



LASER SURFACE HARDENING OF BEARING STEELS

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**SCHOOL OF MECHANICAL AND AEROSPACE
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LASER SURFACE HARDENING OF BEARING STEELS

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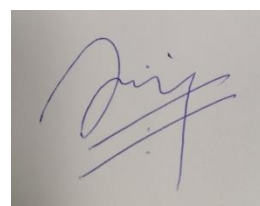
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Assoc. Prof. Wei Zhou

Authorship Attribution Statement

This thesis contains material from 3 paper(s) published in the following peer-reviewed journal(s) where I am the first author.

1. Part of Chapter 5 is published as N. Maharjan, W. Zhou, Y. Zhou, Y.C. Guan, and N. Wu, "Comparative study of laser surface hardening using continuous laser and pulsed lasers with ms, ns, ps and fs pulse duration," *Surface & Coatings Technology*, vol. 366 (pp311-320), 2019. DOI: 10.1016/j.surfcoat.2019.03.036

The contributions of the co-authors are as follows:

- Assoc. Prof. Wei Zhou conceptualized the idea and edited the manuscript drafts.
- I wrote the drafts of the manuscript. I performed all the experiments and characterization studies. I also analyzed the data with the help from Assoc. Prof. Wei Zhou.
- Dr. Yu Zhou assisted in revising the manuscript drafts.
- Prof. Yingchun Guan assisted in nanosecond and picosecond laser treatment and helped in interpreting the results and editing the manuscript drafts.
- Dr. Naïen Wu provided millisecond and continuous laser for the experiment and supervised the experimental trials.

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The contributions of the co-authors are as follows:

- Assoc. Prof. Wei Zhou conceived the idea, provided the initial project direction and edited the manuscript drafts.
 - I prepared the manuscript drafts. I designed the experiments together with Assoc. Prof. Wei Zhou and performed laser hardening trials at Precision Laser Solutions Pte. Ltd. All laboratory works including metallography, hardness testing and microscopy were conducted by me in Materials Lab 1 and 2, School of Mechanical and Aerospace Engineering. I also analyzed the data and performed numerical modelling.
 - Dr. Yu Zhou assisted in providing research guidance and revising the manuscript drafts.
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The contributions of the co-authors are as follows:

- Assoc. Prof. Wei Zhou suggested the material for the study, supervised the project and edited the manuscript drafts.
 - I wrote the drafts of the manuscript. I performed all the experiments and characterization studies including microscopy and sample preparation. I also analyzed the data with the help from Assoc. Prof. Wei Zhou.
 - Dr. Yu Zhou assisted in revising the manuscript drafts.
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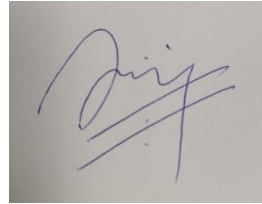
- Assoc. Prof. Wei Zhou supervised the project, assisted in interpretation of the results and revised the manuscript drafts.
- I was responsible for performing all the laser experiments and characterization studies in the lab. I also analyzed the data and prepared manuscript drafts.
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Apart from above papers, 2 more papers have been published in peer-reviewed journals (with me as co-author), but has not been included in the thesis.

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Abstract

Laser surface hardening has emerged as a promising technique to improve the wear resistance of machine components such as bearings, gears and camshafts. However, a lack of thorough understanding of the underlying mechanism coupled with the stringent requirements on surface properties still hinders its widespread application in industries. This thesis investigates various aspects of laser surface hardening of bearing steels (such as effect of operating parameters and laser types, microstructural changes, corrosion properties and improving effectivity) with an aim to elaborate the underlying mechanism and improve surface properties.

The laser hardening has been demonstrated using a continuous wave fiber laser which produces hard outer case owing to the martensitic transformation due to rapid heating and self-quenching. Hardness as high as 844 HV is achieved near the surface with depths up to 500 μm . A parametric study on the effect of various laser operating parameters such as defocus distance, power, speed and overlapping has been carried out which can be a significant input for designing of laser hardening system. Moreover, millisecond laser is shown to have similar hardening effect as continuous wave laser using lower power than continuous wave laser.

Further investigations with ultrashort pulsed lasers exhibit ablation capability than surface hardening. This can have potential application in surface cleaning and repair. Additionally, the corrosion properties of gradient microstructure produced by laser hardening are also explored by performing layer-by-layer electrochemical tests. The study shows that an improved corrosion resistance is found at the surface layer due to formation of chromium rich oxide layer and phase transformation, while the sub-surface does not show significant improvement in corrosion properties.

Abstract

Moreover, a novel gas assisted laser hardening is proposed to improve the effectiveness of laser hardening and achieve superior surface properties. The tests are performed in a specially designed chamber for better controllability of the process. Among different gases used, propane is found to have profound beneficial effect on the steel surface with maximum hardness reaching as high as 900 HV even for low carbon steel. This is attributed to the influx of carbon from the gas into steel which forms a carburized region near the surface. Depending on the parameters used, different microstructures are obtained in the near surface region ranging from eutectoid to eutectic composition. The potential applications of this technique to modify surface properties are also discussed.

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List of Symbols and Abbreviations

Symbols

I	Absorption rate
A_{c1}	lower austenitization temperature
A_{c3}	higher austenitization temperature
M_s	martensite start temperature
M_f	martensite finish temperature
D_b	Beam diameter
v	Process speed
kW	kilowatt
h	Displacement
P	Power
α	Ferrite
α'	Martensite
γ	austenite
E_{corr}	Electrochemical corrosion potential
j_{corr}	Corrosion current density
G	solidification gradient
R	Velocity of solid-liquid interface / solidification rate
$A(z)$	Absorption at depth z
K	Equilibrium constant
T	temperature
T_0	Ambient temperature
T_p	Peak temperature
t	time
f_c	Activity coefficient of carbon
P_{CO}	Partial pressure of carbon monoxide
P_{CO_2}	Partial pressure of carbon dioxide

List of Symbols and Abbreviations

J	Diffusion flux per unit cross section area per unit time
$\frac{\delta C}{\delta x}$	Concentration gradient
β	Mass transfer coefficient
E_a	Activation energy
α_l	Thermal diffusivity of material
g	Acceleration due to gravity
P_e	Peclet number
G_r	Grashof number
M_a	Reynold's number
ϕ_0	Peak fluence
ϕ_{th}	Threshold fluence
E_p	Pulse energy
ω_0	Spot diameter
λ	Thermal conductivity
$2L$	Diameter of pearlite colony
τ	Characteristic time for diffusion of carbon
C_p	Carbon potential of atmosphere
C_s	Carbon potential at the steel surface
ΔT_0	Temperature interval between liquidus and solidus

Abbreviations

BC	Band Contrast
BCC	Body Centered Cubic
BCT	Body Centered Tetragonal
CL	Carburized Layer
CNT	Carbon nanotube
CO ₂	Carbon dioxide
CW	Continuous Wave
EBSD	Electron Back-Scattered Diffraction
EDS	Energy Dispersive Spectroscopy
FCC	Face Centered Cubic
FFD	Free Ferrite Depth
GPa	Gigapascal
HAB	High Angle Boundary
HAZ	Heat Affected Zone
HV	Vickers hardness
IPF	Inverse Pole Figure
L/min	Liter per min
LAB	Low Angle Boundary
LHZ	Laser Hardened Zone

List of Symbols and Abbreviations

LIPSS	Laser Induced Pulsed Periodic Patterns
LMZ	Laser Melted Zone
Nd:YAG	Neodymium-doped Yttrium Aluminium Garnet
PDP	potentiodynamic polarization
XRD	X-Ray Diffraction

Chapter 1: Introduction

1.1 Background

The surface properties of a component are often a critical factor in determining its performance. The requirement for exceptional surface properties in applications such as tribology, biomedicine and aerospace, has ushered the scientists and the engineers to envisage innovative ideas to manipulate the surface and achieve the desirable efficiency [1–3]. These modifications might include modifying surface composition, microstructure, chemical reactivity, wetting, adhesion, lubrication, film formation, topology and so on. The ability to engineer such modifications, not only improves the integrity of the component, but also allows the same material to be used in diverse engineering applications.

The recent development of laser technology has opened new opportunities for surface processing of materials [4]. Apart from conventional cutting [5] and welding [6], lasers have emerged as a promising technique for innovation in surface material processing. Lasers, with their highly coherent monochromatic beam and unrivalled energy capacity, are excellent surface heating tools. A high-power laser can be directly subjected to the desired area such that it will only affect the irradiated area while virtually unaffected the bulk properties of the material [7]. Due to this property, lasers have been employed for localized processing applications such as hardening, cleaning, alloying, texturing and surface heat treatment. In addition, with the ease of automation and safety, they can be readily incorporated in industries for various purposes to increase production efficiency.

Surface hardening of steels has enjoyed considerable interest in the manufacturing industries as it offers the chance to improve components with idealized surfaces and bulk properties such as cams, bearings and shafts. Steel, being considered as an indicator of economic progress, is an integral

element of most systems. It is cheap, strong and durable and its properties can be altered significantly from a very soft, tough state to a very hard and stiff state just by a simple heat treatment operation to suit a specific application [8]. It is therefore, of little surprise that lasers are being used for surface hardening of steel [9,10].

1.2 Motivation

Laser surface hardening offers short processing time, flexibility in operation and economy in comparison to conventional counterparts to modify surface behavior of steels and prevent wear and corrosion [11]. It does not require a separate quenching medium as the bulk of material itself acts as heat sink which makes it an attractive solution for manufacturers. Even though a lot of studies have been performed in laser hardening, the investigations on underlying mechanisms are relatively undervalued compared with the booming laser development.

With the expensive laser systems such as fiber lasers, Nd:YAG lasers and ultrashort pulse lasers becoming affordable for use in even medium and small enterprises, it has become essential to update our knowledge on their possibilities for surface modifications. These compact laser systems can be seamlessly incorporated with the existing industrial robotic systems to achieve the desired production efficiency. However, due to this lack of thorough understanding of the laser steel interaction, the real industrial application of the process still relies on hit-and-trial method, which is very expensive and ineffective. Therefore, there is a dire need to develop the basic understanding of the process and utilize the knowledge to pave the way for its industrial application at economic cost.

Furthermore, the extreme operational conditions experienced by machine components put a stringent demand on their surface properties. Components like gears, bearings and shafts operating in harsh conditions require superior wear and corrosion properties. These requirements can be easily met using laser-based surface processing techniques. Interaction of laser beam with the

steel surface can induce rapid phase transformation at the surface producing phases with better corrosion and wear resistance than base material [12]. In addition, lasers also offer opportunity to explore innovative methods to improve the surface hardness and microstructure of the components. However, despite some studies done in the past, there are still a lot of avenues to explore in this direction.

This thesis demonstrates the rapid phase transformation of various steels during laser surface hardening, and analyzes the corresponding phase transformation, microstructural evolution and surface performance of the hardened region. Systematic studies have been performed to investigate the non-equilibrium kinetics of laser hardening process and the influence of various operating parameters on hardening of the steel. Furthermore, the feasibility of using short pulse lasers, including nanosecond and femtosecond lasers, for surface hardening is also explored. The ablation mechanism during short pulse lasers was found to be suitable for surface cleaning which can be useful for remanufacturing and surface preparation prior to other processes such as welding and coating. Moreover, a novel laser surface hardening technique using special carburizing gases is also discussed which can produce ultrahigh hardness at the surface than any other conventional processes.

1.3 Objectives

With an aim to elucidate the mechanisms of laser hardening process, the following were set as the main objectives of the project:

- To understand the non-equilibrium phase transformation and microstructural changes occurring in the steel during laser surface processing and the influence of operating parameters on its properties
- To explore the surface properties before and after laser treatment
- To investigate the feasibility of using short pulse laser for surface processing applications

- To achieve steel surface with superior hardness and excellent surface properties for application in machine components such as bearings, shafts and cams.

1.4 Scope

Laser surface processing is a broad subject and covers different aspects of laser-material interactions. Depending on the laser parameters and the material properties, different phenomena occur during laser processing such as surface melting, hardening, phase transformation, de-carburization, ablation, surface oxidation and so on. The major focus of this thesis is on laser surface hardening of steels for possible application in bearing and tooling industries.

As such, an elaborative technology benchmarking study on laser heat treatment technology is conducted to identify the technology readiness level of the process. After identifying the current challenges, the study concentrates on exploring the use of various types of lasers to meet the industry demand of achieving high quality surface and optimizing the process. For this, the basic underlying mechanism of hardening is investigated in detail and probable new methods such as coating and surface gas carburizing are attempted. The study focuses on expediting the knowledge on laser hardening mechanism and developing methods to improve surface hardness. On realizing the tremendous potential of short pulse laser ablation for surface cleaning, further studies are carried out in this direction as well which can be beneficial for remanufacturing applications. Other laser surface processing mechanisms like texturing, adhesion and wettability do not fall within the scope of this study.

After defining the scope, the followings are set as the deliverables of the project:

- Literature review on the state-of-the-art heat treatment and laser technology

- An in-depth understanding of microstructural changes occurring during laser hardening
- Methods to improve surface hardness and surface mechanical properties of steels using laser
- Recommendations for future improvements of the process

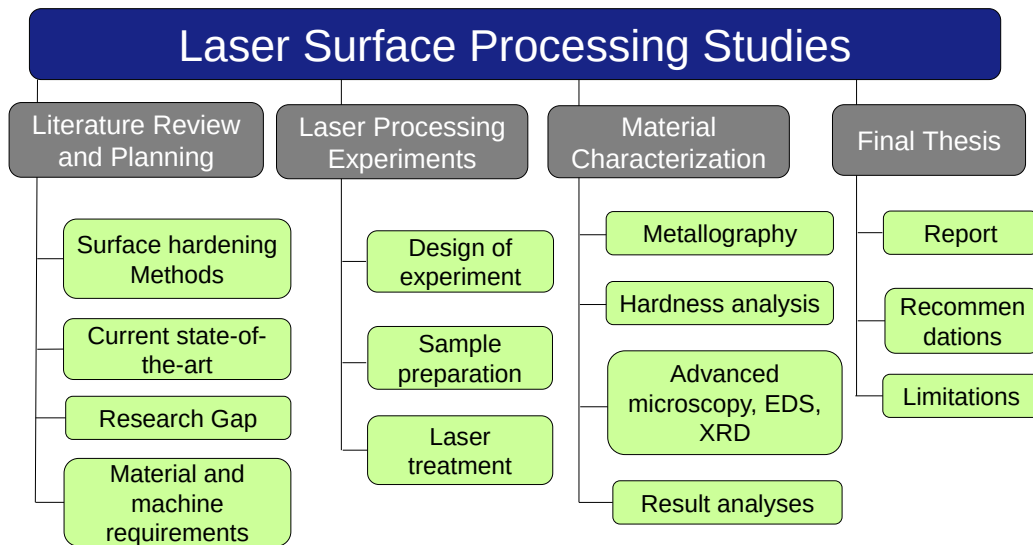


Figure 1.1: Work Breakdown Structure for the project.

1.5 Thesis Outline

This dissertation has been organized as follows. A brief background on laser surface processing of steels and main objectives of the current study are presented in Chapter 1. Chapter 2 provides an elaborative review on existing literature related to laser surface hardening and current state-of-the-art. The existing technology is critically reviewed and research gaps are identified. In Chapter 3, the materials and methodology used for the study are presented. Chapter 4 focuses on fundamentals of basic laser hardening mechanism using 50CrMo4 steel as reference and discusses the influence of various operating parameters on surface hardening. The feasibility of using pulsed lasers is explored in Chapter 5 which also investigates on possibility of using pulsed laser ablation for surface cleaning. Furthermore, the corrosion behavior of hardened steel surface is presented in Chapter 6. Chapter 7

Chapter 1: Introduction

details methods of improving surface hardness by various techniques such as underwater hardening, using graphite coatings and laser gas alloying. Finally, the major conclusions from this research work with a brief outline of possible further researches are summarized in Chapter 8.

Chapter 2: Literature Review

2.1 Laser

Light Amplification by Stimulated Emission of Radiation (laser) has revolutionized our way of living. The introduction of laser technology in 1960s brought a massive interest in this field with possibility of its use in all kinds of field. At that time, laser was considered as a step into the future and a tool looking for an application. With industries pushing for high power lasers for application in material processing, billions of dollars were investigated to develop high power lasers. Now, we have lasers capable of doing just anything from ablation and material deposition to drilling, cutting, joining, producing metallurgical changes and inducing stresses, as well as texturing and cleaning surfaces. They are also flexible enough to be used in any material like metals, glass, plastics or even skin, which gives them a competitive advantage than other conventional tools. With the talks of Industry 4.0 and digitized manufacturing, laser light will be a perfect tool to match the requirement of speed, directness, flexibility and interconnectivity demanded by the factory of the future [13].

2.2 Historical overview of industrial lasers

Lasers have become an essential tool in manufacturing industries. Ever since the invention of the first working ruby laser by Maiman in 1960 [14], much has been discussed on its potential as a tool for future manufacturing.

In the 60s and 70s, first generation of CO₂ lasers [15] and Nd:YAG lasers [16] were developed which were unreliable, bulky and required high maintenance cost. Therefore, they were primarily adopted for scientific use and research. Industrial applications were limited to those that could not be achieved by

conventional technologies like drilling holes, packaging and alignment applications.

The 80s and 90s saw a rapid improvement in laser technology with development of new lasers such as diode pumped solid laser [17–19] and excimer lasers [20]. The car production and sheet metal cutting industries soon realized the advantage of this new technology and started utilizing lasers in their processing. This created a boom in laser processing industries and a lot of companies entered the market like TRUMPF, Polaroid, Spectra Diode Labs, IPG Photonics and so on.

Disk lasers [21] and fiber lasers [22] were soon introduced in 90s and 2000s which opened a whole new avenue for industrial application of lasers. They made the laser technology accessible for small and medium scale companies. Now, laser processing is performed on virtually every product manufactured in at least one part of its manufacturing cycle. Some major application areas are semiconductor, packaging, marking, consumer good, energy generation, transport, aerospace, defense, medicine and so on.

The lasers used in material processing utilizes lasers as a source of heat generation for cutting, welding, machining and surface modifications. Figure 2.1 shows the application of different lasers in industries. Now, the studies are pushing towards even higher power density, ultrashort laser pulses and novel applications of laser. Researchers are investigating to utilize other laser properties such as polarization, phase, pulse length and coherence.

One example is frequency comb generated by ultrafast lasers with potential application in precision metrology [23]. The other significant trend is the use of laser in additive manufacturing [24]. The high-power laser provides an excellent tool for rapid production of components while its capability to easily be automated and controlled numerically crowns its unanimity as an ideal tool for digitalized manufacturing. It is undeniable that lasers will play a significant role in shaping future of manufacturing industries.

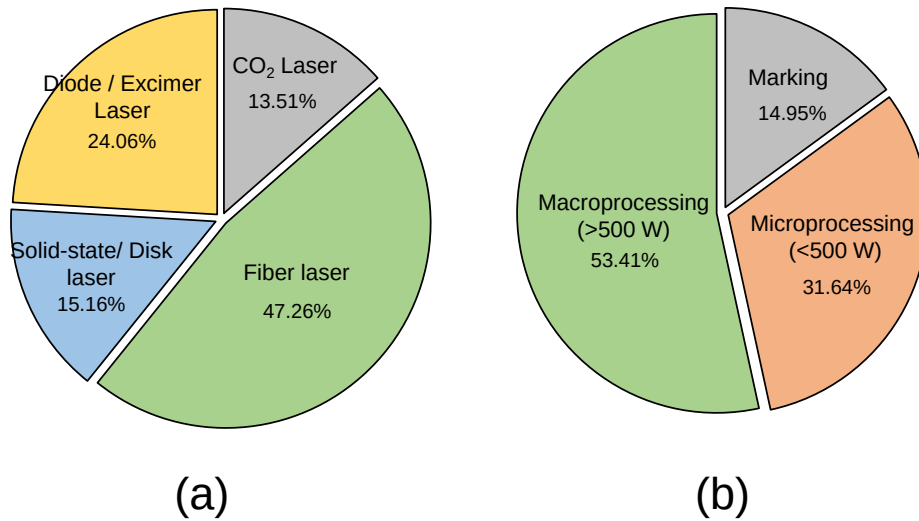


Figure 2.1: Lasers used for different industrial applications: (a) Types of lasers used in material processing industries; and (b) various industrial applications of lasers. The percentage represents the revenues generated from industrial lasers in the year 2017 [25].

2.3 Interaction of laser beam with material

The interaction of laser beam with material involves a complex phenomenon and can generate a range of change in the material [4]. A laser is basically a coherent beam of electromagnetic radiation with electric field and magnetic field perpendicular to each other propagating in space (see Figure 2.2). When the laser is irradiated over the surface, part of the radiation is reflected from the surface, the other is transmitted through the material and the remaining is absorbed by the atoms.

As the beam passes through the material, the particles of the material are excited by electric field which results in forced vibration of particles. The force induced by electric field is generally not strong enough to vibrate an atomic nucleus. However, the photons can be absorbed by the free or bound electrons via inverse Bremsstrahlung process. This causes electrons to vibrate randomly. The excited electrons will either re-radiate energy in all

directions or be restrained by the lattice phonons. Especially in solids where the atoms are compact, the latter case occurs, and the vibration is coupled through the structure which is detected as heat [4].

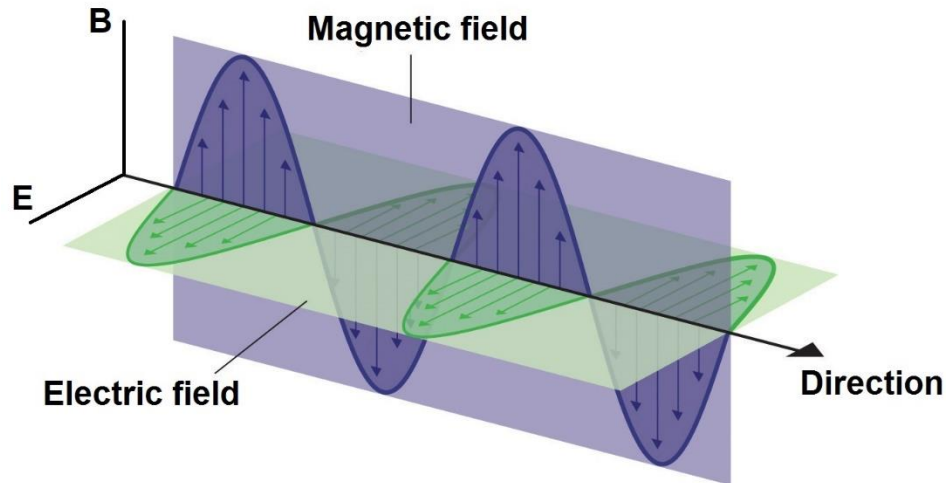


Figure 2.2: Electric and magnetic field vectors of an electromagnetic radiation.

The intensity of vibration depends on the energy of the incident laser beam and absorption rate. The power density determines the energy irradiating over a certain area and higher the density, higher will be the atomic vibration. The laser offers the highest power density available to the industry today which can only be rivalled by an electron beam. Such high power density can evaporate any material. And unlike electron beam, X-rays are rarely emitted during laser material processing (possible in only extreme cases about 1×10^{15} W power) which eliminates the need for protection against this hazard. On the other hand, just by defocusing the beam (either by changing beam optics or placing the component at out-of-focus position), the power density can be lowered to such an extent that it has no heating effect on the material. This makes laser a versatile tool capable of inducing any specified thermal effect to the material [4].

The absorption rate of laser beam varies exponentially as given by Beer Lambert's law, $I = I_0 \exp(-\alpha z)$, where α is the absorption coefficient which depends on the medium, wavelength and intensity of radiation. If sufficient energy is absorbed, then the intense vibration results in stretching of

molecular bonding beyond the point that it is no longer capable of exhibiting the mechanical strength and the material is said to be molten. An even higher absorption of energy results in strong molecular vibrations and ejection of the molecules due to further loosening of bonding, defined as ablation. The vapor can still absorb the radiation but only slightly since it will have bounded electrons. If the gas is sufficiently hot, the gas forms plasma in which electrons and ions are free and can absorb the radiation strongly.

On the other hand, the lower power density and energy absorption, which is not enough to cause melting, can alter the properties of the laser irradiated area. The energy might not be sufficient to rigorously stretch the molecular bonding; but it can be strong enough to bring transformation in the microstructure of material. This solid-state phase transformation can produce effects such as hardening or softening in metals. In some instances, such as laser cleaning, the power density is deliberately lowered so that energy is not absorbed by the base material or insignificant to bring about any change in the material; while the surface contaminants are ablated by direct absorption of the laser energy [26].

Therefore, depending on the power density of the laser beam and absorption coefficient of the material to the beam, the strength of molecular vibration differ which produces different effects on the material ranging from heat treatment to cutting, welding and direct material removal (see Figure 2.3). In this thesis, I will be focusing on the use of laser as a heat source for surface modification.

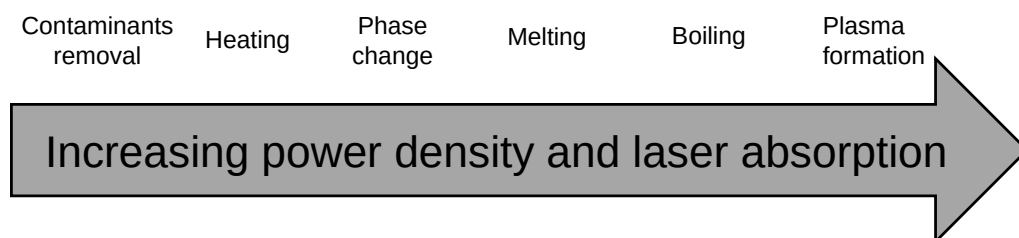


Figure 2.3: Different effects produced on the laser irradiated surface with increasing rate of power density and laser absorption.

2.4 Laser surface hardening

Laser surface hardening is a surface modification process used to selectively enhance the surface hardness and wear resistance of highly stressed parts such as bearings, cams and gears by phase transformation. The hardening is achieved by rapidly heating the surface with a laser beam. On moving the laser beam away, the bulk of the material acts as a large heat sink leading to rapid quenching and phase transformation of the heated surface. The result is a hard surface with virtually unaffected bulk material properties.

Depending on the laser intensity and material used, different surface engineering processes can be achieved as shown in Table 2.1 [27]. A detailed study of all these processes is out of the scope of this work and the current research will only focus on laser surface hardening.

Generally, laser transformation hardening is a solid-state process with no melting of the surface. However, hardening can still be achieved by partial melting and rapid solidification of the surface in which case it is termed as laser surface hardening or just laser hardening. In this thesis, the latter definition of laser hardening is inferred in most cases.

Laser hardening has numerous characteristic features that makes it suitable for adoption in manufacturing industries. Some of the distinct features are

- Fast and selective heat treatment of components
- Self-quenching process due to heat conduction to cold interior of the part, thus eliminating the need of using an external quenching medium
- Negligible part distortion and suitable for complex parts as well
- Low heat input energy to obtain desirable surface hardening effect
- No post processing
- Easy automation and numeric control to obtain required case depth
- Improved fatigue life and corrosion resistance

Table 2.1: Various surface engineering techniques similar to laser hardening [27].

Technique	Laser source	Description
Shock hardening	CO ₂ , Fiber, Nd:YAG, Disc, Excimer	Induces shock waves at surface using laser pulses to create hardened layer
Laser glazing	CO ₂ , Fiber, Disc, Nd:YAG, Diode, Excimer	Produces ultrafine microstructure in glasses
Laser cladding	CO ₂ , Fiber, Disc, Nd:YAG, Diode	Deposits a thin layer of second material onto a surface
Surface alloying	CO ₂ , Fiber, Disc, Nd:YAG, Diode	Selective addition of alloy to change surface properties
Surface impregnation	CO ₂ , Fiber, Disc, Nd:YAG, Diode	Fusion with addition of a solid fraction, e.g. Tungsten carbides
Surface texturing	CO ₂ , Fiber, Disc, Nd:YAG, Excimer	Develop patterns on surface
Photochemical modification	Excimer	Produces local changes for marking, bonding or change of surface hydrophobicity
Surface ablation	Excimer, Fiber, CO ₂ , Nd:YAG	Controlled removal of surface layer without damaging the substrate
Surface refining	Excimer	Rapid, shallow melting to vaporize inclusions and impurities

It is due to these advantages laser hardening is becoming recognized in industries as a suitable technique for surface modification of small and complex engineering components.

2.4.1 Laser hardening mechanism

Laser hardening process is basically a localized heat treatment process with laser beam acting as a source of heat. When a ferrous surface is irradiated with a high-power laser beam, the surface temperature rapidly rises above the austenitization temperature with rest of the component acting as a heat sink. This changes the atomic lattice structure of the surface while the bulk material is still at the room temperature. On moving the laser beam away, the heated surface undergoes “self-quenching” as heat dissipates to the bulk material in a very short time leaving no time for atoms to re-arrange. This produces a hard structure on the surface [9].

The process involves following mechanisms:

2.4.1.1 Austenitization

Steel is basically an alloy of iron and carbon with carbon ranging from 0.02 wt% to 2.11 wt%. The plain carbon steel having a eutectoid carbon percentage of 0.76 wt% has a pearlitic microstructure consisting of ferrite (α phase) and cementite (Fe_3C). Hypereutectoid steel has more than 0.76 wt% C and consists of pearlite and pro-eutectoid cementite. On the other hand, hypo-eutectoid steel, containing less than 0.76 wt% C consists of pro-eutectoid ferrite grains and pearlite colonies.

When laser hardening is performed, the temperature of the surface rises above the austenitization temperature (A_{c3}). At such high temperature, the body centered cubic ferrite matrix (α -phase) transforms to face centered cubic austenite (γ -phase). Austenite has higher solubility of carbon than ferrite and can dissolve up to 2.1% carbon at a temperature of 1147°C [8]. Under equilibrium condition, the austenitization (transformation of ferrite to austenite) for hypo-eutectoid steel starts at A_{c1} temperature and is completed at A_{c3} temperature as shown in the phase diagram in Figure 2.4. Heating rate as high as 1000 K/s is common during laser hardening with a steep temperature gradient [28]. The higher heating rate during laser hardening not only shifts the A_{c3} line up towards higher temperature [29], but also switches the

mechanism of austenite formation from carbon diffusion control to a massive mechanism [30]. Therefore, process parameters are generally set to produce a high peak temperature to achieve complete austenitization. However, care must be taken so that the peak temperature does not exceed the melting point of the steel.

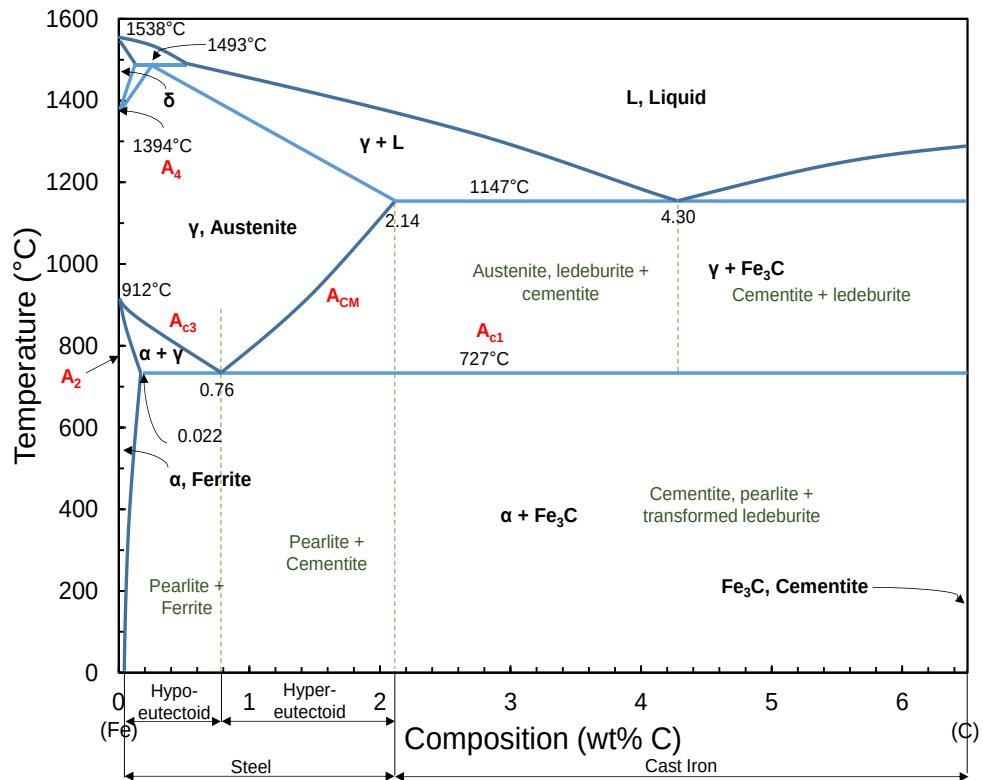


Figure 2.4: Equilibrium Iron-carbon phase diagram.

2.4.1.2 Homogenization

The transformation of ferrite to austenite, dissolution of cementite (Fe₃C) and carbon diffusion in austenite are all time dependent which means the high temperature must be maintained for sufficiently long period to allow diffusion of atoms and microstructure homogenization [31]. Thermal cycle during laser hardening is much shorter than conventional heat treatment. It lasts only for a few seconds or a fraction of second which is not enough for complete dissolution and diffusion of carbon in austenite. Such insufficient time can leave austenite with lower carbon content than in homogenized case reducing

the hardness of the martensite formed. On the other hand, prior-austenite grain size is also proportional to the time available for homogenization which directly influences the block and packet size in martensite [32].

2.4.1.3 Martensitic transformation

Under equilibrium condition, the cooling from high temperature is slow enough for carbon atoms to re-arrange and form a mixture of ferrite and cementite from austenite at room temperature. However, the cooling is very fast during laser hardening with the bulk material acting as heat sink. The cooling rate can reach up to 10^4 - 10^7 K/s. At such high cooling rate, carbon atoms are trapped in the lattice and results in formation of martensitic phase (α' phase) (Figure 2.5). Martensite has body-centered tetragonal (BCT) lattice structure due to slight shift of iron atoms to adjust for trapped carbons, thus providing a barrier to slip. Therefore, the high internal stresses inside the BCT lattice make martensite hard but also brittle [33].

