, 8-10]. Interstitial diffusion of boron achieves saturation in metallic materials, leading to the formation of metal-borides. High hardness and high resistance to abrasion (compared to other thermo-chemical treatments like carburizing and nitriding) are the major characteristics of boronizing treatment. Therefore, this process promises better tribo-mechanical performance [2, 7, 9, 24-28]. Moreover, the boronizing treatment enhances corrosion resistance (in different alkaline and acid medium) and high-temperature oxidation resistance of steels [2, 11, 26, 29-38].

2.2.1 Working Principle of Boronizing

Boronizing process uses thermal energy for chemical reactions at the surface of metallic components, resulting in the absorption of boron atoms into the material's lattice. After attaining a suitable temperature, diffusion of boron starts, and it reacts with the substrate-atoms, leading to the formation of metal-borides. The iron-based alloys form two kinds of iron-borides, i.e., FeB and Fe₂B. Concentration of boron decreases gradually as we progress from surface to the bulk. If the boron potential surrounding the steel is high enough, the FeB (boron rich phase) is formed at the surface, followed by Fe₂B (an iron-rich phase) layer and then nonreacted substrate material. The FeB phase (orthorhombic crystal structure) contains ~16.23 wt.% B; and Fe₂B (tetragonal crystal structure) has ~8.83 wt.% B. As a result of boronizing, either a single-phase structure (Fe₂B) or dual-phase structure (FeB and Fe₂B) forms, depending on various process parameters such as the availability of boron-potential, boriding method, chemical composition of the substrate, process duration, and temperature. The single-phase structure of boronized layer is more desirable than the dual-phase structure because the formation of cracks/delamination (especially between FeB and Fe₂B layers) is more susceptible in dual phase due to the difference in coefficient of thermal expansions (α) of Fe₂B ($\alpha_{Fe_2B} = 5.1 \times 10^{-6}$ /°C) and FeB ($\alpha_{FeB} = 23 \times 10^{-6}$ /°C) [2, 7-13, 39-43].

Figure 2.3 shows the growth of boronized layer schematically through the principle of diffusion. The conventional boronizing process occurs in two stages, which are elaborated as follows [7, 8, 44, 45]:

- Stage 1: Chemical reaction occurs between the boron atoms and substrate surface (steel). Under the influence of temperature and time, nuclei of the boride phase form at surface. Fe₂B nuclei grow preferentially in inward direction and form thin boride columns. As the process continues, Fe₂B dominated layer forms. Nucleation of the Fe₂B phase can occur at various defect points/sites, which are either in macro-range (e.g., surface roughness, scratches etc.) or micro-range (e.g., grain boundaries, dislocation, etc.). Furthermore, the FeB phase can form at the surface if excess boron concentration is available.
- **Stage 2**: Thickness of boronized layer increases due to the diffusioncontrolled reactions. Generally, an increase in thickness of the layer follows the parabolic-rate law:

$$y^2 = k \times t \tag{2.1}$$

where *y* is the boride layer thickness, *k* is the constant, and *t* is the time of boronizing treatment. Fe₂B phase has a body-centred tetragonal (bct) structure, and the diffusion of boron atoms is likely to occur in [001] crystallographic direction. As mentioned above, depending on the process parameters, the dual-phase formation is possible, where FeB phase is likely to form along [002] crystallographic direction [38, 44, 46, 47].

Yu et al. [48] proposed the growth model for forming the FeB/Fe₂B dual-phase structure. This model is based on the following six physiochemical steps, which occur during the boronizing of steels:

- I. B (free) \rightarrow B (adsorption).
- II. B (adsorption) + Fe \rightarrow FeB, or B (adsorption) + 2Fe \rightarrow Fe₂B.
- III. B atoms jump through FeB or Fe₂B lattice (from high to low chemical potential) at B/FeB or B/Fe₂B interface.
- IV. $Fe_2B + B \rightarrow 2FeB$ (at FeB/Fe₂B interface).
- V. $2Fe + B \rightarrow Fe_2B$ (at Fe₂B/Fe interface).
- VI. $2FeB \rightarrow Fe_2B + B$ (phase transformation during growth).



Figure 2.3: Schematic depiction of the boronized layer growth [49].

2.2.2 Techniques of Boronizing

The boron source in the conventional routes of boronizing is in the form of solid, liquid, or gaseous media. Pack-boronizing uses a solid-state boron medium, and it is more popular due to its easy operation, availability of boron source, and low cost. However, this approach has some limitations, like non-homogenous/uncontrolled boron potential in the pack-mixture [19, 26, 43, 50-52], which creates hurdles in predicting the growth kinetics of iron-borides. On the contrary, growth kinetics can be well predicted for gas boriding [14, 29, 53-55].

Different physical and chemical routes are available as alternates to conventional boronizing. With technological developments, different materials can easily be boronized, which are otherwise tricky to boronize using traditional techniques [56-60]. Figure 2.4 summarizes the various methods of boronizing [9, 10]. Successful boronizing of metals/alloys is possible due to the high temperature in these processes. The current work has adopted the pack-boronizing technique, which is described in the subsequent section. Other techniques are beyond the scope of this work, and therefore, they are not explained in this chapter.



Figure 2.4: Flow chart describing various boronizing techniques [9, 10].

2.2.3 Pack Cementation Technique of Boronizing

Powder-pack boronizing is a solid-state boriding technique carried in the presence of a powder-mixture containing (i) boron source, (ii) activator, and (iii) diluent. Amorphous boron, ferroboron, or boron-carbide (B₄C) are widely used boron sources. An activator in the mixture is important because it regulates and accelerates boron's availability to the material surface. Commonly used activators in pack-boriding are NaF, AlF₃, KBF₄, Na₂B₄O₇, etc. Diluent plays a key role in eliminating the sintering risk of boronizing mixture and lowering the boron potential to the surface (to avoid the formation of FeB layer) [7-10]. Table 2.1 summarizes the literature (where powder-pack boronizing technique was used) for boronizing parameters and the resulting phases in the boronized layer of various alloys.

Process of boronizing is accompanied by the formation of active boron atoms from the boronizing pack-mixture [9, 10]. B₄C is a popular source of boron during pack-boronizing (Table 2.1). Despite the higher cost, the use of B₄C with a certain amount of activators and diluents is proved to be an efficient way of obtaining metal-borides. Boron source (B₄C) reacts with oxygen in pack-mixture and forms B₂O₃. Commercially available B₄C powder contains a certain amount of B₂O₃, which can act as an activator during the later stages of pack-boronizing [61]. The possible chemical reactions are as follows:

$$5B_2O_3 + B_4C \to 7B_2O_2 + CO$$
 (2.2)

At elevated temperature, B_2O_3 and B are separated via the following reaction:

$$3B_2O_2 \rightarrow 2B_2O_3 + 2B \tag{2.3}$$

The B atoms thus formed interact with the metal (M) to form a solid solution (M-(B)) or metal borides (M_x-B_y) :

$$\mathbf{B} + \mathbf{M} \to \mathbf{M} - (\mathbf{B}) \tag{2.4}$$

$$yB + xM \rightarrow M_x - B_y$$
 (2.5)

Finally, the entire chemical reaction is summarized as:

$$3B_2O_3 + 2\frac{x}{y}M + 3C \rightarrow 2B_2O_3 + \frac{2}{y}M_x - B_y + 3CO$$
 (2.6)

Voroshnin et al. [9] proposed the mechanism pack-boriding using the halide source as an activator, which forms boron-halides (BF_2 or BF) at elevated temperature. These halide gases are responsible for the transport of boron atoms to the metal surface, leading to the formation of borides:

$$\frac{n}{2}BF_2 + \frac{nx}{6y}M \rightarrow \frac{n}{3}BF_3 + \frac{n}{6y}M_x - B_y$$
(2.7)

$$3BF + 2\frac{x}{y}M \rightarrow BF_3 + \frac{2}{y}M_x - B_y$$
 (2.8)

Sr. No.	Ref.	Substrate	Powder composition	Commercial name of the powder	Process parameter	Observed phases
1	[50]	AISI 316L steel	20% $B_4C + 10\% \ KBF_4 + 70\% \ SiC$	-	Temperature: 900°C Duration: 2-6 h	FeB, Fe ₂ B, CrB, Cr ₂ B
2	[62]	Iron based PM material	$\begin{array}{c} 10\% B_4C + 5\% KBF_4 + 80\% SiC \\ + 5\% C \end{array}$	-	Temperature: 850, 950, 1050°C Duration: 3-10 h	Fe ₂ B at 850 and 950°C and FeB/Fe ₂ B at 1050°C
3	[19]	ASTM F1537	-	Ekabor 2	Temperature: 950, 1000°C for 6 h Duration: 6,10 h	CoB/Co ₂ B
4	[63]	AISI H13 steel	95 vol.% Nanoboron powder + 5 vol.% KBF ₄	-	Temperature: 800,900, 1000°C Duration: 2-6 h	Fe ₂ B at 800°C, FeB/Fe ₂ B at 900 and 1000°C
5	[51]	AISI 1020 steel	5% $B_4C + 5\% KBF_4 + 90\% SiC$	Ekabor 1-V2	Temperature: 1000°C Duration: 4 h	Fe ₂ B
6	[43]	AISI 12L14 steel	20% B ₄ C + 10% KBF ₄ + 70% SiC	-	Temperature: 850, 1000°C Duration: 2-8 h (under argon atmosphere)	Fe ₂ B
7	[52]	AISI O1 steel	-	Durborid	Temperature: 850-1000°C Duration: 2-8 h	Fe ₂ B
8	[64]	Fe-15Cr alloy	B powder + 5% KBF ₄	-	Temperature: 850-950°C Duration: 12 h	(Fe, Cr)B, (Fe, Cr) ₂ B
9	[65]	AISI H13 steel	-	Ekabor 2	Temperature: 800, 900, 1000°C Duration: 2-6 h	Fe ₂ B, Mn ₂ B, Cr ₅ B ₃ (at 800°C); FeB, Fe ₂ B Mn ₂ B, Cr ₅ B ₃ (at 900 and 1000°C)

Table 2.1: Summary of the literature for the composition of boronizing pack-mixture, process parameters, and the obtained phases in

 the boronized layer of various alloys.

10	[66]	99.95% Pure Co	$8\% B_4C + 4\% KBF_4 + 88\% SiC$	LSB-2	Temperature: 850, 900, 950°C Duration: 2-8 h	Co ₂ B and Co ₂ Si
11	[67]	DC53 tool steel	-	LSB-1A	Temperature: 950°C Duration: 7 h	Fe ₂ B
12	[26]	AISI 5140	-	Baybora-1	Temperature: 950°C Duration: 4-6 h	FeB/Fe ₂ B
13	[68]	AISI H13	95% B ₄ C +5% NaBF ₄	-	Temperature: 800, 900, 1000°C Duration: 2-6 h	Fe ₂ B at 800°C, FeB/Fe ₂ B at 900 and 1000°C
14	[69]	Pure Ti	10% B ₄ C + 10% KCl + 10% Al + 70% Na ₂ B ₄ O ₇	-	Temperature: 860, 880, 900, 920°C Duration: 5-20 h	TiB and TiB ₂
15	[70]	SAE 1020 steel	22.5% H ₃ BO ₃ + 5% KBF ₄ + 72.5% SiC	-	Temperature: 850, 900, 950°C Duration: 4-12 h	Fe ₂ B
16	[71]	Inconel 718	90% B ₄ C + 10% KBF ₄	-	Temperature: 900, 950°C Duration: 2-6 h	Ni ₂ B, Ni ₃ B, Cr ₂ B, Ni ₄ B ₃
17	[72]	AISI 9840	33.5% B ₄ C + 5.4% KBF ₄ + 61.1% SiC	-	Temperature: 850-1000°C Duration: 2-8 h	Fe ₂ B
18	[73]	AISI M50 bearing steel	-	Ekabor-1	Temperature: 850, 950, 1050°C Duration: 2-8 h	FeB/Fe ₂ B
19	[74]	GS18, GS22, GS32 gear steel	-	Ekabor-2	Temperature: 850, 900, 950°C Duration: 2-6 h	FeB/Fe ₂ B, CrB, Cr ₂ B
20	[75]	Vanadis-6 steel	-	Ekabor®	Temperature: 900°C Duration: 5 h	FeB/Fe ₂ B
21	[76]	Ni ₃ Al		Ekabor-Ni	Temperature: 800, 850, 900, 950°C Duration: 2-8 h	Ni ₃ B, Ni ₄ B ₃

2.3 Iron-Boron System

Figure 2.5 shows the iron-boron (Fe-B) phase diagram. Two eutectic reactions occur at 1196°C (17 at.% B) and 1499°C (63.5 at.% B) [77-79]. Two compounds with Fe:B ratio of 1:1 and 2:1 are present in the Fe-B system. Fe₂B phase corresponds to CuAl₂ structure with a tetragonal unit cell containing 12 atoms, while FeB phase has an orthogonal unit cell containing 8 atoms [80, 81]. Table 2.2 summarizes the structural and physical properties of Fe₂B and FeB phases. The existence of two other phases, FeB₂ and Fe₃B, are discussed in different studies [82], [83]. As per our literature review, their presence in the boronized layer of steel has practically not shown so far in any literature. Fe₃B compound can have Fe₃C and Ni₃P crystal structure [83].



Figure 2.5: Fe-B Phase diagram [10].

Characteristics	Fe ₂ B	FeB
Composition (wt.%)	8.83	16.23
Crystal Structure	Body-centered tetragonal (a= 5.078 Å, c=4.249 Å)	Orthorhombic (a= 4.053 Å, b= 5.495 Å, c=2.946 Å)
Density (g/cm ³)	7.43	6.75
Microhardness (GPa)	16-20	19-21
Young's modulus (GPa)	285-295	590
Melting point (°C)	1650	1390

Table 2.2: Structural and physical properties of Fe₂B and FeB phases [8].

2.3.1 Migration of Boron

Heating of iron in the presence of boron-yielding substance results in the formation of boron enriched surface layer. Thomas et al. [84] and Campbell et al. [85] concluded that the phenomenon of boron diffusion in steel matrix is identical to that of carbon in steel. In 1953, Busby et al. [86, 87] originally did the classical study of boron diffusion and proposed its diffusion coefficients in austenite (γ -Fe) and ferrite (α -Fe) phases. However, in 1995, Wang et al. [88] claimed relatively more accurate diffusivities (D, in m²/s) of boron in γ -Fe (fcc) and α -Fe (bcc) phases by performing experiments on different steels:

$$D_{\gamma} = (2.6 \pm 0.8) \times 10^{-7} \, e^{(-26500 \pm 800)/\text{RT}}$$
(2.9)

$$D_{\alpha} = (1.5 \pm 0.6) \times 10^{-7} \, e^{(-21200 \pm 900)/\text{RT}} \tag{2.10}$$

The above equations indicate that the activation energies for the diffusion of boron in γ -Fe and α -Fe are approximately 26,500 (± 800) and 21,200 (± 900) cal/mol, respectively. Similar to the diffusion of other interstitial elements (like C and N), the diffusivity of boron in α -Fe is faster

than in γ -Fe because the activation energy barrier is more for the lattice having more close-packed crystal structure (i.e., γ -Fe).

2.3.2 Formation of Iron-borides

Various interlinked parameters such as dissemination of boron in the iron matrix, morphology of the resulting phases, elemental redistribution, and chemistry of the localized region play a key role in defining the mechanical properties of boronized steels. Nucleation and growth of borides depend on the boron potential in the boronizing media, process temperature, duration of boronizing, alloying elements in the material, solubility of boron, crystal structure of the substrate, segregation of boron at grain boundaries, lattice defects, dislocation, etc. [9, 10]. At ~900°C, the solubility of boron is 0.02 wt.% in γ -Fe and 0.008 wt.% in α -Fe [8, 77-81, 89]. Goldhoff et al. [90] confirmed the segregation of boron at austenite grain boundaries. Migration of boron atoms changes from the lattice position to the grain boundaries at high temperature, leading to boron-rich region formation. As mentioned above, Fe₂B and FeB phases form if the iron matrix contains more than ~8.83 and ~16.23 wt.% B, respectively [8].

Columnar structure of iron-borides is due to the anisotropy of boron diffusion coefficients in iron-borides [38, 46, 91, 92]. Also, it has been found that the presence of high compressive stresses towards the surface also governs the strong anisotropy of boride layers [14]. The formation of a very hard FeB phase (having a hardness of about 2000 HV) is generally not desirable due to the possibility of its sudden failure under cyclic loading conditions. Microstructure, hardness-depth profiles, and residual stress variation with the depth of boronized AISI 304 steel are shown in Figure 2.6. Compressive residual stress is associated with the Fe₂B phase, while tensile stress is associated with the FeB phase [93, 94]. A considerable variation in the coefficients of thermal expansion of the borides and residual stresses at FeB/Fe₂B interface increase the possibility of developing cracks

at the surface, interface, and within the borides [38]. Therefore, for low brittleness and better adherence of boronized layer to the substrate material, formation of a single-phase iron-boride (Fe₂B) layer (with saw-tooth morphology) is generally desired which in turn extends their viabilities in friction based applications [13, 26, 43, 95]. Proper selection of process conditions can lead to the formation of a single-phase iron-boride layer [13, 43, 96]. Different authors suggest that the dual-phase structure can also be dissociated into a single-phase through special annealing processes at variable elevated temperatures and using salt bath treatments [97-100].

The presence of alloying elements in steels can affect the formation of iron-borides. In alloy steels, components tending to form borides (e.g.,



Figure 2.6: Optical micrographs of the cross-section of AISI 304 steel boronized at 950°C for (a) 2 h, (b) 6 h, and (c) 10 h. (d) Nano-hardness versus depth profiles of these specimens. (e) Variation of residual stress (obtained by nanoindentation) with a depth of boronized layer (containing FeB and Fe₂B phases: see (a)-(c)) [93].

Cr, Ni, Mn, etc.) can be absorbed/accommodated in Fe-borides [8, 9, 101-103]. The effect of alloying elements on the boronizing behaviour of steels is further discussed in Section 2.5.1.

2.4 Boronizing of Non-ferrous Alloys

Apart from iron and its alloys, boronizing treatment is successful for various other metallic systems. Surface hardening of nickel and its alloys using the boronizing technique was extensively studied by various researchers. Campos-Silva et al. [104] investigated the effect of packboronizing treatment on Inconel 718. Paste-boriding of Inconel 718 was also successfully achieved by Deng et al. [16]. A silicide-free boronized layer (containing Ni₂B and Ni₄B₃ phases) was formed after boronizing. The presence of a hard nickel-boride layer reduces wear rate at ambient and high temperatures [15]. Piasecki et al. [60] carried out laser surface alloying of Inconel 600 alloy in the presence of boron and CaF₂, where a eutectic mixture of nickel-borides, nickel solid-solution, and CaF₂ were observed in the boronized layer. The presence of CaF₂ in the tribo-film decreases wear rate of the alloy. Gas-boriding of Nimonic 80A alloy at 920°C for 2 h in the gas-mixture of N₂-H₂-BCl₃ was performed by Makuch et al. [105], where a hard boride layer (containing a mixture of nickel and chromium borides) was formed.

Usta et al. [21] performed pack-boronizing of niobium, tungsten, and chromium-based alloys. High hardness of ~2500 HV was observed for the niobium- and tungsten- borides, and that of chromium-boride was ~1700 HV. Kul et al. [106] successfully performed salt-bath boriding of ductile cast-iron using the molten salt of borax and reducing agents (Na₂CO₃, CaCl₂, NaCl, NaOH, B₄C, SiC, Al and ferrosilicon). Cengiz et al. [22] investigated the boronizing behaviour of CoCrFeNi high entropy alloy (HEA) containing refractory elements (Ti and Nb), where the presence of various borides like FeB, Fe₂B, Co₂B, and Cr₅B₃ was observed in the layer. Moreover, due to the refractory element in the HEA, TiB_2 and NbB_2 phases were formed in CoCrFeNiTi and CoCrFeNiNb alloys, respectively. The thickness of the boronized layer was decreased due to the presence of refractory elements. Pack-boronizing of pure vanadium was performed in a controlled atmosphere by Tarakci et al. [103], where a single-phase boride layer (VB₂) had dense, compact, and relatively smooth morphology. Such a boride surface showed a very high hardness of ~3700 HV.

2.5 Factors Affecting Boronizing Behaviour

2.5.1 Effect of Alloying Elements in Iron-based Alloys

The total concentration of elements in steels influences the morphology of iron-borides, as shown in Figure 2.7 [50, 107-111]. For example, in the case of steels containing < 5 wt.% concentration of alloying elements, the iron-borides show saw-tooth morphology and the interface between boride and non-treated core is quite irregular (Figure 2.7(a)-(c)). In the case of steels containing ~17 wt.% alloying elements, Fe₂B shows a less sharp saw-tooth appearance, but the boundary between the borides is still irregular (Figure 2.7(d) and (e)). The total concentration of elements in stainless steel is considerably high (> 30 wt.%), and it shows quite smooth FeB/Fe₂B and Fe₂B/core interfaces (Figure 2.7(f)).

Elements like C, Si, and Al do not show any solubility in the borides, and therefore, they can be entirely discarded by the growing iron-borides [7, 8, 108, 112-114]. If the concentration of Si and Al exceeds 0.8 wt.%, formation of the soft ferrite phase is possible beneath the boride layer, which has an inadequate load-bearing capacity. Discarded Si by iron-boride can form FeSi_{0.4}B_{0.6} or FeSiB₂ type precipitates, and C can form Fe₂₃(B, C)₆ and Fe₃(B, C) precipitates between the boride columns or in front of the growing boride [8, 11]. Elements like Cr can be dispersed into the boride phase, resulting in the formation of (Fe, Cr)B or (Fe, Cr)₂B phases [64, 113-115]. Cr in steel can promote the FeB phase's growth, while Ni and Cu elements' presence obstructs it [108, 115]. Ni tends to get diffused into the iron-boride phase, which can later hinder boron diffusion into the growing iron-boride. Precipitation of Ni₃B can occur at Fe₂B/substrate interface [8, 114]. Ni in the iron-boride phase can reduce its hardness, while Cr can increase its hardness [11]. Other alloying elements like Mn, W, and V in the steel can reduce the thickness of iron-boride columns [21, 101-103, 116].



Figure 2.7: Effect of alloying elements and their concentration in steels on the morphology of iron-borides. Total concentrations of alloying elements are as follows: (a)-(c) < 5 wt.% (low alloy steels), (d)-(e) ~17 wt.% (high carbon high alloy steels), and (f) > 30 wt.% (high alloy steel) [50, 107-111].

