

IMPACT OF DIFFUSION COATING AND LASER TREATMENT ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF STEEL

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Abstract

Surface modification of steel is a crucial process in various industries, including automotive, construction, and aerospace. This process involves altering the outer layer of steel to enhance its properties such as corrosion resistance, wear resistance, and hardness. Different methods of surface modification can be employed, such as electrochemical processes, materials processing advancements, and the creation of special physical and chemical properties. This review paper provides a comprehensive analysis of surface modification techniques for steel, focusing on diffusion methods (nitriding, boronizing, and carburizing) and laser treatments (laser surface hardening, laser surface melting, and laser cladding). These methods enhance the microstructure and mechanical properties of steel components, offering improved surface hardness, wear resistance, and fatigue strength. Diffusion techniques alter the surface layer through the introduction of specific elements, creating hard, wear-resistant cases. Laser treatments provide precise, localized modifications with minimal distortion and a variety of coating possibilities. The review explores the process procedure, advantages, and limitations of each method, as well as their influence on the microstructure and mechanical processes. By evaluating these techniques, this paper aims to guide the selection of appropriate surface modification methods for optimizing steel performance and extending the lifespan of components in demanding environments.

Keywords: *Surface modification, steel, microstructure, diffusion coatings, laser treatment.*

Introduction

Steel is primarily composed of iron (Fe) alloyed with carbon (C) and other elements in varying proportions. The composition of steel can vary widely depending on its intended application, with additional alloying elements added to impart specific properties such as strength, hardness, corrosion resistance, and more. Its utilization spans from minor tools, kitchenware, and fasteners to substantial machinery such as excavators, military gear, structural elements, and automotive components. The composition of steel determines its crystal structure, microstructure and mechanical properties. Iron is the primary component of steel, providing its structural integrity and strength. The microstructure of steel is predominantly ferritic (α -iron) at lower temperatures, characterized by a body-centered cubic (BCC) crystal structure. As the temperature increases, iron undergoes phase transformations, transitioning to austenitic (γ -iron) and then to other phases depending on alloying elements and cooling rates. Carbon is a crucial alloying element in steel that significantly influences its microstructure and properties. At low carbon concentrations, steel is softer and more ductile, with a ferritic or pearlitic microstructure. As the carbon content increases, the steel becomes harder and stronger due to the formation of additional phases such as martensite, bainite, or tempered martensite. These phases contribute to various mechanical

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properties, including hardness, tensile strength, and toughness [1]. Beyond iron and carbon, steel often contains alloying elements such as manganese (Mn), chromium (Cr), nickel (Ni), molybdenum (Mo), vanadium (V), silicon (Si), and others. These alloying elements play essential roles in refining the microstructure and enhancing specific properties of steel. Manganese improves hardenability and strength and facilitates the formation of fine-grained structures. Chromium enhances corrosion resistance, hardness, and wear resistance. Nickel increases toughness, strength, and resistance to corrosion and high temperatures. Molybdenum improves hardenability, strength, and creep resistance. Vanadium refines grain size, enhances strength, and improves hardenability. Silicon promotes deoxidation and improves strength and electrical conductivity [2-7].

Steel, renowned for its versatility and ubiquity across industries, owes much of its functional diversity to the intricate relationship between its microstructure and mechanical properties. Over the years, advancements in surface modification techniques have emerged as pivotal strategies for tailoring the performance characteristics of steel components. This intersection of surface modification and steel microstructure has garnered significant attention due to its profound implications on material behavior, durability, and functionality. Understanding how surface modifications influence the microstructural evolution and mechanical response of steel is paramount for optimizing the performance of engineered components across a spectrum of applications, spanning from automotive and aerospace to construction and energy sectors. This exploration delves into the multifaceted effects of surface modification processes on the microstructure and mechanical properties of steel, shedding light on the intricate interplay between surface engineering and material performance in the realm of steel metallurgy.

Surface modification, in a broader context, encompasses all forms of surface treatments and coatings that lead to alterations in the composition and microstructure of the surface layer. These techniques play a crucial role in enhancing the mechanical properties and performance of steel components across various industrial applications. The demands for improved wear resistance, fatigue life, and corrosion resistance in steel have driven the development of advanced surface treatment methods. These methods aim to alter the microstructure and composition of the steel surface, creating layers with superior hardness and strength while preserving the desirable properties of the underlying material.

In this review paper, we focus on two broad categories of surface modification techniques: diffusion coating methods and laser treatments. The diffusion coating methods discussed include nitriding, boronizing, and carburizing, which involve introducing specific elements into the steel surface to achieve desired properties. Nitriding is a surface-hardening process used to improve the wear resistance, fatigue strength, and corrosion resistance of ferrous materials, particularly steels. The process involves the diffusion of nitrogen into the surface of the metal, typically at elevated temperatures in a nitrogen-rich atmosphere. Boronizing, also known as boriding involves the diffusion of boron atoms into the surface of the material to form hard boride layers. It is a widely used surface treatment method in industries such as automotive, aerospace, and tool manufacturing to improve the performance and longevity of metal components subjected to high wear and corrosion environments. Carburizing involves increasing the carbon content of the surface layer to improve hardness and strength [8-10].

On the other hand, laser treatments offer precise and localized surface modifications through high-energy laser beams. This review explores laser surface hardening, laser surface melting, and laser cladding, each providing unique advantages in modifying the steel surface. Laser surface hardening enhances the hardness and wear resistance of the treated areas, while laser surface melting refines the microstructure and reduces defects. Laser cladding allows for the deposition of high-performance materials onto the steel surface for improved properties [11, 12].

This review aims to evaluate six surface modification processes and their impact on the microstructure and mechanical properties of steel. The microstructure of steel is intricately linked to its composition, with alloying elements influencing phase transformations, grain size,

distribution of phases, and mechanical properties. Through careful control of composition and processing parameters, engineers can tailor the microstructure of steel to meet specific performance requirements for a wide range of applications, from structural components to automotive parts, tools, and machinery.

This review aims to provide a comprehensive evaluation of these surface modification methods and their impact on the microstructure and mechanical properties of steel. By analyzing the advantages, limitations, and applications of each technique, this paper seeks to offer insights into the most effective methods for specific industrial needs and guide future research and development in the field of steel surface modification.

Diffusion Coating Techniques

Nitriding

Nitriding is a heat-based chemical treatment whereby nitrogen, either in its atomic or ionic state, permeates the surface of a metal through diffusion [13]. Specifically with steels, this process relies on the ability of nitrogen to dissolve into iron. This process is widely used in various industries such as automotive, aerospace, and tooling due to its ability to enhance wear resistance, fatigue strength, and corrosion resistance of the treated components.

Medium-carbon steels are commonly employed for nitriding, containing robust nitride-forming components like aluminium, chromium, vanadium, tungsten, and molybdenum. These additives play a crucial role in nitriding as they create nitrides that remain stable under nitriding temperatures. Conversely, alloying elements like nickel, silicon, and manganese have less significance in determining the properties of the nitrided diffusion coatings. While alloy steels can indeed form iron nitrides when exposed to nascent nitrogen, the quality of the resulting nitrided layer is superior in steels containing one or more of the primary nitride-forming alloying elements. Gas, plasma and salt bath nitriding are the main methods for obtaining of nitrided diffusion coatings on steels with widely industrial application. Gas nitriding is the most common method, where the metal is heated in an atmosphere of ammonia or other nitrogen-rich gases [14]. Gas nitriding allows for precise control over the nitriding process parameters. In plasma nitriding, the metal component is placed in a vacuum chamber where a high-voltage electrical discharge is used to ionize the nitrogen gas, creating a plasma [15]. The ionized nitrogen atoms then bombard the surface of the metal, facilitating nitriding. Plasma nitriding offers faster processing times and can achieve greater depths of nitriding compared to gas nitriding. The salt bath method involves immersing the metal component in a bath of molten salts containing nitrogen-rich compounds [16]. The temperature and composition of the salt bath are carefully controlled to facilitate the nitriding process.

Nitriding processing procedure

Before nitriding, the metal surface needs to be cleaned thoroughly to remove any contaminants such as oil, grease, or scale. This ensures proper adhesion of the nitride layer. Then the metal component is placed in a sealed furnace or chamber that's filled with an ammonia-rich atmosphere or a nitrogen-containing gas. The temperature typically ranges from 450°C to 600°C for period of 1 to 100 hours depending on the material and the desired properties (such as the depth and the thickness of the layer). At the elevated temperature, nitrogen atoms diffuse into the surface of the metal and form nitrides with the base material. After the desired nitriding time, the metal component is cooled slowly to room temperature to relieve any stresses that may have built up during the process. This can be done either by quenching in a controlled environment or by allowing the part to cool naturally in the furnace [17].

Effects of nitriding on the microstructure and mechanical properties

The microstructure of nitrided steel depends on the specific nitriding process employed, as well as the composition of the steel itself. In gas nitriding, steel is heated in an atmosphere of

ammonia gas at elevated temperatures (typically between 500°C and 600°C). During this process, nitrogen diffuses into the surface of the steel forming iron nitrides, primarily gamma prime (γ' -Fe₄N) phase, some epsilon (ϵ -Fe_{2.3}N) phase, or a two phase mixture $\gamma'+\epsilon$. The microstructure typically consists of a compound layer (white layer) and a diffusion layer beneath it. The compound layer mainly comprises iron nitrides, while the diffusion layer contains nitrogen-rich austenite or martensite, depending on the steel composition and process parameters. Fig. 1 shows the typical structure of nitrided low alloy steel [18].