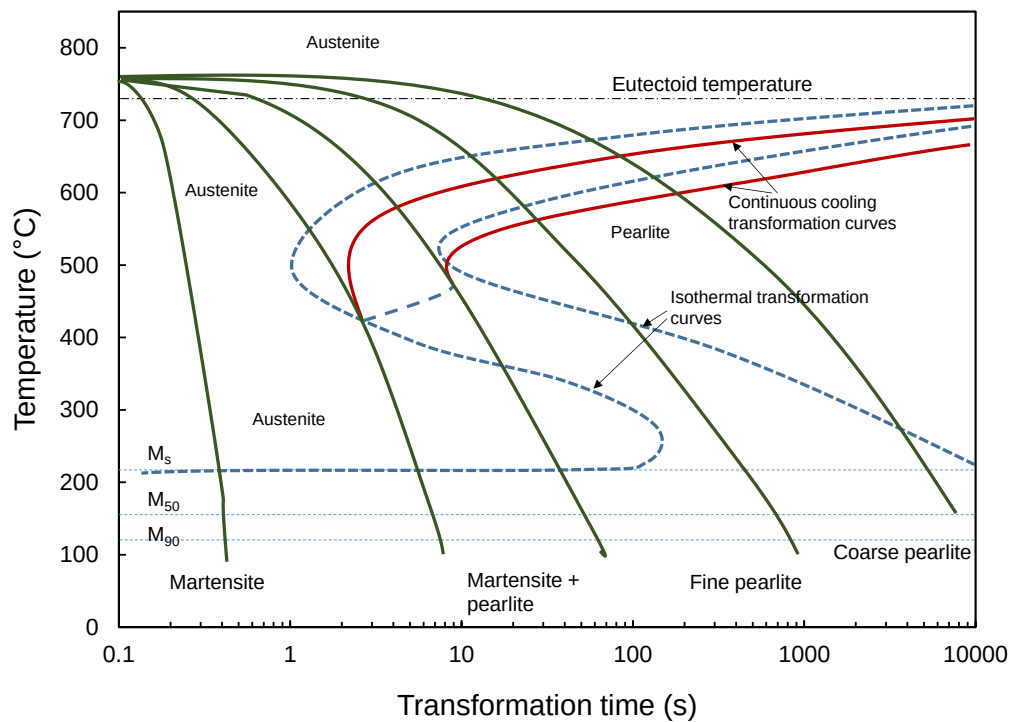


Figure 2.5: A typical continuous cooling transformation (CCT) diagram for eutectoid steel with 0.77 wt% carbon [34].

During cooling, the martensite transformation starts at a certain temperature called martensite start temperature, M_s and finishes at a lower temperature called martensite finish temperature, M_f , as shown in CCT diagram in Figure 2.5. Figure 2.6 shows that M_s and M_f decreases significantly with increasing carbon content in Fe-C alloys and carbon steels. Addition of alloying elements also reduces the M_s temperature. Higher carbon content or presence of alloying elements increases the shear resistance of austenite and, therefore, a greater driving force is required to initiate the martensite transformation [35]. It is also interesting to note that the cooling rate during laser hardening is generally high enough for martensitic transformation even in low carbon steel.

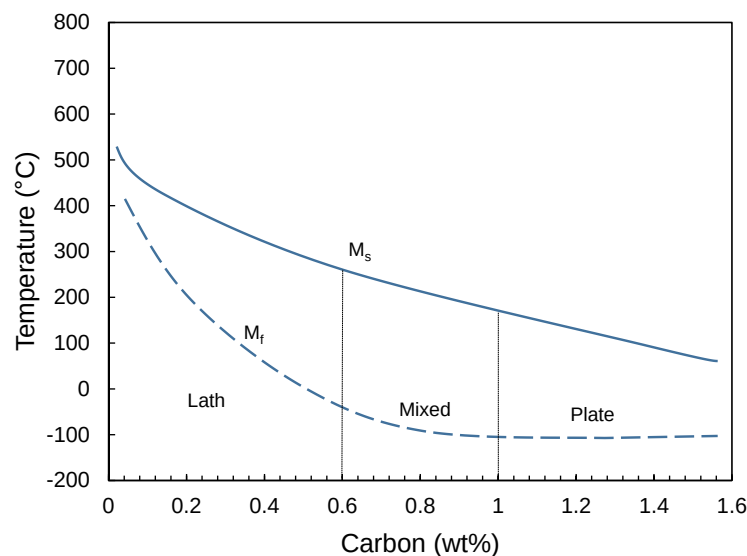


Figure 2.6: M_s and M_f temperatures as functions of carbon content in steels [35,36].

2.4.2 Laser hardenable steels

Generally, any steels that can be hardened by conventional heat treatment can also be hardened by laser hardening method. The commonly used materials in laser hardening are plain carbon steels (AISI 1040, AISI 1045) [37–39], low alloy steels for dies (AISI 4140, x40Cr13, AISI 5135) [40,41], heavy duty and ball bearing steels (AISI 52100) [42], tool steels (X210CrW12, AISI H13) [43,44], martensitic stainless steel (AISI 420, 440C) [45,46] and other steels [47,48]. The maximum attainable surface hardness depends on

the carbon content of the steel [49]. Higher carbon content increases hardenability of the steel i.e. the ability of steel to form martensite on quenching. As a result, the maximum attainable hardness is increased. During laser hardening, this is primarily dictated by the operating parameters used. The laser hardening has also been applied for surface hardening of non-ferrous materials like zirconium and niobium alloys used in pressurized tubings in power generation [50] and titanium alloys used in biomedical implants [51].

2.4.3 Parameters affecting hardening

The laser hardening process is a complex phenomenon and is affected primarily by the material properties and laser operating parameters.

2.4.3.1 Material properties

Composition and microstructure

The hardness of the surface after laser treatment depends primarily on the hardness of the martensite formed. The hardness is directly proportional to the amount of carbon content in the steel (see Figure 2.7). However, at higher carbon content, there is a high possibility of formation of retained austenite at room temperature which can reduce the hardness [52]. The presence of alloying elements such as Ni, Mn, Cr and Mo also increases the volume of retained austenite. They form alloy carbides which requires higher temperature and longer austenitization time for dissolution [31]. In addition, alloying elements tend to increase the thermal conductivity of the steel with increase in temperature [53]. Increased thermal conductivity results in higher penetration depth, but a lower peak temperature at the surface.

Apart from alloying elements, the initial microstructure significantly affects the diffusion of carbon and thus, the resultant hardening effect. For eutectoid steel, the carbon diffusion depends on the interlamellar spacing in pearlite. The carbon diffusion is more efficient in microstructure with finer initial grain resulting in formation of martensite with negligible retained austenite.

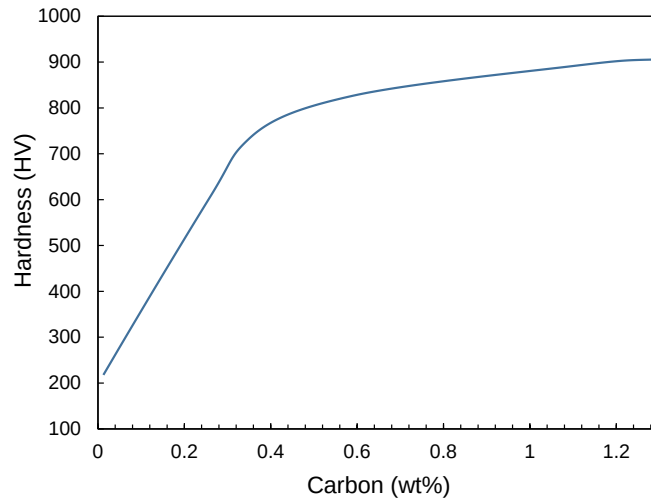


Figure 2.7: Typical martensitic microstructure hardness as a function of steel carbon content after quenching [52].

Surface condition and absorptivity

The capacity of a material to absorb laser energy is greatly affected by the surface texture and initial surface condition [54]. Surface roughness leads to multiple reflection of laser beam in the undulations. The multiple reflection results in effective absorption of energy. It is for this reason that sand blasting improves laser absorptivity. However, if the average surface roughness is less than the beam wavelength, the absorption of radiation will not be affected since the surface will be perceived as flat.

The absorptance of steel increases with increasing levels of surface oxide. As shown in Table 2.2, oxides have higher absorptivity than the steel surface. Thus, the presence of surface oxides increases absorption of laser beam at the surface facilitating laser hardening process. Pantsar and Kujanpää [55] reported that growth of absorbing oxide layer enhances absorptivity significantly reducing the laser power required for hardening by as much as 50%. Interestingly, in stainless steels, the oxide layer growth is limited owing to their high corrosion resistance which limits the increase in absorptivity. Moreover, a relatively clean metal surface of cold rolled mild steel is more reflective than a pickled and oiled hot rolled surface.

Table 2.2: Absorptance of different iron oxides and steels for laser beam with different wavelengths and different surface conditions [56]. Note that the absorptance of hot rolled steels is higher than those of cold rolled ones due to presence of oxides on the surface.

Material	Absorptance	
	$\lambda = 1053 \text{ nm}$	$\lambda = 527 \text{ nm}$
FeO	81%	80%
Fe ₂ O ₃ (hematite)	69%	97%
Fe ₂ O ₃ (magnetite)	80%	83%
Mild steel (cold rolled)	52%	67%
Mild steel (hot rolled, pickled)	68%	78%
Stainless steel (cold rolled)	37%	44%
Stainless steel (hot rolled)	56%	65%

Geometry

The surface geometry determines the heat flow during hardening. Typically, a flat surface to be laser hardened has a large bulk material size which works as a huge sink resulting in high quenching rate and desired hardness. However, the geometry of a component might not be always flat.

Take cam used in automobile as an example. The convoluted surface geometry of the cam pieces coupled with their low wall thickness presents a challenging aspect for laser hardening. Depending on the geometry, it needs to be ensured that the laser beam always provides the optimum heat input as it travels over the component, in both the flat and the curved sections.

If the same beam processing parameters are used for hardening, some areas of the component might be overheated with even melting occurring at the finer edges and contour steps; and some areas might receive low laser power which cannot produce required hardening depth [57]. Therefore, a controlled hardening must be performed in such case to obtain optimum hardening.

2.4.3.2 Laser operating parameters

Wavelength

The absorptivity of laser beam by a material is strongly dependent on its wavelength. Figure 2.8 shows the absorption of radiation at different wavelengths for different materials. Steel is very reflective to CO₂ laser beam which has wavelength of around 10.6 μm . Therefore, some absorptive coating or a black paint is used to increase surface absorptivity during CO₂ laser treatment. The absorption normally increases with decrease in wavelength. It is for this reason the Nd:YAG, diode and fiber lasers operating at lower wavelengths have higher absorptivity and higher efficiency. Although coatings are not required for such lasers, it has been found that coating can still improve the surface absorptivity to as high as 85% in steel [58].

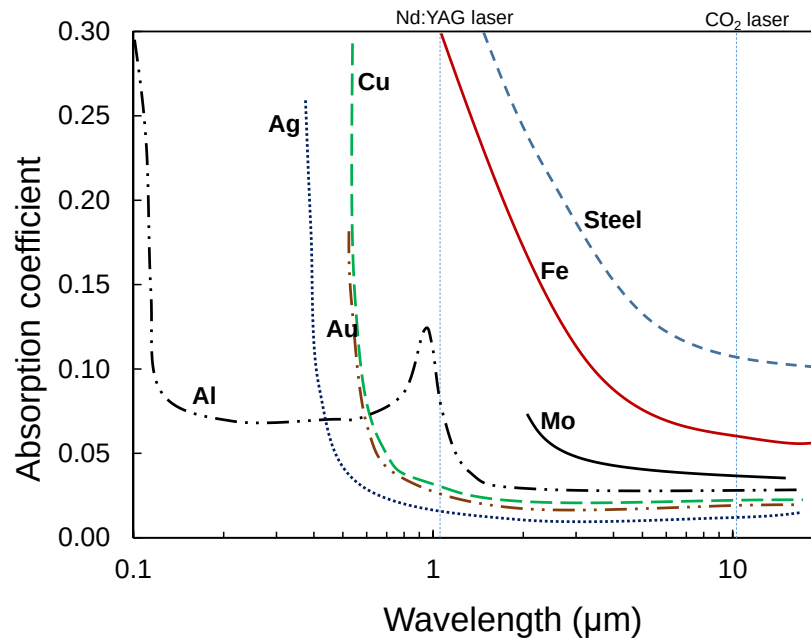


Figure 2.8: Graph showing the absorption of laser radiation at different wavelengths for different metals [59].

Power density

Laser power density has been previously termed as the ratio of laser power to the product of beam diameter and process speed in some literature [60–62].

Although this definition is still used to include the effect of speed in the power density term, it should describe the intensity of laser beam in a defined area. Therefore, a more correct description would be to define it as the ratio of laser power to the area of the beam.

Generally, a power density of 10^3 - 10^5 W/cm² is used for laser hardening as it brings about only the hardening effect without surface melting [63]. As can be seen in Figure 2.9, laser hardening requires a lower power density and longer interaction time. In practice, however, hardening can be achieved even by using higher power density at short interaction time. Highly hardenable steels can be treated with low power density and a longer interaction time to produce a homogeneous microstructure with significant hardened depth. For steels of low hardenability, a higher laser power density and short interaction time is preferred to achieve a faster cooling rate required for martensite formation [64].

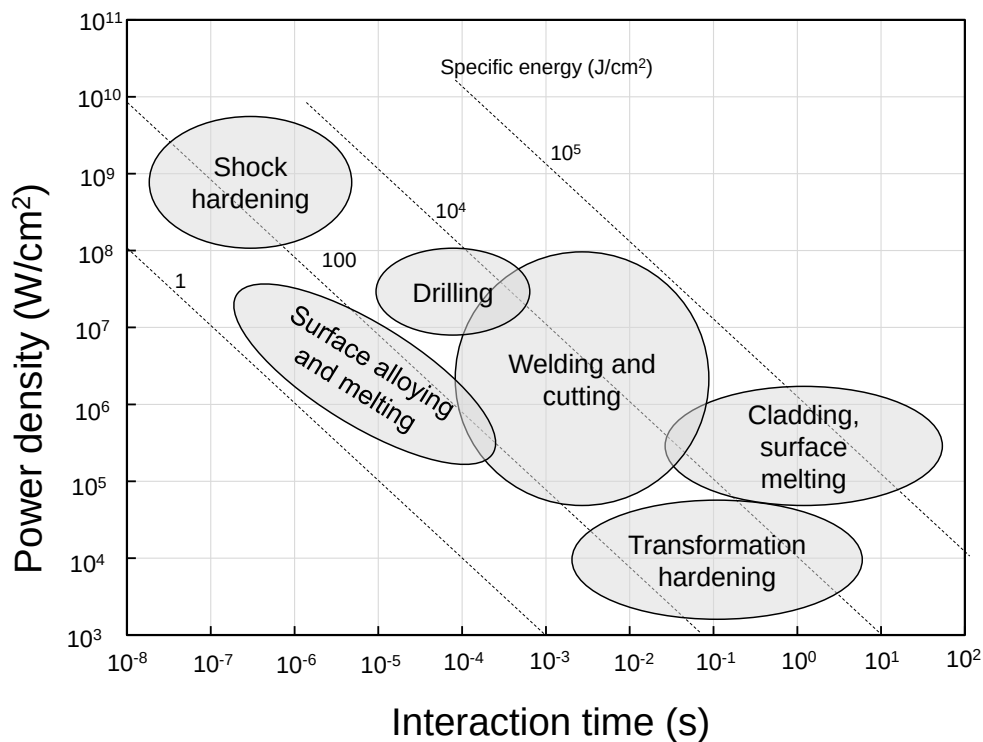


Figure 2.9: Interaction time and power density required for various laser processing methods [63].

Process speed

The process speed determines the time for laser to interact with steel and greatly affects the hardening process. Generally, process speed is optimized such that the interaction time is long enough for microstructure homogenization and formation of martensite on cooling. Too slow speed may result in surface melting while too fast speed can leave the surface unaffected. Therefore, an optimized speed is generally determined experimentally before validating the system for industrial use.

Laser beam shape

The laser beam shape is chosen such that the power is uniformly distributed across the whole beam profile. The uniform power distribution produces equal hardening depth across the width of the beam. A Gaussian power distribution generates a hemispherical hardened zone and may cause melting at the surface exactly below the beam center position. Therefore, a rectangular beam profile is generally preferred in laser hardening which can produce a uniform hardened width over a large area (see Figure 2.10) [65]. Shaping optics have also been used to generate varieties of shaped beams that has high coverage rates and uniform hardening depth.

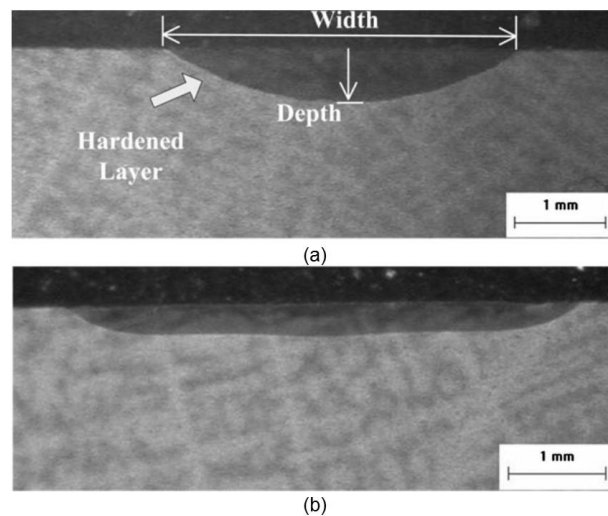


Figure 2.10: Cross section microstructure of hardened layers produced by a Gaussian beam and a shaped beam in 42 CrMo cast steel [40].

Process gas

Use of process gas is not mandatory for laser hardening; but it has two main advantages. First, it minimizes oxidation in the laser hardened surface, thus preventing increase in absorptivity and surface overheating. Second, it protects the optics from being contaminated during the process. Generally, argon is used as a shielding gas during laser hardening due to its inert nature [66–68]. The gas is supplied at the hardened area using a nozzle at the rate of 5-20 L/min. Use of carburizing gases might result in surface reaction inducing carbon at the surface producing a very high hardness during rapid heating and cooling during laser hardening. But, no studies were found in this direction.

Overlapping

The component to be hardened is usually larger than the size of beam. Therefore, multiple hardening tracks are used to harden the whole area. However, during multitrack hardening, the hardened zone might get tempered depending on the percentage of overlap. This produces a tempered microstructure in the overlapping zone which has lower hardness [69]. The result is a non-uniform hardness across the surface. It has been found that a minimum overlapping percent generally produces a more uniform surface properties and better corrosion behavior [12].

2.4.4 Industrial applications of hardening

Laser hardening is basically a surface heating method and doesn't require high beam quality. Although the basics for laser hardening was established a long time ago, industry has been slow to adopt this technique for applications other than manufacturing of small components. This could be probably due to the previously high cost of the laser systems and associated complexity of the process. With invention of new lasers, this forgotten technology has been gaining renewed interest for use in processing of heaving duty components and complex geometries [70]. Some applications of laser hardening in industries are shown in Figure 2.11 and Table 2.3.

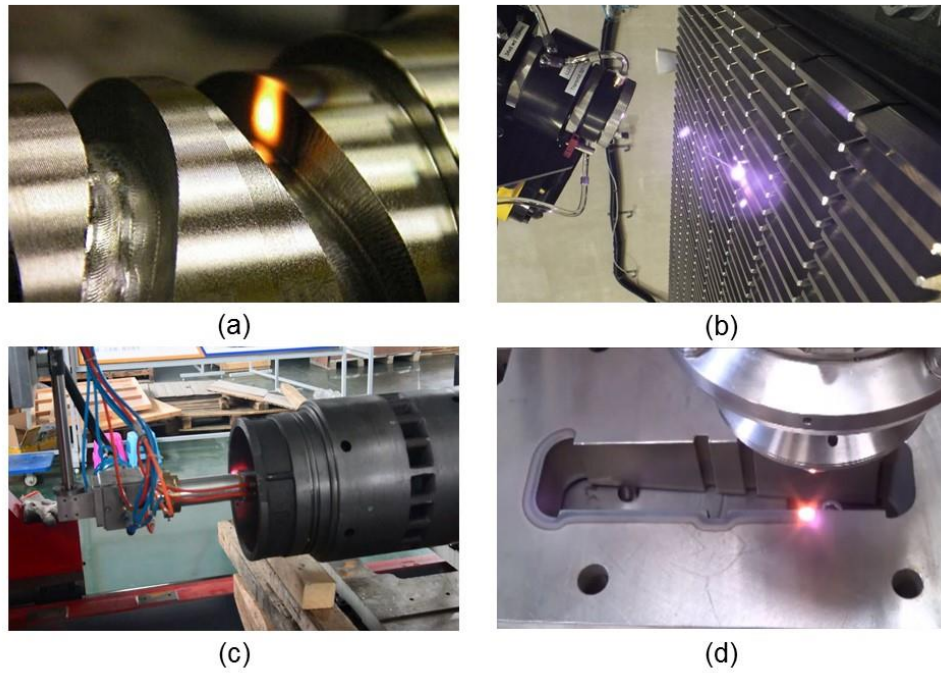


Figure 2.11: Typical laser hardening applications showing hardening of (a) camshaft [57]; (b) gear teeth [71]; (c) automobile engine inner cylinder liner [72]; and (d) stamping die [73].

Table 2.3: Applications of laser hardening in various industries.

Component	Industry	Material	
Bearings	Automotive, Energy generation	AISI 52100	[74]
Blanking die	Automotive	Tool steel	[75]
Gear teeth	Machinery	AISI 1060 / low alloy steel	[76]
Camshaft	Automotive	Grade 17 cast iron	[57]
Torsion springs	Automotive	DIN 58CrV4 steel	[77]
Engine valve	Automotive	Tool steel	[78]
Turbine blade edge	Power generation	Martensitic stainless steel	[79]
Drive Shafts	Machinery	steel	[80]
Engine components	Automobile	Steel, cast iron	[81]
Press brake tools	Machinery	steel	[82]

2.4.5 Competing techniques

Laser hardening technology is not the only method that can be used for surface modifications in industries. It competes with many other established methods of surface treatment. While each technique has its own unique advantages and limitations (see Table 2.4), the laser hardening technique offers a competitive advantage in terms of speed, precision, controllability and automation. A brief overview of other surface engineering techniques is presented below:

2.4.5.1 Flame hardening

As its name suggests, this method uses an oxy-acetylene (or any other high temperature gas) flame to heat the steel surface above upper critical temperature before quenching it in water or other quenching medium. It is one of the oldest technique used for surface heating. The process is fast, low cost and effective for hardening of alloy and tool steels. It is traditionally used to harden gear wheels, lathe guides, blanking tools, moulds, cam shafts and other machine components. The process uses a flame with very high heat input and is difficult to be controlled precisely. Thus, the generated case depth may not be uniform. The high heat input can also cause distortion and surface melting requiring for post treatment. Moreover, the need to use of an external quenchant adds further limitation to the method. All these can be overcome using lasers.

2.4.5.2 Induction hardening

Induction hardening uses heat generated by resistance to eddy currents produced from electromagnetic induction to heat up the metal surface. It produces a deep hardened region without surface melting and has relatively high coverage rates. The method is particularly suitable for components such as gears, wheels and shafts which can be positioned inside the induction coil to generate the hardening effect. The process is also easy to use and can be controlled by the eddy current strength. However, it cannot produce desired result for hardening of complex geometries and localized areas. In such

cases, laser hardening with localized heat input is more suitable. On the other hand, some distortion may be produced during induction hardening due to relatively larger heat input. Moreover, the induction hardening process cannot produce shallow hardening depth. This can be easily solved with limited energy input of laser hardening.

2.4.5.3 Arc hardening

This process is similar to flame hardening. Instead of flame, it uses a welding arc or plasma arc. The low capital cost involved makes this method lucrative for simple hardening applications. It has similar drawbacks as flame hardening; but has the advantage that the process is more controllable compared to flame hardening.

2.4.5.4 Electron beam hardening

Heating can also be generated by scanning a defocused electron beam on the surface. The heat source is similar to a laser beam except that it uses electron beam rather than an electromagnetic beam. The beam can be easily controlled to have heating at a particular location and thus, even complex geometries can be hardened easily. In addition, no absorptive coating is required as in conventional laser hardening. However, the process requires vacuum condition. Although it removes the possibility of surface oxidation, it might not be suitable for a very large component. Moreover, the vacuum requirement adds extra cost and also, delays the production process.

2.4.5.5 Hardening by diffusion

Diffusion methods introduce hardening elements such as carbon, nitrogen or boron on the surface of steel. The method requires an enclosed chamber which is heated to a high temperature such that the hardening elements from a source is introduced in the steel surface. The method is normally applied for low carbon, low alloy steels to produce a relatively thick, wear resistant surface [83].

Carbon is the most commonly used element to increase surface hardness. The process of introducing carbon to the surface (esp. low carbon steel) at temperatures between 850 to 980°C is known as carburizing. The carbon source is either a gas (gas/plasma carburizing), liquids (salt bath carburizing) or solid compounds (pack carburizing). The case hardness in carburized steel is primarily determined by the amount of carbon while the case depth is a function of carburizing time, steel chemistry and available carbon potential at the surface.

Similarly, another surface hardening heat treatment method, called nitriding, introduces nitrogen into the steel surface at a temperature range (500 to 550°C) while it is in the ferritic condition. Since nitriding does not involve heating into the austenite phase and rapid quenching to form martensite, nitride components undergo minimum distortion. It also improves corrosion resistance of the surface.

When carbon as well as nitrogen are introduced into the austenite of the steel during surface hardening heat treatment process, the method is called carbonitriding. It is similar to carburizing in that the surface composition is altered and high hardness is achieved by quenching to form martensite. However, presence of nitrogen enhances hardenability. Thus, the method can achieve exceptionally high hardness in low carbon steel comparable to that of high alloy carburized steel without the need for drastic quenching, minimizing potential for cracks and distortion.

The diffusion methods are very effective for batch processes when several components need hardening over the entire surface as in automotive and tooling industries. Generally, a mask is required if certain areas are not to be hardened which is time consuming and expensive. The equipment cost is relatively low. However, fuel cost is a concern since gas is used inefficiently to heat entire surfaces. In addition, the exhaust gas after the process needs to be disposed properly adding up to the cost of the process. In many cases, a combination of laser hardening and gas hardening is shown to produce superior properties than those of individual treatments [84,85].

2.4.5.6 Shot peening

Shot peening generates a hardened surface by bombarding the surface with hard steel balls. The balls impact on the surface and the energy transfer during the cold working process alone produces the hardening effect. Thus, the negative effects of heating are eliminated in this process. It also generates compressive residual stresses on the surface. However, the hardening depth is too shallow and non-uniform.

Table 2.4: Comparison of different surface hardening methods [9].

Parameters	Laser	Flame	Induction	Arc	Electron beam	Carburizing
Maximum depth, mm	1.5	10	5	10	1	3
Distortion	Very low	High	Medium	Medium	Very low	Medium
Flexibility	High	High	Low	High	Medium	Medium
Precision	High	Low	Medium	Low	High	Medium
Operator skill	Medium	High	Medium	High	Medium	Medium
Environmental impact	Low	Medium	Low	Medium	Low	High
Quenchant required	No	Yes	Sometimes	No	No	No
Material flexibility	High	Medium	Medium	Medium	High	Low
Productivity	Medium	Low	Medium	Low	Medium	High

2.4.6 State-of-the-art on laser hardening

2.4.6.1 Past studies

Laser hardening technique has been around for decades; but understanding and mastering it for industrial applications is still in infancy. Since it is basically a thermal process dictated primarily by diffusion of carbon, many of the earlier studies were devoted in predicting the temperature profile during the process by solving the heat transfer equation and understanding the microstructural phase transformation brought about by the thermal distribution. Steen and Courtney [60] were among the pioneers who conducted a detailed study on laser transformation hardening of steel. They used a 2 kW continuous wave CO₂ laser to harden the surface of EN8 (AISI 1040) steel. Three major

parameters viz. the laser power P , beam diameter D_b and process speed, V were experimentally studied to understand their effects on hardening. Based on the experimental fit of data, the hardening depth was correlated with the parameter $P/\sqrt{D_b V}$ and the start of surface melting was determined to be a function of $P/D_b^2 V$. In addition, they also presented operating charts of the laser power against the scan velocity for various laser beam diameters. However, these relationships are empirical in nature and they did not give any physical or analytical explanation.

Mazumdar and Steen [86] proposed a 3-D heat transfer model for laser material processing with a circular shaped moving heat source with a Gaussian distribution of heat intensity using a finite difference method. The model was used to predict the surface melting, HAZ and thermal cycles during laser-material interactions. In 1983, Kou et al. [87] performed both theoretical and experimental study of heat flow and solid state transformations during laser hardening of AISI 1018 steel. They developed a three-dimensional heat flow model using finite difference method and explained the microstructure evolution with the help of calculated peak temperature, heating and cooling rates.

A detailed analysis on laser transformation hardening of hypo- and hyper-eutectoid steels was performed by Ashby and Easterlung [61] and Li et. al. [62] respectively. They used a continuous wave CO₂ laser and varied the beam diameter and scanning speed. In addition to the process parameters, the effect of material properties in hardening was also studied by combining the approximate solutions of heat flow equation with kinetic models to predict the microstructure and hardness of plain carbon steels after laser surface treatment. Based on their analyses, they developed “laser-processing maps” as shown in Figure 2.12 to determine the optimum combination of process variables required to obtain the desired microstructure and hardness.

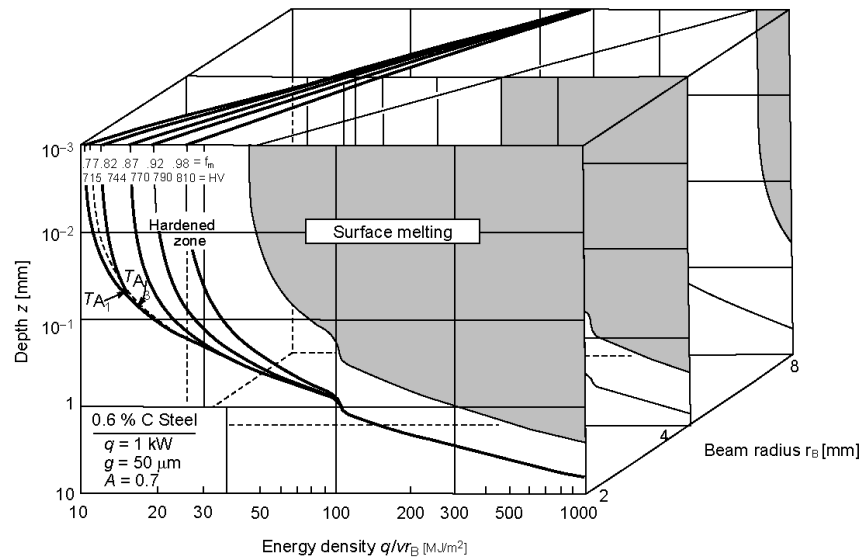


Figure 2.12: Laser processing map for 0.6 wt% carbon steel [61].

Extending the Mazumdar and Steen model, Davis et al. [88] examined the significance of austenite homogenization for laser transformation hardening of steel. They identified the following criteria for surface transformation hardening in their analyses: (1) the material must reach at least A_3 temperature of steel for austenitizing; (2) there should be enough time for carbon diffusion to occur when the steel is above A_3 temperature; and (3) the quenching must be rapid to transform austenite into martensite (cooling rate of $\sim 1000^\circ\text{C/s}$). Ohmura et al. [89] used computer simulations to analyze the time dependence of heat flow, carbon diffusion in austenite and quenching process. Using the model, they were able to theoretically determine the best combination of the process variables for the laser transformation hardening.

In other work, Devgan and Molian [90] used a continuous wave CO_2 laser to study the microstructure, hardness, case depth and wear characteristics of laser treated 52100 bearing steel. They concluded that the laser treatment resulted both in improved hardness and sliding wear resistance over conventionally quenched and tempered steel. Furthermore, the material removal during wear test was found to occur by abrasion and delamination for conventionally heat-treated specimens while by fatigue in laser treated

specimens. Nevertheless, they failed to provide any physical explanation as to why it occurred. Shiue and Chen [91] studied laser transformation hardening in tempered 4340 steel. Their main aim was to investigate the detailed microstructural features using TEM in the laser-treated regions of AISI 4340 steel that had originally been tempered at different temperatures. They discovered that the initial microstructure greatly affects hardness and hardening depth. Lower the tempering temperature, deeper the hardened zone, and narrower the transition zone in the hardness profile. The faster process speed was found to cause smaller martensite sizes (lath and twin) and the less autotempering effect in the surface layer with higher surface hardness value compared to slower speeds.

Jacot and Rappaz [92] developed a diffusion-based model for the prediction of phase transformation during hardening. Later, they proposed a joint model to describe the dissolution of pearlite and the transformation of pro-eutectoid ferrite to austenite during heating phase, and the homogenization of austenite at high temperature and its growth [93]. They concluded that the austenitic transformation completion temperature (A_{c3}) depended on the carbon content and the heating rate. It increased with the increase in heating rate between two extreme values, 770°C and 912°C, for a Ck45 medium carbon steel i.e. faster rate of heating required higher temperature to complete the austenitic transformation. Furthermore, the austenite homogenization temperature was found to increase from 800°C to 1200°C with the increase of the heating rate from 0.1 K/s to 1000 K/s [92].

Selvan et al. [37] studied the potential application of laser hardening in automobile industries. They used AISI 5135 steel to evaluate the hardened microstructure and found that laser surface hardening produces wear resistant and a very hard surface layer consisting of metastable martensite and carbides.