2.5.2 Effect of Pack-boronizing Process Related Factors

The effect of the addition of rare-earth (RE) elements (like Hf, Ta, Ti, Nb, etc.) and their oxides (such as La₂O₃, Ce₂O₃, CeO₂, Nd₂O₃, etc.) in the pack-mixture on boronizing kinetics was extensively studied by different authors [22, 117-125]. However, their role in boronizing treatment has not

fully understood. The presence of RE elements/compounds in the packmixture can enhance the boronizing rate, increase the thickness of boride columns, and lead to single-phase iron-boride formation (Fe₂B), which in turn improve the mechanical response of boride columns under load and sliding conditions [123]. The role of RE elements/compounds on boronizing kinetics is summarised below [100-108]:

- 1. Dissociation of KBF_4 in the traditional boronizing pack-mixture (together with rare earth elements) causes the formation of BF_3 , which can liberate an additional amount of boron to enhance the boronizing rate.
- 2. They further improve the boron diffusion into the substrate by bringing down the barrier created by metal oxides at the surface.
- 3. Lattice distortion by the diffusion of RE elements into the material promotes boron diffusion.

Xu et al. [124] carried out pack-boriding by adding RE elements and chrome in the pack-mixture, which reduces layer's brittleness by forming RE-Cr-B phase and improves the wear resistance of the treated specimen. Su et al. [125] studied the influence of Nd₂O₃ addition on the boronizing behaviour of AISI 1045 steel, where an increase in the thickness of boride column at high temperature (860-940°C) and restriction to its growth at low temperature (780-820°C) were observed.

The response of non-ferrous alloys to the RE additions in packmixture was also investigated in the literature. Zhu et al. [120, 122] studied RE's effect on Ti-alloy's boronizing kinetics. An increase in the TiB layer thickness and the boronized layer's total thickness (containing TiB and TiB₂) was observed. Such thickness increase was associated with the increased concentration of substitutional vacancies (due to the addition of RE elements), leading to an enhancement in the boron diffusion into the Tiboride phases. The effect of nano-boron powder in the pack-boronizing mixture was studied by Erdogan [63] and Gunen et al. [126], where the layer's higher thickness and an increased proportion of FeB/FeB+Fe₂B were observed. Joshi et al. [127] studied the influence of container design on the pack-boriding of AISI 4140 steel. The medium-sized container was suitable for forming the single-phase boride layer, and the larger container produced a boride layer with dual-phase architecture.

2.6 Role of Prior and Subsequent Surface Treatments in Boronizing

Properties and performance of materials processed using conventional boronizing treatment can be enhanced by deploying certain pre- and post-surface treatments. In this regard, various physical and chemical routes were successfully attempted [128-131].

2.6.1 Role of Prior Surface Treatment

Surface deformation using different techniques (like surface mechanical attrition treatment (SMAT), shot peening, cold rolling, etc.) was attempted in literature before boronizing treatment [128-131]. Surface deformation can lower the activation energy of boron diffusion, and hence, it improves the boronizing kinetics of steels. As an example, low temperature (600°C) boriding of air-blast shot-peened (ABSP) AISI H13 tool steel resulted in the formation of a thicker (and more wear-resistant) boride layer than that of the non-treated specimen [130, 131]. Similar improvement in the kinetics of boronizing was observed due to the SMAT processing of AISI 304, H11, and EN8 steels [128, 129, 132]. Mechanical activation (through repeated cold working) of the AISI 4140 steel surface also enhanced the boronizing kinetics [133].

Lee et al. [134] carried out duplex surface treatment of AISI 403 steel using pack-chromizing and pack-boronizing, which improved its high-

temperature performance. Pack-chromizing formed the Cr-diffused layer of \sim 130 µm thickness, and the subsequent diffusion of boron resulted in the formation of \sim 50 µm thick hard layer (hardness: \sim 2300 HV). Such a hard layer showed the presence of FeB, Fe₂B, and CrB phases, and the wear resistance of the duplex treated steel was \sim 1.5 times that of the non-treated steel. A similar kind of work was performed by Kulka et al. [135], where the boro-carburized layer was successfully obtained using carburizing and laser-boriding of 17CrNi6-6 steel.

2.6.2 Role of Subsequent Surface Treatment

Post-treatment of boronized material includes thermochemical treatments, conventional annealing processes, laser surface modification, and multilayer coatings. Thermo-chemical treatments like plasma-nitriding were performed on the boronized steel by Gomez-Vargas et al. [117] and Habibolhzadeh et al. [136, 137]. Formation of c-BN (cubic boron nitride), iron-nitride and Fe₂B was observed in the surface layer. Such a multi-component layer can eliminate the spallation and crack formation, leading to superior wear performance (compared to the boronized specimen) [136] [137].

The effect of diffusion annealing on boronized alloys' performance was investigated in various studies [18, 97-99, 138-140]. Diffusion annealing can be performed at elevated temperature (say 1000°C) by embedding the boronized specimen in SiC powder [98]. The major effect observed in such studies was the enhancement in fracture toughness of the material due to the microstructure's modification.

Borided Inconel-718 was subjected to post heat-treatments (solution treatment, followed by two-step aging) to achieve a good combination of strength and ductility [16]. Such heat-treatments increase boron diffusion and resulted in new borides (like Fe₂B and CrB) in the layer, which caused

a better wear performance than the original nickel-boride layer. In ferrousalloy, post-heat-treatment enhances corrosion resistance of boronized AISI 304 steel [35].

Laser treatment of boronized surface is also gaining importance due to its ability to modify the surface microstructure within a short duration. Bartkowska et al. [141] performed the laser modification of boro-nickelized steel. In this case, multi-component layer was produced by Ni plating and diffusion annealing of the boronized steel substrate, which was followed by the laser surface modification. Laser re-melted surface possesses better wear resistance, low-cycle fatigue resistance, and cohesive strength of the boro-nickelized layer. In another study, laser surface modification of polyphase boride layer on Vanadis-6 steel was performed by Bartkowska [28]. Shankar et al. [142] successfully modified FeB coating on AISI 304L steel using laser surface modification. Overall, enhancement in surface hardness and tribological performance were observed after such laser treatment.

Multilayer architecture is another prominent approach (as a posttreatment) to enhance the tribological response of the boronized surface. Almeida et al. [143] performed pack-boronizing treatment of AISI M2 steel, and then, a multilayer AITiN/CrN film was deposited on it using cathodic arc physical vapour deposition (CAPVD) technique. Such deposited coating showed the highest wear resistance compared to the boronized and quenched–tempered M2 steel. Cuao-Moreu et al. [144] deposited (using the sputtering technique) AlCrON coating on the boronized ASTM F-75 cobalt alloy. Such coating increased the wear resistance by ~7 times and ~1.5 times that of the non-treated and boronized specimens, respectively. Johnston et al. [145] performed plasma-boriding of the cobalt-chromium alloy to increase its compatibility for the formation of nanostructured diamond. Similarly, Ballinger et al. [146] synthesized a metal-boride interlayer to deposit a nanostructured diamond film on AISI 316 and 440C steels.

2.7 Mechanical Response of Iron-borides

Many engineering applications demand the optimum designing of a material surface with different mechanical, physical, chemical, and dimensional properties. Figure 2.8 shows the list of some material properties desired in various applications.



Figure 2.8: Flow chart corresponding to the desired material properties for various applications [1, 8].

Nanoindentation technique has become a versatile tool in recent years to characterise the mechanical properties of the material in micro and nanoscale [38, 147-151]. Based on the concepts introduced by Olive and Pharr [147, 148] and Doerner and Nix [149], different parameters can be calculated through the analysis of load versus nanoindentation-depth plots. Various properties, such as hardness (H), young's modulus (E), fracture toughness (K_c), etc., are possible to measure using this technique.

Kulka et al. [38] studied the boronized Armco iron, where FeB phase showed the higher hardness and young's modulus ($H = 20.95 \pm 0.93$ GPa and $E = 308.86 \pm 26.44$ GPa) than Fe₂B phase ($H = 17.42 \pm 0.80$ GPa and $E = 252.96 \pm 15.57$ GPa) under the load of 50 mN. Campos-Silva et al. [151] studied the indentation size effect on Fe₂B layer formed on the boronized AISI 1018 steel. Dependency of boride hardness on the loading condition (from 10 to 500 mN) was confirmed. Rodriguez-Castro et al. [150] performed a nanoindentation study on the boronized D2 steel for the mechanical behaviour analysis. Their findings correlate the dependency of thermal residual stresses and hardness for FeB and Fe₂B layer on the boronizing time and temperature. They also estimated the indentation size effect on the FeB and Fe₂B layer in the loading range 10-300 mN, which is analogous to the study by Campos-Silva, and projected real hardness using the elastic recovery (ER) model.

Fracture toughness is another property that governs the material's resistance to failure. Fracture toughness defines a material's ability to resist crack propagation under variable loading conditions. Micro-indentation is one of the techniques used to evaluate the fracture toughness of the surface layer. When a material surface is indented, based on indenter's geometry, and applied load, the formation of cracks can occur in the layer. Fracture toughness of materials with and without boride presence was evaluated in several studies [14, 38, 53, 152-154]. Kulka et al. [38] observed higher fracture toughness of Fe₂B layer ($K_c = 2.42 \pm 0.66$ MPa·m^{1/2}) than FeB layer ($K_c = 1.79 \pm 0.70$ MPa·m^{1/2}) formed on the boronized Armco iron. The difference in mechanical properties and thermal expansion coefficients of FeB and Fe₂B phases can facilitate easy crack propagation and cause failure at FeB/Fe₂B junctions.

As mentioned above, compressive, and tensile residual stresses are evident in the treated surface of steels (Figure 2.6(f)), depending on the nature of the boronized layer (i.e., single phase or dual phase boride layer). Various techniques like X-ray diffraction (XRD), synchrotron radiation, strain gauge, and nanoindentation are used to measure the residual stresses in the material [18, 93, 155-157]. Golanzki et al. [155] revealed the existence of tensile stress in the FeB phase, and it transforms to compressive stress with an increase in depth from the surface. Babushkin et al. [156] observed that the intensity of compressive stress increases up to a certain depth, and consequently, it starts decreasing. Here, the composition of boronizing media and heat-treatment cycle (after boronizing) had influenced the distribution of residual stress in the boronized layer formed on steels. Furthermore, the residual stress of tensile nature was observed in the core region because it shrinks more (compared to the boride region) upon cooling due to its larger expansion coefficient. Payne et al. [158] calculated the residual stresses in the Fe₂B layer (formed on AISI 1018 steel) using the synchrotron radiation method. Here, the boronized layer showed compressive residual stress of about 237 MPa and that for the nonboronized region was about 150 MPa. Various researchers have deployed a nanoindentation technique for the measurement of residual stresses. Campos-Silva et al. [151] evaluated the residual stress in the Fe₂B layer formed on AISI 1018 steel, where compressive residual stress was ranged between 351 to 471 MPa. On the other hand, the findings of Campos-Silva [71] are based on evaluating the dependency of residual stress distribution as a function of boride layer thickness. Compressive residual stresses of magnitude between 1000 and 1400 MPa was evident for borided AISI 316L steel [159]. Delgado-Brito et al. [98] characterized the performance of the cobalt-boride layer after diffusion annealing process. Diffusion annealed specimen showed the changing magnitude of compressive residual stresses with an increase in thickness of the cobalt-boride layer. Similar observations were drawn by Pala et al. [157] for the residual stress distribution, which is decreasing with increasing boride layer thickness. Cong-Xin et al. [160] showed the variation of residual stress as a function of heat treatment and correspondingly its effect on the wear performance. A decrease in residual stresses after various heat treatment can be achieved and thus enhancing wear performance. In short, in the boronized steels, the FeB layer is generally associated with tensile stress, and the Fe₂B layer is associated with the compressive stress.

2.8 Tribological Response of Metal-borides

Many engineering applications involve the relative motion between two bodies. Therefore, the tribological response of surface-treated materials is a crucial property. Such study consists of an understanding of the principle of friction, wear, and lubrication. Mechanical components experience wear at a different scale (from mild to severe) when subjected to various loading extents during service. The characteristics of material surface (like surface roughness, hardness, microstructure, surface energy, and surface chemistry) have an essential role in governing material degradation during wear.

The surface deterioration becomes severe under harsh operating conditions like high temperature, cyclic loading, corrosive media presence, etc. Based on surface degradation mechanisms, the key factors responsible for causing a surface failure are grouped into two categories, viz, chemical, and physical (Figure 2.9).

The response of metal-boride to different wear types (like erosion, abrasion, adhesion, etc.) under sliding and reciprocating conditions (at ambient and elevated temperatures) was investigated in various studies, where an exceptional performance of materials was reported [13, 43, 50, 65, 72, 109, 161, 162]. The boronized surface's high hardness is the principal reason for such behaviour [13, 43, 50, 65, 72, 109, 161, 162]. However, the FeB phase's brittleness contradictorily outruns the boronized layer's advantage concerning the response against friction [43, 72, 95, 161].

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Figure 2.9: Flow chart corresponding to the key factors responsible for causing a surface failure [1].

A higher value of the friction coefficient (which is abbreviated in the subsequent text as CoF or COF) during sliding wear was observed for the boronized surface than the non-boronized AISI M2 steel [161]. An increase in load from 4 to 12 N caused a decrease in CoF; however, further increment in load caused a CoF rise, where the wear mechanism was dependent on the applied load. Abrasive wear was observed under 4-12 N load, and subsequently, it was transformed into the fracture and abrasive wear under 20 N load. In other studies of AISI 12L14 and AISI 9840 steels, the Fe₂B layer was formed after pack-boriding [43, 72]. The wear studies (under 5 N with 0.08 m/s sliding velocity) showed a lower CoF value for the boronized specimens than the non-boronized specimens. Formation of oxides (scale) and wear debris have an essential role in governing the tribological behaviour of the boronized steels [63, 161].

The dual-phase FeB-Fe₂B layer's sliding wear behaviour was investigated in different studies [50, 65, 162]. Fernandez-Valdes et al. [50] studied the wear performance of dual-phase boride layer on AISI 316L steel (under 5 N load and 0.1 m/s sliding velocity), where the wear rate of

boronized specimen was reduced by ~10 times that of the non-boronized specimen. In the iron and low alloy steel studied by Martini et al. [163], the dual-phase boride layer (FeB/Fe₂B) showed better performance than the nitrided and WC-Co coated specimen under dry sliding wear condition.

The high-temperature tribological behaviour of the single-phase boride layer (under 3 N load) on AISI 4140 steel was studied by Cimenoglu et al. [109], where superior wear resistance was observed at room temperature; however, it was decreased with an increase in temperature. This behaviour was linked to the thermal stresses in the layer. Dry sliding wear performance of non-boronized and boronized H13 tool steel was explored at room and elevated temperatures (under 5 N load) by Gok et al. [65], where the boronized specimen showed the dual-phase boride layer formation, and the material loss of the boronized specimen was significant at elevated temperature than that of room temperature. Moreover, the boronized specimen was degraded by plastic deformation at room temperature; however, the wear mechanism was changed to micro-cracks, extrusion, and oxidation at elevated temperature.

Reciprocating wear response of dual-phase (FeB-Fe₂B) boride layer on AISI 1018 steel was studied by Carrera-Espinoza et al. [164]. Such study was performed under dry and lubricated conditions at a constant load of 5 N and a sliding speed of 5 mm/s. As compared to the dry condition, CoF and wear rate of specimens were reduced under lubricated condition by 86% and 90%, respectively.

2.9 Concluding Remarks

This literature survey indicates that, boronizing is a promising surface treatment to enhance the various properties of steels. The alloying elements have an essential role in defining the morphology of boronized layer. Boron diffusion and the formation (i.e., nucleation and growth) of boride phase cause the migration of alloying elements. Some elements (like
Cr, V, Mn) tend to accommodate in the iron-boride; however, some elements (like C, Si, Al) are rejected by the iron-boride during its growth. The composition and migration behaviour of alloying elements during the layer growth can affect the boride's morphology and the boride/matrix interface's nature. Therefore, understanding the effect of boron, multiple alloying elements, and processing parameters on the microstructure development and distribution kinetics of the elements during the layer growth is one of the critical challenges. Such behaviour of steel can affect the localised mechanical properties of the boronized layer. The combination of microstructural variation (with depth), localised mechanical behaviour, and oxidation resistance of phases (i.e., boride and the surrounding boride-free matrix regions) can affect the tribological characteristics of the boronized steels.

Pre-/post-boronizing treatment can enhance the performance of the boronized steels, as suggested by literature. In duplex surface treatments, a surface modification technique (like boronizing) can be combined with the coatings (hard or soft coatings) to achieve optimum tribological properties. Such process-route can improve the load-bearing capacity and wear resistance of steel substrate. In this regard, the boronizing treatment can enhance steel's load-bearing ability, and the diamond-like carbon (DLC) coating can reduce the frictional related dilemmas.

The present thesis is focused on: (i) the effect of pack-boronizing on the migration behaviour of alloying elements and the accompanying mechanism of microstructure development in low alloy steel, (ii) the effect of boronizing on various properties (mechanical, oxidation, and wear), and (iii) investigating the role of advanced coatings like DLC/CrN on the tribological behaviour of low alloy steel.

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The current chapter deals with the experimental methodologies associated with specimen preparation, boronizing treatment, and characterization. Furthermore, the experimental strategy adopted to achieve the desired goals is also summarised in the flow-chart (Figure 3.1). Only essential/general aspects of experimentations are elaborated in this chapter, and the specific details of experiments involved in different studies are mentioned in the respective chapters.

3.1 Materials

The present study exclusively focuses on low alloy steels. Commercially available 34CrAlMo5-10 (EN41B) and AISI 4140 steels were used in this work. Table 3.1 mentions the typical composition of these steels in wt.%. Specimens with different dimensions were prepared for boronizing as per the requirements of the studies.

Table 3.1: Composition (in wt.%) of steels used in this thesis.

Steel Grade	С	Cr	Mo	Mn	Si	Р	S	Al	Ni	Fe
34CrAlMo5	0.4	1.4	0.1	0.5	0.2	0.0	0.0	0.9	0.1	Bal
-10 (EN41B)	0	5	4	7	7	4	4	1	1	
AISI 4140	0.4	0.8	0.2	0.5	0.2	0.0	0.0			Bal
	3	1	5	7	5	4	4	-	-	•

3.2 Pack-boronizing

Pack-boronizing of the steel specimens was carried out using the commercially available powder mixture. Generally, the boronizing powder

contains ~5% B₄C (boron source), ~5% KBF₄ (activator), and 90% SiC (used as a diluent). Following steps were adopted in the boronizing process:

Step 1: Stainless steel containers with dimensions of about 100 mm (diameter) \times 120 mm (height) \times 5.5 mm (thickness) were selected for packboronizing. Pre-conditioning of these containers was performed at 1000°C for 8 h. Pre-conditioning involves the boronizing of the container (without specimens) to avoid the utilisation of boron potential by the container during boronizing of the actual specimens to be investigated [1].

Step 2: Specimen was subjected to grinding and polishing treatments (before boronizing) using SiC polishing papers. Polishing was performed up to 1000 mesh SiC paper. Such a polished specimen was cleaned with a soap solution, and subsequently, it was ultrasonically rinsed in acetone.

Step 3: The prepared specimen was embedded in multilayer architecture, where the principal layer (20-30 mm thickness) was the boronizing powder layer, which was in direct contact with the specimen. Subsequent layers were the SiC powder layer (~20 mm thickness), a thin sheet of glass wool, and an alumina powder layer (~5 mm). The remaining volume of the container was filled with fine sand. The main purpose of such multilayers was to protect the principal layer from atmospheric contact.

Step 4: The container was kept inside the muffle furnace for boronizing treatment. The required temperature of the boronizing process was achieved in three stages, where the temperature was raised initially to 650° C (at the rate of 4.5° C/min), followed by 15 min holding. Subsequently, the temperature was increased to the desired boronizing temperature at the rate of 5° C/min.

Step 5: The process of boronizing ends with air cooling of the container. The specimen was taken out from the mixture after cooling the container.

3.3 Characterization of the Boronized Specimens

3.3.1 Specimen Preparation

Boronized specimens were cut using CNC Wire-cut EDM for various investigations. In microstructural studies, the cross-section of specimens was hot mounted using Bakelite powder. Such mounted specimens were ground and polished up to 2500 mesh SiC emery paper and subsequently polished using diamond paste (up to 0.25 μ m size). Such polished specimens were cleaned with a soap solution and then ultrasonically rinsed in acetone.

3.3.2 Optical Microscopy

Metallographically prepared specimens were etched using 2% Nital solution (2% HNO₃ + 98% ethanol). Optical microscopy of the boronized specimens was performed using an inverted microscope (Make: Zeiss Axio Vert.A1). The thickness of the boronized layer was measured at ten different locations of the specimen's cross-section, and the average value of such reading is presented.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was carried out using Field Emission-Scanning Electron Microscope. SEM micrographs were collected at 15 kV accelerating voltage. Information about the elements was collected using energy dispersive spectroscopy (EDS) at 20 kV accelerating voltage.

3.3.4 Electron Backscattered Diffraction (EBSD)

Specimen preparation for EBSD analysis involved polishing the specimen's cross-section up to 4000 mesh emery paper, followed by diamond polishing with 1 µm paste for 8 min duration. Final polishing was

achieved using the standard colloidal silica (0.4 μ m size) suspension for 25 min. Microstructural analysis of the prepared specimen was carried out using Hitachi 3400 SEM containing EBSD detector (Bruker e-flash). All the measurements were carried out at the following parameters: 20 kV acceleration voltage, 10 mA current density, and ~1 μ m step size. ATEX [2] and MTEX software was used to process the acquired images.

3.3.5 X-ray Diffraction (XRD)

A Bruker D2-phaser high-resolution X-ray diffractometer equipped with a Cu-K_{α} radiation source was used for the phase identification of specimens. The range of 2 θ used to record the diffraction pattern was 20-90° (with a step size of 0.02°). X-pert PRO software was used to analyse the obtained diffraction pattern.

3.3.6 Electron Probe Microanalysis (EPMA)

Concentration of different elements in the boronized layer was determined using EPMA. JEOL JXA-8530F instrument (having 3 WDS and 1 EDS channels) was used for the EPMA measurements. The accelerating voltage and the beam current were 15 kV and 50 nA, respectively. The measurements were done within the boride column and the adjacent non-boride region. Elemental mapping of the boronized layer was performed to understand the distribution of B, Fe, Al, Cr, and Mo. Each map covers the area of 140 μ m × 180 μ m, where the measurements were taken using an acceleration voltage of 15 kV, beam current of 50 nA, and dwell time of 10 ms/point at the intervals of 0.5 μ m.

3.3.7 Glow Discharge Optical Emission Spectroscopy (GDOES)

Variation in composition with depth of the specimen is possible to obtain using the GDOES technique. GDOES enables the determination of

composition across the depth of the specimen. A minimum layer thickness of < 50 nm to the maximum of hundreds of microns is possible to investigate with this technique [3]. In the GDOES technique, ejected atoms (from the surface) are in the excited state. Photoelectric sensors detect such atoms for the specific wavelength (due to the optical emission after decaying to the fundamental state [3].