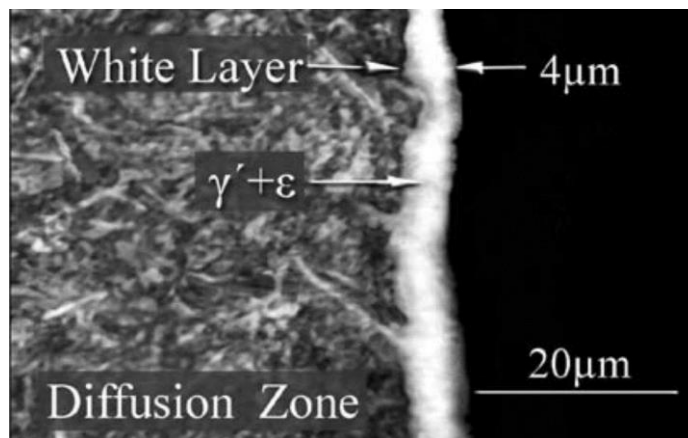


Fig. 1. Microstructure of nitrided 30CrNiMo8 low-alloy steel [18]

In plasma nitriding, the steel is exposed to a glow discharge plasma at lower pressures, typically around 400-600°C. This process provides greater control over the nitriding parameters and can produce a more homogeneous and controlled nitrided layer. The resulting microstructure is similar to gas nitriding but may exhibit finer precipitates due to the more controlled process conditions.

The formation of γ' and ϵ phases strongly depends on the processing parameters. In [18,19], various types of steels underwent nitriding, revealing a dual phase microstructure comprising γ' -Fe₄N and ϵ -Fe_{2.3}N phases. However, the intensity of these phases varied with changes in nitriding temperatures. In [18], the intensity of the ϵ -Fe_{2.3}N phase increased as the temperature rose. Conversely, in [19], the ϵ -Fe_{2.3}N phase emerged at lower temperatures (400-500°C), while the γ' -Fe₄N phase predominated at higher temperatures around 560°C. In some cases, nitriding at much lower temperatures or with lower nitrogen potential led to the formation of the α -FeN phase. In [20], the intensity of the α -Fe phase was more pronounced at lower nitriding temperatures (350°C). In [21], varying the nitrogen potential resulted in the formation of the α -Fe phase at a lower nitrogen potential.

The type of steel can also yield different microstructures during nitriding. Stainless steel leads to the formation of the expanded austenite phase (also known as the S-phase) and the CrN phase. In [22], the S-phase predominated at lower temperatures and weakened with increasing temperatures. At higher temperatures ($\geq 460^\circ\text{C}$), a single CrN phase was observed. Moreover, processing parameters also influence the mechanical properties of the nitrided steel, including hardness, corrosion, and wear resistance. Iron nitrides corrode more slowly than iron, and the formation of a "white layer" on the steel surface significantly enhances corrosion and wear resistance. Microhardness decreases with increasing temperature [18,19]. Additionally, the best wear resistance was demonstrated in the presence of the ϵ -Fe_{2.3}N phase or a combination of γ' -Fe₄N and ϵ -Fe_{2.3}N phases. Enhancing nitrogen diffusion on the steel surface during nitriding can be achieved by pre-treating the steel through annealing, quenching, or tempering, or by utilizing

ultrasonic cold forging technology [21, 23]. Pre-treated steel samples exhibited improved hardness and wear resistance after nitriding compared to untreated samples. Furthermore, the S-phase provided superior wear resistance compared to the CrN phase [24]. Despite most researchers varying the nitriding temperature, Terres et al. [25] varied the duration of the process from 12 h to 48 h and found that the maximum hardness and highest wear resistance were achieved at 24 h.

Advantages and limitations

Advantages:

1. Improved Surface Hardness: Nitriding creates a hard, wear-resistant surface layer, typically reaching hardness levels of up to 1200 HV (Vickers hardness).
2. Low Distortion: Nitriding is carried out at relatively low temperatures (typically between 500°C and 600°C), which minimizes thermal distortion of the treated components.
3. Corrosion Resistance: The process can improve corrosion resistance by forming a passivating layer on the treated surface, particularly in the case of gas nitriding.
4. Fatigue Strength: Nitriding can enhance the fatigue strength of the treated components due to the compressive residual stresses introduced during the process.
5. Controlled Depth: The depth of the nitrided layer can be controlled precisely based on the treatment duration and temperature.
6. Compatibility with Finished Parts: Nitriding can be applied to finished parts without significant changes to dimensions, making it suitable for components that require precise tolerances.

Limitations:

1. Long Process Time: Nitriding can take a relatively long time (from several hours to days) to achieve the desired layer depth and hardness.
2. Limited Material Compatibility: Nitriding is most effective on certain types of steels and alloys. Other materials may not respond as well to the process.
3. Expensive Equipment: The equipment required for nitriding, particularly plasma and ion nitriding, can be expensive and requires specialized maintenance.
4. Environmental Concerns: Some nitriding processes (e.g., gas nitriding) may involve the use of toxic gases, which require proper handling and disposal.

Boronizing

Boronizing is a thermochemical treatment that involves the diffusion of boron into the surface layer of steel, forming hard boride compounds [26]. Boronizing is typically used in applications where the steel needs to withstand high wear, abrasion, and corrosion, such as in cutting tools, automotive components, and industrial machinery parts. Boriding can be applied to a wide range of ferrous materials including plain carbon steels, low-alloy steels, tool steels, stainless steels, cast irons, and sintered steels. There exist various methods for creating boride diffusion coatings on steel surfaces. Thermochemical boronizing techniques encompass several approaches:

- Pack boriding
- Paste boriding
- Liquid boriding
- Gas boriding
- Plasma boriding
- Fluidized bed boriding

However, only pack and paste boriding have achieved commercial success. Gas and liquid boriding face limited application due to environmental concerns. Pack boriding, the most prevalent method, involves encasing steel parts in a mixture of boriding powder comprising ferroboration, amorphous boron or B₄C, fluxes, and activators (NaBF₄, KBF₄, Na₂B₄O₇). Heating occurs in a heat-resistant steel container at temperatures ranging from 900 to 1050 °C for one to twelve hours,

depending on the desired layer thickness. Typically, case depths range from 0.05 to 0.25 mm for carbon and low-alloy steels, and from 0.025 to 0.080 mm for high-alloy steels [27].

Paste boriding presents an appealing alternative due to lower costs and reduced complexity compared to pack boriding. It is typically executed using a paste containing B_4C as a boriding agent, Na_3AlF_4 as an activator, fluxes, and a binding agent. Process temperatures range from 800 to 1000 °C, with heating primarily conducted via induction or resistance methods. A layer exceeding 50 μm in thickness can be achieved by heating to 1000 °C for 20 minutes [28].

Gas and plasma boriding involve the use of toxic mixtures such as $B_2C_6-H_2$ or BCl_2-H_2 , with associated challenges including explosiveness and limited commercial acceptance. Plasma boriding, despite offering advantages such as lower process temperatures around 650 °C and reduced duration, has not gained widespread adoption. Fluidized bed boriding represents a recent innovation in boriding technology. Conducted in a specialized retort furnace, it utilizes a bed material comprising coarse silicon carbide particles, a specific boride powder, and an oxygen-free gas atmosphere typically composed of a nitrogen-hydrogen mixture. This process offers several advantages, including adaptability to continuous production and reduced operating costs attributed to shorter processing times and lower energy consumption for mass production of boronized components [29].

Boronizing process

Similarly to nitriding, the steel surface needs to be thoroughly cleaned to remove any contaminants such as oils, grease, rust, or scale before boronizing. This can be achieved through processes like degreasing, shot blasting, or pickling. The steel is then placed in a boronizing medium, which typically consists of a powder mixture containing boron compounds such as boron carbide (B_4C) or elemental boron. The boronizing medium may also contain activators or fluxes to facilitate the diffusion of boron into the steel surface. The steel is heated to a temperature typically between 800°C to 1100°C in a controlled atmosphere or vacuum furnace. The exact temperature and duration of heating depend on factors such as the steel composition, desired depth of boron diffusion, and the specific boronizing process used. At the elevated temperatures, boron atoms from the boronizing medium diffuse into the surface layer of the steel. The diffusion process forms hard boride compounds, primarily iron borides (FeB and Fe_2B), within the surface layer. After the boronizing process is completed, the steel is allowed to cool slowly to room temperature. Rapid cooling can lead to thermal stresses and cracking in the boronized layer. Depending on the specific application requirements, the boronized steel may undergo additional post-treatment processes such as quenching, tempering, or surface finishing to further enhance its mechanical properties and surface characteristics.

Effects of boronizing on microstructure and mechanical properties

When steel is subjected to boronizing, boron atoms diffuse into the surface layer of the steel, forming hard boride compounds. Boronizing forms a thin layer of borides on the surface of the steel. These boride layers typically consist of compounds such as FeB , Fe_2B , or other boride phases depending on the specific boriding process parameters. Fig. 2 shows a typical SEM image of borided steel [30]. This layer can exist in either a singular or dual-phase form, composed of specific borides. In a singular phase, it primarily consists of Fe_2B , whereas in a dual-phase, it comprises an outer layer of FeB and an inner layer of Fe_2B . FeB , being brittle and harder, forms a surface layer under significant tensile stress and exhibits a higher coefficient of thermal expansion. Conversely, Fe_2B is preferred due to its reduced brittleness and ability to form a surface layer under substantial compressive stress, which is desirable for high-hardness, low-ductility applications. While trace amounts of FeB are typically found in most boride layers, they are not problematic unless present continuously. To mitigate continuous FeB layers, diffusion annealing after boride formation can be employed. Boronizing can lead to changes in the microstructure of the steel substrate beneath the boride layer. Depending on the boriding process

parameters and the composition of the steel, these changes may include alterations in grain size, phase transformations, and the formation of diffusion zones. Boride layers are significantly harder than the base material, leading to increased surface hardness of the steel. This enhanced hardness improves the wear resistance of the steel, making it suitable for applications involving abrasive wear. Additionally, the hard boride layers formed during boronizing act as a barrier against wear, reducing material loss due to friction and abrasion. This property is particularly beneficial in applications where the steel is subjected to high levels of wear, such as cutting tools, gears, and bearings.