Komanduri and Hou [94] developed a general analytical solution (both transient and quasi steady state) for temperature distribution during laser transformation hardening considering the boundary effects. The analytical

results were compared with the experimental results of Steen and Courtney [60] and operating window for different processing conditions for laser transformation hardening were presented based on the optimization of process parameters for no surface melting and 0.1 mm hardening depth.

Obergfell et al. [95] conducted a systematic analysis of the microstructural changes in laser hardened surface of three different alloy steels 20MoCr4, 20CrMoV13-5 and X20CrMoV12-1 using Nd:YAG laser system. By systematic analysis of laser-affected zone through proper characterization techniques, they were able to classify the effect of dislocation density, different type of carbides and solid solute carbon atoms on strength and hardness of material. Tobar et al. [96] performed a numerical modelling for laser surface treatment of H13 tool steel coupling the solutions of heat conduction equation and phase transformation model based on the Johnson–Mehl–Avrami and Koistinen–Marburger equations. They used a 2.2 kW CO₂ laser to verify their model and obtained a good agreement between the measured value and the calculated ones. In another work, Patwa and Shin [97] developed a predictive model in terms of laser operating parameters and initial microstructure to predict hardness profiles, optimize process parameters and assess the potential of laser hardening for different steels. They showed that the predictions and the measurements of hardness value and case depth matched closely validating their thermo-kinetic model. Another research by the same group used a high power continuous wave Nd:YAG laser to investigate the hardening characteristics of AISI 1045 steel [66]. Instead of using defocusing technique, an optical lens with an elliptical profile was used to obtain a widely uniform beam profile and they reported a maximum hardness of approximately 780 HV using the heat input capacity of $4.90 \times 10^2 \text{ J/cm}^2$. Apart from high power CO₂ lasers, a pulsed Nd:YAG laser was utilized by Mahmoudi et al. [45] to surface harden AISI 420 stainless steel. They obtained a maximum hardness of 490 HV and found that the hardening had beneficial effect on corrosion resistance of the steel.

In most of the researches stated above, a high power CO₂ lasers or Nd:YAG based solid state lasers were used for hardening purpose. These are operated

in either continuous or pulsed mode. However, laser hardening with these lasers is comparatively expensive due to their low efficiency, high capital costs and the frequent need for coating to increase absorption. With the advent of multi-kilowatt high power diode lasers, it has emerged as a new and powerful tool for laser transformation hardening. The high power diode lasers have wavelength of around 800-900 nm which is absorbed effectively by steel surface compared to longer wavelengths of CO₂ laser. Other advantages include a higher electrical to optical efficiency (20-35% of diode laser compared to 10-15% and 1-5% of CO₂ and Nd:YAG lasers respectively), low capital cost with almost zero maintenance and compact size which allows it to be integrated into conventional machining tools. In addition, compared to the Gaussian beam produced by CO₂ laser, it generates a uniform beam profile which suits perfectly for hardening applications [70].

Pashby et al. [10] studied hardening on plain carbon and alloy steel using a 1.2 kW diode laser. A simple design of experiment was conducted to observe the effect of laser power and speed on hardening process. They obtained a range of power-speed combination producing 200 μm case depth (defined arbitrarily as the maximum depth with hardness value greater than base level by 50 HV) and found that a greater depth of hardening was obtained for alloy steel than for carbon steel due to presence of alloying elements. Lee et al. [43] used a 200W fiber laser to improve the surface hardness and wear properties of AISI H13 tool steel. They obtained a maximum hardness of 480-510 HV. A comparative study of high power diode laser and CO₂ laser surface hardening on AISI 1045 was performed by Li et al. [38]. They obtained a uniform hardness without surface melting with high power diode laser. For CO₂ laser, surface melting occurred in the center. Another work by Sorgente et al. [98] on laser hardening of 52100 bearing steel revealed that both the surface roughness and the initial steel microstructure affect the achieved hardness values and depth of hardening.

2.4.6.2 Current trends

Although laser hardening is not as popular as other laser processing techniques such as cutting, drilling, marking, the technology is slowly realizing its potential. It has been adopted for surface hardening during remanufacturing of turbine components after cladding, hardening of crankshafts and improving surface characteristics in various large and small machine components. Recently, more studies are focused towards analytical modelling and computer simulations to predict hardness profile and depth as well as to determine optimum condition [99–109]. Back-tempering during multitrack hardening is a major issue during process optimization which produces a softened/tempered overlap zone sandwiched between hardened region. Various models have been developed to address this issue [41,69,110–112]. This, not only saves the resources required for doing experiment, but also speeds up the production saving time.

Similarly, another area that is actively pursued is understanding the phase transformation and non-equilibrium kinetics during laser hardening. In-situ monitoring and feedback control can be used in industry to ensure the repeatability of the process and achievement of required hardening depth in complex engineering parts without doing any metallographic characterization [65]. Lusquinos [113] used a pyrometer to both monitor and control (through close-loop feedback) the temperature rise during laser hardening of AISI 1045. Farshidianfar et al. [114] developed an automated real-time thermal monitoring system to directly control the thermal processes occurring during laser treatment online. An elaborative review of different online measuring techniques based on IR pyrometers and CCD camera for laser hardening of different engineering parts has been present by Bonß [115].

Apart from this, many new avenues such as the hardening of very low carbon steels having less than 0.1 wt% C and thin steel sheets [47,48,116], effect of using heat sinks [117,118], pulsed laser hardening of different types of steel [119–121], laser beam shaping for hardening engineering parts [40,122], and

laser hardening with scanning optics [39], corrosion and wear properties of hardened surface [45] have been reported.

Even though a lot of studies have been performed, some gaps still exist in the literature regarding the process parameters requirements and influence of material properties. The process often requires a tedious task of performing multiple trials and subsequent characterization to optimize the process for a specific engineering application. It is clear that there's still a lot of room to explore in the field of laser hardening.

In this study, I mainly focused on elucidating the mechanism of laser hardening. Laser surface hardening produces a range of microstructures in the hardened region due to non-equilibrium phase transformation of which very little is understood. I aimed to analyze the effect of various operating parameters on the microstructure obtained and surface properties achieved. Furthermore, I explored the feasibility of pulsed lasers in hardening and investigated the underlying mechanism during interaction of laser and steels. The main objective was to achieve superior surface properties using laser heating technique. To this aim, innovative methods to improve the hardenability and surface hardness of different steels (including low hardenable steels) were implemented. It should be noted here that the specific literature review on the topic of interest will be further presented in the subsequent chapters.

2.5 Summary

This chapter presented an overview of industrial lasers and laser surface hardening of steels. Based on the literature survey in this chapter and the objectives and scopes set for this thesis, the following issues will be addressed in the following chapters:

1. The ability of laser to precisely deposit energy into the material in a short time scale over a spatially confined region on the surface predestines it to be used for surface hardening and other modification applications. With the invention of low-cost high power solid-state and

fiber lasers, the method is gaining renewed interest and becoming popular for various industrial applications. However, laser hardening follows a non-equilibrium phase change mechanism which depends on several parameters such as the power density, process speed, laser wavelength, beam profile and material surface condition. Optimization of processing parameters is generally done to achieve the desired surface hardness and hardened depth. While numerical analysis and modelling have proven to be useful for optimization, further investigation on the underlying mechanism and microstructural evolution is required to apply the method in production process.

2. With the laser hardening technology maturing fast, many different studies have emerged in recent years. The introduction of short pulsed and ultra-short pulsed lasers has brought significant excitement in the scientific as well as industrial community. The interaction of these lasers with steel can provide the potential engineering value through surface modification. There is also a possibility of achieving better surface properties and higher hardness using these lasers than using conventional CO₂ and Nd:YAG lasers. This area is comparatively undervalued and need to be explored further.
3. The laser surface hardening produces a range of microstructure along the hardened zone due to rapid phase transformation. Studies suggest that formation of corrosion-resistive oxide layer and microstructural refinement brought about by laser-induced phase transformation improves the corrosion resistance of the steel. However, the fact that the removal of the near-surface layer might expose the sub-surface to corrosive atmosphere cannot be ignored. More studies should be performed to study the corrosion properties in near surface microstructures.

4. Since the hardness of the material influences the wear resistance and fatigue resistance, it is desirable to have high hardness near the surface. However, high hardness results in brittleness and loss of elongation. Therefore, innovative methods to improve the hardness of the surface should be explored. The methods can be beneficial especially for low hardenable steels like low carbon steels. These steels have low hardenability due to less amount of carbon atoms which cannot be hardened by conventional techniques. Laser-based novel hardening techniques could possibly induce rapid non-equilibrium phase transformation and surface alloying in such steels to improve its mechanical properties at the surface.

Chapter 3: Materials and Experimental Procedures

This chapter describes the materials studied and the characterization techniques used for the study. Different lasers used for surface treatment are also briefly discussed. The specific laser parameters used for experiments are presented in the related chapters.

3.1 Materials

Four grades of steels were used for the study. They were AISI 1020, AISI 1055, 50CrMo4 (AISI 4150) and AISI 52100 steels. The nominal compositions of these steels are shown in Table 3.1 and their as-received microstructures are shown in Figure 3.1.

Table 3.1: Chemical composition of different steels used for the study.

wt%	AISI 1020	AISI 1055	50CrMo4 (AISI 4150)	AISI 52100
C	0.20	0.56	0.51	0.98
Cr	-	0.11	0.95	1.42
Mn	0.32	0.78	0.88	0.35
Si	0.21	0.23	0.23	0.25
P	0.009	0.01	0.04	0.02
S	0.042	0.002	0.040	0.02
Mo	-	-	0.20	-
Ni	0.15	0.07	-	-
Cu	0.15	0.06	-	-
B	-	0.0015	-	-

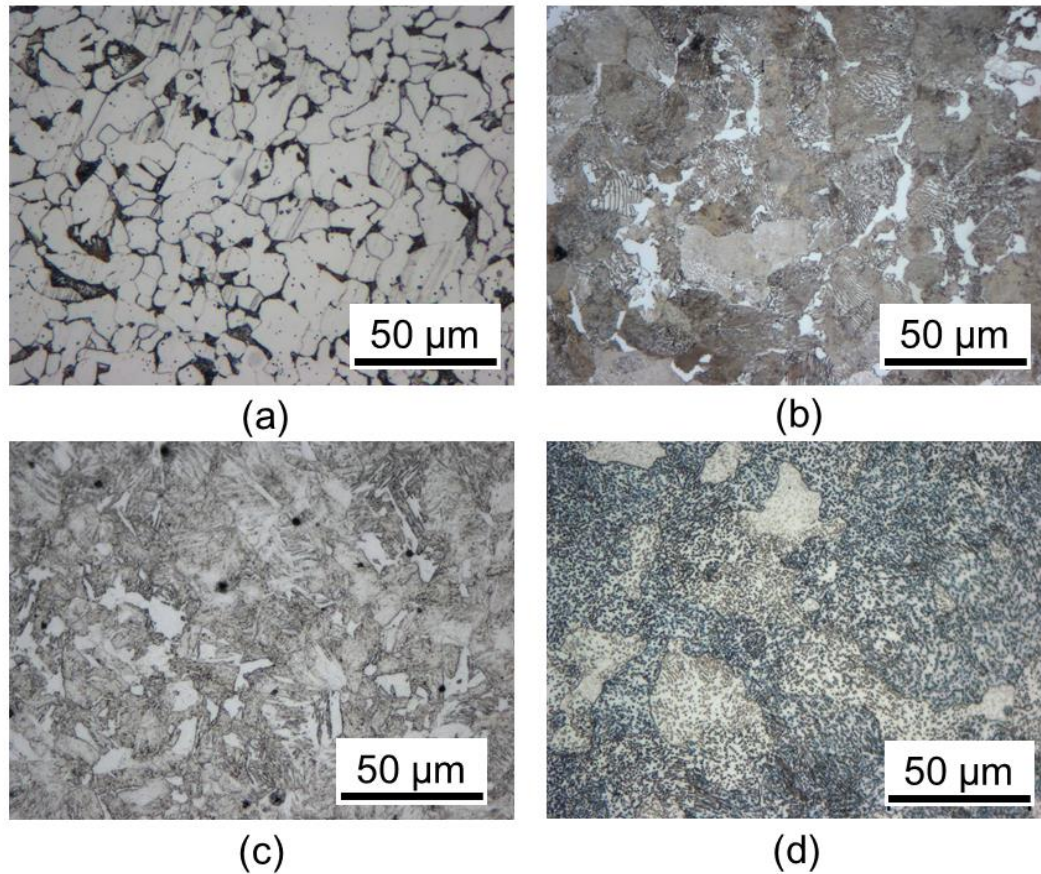


Figure 3.1: As-received microstructure of different steels used in the study – (a) AISI 1020, 140 HV; (b) AISI 1055, 195 HV; (c) AISI 4150 (50CrMo4), 231 HV; and (d) AISI 52100, 213 HV.

AISI 1020 is a low carbon steel with low hardenability generally used in common structures to enhance weldability or machinability properties. AISI 1055 is a medium carbon steel used in springs, shafts, bushings and crankshafts. It was available in hot rolled and normalized form. 50CrMo4 is a medium carbon bearing steel used to produce high toughness components for automobiles and aircrafts, oil pressure vessels and generator shafts. It was available in quenched and tempered condition. Similarly, AISI 52100, obtained in soft annealed condition, is a high-carbon alloy steel with about 1 wt% chromium which is widely used in ball bearings. It is very resistant to wear and plastic deformation.

3.2 Laser systems

The Ytterbium based fiber laser from IPG Photonics (YLR-150/1500-QCW) was used for most of the hardening experiments (see Figure 3.2). The laser had a wavelength of $1.07\ \mu\text{m}$ and could be operated in both pulsed as well as continuous wave mode. It had a maximum power of 250 W in continuous mode. In pulsed mode of operation, the peak power could go up to 1500 W with pulse energy as high as 15 J. The output fiber had a core diameter of $50\ \mu\text{m}$ which carried a single mode laser beam of Gaussian distribution. The laser beam was delivered to the work surface by focusing the beam through a 300 mm focal length lens.

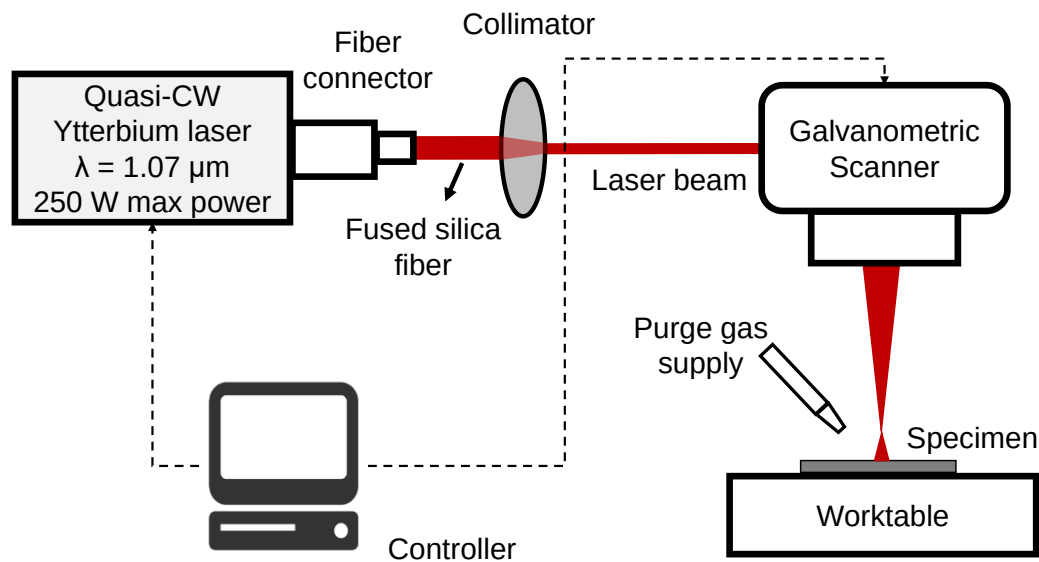


Figure 3.2: General experimental setup for laser hardening experiments.

Apart from the fiber laser, other pulsed lasers were also used for the experiments. The specifications of the lasers are shown in Table 3.2.

Table 3.2: Different lasers used for the experiments.

Laser Type	Wavelength (nm)	Pulse duration	Repetition rate (Hz)	Maximum power (W)
Millisecond	1070	5 – 20 ms	10	1500
Nanosecond	1060	220 ns	5×10^5	90
Femtosecond	790	130 fs	1000	1.5

Different operating parameters such as power, speed, defocus, purge gas and mode of operation were varied in order to design various experimental work based on the scope of the project. The detailed information on each condition used is provided in each chapter and in Appendix B.

3.3 Characterization

3.3.1 Metallography

The microstructures of laser treated samples were characterized following the standard metallography techniques. The samples were carefully cut, mounted, grinded, polished and etched with 2% nital solution for revealing the microstructure before and after laser treatment.

3.3.2 Optical microscopy

The Carl Zeiss Axioskop 2 microscope was used to observe the microstructure of the samples. It uses visible light for illumination (bright field method) and comprises of a system of lenses that can magnify up to 1000x. Digital images were processed using AxioVision 4.3 software.

To observe the samples at lower magnification, SZX7 Stereomicroscope by Olympus was used. It uses separate optical paths with two objective lenses and two eyepiece lenses to give a three-dimensional view of the sample surface. It has eyepiece magnification of 10x and objective lens magnification varying from 0.8x to 5.6x.

3.3.3 Electron microscopy and allied techniques

3.3.3.1 Scanning Electron microscopy (SEM)

Two SEMs JOEL 5600LV and JOEL 7600F system were utilized for studying and characterizing the samples. SEM uses a focused beam of high energy electrons over a surface to create an image. The finer details and topographical information that cannot be obtained by optical microscope can be obtained by using SEM. Heavy etching was performed before SEM imaging since it provides better topological contrast in secondary electron (SE) mode.

3.3.3.2 Energy Dispersive Spectroscopy (EDS)

The EDS system comes as an attachment to the electron microscopes (SEM, TEM, STEM). It collects signal from a volume of matter excited by an electron beam. Higher the voltage larger is the volume from which the signal is detected and lower is the spatial resolution. Since higher volume compromises the lateral resolution of analysis spot, a lower voltage is utilized to improve resolution. However, too low voltage might not generate enough X-rays and is less sensitive. Therefore, the required resolution is optimized by applying proper voltage. For our work, an X-Max Silicon Drift Detector (SDD) developed by Oxford Instruments was used at optimized voltage condition. The EDS system was attached to JEOL 7600F SEM system.

3.3.3.3 Electron Backscattered Diffraction (EBSD) system

EBSD is a SEM based technique that gives information about crystallographic orientation of the sample. It uses a backscatter diffraction camera to detect the backscattered electron from sample surface. The detector consists of a phosphor screen and a CCD camera. The sample is generally tilted 70° to the horizontal such that the incident electron beam is diffracted according to Bragg's Law. The diffracted beam hits the phosphor screen forming diffraction patterns, Electron Backscattered Pattern (EBSP) which is characteristic of the crystal structure and orientation. The pattern can be indexed by Miller indices automatically using computer software. It can be used to identify crystals,

orientation, measure grain boundary misorientations as well as identify phases by comparing the pattern with standard database. In our experiment, Oxford EBSD system was used to study the crystallographic orientation of laser treated sample.

3.3.4 Surface analysis

The surface topography of the laser treated samples were studied using a surface profiler (Talyscan 150) and a confocal microscope (Carl Zeiss Smartproof5). The surface profiler uses an inductive gauge to measure the surface roughness. It has a vertical resolution of 60 nm. For ever higher resolution, confocal microscope is used which uses a spatial pinhole to block out-of-focus light in image formation. It can map multiple two-dimensional images at different depths based on its intensity and reconstruct a three-dimensional image with vertical resolution as high as 1 nm. The technique has been used to analyze the surface morphology before and after laser treatment.

3.3.5 Hardness analysis

3.3.5.1 Vickers microhardness test

Hardness of a material is defined as the resistance to permanent penetration or scratching by another material which is harder. It is one of the important mechanical properties of a material and can be used as good indicator for material selection and quality assurance.

The hardness test is typically performed by measuring the depth of indenter penetration or by measuring the size of an impression left by an indenter. The indenter is made of a hard material usually diamond, tungsten carbide or steel. If the load used for indentation is below 1 kgf (kilogram-force), then the process is called micro indentation hardness testing or simply “micro-hardness testing”. Microhardness testing by Vickers method is the most popular one for metallurgical examination (see Figure 3.3).

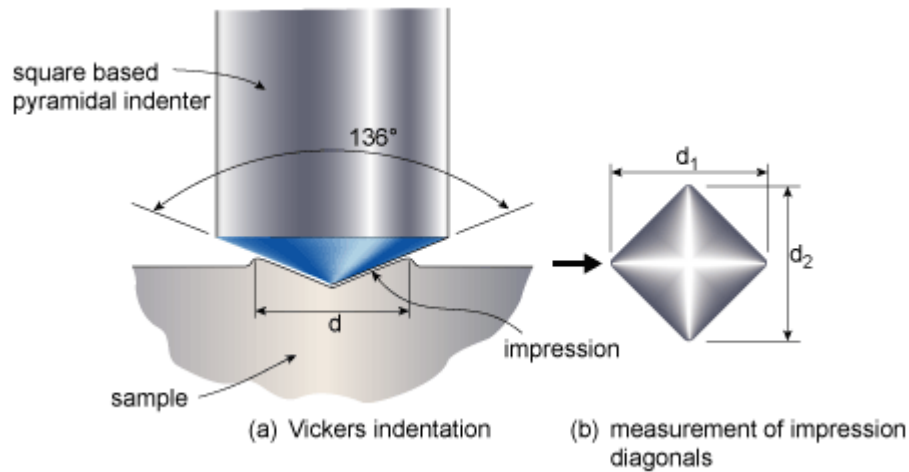


Figure 3.3: Vickers Microhardness test [123].

The Vickers Hardness (HV) is computed by measuring the lengths of diagonal of an indent, which is created by penetrating a diamond pyramid indenter into the specimen surface using a specific load. The loads used range from 10 gf (1 gf) up to 1000 kgf. The test is simple and is often used for testing of almost all solid materials.

The Vickers Hardness value can be calculated as

$$HV = \frac{2P \sin(\frac{\theta}{2})}{d^2}, \quad (3.1)$$

where,

P is the applied load in kg, d is the average length of diagonals $d = (d_1 + d_2)/2$ and θ is the angle between opposite faces of the diamond = 136° .

Since micro Vickers hardness creates a micro-sized indenter, it can be used to measure hardness in a very limited area. The method is specifically beneficial for hardness determination of a particular microstructural phase of materials, such as ferrites and pearlites existing in steels. The hardness values of different phases of steels are different. Thus, it can be used to identify any variation in hardness caused by metallurgical processes such as hardening, welding, and other heat treatment processes, where the larger

indenter used for macro Vickers hardness test limits its application in this case. However, it is to be noted that the sample surface must be properly polished without any scratches to minimize errors in measurement.

In the present study, FM300e series Automatic Microhardness Tester from Future-Tech was used to measure Vickers Hardness of the samples. A loading force ranging from 100 gf to 1000 gf was used with a dwell time of 15 s.

3.3.5.2 Nanoindentation test

Nanoindentation is a technique for measuring the mechanical properties of materials. In conventional hardness measurement, the testing yields only one measure of deformation at one applied force. In contrast to this, nanoindentation test involves mechanical probing of a material surface while continuously monitoring the force and the penetration of the indenter during the process. Such continuous measurement of force and displacement enables to unravel lots of mechanical properties of the material which cannot be achieved by conventional techniques [124].

Nanoindentation, also known as instrumented indentation technique, has already been established as a powerful technique to measure the elastic properties, hardness and fracture toughness of any kind of materials. Ever since the generalized elastic contact theory governing the relationship between load and penetration depth in semi-infinite axisymmetric bodies was proposed by Sneddon in 1965 [125], a number of works have been done to improve the model. With recent advancement, the Oliver and Pharr model [126] for Berkovich indenter has been widely accepted and used for instrumented indentation studies.

The technique can be used to measure young's modulus, hardness, strain rate sensitivity as well as fracture toughness of the material. It is particularly suitable when the area for hardness measurement is too small. There is also a possibility that a material might behave differently at small scales due to

different micro-mechanisms. It's relatively simplicity and ease of sample preparation gives it an advantage over uniaxial compression or tensile testing.

The technique derives nearly all its advantages from continuous measurement of load and displacement during the entire process. The process is either force controlled or displacement controlled. The testing involves following steps:

1. Approach: indenter approaches the test surface until contact is detected.
2. Loading: indenter is pressed into the material until maximum force or penetration is achieved
3. Dwell: the force on the indenter is held constant at peak force for a certain time
4. Unloading: the indenter is slowly withdrawn from the sample until the force becomes about 10% of the peak force, after which it is completely taken out from the sample.

The force and displacement data are continuously recorded and plotted in a compliance curve or P-h (load-displacement) curve as shown in Figure 3.4. When the load is removed from the surface, it generally creates a residual impression on the surface due to plastic deformation. Conventional hardness test measures the size of this residual impression. However, nano-indentation measures the depth of penetration and together with known geometry of the indenter, provides an indirect measure of area of contact at full load, from which hardness can be estimated.

A Berkovich nanoindenter from Agilent technologies (G200 Nano Indenter) was used in our study. The hardness for Berkovich indenter is given by

$$H = \frac{P}{A} = \frac{P}{24.5h_c^2} \quad (3.2)$$

where, P is the maximum loading, A is the projected area and h_c is obtained from the P-h displacement curve. This method was primarily used to measure the hardness in the laser treated area.

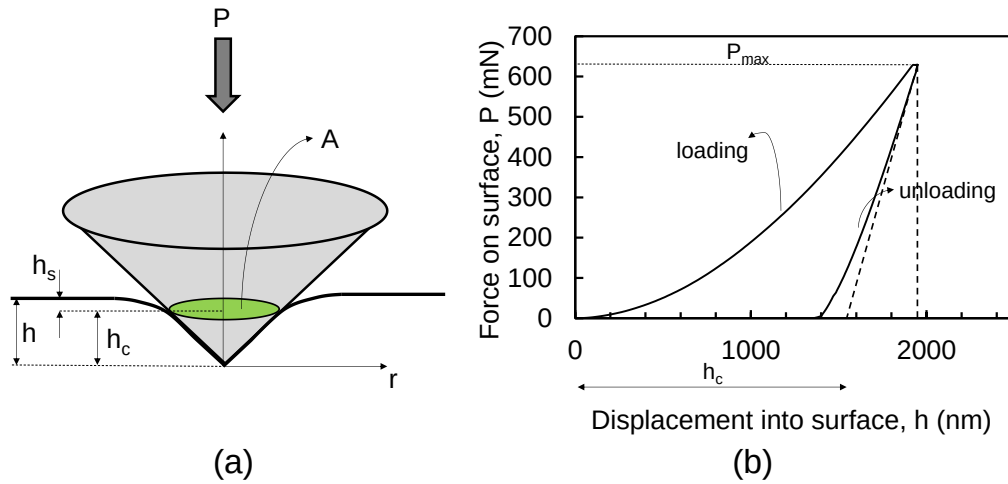


Figure 3.4: Instrumented indentation testing (a) Berkovich indenter penetrating the substrate; and (b) typical P-h curve [127].

3.3.6 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a powerful non-destructive analytical technique used for phase identification of crystalline materials and its crystal properties. It is based on the constructive interference of the monochromatic X-rays and the crystalline sample when conditions satisfy Bragg's law. Bragg's law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Thus, by detecting the diffracted X-rays, the chemical composition and the phase in the sample can be identified.

This study uses X-ray diffractometer (Empyrean XRD from Panalytical) to identify the phases in as-received material and in laser-irradiated surfaces. The diffractometer uses a copper target as a source of X-ray with wavelength $\lambda=1.5404 \text{ \AA}$ (Cu $K_{\alpha 1}$). The scanning angle was in the range of 30° – 120° with a step size of 0.02° and dwell time of 2 s unless otherwise stated. The obtained diffraction data were analysed in MDI Jade6 software.

Chapter 4: Laser surface hardening of 50CrMo4 steel

This chapter describes the surface hardening studies on 50CrMo4 steel. In the first part, laser hardening is performed using a fiber laser and typical hardened microstructure, surface morphology and transformation mechanisms are presented with 50CrMo4 steel as a representative material. The second part discusses the effects of various operating parameters such as beam spot size, power, speed and track overlap on surface hardening. Although other steels were also studied for surface hardening, only the results of 50CrMo4 are presented in this chapter since they all reacted in a similar manner.

4.1 Introduction

Laser surface hardening induces fast and non-equilibrium kinetics which produces a unique microstructure with properties different than that obtained from conventional heat treatment. The developed microstructure has been found to be beneficial for resistance to wear, fatigue and corrosion [12,45,68]. Therefore, the effect of laser hardening on the surface of steel has attracted considerable attention.

Most of the previous studies focused on the improved wear resistance of the surface after laser hardening. However, the underlying phase transformation kinetics and microstructure evolution mechanism is often neglected as discussed in Chapter 2. Therefore, an understanding of as-received microstructure and its response to laser hardening is essential to evaluate the mechanism of laser hardening process.

In addition to understanding the mechanism of microstructure evolution during laser hardening, the choice of suitable operating parameters to achieve desired level of hardening is another challenge. Laser hardening is a complex process involving several parameters. Change in a single parameter can

significantly alter the result obtained. While numerical modelling and simulation is usually employed to optimize the process, investigating the influence of each parameter separately can provide a better insight into the process dynamics.

In this study, a typical microstructure evolution during laser surface hardening was studied using various characterization techniques. The main aim was to study the mechanism of phase transformation and characterize the microstructure evolution induced by laser hardening. To this end, 50CrMo4 steel, which is a commonly used medium carbon low alloy steel, was used as a representative material for the study.

Furthermore, the individual effects of major operating parameters such as beam spot size, power, speed, surface condition and overlapping ratio on hardening morphology are experimentally explored. The results obtained can aid in developing further insights into interaction of laser with steel and can be beneficial for designing of laser hardening system.

4.2 Experimental procedures

4.2.1 Material

The material used for the study was 50CrMo4 steel. Detailed information of the material can be found in Section 3.1.

4.2.2 Furnace heat treatment

The hardening effect of laser requires some benchmark for comparison. To this end, conventional furnace heat treatment was performed in a box furnace. The samples were heated at the rate of 20°C/min up to 860°C and held at that temperature for 20 min. Afterwards, they were cooled either in open air or quenched in water. The microstructure was evaluated using standard metallography technique as discussed in Section 3.3.1. The hardness of the samples was measured with a load of 500 gf and a dwell time of 15 s and the measurements were repeated at least 10 times to obtain an average value.

4.2.3 Laser processing parameters and characterization

The laser hardening was performed using YLR-150/1500-QCW fiber laser. All experiments were performed in open air. In all cases, the laser was operated in continuous mode with the specimen 10 mm below the focal plane position.

A single line was hardened for surface oxidation and melting studies while an area of 10 mm × 10 mm was hardened with an overlap percentage of 42% for investigation of surface topography and XRD. The specific parameters used for specific studies are reported together with the results. For the study of cross-section morphology, a single hardened track with partial surface melting is chosen and investigated in detail. The laser hardening was obtained by operating the laser at 230 W power and 10 mm/s process speed. The microstructure, hardness and grain size of the hardened track was analyzed using optical microscopy, electron microscopy, Vickers and nano-hardness measurements and EBSD.

The samples for EBSD study were cut into a size of 10 x 6 x 5 mm³ using a diamond cutter. They were then polished to a mirror finish with an OP-S colloidal silica suspension for about 5 minutes. The grains could be faintly observed after polishing. The samples were carefully cleaned with alcohol and dried with an air gun. EBSD measurements were carried out in JEOL 7600F FESEM using Aztec detector. The post-processing and analysis of EBSD data was carried out in Channel 5 software from Oxford Instruments.

In order to study the effect of laser parameters, the power, the speed and the beam spot size of the laser were varied. The laser power used was in the range of 100 W to 230 W and the process speed was varied from 10 mm/s to 100 mm/s. The beam spot diameter at the specimen surface was varied by moving the sample surface, which is normal to the direction of laser beam, away from the focal plane by a fixed distance. The detailed experimental conditions used for laser processing are presented in Appendix B1.

4.3 Results and Discussion

4.3.1 As-received microstructure

The microstructure of as-received 50CrMo4 alloy steel before laser irradiation is shown in Figure 4.1. It was received in quenched and tempered condition and had a ferritic microstructure with finely dispersed carbides. Under high magnification, spherical and elongated cementite particles were found randomly distributed in the ferrite matrix. The elongated cementite particles were ferrous carbides (Fe_3C) and the globular carbides were mixed carbides $((\text{Fe},\text{M})_3\text{C}$ with $\text{M} = \text{Cr}, \text{Mo}, \text{Mn}$). The microhardness of this structure was measured to be $260 \pm 20 \text{ HV}_{0.5}$.

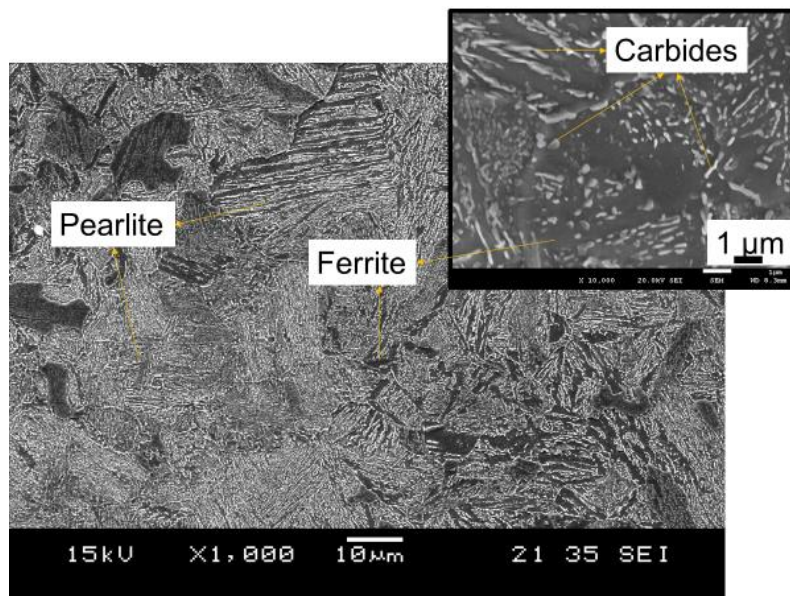


Figure 4.1: Typical microstructure of as-received 50CrMo4 alloy steel, showing carbides at higher magnification (in inset).