Boronized specimens were analysed using GDOES (Make: Horiba GD Profiler 2). Semi-quantitative depth profiles of B, Fe, Cr, Mn, Mo, Ni, Si, and Al were obtained using GDOES.

3.3.8 Microhardness and Nanoindentation

Microhardness measurements across the cross-section of boronized specimens were done using Walter microhardness tester (Model: UHL VMH-002). All the measurements were carried out as per the standard ASTM E-92 with a square-based pyramidal diamond indenter having a 136° face angle of the diamond. The load of 100 g was fixed for all measurements. Hardness value presented is the average of a minimum of three readings at any depth of measurement.

The localised mechanical properties of the boride-columns, matrix (surrounding the columns), and non-boronized core regions were studied using the nanoindentation technique (Make: Hysitron TriboIndenter TI-900). Typically, a standard Berkovich indenter is used in this method. The loading and unloading rate was 0.8 mN/s for all indentations. A constant load of 8 mN was maintained for 10 s during nanoindentation.

3.4 Tribological Study

Dry sliding wear behaviour of the treated and non-treated specimens was carried out on a ball-on-disc tribometer (Model: DUCOM CM-9112). All tests were performed as per the G-99 standard. Details of the wear parameters used for different studies are described in the respective forthcoming chapters. These experiments were performed in an ambient atmosphere. The wear tests were performed at least two times to confirm the reproducibility of the results. The load-cell equipped tribometer (with real-time analysis) was used to measure the frictional force and calculate CoF. Wear loss (wear volume in mm³) of the specimen was obtained by multiplying the wear track's cross-sectional area to its circumferential length. The wear track's cross-sectional area was calculated by getting surface profiles at four different locations (perpendicular to the wear track) using a 2D surface profilometer (Make: Taylor and Hobson; Software: TalyProfile Gold V7.4). Specific wear rate is calculated as per the following standard equation:

$$W_{sp} = \frac{\Delta V}{P \times L} \tag{3.1}$$

where, W_{sp} is the specific wear rate in $\frac{mm^3}{N-m}$, ΔV is the volume loss in mm³, P is the applied load in N, and L is the sliding distance in meter. Wear mechanisms of the specimens were investigated using SEM, EDS, and Raman spectroscopy.

3.5 Oxidation Study

A high-temperature oxidation study of the boronized and nonboronized specimens was performed using the thermo-gravimetric analysis (TGA) technique (Make: NETZSCH TG-209), where the equipment had a resolution of 0.01 μ g. Specimens with a dimension of 4 mm × 4 mm × 1 mm were prepared for oxidation study. A top surface of the specimen was prepared by polishing up to 2000 grit emery paper. The surface was further polished using diamond paste. The polished specimens were cleaned with a soap solution and, after that, ultrasonically rinsed in acetone. Mass-gain of the specimen was recorded automatically (after calibrating with the initial mass of the specimen). The specimen was placed in an alumina crucible (having a melting point > 2000°C). The initial temperature of the chamber was maintained at ~30°C. The chamber's temperature was increased at the rate of 10°C/min to the desired temperature. The total cycle time of the oxidation study was 15 h. These experiments were performed in a protective atmosphere of N₂ gas. SEM and XRD were used to further characterise the oxidized specimens.

3.6 Overall Experimental Strategy

The overall experimental strategy of the current thesis is summarised in Figure 3.1. Low alloy steels and pack-boronizing method were identified for this work. Experiments were planned to investigate (i) the effect of packboronizing on the migration behaviour of alloying elements and the accompanying mechanism of microstructure development in low alloy steel, (ii) the response of boronized layer to wear, nanoindentation, and oxidation, and (iii) tribological response of a DLC/CrN multilayer architecture on the boronized low alloy steel.



Figure 3.1: Experimental strategy of current work.

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Chapter 4

Pack-boriding of Low Alloy Steel: Microstructure Evolution and Migration Behaviour of Alloying Elements

4.1 Introduction

Pack-boriding has emerged as one of the most promising and effective surface modification routes to produce hard boride phases at the surface of the engineering alloys, enhancing its surface properties and thus, making it with- stand against the surface degradation phenomenon such as wear, corrosion, and oxidation [1–3]. Boronizing, a thermo-chemical treatment, is accompanied by the controlled diffusion of boron into the metal surface producing different phases of metal borides (M-B, M = Fe, Cr, Ti, Ni, V, Mo, Mn, W, etc.) [4–14]. A considerable improvement in the quality of the surface layer is possible through combining the boronizing treatment with other surface treatments (like borocaburising, laser treatment on the boronized surface, etc.) [15,16]. Boronizing is a proved lucrative option for many non-ferrous alloys [15,17–19]. However, boronizing of ferrous alloys has got considerable attention due to their wide range of applications [20–22].

Typically, boronizing of iron-based alloys leads to the formation of iron-boride phases on the surface layer [15–17,20–22]. Alloying chemistry has a significant influence on the boronizing behaviour. The effect of various chemical elements on boronizing response of pure iron was a subject of attraction in many kinds of literature [5–12]. Microstructure of

the boronized layer, especially, morphology of borides is dependent on the alloys, where alloying elements can modify the solubility and diffusion of constituents [16,23]. Low alloy steels show saw-tooth morphology of borides [20,22,24]. However, high alloy steels have an almost flat interface between the boride layer and substrate [21,23]. Presence of W and V as alloying elements transforms the saw-tooth morphology into flat boride surface with smooth interfaces, along with the formation of transition zone that is rich in precipitates of W and V [10,11]. There, the alloying elements can lead to the formation of a mixed boride phase in the layer. The boronizing treatment of Fe-Cr alloy causes the formation of (Fe, Cr)B phase at the top and (Fe, Cr)₂B phase beneath it [4]. The presence of Mo within the matrix promotes the precipitation of Mo₂FeB₂ in the boride layer [7,8]. Gencer et al. obtained a boride layer containing FeB, Fe₂B, and precipitates of TiB₂ during boronizing of Fe-Ti alloy [12]. It was noted that the alloying elements could affect the kinetics, hardness, surface roughness, and tribological behaviour of the boride layer [7,8]. Thickness of the boride layer decreases due to the addition of alloying elements [10,11]. Most of the archival literature has given a specific focus on the binary Fe-M alloys. However, the combined effect of alloying elements on the boronized layer of steels is complex and least expounded. 34CrAlMo5-10 steel, popularly known as EN41B, belongs to the category of medium carbon low alloy steels containing C, Cr, Mn, Mo, Ni, Si, and Al as alloying elements. This steel is usually applied in valve stems, connecting rods, shackle pins and casting dies, etc. Understanding the effect of boron, multiple alloying elements, and processing parameters on microstructure development and distribution kinetics of alloying elements during the layer growth is one of the critical challenges. Consequently, the current work presents the effect of pack-boriding on the migration behaviour of alloying elements in low alloy steel and the accompanying mechanism of microstructure development. Pack-borided specimens were investigated using optical microscopy, SEM, EBSD, XRD, EPMA, GDOES, and microhardness.

4.2 Experimental

A medium carbon low alloy steel (34CrAlMo5-10 / EN41B) with the following chemical composition was used: 0.4% C, 1.45% Cr, 0.57% Mn, 0.14% Mo, 0.11% Ni, 0.27% Si, 0.91% Al, 0.04% P, 0.04% S and balanced Fe. Specimens were cut and prepared in a square shape with dimensions $20 \times 20 \times 4$ mm and ground up to 800 mesh size emery paper, followed by diamond polishing and cleaning with acetone before boronizing. A preconditioned stainless-steel container was used to boronize the specimens at 850, 950, and 1050°C for 2, 4, and 6 h using the commercially available BoropakTM powder (typically, the commercially available boronizing powder contains about 5% B₄C as a source of boron + 5% KBF₄ as an activator + 90% SiC as a diluent). The specimens were embedded inside the powder bed at the centre of a container. Top portion of the container was covered with SiC powder. The detailed boronizing process is mentioned elsewhere [20] (see also chapter-3). The container was air-cooled after boronizing.

Cross-section of boronized specimens were metallographically prepared and etched using 2% Nital. The microstructural investigations were performed using an optical microscope (Make: Zeiss Axio Vert.A1), scanning electron microscopy (SEM, Make: Zeiss Supra55), X-ray diffraction (XRD, Make: Bruker D2-Phaser), and microhardness tester (Make: Walter UHL VMH- 002). XRD patterns were recorded using Cu-K_{α} radiation.

In order to obtain the grain structural morphology of the specimen boronized at 1050°C for 4 h, cross-section was prepared using different grit paper (starting from 800 to 4000). Final polishing was done using diamond suspension (1 μ m for 8 min) and standard colloidal silica suspension (0.4 μ m for 25 min). The prepared specimen was observed for the microstructure by a Hitachi 3400 SEM, which contains a Bruker e-flash electronbackscatter-diffraction (EBSD) detector. The followings parameters were used during the measurements: 20 kV acceleration voltage, 10 mA current density, and the step size of $\sim 1 \mu m$. The acquired images were post-processed using ATEX [25] and MTEX software.

Elemental composition of the boronized layer was determined using electron probe microanalysis (EPMA). EPMA measurements were done using a JEOL JXA-8530F instrument having 3 WDS and 1 EDS channels. The accelerating voltage and the beam current were settled as 15 kV and 50 nA, respectively. Line scan was carried out within the boride column and the adjacent non- boride region. Elemental mapping was performed in the boronized layer to understand the distribution of B, Fe, Al, Cr, and Mo. Each map covers the area of $140 \times 180 \,\mu$ m. The measurements were taken under an acceleration voltage of 15 kV, beam current of 50 nA, dwell time of 10 ms/point at the intervals of 0.5 μ m.

Boronized specimens were further analysed using glow discharge optical emission spectroscopy (GDOES, Make: Horiba GD Profiler 2). Semi-quantitative depth profiles of B, Fe, Cr, Mn, Mo, Ni, Si, and Al were obtained using GDOES. This technique allows to observe the surface ejection of atoms in the excited state, which is detected due to optical emission after decaying to the fundamental state by photoelectric sensors for specific wavelength [26].

4.3 Results and Discussion

4.3.1 Phase Analysis, Microstructure, and Hardness

Figure 4.1 shows X-ray diffractograms (XRD) of boronized specimens at different temperatures. The untreated specimen shows the diffracted peaks of ferrite (α -Fe). It was noticed that the characteristic diffraction pattern of Fe₂B is present in all boronized specimens. However, the specimen boronized at 1050°C showed additional small peaks of FeB and SiC. The presence of both iron-borides (FeB and Fe₂B) indicates that
the FeB phase may be formed only in some places on the specimen surface. Therefore, the phase maps shown in Figure 4.3(c)-(d) and the micrograph incorporated in the later portion of Section 4.3 do not show the distinct layer or evidence of FeB (Figure 4.9(d)). Evaporation of boron oxides plays a vital role in controlling the supply of boron for its reaction with steel surface during powder-pack boriding using B₄C as a boron source [16].



Figure 4.1: XRD patterns recorded from the surface of the non-treated and boronized specimens.

Therefore, high temperature can lead to a high boron potential within the pack-mixture, leading to the formation of FeB [16,20,21]. When high boronizing temperature is used, the sticky/diffused layer of boronizing

pack- mixture (which contains SiC) is relatively difficult to remove by cleaning, and therefore, XRD shows SiC peaks at 1050°C.

Figure 4.2(a) and (b) shows the microstructure in cross-section of the specimen boronized at 950°C for 4 h. One can see a columnar morphology of iron-borides in the modified region. The prominent anisotropy of the diffusion coefficient in the tetragonal lattice of Fe₂B is responsible for the formation of columnar morphology [14,23,27]. SEM micrograph shows microstructural features that are difficult to be seen in the optical micrograph (Figure 4.2(a) versus (b)). The boride columns that appear thick in the optical micrographs are formed by clustering thin columns.

A cross-sectional micrograph with the SEM analysis of packborided steel is presented in Figure 4.3(a). This reveals the formation of boride region, which is darker in respect to the non-boronized core. Preferentially oriented grains in the surface region of the boronized crosssection are observed in the IPF map, as shown in Figure 4.3(b). These grains are Fe₂B columns, formed through the diffusion of boron atoms [28], which were noted to grow perpendicular to the surface in a needle-like manner [29]. FeB is not considered due to the detection of its poor signals. IPF map shows that the Fe_2B grains are mostly oriented around {100} and {110} (Figure 4.3(b)). Figure 4.3(e) shows the strong texture of Fe₂B grains toward the horizontal extremities. Iron-boride prefers to grow in the crystallographic direction [001] and by stacking crystal planes {001} [27]. Texture in the Fe₂B phase could occur due to the mutual compression between adjacent grains and the lattice mismatch between the phases [27]. Small grains of Fe_2B are formed near the surface (Figure 4.3(c)-(d)). Random orientation of grains is visible in the area beneath the boronized region (Figure 4.3 (b)).



Figure 4.2: (a) Optical and (b) SEM micrographs in the cross-section of the specimen boronized at 950°C for 4 h. (c) Microhardness-depth profiles for the specimens boronized at 850, 950 and 1050°C for 4 h.

Boronized region consists of iron-boride phase and is surrounded by non- borided matrix. The matrix shows a different contrast in the optical micrograph (Figure 4.2(a) and Figure 4.3) compared to the underneath regions. Tiny boride particles that are apparent in the matrix and on the front of boride columns are generally present at high-angle prior-austenitic grain boundaries [4].

The 'transition zone' is labelled in the vicinity of boronized region that contains boride particles in the non-transformed areas (see the subsequent sections for more details). The total layer is divided into the boronized region and the transition zone [20]. The non-boronized core follows the transition zone.



Figure 4.3: (a) SEM, (b) IPF, (c)-(d) phase maps and (e) Pole figures of the specimen boronized at 1050°C for 4 h. White spots in (c) indicate unindexed areas.

Figure 4.2(c) shows the microhardness-depth profiles of the specimens boronized at 850, 950, and 1050°C for 4 h. The hardness measurements near to the surface (within $\sim 20 \,\mu$ m) are not representative of the real mechanical behaviour; thus, the hardness is recorded after 20 μ m. Maximum hardness of about 1050, 1500, and 1800 HV_{0.1} are detected in the near-surface region at 850, 950, and 1050°C, respectively. At these near

surface regions, it is possible to obtain a constant hardness in the boronized region if the iron-boride columns occupy the entire space of the region [1]. However, the observed decrease in the hardness from the near-surface area to the core (Figure 4.2(c)) is due to the increase in the proportion of non-borided matrix surrounding the iron-boride columns [5,20,30]. Compositional analysis of the specimens borided at 850°C (Section 4.3.3) confirmed that boride fraction in the surface region is less than one (i.e., the surface region is not occupied entirely by the boride phase). Therefore, the lower surface hardness at 850°C is due to the presence of softer non-boride regions surrounding the boride phase. At any depth within the boronized layer, the reduced hardness for lower temperature is due to the smaller fraction of iron-boride.

4.3.2 Compositional Analysis: EPMA

Figure 4.4 shows BSE image and the corresponding EPMA measurements from surface to non-boronized region of the specimen boronized at 950°C for 4 h. The iron-boride phase appears grey coloured in the BSE micrograph (Figure 4.4(a)) because of the significant presence of boron (light element) [1,20]. Porosities are distinguishable in BSE mode due to their blackish appearance. One can see that the region with iron-boride shows the highest boron concentration. Now onwards, the 'depth' term refers to the distance from the surface up to a certain point in the bulk. Concentration of the alloying elements is lower in boride than the non-boronized area suggests that the growing boride significantly rejects Si and Al atoms [31]. The elemental mapping of Al in Figure 4.5(d) shows more concentration of Al in front/surrounding regions of the boride column than the non-boronized region. The relevant GDOES results are discussed later. The fluctuation in the elemental concentration–depth profiles is possible due

to the presence of boundaries/gaps between the clustered thin boride columns at the location of EPMA measurements.



Figure 4.4: (a) BSE micrograph of specimen boronized at 950°C for 4 h. (b) Elemental concentration-depth profiles by EPMA from the surface to the non-boronized region, as shown in (a).

The concentrations of alloying elements, except Si, Al, and C (see also the subsequent section), never reaches zero in the boride phase (Figure 4.4). The concentrations of Cr, Mn, Mo, and Ni show an increasing trend from the surface to the tip of the boride column, which is possible due to the redistribution of the alloying elements (boride has different solubilities for different elements) and nonequilibrium conditions that prevail during the growth of boronized layer [1,23]. A similar trend in the distribution of alloying elements is evident for the boronized Fe-Cr [1] and Fe-Mn [5,6] alloys. The presence of Si and Al in the boronized region at the location of EPMA measurements, especially, near to the surface is associated with their segregation/entrapment between the growing boride columns (see the regions indicated by arrows in Figure 4.5(d)). Boride formed near to the surface could assimilate some Si from the boronizing pack- mixture, which contains SiC powder [20].



Figure 4.5: Distribution of vital elements in the cross-section of the specimen boronized at 950° C for 4 h shown in (a) as BSE micrograph and (b) B, (c) Fe, (d) Al, (e) Cr and (f) Mo as chemical mappings. The coloured scale bars at the right show relative concentration of the elements (low (bottom) to high (top)).

Figure 4.5(b)-(f) shows elemental mapping of vital elements in the boronized region and some portion of the transition zone of the specimens boronized at 950°C for 4 h. The distribution of B and Fe confirms the presence of columnar iron boride in the boronized region due to both chemical signals that follow quite well the morphology previously observed in the SEM micrographs. In the elemental mapping, the near-surface region of the layer does not indicate the formation of a higher B containing ironboride (FeB) phase. Therefore, it agrees with the XRD results shown in Figure 4.1. Boride columns appear dark in the Al mapping. Al enriches the regions between the boride columns and the growing front of the borides. These results confirm that Al does not dissolve in the boride phase, and it is displaced away during phase growth [31]. Unlike the B, Fe, and Al mappings, the Cr and Mo mappings do not show a clear distinction between the boride columns and the surrounding non-boride region, which is due to the presence of Cr and Mo in both the boride phase and non-boride region [1,7]. However, the Cr mapping shows dark patches within the boronized region. These patches are mostly the narrow regions between the ironboride columns, which are occupied by the boride during subsequent growth. For better understanding, Figure 4.5(d) and (e) shows the encircled such regions between the iron-boride columns. The darker appearance indicates the Cr depletion. However, it should be remembered that the ironboride columns do not absorb the entire concentration of the element present in the alloy (Figure 4.4). Hence, some rejection occurs during the growth of boride [23]. Therefore, Cr depletion in the narrow regions between the boride columns hints the faster migration of Cr than the growth kinetics of the iron-boride columns.

Some of the regions indicated by arrows in Figure 4.5 (as an example, Fe and Al mappings) reveal the presence of small non-borided areas trapped between the columns. Open zones are also observed between the boride columns (Figure 4.5(a)). Based on the above observations, the boride phase contains Fe and B with some concentration of Cr, Mn, Ni and

Mo, i.e. the boride formed is (Fe, M)₂B where, M = Cr, Mn, Mo, and Ni [4–7,21,23]. The concentration of the alloying elements in boride column decreases from the core to surface. In the text, Fe₂B designates (Fe, M)₂B for conciseness. Formations of separate borides of alloying elements (like Cr₂B or MnB₂) in the Fe₂B columns are ruled out because of the low concentrations of the alloying elements in the investigated steel [1,5].

4.3.3 Compositional Analysis: GDOES

Unlike the EPMA results, shown in Figure 4.4, a gradual decrease in concentration of B, and some rise in concentrations of the remaining elements (Fe, Cr, Mn, Ni, Mo, Si, and Al) from surface to non-boronized region are observed in GDOES results (Figure 4.6). This difference is ascribed to the fact that the EPMA measurements are done within the boride column (Figure 4.4). However, GDOES gives the results at various depths from a considerably large area (diameter of the crater is ~ 4 mm). Therefore, the obtained results from each depth within the boronized region are the average concentration of the boride phase and the surrounding non-boride area [23]. As an example, the EPMA concentration–depth profile and elemental mapping confirm the absence of Al in the boride, while the concentration of Al in the surrounding regions of boride is higher than the transition zone and core. Therefore, the decreasing trend of Al content from zone-V to I in GDOES (Figure 4.6) is a direct consequence of depleted proportion of non-boride regions towards the surface.

GDOES results (Figure 4.6) show the presence of 5 compositional zones (I to V) in the boronized region. These zones are identified based on the change in slopes (the first derivate of concentration function versus depth or rate of change of concentration versus depth) of GDOES profiles with the distance from the surface or core (Figure 4.7). Most of the alloying elements achieve stability in zone-I. Si and Al contents show a noticeable drop during the transition from zone-II to I. Al content become almost zero

in the zone-I. The Si content above zero in zone-I is possible due to its absorption from the surrounding pack mixture [20]. The plateau in boron concentration profiles (subsequent discussion explains the absence of plateau in boron profile at 850°C) in the zone-I indicates the formation of vastly boride phase and a negligible quantity of non-boride region near to the surface at 950°C. The B and Fe rich regions attempt to wipe the other alloying elements during the growth [23]. The extent of migration of alloying elements is one of the factors controlling the overall concentration of alloying elements at various depths. The growth kinetics of boride columns regulates the extent of wiping [22,23]. In the process of boride formation, the iron-boride phase partially dissolves some of the alloying elements (like Cr, Mn, Ni, and Mo) and entirely discards the other alloying elements (like C, Si, and Al) [31]. GDOES results of the boronized Ti-alloy also showed the rejection of Al by growing boride [32]. In the transition zone-V, the sharpest drop in the concentration of B with an increase of depth is associated with the steepest rise in the concentration of all elements, except Si and Al. Finally, zone-V shows the accumulation of Si and Al.

The variation trend of slopes for concentration–depth profiles of alloying elements at 850°C is analogous to that of the specimen boronized at 950°C (Figure 4.6(b) and Figure 4.7(b)). Even if the concentration–depth profile of B is steeper and variation in the slope with depth is not discerned at 850°C, some similarity in its trend is noticeable in zones-III to V (Figure 4.7). Variation in the slope of B profile becomes distinct as the boronizing temperature increases to 950°C. The slope change in the concentration–depth profiles of all elements, except C, is observed in different zones.



Figure 4.6: GDOES concentration-depth profiles of the elements in the surface layer for the specimens boronized (a) at 950°C for 4 h and (b) at 850°C for 4 h.

In contrast to the other alloying elements, C content in zones-I to IV is absent at 950°C. At lower temperature (850°C), carbon is not found in zone-I to III. The entire absence of C in these zones indicates its faster migration away from the boronized region at both temperatures [23]. Another reason for the lack of C could be its insolubility in the Al- and Sirich matrix. Accumulated Al and Si can form the complex compound in the matrix surrounding the boride columns [31].



Figure 4.7: Variation in the slope of the GDOES concentration-depth profiles (shown in Figure 6) of boron and alloying elements present in the surface layer of the specimens boronized at (a) 950°C for 4 h and (b) 850°C for 4 h.