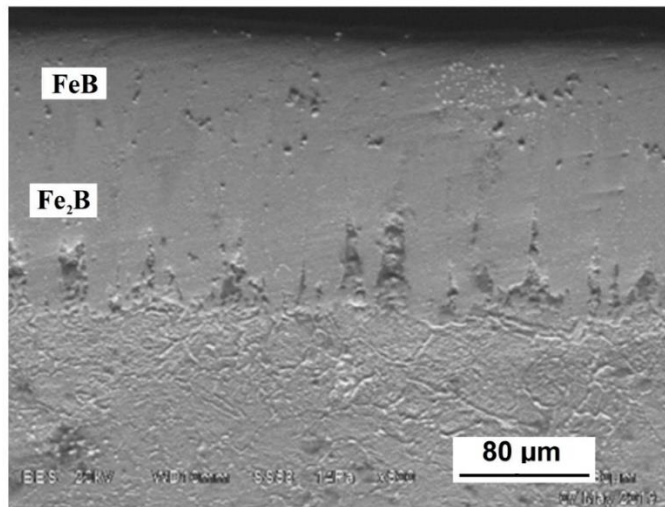


Fig. 2. SEM image of borided steel H21 [30]

During boriding, in addition to the FeB and Fe₂B boride phases, various other phases may form depending on the steel's composition and boriding process parameters. These include CrB, Cr₂B, Cr₃B₄, Ni₃B, and Mo₂B. Studies such as [31, 32] on AISI 904L and 304L stainless steel have shown the formation of CrB, Cr₂B, Ni₃B, and Mo₂B boride phases after 2-4 hours of boriding, owing to the high alloy content of the steel. Prolonged boriding results in the formation of additional phases like Ni₂B and MnB [33]. The variety of boride phases depends on both time and temperature. Research cited in [31] indicates an increase in the number of boride phases with prolonged boriding time and temperature, albeit with a decrease in phase intensities. Notably, boriding significantly enhances hardness and wear resistance, with hardness increasing by up to 10 times and wear resistance by up to 40 times compared to untreated alloys. Time and temperature emerge as critical parameters in boriding, where the presence of FeB phase diminishes over time, while Fe₂B and other boride phases increase. Furthermore, corrosion and abrasion resistance exhibit improvements over time; however, abrasion resistance diminishes with increasing temperature [34].

Advantages and limitations

Advantages:

1. **High Surface Hardness:** Boronizing produces an extremely hard surface layer, often reaching hardness levels of up to 1800 HV (Vickers hardness).
2. **Wear Resistance:** The iron borides formed on the surface significantly improve wear resistance, making boronized components suitable for high-stress applications.
3. **Corrosion Resistance:** Boronized surfaces exhibit good resistance to corrosion, particularly in harsh environments such as saline or acidic conditions.

4. Improved Fatigue Life: The boronized layer can enhance the fatigue life of treated components, increasing their durability.

5. Compatibility with Various Materials: Boronizing can be applied to a variety of materials, including low-carbon steels, tool steels, stainless steels, and some non-ferrous metals.

Limitations:

1. Process Temperature: Boronizing requires high temperatures (typically between 700°C and 1000°C), which may cause distortion or unwanted microstructural changes in the base material.

2. Limited Control Over Layer Depth: While the depth of the boronized layer can be adjusted, the process may be less precise compared to other techniques such as nitriding.

3. Post-Treatment Machining: Due to the extreme hardness of the boronized layer, post-treatment machining can be challenging and may require specialized tools.

4. Process Duration: Boronizing can take several hours to complete, depending on the desired layer thickness and material being treated.

Carburizing

Carburizing is a process used in metallurgy to increase the carbon content at the surface of low-carbon steel, creating a harder and more wear-resistant outer layer while maintaining a softer, tougher core [35]. This process is commonly employed in manufacturing gears, bearings, and other components requiring wear resistance.

Carburizing process

There are two primary methods for carburizing: pack carburizing and gas carburizing. In the pack carburizing method, the steel parts are packed in a container along with a carbon-rich material such as charcoal or carbon powder. The container is sealed to prevent the ingress of air and then heated to high temperatures (typically between 850°C to 950°C) for an extended period, often several hours to several days. During this time, carbon atoms from the pack material diffuse into the surface of the steel parts, forming a carbon-rich layer. In gas carburizing, the steel parts are placed in a sealed furnace or chamber along with a controlled atmosphere containing a carbon-bearing gas, such as methane or propane, along with other gases like hydrogen or nitrogen. The chamber is heated to temperatures typically ranging from 870°C to 980°C. The carbon atoms in the gas diffuse into the surface of the steel, forming a carbon-rich layer. Regardless of the method used, the carbon atoms diffuse into the surface of the steel due to the concentration gradient between the carbon-rich environment and the steel surface. This diffusion process is driven by the temperature and time duration. After the desired carbon content is achieved at the surface, the steel parts are rapidly cooled, or quenched, to room temperature. Quenching involves immersing the parts in a quenching medium such as oil, water, or polymer solution. This rapid cooling helps to "freeze" the carbon atoms in the desired arrangement, creating a hardened surface layer. The hardened steel parts are then often subjected to a tempering process. Tempering involves reheating the parts to a lower temperature (typically between 150°C to 300°C) to relieve internal stresses and improve toughness. This step is crucial for achieving the desired balance between hardness and toughness in the finished component [36].

Effects of carburizing on microstructure and mechanical properties

The primary effect of carburizing is the formation of a carbon-rich layer on the surface of the steel. Carbon atoms diffuse into the surface of the steel, forming a gradient of carbon concentration from the surface inward. This layer is typically referred to as the "case" and is characterized by its higher carbon content compared to the core of the steel. As carbon diffuses into the steel, it alters the microstructure of the surface layer. At elevated temperatures, carbon combines with iron to form iron carbides, such as cementite (Fe_3C). These carbides precipitate

within the microstructure, increasing the hardness of the carburized layer. The microstructure of the carburized layer often consists of martensite, retained austenite, and carbides.

The nonmartensitic microstructures, are variously described as pearlite or quenching pearlite, or either or both lower and upper bainites, or mixtures of all of them. A low-alloy steel is inclined to develop a surface with pearlite, while a high-alloy steel typically results in a bainitic microstructure after quenching. Regardless of the specific nonmartensitic microstructure formed, it will consist of ferrite and carbides.

The resulting microstructure is influenced by the carburizing and quenching heat treatment processes. The depth of the carburized layer can be finely adjusted by manipulating parameters such as temperature, time, and the carbon potential of the carburizing atmosphere. For example, in a study by Xue et al.[37], a comparison of two carburizing methods revealed distinct differences in the microstructure of gear steel. Gas carburized gear steel exhibited twin martensite, retained austenite, and spherical carbides, while low-pressure carburized gear steel showed an absence of carbides in the near-surface layer as indicated in Fig. 3. In the carburizing of M50 bearing steel, it was observed that the austenite content in the surface layer increased after a slight carburizing treatment, leading to a decrease in martensite content. Furthermore, during tempering, retained austenite transformed into martensite, and a significant quantity of uniformly distributed carbides precipitated [38]. The rate of cooling typically determines the precipitation of carbides. Additionally, low-temperature tempering can yield a multiphase microstructure comprising bainite, martensite, carbides, and retained austenite, as indicated in [39].

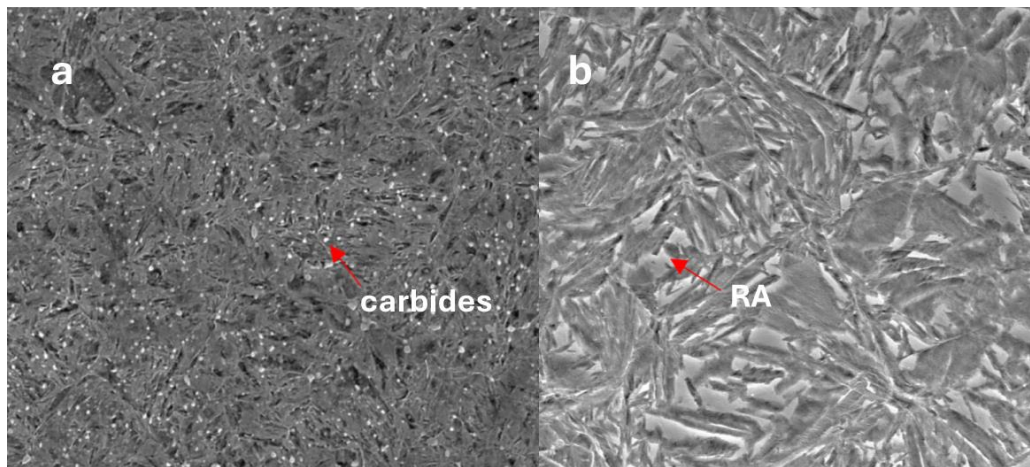


Fig. 3. SEM micrographs showing microstructures: a) in the near-surface carburized layer of the gas carburized gear steel; b) in the near surface carburized layer of the low-pressure carburized gear [37]

The diffusion of carbon and the formation of iron carbides lead to an increase in the hardness of the carburized layer. Martensite, a very hard and brittle phase, forms when the steel is quenched from the carburizing temperature, contributing significantly to the surface hardness. This increased hardness improves wear resistance and extends the service life of the component. In the study conducted by Wei et al.[40], short-time carburizing of M50 steel resulted in a significant increase in hardness, measured at 57.7 HV. Furthermore, research by Yu et al.[38] demonstrated that a reduction in martensite content corresponded to a decrease in the hardness of M50 steel. The hardness of various microstructures, categorized by their carbon content, are presented in Table 1 [41].