The evolution of starting microstructure on heating was determined using computational software Thermo-Calc. A system with chemical composition of 50CrMo4 steel was defined and all possible phases that can form in this system were taken into account. The thermodynamically stable phases and the determination of critical temperature A_{e1} and A_{e3} are shown in Figure 4.2. The A_{e1} and A_{e3} temperature were calculated to be 740°C and 762°C

respectively. It is clear from Figure 4.2 that bcc phase and cementite phase exist at temperatures below 740°C. Cementite here represents $(\text{Fe,Cr,Mn})_3\text{C}$ phase. Although cementite is not an equilibrium carbide phase in many alloy steels, it is kinetically favored since it does not require long range diffusion of substitutional solutes [128]. In the intercritical temperature range, the austenite phase expands at the expense of bcc and cementite phases until the microstructure is fully austenitic. The transformation to austenite is completed at A_{e3} temperature in equilibrium condition.

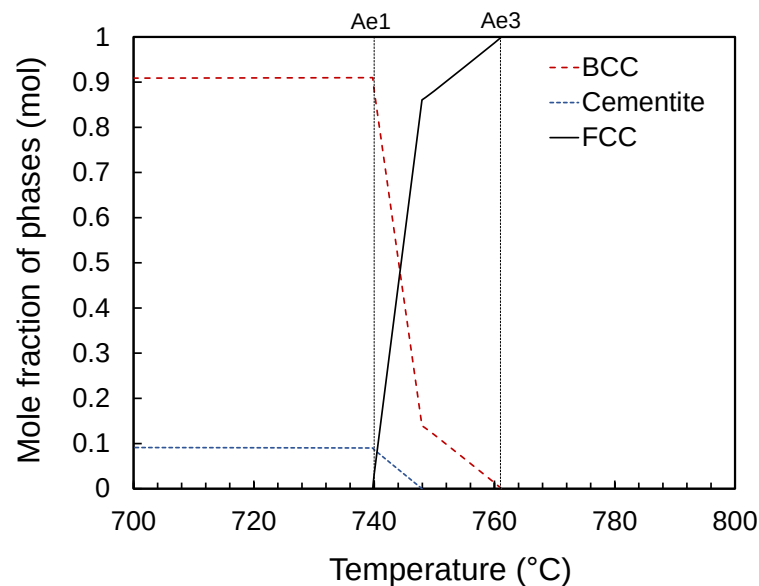


Figure 4.2: Mole fraction and equilibrium phases of the steel during isothermal heating.

However, it is to be noted that heat treatment with laser beams induces faster heating and cooling cycles to the material which is far from equilibrium. Heating rates can go as high as 10^4 K/s or even higher with very short austenitizing times [129], which causes transformation temperatures to rise. In such cases, the designations A_{c1} and A_{c3} are used to represent critical temperatures [8]. Since A_{c1} is the temperature at which first austenite forms, the A_{c1} temperature is not so sensitive to carbide dissolution and carbon content. Thus, it raises slightly. However, A_{c3} temperature is sensitive to the structure and can rise considerably depending on the heating rate [29]. This

produces incomplete austenitization and non-equilibrium microstructures. Nevertheless, the sequence of phase transformation still follows the same sequence as predicted by equilibrium.

4.3.2 Furnace heat treatment

The microstructure of heat treated samples are shown in Figure 4.3. The resulting hardness values were measured to be 260.8 HV, 377.7 HV and 799.0 HV for as-received, air cooled and water quenched samples respectively (see Figure 4.4). The as-received sample consists of ferrite phase and patches of pearlite. When the specimen is heated above austenization temperature, carbon diffusion occurs and the austenite phase appears. The cementite particles start to homogenize in the matrix at such high temperature. On cooling in open air, the atoms in the matrix have enough time to re-organize and form pearlite and ferrite phase. However, quenching in water instantly freezes the matrix leaving no time for carbon to re-arrange. This metastable phase is very hard and brittle and known as martensite. The material is generally tempered to some temperature below re-crystallization temperature to increase its ductility for machinability.

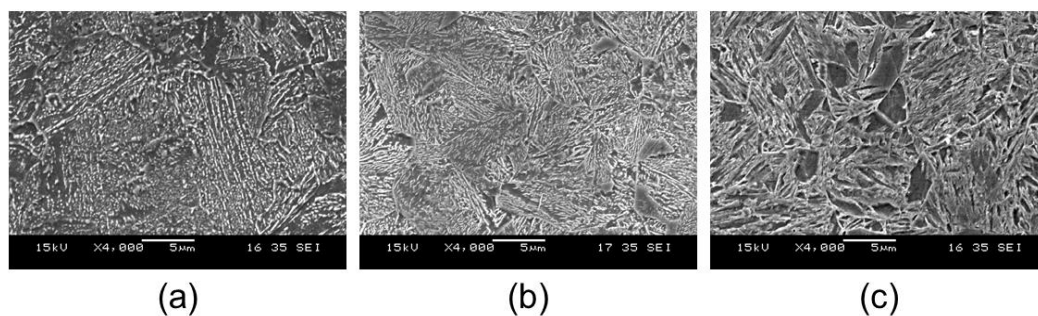


Figure 4.3: Micrographs of 50CrMo4 steel after different furnace heat treatment (a) as-received; (b) cooled in air; and (c) quenched in water.

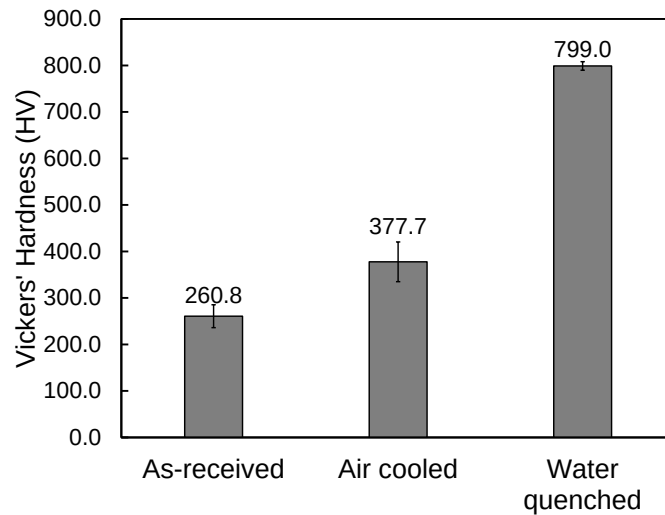


Figure 4.4: Comparison of microhardness values of heat treated steel samples.

4.3.3 Microstructure evolution during laser surface hardening

A schematic diagram of the laser affected area is shown in Figure 4.5. The affected area can be roughly categorized as laser hardened zone (LHZ) and heat affected zone (HAZ). Depending on the operating condition used, the affected area can have both or only one of these zones.

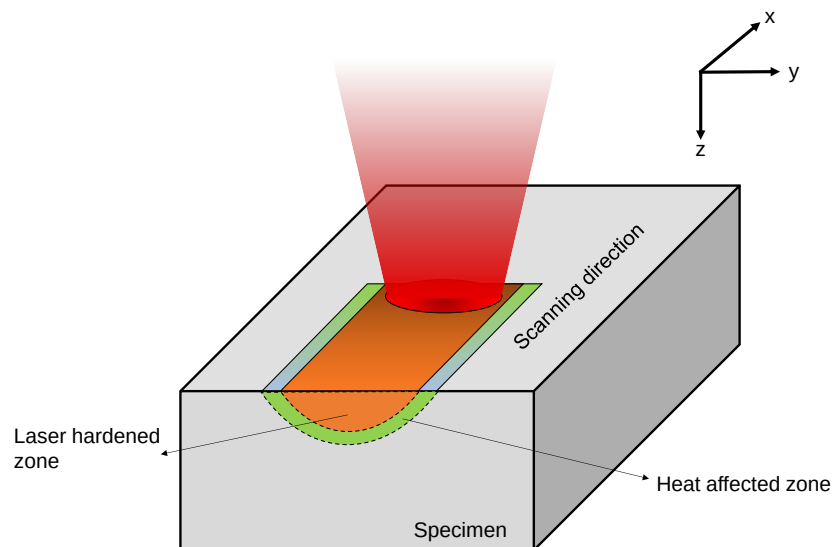


Figure 4.5: Schematic diagram showing laser transformation hardening.

4.3.3.1 Surface morphology

Laser hardening process should ideally result in phase change at the surface and few layers beneath without virtually affecting the surface morphology and topography. However, the hardening is generally accompanied by other visible changes on the surface.

One of the most recognizable changes observed on the surface is change in coloration due to surface oxidation. A typical case is shown in Figure 4.6 in which the laser treatment was performed in air. The surface oxides formed on the laser hardened track can be clearly observed. Figure 4.7 shows the elemental map of the laser scanned line. High amount of oxygen concentrated along the hardened track. Apart from oxygen, other elements such as Cr, Mn and Si are also agglomerated along the scanned track.

Surface oxidation during laser treatment has been reported in the literature [130–132]. The laser heated surface has temperature high enough for oxygen in air to react quickly and form a thin layer of oxide on the surface. Other elements present in steel such as Mn, Cr and Si have higher affinity to oxygen [133] and hence, are segregated during laser heating.

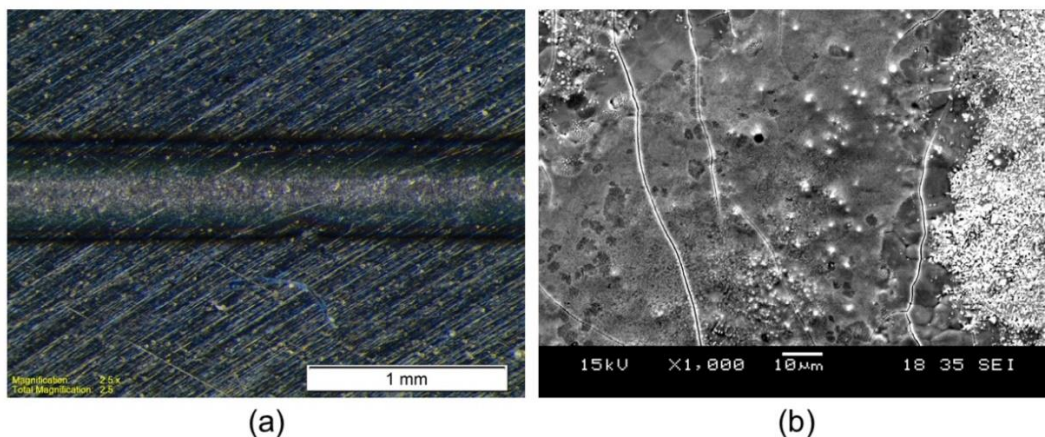


Figure 4.6: (a) A typical laser scan line showing surface coloration and oxidation on the surface. (b) Close-up SEM image of the scanned area showing surface oxides.

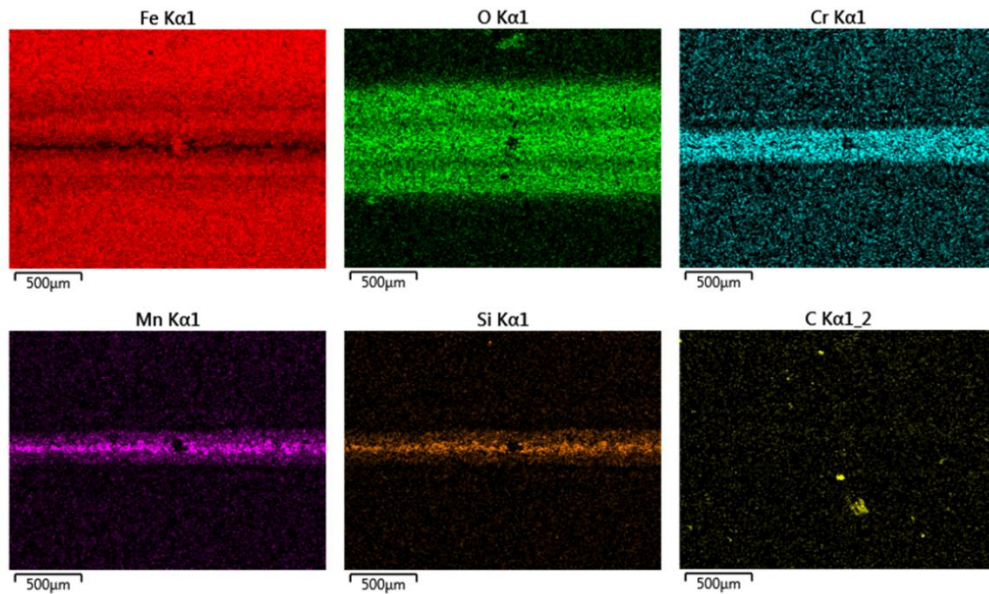


Figure 4.7: Elemental maps of various elements along a typical laser scan line.

In cases where beam absorption is too low, surface oxidation is helpful as it helps to increase the absorptivity of the laser beam by as much as 40% [131]. However, oxidation might deteriorate the surface properties of the steel as it is generally accompanied by decarburization [134]. Therefore, the system must be designed cautiously such that the beneficial absorption effect of surface oxidation is achieved while minimizing its drawbacks.

One of the main challenges in laser surface hardening is melting of the surface. Melting is generally considered as a flaw when dimensional tolerance and surface morphology is a concern. It can be identified by formation of ripple-like structure on the surface (see Figure 4.8), which forms due to flow of molten metal and instant freezing. Melting occurred for cases where power density of the laser was very high ($>18 \text{ J/mm}^2$).

The metal flow during melting distorts the surface and is governed by thermally driven Marangoni effect. When metal is in molten form, the surface tension at the position where the laser irradiates is lower compared to the cooler edges which has higher surface tension. Marangoni flow arises due to such gradient

of surface tension along the interface between two fluids. The radially outward Marangoni flow pushes the molten metal towards the edges creating depression at the center [135]. As the laser moves away, the molten metal rapidly solidifies producing a ripple like effect.

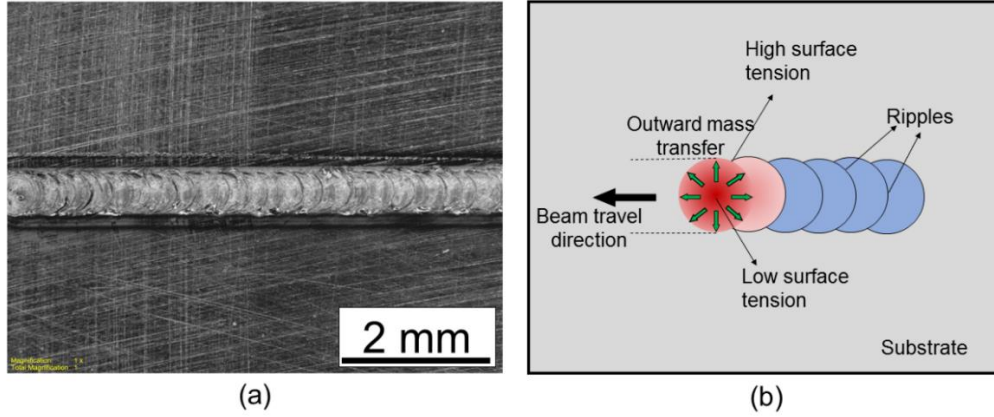


Figure 4.8: (a) A typical laser hardening surface showing melt ripples due to excessive heating; (b) Schematic diagram showing Marangoni effect and ripple formation.

Despite surface melting, the resolidified surface exhibited similar or even higher hardness than LHZ. Therefore, melting can be advantageous as long as surface distortion is within the tolerance level. The higher hardness of remelted surface is attributed to the dissolution of hard carbides owing to higher temperature reached during melting [136].

Further analysis was done to determine the criteria to avoid melting during laser hardening. Based on the work by Komanduri and Hou [94], a simple model to determine the optimal processing conditions for no surface melting in terms of process parameters - power P , process speed v and the beam diameter D was calculated. The model can directly predict the critical process speed for the case of no surface melting and is given as

$$v = A + BP + CP^2 \quad (4.1)$$

where

$$A = -7.0201 + 10.808D$$

$$B = 0.11567e^{(-7.3709D)}$$

$$C = (-18.659 + 118.29D - 246.32D^2 + 171.18D^3) * 10^{-6}$$

(4.2)

In general, surface melting can be prevented by operating the laser at high process speed; but it might as well result in inadequate time for phase transformation. Therefore, along with the critical process speed for no surface melting, a hardening depth of 0.1 mm was considered as sufficient depth since the component would most likely lose its dimensional accuracy if the wear is to exceed this value. The process speed for the case of hardening depth of 0.1 mm is given by

$$v = A_1 + B_1P + C_1P^2$$

(4.3)

where

$$A_1 = 17.279 - 87.148D + 94.249 D^2$$

$$B_1 = -0.0015333 + 0.08384D - 0.12433D^2$$

(4.4)

$$C_1 = (0.31794 - 21.319D + 33.964D^2) * 10^{-6}$$

Thus, by using these equations, a simple relation between process speed, power and beam diameter is obtained. The operating range should be such that the process speed is higher than the critical speed for surface melting and lower than the critical speed for hardening depth of 0.1 mm. The critical process speeds for 0.1 mm depth hardening and no surface melting were calculated for a laser power of 230 W and beam diameter of 0.5 mm. The values were found to be 136.6 mm/s and 112.2 mm/s respectively which provides a very narrow window for processing. However, for a lower power of 150 W, the critical process speeds for 0.1 mm hardening depth and no surface melting were found to be 134.9 mm/s and 52.2 mm/s respectively. The experimental results matched well with the model as discussed later.

Figure 4.9 shows the surface topography before and after laser treatment. The first column in Figure 4.9 shows the topography of as-received surface. The surface appears smooth except for few scratch marks. The second column in Figure 4.9 shows surface topographies after laser treatment using 100 W power and 100 mm/s process speed. The surface appeared flat with little change in waviness. Surface oxides were detected on the surface by EDS which resulted in slight increase in surface roughness. The third column in Figure 4.9 shows the surface after treatment using 230 W power and 100 mm/s process speed. As can be seen, the surface has completely different topography compared to previous ones. It appeared wavy with undulating peaks and valleys. This demonstrates that the surface melted due to excessive laser intensity. Several bumps were spread all over the laser treated surface and varied from a few μm to a size of 60 μm . EDS analysis showed that these bumps were rich in O, Si, Cr, Mn, Fe and C. They were

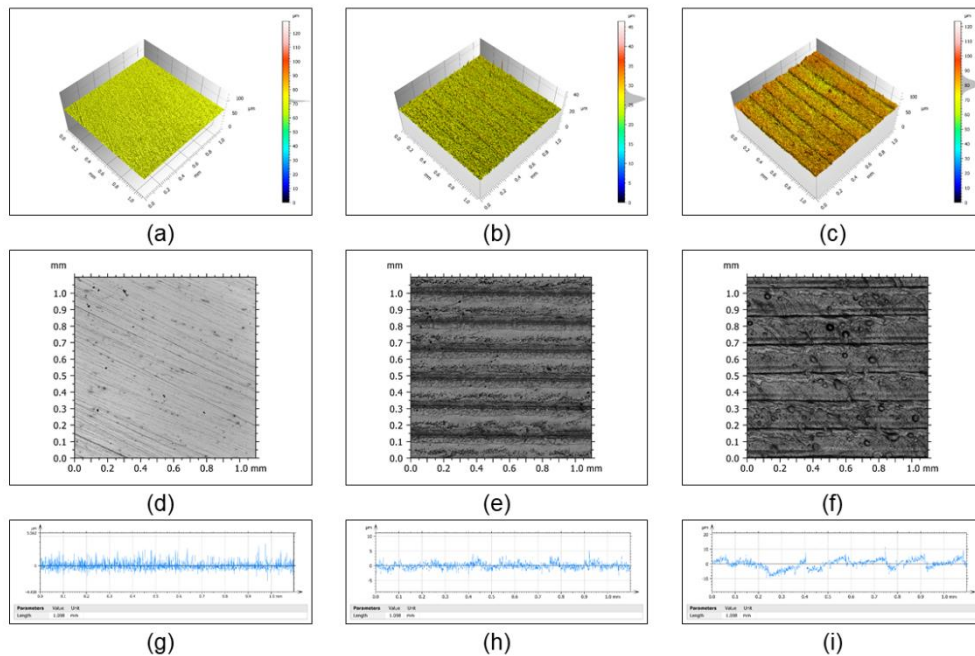


Figure 4.9: Surface topography of (a,d,g) as-received steel surface; (b,e,h) surface treated with 100 W power; and (c,f,h) surface treated with 230 W power. (a,b,c) show 3-D profiles, (d,e,f) show 2-D profiles, and (g,h,i) show line profiles.

The third column in Figure 4.9 shows the surface after treatment using 230 W power and 100 mm/s process speed. As can be seen, the surface has completely different topography compared to previous ones. It appeared wavy with undulating peaks and valleys. This demonstrates that the surface melted due to excessive laser intensity. Several bumps were spread all over the laser treated surface and varied from a few μm to a size of 60 μm . EDS analysis showed that these bumps were rich in O, Si, Cr, Mn, Fe and C. They were

thus identified as metal slag formed due to segregation of elements during rapid heating. The wavy appearance of the surface at high laser power can be attributed to reflow of the melted surface and re-solidification.

X-ray diffraction spectrum of the laser treated surface was obtained to identify the phases formed during laser treatment and compare it with the as-received material. The laser hardening produced similar phases for all conditions. Hence, hardening result with 230W power at 10 mm/s process speed is reported here as a reference for comparison with as-received material.

The diffraction spectrums of both as-received surface and laser treated surface are shown in Figure 4.10. The as-received material basically consisted of ferrite phase (α) while the laser treated surface had martensitic phase (α'), some austenite (γ) and oxides of iron (Fe_2O_3 and Fe_3O_4). XRD analysis also verifies that rapid heating and quenching of the surface layer during laser treatment produces new phases which are harder than the base microstructure. The presence of surface oxides suggests the oxidation of steel surface during laser heating in air.

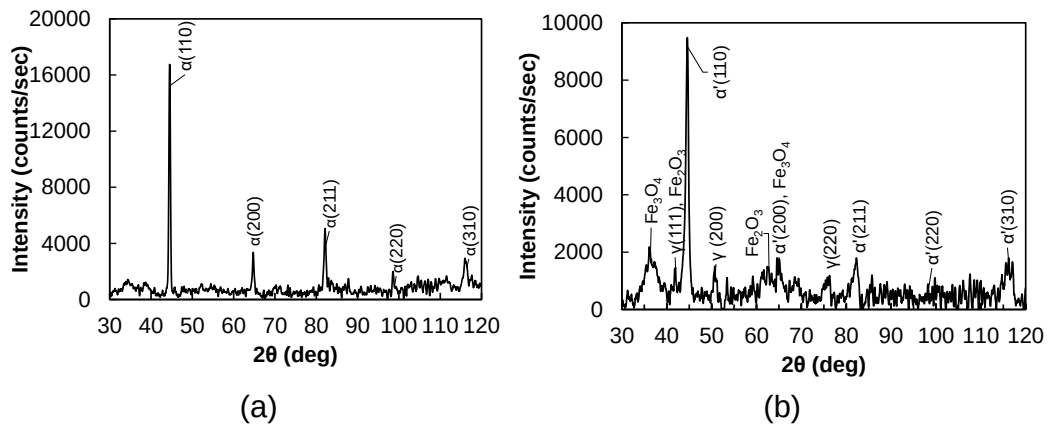


Figure 4.10: XRD diffraction pattern of (a) as-received surface, and (b) laser treated surface. α = ferrite, α' = martensite, γ = austenite.

4.3.3.2 Cross section morphology

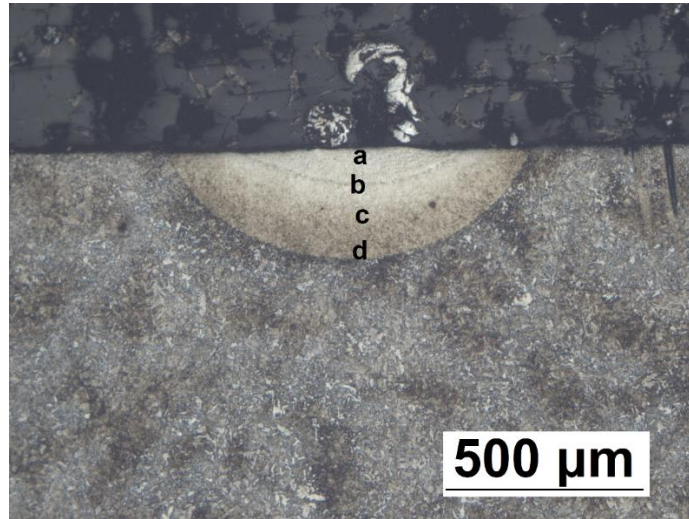


Figure 4.11: Optical micrograph of cross section of laser hardened region obtained using 230 W power at 10 mm/s process speed. The depth and the width of laser hardened region are approximately 290 μm and 930 μm respectively.

A typical microstructure of the cross-section zone of laser hardened layer is shown in Figure 4.11. The laser affected zone can be clearly distinguished from the base microstructure. The structure consists of lath martensite with gradually varying microstructure along the depth (see Figure 4.12). HAZ is minimal or almost absent. Similar microstructures were obtained for all samples.

The base microstructure had a ferritic-pearlitic phase with globular and elongated carbides as shown in Figure 4.12(f). Depending on the extent of self-quenching, the hardened layer had different microstructures along the depth and were identified as laser melted zone (LMZ), LHZ and a transition zone (HAZ) from surface towards depth direction. The LMZ was observed for energy densities of 18.4 J/mm² and higher. In LMZ, the microstructure consisted of lath martensitic structure (Figure 4.12(a)). Due to the high temperature reached at melting point, the atoms in this region can redistribute easily, which on subsequent cooling forms lath martensite.

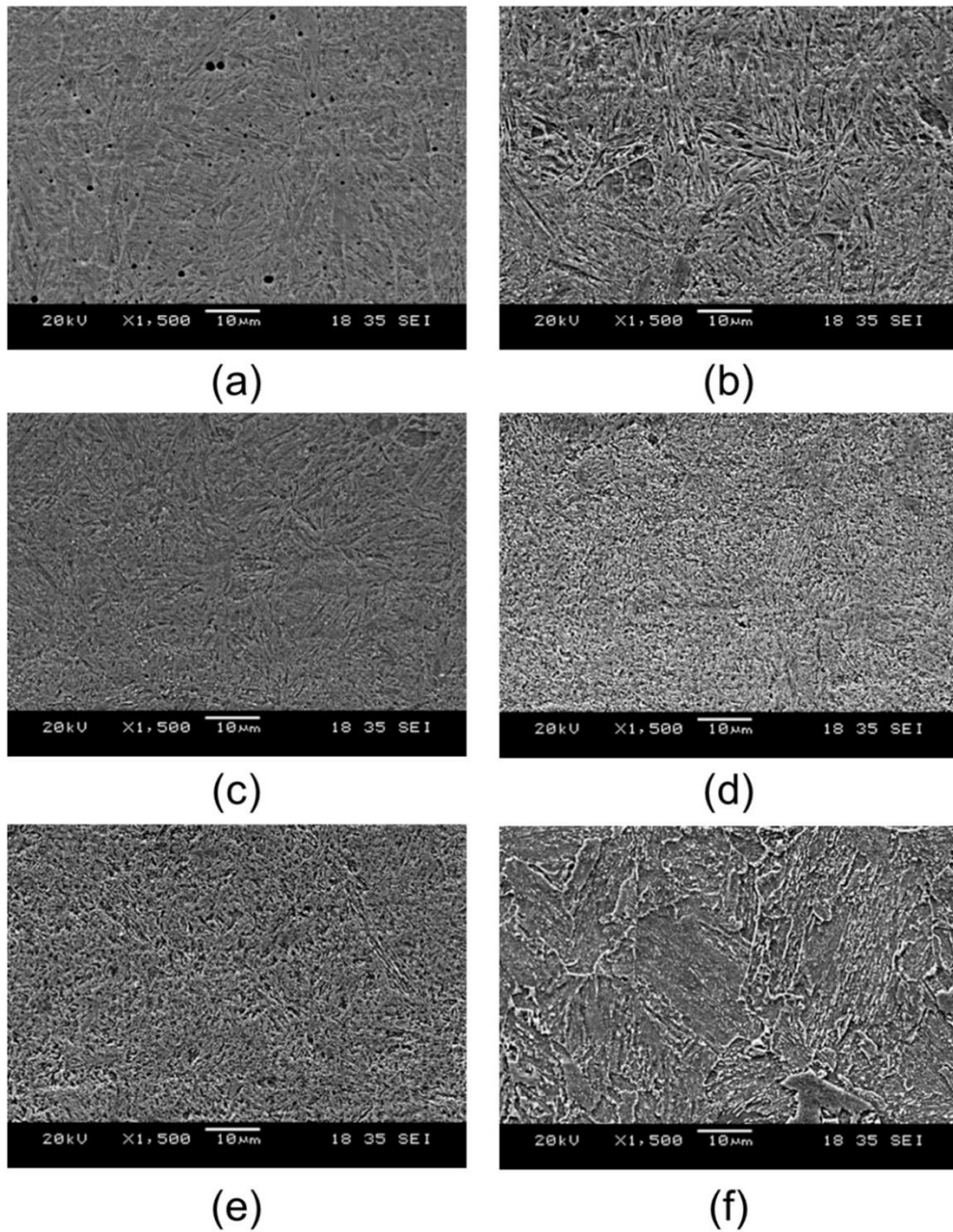


Figure 4.12: SEM micrographs at different position: (a) laser melted zone, shown as 'a' in Figure 4.11; (b) remelted arc, shown as 'b' in Figure 4.11; (c) transformation hardened zone, shown as 'c' in Figure 4.11; (d) lower region of transformation zone showing more spherical carbides; (e) transition zone, shown as 'd' in Figure 4.11; and (f) microstructure of base material. The specimen was etched with 2% nital solution for 5 seconds before observing under SEM.

A distinct arc appeared just beneath the LMZ which appeared as a dark line about 15 μm thick in OM image (indicated as 'b' in Figure 4.11). In this region, a fine structure of lath martensite was found (Figure 4.12(b)). On moving deeper away from the surface, a mixed martensitic structure was observed with a mixture of lath martensite, bainite as well as spherical carbides (Figure 4.12(c)). The stable globular carbides $((\text{Fe},\text{M})_3\text{C}$ with $\text{M} = \text{Cr}, \text{Mo}, \text{Mn}$) were partially dissolved due to rapid heating and cooling and were finely dispersed in the matrix. At the lower end of the LHZ, the martensitic structure with several spherical carbide particles was observed (Figure 4.12(d)). As can be seen in Figure 4.12(e), the transition zone also had similar microstructure. A clear demarcation between the laser affected zone and the base microstructure could be observed.

The average size of these globular carbides was larger than that in the base material. According to the literature, this is due to Ostwald ripening [137]. Presence of spherical carbides indicates undissolved carbide particles during austenitizing prior to quenching because of insufficient time for the dissolution of carbides in the structures present prior to austenitizing [52].

From the microstructure results, it is clear that the heating from laser beam has a decreasing effect on the structure away from the surface. Most of the laser energy is absorbed by the surface and near surface region which increases surface temperature rapidly above its melting point. At such condition, carbon atoms have more mobility and hence, almost all carbides dissolve in the matrix producing a homogeneous austenite phase.

Generally, the cooling rate induced by movement of laser beam is enough for martensitic transformation. The higher cooling rate at the surface explains the formation of fine structures. In addition, the presence of alloying elements suppresses the formation of cementite during quenching. The effect of heating and cooling decreases away from the surface resulting in partial dissolution of cementite particles. Therefore, more spherical carbides appear in the microstructure in lower region of transformed zone and heat affected zone.

Nanoindentation tests were also performed on the polished samples to compare the hardness of laser treated and as-received microstructure. A representative load displacement (P-h) curve for laser treated and as-received microstructure is shown in Figure 4.13. A clear difference can be observed between the load bearing capacity of laser treated region and base material. For the same displacement, the laser treated microstructure could withstand higher load than the base material. The unloading response of both region had almost same slope suggesting that laser treatment does not change the elastic modulus and contact stiffness of the material. The elastic-plastic load curve showed major difference with higher deformation occurring in base material than laser treated microstructure for the same loading. This is attributed to the ductile nature of pearlitic base matrix which can deform more easily. On the contrary, the laser treatment forms a brittle martensitic phase which can withstand a very large load with minimum deformation.

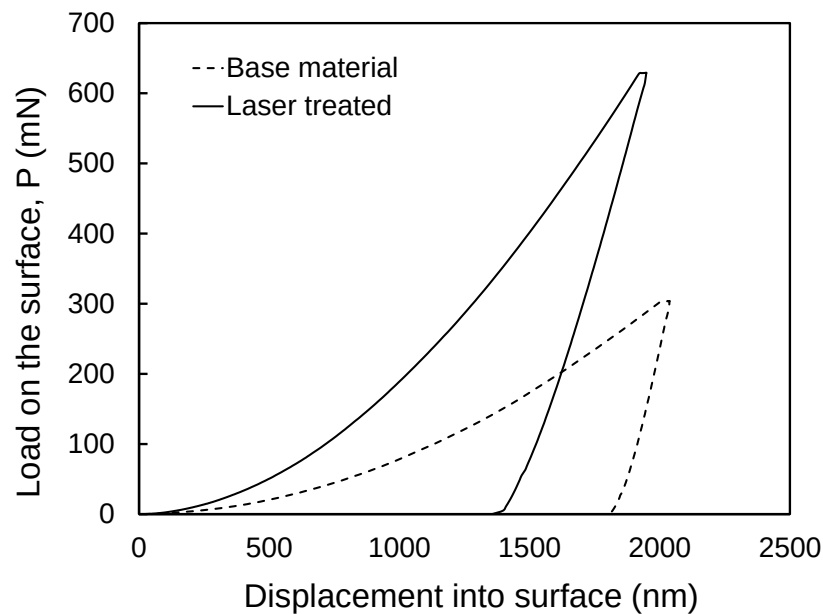


Figure 4.13: A typical load-displacement (P-h) curve for laser treated area and base material.