A sequence of the events occurred during the growth of the boronized region resembles the course of development of zones from V to I. It is because, the journey of layer growth starts with a non-boronized core (i.e., the deeper region near to zone-V) to the layer of fully occupied boride phase (i.e., zone-I). Therefore, the subsequent discussion explains the events occurring from core to surface. As mentioned above, the slope of the GDOES profiles varies systematically, and the pattern for the alloying elements is almost identical at 950°C and 850°C (Figure 4.7). The steeper slope is followed by the shallower slope and vice-versa. The increasing

slope of all elements (either in the positive or negative direction) approaches towards zero and then, increases again. The pattern of slope change for Cr, Mn, and Mo profiles is like a mirror image of the slope profile of B at 950°C. The sequence of slope variation in different zones is identical for Si and Al. Moving from zone-V towards the surface, as the slopes of B, Cr, Mn, Mo and Ni profiles approach towards zero (at the interface of zones-IV and III), the slopes of Si and Al profiles move away from zero and reach the maximum either at the interface of zones-IV and III (for 950°C) or in zone-III (for 850°C). However, the slopes of all elements approach to zero and achieve better stability while moving in zones-II and I. The complete transformation of the surface region to boride causes slight increase in composition (i.e., negative slope) of Cr, Mn, and Mo in zone-I. The slope of B profile becomes positive in zone-I (i.e., B concentration decreases near to the surface) at 950°C, which is possible due to the formation of macrodefects, like porosities [3,6], in the near-surface region. Segregation of Ni occurs at the interface of zones-I and II, which is also evident at the lower boronizing temperature of 850°C. However, EPMA measurements within the boride column do not manifest such segregation in the near-surface region, suggesting that during the transformation of the entire extension of the surface to the boride phase, some fraction of Ni atoms is discarded in the surrounding matrix retaining some in the boride phase.

Even if the trend in the variation of slopes for alloying elements at 850°C is almost comparable to that of at 950°C, the position of the slope peaks concerning each other in different zones is not identical at both temperatures (Figure 4.7). The slope profiles show a backward shift in the peak positions at 850°C. For example, the locations of peaks for Cr, Mn, Mo, and Ni, concerning the position of peaks for Si and Al at the interface of zones-V and IV, are shifted towards the left at 850°C. This observation confirms the role of temperature on the growth behaviour of boride and the compositional adjustments between boride and its surrounding matrix. It

also reflects the difference in migration kinetics among alloying elements during the boronizing process.

The depth corresponding to the maximum accumulation in zone-V (i.e., the intersection of slope profiles to X-axis at Y = 0) is lower for Si than Al. The peak-positions in the slope profiles are at lower depths for Si than Al (however, the difference in the peak positions of Si and Al is smaller at 950°C than 850°C). These results suggest slower migration kinetics of Si than Al.

For Ni, the position of the first peak while moving from zone-V to I occurs at a considerably lower depth than that for Cr, Mn, and Mo. It indicates the absence of Ni migration even though other alloying elements start depleting (during the formation of boride particles). This situation is possible due to the lower migration kinetics of Ni than Cr, Mn, and Mo. Positions of peaks for Cr, Mn, and Mo are almost at the same depth that demonstrates the inconsequential difference in their migration kinetics.

Figure 4.8 shows the normalised concentration–depth profiles of B and their corresponding slope variations for the specimens boronized at 850, 950, and 1050°C for 4 h. The thickness of the layer increases with temperature. For the relative comparison of these concentration–depth profiles at different temperatures, they are normalised by making the maximum B concentration in Fe₂B layer as the unity. A considerable jump in B content near to the surface at 1050°C is possible due to the presence of FeB phase, as detected by XRD (Figure 4.1), at some locations on the surface. Unlike 850 and 950°C, an increasing concentration of B from the core to surface is very gradual at 1050°C, and the slope of the profile approaches towards almost zero at 50% of the boronized layer thickness (thickness of boronized region plus transition zone). This gradual change indicates the presence of unreacted Fe in the broader transition zone. Tiny particles of boride are apparent in areas close to the core and surrounding the boride columns (Figure 4.9 and Figure 4.2(b)). The equilibrium

solubility product (K) of the boride controls the extent of the transition zone [33]. Typically, K increases with temperature [33,34]. Therefore, the tendency for dissolution of boride at higher temperature causes a broader transition zone.

Typically, the growth of boride is faster in the forward direction than the transverse direction causing a columnar morphology (i.e., a sharp change in the average width or volume of boride) [23,24] and therefore, an abrupt change in boron profile is expected in this case. However, at 1050°C, a gradual change in B profile from the surface to the steel core is possible. It is due to the higher rate of nucleation and growth of boride particles in the matrix [4] or accelerated growth of boride columns in the transverse direction as compared to the forwarding direction. Hence, variation in the slope of B profile is a direct indication of boride morphology.



Figure 4.8: (a) GDOES concentration-depth profiles of boron and (b) corresponding slope variations in the surface layer for the specimens boronized at 850, 950, and 1050°C for 4 h.



Figure 4.9: Micrographs in the cross-sections of the boronized specimens. Arrows indicate some of the boride particles formed at grain-boundaries in the transition zone.

Moreover, slope change in the B profiles on different zones indicates a non-uniformity in the growth kinetics of boride columns. The extent of region (above the transition zone) having the slope of B profile, d(B)/dx, close to zero is considerably broader at 1050°C than that of at 950°C (see inserts in Figure 4.8(b)). It may indicate the constant boride fraction (f_B) in this region. At the interface of zones-III and IV (Figure 4.6(a)), for the same value of B on either side, Si and Al contents are lower in zone-III than zone-IV that suggests the possible role of reducing their accumulation for further growth of boride.

Figure 4.9 shows change in the appearance of boride morphology with temperature. Tips of the boride columns show considerable thickening (or blunting) and branching at 1050°C leading to the decrease in gaps between the columns. In contrast, the boride columns are relatively narrow and have sharp tips at 850°C. In case of 950°C, the tips of boride columns are sharper than that of at 1050°C and show more thickening towards the surface than at 850°C. These boride morphologies support the trend in variation of B content (and hence, f_B) with depth in the boronized layer. The continuous rise in the B content even in zone-I at 850°C indicates that f_B is possibly close to 1, but not equal to 1. The boride growth kinetics is concurrent with the change in slopes of the concentration–depth profiles of other alloying elements.

4.3.4 Effect of Process Time

Figures 4.10 and 4.11 show the concentration–depth profiles of various elements and their slopes (rate of change), respectively, of specimens boronized at 950°C for different process times.



Figure 4.10: GDOES concentration-depth profiles of the elements in the surface layer for the specimens boronized at 950°C for 2, 4, and 6 h.

The trend in the variation of slopes is similar to the Figures 4.6 and 4.7. Peaks designated as p1 in Figure 4.11 correspond to depths at (i) the sharp drop in the concentration of alloying elements (i.e., the maximum

slope in the positive direction), and (ii) the sharp rise in B content (i.e., the maximum slope in the negative direction) while moving from core to surface. Peaks labelled as p2 correspond to the accumulation of Al and Si towards the core. For Al and Si, Al-2 and Si-2 designate the depths at p1, and Al-1 and Si-1 assign the depths at p2. Figure 4.12(a) shows depths corresponding to p1 and p2 for the elements present in the boronized steel. The horizontal dashed lines indicate depths for B. As a general observation, depths for Ni, Al, and Si are lower than that of B. For example, Figure 4.12(b) compares the profiles of B and Ni, where the depth that corresponds to the beginning in the drop of Ni content is leftward to the depth corresponding to Al-2 and Si-2, which suggests that the system prefers accumulation of Al and Si over the depletion during the boride formation.

Typically, in surface alloying process, square of the depth is proportional to the duration of process. There, the proportionality constant indicates the rate of events occurring during the process [1,23]. The coefficient of determination (\mathbb{R}^2) for a linear regression of the square of depths for the elements (Figure 4.12(a)) with time is 0.94 ± 0.04. Slope of the linear regression line for boron indicates the boride growth rate. However, the slopes corresponding to other alloying elements show their migration kinetics during the boride growth. Figure 4.12(c) shows such determined rates of the events.

Figure 4.12(c) shows that Cr, Mn, Mo, and C migrate at slightly higher rate than the rate of boride growth causing the lower tendency of these elements to accumulate (in the non-boride areas surrounding the boride columns: see Figure 4.5(e)-(f)) [1,5,6,23]. However, Ni, Al, and Si migrate at a slower rate than Cr, Mn, Mo, and C. The kinetics of migration of Al and Si that cause the accumulation in the transition zone (near the core) is faster than the rate determined at Al-2 and Si-2. The lower migration

kinetics of Al and Si in the matrix than in the transition zone caused higher concentration of these elements in the matrix than the transition zone (for example, see Figure 4.5(d)).



Figure 4.11: Variation in the slope of the GDOES concentration-depth profiles (shown in Figure 10) of the elements in the surface layer for the specimens boronized at 950°C for 2, 4, and 6 h.

At the locations of Al-2 and Si-2, the slope of the B profile approaches to zero (i.e., stagnation in the boride growth: see Figures 4.7 and 4.11). Therefore, f_B is constant at those locations, and the decreased accumulation in the matrix should be responsible for sharp depletions in overall concentrations of Al and Si at Al-2 and Si-2 locations, respectively. Concentrations of alloying elements affect the growth kinetics of borides [7,9]. The lower migration kinetics of Al and Si at the locations where stagnation in the boride growth occurs suggest that the reduction in accumulation in the matrix is required to overcome the stagnation and, hence, to generate a further growth of boride.



Figure 4.12: (a) Depths corresponding to p1 and p2 (shown in Figure 11) for the elements present in the specimens boronized at 950°C for 2, 4, and 6 h. (b) Magnified view of the B and Ni profiles near to the non-boronized core of the specimen boronized at 950°C for 4 h. (c) Rates determined using the data shown in (a) for the elements present in the steel.

4.3.5 Theoretical Interpretation of EPMA and GDOES Results

The discussion mentioned in the previous sections is further apprehended as follows. Due to the columnar morphology of iron-boride, GDOES measures the composition of boride and the surrounding nonboride regions (matrix) at every depth. Therefore, trend in the concentration–depth profiles of various elements (Figure 4.6) and their slopes (Figure 4.7) are directly associated with the variation in compositions and proportions of boride and matrix. Assume, i is the alloying element in steel, which is further subclassified as *i*-*B* (element present in boride (i.e., Cr, Mn, Mo, and Ni)) and *i*-*NB* (element absent in boride (i.e., Si and Al)). Carbon is excluded because of its absence in the pack-borided surface region. It is considered, the concentrations of alloying element i at depth j in the boride phase and the matrix are $c_B^{i,j}$ and $c_m^{i,j}$ respectively (here, *i* can be *i*-*B* or *i*-*NB*). If f_B and f_m are the fractions (concerning weight or volume) of boride and matrix respectively, $f_B + f_m = 1$. The total composition of i at depth j is given by,

$$c_t^{i,j} = c_B^{i,j} \cdot f_B + c_m^{i,j} \cdot f_m \tag{4.1}$$

EPMA (Figure 4.4) and GDOES results (Figure 4.6) have confirmed that the boride phase contains a lower concentration of the alloying elements than the matrix. Let assume, $\Delta c^{i,j}$ is the difference in the composition of matrix and boride, i.e., $\Delta c^{i,j} = c_m^{i,j} - c_B^{i,j}$. Therefore,

$$c_t^{i,j} = (c_m^{i,j} - \Delta c^{i,j}) \cdot f_B + c_m^{i,j} \cdot f_m$$
 (4.2)

which, further is simplified as

$$c_t^{i,j} = c_m^{i,j} - (\Delta c^{i,j} \cdot f_B)$$
(4.3)

In the case of *i*-*B*, $\Delta c^{i-B,j}$ has a positive value, and it increases from the core to surface. However, in the case of *i*-*NB*, $c_B^{i-NB,j} \approx 0$ (confirmed by EPMA and GDOES results). Hence,

$$c_t^{i-NB,j} = c_m^{i-NB,j} \cdot f_m \tag{4.4}$$

As established in the previous section, the migration rate of i-B is almost close to the rate of boride growth, which indicates that the rejection of i-B by the growing boride and its migration in the matrix strike at the same rate. Therefore, $c_m^{i-B,j}$ remains constant during the boride growth (as a confirmation, varying contents of the elements in the matrix is not evident in Figure 4.5(e)-(f)).

In zone-II, *i*-NB has almost horizontal concentration–depth profiles (i.e., slope = 0) with an increased f_B (or decreased f_m). A considerable increase in $c_m^{i-NB,j}$ (see Eq. (4.4)) is required to maintain this situation. Figure 4.5(d) confirms this by showing the higher concentration of Al in the matrix. Accumulation in the matrix indicates that the rejected *i*-NB diffuse away from the growing boride front at a slower rate causing $c_m^{i-NB,j}$ as a variable during the boride growth.

Concisely, the trend of alternate steeper and shallower slopes of $c_t^{i-B,j}$ profiles are related to the variation in f_B and $c_B^{i-NB,j}$ (Eq. (4.3) and constant $c_m^{i-B,j}$). In other word, profiles of $c_t^{i-B,j}$ are mainly dependent on the composition and morphology of boride, which explains why the Cr, Mn, and Mo profiles appear like the mirror images of the B profiles (Figures 4.6, 4.7, 4.10, and 4.11). However, the pattern of variation in the slopes of the $c_t^{i-NB,j}$ profiles are associated with the changes in the morphology of boride (linked to f_B) and chemical structure of matrix ($c_m^{i-NB,j}$) (Eq. (4.4)). Here, the morphology of boride is a common factor in controlling the trends in $c_t^{i-B,j}$ and $c_t^{i-NB,j}$ profiles.

4.3.6 Mechanism

The obtained results indicate the occurrence of the following events during pack-boriding of the 34CrAlMo5-10 low alloy steel surface.

In the boriding pack-mixture, activator (KBF₄) generates boron halide gases (like BF₃), which (along with O_2 trapped in the boriding mixture) reacts with the source of boron (B₄C) and diluent (SiC), and generate a favourable atmosphere for the boronizing of steel through the following reaction [16,20,22,35]:

$$B_4C + 3SiC + 3O_2 \xrightarrow{BF_3, SiF_4} 4B + 2Si + SiO_2 + 4CO$$
(4.5)

Like the other surface alloying techniques [36,37], boron enters the steel surface $(B \rightarrow [B])$ due to its high chemical potential in the surrounding pack-mixture, and then, achieves a steady-state. The dissolved boron at surface reacts with the elements (M) present in the steel through the reaction (4.6):

$$[B] + 2M \rightarrow M_2B \tag{4.6}$$

Initially, boride starts nucleating at the high-angle austenitic grain boundaries [4] and multiple locations on the surface (Figure 4.13(a)). The nucleating and growing boride particles discard alloying elements because the boride has low or no solubility for most of the alloying elements present in the steel (Figures 4.4–4.6) [4–13]. Boride has the lower solubility (as compared to non-boride region or core) for Cr, Mn, Mo and Ni, and almost zero solubility for C, Si, and Al. The overall content of the elements at any depth within the boronized layer depends on the composition and proportions of boride and matrix. Due to the formation of iron-boride, B content increases sharply during the initial stages causing the sharp decrease in the overall content of Cr, Mn, Mo, and Ni without much change in their concentration in the matrix. Here, a delay in the reduction of Ni content is possible due to its lower migration kinetics. However, the overall content of Si and Al increases with increasing B content due to the sharp increase in their concentration in the matrix. Figure 4.13 shows the difference in composition of matrix region (surrounding the boride) and the core using the grey and white colours, respectively. Accumulation of Al occurs before Si. Initial boride formation leads to a significant reduction of C content, which is finally displaced away from the borides [23]. However, further formation of boride particles leads to increase in the C content to some

extent (due to the sudden rise in the supply of rejected carbon by the growing boride particles) and subsequently, sharp depletion to almost zero content [23]. Rejected C in front of the growing boride can form cementite (Fe₃C) or borocarbides (Fe₃(B, C)) in the transition zone [4,16,20,38]. The following sequence of migration kinetics (MK_i) of the alloying elements, i, causes these differences in their response during the growth of boride: $MK_{Cr/Mn/Mo/C} > MK_{Ni} > MK_{Al} > MK_{Si}$. The transition zone is the region containing boride particles and the matrix containing the accumulated or rejected (by boride) alloying elements. A higher boronizing temperature increases the extent of the transition zone (Figures 4.8 and 4.9). The matrix region (grey shaded regions shown in the schematic diagrams in Figure 4.13) could penetrate/extend in the transition zone at high boronizing temperature (Figure 4.9(d)). Composition of boride and matrix changes continuously as the boronizing process progresses. The growth of already nucleated borides in the forwarding direction gives them a columnar morphology [001]. It corresponds to a maximum atomic density of B and is the most natural path for the diffusion of B in Fe₂B [24]). In parallel, new boride particles nucleate in the transition zone (which later become a part of the growing boride columns) (Figure 4.13(b)-(e)).

During this growth, the concentration of Si and Al in boride remains almost zero, and their accumulation in the matrix decreases to some extent (to accelerate the boride growth) and then, increases again at a later stage (due to the mismatch between rejection rate and migration kinetics of the elements). The extent of the region accumulated with Si and Al increases during further growth. The concentration of Cr, Mn, Mo, and Ni in ironboride decreases without changing their content in the matrix (because the rejection and migration of these elements occur at the same rate) during the growth of boronized region. During the transformation of the entire region to boride ($f_B = 1$) near to the surface, the concentration of the alloying elements in boride could increase slightly (possibly, to accommodate the change in equilibrium situation from two phases to a single phase). Porosities could form at the interface of boride columns (especially, near to the surface) due to the persistent exposure of the specimen surface at the generated gases and oxygen in the pack-mixture [2,6]. The porosities could increase with boronizing temperature (Figure 4.9) [6].



Figure 4.13: Schematic presentation of the boronizing mechanism: (a)-(e) Steps in the development of microstructure and elemental profiles. Positions of the elemental profiles (concerning each other) are arbitrary.

Due to the continuous supply of boron from the surface, the boundaries of the boride grains at the fully transformed surface can act as the nucleation sites for the formation of small grains of the boride (Figure 4.3).

4.4 Conclusions

- Pack-boriding of 34CrAlMo5-10 (EN41B) steel revealed the presence of mainly (Fe, M)₂B layer, where M = Cr, Mn, Mo, and Ni. The concentrations of the alloying elements in (Fe, M)₂B were increased from the surface to core. The solubilities of C, Al, and Si were found almost zero in iron- boride phase.
- 2) The microstructure in the cross-section of boronized specimens, starting from the surface to core, showed the presence of (i) small grains of iron- boride near the surface, (ii) columnar iron-boride and the surrounding non-boride region (called as 'matrix'), (iii) transition zone that contains tiny boride particles in the non-transformed areas, and (iv) non-boronized core. The morphology of iron-boride and extent of the transition zone were dependent on the temperature. IPF map showed that the columnar grains of Fe₂B were oriented mostly around {100} and {110}. The strong texture of Fe₂B grains was observed in [001] crystallographic direction. Maximum hardness of about 1050, 1500, and 1800 HV_{0.1} were detected in the near- surface region at 850, 950, and 1050°C, respectively.
- 3) EPMA and GDOES proved to be promising tools to elucidate the boride growth behaviour. The trend of variation in slope of boron concentration-depth profile was linked with the boride morphology and process temperature. Concentration-depth profile of boron was steeper, and the change in its slope with depth was not discerned at 850°C. However, the variation in the slope of the boron profile becomes distinct at higher process temperature.

- 4) Pack-boriding of steel led to the formation of a systematic trend in the slope variation of overall concentration-depth profiles of the alloying elements. The steeper slope was followed by the shallower slope and vice-versa. The pattern of change in the slopes of the boride forming alloying elements is connected to the composition and morphology of boride. However, for Al and Si, it was related to the boride morphology and the composition of the matrix.
- 5) The chemical composition of the matrix was dependent on the solubility and migration kinetics of alloying elements. The migration kinetics of the alloying elements and the rate of boride growth were interlinked. The migration kinetics of Cr, Mn, Mo, and C were almost equivalent to the rate of boride growth. However, Ni, Al, and Si were migrated at slower rates. Si showed the lowest migration kinetics among the alloying elements. The migration kinetics of Al and Si was lower in the matrix than in the transition zone, which caused the higher concentration of these elements in the matrix than the transition zone. Carbon was entirely missing in the boronized region. The concentrations of the alloying elements having higher migration kinetics remain constant in the matrix during the boride growth.

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The Response of Boronized 34CrAlMo5-10 (EN41B) Steel to Nanoindentation, Oxidation, and Wear

Chapter 5

5.1 Introduction

Industrial components under harsh (working) conditions experience their deterioration (which could be gradual or abrupt), depending on their surface characteristics [1]. However, the engineering components respond efficiently against failure (caused by wear, oxidation, corrosion, etc.) if the microstructure of their surface is customised or the layers of suitable materials are deposited [2–8]. Boronizing, nitriding, carburising, carbonitriding, nitro-carburising, etc., are widely used thermo-chemical methods in industries to enhance the surface properties of steels.

Surface alloying of steel with boron, which is described as packmethod of boronizing, involves use of boron source (generally, B₄C), activator (like KBF₄), and diluent (mostly, SiC or Al₂O₃), resulting into the formation of hard iron-borides (like FeB and Fe₂B) [8–10]. Steels are typically boronized at elevated temperatures (800–1100°C) during which, boron-halide gases and trapped oxygen in the pack-mixture react with boron source and diluent, generating a boron-rich atmosphere [8–10]. Such atmosphere introduces boron into a steel surface and forms the boronized layer. Iron-based alloys can show the formation of a single-phase or dualphase boride layer (i.e., Fe₂B or FeB + Fe₂B), depending on the boronizing process-parameters like the composition of pack-mixture, temperature, and time [8–11]. Preconditioning of steel container (box) used for the packboronizing is also a vital aspect in governing the formation of phases. If the container utilises the boron atmosphere generated in the pack-mixture, the available boron-potential surrounding the specimen is altered, depending on the size of container [8]. Therefore, the resulting microstructure and depth of the boronized layer are affected. Thickness of the pack-mixture can alter the boron potential in the container [12].

The FeB and Fe₂B phases have different crystal structures (orthorhombic and tetragonal, respectively) and different coefficient of thermal expansion [10, 13], although both iron-borides have a substantial hardness. Due to a weak adhesion between FeB and Fe₂B layers, a single-phase boride (Fe₂B) layer is preferred over the dual-phase (FeB and Fe₂B) boride layer [14–16]. However, the formation of FeB is challenging, especially at high temperatures [12,17,18]. Post-treatments can enhance the surface properties of boronized steel [19].