Table 1. Hardness values for different microstructures [41]

Microstructure	Ferrite	Mixed ferrite & pearlite	Pearlite	Mixed pearlite & bainite	Bainite
Hardness, HV	200 – 250	200 – 300	300	300 – 400	400

Advantages and limitations

Advantages:

1. **Increased Surface Hardness:** Carburizing significantly increases the hardness of the surface layer, providing enhanced wear resistance and improved load-bearing capacity.
2. **Improved Fatigue Strength:** The hard case formed by carburizing improves the fatigue strength of the treated components, making them more durable under cyclic loading.
3. **Controlled Case Depth:** The depth of the carburized layer can be precisely controlled by adjusting the treatment time and temperature, allowing for customization based on application requirements.
4. **Versatile Process:** Carburizing can be performed using various methods such as gas, liquid, and solid (pack) carburizing, providing flexibility in choosing the appropriate technique based on the component and application.
5. **Compatibility with Complex Geometries:** Carburizing can be applied to components with complex shapes and geometries, making it suitable for a wide range of parts.
6. **Retention of Core Properties:** The core of the treated material remains relatively unchanged, retaining its original toughness and ductility.

Limitations:

1. **High Process Temperatures:** Carburizing requires high temperatures, typically between 850°C and 950°C, which may lead to distortion or changes in the microstructure of the material.
2. **Post-Treatment Processes:** Carburized components often require quenching and tempering after the treatment to achieve the desired mechanical properties, which can add time and cost to the process.
3. **Environmental Impact:** Certain carburizing methods, such as gas and liquid carburizing, may involve the use of toxic chemicals or gases, requiring proper handling and disposal to minimize environmental impact.
4. **Limited Material Compatibility:** Carburizing is most effective on low-carbon steels. High-carbon steels and certain other materials may not respond well to the process.
5. **Surface Preparation:** The treated surface may require additional processing, such as grinding or machining, to achieve the desired finish and dimensions.

Laser surface treatment

Laser surface treatment, also known as laser surface modification or laser surface engineering, is a highly precise and controlled method used to alter the surface properties of materials. It involves the use of a high-energy laser beam to heat, melt, or vaporize the surface of a material, leading to changes in its microstructure and properties [42]. Laser surface treatment is employed in various industries, including manufacturing, automotive, aerospace, electronics, and medical. During laser treatment, a high-energy laser beam is directed onto the surface of the material. The interaction between the laser beam and the material depends on several factors, including the laser wavelength, power density, scanning speed, and material composition. When the laser beam strikes the material surface, it rapidly heats the surface layer, causing localized heating, melting, or vaporization, depending on the laser parameters and material properties. The rapid heating and cooling associated with laser treatment induce various thermal effects, such as phase transformations, solidification, and rapid cooling rates. These thermal effects lead to changes in the microstructure and properties of the material surface. Depending on the desired outcome, laser surface treatment can achieve different surface modifications such as hardening, alloying and surface texturing.

Laser surface hardening

Laser surface hardening involves heating the material surface to high temperatures and then rapidly quenching it to induce martensitic transformation, resulting in increased surface hardness and wear resistance [43]. The rapid heating and quenching during laser hardening promote the formation of martensite, which is a very hard and brittle phase of steel. Martensite formation occurs due to the rapid cooling rate, which traps carbon atoms in a supersaturated solid solution, resulting in a high hardness. Austenite, the high-temperature phase of steel, undergoes a phase transformation into martensite during laser hardening. The rapid heating followed by quenching prevents the austenite from transforming into other phases such as pearlite or bainite, leading to a fully martensitic microstructure in the hardened region. In some cases, a small amount of retained austenite may be present in the hardened region after laser hardening. Retained austenite can affect the mechanical properties and dimensional stability of the steel and may need to be addressed through additional post-treatment processes such as tempering.

Laser surface hardening process

The steel surface is cleaned and prepared to ensure optimal laser interaction. This may include removing any oxide layers, contaminants, or coatings that could interfere with the laser treatment. A high-energy laser beam is directed onto the steel surface, typically in a controlled and focused manner. The laser heats the surface rapidly to a high temperature, often above the critical temperature for steel, allowing a phase transformation from the existing microstructure to martensite. The laser beam is typically controlled using a computerized system to move along the desired path or area. This allows for precise and uniform treatment of the surface according to the specific requirements of the component. As the laser beam heats the surface, it creates a temperature gradient, with the surface reaching high temperatures while the underlying material remains cooler. This rapid heating changes the microstructure of the steel, making it harder. Once the laser beam moves away from the treated area, the surface cools rapidly due to heat conduction into the cooler substrate. This rapid cooling, or quenching, transforms the heated steel surface into a hard martensitic microstructure. The treated surface layer exhibits increased hardness and wear resistance due to the formation of martensite. The depth of hardening depends on factors such as laser power, exposure time, and the movement speed of the laser beam. In some cases, the hardened surface may require post-treatment processes such as tempering to reduce residual stresses and improve the overall mechanical properties.

Effects of laser surface hardening on microstructure and mechanical properties

A coarse martensite with retained austenite structure was obtained by [44] after laser treatment of austempered ductile iron by Nd:YAG laser, which subsequently improved the microhardness and wear resistance. The presence of martensite significantly enhances surface hardness, making it crucial for researchers and industry alike to prioritize increasing its formation. Moradi et. al [45] demonstrated that increasing laser power and decreasing the focal point position results in heightened martensite formation and, consequently, increased surface hardness. Furthermore, the study suggests that allowing more time for dissolution, which completely dissolves the delta ferrite phase, and avoiding rapid quenching can further enhance hardness in the treated zone.

Surface hardness is directly influenced by the formation of martensite, with its hardness increasing proportionally with carbon content. For instance, according to [46], it rises steadily from 300 HV at 0.05 %C to approximately 750 HV at 0.5 %C. It's crucial to recognize that the transformations in phases during the laser heating of ferrous alloys are heavily reliant on the initial microstructure of the alloy undergoing treatment. Laser hardening is particularly effective for fine microstructures like pearlite colonies and quenched and tempered microstructures because there is ample time for the carbon to dissolve and homogenize. Conversely, achieving significant hardening in coarse microstructures such as graphite nodules and ferrite matrices may prove challenging due to inadequate carbon dissolution.

The localized heating and rapid cooling associated with laser hardening can result in a finer grain structure in the hardened region compared to the base material. This finer grain size contributes to improved mechanical properties, such as higher strength and toughness. The grain size can decrease by increasing laser power density, provided that no melting occurs. Additionally, the pretempering temperature influences the grain size. In [47], the grain size decreased when the pretempering temperature was raised, especially at pretempering temperatures above 300°C.

Processing parameters for laser hardening, including the type of laser, laser power, and traverse speed, significantly affect the resulting microstructure and mechanical properties of the treated material. In [48], it was observed that the high-power diode laser yielded higher hardness compared to the Nd:YAG laser. Regarding the impact of laser power and traverse speed, [49] suggested that laser power did not exert a significant influence on hardness. However, hardness reached very high levels at a high power of 2.46 kW, leading to surface melting. Conversely, hardness increased with decreasing traverse speed. Overall, laser hardening offers precise control over the microstructure and properties of steel components, making it a valuable technique for enhancing the performance and longevity of critical parts in various industrial applications. However, proper process parameters and post-treatment steps are essential to ensure the desired microstructural characteristics and avoid potential issues such as cracking or distortion.

Table 2. The impact of process parameters on hardness

Parameter	Impact on hardness	Ref
Laser type High power diode laser (1600 W) vs Nd:YAG (700 W)	High power diode laser – 792 HV Nd:YAG – 698 HV High Power diode laser result in higher hardness value due to finer ferrite grains.	[48]
Laser power Laser power was varied from 0.74 – 2.46 kW	The highest hardness value was obtained at 2.46 kW. The relationship between the laser power and hardness is non-linear.	[49]
Traverse speed The traverse speed was varied from 4 – 12 mm/s	The optimum traverse speed for 0.28% C steel is nearer to 4 mm/s, for 0.40% C steel it is within 6–8 mm/s and for 0.46% C steel, it lies between 8 and 10 mm/s.	[49]
Scanning speed The scanning speed was varied from 40 – 200 mm/s	The hardness decreases as the scanning speed was increased from 40 to 200 mm/s.	[50]

Advantages and limitations

Advantages:

1. **Precise Control:** Laser surface hardening offers precise control over the depth and area of hardening, making it ideal for treating specific regions of a component or complex shapes.
2. **Localized Treatment:** The technique allows for localized hardening without affecting the core properties of the material, which helps retain the original ductility and toughness of the component.
3. **Minimal Distortion:** The rapid heating and cooling associated with laser hardening result in minimal distortion of the treated component.
4. **High Hardness:** Laser surface hardening creates a very hard surface layer with increased wear resistance and improved mechanical properties.
5. **Flexibility in Material Selection:** Laser surface hardening can be applied to a variety of materials, including different types of steels and other ferrous alloys.
6. **No Post-Treatment Required:** The process typically does not require further post-treatment, such as tempering, making it a relatively straightforward method.

Limitations:

1. **Equipment Cost:** The high-energy laser equipment required for the process can be expensive and requires specialized training for operators.