In order to study the hardness of the laser treated area, a series of nano-indentations were made on the cross section of laser treated sample as shown in Figure 4.14. The hardness of the laser treated area was quite

high compared to that of the base material. The base material hardness was about 3.51 GPa which increased to as high as 10.72 GPa in the melted zone near the surface (Figure 4.14(b)). The hardness in the laser affected region remained almost same until it suddenly dropped to 3.53 GPa immediately below the laser treated area. The results obtained matched with the microstructure evolution discussed above. The sudden drop suggests a narrow heat affected zone present during laser hardening.

Figure 4.14(c) shows the variation of hardness across the direction parallel to the surface. Two positions were considered – first one at 40 μm and the second one at 170 μm below the surface. The first line passes through the laser melted zone and had slightly higher hardness value compared to the second line. The hardness along the lines was almost constant at the laser treated region.

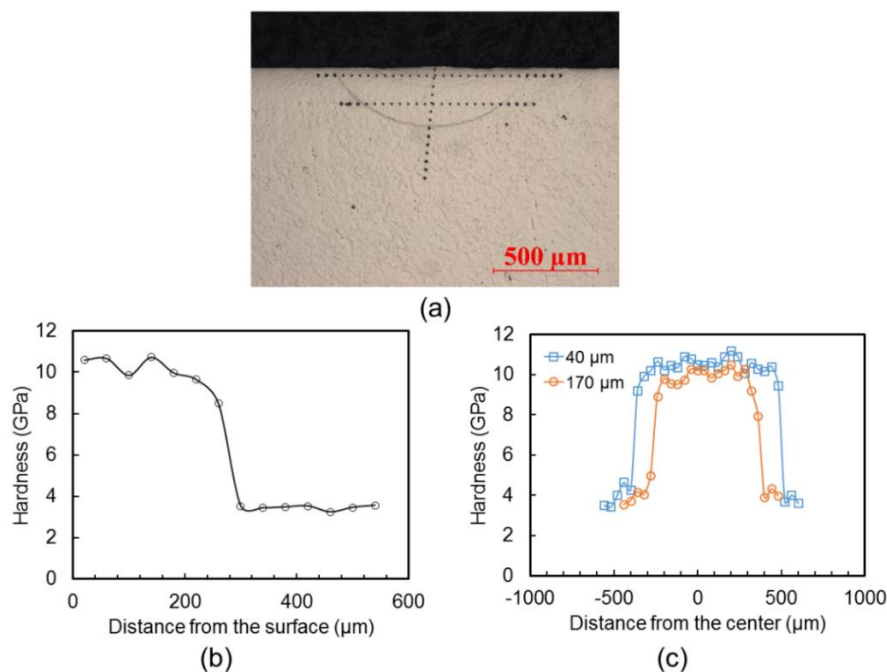


Figure 4.14: Hardness profile analysis. (a) SEM image showing indents made on the specimen, the dotted line represents the extent of surface melting; (b) Graph showing variation of hardness along with depth; and (c) Graph showing variation of hardness across planes parallel to the surface.

In addition to nano-indentation measurements, Vickers microhardness tests were also performed along the depth of laser treated region. The microhardness of the laser treated area along the depth varies as shown in Figure 4.15. The trend is similar to that obtained from nanoindentation experiment with the hardness being very high near the surface and gradually decreasing along the laser treated area with decrease in extent of laser heating until finally dropping down to base material hardness.

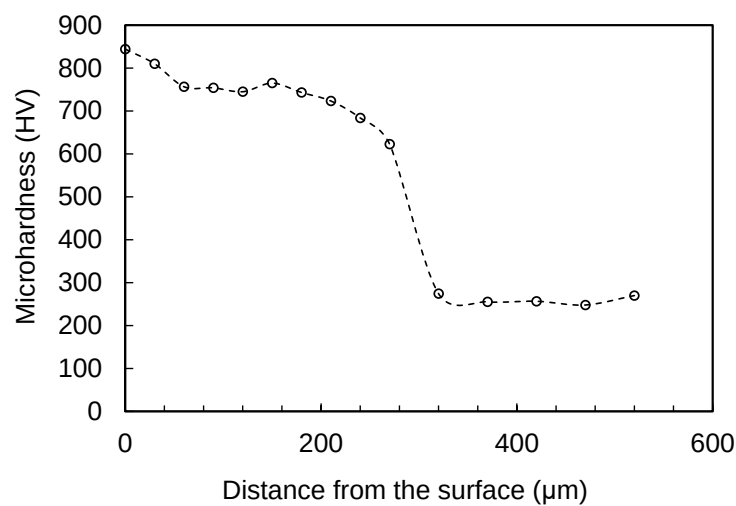


Figure 4.15: Typical hardness profile along the depth of the sample.

A Vickers tip (with 4 sided pyramid) is used for microhardness test while nanoindentation uses a Berkovich indenter (with 3 sided pyramid). Both these tips produce approximately 8% strain in the material during indentation; thus enabling direct comparison of the values [138]. The hardness values can thus be converted to same units using a simple relation [139]. It was found that the hardness value obtained from nanoindentation tests were 1.3-1.5 times higher than the hardness value obtained from Vickers test. For nanoindentation, contact area is defined as the projected area of contact between the sample and the tip. While, for Vickers test, the contact area is the total surface area of tip faces in contact with the sample. Therefore, this difference in contact area definition contributes to higher hardness for nano-indentation.

The other reason could be ascribed to the size effect i.e. hardness decreasing with increase in load [140]. Nanoindentation method uses very small load in the range of mN compared to the loads in the range of N in Vickers test. Generally, the material behavior is more elastic at small loads which might increase the hardness at lower loads.

The hardness of a specimen depends on the distribution of carbide particles in the microstructure and its dissolution during heat treatment. The rate of carbide dissolution depends primarily on austenitization temperature reached and the time for interaction (less effect of heating rate). Since cooling is rapid during laser hardening, the material undergoes diffusionless transformation which provides very little time for carbon re-arrangement and forms martensitic structure. The hardness of the resulting martensite depends on the amount of carbon in the parent austenite.

The physical explanation for high hardness in the laser hardened region was explored in the literature. Obergfell et al. [95] presented a comprehensive method to classify the various hardening mechanisms. Based on their classification, the microhardness obtained can be separated into the effect of different hardening mechanisms as shown in Figure 4.16. In the base material, dislocation hardening (H_{disl}) and precipitation hardening from carbides (H_{carbides}) are the main mechanisms responsible for its hardness. As we move closer to the laser affected area, the temperature reaches between A_{c1} and A_{c3} during heating cycle and the fraction of austenitized and subsequently hardened matrix increases. As a result, the dislocation density in the martensitic matrix increases in this region and hence, hardening effect due to dislocation also increases depending upon the carbon content of former austenite.

As the temperature increases, they suggest that carbide particles dissolve in the matrix and precipitation hardening effect (H_{carbides}) caused by carbides diminishes. On the other hand, it is argued that the dissolution of carbides in the matrix increases the carbon content in the austenite, which further increases the dislocation hardening effect (H_{disl}). The dissolved carbides and

other alloying elements also aid in increasing hardness by solid solution strengthening (H_{ss}). When all of carbides are dissolved at sufficiently high temperature say $A_{c,cd}$, the increase in carbon content in the matrix stops and solid solution strengthening remains constant. The matrix might still be inhomogeneous which becomes homogeneous at a higher temperature $A_{c,hom}$.

Our results match pretty well with this explanation. Therefore, the hardening in the laser treated region is attributed to dislocation hardening of martensitic matrix and solid solution strengthening due to dissolution of carbide in the matrix.

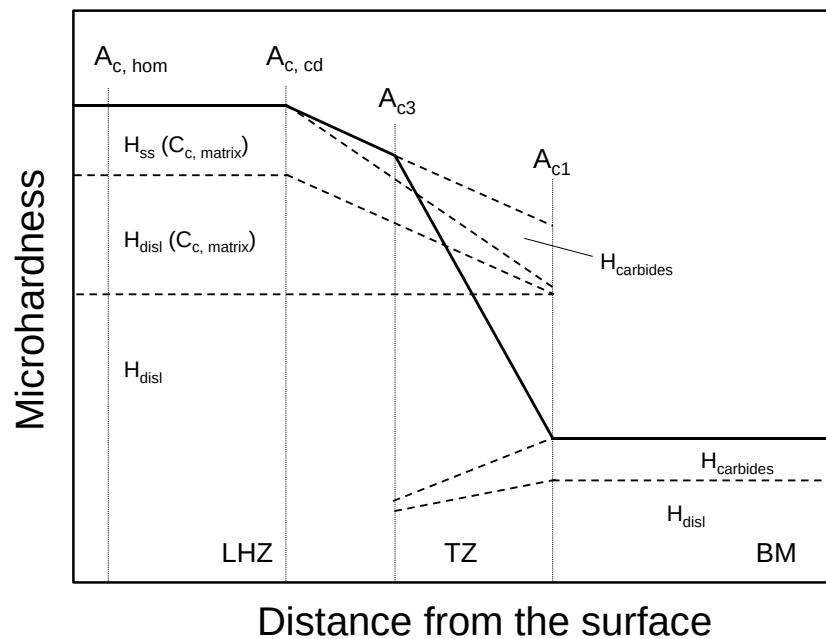


Figure 4.16: Schematic diagram showing different hardening mechanisms contributing to the microhardness values in laser-affected zone [95].

Apart from the hardening mechanisms discussed above, the grain boundary also plays a significant role in hardening of the laser-affected zones. Therefore, electron backscattered diffraction (EBSD) studies were carried out to study the grain boundary effect on hardening of laser affected zones. Figure 4.17 shows the band contrast (BC) image of cross-section of laser treated area. BC is a measure of the intensity of Kikuchi bands and is related to the

quality of the captured pattern image. In BC image, each pixel values range from 0 to 255 (i.e. grayscale) where white represents good quality of the pattern while black represents poor or no Kikuchi bands at all. The grain boundaries usually have high misorientation and hence, produce a darker BC. From Figure 4.17, it can be observed that the laser treated region has lower BC as compared to as-received microstructure. In fact, the grains in parent microstructure can be easily distinguished, but the grains look more refined in the laser treated region.

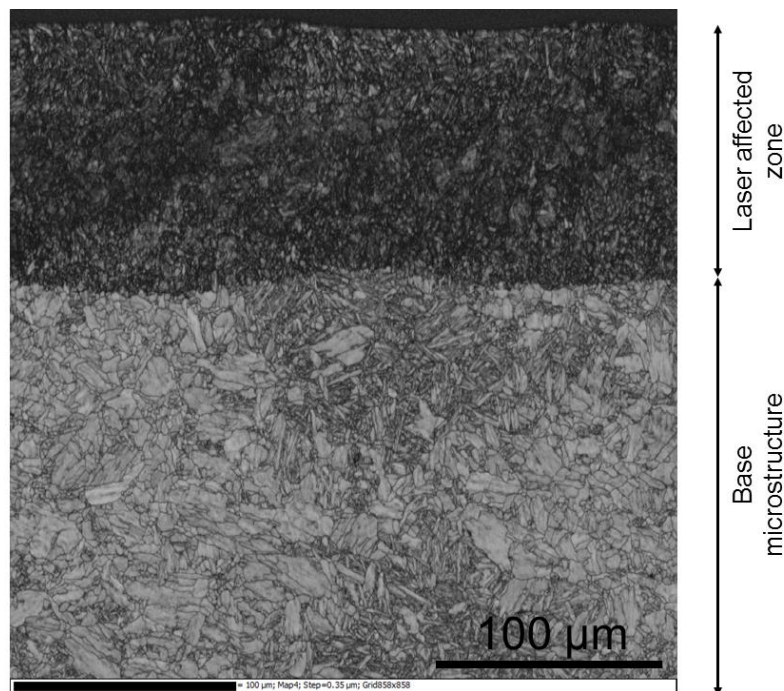


Figure 4.17: Band contrast (BC) image showing laser affected zone and the base microstructure.

The Euler maps of the parent microstructure and the laser scanned region with are shown in Figure 4.18. The Euler maps clearly demonstrate the random orientation of grains suggesting that the material is isotropic. Grain boundaries were defined with misorientation greater than 15° identified as high angle grain boundary (HAB) and greater than 2° identified as low angle boundary (LAB). HAB and LAB are represented by thick black and thin grey lines respectively in Figure 4.18. Few points that were unindexed during the data acquisition were extrapolated based on the orientation of neighboring pixels using the software.

Average grain size was measured using linear intercept method from ASTM Standard E112-12 [141]. At least three images were considered for grain size analysis and 6 lines were drawn on each image to measure the grain size. The average grain size for base microstructure and laser affected zone were calculated to be $5.86 \pm 0.66 \mu\text{m}$ and $2.18 \pm 0.22 \mu\text{m}$ respectively which shows the grain size in the laser treated region to be smaller than the grain size of parent microstructure. Such refinement in grain size also contributes in strengthening of the laser hardened matrix.

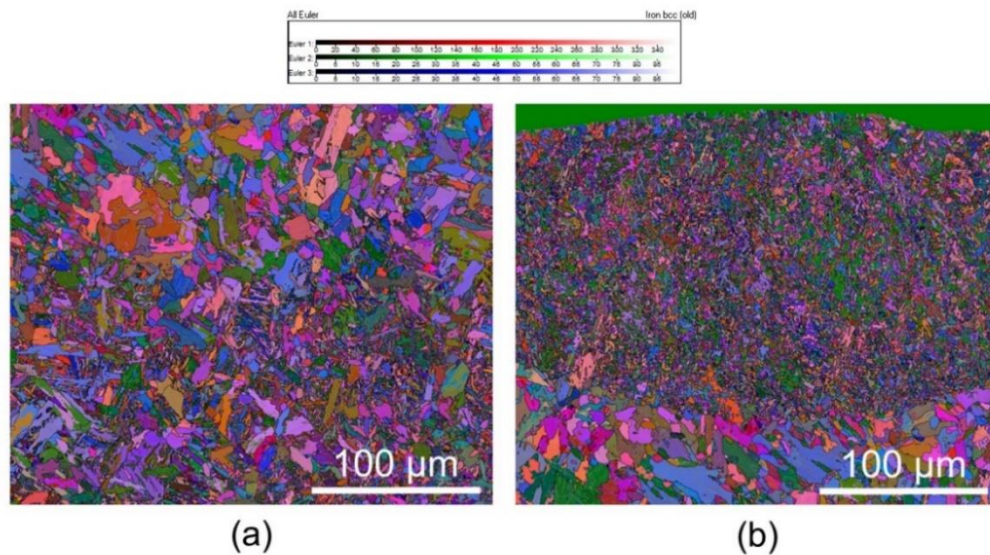


Figure 4.18: Typical Euler maps of (a) base microstructure; and (b) laser treated zone showing the variation in grain size and crystal orientations.

4.3.4 Effect of operating parameters during laser treatment

The size and the properties of the laser transformed zone depends on multitude of factors such as beam spot diameter, energy density [60] and the overlap ratio during multi-track hardening [142]. A systematic study was therefore, performed to study the individual effects of these major parameters influencing surface hardening. The details of the laser parameters used for the experiment can be found in Appendix B1. The effects of these individual factors are discussed below.

4.3.4.1 Effect of beam spot size

The spot diameter of the laser beam at the specimen surface plays an important role during laser treatment. Thus, the effect of spot size was investigated by defocusing the laser beam. The defocusing distance was varied by moving the surface away from the focal plane.

Figures 4.19 and 4.20 show clearly the variation in hardening morphology with change in defocusing distance. The depth of hardening was highest at focused position with value around 120 μm while the width was about 320 μm . The hardening depth decreased with increasing defocusing distance while the width of hardening increased at first and decreased again. The width of hardening remained almost same for 8 mm, 10 mm and 12 mm defocused positions and decreased on further defocusing. At 20 mm defocus position, the hardening width reduced to about 250 μm .

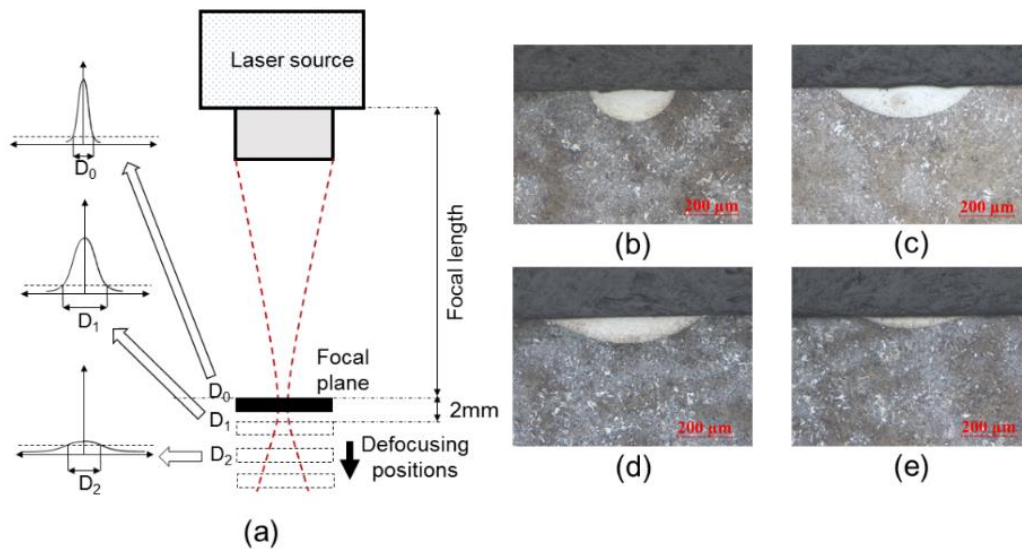


Figure 4.19: (a) Schematic diagram illustrating defocusing of the laser beam; cross-sections of laser-treated samples at varying defocus distance: (b) 0 mm (focal plane); (c) 6 mm; (d) 12 mm; and (e) 18 mm.

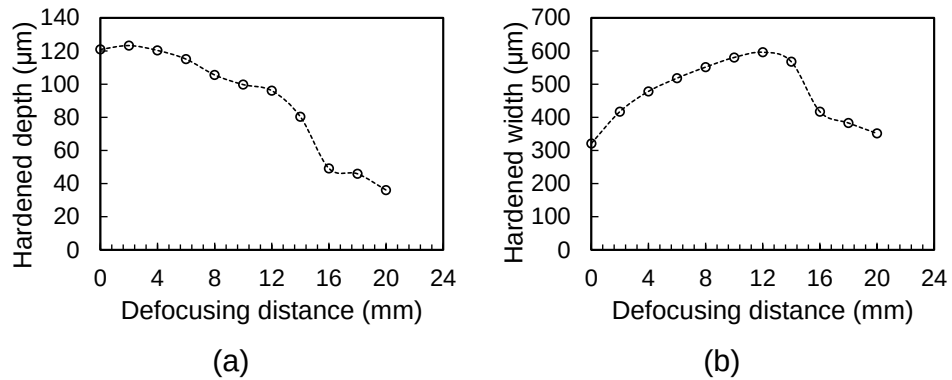


Figure 4.20: Effect of defocus distance on (a) hardened depth and (b) hardened width.

The variation of microhardness at the surface with change in defocusing distance is shown in Figure 4.21(a). The difficulty in measuring the indent size gave a wide variation in data for hardness measurement. Nevertheless, the hardness of the laser transformed zone was found to be almost constant and the value was about 800 HV. As mentioned earlier, the variation of width with change in defocusing can be clearly appreciated from the hardness profile as well. The width of hardening was minimum at focused condition and increased with increase in defocusing distance before reducing again.

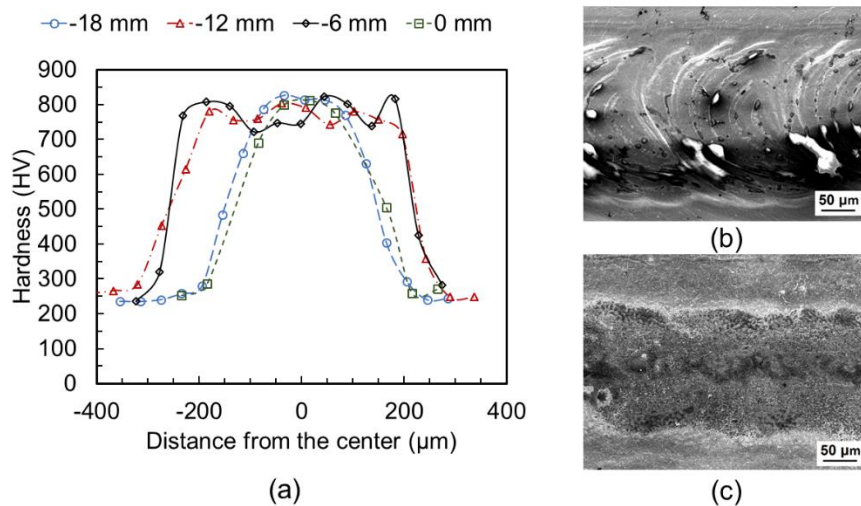


Figure 4.21: (a) Graph showing variation of surface hardness with distance from the center; (b) surface melting at focused position; and (c) surface at 8 mm defocus position with partial oxidation but no melting.

Another interesting phenomenon observed was the melting of the surface as shown in Figure 4.21(b). Surface melting occurred at 0, 2, 4 and 6 mm defocus positions. On increasing the defocusing distance, it was found that no surface melting occurred from 8 mm onwards. It is also noteworthy to point out the surface distortion was observed due to surface melting in focused condition while no distortion was observed for defocused beam condition.

The results obtained can be explained by the nature of Gaussian beam and the spot size. The Gaussian beam has a normal distribution of energy in a plane perpendicular to the beam axis with maximum at its center as shown in Figure 4.19(a). Under focused condition, the Gaussian beam has small beam spot size and a high laser energy density. Hence, the high energy density irradiating on a small spot in the surface of the specimen quickly heats up the material beyond its melting point and results in surface melting.

Contrary to this, during defocused condition, the beam spot size is large and the energy is normally distributed in the spot area with lower intensity at the edge. Such distribution of laser energy results in a lower peak intensity at the center which is high enough to cause phase transformation, but no surface melting. Consequently, a wider hardening track is generated. On further increasing the defocusing distance, the laser energy density at the edge of beam profile becomes too low to bring about any phase transformation in the material and hence, it produces a narrower hardening width comparable to the one in focused condition.

Based on the result obtained, a 10 mm defocus position was used to produce desired surface hardening effect with minimum surface melting for rest of our experiments. The spot diameter at the specimen surface at this condition is about 500 μm .

4.3.4.2 Effect of speed and power variation

The energy density of an irradiated area during continuous wave laser treatment can be estimated by $H = P/Dv$, where P is the power input by the laser, D is the laser spot diameter and v is the process speed. According to

this relation, energy density is directly proportional to power supplied by the laser and inversely proportional to the speed and the spot diameter of the laser. In other words, it gives a combined effect of power, speed and beam spot size during laser hardening. To investigate the individual effects of each of these parameters, each factor should be segregated and studied independently.

Figure 4.22 shows the effect of process speed and laser power on depth and width of hardening. Both the hardening width and hardening depth decreased with increase in process speed. This is expected since increasing the speed would give less time for laser energy coupling and interaction with the surface resulting in less amount of energy transfer. It is also clear from the graph that both the depth and width increase with increase in laser power used. Thus, a higher extent of hardening is obtained by using a lower process speed and a higher laser power.

A bar chart showing the surface hardness variation with different speeds and powers is shown in Figure 4.23. A high hardness is achieved at slower speeds for all power levels used. This suggests that the austenitization time is sufficiently long enough for dissolution of carbides in the microstructure [31] which forms smaller martensite sizes (lath and twin) on cooling [91]. The hardness decreased with increase in speed.

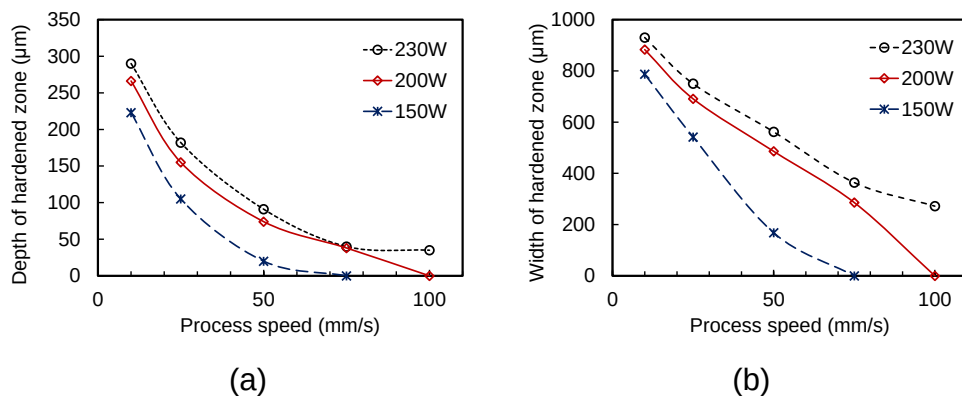


Figure 4.22: Effect of process speed and power on (a) depth and (b) width of hardened zone.

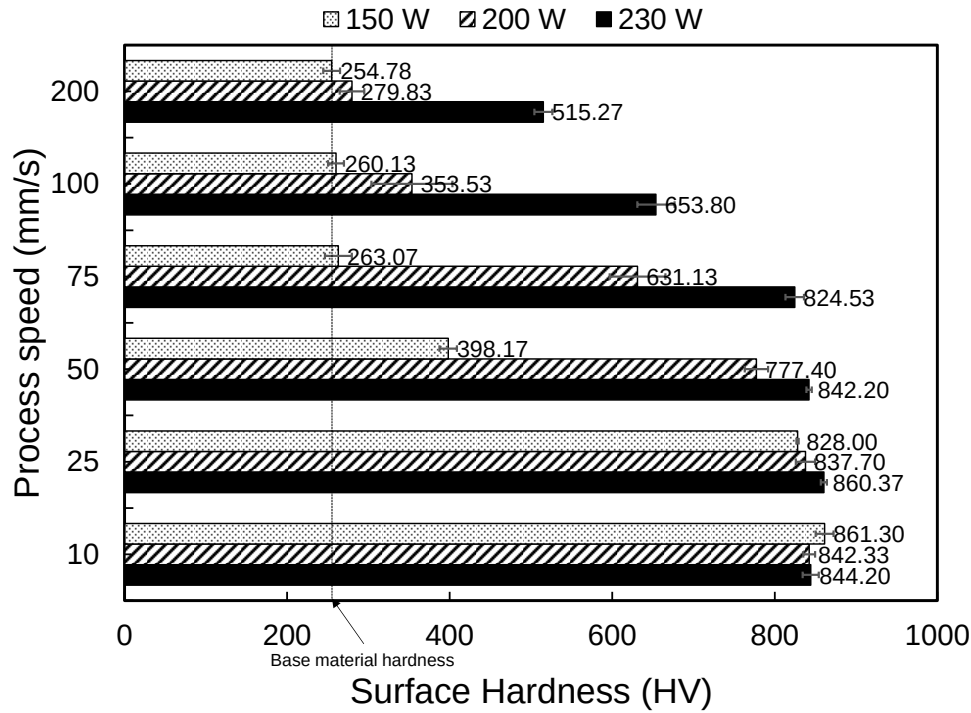


Figure 4.23: Bar chart showing variation of surface hardness at the center of hardened track with different process speed and laser power.

At faster speed, peak temperature does not exceed the critical temperature required for hardening due to shorter time for interaction. Thus, it results only in tempering effect which cannot achieve high hardness value. It is also to be noted that lower hardness is recorded for low power than high power at faster speeds. This can be ascribed inadequate heating at low power.

At 10 mm/s speed, it is observed that the highest hardness is obtained for 150 W laser power instead of 230 W power. The time for austenite homogenization can be considered constant for all power levels since same process speed is used. However, the higher energy density for 200 W and 230 W power can result in surface melting and decarburization effect which slightly lowers its hardness. For other process speeds, this effect is not severe and hence, the general trend of lower hardness with decrease in power prevails.

4.3.4.3 Effect of surface oxide layer

In order to study the effect of surface oxide layer, two normalized samples were taken. One of the samples was polished to P1200 grit surface finish while the other sample had an oxide layer fabricated by heating the sample at high temperature in air for several minutes. The heating formed a thin layer of reddish brown iron oxide layer attached to the exposed surface. The thickness of oxide layer was about 5-20 μm as observed from cross section OM. The surfaces were then laser treated with same laser parameters (230 W power and 10 mm/s process speed).

Figure 4.24 shows the comparison of laser affected area of polished and pre-oxidized specimens. It was found that the sample with oxide layer had higher depth compared to polished sample. This is probably because the oxide layer absorbs more laser energy [130,131,143] and hence more energy is available for hardening. On the other hand, the width of the laser affected area at the surface for pre-oxidized sample was slightly smaller than that of polished sample. This can arise due to surface decarburization more of which is discussed later.

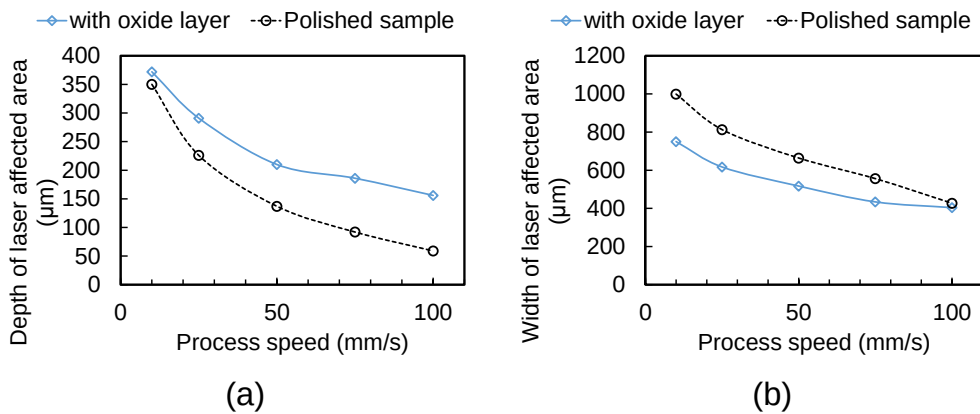


Figure 4.24: Variation of (a) depth; and (b) width of polished and pre-oxidized specimens with process speed.

Figure 4.25 shows the plot of hardness profile of both samples along the depth direction at the center of laser beam irradiation. For polished sample, the hardness is almost constant at around 800 HV with slight decrease along the depth direction. However, for the oxidized sample, the hardness near the surface was lower (around 600 HV) and gradually increased to about 800 HV before finally dropping to base microstructure hardness.

The lower hardness at the surface was attributed to decarburization during laser treatment [144,145]. In addition, the oxide layer on the surface during laser irradiation helps in absorption of laser energy. Pantsar and Kujanpaa [55] reported that surface oxidation enhances absorptivity significantly, thereby increasing process efficiency by as much as 50%. Therefore, abundant heat energy is available at the surface which can result in further oxidation and surface decarburization. The decarburized layer is removed during grinding and polishing and hence no decrease in hardness is observed for the polished sample.

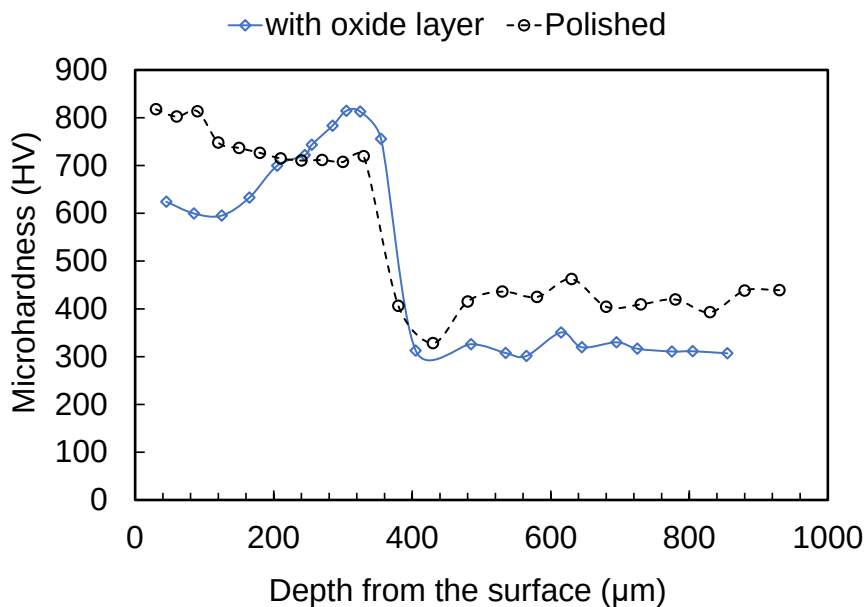


Figure 4.25: Comparison of hardness profile along depth for different surface conditions.

4.3.4.4 Effect of overlapping

In real application, the dimension of the surface to be hardened is generally larger than the spot diameter of laser beam used for hardening. So, several overlapping tracks are required to harden the whole surface. Generally, softening occurs in the overlap zone of hardened surface which is a challenge in surface hardening.

The cross-section micrograph in Figure 4.26 shows the laser affected area during one overlap arrangement at different overlap ratios. The area hardened by second track is obviously larger than that by the first track. Moreover, the distance between the successive tracks significantly affects the hardening obtained. Figure 4.27 shows the variation of hardness at the surface for different overlapping ratios. Except for 0% overlap, the hardness of the first track was lower compared to hardness of the next track for all other cases.