Wear and oxidation resistance of the plain-carbon steels (like AISI 1020, 1018) were studied previously [12,14,20–22]. The oxide film formed on the boronized surface can be beneficial in reducing the coefficient of friction [23]. Also, improvement in the oxidation resistance of steels is possible using boronizing treatment [21,24], along with its promising capability to enhance surface properties of steels for biomedical applications [17,18]. Apart from steels, the oxidation resistance and tribological properties of non-ferrous alloys can also be enhanced using the boronizing treatment [25–28].

The composition of steel plays a vital role in governing the morphology of phases in boronized layer. High-alloy steel (like stainless-steel) shows a smooth interface between the iron-boride layer and substrate [17,18]. However, plain-carbon and low-alloy steels show the saw-tooth morphology of iron-borides [8,9,12,14,21]. High-carbon high-alloy steel (like AISI D2) and medium-carbon medium-alloy steel (like AISI H13) shows an irregular boundary between Fe₂B layer and the substrate (i.e., less

saw-tooth appearance of Fe₂B); however, FeB still shows the saw-tooth morphology [13,15]. Boron diffusion and formation (i.e., nucleation and growth) of the boride phase cause the migration of alloying elements [9,11,29]. Different elements have different solubility and migration kinetics in the iron-boride phase and its surrounding regions [9]. In other words, some elements (like Cr, Mn, Ni) present in the steel are accommodated in the iron-boride, and some elements (like C, Al, Si) are discarded during the growth of iron-boride. Moreover, migration kinetics is different for different elements, and therefore, accumulation of the elements can occur in front of the boride [9]. Such behaviour could resist the faster growth of boride in a particular direction in case of high-alloy steels, leading to a smooth interface between the boride layer and substrate. The composition and the migration behaviour of alloying elements during the layer growth can affect the morphology of boride and the nature of interface developed between the boride and matrix. In case of low alloy steels, sawtooth morphology of boride and migration of alloying elements (during the development of a boronized layer) cause a variation in composition and fraction of phases from the surface to core [9]. Such variation can affect the localised mechanical properties of boronized layer. Nanoindentation technique is becoming popular to investigate the nanomechanical behaviour of various materials [30–38]. This technique has potential to investigate the microstructural inhomogeneity of the boronized layer. Microstructural variation (with depth), localised mechanical behaviour, and oxidation resistance of phases (i.e., boride and the surrounding boride-free matrix regions) can affect tribological characteristics of boronized steels.

Medium-carbon low-alloy steels like 34CrAlMo5-10 (EN41B) have a wide range of applications in the automotive, chemical, oil and gas, and pharmaceutical industries. Nitriding is generally employed to EN41B steel to enhance its mechanical properties. However, the boronizing of this steel can give a superior surface hardness (as high as ~1800 HV_{0.1} – see Ref. [9]), which is substantially higher than the nitrided surface [7]. Therefore, boronizing treatment has a capability to widen the applications of EN41B steel, especially for severe conditions of wear. In the current study, a singlephase boride layer (with a negligible presence FeB) is obtained on 34CrAlMo5-10 steel. The effect of boronizing on various properties is the prime objective of this study. High-temperature oxidation behaviour of the boronized and non-boronized specimen is investigated at different temperatures. Tribological characteristics of the boronized and non-boronized specimen test-parameters (loads and sliding speed) are compared in the dry sliding condition. Optical microscopy (2D and 3D), scanning-electron- microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), glow discharge optical emission spectroscopy (GDOES), X-ray photo- electron spectroscopy (XPS), Raman spectroscopy, nanoindentation, 2D surface-profilometer, and tribometer are used to investigate the specimens. Raman spectroscopy provides useful information about the worn surfaces.

Using the XPS technique, room-temperature oxidation response of the boronized specimens (polished to different depths) is investigated. Nanoindentation technique is employed to study the mechanical behaviour (under the constant load) of the boronized and non-boronized regions of the specimen cross-section.

5.2 Experimental

Medium-carbon low-alloy EN41B steel was used in the study. Chemical composition (in wt.%) of the steel is as follows: 0.4 C, 0.57 Mn, 0.27 Si, 1.45 Cr, 0.91 Al, 0.11 Ni, 0.14 Mo, 0.04 P, 0.04 S and the balance is Fe. Specimens with 40 mm diameter and 3 mm thickness were cut from the cylindrical bar. The specimens were subjected to grinding operation up to 800 mesh-size emery paper, and before boronizing treatment, they were cleaned using acetone. Boronizing was carried out at 1050°C for 4 h in a preconditioned stainless-steel container using commercially available
BoropakTM powder as the boron source. The boronizing pack-mixture generally contains about 5% B₄C, 5% KBF₄, and balance SiC/Al₂O₃ [8,9]. The steel container was air-cooled after boronizing treatment. Detailed procedure of boronizing is explained in chapter-3.

Cross-section of the boronized specimens was polished up to 2500 mesh-size emery paper, followed by polishing up to 0.25 μ m diamond paste. After polishing, specimens were rinsed with soap-solution. Etching was performed using a 2% Nital solution. Boronized and non-boronized specimens used for the roughness measurements and other tests (like adhesion, oxidation, and wear) were polished up to 2000 mesh-size emery paper, followed by 3 μ m diamond paste polishing.

Microstructural investigations of the cross-section of boronized specimens and surface morphology of the oxidised and wear-tested specimens were performed using an optical microscope and scanning-electron-microscopy (SEM, JEOL JSM-7610F-Plus). X-ray diffraction (XRD) patterns of non-boronized, boronized, and oxidised specimens were recorded using Cu-K_{α} radiation. Rockwell-C indentations were taken on polished surface of the boronized specimen to confirm the adhesion of boronized layer using the VDI 3198 standard [39].

Elemental composition across the boride column was determined using EDS line-scan (JEOL JXA-8530F instrument), where the accelerating voltage was 15 kV, and a beam current was 50 nA. Glow discharge optical emission spectroscopy (GDOES-GD-Profiler 2-HORIBA) was used to obtain the semi-quantitative depth profiles of B, Fe, Cr, Mn, Mo, Ni, Si, and Al in the boronized region. In the GDOES technique, ejected atoms (from the surface) are in the excited state. Photoelectric sensors detect such atoms for the specific wavelength (due to the optical emission after decaying to the fundamental state) [40].

In the X-ray photoelectron spectroscopic (XPS) study, specimens were exposed to sputtering by Ar^+ ion to clean the surface before analysis. Sputtering was performed for 1 min maintaining Ar pressure of 1.5×10^{-4} mbar, 300 eV energy, current density of 0.5 mA/cm², and 90° incidence angle of the ions. After the cleaning process, the specimens were transported to the XPS analysis chamber (work pressure $< 10^{-6}$ Pa). Such transport was done without exposing the specimens to the atmosphere. XPS spectra were obtained using a hemispherical analyser (Thermo Alpha 110) in the constant pass mode (20 eV pass energy) and using an X-ray tube with Al target (K_{α} energy \approx 1486.6 eV). The electron inelastic collision background was removed from the spectra by the Shirley method [41]. The relative chemical concentrations were obtained after the correction in the areas of XPS peaks (using the appropriated sensitive factor given by Wagner et al. [42]). Voigt curves were applied considering Gaussian and Lorentzian contributions to determine the position and area of peaks in the spectrum (i.e., the identification of elements and their concentration) [43].

The nanoindentation method (using a Hysitron TriboIndenter TI-900) was used to study the localised mechanical properties of boride columns, matrix surrounding the columns, and non-boronized core regions. This method uses a standard Berkovich indenter. Loading and unloading rate of 0.8 mN/s were applied for all indentations. A constant load of 8 mN was maintained for 10 s during the nanoindentation. Four indentations were taken along the two iron-boride columns, where the vertical and horizontal gaps between the indentation-sites were ~50 µm. Additional indentations were randomly taken in the matrix and core regions. Hardness (H), modulus (E), strain-rate sensitivity (m), and activation volume (V) were determined for boride, matrix, and core regions. Typically, the hardness during indentation is given by Equation (1):

$$H = \frac{P}{A} \tag{5.1}$$

where P is the applied load (in μ N or mN), and A (in nm²) is the projected area of the indent. The projected area depends on the contact depth (h_c in nm). The area function of the Berkovich indenter can be expressed as follows [44]:

$$A(h_c) = 24.50h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \dots \dots + C_8h_c^{1/128}$$
(5.2)

where C_1 to C_8 are constants, and their values depend on the discrepancy in the geometry of Berkovich indenter (for example, blunting of the tip). The first term in Equation (5.2) is the dominant term, and it corresponds to the perfect geometry of Berkovich indenter. This term extensively contributes to determining the impression-area of indentation. Calibration to the area function is based on the calculation of constants by performing many indentations on the material surface [32].

During the constant loading, hardness variation with the holding time (t) was calculated using the instantaneous area (Equation (5.2)) corresponding to the instantaneous contact depth [32]. Indentation strain-rate ($\dot{\varepsilon}$) is generally given by the following equation [35]:

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{1}{h}\frac{dh}{dt}$$
(5.3)

Creep displacement (h) versus time (t) plots were fitted using the following empirical function [45]:

$$h_t = h_0 + a(t - t_0)^b + ct (5.4)$$

where, h_t is the instantaneous contact depth, h_0 is the initial displacement (after reaching the constant load) at t_0 , and a, b, c are fitting constants. Strain-rate sensitivity (SRS), m, can be experimentally defined as [32,35,36]:

$$m = \frac{\partial \log (H)}{\partial \log(\dot{\varepsilon})} \tag{5.5}$$

The SRS of boride, matrix, and core regions were calculated by fitting the linear portion of the double logarithmic plots of hardness and strain-rate. Furthermore, the activation volume (which indicates the plastic volume involved during deformation) for the boride, matrix, and core was calculated using the following expression [36,46]:

$$V = \frac{2.8\sqrt{3}kT}{mH} \tag{5.6}$$

where k and T are Boltzmann constant and absolute temperature, respectively. Activation volume is generally expressed in terms of b^3 , where b is the Burgers vector [36,46]. The activation volume is linked to the number of atoms involved in moving the dislocation against the obstacles along the slip planes.

A high-temperature oxidation study was performed at 200, 550, and 850°C in a laboratory atmosphere using TGA (NETZSCH TG-209). Specimens of dimensions $4 \times 4 \times 1$ mm were kept in an alumina crucible. The initial temperature of the chamber was 30°C. The temperature of specimens was increased at the rate of 10°C/min to the oxidation temperature in a protective N₂ atmosphere. The total cycle time of oxidation was 15 h.

Dry sliding wear tests were performed on the boronized and nonboronized specimens. The parameters used for the wear test are summarised in Table 5.1. Worn surfaces of the specimens were investigated using SEM, 3D optical microscope (Olympus, DSX 1000), and Raman spectroscopy (Horiba, LabRAM HR Evolution). The He–Ne laser (excitation wavelength: 532 nm) was used to obtain the Raman spectra. Contact type surface profilometer (Taylor and Hobson, 2D Stylus Profilometer) was used to obtain the wear-track profiles. Wear-track profiles were measured at four different locations. The wear loss (wear volume) was calculated by multiplying together the area of profiles (i.e., the area of cross-sections of wear track) and the length of wear-track. The specific wear rate was calculated by dividing the wear volume by applied load and sliding distance.

Parameters	Details			
Type of test	Dry sliding wear			
Instrument	Pin-on-disc (DUCOM CM-9112)			
Testing-standard	ASTM G-99			
Specimen condition	Boronized and non-boronized steel			
specimen condition	(34CrAlMo5-10/EN41B)			
Geometry and dimensions of the	Round disc: ϕ 40 mm \times 3 mm			
specimen	(thickness)			
Counter surface (Ball material)	Alumina (Al ₂ O ₃)			
Diameter of ball	φ 10 mm			
Normal load	20, 40, and 60 N			
Sliding speed	0.3 and 0.5 m/s			
Sliding distance	1000 m			
Atmospheric condition	Ambient temperature ($\approx 38 \pm 2^{\circ}$ C)			

Table 5.1: Parameters used for the dry sliding wear studies.

5.3 Results and Discussion

5.3.1 Phase Analysis, Microstructure, Elemental Distribution, and Adhesion Strength

Figure 5.1(a) shows XRD patterns of non-boronized and boronized (at 1050°C for 4 h) surface of EN41B steel. The diffraction pattern of the non-treated specimen shows peaks of the ferrite (α -Fe) phase. However, the boronized specimen indicates the major peaks of Fe₂B and minor peaks of FeB. Optical and SEM micrographs of a cross-section of the boronized

specimen are shown in Figure 5.1(b) and (c), respectively. A major portion of the boronized region shows a columnar Fe₂B, but there is no clear sign of a separate FeB layer. However, the negligible presence of FeB is possible at few locations (which are difficult to trace in micrographs due to the presence of a porous region near the surface). As a result of the anisotropy of boron diffusion in the tetragonal lattice, Fe₂B possesses a columnar morphology [13,47]. Average length of the boride columns depends on boronizing temperature, time, and composition of a pack-mixture [8]. Long boride columns are formed by clustering smaller columns during their growth (Figure 5.1(b)), with maximum length of these clusters reaching up to 200 μ m. Development of the boronized layer involves nucleation and growth of boride and redistribution of alloying elements, leading to the formation of 'transition zone' between the boronized region and core [8,9]. This zone contains fine boride particles, which nucleate mostly at grain boundaries and in the areas between boride columns (Figure 5.1(b) and (c)).

The entire architecture of cross-section of the boronized specimen comprises of the following zones (Figure 5.1(b) and (c)): (i) boronized region containing boride columns, boride particles, and matrix surrounding the columns, (ii) transition zone, and (iii) core. A non-transformed matrix in zones-(i) and (ii) has a different appearance than the core in optical micrograph (after 2% Nital solution reaction) (Figure 5.1(b)), which is possible due to a difference in their chemistry (caused by the elemental redistribution [9]).

Figure 5.1(d) shows the micrographs of Rockwell-C indentation taken on a polished boronized surface to confirm the adhesion of the boronized layer as per the norms mentioned under VDI 3198 standard [39]. Radial cracks are observed at the perimeter of indentation. Cohesion strength of the boronized layer resembles HF3 quality (due to the indication of delamination at some places along the indentation periphery), which is an acceptable level of interfacial adhesion [39].



Figure 5.1: (a) XRD patterns of the boronized and non-boronized specimens. (b) Optical and (c) SEM micrographs of the cross-section of boronized specimen. (d) Optical micrographs are indicating the Rockwell indentation on the boronized surface. (e) BSE micrograph of the cross-section of boronized specimen demonstrating the position of EDS line-scan and the corresponding elemental distribution.

Distribution of boron and other alloying elements within the boronized region is studied using the EDS line-scan across a boride column, as shown in Figure 5.1(e). Initial data-points on EDS line-scan (up to ~90 μ m depth) are within the boride phase, and rest of the points are either in the non-transformed matrix or at the boride/matrix interface. Typically, Fe₂B phase contains about 8–9 wt.% B [8,10]. The observed boron content in the boride phase is close to this value. Somewhat lower B content, especially near the surface, is due to the presence of pores, trapped regions of a non-transformed matrix (between the clusters of boride-columns), and the boundaries between boride columns. Alloying elements like Cr and Mn show a clear indication of their (limited) solubility in the boride phase.

Furthermore, the GDOES results shown in Figure 5.2 confirm that Cr, Mn, Mo, and Ni have partial solubility in the boride-dominated region. These alloying elements tend to form boride phase [11,25,48], and therefore, their presence in the steel results in the formation of mixedboride, M_2B (M = Fe, Cr, Mn, Mo, and Ni) [9,29]. A gradual drop in B concentration-depth profile indicates a decrease in the average boridefraction from the surface to the core. Overall concentrations of the elements given by GDOES are strongly linked with the fraction and chemistry of boride-occupied and boride-free regions [9]. Formation of pores near the surface (Figure 5.2(a) and Figure 5.3(a)) causes the displacement and accumulation of elements at the interface of porous region and boridedominated region (Figure 5.2(b) and (c)). Al and Si contents decrease sharply (close to zero) as the depth reduces from $225 \,\mu m$ to $125 \,\mu m$. Further, Al content depletes to zero below 50 µm depth. Some Si content is observed near the surface region, which is possible due to the presence of Si comprising compounds in the boronizing pack-mixture. The solubility of Al, Si, and C in the iron-boride phase is almost zero [9,10,13], and therefore, the growing boride rejects these elements entirely. Concentration of elements in the matrix of the boronized region depends on the extent of rejection (by boride phase) and migration kinetics of the elements.

Indication of constant Al and Si content within a certain thickness below 125 μ m depth is due to their slow migration (and hence, accumulation/stagnation in matrix) during the growth of boride. Ref. [9] explains thoroughly the migration behaviours of various alloying elements during pack-boriding of the low alloy steel.



Figure 5.2: Glow discharge optical emission spectroscopic (GDOES) concentration-depth profiles of various elements in the surface layer of the specimen boronized at 1050°C for 4 h.

5.3.2 Nanoindentation Analysis

Nanoindentation study is performed to understand the mechanical response of boride, matrix (surrounding the boride-columns), and core regions under the loading-unloading and constant loading (8 mN) conditions. Figure 5.3(a) shows sites of nanoindentation (indicated by numbers 1–6) at different depths. Matrix regions are also displayed in

Figure 5.3(a). Indentations 1–4 are taken on two different boride columns. However, the locations of indentations 5 and 6 are present within matrix surrounding the boride columns. Indentations 7 and 8 are taken at random sites in the non-boronized core (on the ferrite-grains). Figure 5.3(b) shows the loading-unloading curves for various indentations. During indentation process, load increases linearly for 10 s until it reaches the maximum loading condition of 8 mN, where it is held for the next 10 s (to eliminate a creep effect within the investigated region [37]). The indentation cycle ends with unloading in another 10 s.

Table 5.2 shows the maximum penetration depth (h_{max}) and calculated values of hardness (H), reduced modulus (Er), and elastic modulus (E) for the indentations taken at locations 1–8. Elastic modulus of boride is in the range of 278–309 GPa. The maximum depth of indentations in the boride, matrix, and core regions is about 145-152 nm, 224-249 nm, 266–273 nm, respectively. However, the value of h_c (after unloading) is 104-111 nm for boride, 189-210 nm for matrix, and 250-265 nm for core regions. Variation in the penetration depth within boride, matrix, and core regions is linked to their hardness (Eqs. (5.1) and (5.2)). A small deviation in the mechanical properties within the boride columns is possible due to the presence of pores and intercolumnar boundaries [37]. Mechanical behaviour of the locations 5 and 6 is significantly different than the other locations present within the boronized region. Penetration depths of these indentations are considerably higher than the indentations in boride columns, which confirms a relatively softer nature of areas at locations 5 and 6. However, these regions have somewhat higher hardness and lower modulus than the core (Table 5.2). This behaviour is linked to the different chemistry of the matrix regions from the core.



Figure 5.3: (a) SEM micrograph of the cross-section of boronized specimen indicating the locations of nanoindentations and matrix regions. (b) Nanoindentation load vs. penetration depth profiles corresponding to the locations shown in (a). Actual and fitted profiles of creep displacement vs. holding time (under 8 mN load) for (c) boride, (d) matrix, and (e) core regions.

Apart from the hardness and modulus, a variation in other nanomechanical properties of boride columns, matrix, and core are also observed in Figures 5.3 and 5.4. The unloading curve of a loaddisplacement plot is useful in understanding an elastic-plastic nature of material [37]. The difference in the slopes of loading region and unloading region of the curves (Figure 5.3(b)) confirm the presence of elastic-plastic deformation at the contact zone. The h_f /h_{max} (i.e. (final displacement) / (maximum displacement)) ratios are lower for the boride columns than the matrix and core (Table 5.2), which indicates a higher elastic recovery and higher residual stress in the boride regions. Such behaviour is associated with the higher H/E ratio (Table 5.2), which is proportionate to the elastic strain, and the flexible nature [33] of boride. The value of h_f /h_{max} ratio for indentations 1–4 does not have any considerable difference. This observation and the other properties mentioned above indicate that, the localised mechanical behaviour of boride columns at different locations is almost identical. The values of h_f /h_{max} ratios for the matrix are somewhat lower than the values for core (Table 5.2). In other words, elastic recovery of the matrix is somewhat higher than the core (but it is lower than the boride).

Under constant load (8 mN), fitted (Equation (5.4)) creep displacements with the holding time (total duration of 10 s) are shown in Figure 5.4(a) for boride, matrix, and core, where the correlation factors (\mathbb{R}^2) are 0.998, 0.962, and 0.983, respectively (Figure 5.3(c)–(e)). During the initial period, strain-rate (Equation (5.3)) is high, but it subsequently drops and achieves a steady-state below 0.003 s⁻¹ (Figure 5.4(b)). As compared to the matrix and core, the localised boride region (beneath the indenter) experiences a somewhat higher strain-rate under 8 mN load. Such behaviour is possible due to the porous and brittle nature of the boride region.

Table 5.2: Maximum penetration depth (h_{max}) and calculated values of hardness (*H*), reduced modulus (E_r), elastic modulus (*E*), *H/E* ratio, and h_f/h_{max} ratio (i.e., (final displacement) / (maximum displacement)) for the indentations taken at different locations under 8 mN load.

Indentation No.	Location	h _{max} (nm)	H (GPa)	E _r (GPa)	E (GPa)	Ratio <i>H/E</i>	Ratio h _f /h _{max}
1	Boride phase	145	30	255	302	0.10	0.45
2	Boride phase	152	26	239	278	0.09	0.52
3	Boride phase	149	28	242	283	0.10	0.48
4	Boride phase	145	29	256	303	0.10	0.48
5	Matrix (surrounding boride)	224	9	164	177	0.05	0.71
6	Matrix (surrounding boride)	249	7	137	144	0.05	0.75
7	Non- boronized core (ferrite grains)	286	4	168	182	0.02	0.86
8	Non- boronized core (ferrite grains)	274	5	167	181	0.03	0.84



Figure 5.4: Representative graphs for boride, matrix, and core regions under 8 mN load. (a) Fitted creep displacement vs. holding time. (b) Creep rate vs. holding time. Double logarithmic graphs representing the strain-rate vs. hardness for (c) boride, (d) matrix, and (e) core regions. (f) Comparison of the average values of h_f / h_{max} ratio, SRS (m), and activation volume (in terms of b^3 , where b is Burgers vector) for boride, matrix, and core regions.