2. Limited Depth: The depth of hardening achieved through laser surface hardening is typically shallow, which may not be suitable for applications requiring deep case hardening.

3. Surface Roughness: In some cases, the treated surface may exhibit increased roughness, which may require additional finishing steps.

4. Safety Concerns: The high-energy laser beam can pose safety risks, requiring appropriate safety measures and protective equipment for operators.

5. Limited Material Compatibility: While laser hardening is versatile, not all materials respond well to the process. The technique works best with specific materials such as steels.

Laser surface melting

Laser surface melting relies on swiftly traversing the surface with a concentrated beam, achieving power densities ranging from 104 to 107 W/cm². Rapid cooling rates, reaching up to 108 – 1010 K/sec, facilitate the development of intricate patterns, uniform microstructures, expanded solid solubility thresholds, and the emergence of non-equilibrium phases including metallic glasses or amorphous phases. These outcomes yield corrosion resistance levels 10 to 100 times superior to crystalline structures [51].

Laser surface melting process

The steel surface is cleaned and prepared to ensure optimal laser interaction. This may involve removing any oxide layers, contaminants, or coatings. A high-energy laser beam is directed onto the steel surface, rapidly heating it to a temperature above the melting point of the material. The laser beam can be precisely controlled to focus on specific areas. As the laser beam heats the steel, the surface melts, creating a thin layer of molten metal. The depth of the molten layer is typically shallow, usually on the order of micrometers to millimeters, depending on the laser parameters and the material being treated. Once the laser beam moves away from the treated area, the molten metal cools rapidly due to heat conduction into the cooler substrate. This rapid cooling or quenching results in solidification of the melted layer. The rapid solidification leads to a fine, homogeneous microstructure with reduced segregation and defects. This can result in improved hardness, wear resistance, and other mechanical properties. The solidified surface typically has a smooth, fine finish due to the melting and rapid solidification process. This can reduce roughness and improve the aesthetics of the treated component. Depending on the application, the treated surface may undergo additional post-treatment processes, such as tempering or mechanical finishing, to further optimize the properties and performance.

Effects of laser surface melting on microstructure and mechanical properties

Laser melting can result in a fine and equiaxed grain structure in steel. This occurs due to the rapid solidification that happens during the process. The high cooling rates associated with laser melting prevent the formation of large grains, leading to a more uniform and refined microstructure compared to traditional manufacturing methods. The fine grains produced from laser melting strengthen materials. Similar to the laser hardening process, the parameters of the process affect the resultant microstructure in the laser melting process. In [52], higher scanning speed led to the formation of fine grains, which contributed to the strengthening of the treated material.

During solidification, elements within the steel alloy may segregate, leading to variations in composition across the microstructure. Laser melting can help reduce microsegregation due to the rapid solidification rates, resulting in a more homogeneous distribution of elements within the steel. The phenomenon of microsegregation was observed in [53]. They obtained columnar grains of austenite with intercellular segregation of Mo, Cr, and Si microstructure, resulting in the formation of non-equilibrium eutectic ferrite. This segregation contributed to the improvement in the yield strength and ultimate tensile strength of the 316 L steel.

Depending on the composition of the steel, laser melting can induce martensitic transformation in certain regions of the microstructure. Martensite is a metastable phase of steel characterized by a highly stressed and hardened structure. The rapid heating and cooling cycles involved in laser melting can promote the formation of martensite, particularly in regions subjected to high temperature gradients. However, depending on the steel composition, the martensite phase may form as a mixture with other phases such as bainite or austenite, thereby affecting the mechanical behavior of the steel. In [54], fabricating low-alloyed steel via laser melting deposition resulted in a mixture of lower bainite and martensite microstructure on the surface and tempered martensite in the interior as shown in Fig. 4. The size of the martensite increased with higher laser power. The tempered martensite phase exhibited higher hardness compared to the phase with the mixture of bainite and martensite.

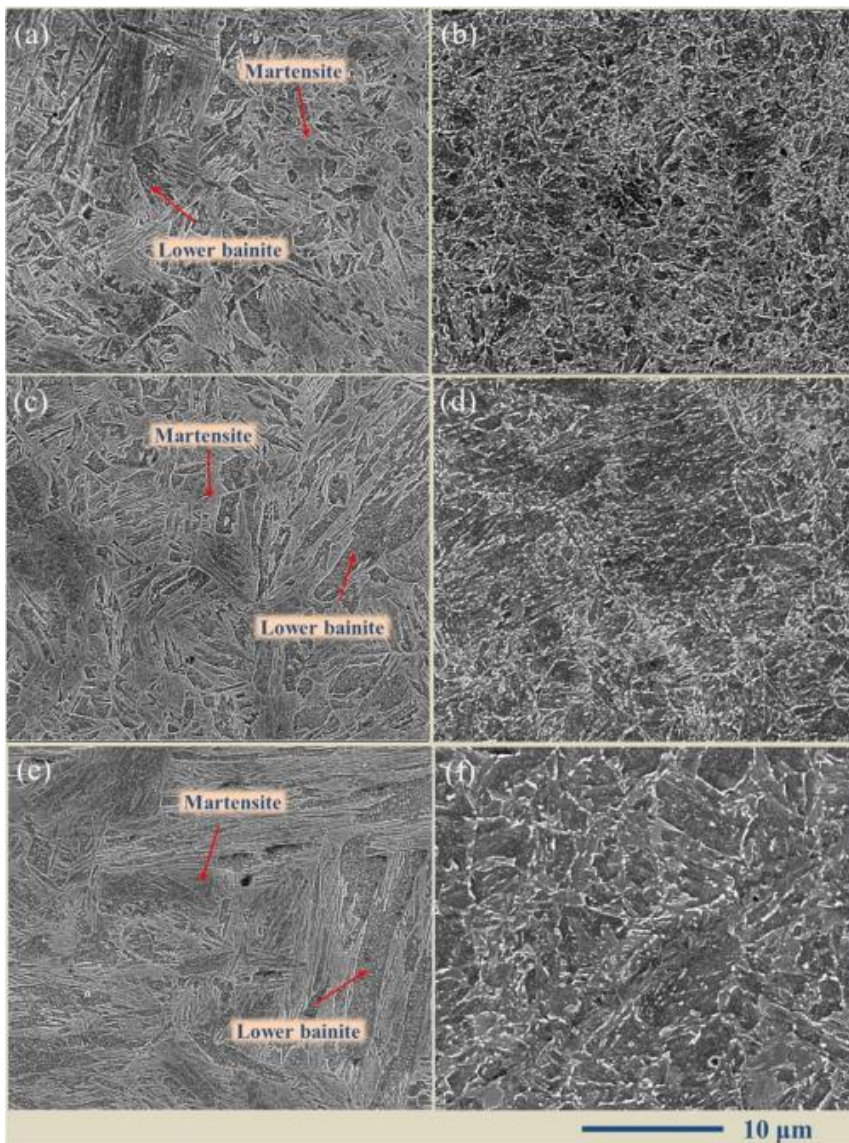


Fig. 4. Surface microstructure: a) 1500 W; c) 2000 W; e) 2500 W laser powers.
Interior microstructure: b) 1500 W; d) 2000 W; e) 2500 W laser power [54]

Laser melting can influence the texture of the steel microstructure, affecting its mechanical properties. The directional solidification inherent in the process can lead to preferred crystallographic orientations, resulting in anisotropic mechanical behavior. Understanding and controlling texture development is essential for optimizing the performance of laser-melted steel components. For instance, the change of scanning strategy from simply alternating strips to alternating strips with re-melting after each layer changed one-component cube texture to partially fiber texture which consequently affected the mechanical behavior of the steel [53].

Despite its advantages, laser melting can also introduce defects into the microstructure of steel, such as porosity, lack of fusion, and microcracks. These defects can significantly impact the mechanical properties and performance of the final component. Process optimization, including parameters such as laser power, scanning speed, and powder characteristics, is essential to minimize the occurrence of defects and ensure the integrity of the microstructure.

Laser melting can significantly influence the microstructure of steel, leading to refined grain structures, reduced microsegregation, potential martensitic transformation, residual stresses, texture development, and the formation of defects. Understanding these effects and optimizing process parameters are crucial for achieving desired mechanical properties and performance in laser-melted steel components.

Advantages and limitations

Advantages:

1. **Refined Microstructure:** Laser surface melting creates a fine and homogenous microstructure due to rapid solidification, which can improve hardness, toughness, and wear resistance.
2. **Reduced Segregation:** The process can reduce chemical segregation and other inhomogeneities in the material, leading to improved mechanical properties.
3. **Minimal Distortion:** Since the laser treatment is localized and the substrate absorbs the heat quickly, there is minimal distortion of the treated part.
4. **Surface Cleaning:** Laser surface melting can eliminate surface defects such as porosity and oxides, leading to a smoother, cleaner finish.
5. **Compatibility with Alloying Elements:** Additional alloying elements can be introduced into the molten pool to tailor the properties of the surface layer for specific applications.
6. **Versatility in Applications:** The technique can be applied to various materials, including different types of steels and alloys, and can be used for different objectives such as wear resistance, corrosion resistance, or surface finishing.

Limitations:

1. **Limited Depth of Treatment:** Laser surface melting typically affects only the very top layer of the material, with treatment depths usually in the range of micrometers to millimeters.
2. **High Equipment Cost:** The high-energy laser systems required for this process can be expensive, and their maintenance may be complex.
3. **Surface Roughness:** Although the process can improve surface finish in some cases, it can also create surface roughness depending on the process parameters, which may require additional finishing steps.
4. **Material Compatibility:** Not all materials respond well to laser surface melting, and the process may cause unwanted changes in the microstructure of certain materials.
5. **Safety Concerns:** The use of high-energy lasers poses safety risks for operators, requiring proper safety measures and training.