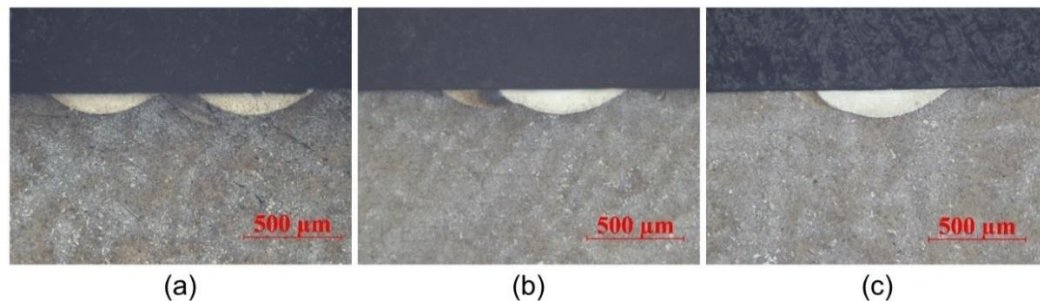


Figure 4.26: Cross section micrograph showing overlapping tracks at different overlap percent: (a) 0%; (b) 33.33%; and (c) 66.66%.

The effect can be explained by the back-tempering effect due to heating from the successive scan. When the tracks are not overlapping, the heating from the successive track has negligible effect on hardening from previous track. As the overlapping increases, part of the martensite formed during first scan transforms to tempered microstructure due to the heating from second track (see Figure 4.28). The tempered microstructure has lower hardness than martensite.

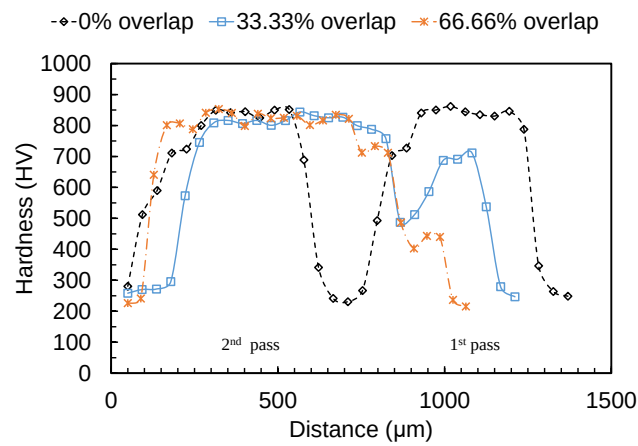


Figure 4.27: Variation of surface hardness for different overlap ratios.

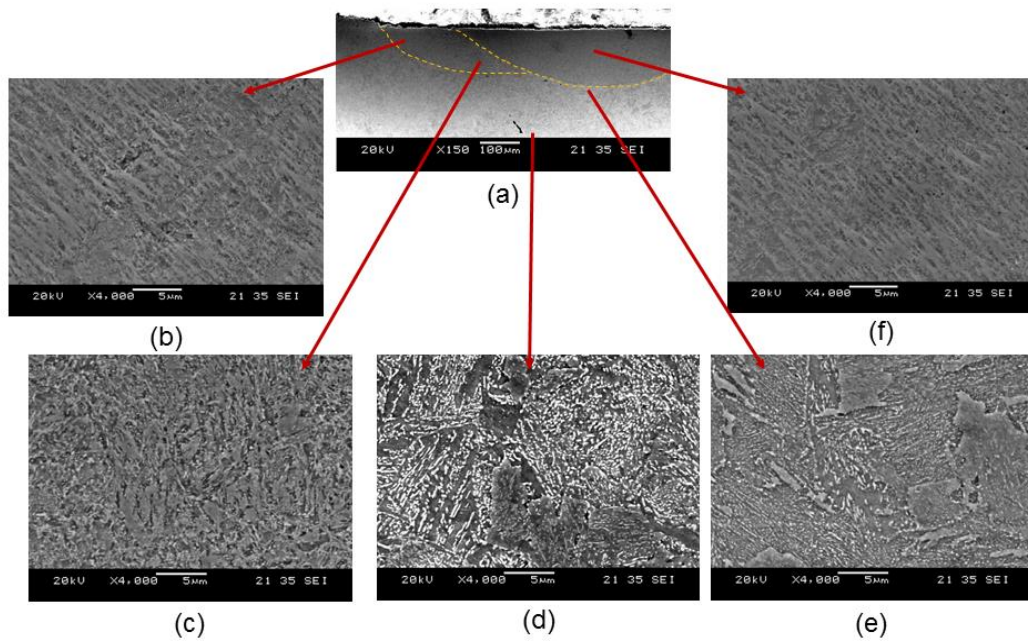


Figure 4.28: Microstructure in the hardened zone of multitrack scanned sample: (a) Overview; (b) martensite in hardened zone in the first track; (c) tempered zone; (d) base microstructure; (e) heat affected zone; and (f) martensite in hardened zone of second track.

On the other hand, the region near the first track is pre-heated to a temperature above room temperature during the hardening of first track. When the second scan passes through the pre-heated region, the austenitization temperature is achieved at a larger area than first scan. This would, in turn,

increase the laser hardened area as well as the hardness value in the second track. The peak austenitization temperature will also increase due to preheating. Figure 4.29 shows schematically a possible thermal cycle experienced by a point in the hardened region of the second track.

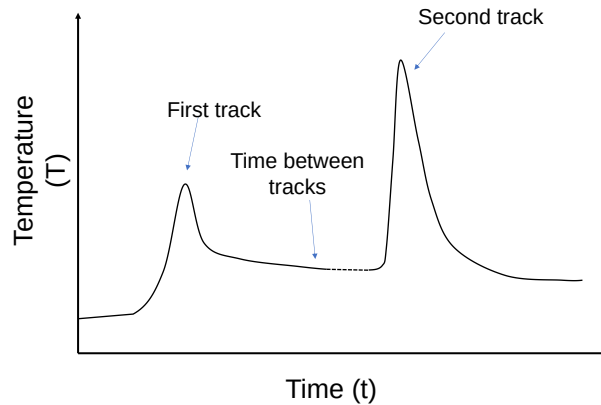


Figure 4.29: Thermal cycle of a point in hardened region of second track.

4.3.4.5 Effect of initial microstructure

The properties of martensite formed during rapid cooling of laser hardening depend on the properties of austenite prior to quenching [52]. At sufficiently higher temperature, ferrite transforms directly into austenite without much carbon diffusion. The properties of austenite formed in such case depends on the maximum austenitization temperature reached and the time available for complete dissolution of carbides in the matrix. The alloy carbides in alloy steel are thermodynamically more stable and require higher temperature and longer austenitization time for complete dissolution [95]. Since the extent of carbide dissolution has significant effect on hardness of martensite, the factors affecting the carbide dissolution during austenitization must be properly investigated.

The initial distribution of carbides in the microstructure could affect the dissolution of carbides. Therefore, samples with different initial microstructure were produced by heat treatment. The initial microstructure of as-received, normalized and water quenched samples are shown in Figure 4.3 and the

laser treatment parameters are presented in Section 4.2.3. For all samples, the laser affected zone was clearly observed as a crescent shaped region after etching with 2% nital solution. Figure 4.30 shows a typical microstructure of laser hardened zone. The structure consists of lath martensite with gradually varying microstructure along the depth. Heat affected zone was minimal or almost absent. Similar microstructure was obtained for all samples.

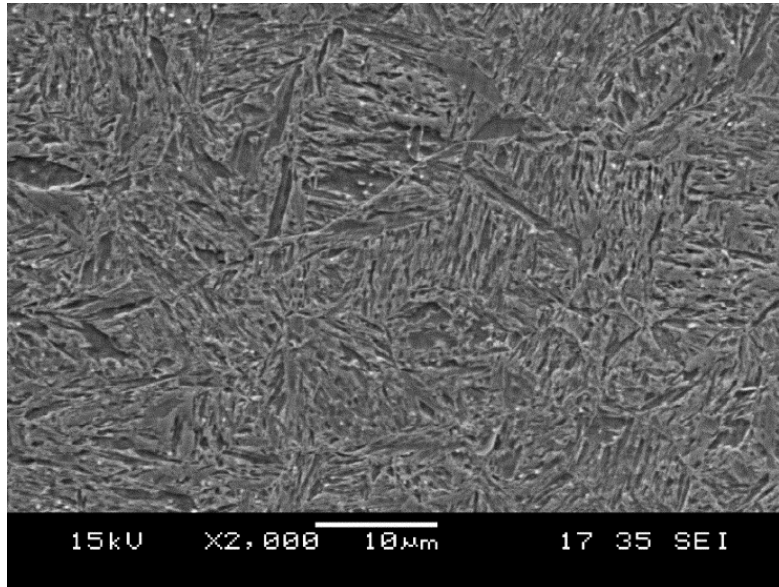


Figure 4.30: A typical martensitic structure in laser hardened zone showing martensitic structure.

Figure 4.31 shows the depth and width of laser affected area as determined from optical micrograph. It is observed that the depth and width did not vary much for normalized and water quenched samples. The as-received sample had slightly lower depth and width. The variation in hardness along the depth was also measured for the samples. Figure 4.32 shows the hardness distribution along the depth of laser treated samples. For all samples, the hardness in the laser treated area is high compared to parent microstructure hardness with the value decreasing gradually as distance from surface increases.

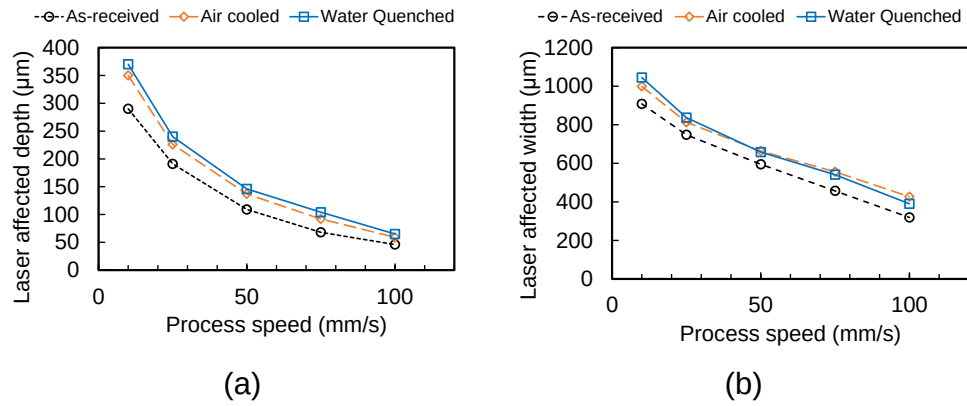


Figure 4.31: Variation of (a) Depth and (b) Width with process speed.

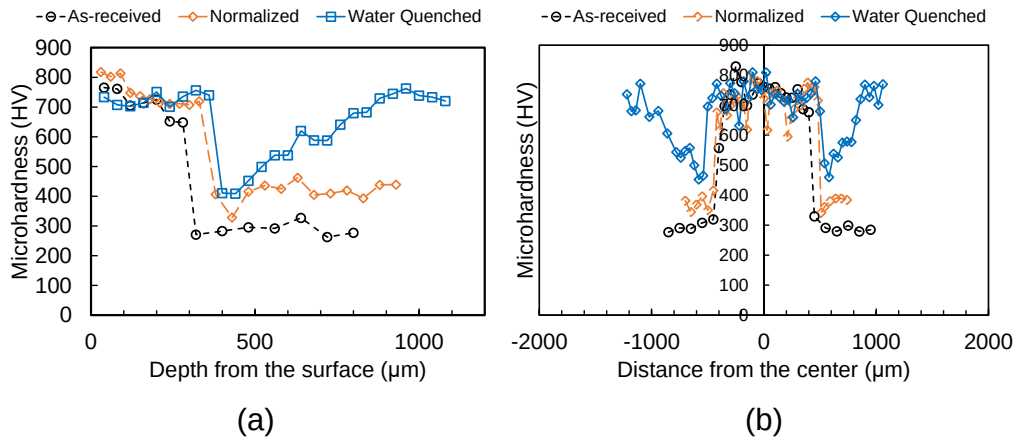


Figure 4.32: Variation of hardness along the (a) depth below the surface; and (b) center line at the surface.

Since the same laser parameters and surface conditions are used for all samples, it can be assumed that the material undergoes same heating and cooling cycle. Thus, the achieved hardness can be related to the initial microstructure of the specimen. From the results, there is not a significant variation in the hardness obtained in the laser treated region. A slightly higher hardness was obtained for normalized sample which can be attributed to matrix homogenization. For the same austenitization temperature and cooling rate, the homogenized microstructure would form a finer structure producing harder martensite compared to non-homogenized structure, however, the difference is not significant in this case.

Water quenched sample already has a very high hardness. Under laser irradiation, laser energy heats up the metastable martensitic structure releasing the trapped carbon particles. These carbon particles dissolve in the matrix during the heating cycle. On rapid cooling due to movement of laser beam, martensite re-forms in areas heated above austenitization temperature. On the other hand, the energy conducted inside the material heats up the matrix due to heat transfer. As a result, the area heated below austenitization temperature undergoes tempering and forms a lower hardness structure. Therefore, a hardness gradient is achieved in the heat affected zone with hardness gradually increasing to quenched hardness in the bulk material.

From the microstructure observed and the hardness profile obtained, it can be concluded that the initial heat treatment had very small effect on maximum hardness obtained in the laser treated region.

4.4 Summary

Laser surface hardening of 50CrMo4 steel was studied using continuous wave fiber laser and the effects of various operating parameters were analyzed. The main findings from the study are listed below:

1. Laser surface hardening produces a distinct microstructural change in the laser affected area with a non-homogeneous microstructure due to difference in heating and cooling rates along the depth. The rapid heating and cooling produces martensitic structure near the surface due to phase transformation which has high hardness and superior mechanical properties compared to base microstructure of ferrite and pearlite. The transformation is rapid and selective with little or no heat affected zone and therefore, can be used for applications where wear resistant surfaces are required such as gears, cams, shafts and bearings.

2. Depending on the intensity of laser beam, surface oxidation and melting might occur during the hardening process. Surface oxidation produces element segregation and formation of Fe-Mn-Cr-O oxides on the surface. The surface oxides appear as thin layers or bumpy structure rich in Mn, Cr, Si and O. Similarly, melting results in formation of surface ripples and wavy surface topography which is generally not desired in laser hardening process. Therefore, critical processing condition to prevent surface melting during laser hardening was evaluated. Based on Komanduri and Zou's model, the critical process velocities for 0.1 mm hardened depth and no surface melting were determined to be 134.9 mm/s and 52.2 mm/s respectively for a constant laser power of 150 W and 0.5 mm beam spot size.
3. The size of laser affected zone is determined by amount of dissolving carbides and distribution of carbon content in the austenite matrix. The laser affected zone could be divided into laser hardened zone and heat affected zone along the depth direction. The hardness was found to be very high compared to base material hardness with hardness gradually decreasing along the depth. Such high hardness is attributed to the combined effect of various hardening mechanisms including dislocation hardening, solid solution strengthening, grain boundary hardening and precipitation hardening.
4. The choice of process parameters for laser surface hardening is generally based on experience rather than on their influence on the resulting microstructures. Therefore, individual effects of major operating parameters were investigated. The findings are presented below:
 - The beam spot diameter only affects the hardened depth and width. For the range of defocusing distance selected, the surface hardness

at the center of the beam spot remains constant at about 800 HV irrespective of the spot size since it undergoes same austenitization process.

- In general, slow process speed produces high hardness value at the surface. The power in such cases has very little effect given that it is sufficient to ensure heating to austenitization temperature. At high power, however, care must be taken that superheating does not occur which can result in surface melting.
- Presence of oxide layer on the surface increases surface absorptivity. Increased energy absorption contributes to increase in laser affected depth. However, the maximum hardness does not change. Instead, it might result in melting of the surface. Moreover, the hardness at the pre-oxidized surface can decrease due to possibility of decarburization from the surface.
- Overlapping of laser hardening tracks results in backtempering which produces lower hardness in the previously hardened track. Higher the overlapping percent, higher is the softening effect.
- The initial heat treatment has very little effect on maximum hardness obtained in the laser treated region.

Chapter 5: Interaction of pulsed laser beam with steel

Pulsed lasers produce an extremely high instantaneous intensity at short pulses which causes phenomena such as multiphoton absorption and optical breakdown [146]. Thus, they are thought to be unsuitable for surface hardening application whereby a phase transformation effect is desired rather than material removal. Nevertheless, pulsed lasers seem to be beneficial for intricate parts with complex geometry in which continuous wave lasers might produce non-uniform hardening due to complex shape of the parts.

In this chapter, the effects of millisecond, nanosecond and femtosecond pulsed lasers on surface modification of various steels are systematically explored. Different laser pulses interact differently with different material and produce a range of effects. Since the main aim of this study is to investigate the feasibility of pulsed laser-based surface hardening, typical steels used in industries are employed to exhibit the possibility of hardening and the results should be applicable to all steels in general. The hardening effect of millisecond pulse laser is investigated experimentally and analytically. Furthermore, the feasibility of hardening using nanosecond and femtosecond laser hardening is explored. Apart from surface hardening, the interaction between short laser pulses and the steel produced various phenomena such as melting, topography changes and surface ablation. The possible application of surface ablation in laser surface cleaning is further investigated.

5.1 Introduction

5.1.1 Hardening using millisecond laser

Laser surface hardening generally employs continuous wave (CW) CO₂ lasers, Nd:YAG lasers and high power diode lasers to produce hard outer case. The higher energy input with CW lasers provides the required heating effect for phase transformation hardening. While CW lasers still dominate this

field, pulsed lasers are also increasingly being implemented for surface hardening applications due to their wider scope for selective hardening and better process control.

Generally, pulsed lasers with lower repetition rate and pulse duration in millisecond range seem suitable for phase transformation hardening [43,45,98,147–156]. Danileiko et al. [150] used 4 ms quasi CW Nd:YAG laser at 50 Hz frequency for pulse-periodic laser heating and found the cyclic cumulative nature of carbon dissolution during laser heating. They pointed out the beneficial effects of pulsed laser for hardening applications because of additional controlling parameters like pulse duration and frequency which give more flexibility to ensure better homogenization of austenite phase, microhardness and hardening depth. In 1999, Xu et al. [151] used a high power pulsed Nd:YAG laser of 2 ms pulse duration and 200 Hz frequency to harden surfaces of AISI 1045 steel and grey cast iron. They could achieve a case depth of 0.6 mm with Rockwell C61 and 40 without surface melting for laser treated 1045 steel and grey cast iron respectively.

Further studies on three-dimensional model for pulsed laser transformation hardening was done by Wu et al. [152]. Their results revealed that temporal pulse shape had great effects on the hardening parameters. Similarly, Habedank et al. [153] performed both experimental and simulation studies on pulsed laser hardening and discovered that hardening with low-pulse frequencies (25-100 Hz) produced a higher hardening depth compared to that by CW laser and could generate compressive residual stresses leading to higher endurance limits. Miokovic et al. [119] did an elaborate investigation on microstructural changes and hardening mechanism during laser hardening with cyclic temperature changes. Their results suggest that increasing number of cycles during hardening leads to varying amount of retained austenite in the hardened zone due to dissolving of carbides and non-uniform distribution of carbon in the matrix.

Similarly, Yilbas and co-workers [155] investigated the laser consecutive pulse heating of solid surface and the influence of pulse parameters on the melting

and mushy zone formation in irradiated region by numerical simulation. Mahmoudi et al. [45] studied the effect of peak and average laser powers on surface hardening of AISI 420 stainless steel with a pulsed Nd:YAG laser at 15 Hz frequency and argued that the laser peak power is a more important parameter than the average power. Nath et al. [156] utilized repetitive laser pulses for surface hardening of AISI 1055 steel and found the average heating rate to be lower and the soaking time above austenitization temperature longer than those in CW laser hardening process. They argued that these effects could increase the depth of hardness and facilitate better homogenization of austenite.

Jiang et al. [147] recognized the laser pulse energy as the most important parameter for spot hardening of AISI 01 tool steel. They found that short laser pulse durations below 8 ms tend to produce shallower hardening zones and recommended to use pulse duration higher than 8 ms for hardening. Similar results were obtained by Yasavol et al. [157] who reported that increase of the laser energy and reduction of the process speed results formation of deeper melt pool. Recently, Shuja et al. [149] studied influence of duty cycle on temperature rise during surface hardening. They found an increment in hardened width size with increase in duty cycle and irradiated spot diameter size.

From above discussion, it is evident that millisecond pulsed lasers with frequency ranging from 0.25 – 100 Hz carry potential to be used for surface hardening. In most cases, pulsed laser treatment is accompanied by surface melting which makes it a combination of both laser transformation hardening and surface melting – referred simply as laser hardening. Surface melting with pulsed laser can be beneficial as it results in fine homogeneous structures due to rapid solidification rates [158]. This is especially true for materials that cannot achieve high hardness through martensite transformation due to incomplete carbide dissolution during short interaction time of transformation hardening [157]. In addition, pulsed lasers can easily treat intricate parts with complex geometry where CW lasers might produce non-uniform hardening due to complex shape of the parts [57].

The current study was carried out to gain a good understanding of the interaction between millisecond pulsed laser and steel. Experimental studies were carried out using AISI 1055 steel, a commonly used plain carbon steel so that the effect of alloying elements could be suppressed during exploration of the underlying hardening mechanism.

5.1.2 Nanosecond laser hardening

Surface hardening using laser utilizes the thermal effect of laser to austenitize the surface and quench it afterwards to achieve hard outer surface. Long pulsed lasers have pulse time longer than the thermal relaxation time for metals (about 10^{-12} - 10^{-13} s) [146]. Thus, they can produce photothermal effect on the material i.e. the absorbed energy is transformed into heat. Since nanosecond lasers have longer pulse duration than laser-induced excitation time and the thermal relaxation time, it is possible to achieve the hardening effect from heat dissipated during the process.

Buling et al. [148] used a pulsed solid-state laser with 1064 nm wavelength, 30 kHz repetition rate and 80 ns pulse duration to improve the adhesive properties of the bearing steel surface. They achieved a very hard surface with hardness higher than 900 HV and maximum depth up to 23 μm . Such changes were attributed to the microstructural changes occurring due to near surface re-austenitization and rapid quenching. A dark etching zone appeared beneath the hardened zone with intermediate hardness up to a depth of 32 μm due to re-tempering which is similar to that in millisecond laser hardening. The study indicates the potential of using nanosecond laser for surface hardening.

However, not many publications are available on utilizing nanosecond laser pulses for surface hardening. This is because the material response will also be dependent on local material heating and cooling rates, maximum temperature reached and temperature gradients. The heating rates can reach as high as 10^9 K/s for nanosecond lasers and at fluences well above ablation threshold of the material, it can result in ablation of material by direct

deposition of laser energy [159]. A careful control of operating parameters is required to demonstrate the hardening using nanosecond laser. Moreover, non-equilibrium microstructure with different properties than conventional CW laser hardening might be generated due to short nanosecond pulses. Therefore, studies were carried out to investigate the feasibility of laser hardening using nanosecond laser.

5.1.3 Femtosecond laser interactions

5.1.3.1 Hardening using femtosecond laser

Femtosecond laser pulses are characterized by incredibly high peak intensities and interact with materials on a timescale faster than the heat diffusion in the material [159]. The fast interaction between laser and material coupled with high laser intensity facilitates photochemical ablation on the surface i.e. the removal of material from the surface by direct absorption of energy. The removal is often precise and occurs by direct ionization, bond-breaking, critical phase separation and rapid phase explosion [160].

The excess energy remaining in the material after ablating the surface might lead to thermal effects in the surrounding volume of material [161,162]. One of such examples is semiconductor annealing using ultrashort pulses which has been well established in microelectronics and photovoltaic industries to improve crystallinity and material performance [163–165]. In metals, Hirayama and Obara [166] studied the heat effects of metals ablated with femtosecond laser pulses and found the amorphous metal formation in the ablated area which they attributed to rapid melting and quenching. Moreover, Dumitru et al. [167] found evidence of crystalline structure change in the immediate vicinity of femtosecond laser induced microholes, with the extent of modified zones increasing with increase in fluence. They reported an increase in hardness near the microholes with hardness as high as 11.6 GPa for AISI 52100 steel and 20.5 GPa for AISI M3 steel.

It was therefore envisaged that the residual energy from ablation can bring changes such as phase transformation and hardening on the remaining

surface. Experiments were carried out to investigate hardening during femtosecond laser irradiation.

5.1.3.2 Ablation during femtosecond laser interaction with steel

Although the hardening effect of femtosecond pulses might not be useful for practical application, the ablation effect can be used to remove surface contaminants which could be useful for surface cleaning as well as damage layer removal remanufacturing industries. The ablation during femtosecond pulse interaction with material is very precise and it creates minimal damage to the substrate. Therefore, further studies were performed on feasibility of using femtosecond laser for surface cleaning applications.

Ultrashort laser pulses are rarely used for cleaning of engineering components. This is possibly due to low material removal rate and high peak power. However, preliminary studies show that the contaminants can be effectively removed by operating the ultrashort pulses in near ablation threshold region in defocused condition [168]. Thus, there is an opportunity to employ short-pulse based ablation for damage removal applications.

Ablation occurs when the laser fluence exceeds the ablation threshold of the material. Since cleaning requires near-threshold operation to prevent excessive damage to the substrate, determination of exact ablation threshold is essential for successful removal of the material by ablation.

Keeping this in mind, the morphological changes during near ablation threshold fluence and high fluence during ultrashort pulse material interaction is explored in this study. The surface modifications during near ablation threshold fluence and high fluence operation are carefully investigated. In addition, the ablation threshold of bearing steel is determined using the diameters measurement method. The incubation effect on ablation threshold is also presented. Special attention is paid to understand the effect of laser fluence on morphological evolution and surface oxidation induced by laser treatment.

5.2 Experimental procedures

5.2.1 Millisecond laser

AISI 1055 steel of dimension 50 x 25 x 16 mm³ was irradiated with laser beam from Ytterbium based fiber laser (YLR-150/1500-QCW) which can be operated both in continuous and pulsed mode. The details of steel and the laser are already presented in Chapter 3. A defocus distance of about 10 mm was maintained for all laser experiments and all experiments were carried under argon gas protection with the flow rate of 15 L/min. A single line tracks of 10 mm were drawn on the sample surface using a galvanometric scanner. The laser beam used had a Gaussian shape with 0.5 mm spot diameter at the surface.

In order to study the effect of mode of operation, the laser was operated in both continuous and pulsed mode. Pulsed mode of operation was performed at a fixed frequency of 10 Hz and different peak power (107 – 1500 W), process speed (0.5 – 5 mm/s) and pulse width (5-20 ms). The details are presented in Appendix B2 and Table 5.1. Microstructural analyses were carried out using stereomicroscopy, optical microscopy and electron microscopy. Microhardness measurements were made on the transverse sections using Vickers' hardness indenter at 100 gf and 15 s dwell time.

5.2.2 Nanosecond laser

A Nd:YAG pulsed laser with 1060 nm wavelength, 220 ns pulse duration and 500 kHz frequency was used to harden 50CrMo4 steel surface. The laser was operated using a Gaussian beam spot of 120 µm at the process speed of 200 mm/s. A 2D galvanometric scanner was used to scan over an area of 10 x 10 mm² with 50% track overlap as shown in Figure 5.1. Laser power was varied from 30 W to 90 W. The details of experimental conditions are provided in Appendix B2.

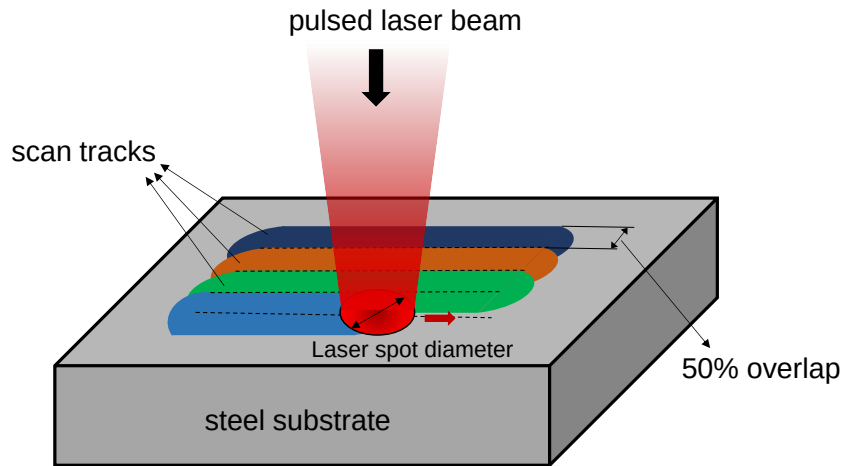


Figure 5.1: Laser hardening scheme showing overlapping of scan tracks.

5.2.3 Femtosecond laser

The material studied was AISI 52100 bearing steel. The details of the steel can be found in Chapter 3. The specimen surface was ground with progressively finer SiC papers (P120, P180, P320, P400, P800, P1200) and polished with 9 μ and 3 μ diamond suspension followed by a final oxide polishing with 0.04 μ m colloidal silica. The average roughness after final polishing was measured to be about 20 nm. Before laser treatment, the sample was cleaned with alcohol, dried with an air gun and placed in the manually controlled X-Y translation stage of the experimental setup.

Figure 5.2 shows the schematics of experimental setup. The Quantronix Integra C-1.0 femtosecond laser (with a center wavelength of 790 ± 10 nm and pulse duration of 130 fs) was used for laser irradiation. The laser was operated at 1000 Hz repetition rate with peak fluence varying in the range of 0.100 J/cm² to 9.000 J/cm². The laser beam approximates a Gaussian shaped intensity distribution at the center. An objective lens of 100 mm focal length was used which created a beam spot radius of about 26.48 ± 1.39 μ m at the

$1/e^2$ intensity. The sample was placed in the focal plane and irradiated under normal incidence by linearly polarized laser in air.

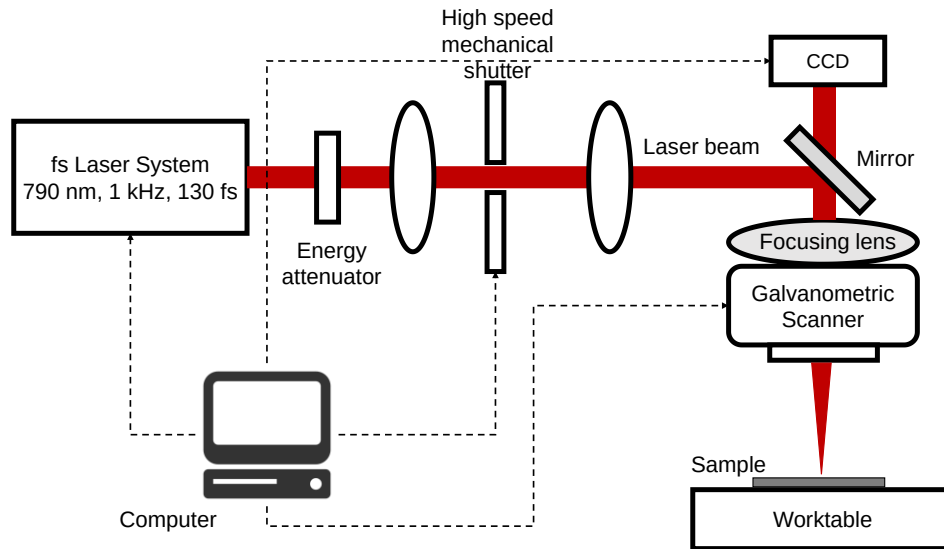


Figure 5.2: Schematics of experimental setup for ablation studies.

It was soon realized that the femtosecond laser did not produce any hardening effect. Instead it resulted in surface ablation. To investigate this further, ablation craters were created on the sample surface at different peak fluences and number of shots as shown in Appendix B2. The number of laser shots striking the surface was controlled by means of computer controlled fast optical shutter. The average power of the laser beam was measured just above the sample surface using PM3 5500 E16R power-meter from Coherent Inc. and pulse energy was calculated as the ratio of average power to repetition rate.

After laser irradiation, the ablation morphology of irradiated area was investigated using Carl Zeiss AxioCAM optical microscope (OM) and JOEL 5600 LV SEM equipped with Energy Dispersive X-ray Spectrometer (EDS). The surface measurements were carried out in OM and SEM images using freely available image processing software ImageJ.

5.3 Results and Discussion

5.3.1 Hardening using millisecond laser

5.3.1.1 Experimental studies

Although average laser power for surface hardening is comparatively lower in pulsed mode than in CW mode, peak power is considerably high. At such high peak power, the surface of the steel reaches to a very high temperature above the melting point. This is evident by formation of melt beads on the surface as shown in Figure 5.3. Melt bead is the melted spot at the surface formed due to rapid heating by single laser pulse. The melted beads had characteristic folds/ripples and formed due to sudden freezing of the molten metal. Such melt beads were observed in almost all the cases except for pulse energies lower than 2 J. For all the considered conditions, the obtained surface layers did not show any evidence of cracks and porosity. At higher pulse energies, the size of the melt beads was larger than at lower pulse energies. Figure 5.4 shows the increase in melt bead size with increase in pulse energies. This is because of the higher energy deposition at higher pulse energies which affects larger area at the surface.