The strength of many materials depends on strain-rate. Not only metals but also brittle materials like ceramics display a strain-rate sensitivity [30–32,49,50]. Some ceramics demonstrate an increase in peak (or failure) strength with an increase in strain-rate [51]. Microstructural features play an essential role in governing the SRS of ceramics [50]. Wang et al. [31] observed a rate-sensitive nature of the compressive strength of porous SiC. SRS of brittle materials depends on the rate of crack growth and toughness of the material [51]. Under the applied load, densification (elimination/closure) of defects (or discontinuities) in ceramics can promote strain-hardening and hence, SRS can increase [30,32]. Figure 5.4(c)–(e) shows the double logarithmic plots between strain-rate and hardness for boride, matrix, and core regions. Reciprocal of the slope of the linear portion of these plots gives the strain-rate sensitivity (see Equation (5.5)). Strainrate sensitivities (SRS) of the boride column, matrix, and core are marginally different from each other at room temperature (Figure 5.4(f)). Nanoindentation results of iron-boride columns show a positive value of SRS, and it is somewhat higher than the SRS of matrix and core (Figure 5.4(f)). As mentioned above, porosity and inter-columnar boundaries are present in the boride columns (Figure 5.1(b) and (c)). During the penetration of indenter in boride, densification of localised region can enhance its failure strength and diminish nucleation/growth-rate of cracks, which can promote the strain hardening of boride regions. Due to an orientationdifference between the boride columns [9], inter-columnar boundaries in the boride region can offer a localised resistance to the propagation of cracks.

The activation volume of dislocation nucleation in boride, matrix, and core regions are shown in Figure 5.4(f). At a constant temperature, the activation volume is linked to the hardness and SRS of the investigated regions (see Equation (5.6)). Generally, a too-small value of activation volume indicates that point-like defects can act as the source of plastic initiation, and larger volume suggests the involvement of several atoms to migrate the dislocation [34]. At room temperature, the activation volume is

considerably small for the boride regions, which indicates a high resistance to the dislocation nucleation/movement.

During the growth of boride columns, redistribution of the alloying elements occurs, and therefore, the matrix surrounding the boride columns have a different chemistry than the core [9]. The nanomechanical properties of the matrix are strikingly different than the core (Table 5.2 and Figures 5.3 and 5.4), which suggest the role of elemental redistribution.

5.3.3 Room-temperature Response of Boronized Specimen: XPS Study of Polished Surfaces

X-ray photoelectron spectroscopy (XPS) of the specimens polished to different depths ($D_1 - D_5$: see Figure 5.1(c)) helps in understanding the role of varying microstructures of the boronized region (concerning the chemistry and fraction of phases) on room-temperature oxidation behaviour. Figures 5.5–5.7 show the XPS spectra of Fe, B, Cr, and O for D_1 – D_5 depths. The D_1 depth is close to the boronized surface, and D_5 is close to the core. XPS peak-fitting for different elements gives information about the chemical state and composition of the surface film (formed due to environmental exposure). Fitted peaks of Fe (2p_{3/2}), B (1s), Cr (2p_{3/2}), and O (1s) are superimposed on the original XPS spectra in Figures 5.5–5.7.

Deconvoluted peaks at ~187.9 eV binding energy in the XPS spectra of B and the binding energy between 707.01–707.04 eV in the Fe spectra correspond to iron-boride (Fe₂B) [51]. Indications of borides in the case of deeper surface (D₄ and D₅) are due to the presence of boride particles in the matrix (or tails of boride columns). Presence of boron-oxide on D₂ – D₅ surface (peak position at ~191.4 eV) is evident in B(1s) spectra. Indication of Ni-boride in the boron spectra (peak position at ~189.8 eV) supports the elemental analysis discussed in Section 5.3.1, and it confirms the formation of mixed boride (M₂B) phase. Ref. [18] reported the similar

observation of Ni-boride in the XPS spectra of B recorded from the surface of boronized AISI 316L steel.



Figure 5.5: XPS spectra and fitted peaks of B, Fe, and Cr corresponding to the surface at depths D_1 and D_2 within the boronized region.

Apart from the indications of iron-boride, Fe $(2p_{3/2})$ spectra show the deconvoluted peaks corresponding to Fe²⁺ in FeO_x and Fe³⁺ in Fe₂O₃. Most of the Fe present in the matrix (surrounding the boride columns) could form these oxides. In boride columns, Fe bonds with B, and during exposure of the surface to an environment, the confrontations between O–B and O– Fe are viable. The presence of boron-oxide suggests that some B atoms are detached from Fe. Therefore, some proportion of the Fe-oxides could have formed by the detached Fe from B. Elemental Fe, and iron in boride share almost the same peak position in the XPS spectrum of Fe ($2p_{3/2}$) [18,52,53]. Therefore, a signal from the nonreacted Fe (in the boride-free matrix) beneath the layer of oxides is possible (if the layer is sufficiently thin).



Figure 5.6: XPS spectra and fitted peaks of B, Fe, and Cr corresponding to the surface at depths D_3 to D_5 within the boronized region.



Figure 5.7: (a)–(e) XPS spectra and fitted peaks of O (1s) corresponding to the surface at depths $D_1 - D_5$ within the boronized region. (f)–(h) Relative total concentration of Fe, O, B, and Cr corresponding to the surface at depths $D_1 - D_5$.

Deconvoluted Cr $(2p_{3/2})$ spectra show the presence of peaks corresponding to Cr–Cr, and Cr³⁺ in Cr₂O₃. Chromium in the matrix mostly contributes to the formation of Cr₂O₃. Jordan et al. [54] studied the corrosion behaviour of Cr-boride coating, where corrosion resistance of the coating is due to the formation of Cr-oxide passive film. This observation suggests that Cr-oxides are more stable than Cr-borides. Therefore, some of the Cr in (Fe, M)₂B phase (i.e., mixed boride) can also contribute to the formation of Cr_2O_3 . The peak corresponding to the elemental Cr is related to its presence beneath the oxide layer (in a boride-free matrix).

Deconvolution of O(1s) spectra in Figure 5.7(a)–(e) shows the prominent peak at ~ 531.2 eV corresponding to metal oxides (M_xO_x). The presence of contaminants is also evident from the deconvoluted spectra of oxygen [55].

Figure 5.7(f)–(i) shows the calculated relative total concentration of Fe, B, Cr, and O for $D_1 - D_5$ surface. Round brackets are used to specify these elements as their relative total concentrations. Region of XPS scan for each surface covers the boride and boride-free matrix. Higher (Fe) and (B) on the D_1 surface confirm the higher proportion of the iron-boride phase. Due to the decrease in boride fraction, the relative concentration of boron shows a decreasing trend from D_1 to D_5 . A considerable drop in (B) on the D_5 surface indicates the domination of a boride-free matrix and substantial depletion of boride (as compared to other surfaces).

The trends of (B) and (O) for $D_1 - D_5$ surface display their competition to form bonds with Fe (Figure 5.7(g)). As mentioned above, the surface layer on $D_1 - D_5$ consists of Fe-oxides and Cr-oxide (Figures 5.5 and 5.6). Decrease in (Fe) with increasing depth from D_1 to D_2 is associated with an increase in (O) and (Cr). These trends suggest a rise in Cr-oxide proportion (i.e., a drop in the proportion of Fe-oxides) in the oxide layer on the D_2 surface. The highest (Cr) and the lowest (O) indicate the thinnest oxide layer on the D_3 surface (Figure 5.7(g) and (i)). Therefore, more signal comes from the metallic Cr beneath the oxide layer (Cr–Cr bonds in matrix regions). Almost the lowest (Fe) for the same surface indicates a possibility of Cr-oxide dominance in the layer. This behaviour of D_3 is possible due to the presence of higher Cr in the mixed-boride columns located at a deeper boronized layer (Figure 5.1(e)) [9] or due to the optimum chemistry and fractions of boride and matrix. As the depth increases from D_3 to D_4 , the content of (O) and (Fe) increases, and (Cr) decreases. Such trends indicate an enrichment of the surface layer with Fe-oxides. The highest (O) on the D_5 surface is associated with the lower concentrations of other elements. This behaviour is linked with the lower proportion of boride (i.e., the higher fraction of boride-free regions) and the higher proportion of oxides.

Concisely, the oxidation resistance of the steel surface at room temperature is enhanced by the presence of a higher proportion of mixedboride (preferably, with higher Cr content) and the oxide layer enriched with Cr_2O_3 . The depletion of boride content on the steel surface raises the proportion of oxides.

5.3.4 High-temperature Oxidation Behaviour

Prior to the high-temperature oxidation study, boronized specimens were polished to remove surface contamination from the pack-mixture. Figure 5.8(a) shows the mass-change with time for the boronized and nonboronized specimens subjected to the TGA temperatures of 200, 550, and 850°C for a total duration of 15 h. In Figure 5.8(a), mass-change is of expressed in per unit area the specimen (i.e., $\Delta m/A$). The discernible difference in the behaviour of mass-change of nonboronized and boronized specimens is observed at different temperatures.

Oxide scale on the specimen exposed to 850°C spalls easily if not handled carefully after the oxidation. However, the scale is intact on the specimens subjected to lower temperatures. A substantial rise in the massgain indicates the thickening of oxide scale at elevated temperatures. During the continuous growth, the volume of oxide scale increases at localised regions resulting in the formation of compressive stresses, and hence, spallation of the scale is plausible [56]. However, spallation of the oxide scale on the boronized surface does not occur at higher temperatures, which is possible due to the lower thickness of the scale. Dokumaci et al. [28]





Figure 5.8: (a) TGA plots of mass-gain per unit area (Δ m/A) of the nonboronized and boronized specimens at 200, 550, and 850°C. (b) XRD patterns of the specimens oxidised at 550 and 850°C.

The mass-change of specimens occurs in two steps (Figure 5.8(a)): (i) non-iso- thermal oxidation (mass changes during the rise in temperature to the set-point) and (ii) isothermal oxidation (mass changes at constant temperature). Unlike the specimens at 200°C, boronized specimens show a lower mass-gain than the respective non-boronized specimens at 550 and 850°C. At 550°C, mass gained by the non-boronized specimen is almost twice that of the boronized specimen. However, the difference in masschange between the non-boronized and boronized specimens is substantially reduced at 850°C. Mass-change of the specimens at 200°C is significantly lower than the specimens exposed to elevated temperatures (Figure 5.8(a)). During the initial stage of oxidation at 200°C, pores, and openings at grain- (or intercolumnar) boundaries in the boronized layer provide an easy path for oxygen to form oxides. Therefore, the boronized specimen shows higher mass-grain than the corresponding non-boronized specimen. Subsequently, downward-fluctuation of mass-change in the isothermal stage can be attributed to a release of gases entrapped/adsorbed in pores/openings. Further oxidation of the specimen causes a rise in the mass-change.

Figure 5.8(b) shows XRD patterns of the oxidised surface of the non-boronized and boronized specimens. Generally, the stoichiometry of iron-oxide formed on the surface depends on temperature and oxygen potential in the surrounding environment. Oxidised iron-based alloys frequently show a formation of Fe_2O_3 and Fe_3O_4 in the scale [56,57]. In the current work, XRD patterns of the non-boronized specimens comprise mostly Fe₂O₃ phase at elevated temperatures (Figure 5.8(b)). However, the oxide scale formed on the boronized specimens shows the presence of ironborates like Fe₃BO₆, Fe₃BO₅, Fe₂BO₄, and FeBO₃ (Figure 5.8(b)). The presence of iron-oxide is also possible on the scale. Iron-borates are present in the pseudo-binary phase diagrams of iron-oxide $(Fe_2O_3 \text{ or } FeO_x)$ – boronoxide (B_2O_3) system [58]. Phase diagram of Fe₂O₃ – B₂O₃ system shows the presence of Fe₃BO₆ and FeBO₃, and FeO_x-B₂O₃ system reveals the presence of Fe₃BO₅ and Fe₂BO₄. The XRD patterns do not show any peak corresponding to B_2O_3 (Figure 5.8(b)) because of its non-crystalline nature [24,28]. However, XPS results in the previous section support the possibility of its formation.

XRD patterns of the specimens exposed to 200°C are not shown because noticeable peaks of oxides are absent, and (as mentioned above) mass-change of the specimens is substantially lower at 200°C (Figure 5.8(a)). Furthermore, a noticeable oxide scale is not observed on the surface of specimens at 200°C. However, in case of the boronized specimen, oxides can form only at limited locations on the surface due to the presence of pores or openings at grain boundaries (Figure 5.9(a)). In contrast to the specimens exposed to 200°C, the oxide scale covers an entire surface during the oxidation at 550 and 850°C (Figure 5.9(b)-(e)).

SEM micrographs in Figure 5.9(d) and (e) show the morphology of Fe₂O₃ scale formed on non-boronized specimens at 550 and 850°C, respectively. Iron-oxides in the form of irregular shaped platelets and crystals (with various geometries) are evident on the surface at 550°C. However, at 850°C, the surface is mostly covered with iron-oxide plates (with thin cross-section) and needles. Some of the thin plates are grown almost perpendicular to the surface, and therefore, they look like needles. Morphology beneath the plates and needles appears as an interconnected network of irregular shaped small islands (see insert in Figure 5.9(e)).

During the oxidation of boronized specimens, iron-boride reacts with oxygen to form iron-borates. In another possibility, iron-oxides and B_2O_3 form, and simultaneously, they react with each other to form ironborates. The layer of amorphous B_2O_3 (which has a melting temperature of about 450°C [21]) and crystalline iron-borates restrict the diffusion of oxygen (from surrounding) and iron (from the substrate) leading to the improved oxidation resistance. SEM micrographs of the boronized surface after oxidation at 550°C show the clusters of small globules of oxides (Figure 5.9(b)). These clusters are present on the oxide layer, where multiple cracks are visible (suggesting the formation of glassy B_2O_3).

These cracks are possible to form due to the mismatching of thermal expansion coefficients of the oxide scale and the iron-boride layer. Cracks and pores on the oxide scale are filled (or covered) by the clusters of oxides, which further restricts the oxidation of the surface.



Figure 5.9: Scanning electron micrographs of the boronized surface after the oxidation at (a) 200, (b) 550, and (c) 850°C, and the micrographs of the non-boronized surface oxidised at (d) 550 and (e) 850°C.

During the initial stage of oxidation of boronized specimen at 850° C, there is a possibility of liquid or gaseous B₂O₃ to react with ironoxides to form iron-borates (Figure 5.8(b)). These borates show several morphologies like whiskers, needles, rods, and plates of different shapes (Figure 5.9(c)). During exposure of the specimen for longer duration at the higher temperature (850°C), partial dissociation of iron-borates to ironoxides and B₂O₃ liquid (which evaporates above 800°C [21,24]) reduces the effectiveness of surface layer in improving the oxidation resistance. The formation of large pores in the oxide scale can be attributed to the evaporation of some proportion of B_2O_3 liquid (Figure 5.9 (c)). Fluctuations in mass-change curves (Figure 5.8(a)) could be associated with the occurrence of various reactions on the specimen surface and the growth (kinetics) of different oxides into the diverse morphologies.

5.3.5 Dry sliding Wear Behaviour

5.3.5.1 Surface Roughness and Wear Loss

As mentioned above, pack-mixture forms an adherent layer (which contains SiC and residual products of heat-treatment) on the specimen surface during boronizing. Such layer sticks to the surface, and it is not a part of the boronized layer. Therefore, like the high-temperature oxidation study, mild polishing was performed to eliminate the effect of such deposited layer on wear behaviour of the specimens. As shown in Figure 5.10(a), average surface roughness of the boronized and non-boronized specimens is about 0.32 and 0.02 μ m, respectively. Presence of pores/cavities on the polished surface causes higher roughness of the boronized specimens (Figure 5.10(b)).

Figure 5.11(a)–(d) shows the two-dimensional depth profiles of wear-scars formed on the surface of non-boronized and boronized specimens. Significantly lower depth of wear-scars confirms the superior wear resistance of the boronized specimens. The maximum depths of wear-scars for the non-boronized and boronized specimens under the identical wear conditions (i.e., 60 N and 0.3 m/s) are about 175 and 58 μ m, respectively. Lower depths of the scars for specimens subjected to the higher sliding velocity are due to the smaller duration of sliding to cover a constant distance of 1000 m (i.e., when the velocity is 0.3 and 0.5 m/s, sliding occurs for 3333 and 2000 s, respectively).



Figure 5.10: (a) Two-dimensional surface roughness profiles of the nonboronized and boronized specimens. (b) SEM micrographs of the polished surface of boronized specimen.

Unlike the boronized specimens, the pileup of material (plastically deformed and displaced material) at the periphery of wear-tracks is significant for the non-boronized specimens (see the regions indicated by dashed-ellipses in Figure 5.11(a) and (c)). Accumulation increases with load under lower sliding speed, which is consistent with the tendency in wear-scar depth. However, such a trend in the pileup formation is absent under higher sliding-speed. In the case of boronized specimens, the pileup of plastically deformed material is not observed due to the brittle nature (Section 5.3.2) of the boride-dominated surface region. However, under higher load (especially under higher sliding velocity), the broad hump is visible at the periphery of wear-tracks (Figure 5.11(d) and (e)), which is possible to transpire due to the considerable elastic recovery of boride phase (Section 5.3.2).

Wear-scar depth profiles of boronized specimens show considerable asymmetry, where the depth is more towards the outer periphery than the inner edge (Figure 5.11(b) and (d)–(f)). Such behaviour is more pronounced at higher load and higher sliding velocity. Abrasion starts at relatively brittle regions (or locations) with a significant stress concentration [23,59]. Brittle particles (debris) of boride are dragged towards the outer periphery (due to the centrifugal force), which can cause nonuniform wear and asymmetric depth-profile of wear track.

Figure 5.12 represents the volume loss (i.e., wear loss) and specific wear rate of non-boronized and boronized specimens studied under various sliding conditions. Volume loss and specific wear rate of boronized specimens are significantly lower than the corresponding non-boronized specimens under the investigated wear conditions. Under higher sliding velocity, volume loss of the non-boronized and boronized specimens (under each load) is lower than the corresponding specimens tested under lower sliding speed. In the case of boronized specimens, the ratio of wear loss under 0.5 m/s sliding speed to 0.3 m/s sliding speed is 0.81 for 20 N, 0.75 for 40 N, and 0.28 for 60 N (Figure 5.12(a) and (b)). As mentioned above, such behaviour is linked to a smaller duration of sliding to cover 1000 m distance under 0.5 m/s sliding speed. Another reason for the reduction in wear loss can be as follows. Under higher sliding speed, specimen surface experiences a higher strain-rate. Due to the positive value of strain-rate sensitivity (see Section 5.3.2), increase in the yield strength for non-boronized surface (m ≈ 0.007) and increase in peak-strength/failurestrength for boride-dominated surface (m ≈ 0.011) are possible to reduce the wear loss under higher sliding speed.

Wear loss of non-boronized specimens increases with load under 0.3 m/s sliding speed, where the loss at 40 and 60 N loads is about 2–4 times the loss at 20 N load. Under 0.5 m/s sliding speed, wear loss of non-boronized specimens increases as load increases from 20 to 40 N. Subsequently, it decreases with an increase in load to 60 N (Figure 5.12(b)). For the same sliding speed (i.e., 0.5 m/s), the specific wear rate of non-



Figure 5.11: (a)–(d) Two-dimensional depth profiles of wear-tracks formed on the surface of non- boronized and boronized specimens during wear study under different loads (P = 20, 40, and 60 N) and sliding speeds ($v_s =$ 0.3 and 0.5 m/s). (e)–(f) Three-dimensional optical images along with the colour mapping for varying degrees of depths in different regions of weartrack.

-boronized specimens decreases consistently with an increase in load (Figure 5.12(d)). Such behaviour can be linked to the formation of oxide

scale (Section 5.3.5.2) during sliding (due to the localised surface heating), which can reduce the coefficient of friction and wear loss [23].

In the case of boronized specimens, volume loss under 20 N load is the lowest. Due to the higher surface roughness of the boronized specimens, surface asperities can be broken under lower load (e.g., 20 N). Such debris can increase friction to some extent; however, they are still unable to cause significant wear loss under 20 N load. The volume loss increases with increasing load under both sliding velocities. However, specific wear rate remains almost unchanged under 20 and 40 N load (Figure 5.12(c) and (d)). Such behaviour is allied to the formation of a tribo-oxides scale on the worn surface (Section 5.3.5.2). The oxide film formed on the boronized surface during sliding wear can reduce friction [23]. Under the lower loading conditions (20 and 40 N), the oxide scale remains adherent to the surface for a relatively longer duration, which restricts the abrasion of surface and reduces the extent of material loss. In other words, the presence of oxide scale can reduce the frictional force under lower loads (20 and 40 N), and therefore, the proportionate rise in the volume loss with an increase in load from 20 to 40 N is insignificant (Figure 5.12(a) and (b)). However, specific wear rate of the boronized specimens increases with a further increase in load to 60 N (Figure 5.12(c) and (d)). Under high load (say, 60 N), boronized surface experiences a higher degree of fracturing, abrasion, and oxidation, leading to a considerable rise in the volume loss and specific wear rate (Section 5.3.5.4).



Figure 5.12: (a)–(b) Volume loss (wear loss) and (c)–(d) specific wear rate of the non-boronized and boronized specimens studied under different wear conditions. (e) The ratio of wear loss of non-boronized specimens to the wear loss of boronized specimens under different loads and sliding speeds.

The maximum wear-resistance of the boronized surface is ~ 46 times the wear-resistance of non-boronized surface studied under the same wear conditions (Figure 5.12(e)). Under the lower load (20 N), higher sliding speed can cause the domination of surface hardening (considerable value of SRS of boride, as mentioned above) over the brittle fracturing of boronized specimen, leading to the maximum improvement in wearresistance (concerning the non-boronized specimen). Increase in load from 20 to 40 N under 0.3 m/s sliding speed, non-boronized specimens show the sharper increase in wear loss (\sim 51%) than that of the boronized specimens $(\sim 46\%)$ (Figure 5.12(a)), which causes the higher ratio of their wear loss under 40 N load than 20 N load (Figure 5.12(e)). With further increase in load, especially under higher sliding speed, a steeper drop in the tribological advantage gained by the boronizing treatment is observed. Amongst the investigated wear-parameters, the wear resistance under 60 N load is the lowest for the boronized specimens, where the ratio of wear loss of nonboronized specimens to the wear loss of boronized specimens is about 14 and 8 under 0.3 and 0.5 m/s sliding speeds, respectively (Figure 5.12(e)). As mentioned above, such behaviour is linked with the domination of boronized layer fracturing, abrasion, and oxidation.

5.3.5.2 Raman Spectroscopy of Worn Surface and Coefficient of Friction (CoF)

Figure 5.13(a)–(c) shows the characteristic Raman spectra recorded from the wear-tracks formed under the various wear conditions. The presence of Fe₂O₃ and Fe₃O₄ peaks confirms the formation of the tribooxide scale on the worn surface of non-boronized and boronized specimens. The presence of such oxides indicates the occurrence of localised heating during dry sliding of specimens. Figure 5.13(d) corresponds to the Raman spectra recorded from the abraded sites, where brittle fractures have occurred on the wear tracks (Section 5.3.5.4). Such spectra show the peaks corresponding to the friction products, which contain Fe_2O_3 , Fe_3O_4 , B_2O_3 , and H_3BO_3 phases. Beneath the iron-oxides, B_2O_3 and H_3BO_3 phases are possible to exist, and they are uncovered due to the brittle fracture during dry sliding wear of specimens. Unidentified peaks at x and y positions in Figure 5.13(c) and (d) may correspond to impurities or other mixed phases.