Laser cladding

Laser cladding involves melting a powdered or wire-form material, known as the cladding material, onto the substrate using a high-energy laser beam. Laser cladding can achieve a high

level of metallurgical bonding between the cladding material and the substrate, leading to improved mechanical properties and wear resistance [55].

Laser cladding process

The substrate surface is cleaned and prepared to ensure optimal laser interaction and bonding with the cladding material. This may involve removing any contaminants, oxides, or coatings. The cladding material, usually in the form of powder or wire, is fed into the laser beam path. The material is often pre-heated to improve adhesion and reduce thermal shock during deposition. A high-energy laser beam is directed onto the substrate surface at the point where the cladding material is being fed. The laser heats the substrate and the cladding material, causing the material to melt and form a molten pool on the substrate surface. The molten cladding material is deposited onto the substrate, and the heat from the laser allows it to fuse with the substrate material. The laser beam moves along a predefined path, continuously depositing the material layer by layer. The movement of the laser beam and the material feeding system are controlled using a computerized system to ensure uniform and precise deposition of the cladding material. As the laser beam moves away from the treated area, the deposited material solidifies rapidly, creating a strong bond with the substrate. The rapid cooling helps achieve a fine, uniform microstructure in the clad layer. The process can be repeated multiple times to build up the desired thickness of the clad layer. This allows for customization of the material properties based on the specific application. Depending on the application, the clad surface may undergo additional post-treatment processes such as heat treatment or mechanical finishing to optimize properties and performance.

Effects of laser cladding on microstructure and other properties of steel

The rapid heating and cooling rates associated with laser cladding can lead to the formation of a fine-grained microstructure in the clad layer. This fine grain structure often results in improved mechanical properties, such as increased hardness and strength. The parameters of the cladding process have a significant impact on the grain size of the material. Jiao et al. [56] investigated how variations in scanning speed affect the microstructure, hardness, and wear behavior. Their findings indicated that a scanning speed of 200 mm/min led to a smaller grain size, resulting in increased hardness and optimal wear resistance.

The heating and cooling cycles experienced during laser cladding can induce phase transformations in the steel microstructure. Depending on the composition of the steel and the processing parameters, phases such as austenite, martensite, bainite, and retained austenite may form, influencing the mechanical and metallurgical properties of the clad layer. For instance, in [56], the T15M high speed steel alloy resulted in the formation of martensite, retained austenite and carbides phases. In some instances the coating can form small amounts of δ ferrite due to non-equilibrium solidification and fast cooling rate. Therefore, the δ ferrite does not have enough time to completely transform into austenite and is left becoming residual ferrite at room temperature [55].

The laser cladding process parameters are crucial for optimizing the procedure and achieving desired outcomes, but the composition of the cladding material is equally important. A study by Wang et al. [57] highlighted the significance of molybdenum (Mo) content in the cladding material for optimizing the properties of steel and the resultant microstructures are shown in Fig. 5. In Fig. 5 shows that as the Mo content increases, the amount of martensite decreases, while the amount of ferrite gradually increases. Additionally, the coating's microstructure containing Mo is finer than that of the coating without Mo. The microhardness decreases, and the wear resistance of the coating gradually improves with increasing Mo content.

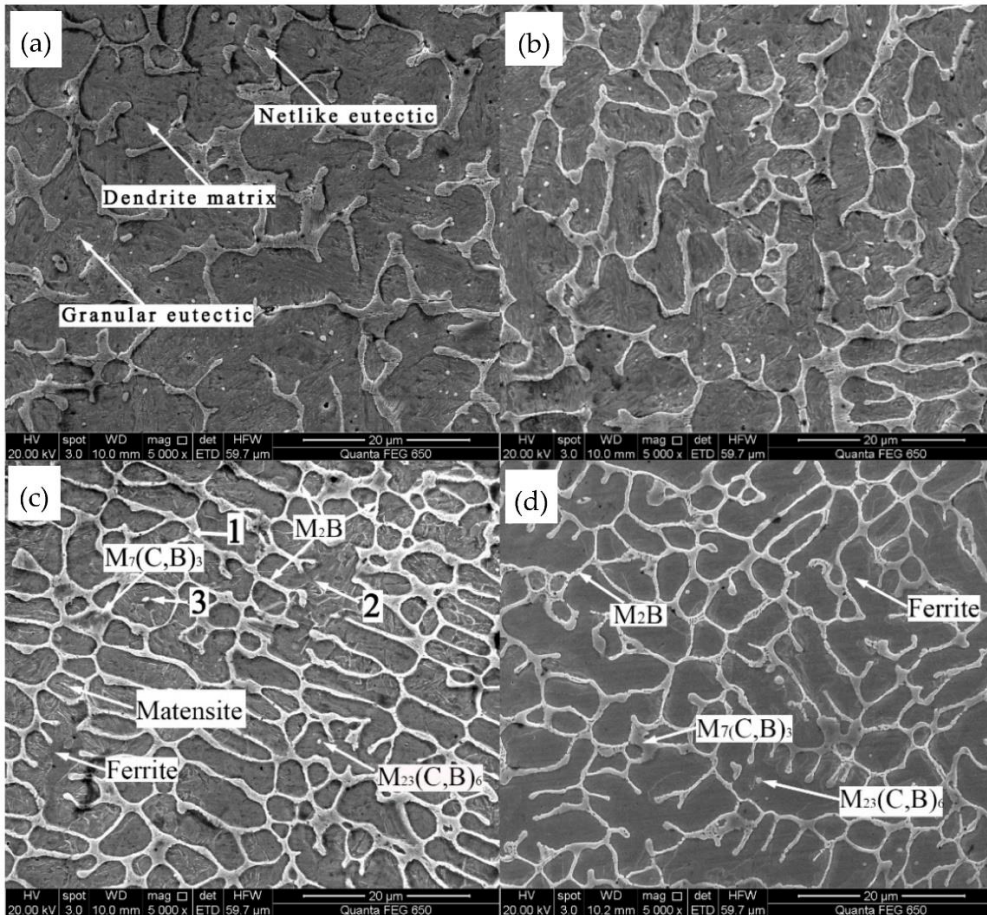


Fig. 5. SEM images of coatings with different Mo content:
 a) Mo-free; b) 2.0 wt. % Mo; c) 4.0 wt. %; d) 6.0 wt. % Mo [57]

Achieving a uniform microstructure throughout the clad layer is essential for ensuring consistent mechanical properties. Proper control of processing parameters such as laser power, scanning speed, and powder feed rate is critical to achieving microstructural homogeneity. In [58], post-cladding tempering at 550 °C for 2 h led to the development of uniform microstructure without fine carbide precipitated along grain boundaries or inter-dendritic regions which improved the hardness level. Further laser reheating (tempering) of the clad zone showed a more refined microstructure which resulted in a significant improvement in hardness.

Depending on the composition of the cladding material and the steel substrate, laser cladding can promote the precipitation of carbides within the microstructure. Carbides can enhance wear resistance and hardness but may also affect other mechanical properties such as toughness and ductility. In [56], more carbides precipitated and large local segregation decreased in the original austenite grain boundary with the increase of the laser scanning speed. Laser cladding involves melting both the substrate material and the cladding material. The extent of mixing between these materials, known as dilution, can significantly affect the microstructure of the clad layer. High dilution can result in changes to the chemical composition and microstructure of the clad layer, potentially altering its properties. In [59], the dilution rates were shown to increase with increasing laser scanning speed due thinner coating thickness and less melted cladding material.

The increase of the dilution rate led to surface cracks, and the corrosion resistance decreases due to these cracks and the formation of the Fe-Ti intermetallic compounds on the coating surface.

Laser cladding can have significant effects on the microstructure of steel, influencing its mechanical and metallurgical properties. Proper control of processing parameters and an understanding of the microstructural changes induced by laser cladding are essential for achieving the desired performance of the clad steel components.

Advantages and limitations

Advantages:

1. **Versatility:** Laser cladding can be applied to a wide range of materials, including metals, ceramics, and composite materials. It is suitable for repairing worn or damaged parts, as well as for coating new components.
2. **Precise Control:** The process allows for precise control over the thickness, composition, and distribution of the deposited layer, enabling customized solutions for specific applications.
3. **Minimal Heat-Affected Zone:** The high precision of the laser beam and the localized nature of the process minimize the size of the heat-affected zone, reducing distortion and preserving the properties of the substrate.
4. **Strong Bonding:** The process creates a strong metallurgical bond between the cladding material and the substrate, ensuring good adhesion and longevity of the coating.
5. **High-Quality Surface:** Laser cladding can produce a smooth and uniform surface finish, reducing the need for post-treatment machining or finishing.
6. **Flexible Geometry:** The technique can be applied to complex geometries and specific regions of a component, offering great flexibility in design and manufacturing.

Limitations:

1. **High Equipment Cost:** The laser equipment required for cladding can be expensive, and the process may require specialized operators and maintenance.
2. **Material Compatibility:** While laser cladding can be applied to a variety of materials, not all materials may be compatible with the process. There can be challenges in matching the properties of the cladding material with those of the substrate.
3. **Process Optimization:** Achieving optimal process parameters can be challenging and may require experimentation to find the right combination of laser power, scanning speed, and material feed rate.
4. **Safety Concerns:** High-energy lasers pose safety risks to operators, requiring appropriate safety measures, including protective equipment and controlled environments.
5. **Production Time:** Depending on the size and complexity of the part, as well as the desired layer thickness, the process can be time-consuming.