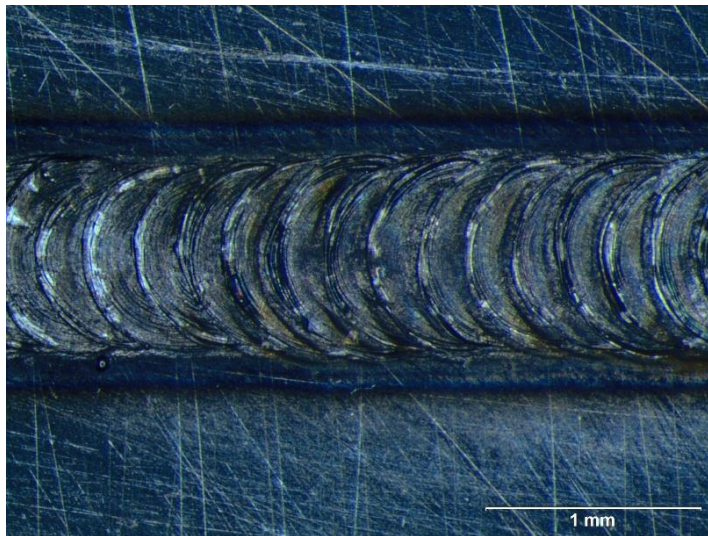


Figure 5.3: Melted surface produced by laser beam with 12.4 J pulse energy, 10 ms pulse duration and 10 Hz frequency.

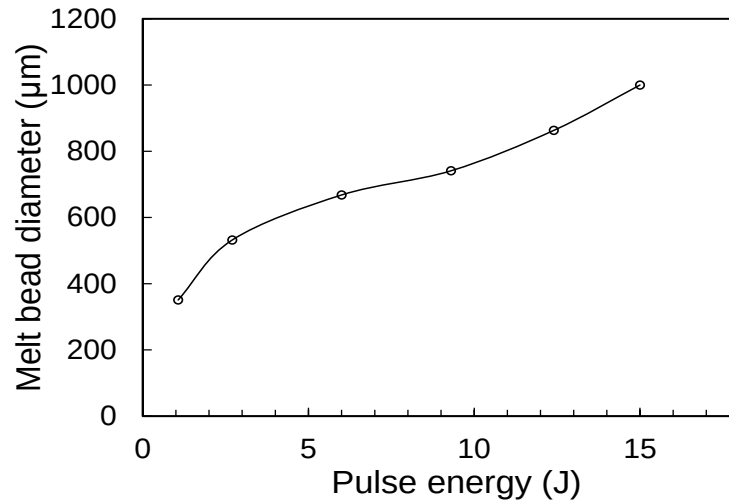


Figure 5.4: Variation of melt bead diameter with laser pulse energy.

Table 5.1: Laser parameters and laser affected zone of AISI 1055 steel.

S. N.	Pulse duration (ms)	Pulse energy (J)	Process speed (mm/s)	Laser affected width (μm)	Laser affected depth (μm)	Bead overlap (%)
1	10	15.00	2	1083	828	76.31
2	10	12.40	2	950	711	76.00
3	10	9.30	2	843	440	70.44
4	10	6.00	2	720	351	68.71
5	10	2.70	2	605	208	60.00
6	10	1.07	2	435	90	37.60
7	10	2.70	0.5	580	198	79.78
8	10	2.70	1	585	214	66.59
9	10	2.70	5	576	204	00.00
10	5	1.35	2	579	158	58.20
12	15	4.05	2	633	261	57.67
13	20	5.40	2	686	291	58.21

Cross section microstructure of the samples showed similar trend. A higher laser affected depth was achieved at higher pulse energies than at the lower pulse energies. The micrographs of transverse section of laser affected area

at different pulse energies are shown in Figure 5.5. The laser affected depth changed from shallow (around 90 μm depth at 1.07 J) to deep zone (with 828 μm depth at 15 J). At even higher pulse energy, cavities were found in the laser affected zone which might have formed due to trapping of air bubbles or shrinkage after solidification.

From the data in Table 5.1, it is observed that for the range of parameters selected, process speed and the pulse duration have almost negligible effect on laser affected area while the variation in pulse energy has the most significant effect. The results are similar to what is reported in the literature [147,157] according to which higher pulse energies lead to more heat input and lower cooling rate which is accompanied by increment in laser affected depth.

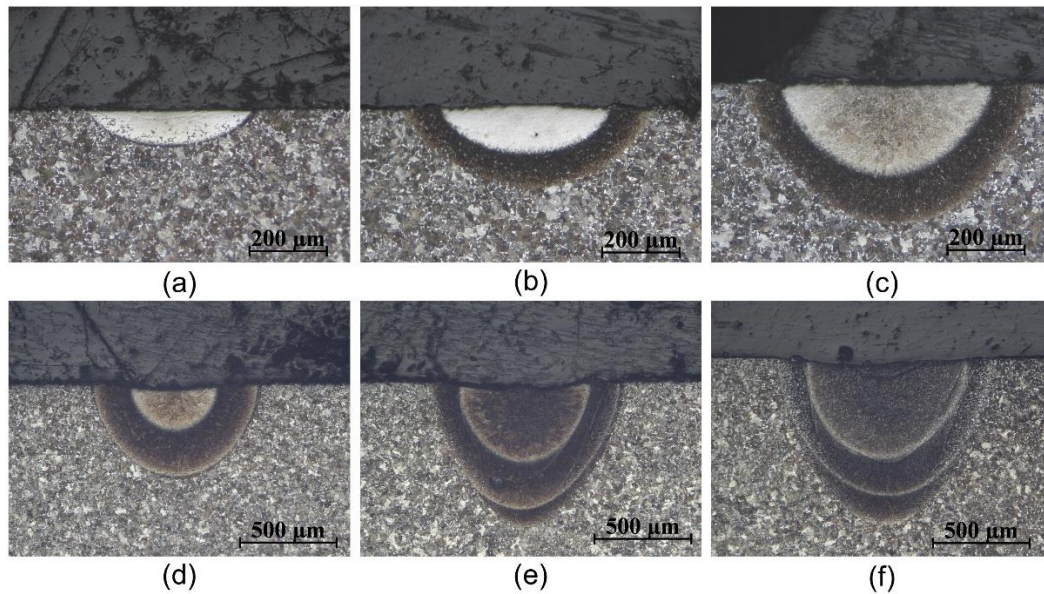


Figure 5.5: Cross section microstructure of specimens after pulsed laser treatment at different pulse energies, (a) 1.07 J; (b) 2.7 J; (c) 6 J; (d) 9.3 J; (e) 12.4 J; and (f) 15 J. 2 mm/s process speed, 10 ms pulse duration and 10 Hz frequency were used in all cases.

Figure 5.6 illustrates the microstructure of different zones of laser affected area processed at laser pulse energy of 15 J, pulse duration of 10 ms and process speed of 2 mm/s. The parent microstructure consists of pearlite and

ferrite as shown in Figure 5.6(d). The laser hardened area had a distinct microstructure from base materials with arc shaped striations in the laser affected zone. These striations relate to the maximum heat affected depth for individual laser pulses and were absent during CW laser treatment. The microstructure near the surface consisted of upper bainitic microstructure with large volume fraction of acicular ferrite. In the intermediate zone between the striations, the microstructure was similar to that near the surface, but the ferrite phase grew at certain locations forming almost equiaxial ferrite.

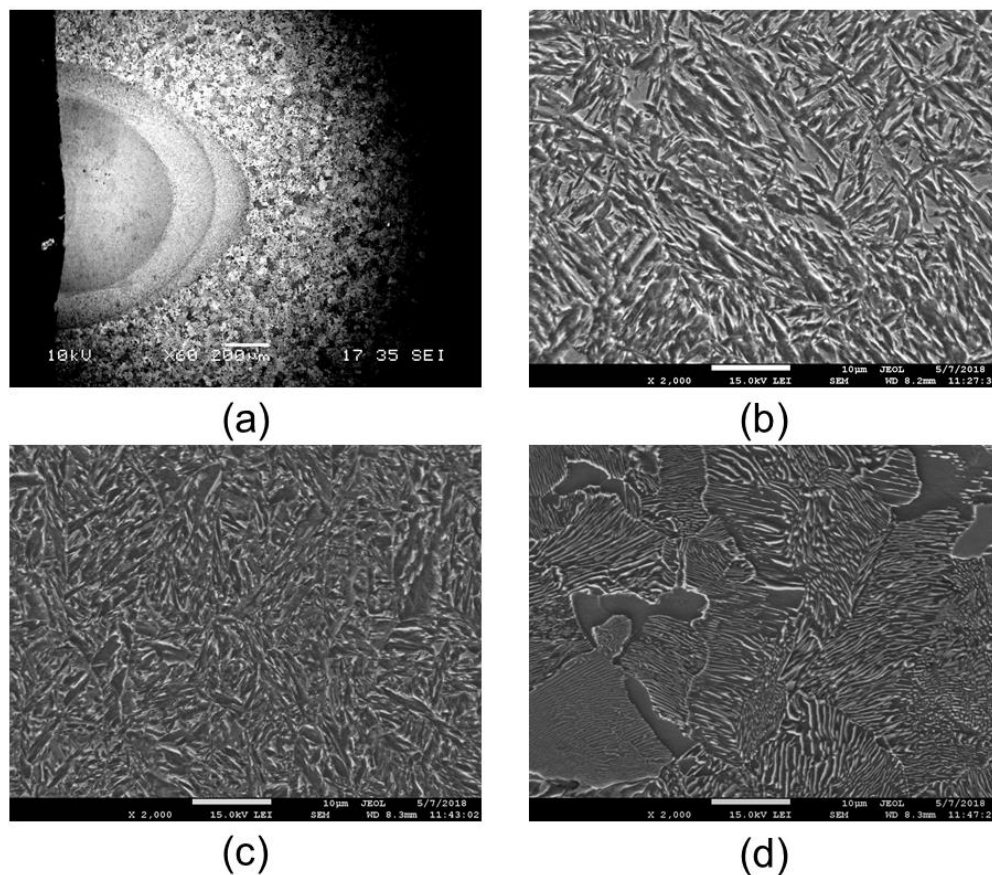


Figure 5.6: SEM micrographs showing cross section of laser treated area at 15 J pulse energy, (a) Overview image; (b) bainitic microstructure near the surface; (c) tempered microstructure in the intermediate zone; and (d) pearlitic matrix of parent microstructure.

During high energy pulse laser treatment, higher energy deposition by consecutive laser pulses results in slower cooling rate [157]. Hence, instead

of martensitic transformation, it produces intermediate temperature range resulting in bainitic transformation. Especially in plain carbon steels, the transformation regions for proeutectoid ferrite/pearlite and bainite are continuous and overlap with decreasing temperature [169]. Moreover, the rapid heating and cooling imposed by laser beam results in non-equilibrium kinetics [135]. Therefore, it is difficult to pinpoint the exact start of bainite transformation. The increase in volume fraction of ferrite in the intermediate zone could be attributed to the tempering effect of heating from successive laser pulses.

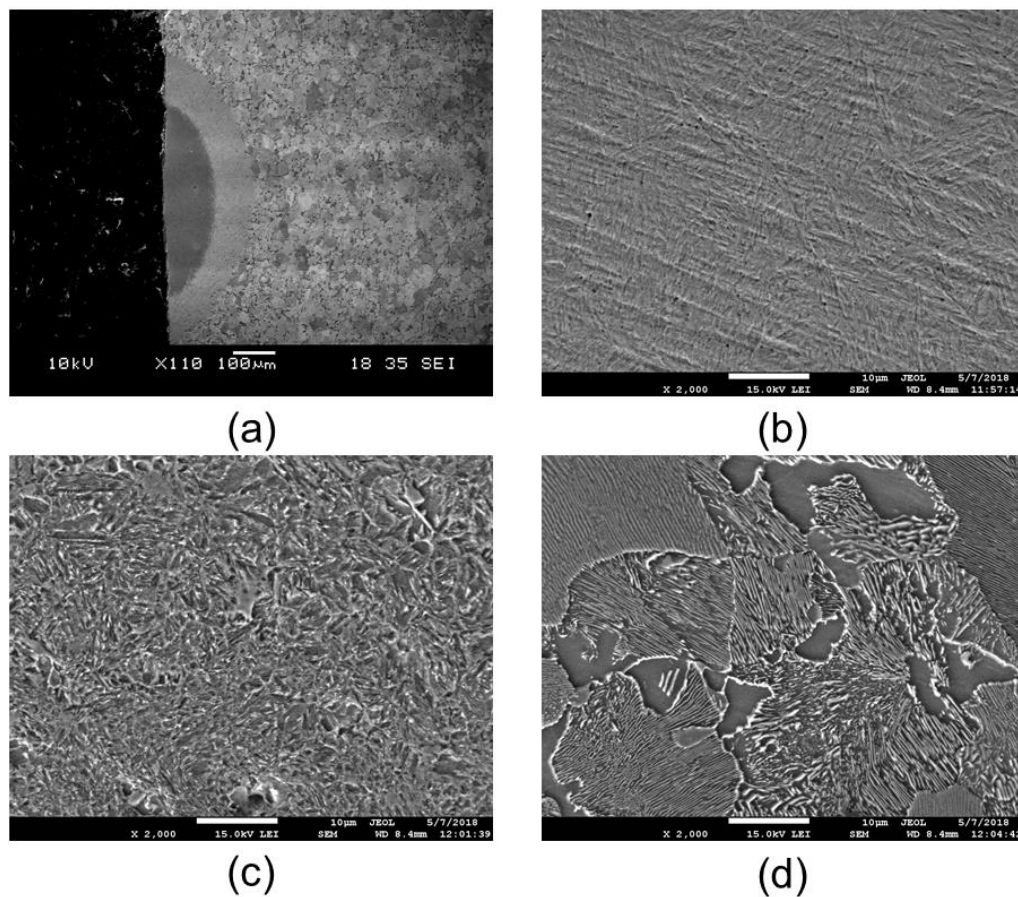


Figure 5.7: SEM micrographs showing cross section of laser treated area at 2.7 J pulse energy, (a) Overview image; (b) martensitic microstructure near the surface; (c) mixed microstructure in the intermediate zone; and (d) pearlitic matrix of parent microstructure.

Figure 5.7 shows the microstructure observed at laser affected area processed at laser pulse energy of 2.7 J, pulse duration of 10 ms and process speed of 2 mm/s. The laser affected depth is lower than for high pulse energy due to lower energy deposition. The microstructure is primarily martensitic in the laser hardened zone; while in the intermediate zone, it consisted of martensite, bainite, ferrite and cementite. The lower pulse energy results in faster cooling rate leading to formation of martensite near the surface. The mixed microstructure in the intermediate zone is due to the tempering effect of successive laser pulses as in the case of higher pulse energy.

To understand more about the microstructural changes, hardness measurements were performed in the laser affected area. The plot of hardness is shown in Figure 5.8. The hardness of the surface treated with 15 J pulse energy did not increase significantly compared to the base material hardness. This result indicates the formation of upper bainitic microstructure as observed from the microstructure in Figure 5.6(b).

Baozhou and Krauss [170] have shown that the strength of upper bainite is very low (~300 HV) compared to lower bainite (430 – 500 HV) and tempered martensite (540 HV). In addition, the fact that upper bainite forms generally at the intermediate isothermal transformation temperature range of 430°C suggests slower cooling rate during high energy laser treatment. A slight increase in hardness in the intermediate zone can be attributed to the tempering effect due to overlapping of laser pulses [41].

Corresponding to the microstructure observed, the specimen treated with lower pulse energy of 2.7 J had a higher hardness near the surface. The hardness value was around 750 HV up to a depth of 100 μm after which the hardness decreased to about 450 HV. The hardness remained at this value up to a depth of about 200 μm after which it reduced the parent microstructure hardness. The depths correspond to the martensitic zone near the surface and intermediate zone with mixed microstructure as seen in SEM micrographs in Figure 5.7.

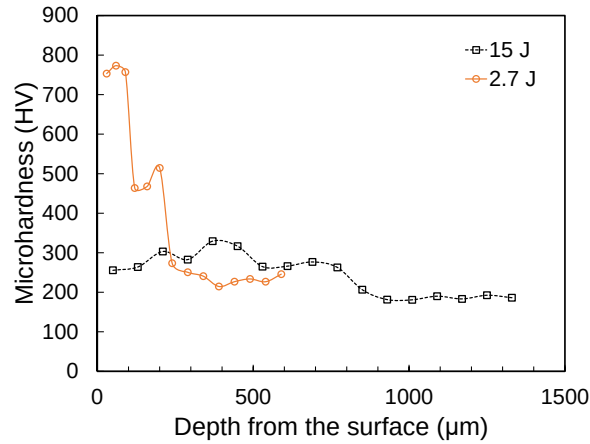


Figure 5.8: Hardness profile along the depth for surface treated at different pulse energies.

The influence of pulse duration on laser hardening was also studied. Microhardness profiles are presented in Figure 5.9 which shows that the depth of hardness reduces with the reduction of pulse duration. This is because the average laser power decreases and the heat loss during laser off period increases with the reduction of pulse duration [156]. For 5 ms pulse duration, intermediate zone was not observed. The hardness in the affected zone was also slightly lower than with 10 ms pulse duration probably due to insufficient heating above austenitization temperature. On the other hand, longer pulse duration of 20 ms provides more time for the material heat up and cool down avoiding martensitic transformation. Therefore, it produces a lower hardness in the laser affected zone than with shorter pulse duration.

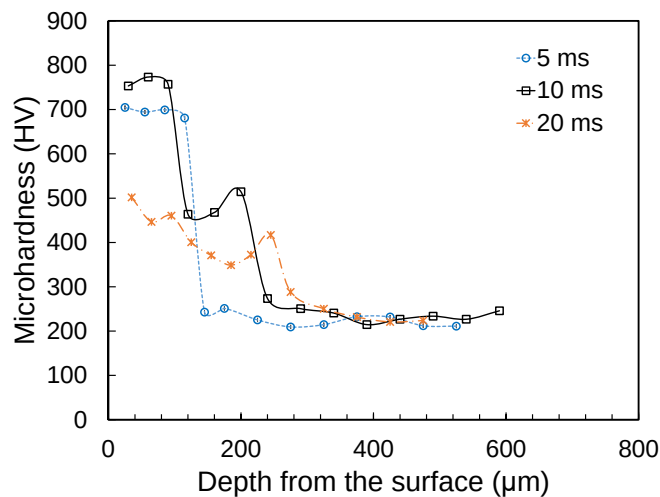


Figure 5.9: Hardness profile along the depth for various pulse duration.

5.3.1.2 Analytical modelling

Laser surface treatment utilizes laser as a source of heat to raise the temperature of the surface. When the temperature increases above A_{c1} temperature, pearlite colonies in hypoeutectoid steel transform to austenite. The transformation occurs by diffusion of carbon from eutectoid cementite plates into eutectoid ferrite plates within pearlite colonies. If the pearlite plate spacing in a colony is λ , the lateral diffusion of carbon over a distance λ would be sufficient to convert colony to austenite. This forms austenite containing $c_e = 0.8 \text{ wt\% carbon}$.

The fast heating rate during laser treatment quickly rises the surface temperature above A_{c1} temperature. At higher temperature, carbon tries to homogenize in the matrix. The extent of carbon diffusion from high to low concentration region depends on time and temperature for which the surface layer is held above A_{c1} temperature [171]. Depending on the superheated temperature, part or all of proeutectoid ferrite may transform to become austenite with negligible carbon content, c_f . When the temperature reaches A_{c3} temperature, the transformation of proeutectoid ferrite to austenite is completed. On subsequent cooling, all material with carbon content higher than a critical value c_c ($\sim 0.05 \text{ wt\%}$) converts to martensite.

Jacot and Rappaz [92] suggest that with faster heating rate as in laser surface treatment, the A_{c3} temperature is raised to a higher value and thus, complete homogenization of austenite may not occur. In addition, a finite time is required for carbon dissolution in pearlite colonies and some additional time for homogenization of carbon in austenite. According to Ashby and Easterling [61], this time is determined by the kinetic strength of heating cycle. All these indicate that a finite soaking time above the phase transformation temperature is necessary to get a uniform distribution of carbon in austenite microstructure [156].

The time required for carbon to diffuse in pearlite structure can be estimated by [61]

$$L\lambda = 2D_0\alpha\tau\exp\left(-\frac{Q}{RT_p}\right) \quad (5.1)$$

where, $2L$ is the diameter of the pearlite colony, λ is the average pearlite plates spacing, τ is the characteristic time for diffusion of carbon, and D_0 , Q , R and T_p respectively are the pre-exponential carbon diffusivity, activation energy for transformation, gas constant, and peak temperature.

The term, $\alpha\tau\exp(-Q/RT_p)$ represents the kinetic strength of heating cycle. The constant α is approximated as

$$\alpha \approx 3 \sqrt{\frac{RT_p}{Q}} \quad (5.2)$$

Furthermore, the diameter of pearlite colony can be related to austenite grain diameter by [156]

$$2L = \frac{g}{f_i^{1/3}} \quad (5.3)$$

where $f_i = c/c_e$, c = carbon wt% of the steel specimen and $c_e = 0.8$ wt% i.e. carbon content in eutectoid steel.

The pearlite colony diameter and lamellae spacing in pearlite was determined using SEM image. In order to reduce the complications of measurements which usually arise due to variation of spacing within a given pearlite colony or between different colonies or even due to metallographic sectioning plane, a robust method proposed by Vandervoort and Roos [172] was utilized to measure the average values. From the micrographs, the average pearlite colony diameter, $2L$ and pearlite lamellae spacing, λ , were determined to be $20 \mu\text{m}$ and $0.34 \mu\text{m}$ respectively.

The time required for carbon diffusion in pearlite for these values is estimated using equation (5.1) at different temperatures in A_{c1} – A_{c3} interval and is tabulated in Table 5.2. Other values required for the calculation are taken from literature [61]. From estimated time, the diffusion of carbon in pearlite above

A_{c1} is very fast (in the range of microseconds). During fast heating as in laser treatment where heating rate can go as high as 10^4 K/s, the process can be assumed to be instantaneous.

The diffusion of carbon from high concentration austenite (with eutectoid carbon content) to proeutectoid ferrite and low concentration austenite is governed by Fick's 2nd law. The characteristic time for diffusion of carbon in proeutectoid ferrite and austenite can be estimated using an approximate solution given by [61]

$$x = \frac{2}{\sqrt{\pi}} \ln \left(\frac{c_e}{2c_c} \right) \sqrt{\alpha \tau \exp \left(-\frac{Q}{RT_p} \right)} \quad (5.4)$$

where x is the distance up to which carbon content in proeutectoid ferrite/austenite reaches a critical value, c_c by diffusion from high carbon content ($c_e = 0.8$ wt.%) austenite in time, τ . The critical value is taken as $c_c = 0.05$ wt% for martensite to form.

Table 5.2: Characteristic time for carbon diffusion in hypo-eutectoid steel at different temperatures.

Peak temperature (K)		1000	1113	1183	1273	1473	1673
Characteristic time for carbon diffusion	in pearlite	442.3 μs	158.0 μs	91.8 μs	49.8 μs	16.6 μs	7.13 μs
	from pearlite to pro-eutectoid ferrite	3.72 ms	1.33 ms	0.77 ms	0.42 ms	0.14 ms	0.06 ms
	from pearlite to austenite	21.7 s	4.0 s	1.6 s	0.6 s	0.1 s	0.02 s

For homogenization, carbon should diffuse across whole austenite grain. Thus, equating x as radius of austenite grain ($g/2$), the characteristic time for diffusion of carbon in ferrite and low-concentration austenite is calculated for different temperatures above A_{c1} as shown in Table 5.2. The obtained results show diffusion of carbon in austenite is relatively slower than in ferrite and

therefore, longer austenitization time is required for complete homogenization. At higher heating rate, the time required is even longer as pointed out by Jacot and Rappaz [93].

When the laser beam moves away, rapid cooling occurs in the heated zone which produces displacive transformation rather than diffusive. In such cases, cooling rate becomes more important rather than the kinetic strength. Cooling rates in excess of 10^3 - 10^5 K/s is common during laser surface treatment [173]. Even higher cooling rate can be obtained by using short pulses [4]. Such high cooling rate is sufficient for austenite having carbon content more than critical value c_c to transform to martensite.

The volume fraction of martensite can be estimated by [61]

$$f = f_m - (f_m - f_i) \exp\left(\frac{6f_i^{\frac{2}{3}}}{g} x\right) \quad (5.5)$$

where, f_m is the maximum volume fraction of martensite permitted by the phase diagram. It can be determined by

$$\begin{aligned} f_m &= 0 \text{ if } T_p < A_{c1} \\ f_m &= f_i + (1 - f_i)(T_p - A_{c1})/(A_{c3} - A_{c1}) \text{ if } A_{c1} < T_p < A_{c3} \\ f_m &= 1 \text{ if } T_p > A_{c3} \end{aligned} \quad (5.6)$$

The average microhardness of the quenched surface can then be estimated by [61]

$$H = 1667c - 926c^2/f + 150 \quad (5.7)$$

Based on equations (5.5) -(5.7), average microhardness corresponding to $f = 1$ is estimated to be 784 HV which is almost same to the hardness value measured near the surface for hardened region. Since the carbon content in

martensite will vary along the depth, the microhardness is expected to decrease along the depth with decreasing influence of laser heating.

An additional thing to note during pulsed laser hardening is the accumulation of heat from each pulse [150,156]. This increases diffusion of carbon in the matrix pushing forward the boundary having critical value of carbon, c_c . Therefore, a higher depth of hardening can be obtained even with lower average power compared to CW laser. For example, with an average laser power of 27 W, the hardening depth of about 200 μm is obtained which is comparable to depth achieved by CW laser of 250 W power. However, it is to be noted that at high power, longer soaking time can result in austenite grain growth, softening and can even result in onset of melting [156,157].

5.3.2 Surface hardening using nanosecond laser

The topographical changes on the steel surface due to laser treatment was analyzed using white light interferometry. Figure 5.10 shows the surface profile obtained and the surface parameters are presented in Table 5.3.

As can be seen, the laser treatment with low power of 30 W did not show any obvious change in surface morphology. Increasing the laser power led to formation of rougher surface. A higher surface roughness was obtained for 60 W laser power than for 90 W laser power. Careful observation revealed the presence of some deep craters in the 60 W laser treated sample which increased its average surface roughness.

The craters during 60 W laser treatment probably formed from higher absorption of laser energy by contaminants on the surface. The surface is always prone to some contamination even though careful cleaning and precautions are taken. These surface contaminants absorb more energy leading to localized melting and outflow of molten metal. The metal outflow can be verified by increase in height of the surface around the periphery of the crater.

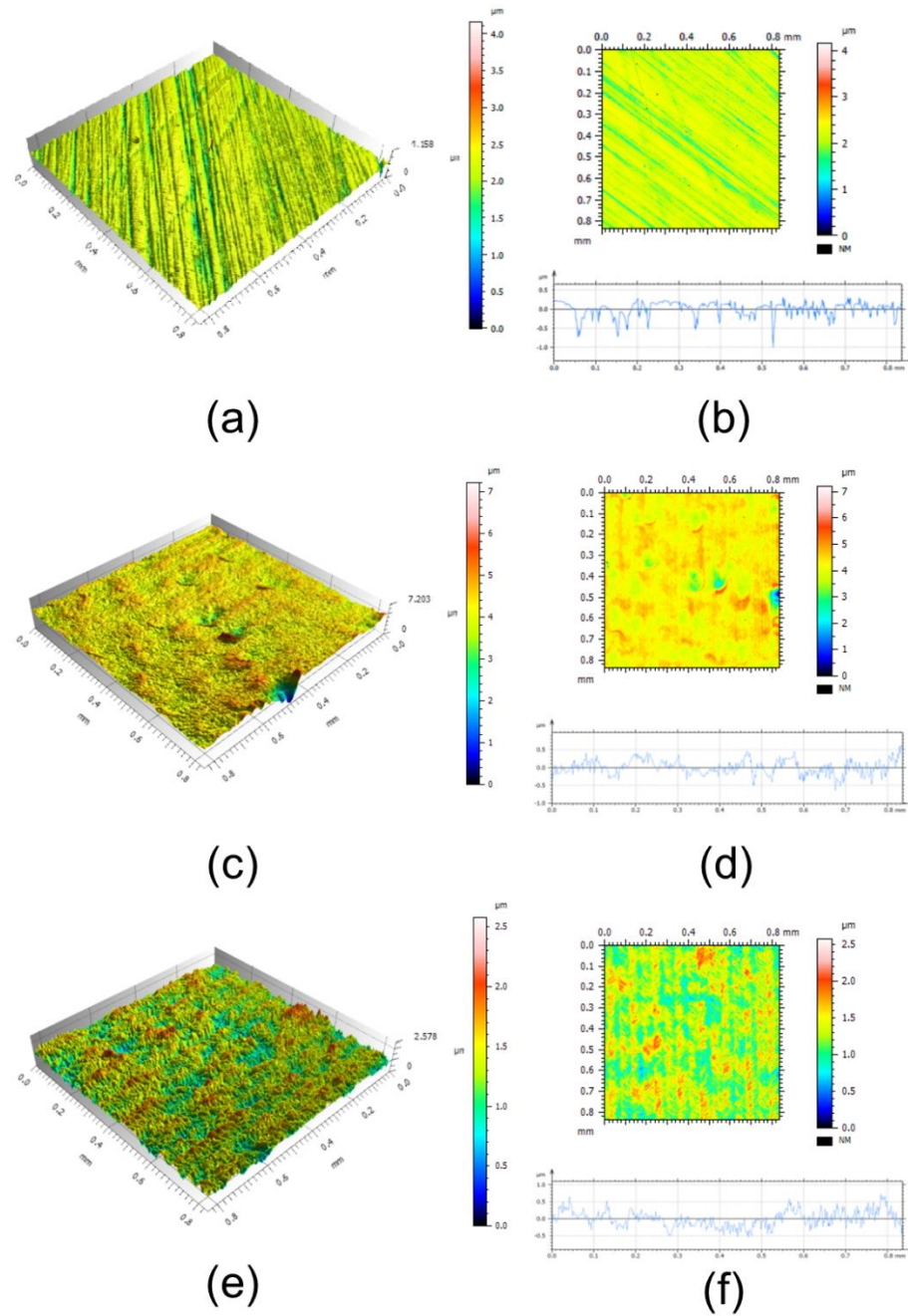


Figure 5.10: 3-D (a,c,e), 2-D and 1-D (b,d,f) surface topography of laser treated surfaces at different average powers: (a,b) 30 W; (c,d) 60 W; and (e,f) 90 W.

Table 5.3: Surface topographic parameters for surfaces treated with different laser power measuring using white light interferometry: S_a = average surface roughness value and S_q = root mean squared surface roughness value.

Laser power (W)	S_a (nm)	S_q (nm)
0 (Untreated surface)	125	168
30	119	203
60	227	329
90	191	240

In 90 W laser treated samples, the laser scan lines overlap could be clearly observed as the edge of laser spot created stuck out fins of about 2 μm higher height than the surface. These fins were about 60 μm apart and corresponded well with the 50% overlapping used for laser hardening. Similar effect was observed in 60 W laser treated sample, but it was less distinct due to lower power used. The 30 W laser treated sample did not exhibit any such changes but only a smooth surface.

Figure 5.11 shows the variation of surface hardness with average laser power. The hardening effect was non-existent for 30 W power while surface hardness higher than 600 HV was obtained for both 60 W and 90 W laser power. The hardness had sinusoidal variation along the surface. This can be attributed to the tempering effect due of overlapping of scan tracks as discussed in Section 4.3.4.4.

Similar hardness values obtained for 60 W and 90 W laser power indicates similar microstructure changes occurring in both cases. Both the sample had similar microstructure except for the difference in depth of laser affected area. The laser affected depth was about 50 μm for 90 W laser power treated sample while it was just 20 μm for 60 W laser power treated sample. This is understandable as higher power would provide higher energy to the substrate which can penetrate deeper into the material. No change in microstructure

was observed for 30 W laser treated sample which is consistent with the hardness and surface topography studies.

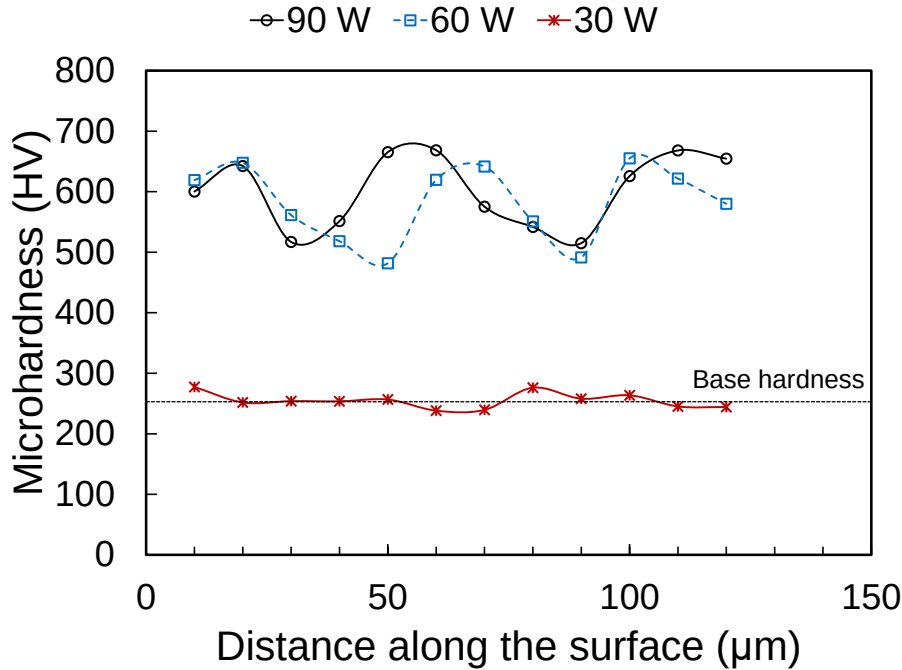


Figure 5.11: Variation of surface hardness along the surface.

Further investigations were carried out to study the cross-section microstructure of laser treated samples. Figure 5.12 shows a cross-section microstructure after nanosecond-pulse laser irradiation with 90 W laser power. The laser affected area could be clearly distinguished and was broadly categorized into laser hardened zone, overlap zone and heat affected zone.