In the case of boronized specimens, various compounds form on the worn-surface due to frictional heating (localised heating at contacting surfaces) and subsequent cooling. Above results suggest the occurrence of following steps during wear study [23,60,61]: (i) oxidation of Fe₂B to form Fe and B_2O_3 ; (ii) oxidation of Fe to Fe_2O_3 and Fe_3O_4 ; and (iii) hydration reaction, where H₃BO₃ forms due to the reaction of B₂O₃ with moisture present in the atmosphere (such reaction could occur during cooling of a localised area of the worn surface). Apart from these reactions, oxidation of matrix surrounding the boride phase is possible during sliding wear because matrix regions have relatively weak oxidation resistance (like nonboronized surface) than the boride phase (Section 5.3.3 and 5.3.4). With an increase in the depth from the surface of the boronized specimen, the fraction of boride decreases (i.e., the fraction of boride-free matrix region increases) (Figure 5.2(a)). It is observed that some of the non-transformed (to boride) matrix regions are trapped between the clusters of the boride columns, and they are present nearer to the surface (Figure 5.3(a)) [9]. Therefore, with an increase in wear loss, the contribution of oxidised matrix regions in the overall tribo-oxide scale can be perceptible.

Figure 5.14 presents a variation in coefficient of friction (CoF) with time under different study conditions. An initial steep rise in the CoF of boronized surface occurs as a result of the running-in period, where surface roughness, porosity, and nature of contact between the asperities of mating surfaces play a vital role [12,16]. After passing through a running-in period, fluctuations in CoF under different study conditions are attributed to the oxide-scale formation, plastic deformation, and grooving of the surfaces [26]. With the rise in load and sliding velocity, relatively better uniformity in CoF is evident for the specimens (Figure 5.14(c)–(f)) due to the establishment of better contact between the sliding surfaces.

During an initial stage of surface contact (i.e., during the running-in period) and sliding under lower loads (Figure 5.14(a) and (b)), the formation of oxide film is constrained by a limited rise in temperature (caused by the localised frictional-heating under dry sliding condition [23]). Such surface has a thin oxide scale. A swinging nature of CoF is associated with the formation and exfoliation of oxide scale. Under lower loads, uniformity of oxide scale (on the worn surface) is less (Section 5.3.5.4), which can cause a rise in CoF during sliding. As the oxide scale or strain-hardened surface or brittle phases flake off, CoF can rise (Figure 5.14(d)–(f)) due to the direct contact between the mating surfaces. As the sliding duration progresses, thick oxide film spreads over the worn surface, and it brings the dynamic stability to CoF [23].

Higher roughness of the boronized surface (Figure 5.10(b)) dominates at 20 N load, which causes a higher CoF than the non-boronized surface (Figure 5.14(a) and (d)). The fracturing of asperities on the rough surface forms wear debris, which can further contribute to the rise of CoF. However, as mentioned above, such an increase in CoF is unable to cause a significant wear loss of hard boride surface under lower load (Figure 5.12(a) and (b)). Generally, during sliding motion, adhesion and deformation of contacting surfaces increase the CoF [62]. However, these components of CoF are minimised if sliding surfaces have high hardness. Therefore, an increase in surface hardness can cause a decrease in CoF [62]. Under 40 and 60 N load and 0.3 m/s sliding speed, the enhanced contact between the surfaces and the high hardness of boronized surface cause the lower CoF than the non-boronized specimens (Figure 5.14(b)–(c)). The formation of continuous oxide film on the boronized surface (during sliding wear) can also contribute to reducing the CoF under higher loads [23].



Figure 5.13: Raman spectra of wear-tracks on (a) boronized and (b) nonboronized specimens studied under 60 N load. (c) Raman spectra of weartracks on boronized specimens worn under 20 and 40 N loads. (d) Raman spectra recorded from the abraded sites, where brittle fractures occur on the wear-tracks.



Figure 5.14: Variation in the coefficient of friction (CoF) with time for nonboronized and boronized specimens studied under the different wearparameters.

Under the applied load, shear stress (frictional stress) increases with an increase in sliding velocity [63], leading to an increased probability of brittle fracturing of the boronized surface. Therefore, the role of wear-debris dominates under higher sliding speed (due to the brittle fracture of oxide scale and iron-boride) and causes a jump in CoF (exceeding that of nonboronized specimens) after sliding for some duration (beyond 600–700 s: see Figure 5.14 (d)–(f)).

Under 20 N load, smoother surface of the non-boronized specimen (Figure 5.10(a)) has lower CoF than the boronized specimen (Figure 5.14(a)
and (d)). With an increase in sliding velocity, a slight rise in CoF of the nonboronized specimen is observed under 20 N load. In case of metals, an increase in adhesion strength with an increase in load can cause a rise in the CoF [64]. For 0.3 m/s sliding speed, as the load increases to 40 N, the CoF of non-boronized specimen increases. Such behaviour is possible due to the formation of discontinuous oxide scale, increase in surface deformation, the formation of deep grooves, adhesion, and delamination (enabled by the softer nature of the non-boronized specimen surface). However, CoF of the non-boronized surface decreases with an increase in load under 0.5 m/s sliding speed (Figure 5.14(d) and (e)), which can be caused by the higher localised heating and formation of continuous oxide film. As compared to 40 N load, CoF of non-boronized surface under 60 N load is either reduced (for 0.3 m/s sliding speed: see Figure 5.14(b) and (c)) or remained the same (for 0.5 m/s sliding speed: see Figure 5.14(e) and (f)). Such behaviour is linked with better coverage of the specimen surface by oxide film [23].

5.3.5.3 Worn Surface Morphology and Wear Mechanism of Nonboronized Specimens

Surface morphology and characteristics of worn surface of the nonboronized specimens studied under various wear-parameters are analysed using SEM micrographs shown in Figure 5.15. Oxidative wear [65,66] is the dominating wear phenomenon observed for these specimens. Frictional heat produced during the rubbing of contacting surfaces causes the formation of a tribo- oxide layer on the non-boronized specimens. Such oxide layer possesses mainly Fe_2O_3 and Fe_3O_4 (Figure 5.13(b)).

SEM micrographs show the wear-tracks with plateaus of oxide scale and deeper grooves (Figure 5.15). Due to the malleable nature of the surface and continuous rubbing action of hard alumina ball (counter surface) on wear-tracks, non-boronized specimens encounter severe plastic deformation [12,59] and the formation of grooves. Due to the frictional heating, thickness of the tribo-oxide scale can increase as the sliding duration progresses. Consequently, internal stresses developed within the scale (in conjunction with external load) lead to its delamination and conversion into debris. Furthermore, such fragments incorporate into the oxide scale and thereby, increase its brittleness [23]. As discussed in the previous section, the non-uniformity of oxide scale on the wear track leads to turbulence in the contact between tribo-pair. Such interaction results in cyclic stress, and hence, delamination occurs at the contact zone (Figure 5.15) [23,65].

Under the applied test conditions, as the wear test progresses, distortion of the worn surface increases. Sliding speed and the applied load have a significant role in controlling the distortion of the worn surface. Distortion dominates with an increase in loading conditions [65]. For the lower sliding velocity, the larger contact area is possible to develop due to a longer duration of the test to cover the fixed sliding distance [65]. Therefore, substantial distortion (Figure 5.15(b) and (c)) and more wear loss are the characteristics of higher loading with lower sliding speed (Figure 5.11(a) and Figure 5.12 (a)). Various characteristic appearances of the delaminated oxide scale are observed on the worn surfaces (Figure 5.15). Under 20 N load, the delamination sites with short contours are seen on the worn surface. However, the specimens studied under higher loads show the delamination sites with more extended contours. Pulverisation of oxide scale into fine debris occurs during the wear test, especially at the higher load (Figure 5.16(a)). Such wear debris contains Fe-oxides (Figure 5.13(b)) and ferrite [22].



Figure 5.15: SEM micrographs of the worn surface of the non-boronized specimens studied under different wear-parameters. Dashed ellipses indicate the delamination of the oxide scale.

5.3.5.4 Worn Surface Morphology and Wear Mechanism of Boronized Specimens

In the case of worn surface of boronized specimens, a relatively smooth wear track is easily distinguishable from the surrounding rougher regions (Figure 5.17). Under the action of a constant loading, surface asperities on the boronized surface break during the initial stage and then, separate from the surface in the form of wear debris. These events result in the development of flat contacts between the mating surfaces. Due to the continuous rotation of the disk (specimen), most of the fragments (debris) produced during the initial stage of contact are pushed away from the mating surfaces. Welding of the debris to the surface is unlikely because of the brittle nature of the boronized surface. Some of the debris can accumulate in the wear-tracks and cause the asymmetric wear-track profiles (Figure 5.11(b) and (d)–(f)).



Figure 5.16: Wear debris of (a) non-boronized and (b) boronized specimens tested under 0.3 m/s sliding velocity and 60 N load.

The physical appearance of the worn surface of boronized specimens is significantly different from non-boronized specimens (Figures 5.15, 5.17, and 5.18). Unlike the non-boronized specimens, deformed grooves parallel to the sliding direction are negligible in case of boronized specimens (Figure 5.17), which is attributed to the high hardness of boride dominated surface. During dry sliding, the boronized surface experiences oxidation, abrasion, fatigue, and brittle fracture. Oxidation of the boronized surface begins after the development of proper contact between the tribopair. Since both contacting surfaces (i.e., boronized surface and alumina counter surface) have brittle nature, their engagement under dry sliding conditions can result in a noticeable temperature rise at the contact zone [65,67]. The phenomenon of surface oxidation of boronized surface during

wear is like the non-boronized surface (discussed above). Initially, the oxide scale developed at the surface acts as a barrier for further wearing [15,23].



Figure 5.17: SEM micrographs of the worn surface of the boronized specimens studied under different loads and 0.5 m/s sliding velocity. WTW indicates the width of the wear track.



Figure 5.18: (a)–(d) SEM micrographs of the boronized surface worn under different loading conditions at 0.3 m/s sliding velocity. (e)–(f) SEM micrographs of the cross-section of wear-tracks formed on the boronized surface.

Patches of the tribo-oxide scale are observed on the wear tracks (Figure 5.17(b) and (c)). These patches can be formed initially due to the oxidation of boride-free matrix regions because they have relatively deprived oxidation resistance (like non-boronized surface) than the boride phase (Section 5.3.3 and 5.3.4). The temperature of the contact zone can increase with an increase in the applied load [68]. Therefore, increase in

coverage of the tribo-oxide scale on wear tracks is possible with increase in load. Under 60 N load, the entire worn surface is covered with the patches of oxide scale (Figure 5.17(c)).

Periodically spaced ridges labelled as 'creased surfaces' are found on the worn surface of non-boronized (Figure 5.15(b)) and boronized specimens (Figure 5.17(e) and Figure 5.18(c)). The creased surfaces have ridges perpendicular to the wear direction. Such features on the oxide layer are also called 'corrugation bands' [23] or 'striations' [60], which are formed as a result of shredding of the oxide film adherent to the sliding surface [23]. These surfaces are believed to restrain the further growth of oxide film and cause a rise in friction coefficient [23]. As the test progresses, a transition from oxidation wear to abrasion (by wear debris) occurs [26]. This transition causes a substantial rise in the frictional force between the tribo-pair, especially under higher sliding speed and higher loads (Figure 5.14(d)–(f)). Therefore, higher wear-rate is observed for the boronized specimens under 60 N load (Figure 5.12).

Typically, the failure of boronized surface occurs due to its brittle fracture [16,23,26]. Fracture toughness of the boride phase plays a significant role in governing the wear mechanism [16]. Depth profiles of wear-tracks (Figure 5.11) and wear-rates (Figure 5.12) indicate that the severity of surface damage of the boronized specimens increases under the application of high load (60 N) and sliding for a longer duration. In Figure 5.11(e) and (f), three-dimensional optical images along with the colour mapping show a varying degree of surface distortion (from mild to severe) in different regions of the wear-track. As mentioned above, distortion of the worn surface of boronized specimens depends on the load and sliding speed (Figures 5.17 and 5.18). Shear stress developed at the contact zone between the specimen and the counter surface acts as a driving force for the fragmentation of brittle surfaces [27]. Due to the brittle nature of boride (Section 5.3.2), when the contact stress exceeds beyond the threshold stress,

cracks initiate at the surface, and they propagate within the boronized layer to cause a brittle failure during the wear [20]. Thin boride columns, intercolumnar boundaries, and pores are the primary sites for the nucleation and propagation of cracks. Therefore, the indications of cracking are observed at various locations on the worn surface of boronized specimens (Figures 5.17 and 5.18). During sliding, every location on the wear track experiences a continuous cycle of loading and unloading. Such activities cause the propagation of nucleated cracks (even under lower load) in different directions within the boronized region, resulting in the spallation [15]. The worn surface of the specimen studied under 20 N load shows the small patches of brittle fracture (Figure 5.17(a)). However, as the load increases, these small patches of brittle fracture cluster together (to cause a severe fracturing) and create valleys of brittle failure (Figure 5.17(b)–(f)). Cracks on the sub-surface regions are evident in the case of specimens tested under the higher loading conditions (Figure 5.17(f) and Figure 5.18(d) and (f)). Such cracks can cause sub-surface delamination.

The formation of FeB on the Fe₂B layer at a few locations is possible in case of the boronized specimens (Figure 5.1(a)). Generally, the FeB layer has compressive residual stress at a low boronizing temperature (about 800– 900°C) [69]. However, at high boronizing temperature, FeB layer has the tensile residual stress [70], and it has poor adhesion with the underneath Fe₂B layer (due to their different crystal structures and coefficients of thermal expansion [8]). Therefore, the FeB formation expediates cracking [15,16]. However, in the current work, a separate layer of FeB on the specimen is not evident (Figure 5.1(b) and Figure 5.3(a)). Due to the considerable elasticity of Fe₂B (Section 5.3.2), single-phase boride layer can accommodate compressive residual stress [71] and can have better adhesion with the substrate (Section 5.3.1). Due to high hardness (Table 5.2) and presence of compressive residual stress [71], single-phase Fe₂B layer is a better candidate against wear (as it has a lower tendency for the crack initiation and propagation) [16]. Furthermore, the load-bearing capacity of thick boronized layer is better than the thin layer [20]. Due to the absence of a separate FeB layer and the presence of thick boronized layer, fracturing and overall wear loss of the specimens are less severe in the present work. Wear loss of boronized specimens is minimum 8 and maximum 46 times better than the non-boronized specimens (Figure 5.12 (e)).

As mentioned above, tribo-oxidation and brittle fracture coincide during dry sliding wear of the boronized specimens. Coarse debris pulled off from the worn surface of the boronized specimen are shown in Figure 5.16(b). Typically, the size of wear-debris produced under the higher load is more massive because of their direct peeling from the surface [72]. However, such debris of oxides and boride are crushed during continuous sliding under load, leading to the formation of smaller and irregular shaped particles (Figure 5.16(b)). Regions of the wear debris show signs of brittle fracture (see the inserted micrograph in Figure 5.16(b)). The cross-sectional view of wear-track (Figure 5.18(e) and (f)) shows the accumulation of debris at sub-surface, where the brittle fracture has occurred, which can cause severe damage to the surface [14,23]. In the case of boronized specimens, brittleness of the tribo-oxide scale is higher due to the accumulation of fragmented borides (hardened debris) in the oxide scale.

5.4 Conclusions

1) Cross-section of the 34CrAlMo5-10 (EN41B) steel specimen boronized at 1050°C for 4 h showed the following two distinct regions in the boronized layer: (i) boronized region, which contains (Fe, M)₂B columns and boride-free matrix, and (ii) transitions zone containing fine boride particles at grain boundaries and in the regions between boride columns. The maximum length of the clusters of boride columns was as high as ~200 μ m. The matrix regions (surrounding the boride columns) had a different chemistry than the non-boronized core.

- 2) Nanoindentation study revealed the difference in the mechanical behaviour of boride, matrix, and core regions. Boride showed the maximum elastic recovery after the release of the load on the nanoindenter. Strain-rate sensitivity of different regions of the specimen cross-section varies between 0.005 and 0.011. The boride phase was relatively more sensitive to the strain-rate than matrix and core. The nanomechanical properties of the matrix are strikingly different than the core, suggesting a role of the elemental redistribution. According to VDI 3198 standard, cohesion strength of the boronized layer resembles HF3 quality, which was an acceptable level of interfacial adhesion.
- 3) X-ray photoelectron spectroscopic study revealed the presence of Feoxides, Cr₂O₃, and B₂O₃ in the oxide layer formed on the boronized specimens at room temperature. The oxidation resistance of the steel surface at room temperature was enhanced by the presence of higher proportion of mixed-boride (preferably, with higher Cr content) and the Cr₂O₃ enriched oxide layer.
- 4) Boronized specimens had superior oxidation resistance than the nonboronized specimens at 550 and 850°C. At 550°C, mass gained by the non-boronized specimen was almost twice that of the boronized specimen. The morphology of the oxidised surface was dependent on the temperature. Oxide scale consisting of various iron-borates like Fe₃BO₆, Fe₃BO₅, Fe₂BO₄, and FeBO₃ protects the boronized surface from oxidation at elevated temperatures. At 200°C, the weak oxidation resistance of the boronized specimen was caused by the macro-defects in the surface layer.
- 5) The maximum wear resistance of the boronized surface was ~46 times the wear resistance of non-boronized surface (studied using the same wear-parameters) under the dry sliding conditions. A steeper drop in the tribological advantage gained by the boronizing treatment was

observed with an increase in load, especially under higher sliding speed. Amongst the investigated wear-parameters, an improvement in the wear resistance under 60 N load was the lowest (i.e., about 8 times the wear resistance of non-boronized surface) for the boronized specimens. The CoF of boronized surface was higher than the non-boronized specimen under higher sliding-speed.

- 6) Oxidative wear was the resultant wear-phenomenon for the nonboronized specimens. The worn surfaces of non-boronized specimens showed the delamination, surface creasing, and grooves. However, the boronized specimens experience damage due to the surface oxidation, abrasion, fatigue, and brittle fracture during wear study. The Raman spectroscopy confirmed the presence of Fe₂O₃, Fe₃O₄, B₂O₃, and H₃BO₃ in the tribo-oxide scale formed on the worn surface of boronized specimens.
- Overall, the boronizing treatment was beneficial for EN41B steel to obtain the superior surface hardness (5–6 times the hardness of core), enhanced oxidation resistance, and high wear resistance.

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Wear Behaviour of Boronized and Duplex-Treated AISI 4140 Steel against DLC-Coated Boronized AISI 4140 Disc

Chapter 6

6.1 Introduction

Wear is the most common reason for the mechanical failure of the engineering components. It involves many complex surface interactions which could be mechanical as well as a chemical in nature. It is well fact that, wear and friction are interlinked phenomena. Although elimination of wear is a difficult task, it can be minimized using the surface modifications and coating technologies. These technologies are implemented and being researched for the applications in automotive, oil, gas, aerospace, and biomedical sectors [1-4].

Two basic types of coatings are widely used to control the wear and friction: hard coatings and soft coatings. Hard coatings include oxides, carbides, nitrides, borides, and carbon-based coatings (for example, diamond, low hydrogenated diamond-like carbon (DLC), etc.). Soft coatings include polymers, soft metals, halides, and sulphates of alkaline earth metals, etc. Soft coatings also include highly hydrogenated DLC and lamellar solids like graphite, MoS₂, and WS₂. Generally, a carbon-based coating helps to achieve the low friction [5-10]. In duplex surface-treatments, a surface modification technique is combined with the coatings to achieve the optimum tribological properties. The duplex treatments

improve the load-bearing capacity and wear resistance of the substrate, which prevents the surface from cracking and delamination [6,11,12].

Boronizing and DLC coatings techniques are gaining popularity in recent years [2,4,6,13-21] due to their potential for enhancing the wear and corrosion properties and hence, widening their industrial applications. Under a given condition, wear behavior can depend on the combination of surface engineering methods that are applied to the contacting surfaces. Current work deals with the wear behavior of various specimen conditions against the boronized plus DLC coated counter-surface under different loading conditions (Table 6.1). This study can be useful in the applications like a cup and cone bearings, ratchet and pawl, scissor assembly, etc., where the wear properties are important.

6.2 Experimental

Chemical composition of the AISI 4140 steel used in this study is as follows: 0.43 wt.% C, 0.81 wt.% Cr, 0.25 wt.% Mo, 0.57 wt.% Mn, 0.25 wt.% Si, 0.04 wt.% P, 0.038 wt.% S and Fe as balance. The following steelconditions were used for the investigation (designation of the specimens is mentioned in the brackets): hardened-tempered plus DLC-coated (HT-DLC), as-boronized (AB), boronized plus polished (B-P) and boronized plus DLC-coated (B-DLC). In case of DLC coating, CrN interlayer was used. In the subsequent text, 'DLC coating' term is used for the 'DLC with CrN interlayer.

Cylindrical specimens (10 mm (diameter) X 10 mm (length)) were used for the metallographic studies. Pins with 5 mm tip radius, 10 mm diameter and 25 mm length were prepared for the wear test. The disc of AISI 4140 steel with a diameter of 200 mm and thickness of 7 mm was used as the counter-surface in the wear test. In the subsequent text, 'specimen' word means the cylindrical specimen or pin or disc. HT specimens were prepared using the steel austenitized at 850 °C for 0.5 h (followed by water quenching) and tempered at 350 °C for 1 h (followed by air cooling). Before boronizing treatment, the specimens were ground on 800-grade emery paper followed by diamond polishing. Polished specimens were cleaned with a soap solution and acetone. Boronizing treatment was performed at 950 °C for 4 h in the preconditioned mild-steel container using the pack-method [14] (see also chapter-3). The container was air-cooled after boronizing. The surface roughness of the as-boronized specimens was $0.61 \pm 0.07 \ \mu m$ (R_a). Boronized specimens were diamond polished to the roughness of $0.14 \pm 0.03 \ \mu m$ (R_a) for subsequent DLC coating, and also, to make the B-P specimens. Plasma-assisted chemical vapor deposition (PACVD) method was used to deposit the hydrogenated DLC (a-C:H) coating with CrN interlayer on the boronized specimens. The total thickness of the coating was about 3-4 μm .

The standard metallographic procedure was adopted for the microstructural investigations using an optical microscope and scanning electron microscope (SEM). The coating thickness of the boronized specimens was measured at ten different locations using an optical microscope, and their arithmetic average is reported. The thickness of the DLC coating was measured using SEM. Compositional analysis of the boronized layer was done using electron probe microanalysis (EPMA). Smoothly polished surface (without etching) was used for the EPMA measurements using JEOL JXA-8530F instrument. Vickers microhardness tester was used for the hardness measurements.