Future Directions and Limitations

There are several focus areas to enhance and optimize the surface modification of steel which can be used as a guide for future directions by researchers. Some of the future directions for diffusion coating techniques may include:

1. *Development of advanced diffusion coating techniques:*
 - Development of more efficient plasma processes, such as low temperature plasma nitriding to reduce thermal distortion, plasma assisted boronizing methods to improve control over the process, and exploration of plasma-assisted carburizing.
 - Development of laser-assisted nitriding and boronizing processes to achieve precise and localized surface modification.
 - Establish hybrid techniques: combining two or more coating techniques to enhance the overall performance of the steel.

- Development of low-pressure carburizing techniques to improve uniformity, reduce cycle time, and lower distortion.
- 2. *Establish control and monitoring techniques:*
 - Development of real-time monitoring techniques to precisely control all process parameters.
 - Utilizing advanced computational models and simulations to predict the process outcome and optimize process parameters.
- 3. *Environmental and economic consideration:*
 - Development of environmentally friendly nitriding, boronizing and carburizing processes that minimize the use of hazardous chemicals and reduce environmental impact.
 - Optimization of nitriding processes to reduce energy consumption and overall costs while maintaining or improving surface properties.
- 4. *Research in surface engineering and nano-technology:*
 - Research on creating nanostructured nitride, boronized or carburized layers to achieve superior surface properties, or the addition of functional properties such as improved thermal stability, oxidation resistance, and self-lubricating characteristics.
- 5. *Material-specific studies:*
 - Research on steel and alloy compositions that respond favorably to each process and develop customized process cycles for different types of steel to optimize surface properties for specific applications.

Future directions in laser treatment may include:

1. *Development of Advanced laser technology:*
 - Implementation of high-power and ultrafast laser systems to improve the efficiency and precision of laser surface treatments.
 - Exploration of fiber and diode lasers for their advantages in energy efficiency, flexibility, and precise control over the hardening process.
2. *Process control and monitoring:*
 - Implementation of real-time monitoring systems, such as thermal imaging and pyrometry, to continuously observe and control the temperature and other parameters during laser hardening.
 - Development of adaptive control algorithms that can adjust laser parameters on-the-fly to ensure consistent hardening quality across different parts and geometries.
3. *Laser Path Optimization:*
 - Development of advanced path planning algorithms that optimize the laser scan path to reduce processing time, energy consumption, and thermal distortion.
4. *Hybrid Techniques:*
 - Combining laser hardening with other surface modification techniques such as carburizing, nitriding, or coating to enhance overall surface properties and performance.
5. *Modeling and Simulation:*
 - Utilization of advanced computational models and simulations to predict the outcomes of laser surface treatment processes, optimize parameters, and minimize trial-and-error in process development.

Conclusions

In this review paper we have explored various surface modification techniques to enhance the performance and longevity of steel components. The diffusion methods, including nitriding, boronizing, and carburizing, have been assessed for their ability to improve surface hardness, wear resistance, and fatigue strength while maintaining the core toughness of the material. Additionally, the impact of these techniques on the microstructure was examined. Laser-based

treatments, including laser surface hardening, laser surface melting, and laser cladding, have been evaluated for their precision and versatility. In laser surface treatments, several factors, including grain size, phase transformation, microsegregation, and texture in laser surface melting, as well as the presence of other materials such as molybdenum in laser cladding, affect the resultant microstructure. These factors can be controlled by adjusting processing parameters, which in turn influence the microstructure. This review comprehensively discusses the impact of these factors. The following conclusions can be made regarding each modification technique:

1. Diffusion techniques offer precise control over case depth and properties but may involve high temperatures and extended process times.

2. In nitriding, nitrogen diffuses into the steel surface, forming iron nitrides γ' -Fe₄N and ϵ -Fe_{2.3}N, which enhances corrosion and wear resistance. The intensity of these phases varied with changes in processing parameters. Literature indicates that the ϵ -Fe_{2.3}N phase offers the best wear resistance.

3. Boronizing results in the formation of boride layers FeB and Fe₂B, significantly increasing the steel's hardness. The Fe₂B layer is preferred due to its lower brittleness, high hardness, and low ductility. Processing time and temperature are critical for controlling the formation and intensity of the boride phases.

4. Carburizing creates a carbon-rich layer on the steel's surface, where high carbon content combines with iron to form iron carbides, altering the microstructure and increasing the steel's hardness. The resultant microstructure often includes martensite, retained austenite, and carbides. Processing parameters such as temperature, time, and the carburizing method itself play key roles in determining the final microstructure.

5. Laser surface hardening provides localized treatment with minimal distortion. The resulting microstructure is usually martensite, which affect mechanical properties.

6. Laser surface melting refines the microstructure for improved mechanical properties. Laser surface melting may form martensite phase as a mixture with other phases such as bainite or austenite, depending on the composition of the steel, thereby affecting the mechanical behavior of the steel.

7. Laser cladding offers a robust method for applying high-performance coatings with strong adhesion and controlled thickness. The resultant grain-size plays affect the mechanical properties significantly and can be controlled by process parameters.

8. Diffusion coating is preferred for applications needing high-temperature resistance and uniform coatings, while laser surface treatments are chosen for their precision, speed, and minimal thermal impact on the substrate.

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References

- [1] P. Sankara, **Corrosion Control in the Oil and Gas Industry**, Gulf Professional Publishing, Canada, 2014, p. 133.
- [2] S. Karan, **Subsea Valves and Actuators for the Oil and Gas Industry**, Gulf Professional Publishing, USA, 2021, p. 421

- [3] M. Sabzi, M. Farzam, *Hadfield manganese austenitic steel: a review of manufacturing processes and properties*, **Mater. Res. Express**, 6, 1065c2, 2019.
- [4] I. El-Mahallawi, R. Abdel-karim, A. Naguib, *Evaluation of effect of chromium on wear performance of high manganese steel*, **Materials Science and Technology**, 17:11, 2001, p. 1385-1390.
- [5] S. U. Koh, J. M. Lee, B. Y. Yang, K. Y. Kim, *Effect of Molybdenum and Chromium Addition on the Susceptibility to Sulfide Stress Cracking of High-Strength, Low-Alloy Steels*, **CORROSION**, 63 (3), 2007, p. 220–230.
- [6] K. Han, T.D. Mottishaw, G.D.W. Smith, D.V. Edmonds, A.G. Stacey, *Effects of vanadium additions on microstructure and hardness of hypereutectoid pearlitic steels*, **Materials Science and Engineering: A**, 190, 1–2, 1995, p. 207-214.
- [7] T. Ros-Yañez, Y. Houbaert, O. Fischer, J. Schneider, *Production of high silicon steel for electrical applications by thermomechanical processing*, **Journal of Materials Processing Technology**, 143, 2003, p 916-921.
- [8] F.Z. Benlahrechea, E. Nouicer, *Improvement of Surface Properties of Low Carbon Steel by Nitriding Treatment*, **ACTA PHYSICA POLONICA A**, 131, 2017, p. 20-23.
- [9] H. Wang, Y. Zhao, X. Yuan, K. Chen, R. Xu, *Effects of Boronizing Treatment on Corrosion Resistance of 65Mn Steel in two Acid Mediums*, **Physics Procedia**, 50, 2013, p. 124-130.
- [10] S. R. E. Hosseini , Z. Li, **In Encyclopedia of Iron, Steel, and Their Alloys**, Taylor and Francis, New York, 2016; p. 1-24.
- [11] I.R. Pashby, S. Barnes, B.G. Bryden, *Surface hardening of steel using a high power diode laser*, **Journal of Materials Processing Technology**, 139, 1–3, 2003, p. 585-588.
- [12] Y. Bai, D. Wang, Y. Yang, H. Wang, *Effect of heat treatment on the microstructure and mechanical properties of maraging steel by selective laser melting*, **Materials Science and Engineering: A**, 760, 2019, p. 105-117.
- [13] J.R Davis, **Surface Engineering for Corrosion and Wear Resistance**, ASM International, Materials Park, Ohio, USA, 2001.
- [14] N. D. Nam, N. A. Xuan, N. Van Bach, L. T. Nhung, L. T. Chieu, *Control Gas Nitriding Process: A Review*. **Journal of Mechanical Engineering Research & Developments**, 42(1), 2019, p. 17-25.
- [15] L.F. Zagonel, C.A. Figueroa, R. Droppa, F. Alvarez, *Influence of the process temperature on the steel microstructure and hardening in pulsed plasma nitriding*, **Surface and Coatings Technology**, 201, 1–2, 2006, p. 452-457.
- [16] B. C. Kumar, P. S. Charan, K. Jayakumar, D. Alankrutha, G. Sindhu, R. Subbiah, *Assessment of wear properties on low temperature molten salt bath nitriding on austenitic stainless steel*, **Materials Today: Proceedings**, 27, 2, 2020, p. 1541-1544.
- [17] D. Pye, **Practical Nitriding and Ferritic Nitrocarburizing**, ASM International, Materials Park, Ohio, USA, 2003.
- [18] S. Ahangarani, F. Mahboubi, A.R. Sabour, *Effects of various nitriding parameters on active screen plasma nitriding behavior of a low-alloy steel*, **Vacuum**, 80, 9, 2006, p. 1032-1037.
- [19] L.N. Tang, M.F. Yan, *Influence of Plasma Nitriding on the Microstructure, Wear, and Corrosion Properties of Quenched 30CrMnSiA Steel*. **J. of Materi Eng and Perform**, 22, 2013, p. 2121–2129.
- [20] B. Wang, X. Zhao, W. Li, M. Qin, J. Gu, *Effect of nitrided-layer microstructure control on wear behavior of AISI H13 hot work die steel*, **Applied Surface Science**, 431, 2018, p. 39-43.