Wear testing of the specimens was performed using the pin-on-disc method. ASTM G-99 standard was followed to carry out this test [22]. Table 6.1 shows the pin-on-disc test parameters. Two pins were tested for each specimen condition, and the arithmetic average of their results is reported. Significant wear of the pins and zero wear of the B-DLC disc were assumed in the wear test. The worn-out surface of the tested pins was investigated using the optical microscope, SEM and EDS (energy-dispersive spectroscopy). The wear volume loss, specific wear rate and the depth of wear-scar were calculated using the following equations [15]:

Wear volume loss
$$(mm^3) = \frac{\pi \times d^4}{64 \times R}$$
 (6.1)

 $Specific wear rate (mm³/Nm) = \frac{Wear volume loss}{Normal load \times Sliding distance}$ (6.2)

Depth of wear scar (mm) =
$$R - \sqrt{R^2 - (d/2)^2}$$
 (6.3)

where R is the radius of the pin (mm) and d is the diameter of wear-scar (mm).

Parameters	BoronizedplusDLC coated(B-DLC)	As-boronized (AB)		
Load (N)	10, 15	100, 150		
Velocity (m/s)	0.3	1		
Total distance (m)	500	1000		
Humidity (%)	45 ± 5			
Test pin diameter (mm)	10			
Temperature (°C)	26 ± 5			
Environment	Air			
Disc material	AISI 4140 steel			
Surface condition of disc	Boronized plus DLC (a-C:H) coated			
Disc surface roughness, R _a (µm)	0.14 ± 0.03			

Table 6.1: Pin-on-disc sliding wear test parameters.

6.3 Results and Discussion

6.3.1 Microstructural Analysis of Treated Specimens

The microstructure of hardened-tempered (HT) specimen shows the tempered martensite (Figure 6.1(a)). The hardness of the HT specimen is about 458 HV. Columnar morphology of Fe₂B is observed near the surface of the boronized specimen (Figure 6.1(b)). A separate layer of FeB is not visible in the micrograph. Average thickness of the boronized layer is 154 \pm 20 µm. The boronized layer shows the presence of crack-like openings and porosities. The density of these defects is nearer to the surface region. Small porosities are accumulated at the interface of Fe₂B columns to cause the crack-like openings. Brittle nature of the iron-borides could provide an easy opening/cracking of the boride-columns. Therefore, the generated gases and the oxygen present in the boronizing pack-mixture could be adsorbed at the interface of boride-columns (especially, near to the surface of the specimen) and causes the formation of defects in the boronized layer. Surface hardness of the boronized specimen is about 1400 HV_{0.1}. The hardness of the DLC coating is about 1500 HV_{0.1}.

Figure 6.2 shows the location of EPMA measurements and the corresponding elemental composition-depth profiles across the boronized layer. Boride regions have high boron content (indicated by A and C at the location of EPMA measurements). Some decrease in the boron content with the distance from the surface is observed in the boride regions (downward slope in the boron content is visible in the regions A and C). The boride regions contain about 6-8 wt.% B. At B and E locations, EPMA measurements are partially in the iron-boride as well as in the non-boronized region. Therefore, the boron content is somewhat lower at B and E than in the iron-boride regions. The Si content in region D is higher than the regions A and C. Slight increase in the Si content is also seen in the region B (where EPMA measurement is partially in the non-boronized region). These observations confirm the marginal absorption of Si in the

iron-boride, and Si is displaced towards the growing front of the iron-boride during boronizing. Such accumulated Si in front of the boronized layer can lead to the formation of transition-zone [14].



Figure 6.1: (a) Secondary electron (SE) micrograph of HT and (b) backscattered electron (BSE) micrograph of boronized (950°C, 4 h) AISI 4140 steel.

SEM micrographs in Figure 6.3 show of the cross-section of DLC coated boronized steel and the morphology of DLC coated surface. Micrograph of the cross-section at higher magnification (Figure 6.3(b)) shows the CrN interlayer and the top layer of the DLC coating. EDS analysis confirms the high percentage of Cr and N in the interlayer and high carbon content in the top layer. The total thickness of the coating is about 3-4 μ m (comprising of ~2 μ m CrN interlayer and 1-2 μ m DLC layer). Figure 6.3 (c) and (d) shows the surface morphology of the DLC coating, where protuberances of different sizes are seen. EDS analysis of these protuberances confirms the presence of high C, N, and Cr. High N and Cr indicates that these protuberances emerge from the CrN interlayer, and high C is due to the surrounding DLC coating.

Rockwell 'C' adhesion test (VDI 3198 standard) of the DLC coated boronized steel disc does not show the delamination of the coating around the indentation-marks (Figure 6.4). This result confirms a very good coating adhesion (HF1 scale).



Figure 6.2: (a) BSE micrograph of boronized (at 950°C for 4 h) AISI 4140 steel indicating the location of EPMA measurements, and corresponding (b) elemental composition-depth profiles.

6.3.2 Tribological Study

6.3.2.1 DLC Coated Pins Against Duplex Surface-treated AISI 4140 Steel Disc

Table 6.2 shows the tribology results of the B-P, B-DLC, and HT-DLC pins against the duplex surface-treated (B-DLC) AISI 4140 steel disc at 10 and 15 N normal loads, 0.3 m/s sliding velocity and 500 m sliding distance. B-P pins show the most inferior wear properties due to their lower surface hardness than the DLC coated counter disc. HT-DLC pins have the better wear properties than the B-P pins. However, B-DLC pins show the

best wear properties. At 10 N load, the specific wear rate of B-DLC pins is ~30 times lower than the B-P pins and ~4 times lower than the HT-DLC pins. Wear properties of the B-DLC, and HT-DLC pins are enhanced with increasing load.



Figure 6.3: SEM images of the (a) cross-section of B-DLC specimen, (b) magnified view of the cross-section of B-DLC specimen and EDS results corresponding to the locations marked as '1' and '2', and (c) and (d) surface morphology of the DLC coating and EDS results of the indicated protuberances.

The depth of wear-scar is linked with the volume loss of the pin due to the wear. The higher depth of the wear-scar indicates the higher volume loss. In case of the DLC coated pins, the depth of wear-scar is lower for the B-DLC pins than the HT-DLC pins, which is due to the higher hardness of the boronized surface than the HT surface. The higher hardness of the boronized layer offers the better support to the DLC coating. A small increase in the load (i.e., from 10 N to 15 N) further reduces the depth of wear-scar for the B-DLC and HT-DLC pins. The depth of wear-scar is maximum in the absence of DLC coating on the pins (B-P pins), which indicates the important role of DLC coating (with CrN interlayer) in reducing the depth of wear-scar. DLC coated pins show the considerably lower COF than B-P pins. Within the DLC coated pins, COF is lower for B-DLC pins than HT-DLC pins due to the lubricating property of DLC from both contacting surfaces (i.e., pin and disc). The presence of protuberances from the CrN interlayer (Figure 6.3(c) and (d)) along with the surrounding DLC could also be responsible for the enhanced lubrication and lower COF. The lubrication is effective if the stronger surface supports the DLC coating.



Figure 6.4: (a) Optical image of VDI 3198 indention taken on the DLCcoated boronized AISI 4140 disc. (b) Magnified view of the region highlighted by a rectangle in (a).

Figure 6.5(a)-(e) shows the optical images of the worn-out surface of the pins. In case of the DLC coated pins, EDS analysis of the worn-out area shows the presence of high carbon, which is the indication of carbonaceous transfer layer on the surface (Figure 6.5(f)). The optical images clearly show the presence of transfer layer around the worn surface of the DLC coated pins. The absence of boron in the EDS results confirms that the DLC coating is not removed completely on the worn-out surface, and the underneath boronized layer is not exposed to the surface. The depth of wear-scar for the DLC coated pins is less than the thickness of the DLC coating (Table 6.2). Therefore, the presence of high carbon and the absence of boron on the worn-out surface is in good agreement with the small depth of wear-scar.

Table 6.2: Wear results of the various pins against the boronized plus DLC coated AISI 4140 steel disc at 10 and 15 N normal loads, 0.3 m/s sliding velocity and 500 m sliding distance.

Pin condition	Disc condition	Load (N)	Depth of wear-scar (µm)	Specific wear rate (×10 ⁻⁸ mm ³ N ⁻¹ m ⁻¹)	COF
B-P		10	5.95	11.12	0.13
B-DLC		10	1.09	0.37	0.09
HT-DLC	B-DLC	10	2.28	1.64	0.1
B-DLC		15	1.01	0.21	0.08
HT-DLC	-	15	1.47	0.45	0.1



Figure 6.5: Optical images of the worn-out surface of (a) B-P pin at 10 N, (b) B-DLC pin at 10 N, (c) B-DLC pin at 15 N, (d), HT-DLC pin at 10 N, (e) HT-DLC pin at 15 N, and (f) EDS results of the worn-out region marked on the SEM insert for B-DLC pin at 15 N.

6.3.2.2 Non-coated Boronized Pins Against the Duplex Surface-treated AISI 4140 Steel Disc Using Aggravated Conditions

To understand the capability of boronized surface in wear behavior against the duplex surface-treated (B-DLC) steel disc, testing was done in the aggravated wear-conditions, where the unpolished boronized pins (i.e., as-boronized, AB, pins) were tested at higher loads (100 and 150 N), accelerated sliding velocity (1 m/s) and increased sliding distance (1000 m). Figure 6.6 shows the wear-results of these pins (wear-results of the B-P pins mentioned in Table 6.2 are also shown in this figure for comparison). The depth of wear-scar at 100 and 150 N for the AB pins is higher than the B-P pins at 10 N. This indicates the higher volume loss of the AB pins due to the aggravated conditions and somewhat lower hardness of the boronized layer (~1400 HV_{0.1}) than the DLC coating (> 1500 HV_{0.1}). However, the 'specific wear rates' of the AB pins at higher loads are significantly lower than the B-P pins. It should be noted that an increase (or decrease) in the depth of wear-scar not necessarily increase (or decrease) the specific wear rate because latter considers not only the volume loss (due to the wear) but also the normal load and sliding distance. Therefore, the volume loss for AB pins is quite low considering the higher load and sliding distance. In fact, the specific wear rate and the depth of wear-scar are decreased further with an increase in the load from 100 to 150 N. Under these loads, COF is higher for the initial sliding distance because of the non-polished condition of the pins. However, it subsequently decreases with further distance. Additionally, the COF is decreased with increasing load.

The improvement in the wear behavior at aggravated wearconditions is linked with the duplex surface-treatments of the steel disc. Here, DLC coating on the disc helps in reducing the friction, and the presence of boronized layer on the disc (beneath the DLC coating) and pin improve the load-bearing capacity. Higher loads and higher velocity promote the graphitization of the DLC coating and the formation of the transfer layer, which subsequently reduces the COF and specific wear rate [23,24]. Figure 6.7(a) and (b) are the optical images of the worn-out surface of the as-boronized pins. The worn-out surfaces show the presence of a transfer layer, which comes from the counter surface of the DLC coated boronized disc. Figure 6.7(c) shows the SEM and EDS results of the wornout surface. EDS results show the presence of high carbon and boron on the surface. The presence of high carbon confirms the transfer of a carbonaceous layer from the DLC coating on the disc. An indication of the high boron content is due to the presence of the boronized layer on the pin. In Figure 6.7(d), SEM micrograph of the worn-out surface of the pin (tested

at 150 N) shows the shallow grooves, which are formed during sliding of the pin against the disc.



Figure 6.6: (a) Specific wear rate, (b) depth of wear scar and (b) COF versus sliding distance for the AB pins against the DLC-coated boronized AISI 4140 steel at 100 and 150 N. The results of B-P pins (Table 6.2) are also shown in (a) and (b).

The observed cavity on the surface is originally present in the boronized layer (see Figures 6.1(b) and 2(a)). Brighter patches in the micrograph are the non-boronized or partially-boronized regions between the boride columns. The absence of the cracks on the worn-out surface confirms the good load bearing capacity of the boronized layer.



Figure 6.7: Optical images of the worn-out surface of AB pins (a) at 100 N and (b) 150 N. (c) EDS results of the worn-out region marked on the SEM insert for the AB pin at 150 N. (d) Magnified SEM image of the worn-out region of AB pin at 150 N.

6.3.2.3 Mechanism

Boronized layer on the steel surface helps in enhancing the load bearing capability due to the high hardness of iron-borides. The hard layer avoids the formation of surface cracks and delamination during the relative motion of the contacting surfaces under load. Generally, the high hardness reduces the wear loss [14]. COF between the contacting surfaces is also an important factor in controlling the wear. DLC coating on the hard surface gives the advantage in improving the overall wear behavior. Carbonaceous transfer layer from the DLC coating reduces the friction [2,6]. Reduction in the COF depends on the roughness, hardness, and adhesive strength of the DLC coating. When a high load is used, the contact stresses are concentrated in the small area of the coating, which originate high shear stresses and more wear loss [2]. Wear performance of the steel depends on the combination of surface-conditions of both contacting surfaces (HT-DLC, AB, B-P, B-DLC). The hard surface beneath the DLC coatings is useful in improving the wear properties. Two approaches are used in the current work to obtain the hard surface beneath the DLC coating – (i) hardening-tempering and (ii) boronizing. The approach that gives the higher hardness of the underlying surface imparts the better wear properties. The lubrication effect of the DLC coating is effective if the stronger surface supports it. The hard boronized layer not only supports DLC coating but also promotes the transfer of carbonaceous layer to the counter surface, causing only DLC layer to play a part in the contact mechanism and helps to reduce the friction. Therefore, the boronized surface outperforms the hardened-tempered surface (B-DLC pins show the better wear properties than the HT-DLC pins).

In case of the boronized surface against the DLC coated countersurface, lubricious layer transfers from the disc to the boronized surface of the pin. However, this transfer layer is not sufficient to offer the best lubricity and therefore, the higher hardness of the one contacting surface (i.e., DLC coated disc) causes the wear of another surface (i.e., boronized surface) and increase in the depth of wear-scar (B-P pins versus B-DLC pins). The higher loads and higher velocity promote the graphitization of the DLC coating, and hence, COF and the specific wear rate reduces considerably (AB pins versus B-P pins). If the DLC coating is applied on both contacting surfaces, where the underlying boronized layer supports the coating, wear properties improve enormously due to the interaction of the lubricious transfer layer from both surfaces. Therefore, the wear behavior of B-DLC pins is significantly better than the B-P, and AB pins against the B-DLC coated disc.

6.4 Conclusions

- Wear behavior of the AISI 4140 steel specimens with four different surface conditions (HT-DLC, AB, B-P, B-DLC) were tested against the DLC coated boronized disc of AISI 4140 steel. DLC coating on both contacting surfaces was very effective in enhancing the wear resistance. Higher hardness of the underlying surface imparts better wear properties. The underlying boronized surface outperformed the hardened-tempered surface.
- 2) Best wear properties were observed for the B-DLC pins (the lowest specific wear rate of $0.21 \times 10^{-8} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$). At 10 N load, the specific wear rate of B-DLC pins is ~30 times lower than the B-P pins and ~4 times lower than the HT-DLC pins. The coefficient of friction (COF) of B-DLC pins was in the range of 0.08-0.09.
- Specific wear rate, depth of wear-scar, and COF of the DLC coated pins was found to be decreased with increase in the load.
- 4) Improved performance of the as-boronized (AB) surface against the B-DLC surface in aggravated conditions was observed. Specific wear rate and COF of AB pins were substantially lower at 100 and 150 N loads than the B-P pins at 10 N. COF of AB pins was in the range of 0.07-0.09. However, the COF of B-P pins was about 0.13.
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The current thesis was focused on understanding the packboronizing behaviour of low alloy steels (34CrAlMo5-10/EN41B and AISI 4140). In this study, the effect of alloying elements on the growth behaviour of iron-boride and the corresponding migration behaviour of the alloying elements were investigated. The occurrence of events during boronizing of low alloy steels was systematically proposed in this work. The boride layer's performance was evaluated in terms of its response to oxidation, nanoindentation, and wear. Effect of DLC/CrN multilayer coating on tribological behaviour of the boronized steel was also studied.

7.1 Summary

7.1.1 Microstructure Evolution and Migration Behaviour of Alloying Elements

Low alloy steel specimens boronized at various processing temperatures (850, 950, and 1050°C) and durations (2, 4, and 6 h) were investigated using optical microscopy, SEM, EBSD, XRD, EPMA, GDOES, and microhardness. The boronized layer showed the presence of three zones: (i) boronized region containing finer grains and columnar geometry of (Fe, M)₂B (where M= Cr, Mn, Mo, and Ni), (ii) transition zone comprising of tiny boride particles in the non-transformed areas, and (iii) non-boronized core. The boride grains were oriented primarily around $\{100\}$ and $\{110\}$, as confirmed by EBSD results. Strong texture of boride grains was observed in [001] crystallographic direction. Maximum hardness of about 1050, 1500, and 1800 HV_{0.1} were detected in the near-surface

region at 850, 950, and 1050°C, respectively. The concentrations of the alloying elements in (Fe, M)₂B increased from surface to the core of the specimen. The slope variation pattern of boron concentration–depth profile (obtained using GDOES) was linked to the boride morphology and process temperature. Pack-boriding of steel led to the development of a systematic trend in slope variation of the alloying elements' overall concentration– depth profiles. The composition and morphology of boride affected the boride-forming alloying elements' slope variation trend. However, for Al and Si, the slope variation trend was connected to the boride morphology and the composition of the matrix. The chemistry of the matrix was strongly dependent on the migration kinetics of the alloying elements during the boride growth.



Figure 7.1: Summary of microstructure evolution and migration behaviour of alloying elements in the boronized 34CrAlMo5-10/EN41B steel.

The migration kinetics of Cr, Mn, Mo, and C was almost equivalent to the rate of boride growth. However, Ni, Al, and Si were migrated at a slower rate. Si showed the lowest migration kinetics amongst the alloying elements in the steel. The concentrations of the alloying elements having higher migration kinetics remained constant in the matrix during the boride growth. Finally, the mechanism of microstructure development during boronizing was proposed. The summary of these results is presented in Figure 7.1.

7.1.2 The Response of Boronized Steel to Nanoindentation, Oxidation, and Wear

The saw-tooth morphology of boride and the migration of alloying elements (during the development of a boronized layer) in low alloy steels caused a variation in composition and fraction of phases from the surface to core. Therefore, this work also focused on the properties of boronized (at 1050°C for 4 h) and non-boronized low-alloy steel (34CrAlMo5-10) to understand the role of microstructural variations in the boronized layer. Specimens were characterised using microscopy, various spectroscopic techniques, nanoindentation, surface profilometer, and tribometer. Nanoindentation study revealed the difference in the mechanical behaviour of boride, matrix, and core regions. Strain-rate sensitivity of specimen cross-section's different regions varied between 0.005 and 0.011. The boride phase was found to be more sensitive to the strain-rate than the matrix and core. The nanomechanical properties of the matrix were strikingly different from the core, suggesting a role of the elemental redistribution. According to VDI 3198 standard, the cohesion strength of the boronized layer resembled HF3 quality, which was an acceptable level of interfacial adhesion. The oxidation resistance of the steel surface at room temperature was enhanced by the presence of a higher proportion of mixed-boride (preferably, with higher Cr content) and the Cr_2O_3 enriched oxide layer. At 550 and 850°C, boronized specimens revealed higher oxidation resistance than the non-boronized specimens, where the layer of iron-borates (like Fe₃BO₆, Fe₃BO₅, Fe₂BO₄, and FeBO₃) protected the surface. At 200°C, the

weak oxidation resistance of the boronized specimen was caused by the macro-defects in the surface layer. Amongst the investigated wear parameters, the maximum and minimum wear-resistance of the boronized surface was about 46 and 8 times the wear resistance of the non-boronized surface under the dry sliding conditions, respectively. A steeper drop in the tribological advantage gained by the boronizing treatment was perceived with the increase in load, especially under higher sliding speed. The coefficient of friction (CoF) of the boronized surface was higher than the non-boronized specimen under a higher sliding-speed. The summary of these results is presented in Figure 7.2.



Figure 7.2: Summary of the response of boronized 34CrAlMo5-10/EN41B steel to nanoindentation, oxidation, and wear.

7.1.3 The Role of DLC/CrN Coating on Tribological Behaviour of Boronized Steel

The average coefficient of friction (CoF) of the boronized surface was not impressive (0.5-0.7) under dry sliding conditions. Therefore, the tribological performance of pack-boronized low alloy steel in conjunction with DLC/CrN coating, when acting combinedly as a multilayer architecture, was investigated in the final stage of this thesis. Wear behaviour of the low alloy steel (AISI 4140) specimens with various surface conditions was tested against the DLC/CrN coated boronized disc of AISI 4140 steel. Specific wear rate and CoF of the as-boronized (AB) pins at 100 and 150 N loads were substantially lower than the boronized–polished (B-P) pins. CoF of AB pins was in the range of 0.07–0.09. However, the CoF of B-P pin was about 0.13. In the case of the DLC/CrN coated pins, the underlying boronized surface outperformed the hardened–tempered surface. The wear properties of the coated pins were improved with an increase in the load. DLC/CrN coating on both contacting surfaces showed the lowest specific wear rate of about $0.21 \times 10-8 \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, which was about 30 times lower than the B-P pins, and CoF was in the range of 0.08–0.09. The summary of these results is presented in Figure 7.3.



Figure 7.3: Summary of wear behaviour of boronized and duplex-treated AISI 4140 steel against DLC/CrN coated boronized AISI 4140 disc.

7.1.4 Overall Summary

The boronizing treatment was beneficial for low alloy steels to obtain superior surface hardness (5–6 times the hardness of core), enhanced oxidation resistance, and high wear resistance. The set of results presented in the current study established a detailed understanding of developing a boronized layer containing the boride region and transition zone. The sawtooth morphology of boride and the migration of alloying elements (during the development of a boronized layer) in low alloy steels caused a variation in composition and fraction of phases from the surface to core. Mechanical and oxidation response of steels was improved after boronizing treatment. This work successfully attempted the establishment of a microstructureproperty correlation of the boronized steels. Duplex surface treatment like DLC/CrN coating in conjunction with boronizing gave additional characteristic to the system in response to different tribological conditions.

7.2 Future Scope

The current study was entirely focused on analysing the growth behaviour and performance of iron-boride system produced on low alloy steel components. A similar study is possible with high alloy steels (like stainless steel). In addition to this, the conventional route of boronizing can be replaced by one of the emerging and alternate routes, for example, plasma, laser, TIG, etc., surface processing. Since these operations utilize high temperature and process is possible to carry out under the inert atmospheric condition, these routes can be advantageous concerning low process time and better surface quality (due to an oxygen-free atmosphere).

Since boronizing is a promising treatment for agricultural components, the actual components can be subjected to field trials. This approach will be beneficial in enhancing the confidence of industries in this technology, especially for Indian market.

DLC coating is used in the present study to enhance the performance of iron-boride. Similarly, other types of coatings (like polymers) can be explored in terms of their effectiveness in enhancing the tribological properties of the boronized surface.