- [21] D. She, W. Yue, Z. Fu, Y. Gu, C. Wang, J. Liu, *The effect of nitriding temperature on hardness and microstructure of die steel pre-treated by ultrasonic cold forging technology*, **Materials & Design**, 49, 2013, p. 392-399.
- [22] G-J. Li, Q. Peng, C. Li, Y. Wang, J. Gao, S-Y. Chen, J. Wang, B-L. Shen, *Effect of DC plasma nitriding temperature on microstructure and dry-sliding wear properties of 316L stainless steel*, **Surface and Coatings Technology**, 202, 12, 2008, p. 2749-2754.
- [23] K. Dimitar, *Improvement of Corrosion Resistance of Steels by Surface Modification*, **Corrosion Resistance**, 2012, p. 295 – 316.
- [24] J. Wang, J. Xiong, Q. Peng, H. Fan, Y. Wang, G. Li, B. Shen, *Effects of DC plasma nitriding parameters on microstructure and properties of 304L stainless steel*, **Materials Characterization**, 60, 3, 2009, p. 197-203.
- [25] M.A. Terres, L. Ammari, A. Chérif, *Study of the Effect of Gas Nitriding Time on Microstructure and Wear Resistance of 42CrMo4 Steel*. **Materials Sciences and Applications**, 8, 2017, p. 493-507.
- [26] J.R. Davis, **Surface Hardening of steels: understanding the basics**, ASM International, ISBN 0-87170-764-0, Materials Park, Ohio, USA, 2022.
- [27] W. Fichtl, *Boronizing and its practical applications*, **Materials & Design**, 2, 6, 1981, p. 276-286.
- [28] K. Kempen, **ASTM Handbook Heat Treating Volume 4**, ASTM International, Materials Park, Ohio, USA, 1991.
- [29] C. Zimmerman, **Boriding (Boronizing) of Metals, Steel Heat Treating Fundamentals and Processes, Vol 4A, ASM Handbook**, ASM International, USA, 2013, p 709–724.
- [30] U. Mishigdorzhniyn, Y. Chen, N. Ulakhanov, H. Liang, *Microstructure and Wear Behavior of Tungsten Hot-Work Steel after Boriding and Boroaluminizing*. **Lubricants** 2020, 8, 26.
- [31] M. Çetin, A. Günen, M. Kalkandelen, M.S. Karakaş, *Microstructural, wear and corrosion characteristics of boronized AISI 904L superaustenitic stainless steel*, **Vacuum**, 187, 110145, 2021.
- [32] O. Bican, S.U. Bayça, H. Kuleyin, R. Gümrük, *Effect of Boronizing on Operating Stability of Steel AISI 304L under Erosion Impact of Hard Particles*, **Metal Science and Heat Treatment**, 63, 3-4, 2021, p. 156.
- [33] S. Ocak-Araz, A. Birden, S.U. Bayca, O. Bican, *Effect of Powder-Pack Boronizing on the Microhardness, Wear, and Corrosion Behaviors of AISI 304L Steel*, **J. of Materi Eng and Perform**, 33, 2024, p. 166–172.
- [34] A. Günen, M. S. Gök, A. Erdoğan, B. Kurt, N. Orhan, *Investigation of Microabrasion Wear Behavior of Boronized Stainless Steel with Nanoboron Powders*, **Tribology Transactions**, 56:3, 2013, p.400-409.
- [35] M.I. Ismail, S.S. Iskander, E.B. Saleh, *Carburizing of steels*, **Surface Technology**, 12, 4, 1981, p. 341-349.
- [36] B. Edenhofer, D. Joritz, M. Rink, K. Voges, **Thermochemical Surface Engineering of Steels**, Woodhead Publishing, Cambridge UK, 2015, p.485–553.
- [37] Y. Xue, Y. Yan, W. Yu, M. Dong, J. Shi, M. Wang, *Microstructure and fatigue properties of 17Cr2Ni2MoVNb gear steel after gas carburizing and low-pressure carburizing*, **International Journal of Fatigue**, 167, Part A, 2023, 107314.
- [38] X. Yu, X. Shen, Y. Wei, W. Zhao, Y. Li, F. Xing, Y. Su, *Effect of Minor Carburizing on Microstructure and Mechanical Properties of M50 Bearing Steel*, **Steel research int**, 93, 2022, 2100767.

- [39] Y. Wang, Z. Yang, F. Zhang, D. Wu, *Microstructures and mechanical properties of surface and center of carburizing 23Cr2Ni2Si1Mo steel subjected to low-temperature austempering*, **Materials Science and Engineering: A**, 670, 2016, p.166-177.
- [40] Y. Wei, X. Yu, S. Wang, X. Shen, W. Zhao, Y. Su, Y. Yang, X. Feng, *Effect of Short-Time Carburizing Treatment on Microstructure and Mechanical Properties of M50 Steel*, **Metals and Materials International**, (2023) 29:1586–1595.
- [41] G. Parrish, **Carburizing: Microstructure and Properties**, ASM International, 1999, USA.
- [42] S.R. Al-Sayed, A.A. Hussein, A.A. Nofal, S.I. Hassab Elnaby, H. Elgazzar. *Characterization of a Laser Surface-Treated Martensitic Stainless Steel*, **Materials**, 2017; 10(6):595.
- [43] J.S. Selvan, K. Subramanian, A.K. Nath, *Effect of laser surface hardening on En18 (AISI 5135) steel*, **Journal of Materials Processing Technology**, 91, 1–3, 1999, Pages 29-36.
- [44] C. Soriano, J. Leunda, J. Lambarri, V. García Navas, C. Sanz, *Effect of laser surface hardening on the microstructure, hardness and residual stresses of austempered ductile iron grades*, **Applied Surface Science**, 257, 16, 2011, p.7101-7106.
- [45] M. Moradi, D. Ghorbani, M.K. Moghadam, M. Kazazi, F. Rouzbahani, S. Karazi, *Nd:YAG laser hardening of AISI 410 stainless steel: Microstructural evaluation, mechanical properties, and corrosion behavior*, **Journal of Alloys and Compounds**, 795, 2019, p. 213-222.
- [46] J. C. Ion, *Laser Transformation Hardening*, **Surface Engineering**, 18(1), 2002, p.14-31.
- [47] G. Shi, P. Ding, J. Liu, H. Yin, J. Wang, *Microstructure and properties of laser surface hardened M2 high speed steel*, **Acta Metallurgica et Materialia**, 43, 1, 1995, p.217-223.
- [48] M. Moradi, M.K. Moghadam, M. Shamsborhan, *How the laser beam energy distribution effect on laser surface transformation hardening process; Diode and Nd:YAG lasers*, **Optik**, 204, 2020, 163991.
- [49] J. Rana, G.L. Goswami, S.K. Jha, P.K. Mishra, B.V.S.S.S. Prasad, *Experimental studies on the microstructure and hardness of laser-treated steel specimens*, **Optics & Laser Technology**, 39, 2, 2007, p. 385-393.
- [50] N. M. Salleh, M. Ishak, M. H. Aiman, Q. Zaifuddin, and M. M. Quazi, *The effect of laser surface hardening on the surface hardness of mild steel*, 2020 **IOP Conf. Ser.: Mater. Sci. Eng.** 788 012014.
- [51] V. C. Bommi, K. M. Mohan, S. Prakash, *Surface Modification of Martensitic Stainless Steel Using Metal Working CO2 Laser*, **Proceedings of International Symposium of Research Students on Materials Science and Engineering**, Chennai, India, December 20-22, 2004.
- [52] J. Liu, Y. Song, C. Chen, X. Wang, H. Li, C. Zhou, J. Wang, K. Guo, J. Sun, *Effect of scanning speed on the microstructure and mechanical behavior of 316L stainless steel fabricated by selective laser melting*, **Materials & Design**, 186, 2020, 108355.
- [53] T. Kurzynowski, K. Gruber, W. Stopyra, B. Kuźnicka, E. Chlebus, *Correlation between process parameters, microstructure and properties of 316L stainless steel processed by selective laser melting*, **Materials Science and Engineering: A**, 718, 2018, p. 64-73.
- [54] X. Kang, S. Dong, H. Wang, S. Yan, X. Liu, B. Xu, *Effect of laser power on gradient microstructure of low-alloy steel built by laser melting deposition*, **Materials Letters**, 262, 2020, 127073.
- [55] K. Li, D. Li, D. Liu, G. Pei, L. Sun, *Microstructure evolution and mechanical properties of multiple-layer laser cladding coating of 308L stainless steel*, **Applied Surface Science**, 340, 2015, Pages 143-150.
- [56] X. Jiao, J. Wang, C. Wang, Z. Gong, X. Pang, S.M. Xiong, *Effect of laser scanning speed on microstructure and wear properties of T15M cladding coating fabricated by laser cladding technology*, **Optics and Lasers in Engineering**, 110, 2018, p. 163-171.

- [57] K. Wang, B. Chang, J. Chen, H. Fu, Y. Lin, Y. Lei, *Effect of Molybdenum on the Microstructures and Properties of Stainless Steel Coatings by Laser Cladding*, **Applied Sciences**, 2017; 7(10):1065.
- [58] G. Telasang, J. Dutta Majumdar, G. Padmanabham, M. Tak, I. Manna, *Effect of laser parameters on microstructure and hardness of laser clad and tempered AISI H13 tool steel*, **Surface and Coatings Technology**, 258, 2014, p. 1108-1118.
- [59] W. Gao, S-C. Wang, K-K. Hu, X-Z. Jiang, H-Y. Yu, D-B. Sun, *Effect of laser cladding speed on microstructure and properties of titanium alloy coating on low carbon steel*, **Surface and Coatings Technology**, 451, 2022, 129029.
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