The high magnification SEM images of these regions are shown in Figure 5.13. Laser hardened zone had a martensitic structure (Figure 5.13(a)). In the overlap zones, the heating effect from successive laser pulses produced tempered martensite with needle-like structure (Figure 5.13(b)). The laser hardened zones and the overlap zones corresponded with the peak and valley of sine wave-like surface hardness curve respectively (see Figure 5.11). Similarly, the heat affected zone beneath the hardened zone had a tempered microstructure with lots of carbides (Figure 5.13(c)). The base material did not show any change in microstructure due to laser heating (Figure 5.13(d)). It consisted of ferritic microstructure with elongated and spherical carbides.

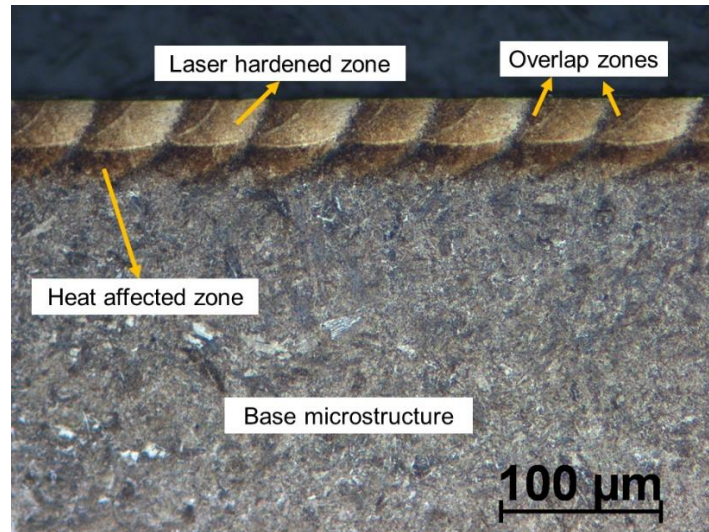


Figure 5.12: Cross section microstructure showing laser affected area during nanosecond laser treatment.

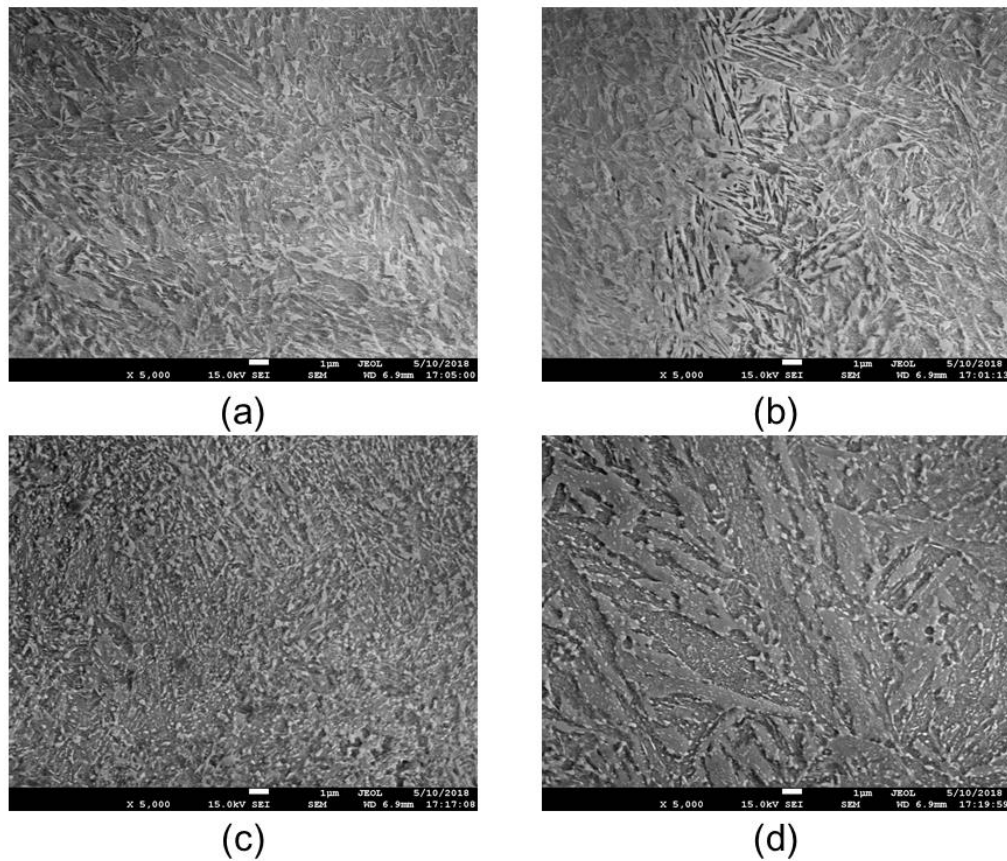


Figure 5.13: SEM micrographs of various regions: (a) Laser hardened zone (LZ) near the surface; (b) tempered zone due to overlapping; (c) heat affected zone beneath LZ; and (d) base microstructure.

The change in microstructure proves the austenitization of the surface layer and rapid quenching due to heat dissipation into the bulk. The overlapping reheats the hardened zone producing tempered microstructure in the overlap zone. This is verified by the microhardness measurement which shows a decrease in the overlapped regions. In addition, etching also revealed darker phases in the overlap zones than laser hardened zone due to presence of tempered microstructure.

Moreover, the heat from nanosecond pulses penetrate the material depending on the thermal penetration depth of the steel. Thus, the sub-surface region just beneath the laser hardened zone is exposed to heating from the laser pulses which is long enough for tempering; but not for austenitization. As a result, tempered microstructure with lots of carbides are formed in the heat affected zone.

Hardness measurements were made on the cross-section to confirm the obtained microstructure. Figure 5.14 displays a series of indents made on the cross-section using nano-indenter. As can be observed, the hardness in the laser hardened region is very high compared to base material hardness. It gradually reduced in heat affected zone and finally reaches base material hardness at depth of about 80 μm . An intermediate hardness (of about 500 HV) was recorded in the overlap zone which was attributed to tempering due to successive laser passes. The results are summarized in Table 5.4, which shows that the obtained hardness co-related well with the microstructure.

Table 5.4: Microhardness values at different zones of the laser treated specimen.

Region	Hardness (HV)
Laser hardened zone	642 ± 45
Overlap zone	500 ± 49
Heat affected zone	473 ± 21
Base region	253 ± 6

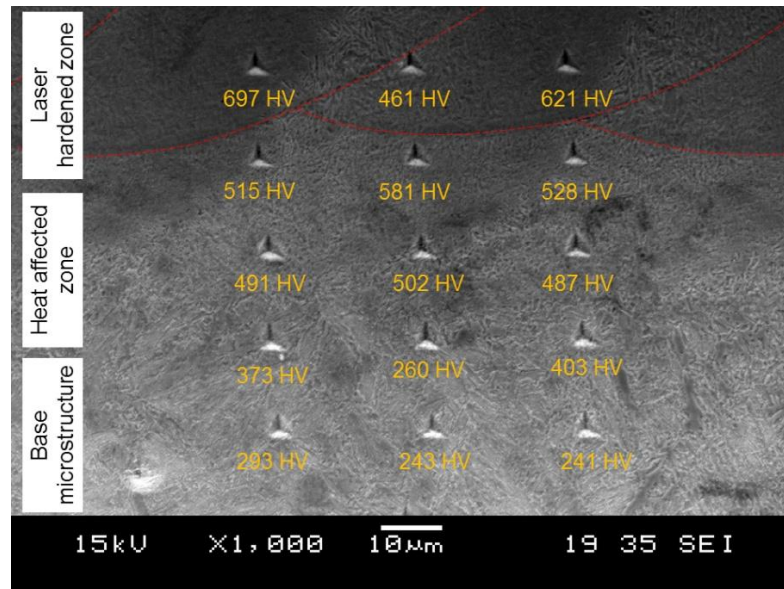


Figure 5.14: Indents made on transverse section of ns laser treated specimen showing variation in hardness along the depth. The specimen was etched with 2% nital after indentation test to reveal the microstructure.

The analysis shows the feasibility of using nanosecond lasers for hardening by carefully controlling the laser power. With the selected setting of 11% duty cycle (220 ns pulse width and 2000 ns cycle), peak temperature at the surface reaches austenitization temperature, but does not exceed melting point. Therefore, the area undergoes local quenching and a hardened surface is formed. However, the fast outflow of pulse energy often exceeds its accumulation and limits its thermal diffusion depth. As a result, only a shallow depth of hardening (of about 80 µm) can be achieved which might not be suitable for industrial application.

5.3.3 Interaction of steel with femtosecond laser beam

As mentioned earlier, femtosecond laser interaction did not produce any noticeable change in hardness for practical application. The maximum heat affected depth was just few micrometers (1-5 µm) depending on the laser parameters used. On the other hand, it was noticed that the ablation during femtosecond pulse irradiation produced a clean surface with precise removal

of surface contaminants and minimal damage to the substrate. This could be useful for surface cleaning as well as damage layer removal in cleaning and remanufacturing industries. Therefore, further studies were performed on feasibility of using femtosecond laser for surface cleaning applications.

5.3.3.1 Determination of ablation threshold

The ablation threshold of a material is an important parameter that determines the damage to the substrate during laser-material interaction [174–176]. The determination of exact ablation threshold would be helpful in choosing the proper parameters for femtosecond laser cleaning. Since there is a lot of variation in ablation threshold value of steel reported in the literature, it was considered necessary to calculate it for the steel sample used in our experiment.

The start of damage to the surface may be assessed by appearance of plasma during irradiation or formation of permanent crater on the surface due to some material removal. The ablation threshold for given steel was determined based on surface diameter measurement method which is a widely accepted technique [177]. Considering a Gaussian spatial distribution of laser intensity, the relation between peak fluence, ϕ_0 and surface crater diameter, D , is given by

$$D^2 = 2\omega_0^2 \ln \frac{\phi_0}{\phi_{th}} \quad (5.8)$$

where, ω_0 is the beam spot radius at $1/e^2$ intensity and ϕ_{th} is the threshold fluence. Peak fluence is used for ablation threshold determination since it determines the extent of damage to the surface and gives a more realistic value for ablation than average fluence. The peak fluence can be derived from pulse energy, E_p and beam spot radius using following equation:

$$\phi_0 = \frac{2E_p}{\pi\omega_0^2} \quad (5.9)$$

The ablation threshold can then be determined by plotting the square of crater diameters, D^2 , against the logarithm of peak fluence, ϕ_0 , as shown in Figure 5.15. Extrapolating D^2 to zero gives the value of ablation threshold fluence.

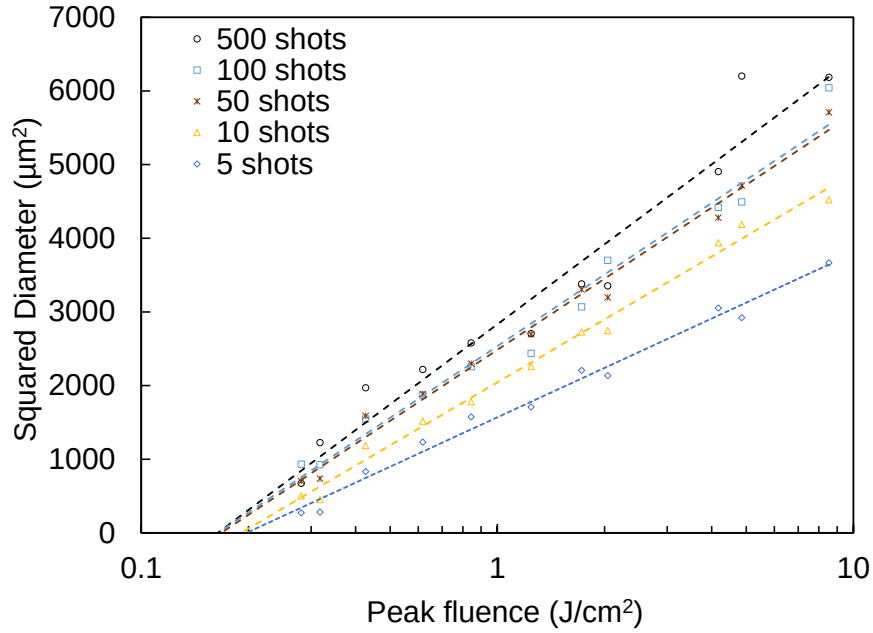


Figure 5.15: Graph of squared diameter, D^2 , of ablation craters in steel as a function of peak fluence, ϕ_0 . The lines represent the least-squares fit according to equation (5.8).

Ablation thresholds for different number of laser shots were determined applying this method. The ablation threshold of steel for 100 laser pulses was calculated to be 0.164 J/cm^2 which is comparable to the values mentioned in literature [175,178].

A reduction in ablation threshold fluence was observed with increasing number of laser shots as shown in Figure 5.15 and Figure 5.16. The reduction can be attributed to incubation effect or damage accumulation effect [175]. Based on the power law, the ablation threshold fluence, $\phi_{th}(N)$, for N laser shots is related to single shot ablation threshold fluence, $\phi_{th}(1)$, by

$$\phi_{th}(N) = \phi_{th}(1)N^{S-1} \quad (5.10)$$

where S is the incubation coefficient. The incubation coefficient is calculated by plotting graph of $N \cdot \phi_{th}(N)$ against N as shown in Figure 5.17. It was calculated to be 0.955 and the single shot ablation threshold was found to be 0.208 J/cm^2 respectively.

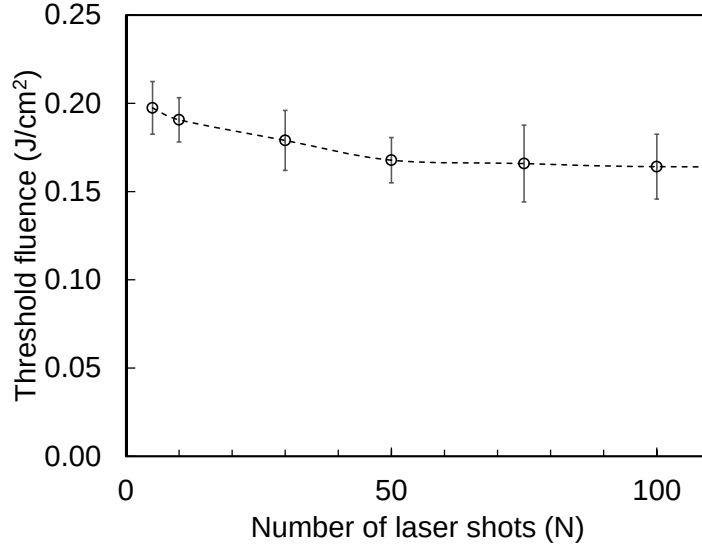


Figure 5.16: Graph showing the reduction in ablation threshold with increase in number of laser shots.

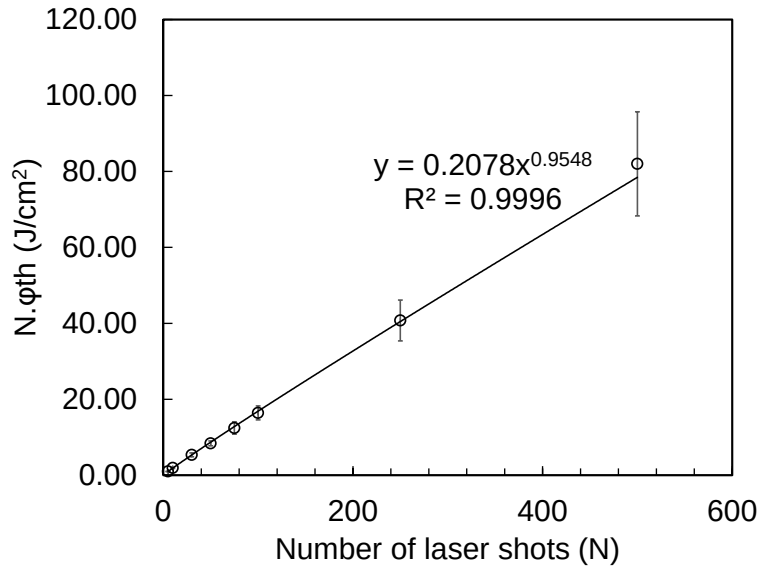


Figure 5.17: Graph of accumulation fluence against number of laser shots. The line represents the least square fit according to equation (5.10).

Different theories are available on mechanisms responsible for incubation [176,179,180]. One explanation is the sudden reduction in surface reflectance after first few laser shots which results in a higher percentage of incident energy being absorbed by the material. On the other hand, the excitation of surface plasmons could also aid in energy coupling mechanism. The overall outcome is the reduction in ablation threshold value. It is however, noteworthy to point out that the ablation threshold does not keep on decreasing and stabilizes after about 70 shots (see Figure 5.16). This is because of the reduction in beneficial effect of reflectance drop after few pulses and decoupling of plasma from the surface.

5.3.3.2 Surface morphology

After determining the ablation threshold fluence, experiments were performed at different fluence values ranging from near ablation threshold to higher fluences. The aim was to remove the surface contaminants with minimal damage to the substrate.

No visible damage occurred to the surface at fluences lower than ablation threshold. As can be seen in Figure 5.18(a), a smooth crater was obtained at a low fluence value just above the ablation threshold. The surface crater did not show any sign of melting. The depth of material removed was about 3 μm for 100 laser pulses as shown in Figure 5.18(c). At very high fluences however, a rough surface recast layer was observed (Figure 5.18(b)). The ablated crater had a deep hole (in the range of tens of micron) at the center with lots of re-solidified metal droplets ejected from the ablation center.

When the femtosecond laser pulse is irradiated on the surface, the incident energy is absorbed by surface electrons via inverse Bremsstrahlung process which results in rapid increase of surface temperature. The heat is then transferred to ions or lattice through electron-phonon coupling [181]. Since the pulse duration for femtosecond laser is shorter than thermal relaxation time and the laser is very intense, the focal area of the interacting surface where fluence value exceeds ablation threshold is directly ablated by spallation and vaporization [135,160,182]. At low fluence regime, the volume expansion of

the irradiated surface changes the internal pressure in the solid material. When tensile stress exceeds the tensile strength limit of the material, fractures parallel to the surface of the solid appear. These fractures initially generate as micro-pores just beneath the surface before coalescing to result in ejection of the topmost surface layer. Studies suggest that spallation occurs at fluences close to ablation threshold (see Figure 5.19) [183].

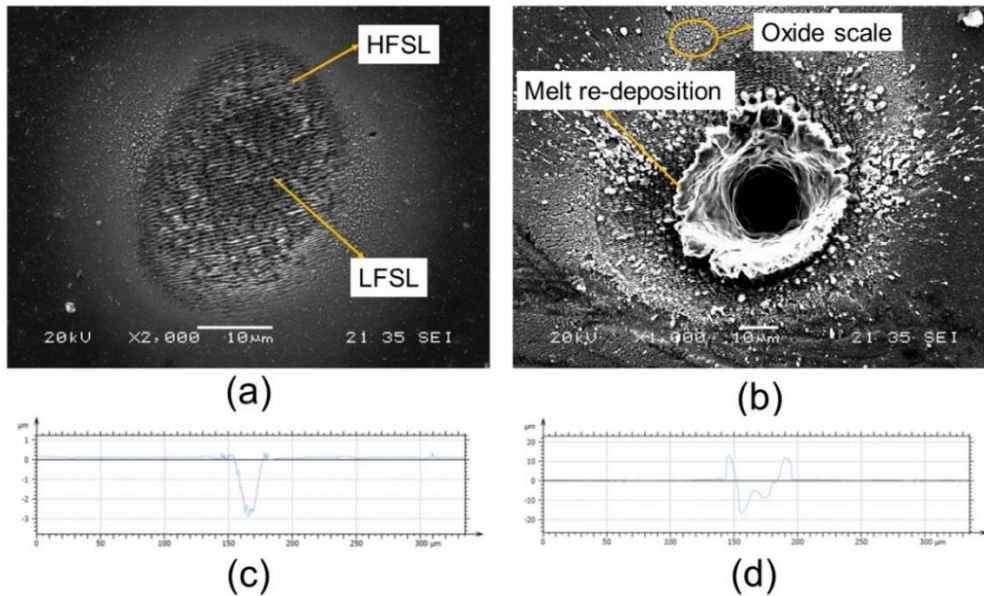


Figure 5.18: Ablated surface of AISI 52100 steel at 100 pulses and different peak fluences: (a) 0.317 J/cm^2 ; (b) 8.522 J/cm^2 ; (c) 2-D profile of (a); and (d) 2-D profile of (b).

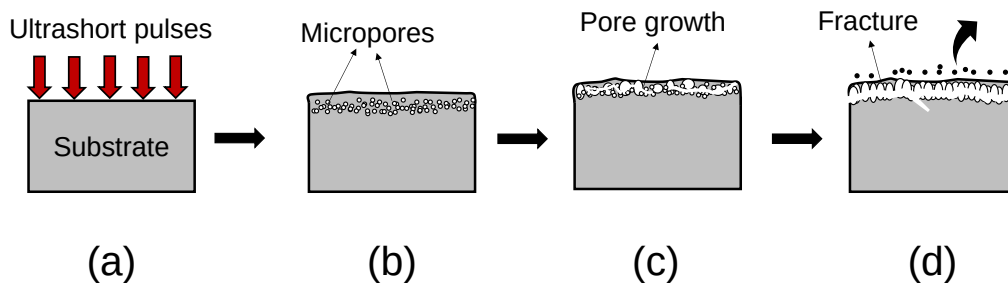


Figure 5.19: Illustration showing ablation by spallation at low fluences – (a) laser irradiation; (b) formation of micropores due to volume expansion; (c) pore coalescence; and (d) fracture and material removal.

At higher laser fluence, more energy is deposited on the surface which results in material being quickly heated above its equilibrium boiling temperature. This causes molten metal to enter meta-stable phase with variation in density and specific heat [175]. This forms a homogeneous nucleation of vapor nuclei in regions of low density. The upward movement of these vapor bubbles results in rapid phase explosion of the material expelling a mixture of vapor and metal droplets away from the center [184]. The rapid cooling and solidification forms a coarse morphology on the ablated surface where a dominant feature is widespread melt formation (see Figure 5.20).

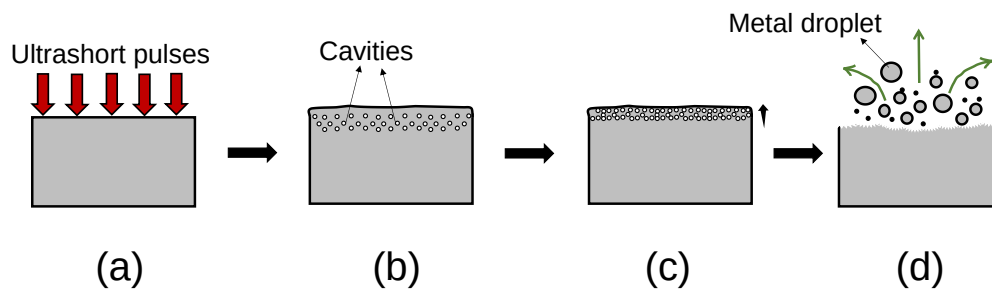


Figure 5.20: Illustration showing ablation by phase explosion at high fluences – (a) laser irradiation; (b) formation of cavities in low density region; (c) upward movement of cavities; and (d) metal droplets and vapor expulsion.

The laser fluence and the number of laser shots are primary factors determining the ablation crater on the surface and hence, affects the removal efficiency. As shown in Figure 5.21, it was found that the surface crater increased rapidly as the peak fluence is increased from near threshold value to about 2 J/cm^2 . After that, the increment in diameter was gradual. Peak fluence increases with increase in pulse energy as seen from equation (5.9). Thus, at high peak fluence, more area of Gaussian intensity profile will lie above ablation threshold. This obviously increases crater diameter. The number of laser shots also had similar effect with diameter increasing rapidly up to 100 shots and then stabilizing after that. This can be attributed to the reduction of ablation threshold due to accumulation of plastic deformation as discussed above.

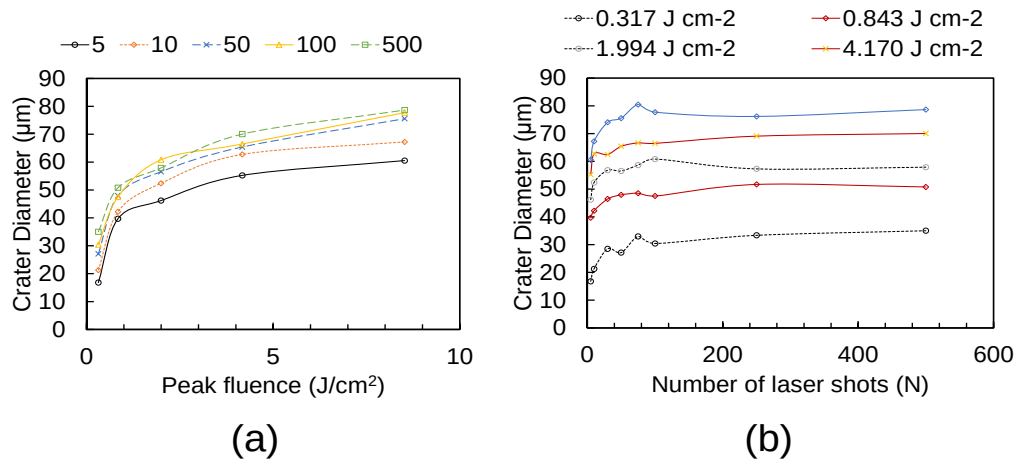


Figure 5.21: Graphs showing variation of ablation diameter with (a) peak fluence; and (b) number of laser shots.

The elemental composition of ablated area was analyzed using EDS to check surface oxidation. At low fluences ($< 1 \text{ J}/\text{cm}^2$), a maximum of 1-2 wt% oxygen was detected in the ablated area. At fluences higher than $1 \text{ J}/\text{cm}^2$, a thin scaly layer formed around the ablated area as shown in Figure 5.18(b). With increase in fluence, the scales became more prominent with oxygen content increasing from 10 wt% to 40 wt%. Table 5.5 compares the results of EDS observation on as-received and typical ablated surfaces. At $0.317 \text{ J}/\text{cm}^2$, the oxygen was not present on the surface while about 22.80 wt% oxygen was detected at $8.522 \text{ J}/\text{cm}^2$.

Table 5.5: Typical elemental composition obtained using EDS on the surface before and after laser irradiation.

Elements	Weight percentage (%)		
	As received	Low fluence ($0.317 \text{ J}/\text{cm}^2$)	High fluence ($8.522 \text{ J}/\text{cm}^2$)
C*	4.15	4.74	2.50
O	-	-	22.80
Si	0.25	0.24	0.24
Cr	1.35	1.41	1.17
Mn	0.36	-	-

Fe	93.89	93.61	73.28
Total	100.00	100.00	100.00

*weight percent for carbon might not be accurate due to contamination of SEM chamber walls or the specimen itself.

When the steel is in contact with air, increase in temperature will generally increase the rate of oxidation. During ablation at low fluence, the heating is insignificant to bring about any increase in surface oxidation. At very high fluence, however, the interaction between air and surface plasma generates a larger hot plume around the ablated surface which enhances the rate of surface oxidation. This results in formation of a thick oxide scales and increases oxygen content on the metal surface.

Careful examination of the ablated areas revealed a periodic ripple patterns on ablated surface as shown in Figure 5.18(a) and Figure 5.22. These ripples are oriented perpendicular to the polarization direction. They had periodicity in the range of 590-630 nm which is close to the wavelength of laser beam. With increase in pulse energy, rough bumps appeared at the center (at fluences more than 1 J/cm²). A rough periodic pattern with periodicity of about 2 μ m appeared at the center with direction normal to the original ripples. These micro-ripples soon disappeared with formation of rough ablation regime at the center due to surface melting. The ripples were visible only at the periphery after irradiation at high fluence.

Similarly, increasing pulse number resulted in formation of two types of surface ripples – one with periodicity around 600 nm at the ablation center and the other with periodicity around 350 nm at the edges. These are often termed as LSFL (Low Spatial Frequency LIPSS) and HFSL (High Spatial Frequency LIPSS) respectively in the literature (see Figure 5.18(a)). Although a clear explanation for formation of these periodic ripples is still lacking, most studies suggest that they are formed due to interaction between surface plasmons and incident laser energy resulting an increase in dielectric constant of air due to plume ejection from laser spot. The detailed investigation of LIPSS formation is beyond the scope of our studies and can be found elsewhere [185–194].

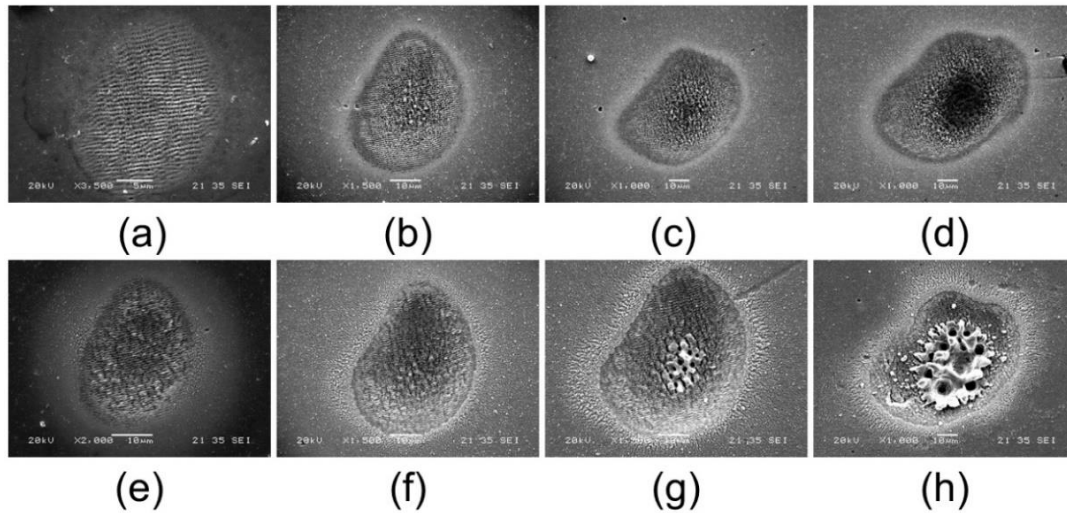


Figure 5.22: SEM images showing morphological evolution of steel surface after irradiation with increasing peak fluences at 10 (a,b,c,d) and 100 (e,f,g,h) laser shots : (a,e) 0.317 J/cm^2 ; (b,f) 0.843 J/cm^2 ; (c,g) 1.223 J/cm^2 ; and (d,h) 1.994 J/cm^2 .

5.4 Summary

The studies on feasibility of hardening using different pulsed lasers were presented in this chapter. The effects of millisecond, nanosecond and femtosecond pulsed lasers on surface modification of various steels were discussed. The major effects on the surface after laser irradiation with different lasers are illustrated in Figure 5.23. The main findings are summarized below:

1. Millisecond laser can achieve effective hardening on steel surface with hardness reaching above 700 HV in the laser hardened zone. The depth of hardened zone was about $200 \mu\text{m}$ for a typical treatment chosen and can vary from $100 - 1000 \mu\text{m}$ depending on the laser parameters used. At higher pulse energies, the longer soaking time and slower cooling rate due to higher energy deposition resulted in softening due to formation of upper bainitic microstructure in the laser affected zone. Effective hardening was obtained at lower pulse

energies with a zone of intermediate hardness just below the hardened zone. Intermediate hardness originated from tempering by successive laser pulses. Interestingly, millisecond laser could produce equivalent surface hardness and hardening depth using about 9 times lower power than in continuous wave laser.

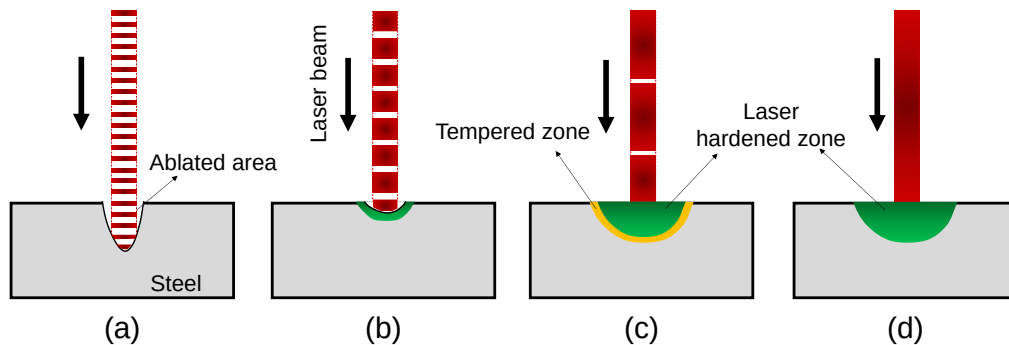


Figure 5.23: Schematics of laser processing using – (a) femtosecond laser showing surface ablation and no hardening effect; (b) nanosecond laser with surface material removal and hardening of surrounding area; (c) millisecond laser showing laser hardened zone and tempered zone; and (d) continuous laser showing hardening of laser affected area.

2. Hardening was found to occur for nanosecond-pulse laser as well and the hardness as high as 642 HV was achieved at the surface. However, the depth of penetration was too shallow (about 50-80 μm) due to insufficient heating by laser pulses. In addition, the change in surface properties and morphology triggered by nanosecond pulses can be advantageous for subsequent operations such as welding and surface cleaning.
3. Due to extremely higher pulse intensities and short pulse duration, femtosecond pulse laser resulted in direct ablation of the steel surface. Attempts were made to exploit the laser ablation for surface cleaning and damage layer removal. The ablation threshold of bearing steel was

determined first and calculated to be 0.142 J/cm^2 . By operating the femtosecond laser at fluence value slightly above the ablation threshold, the damaged surface layer was effectively removed.

Chapter 6: Corrosion studies on laser hardened 50CrMo4 steel

In this chapter, the corrosion behavior of laser hardened 50CrMo4 steel surface is examined using 3.5% NaCl solution. The laser treatment produces a gradient microstructure to a certain depth beneath the surface. Thus, a predefined depth of the hardened surface is removed first by polishing followed by electrochemical corrosion test at each layer to understand the effect of the microstructural changes.

6.1 Introduction

Laser surface hardening has emerged as a promising technique to improve surface properties of steel components in industries. It induces a rapid non-equilibrium phase transformation near the surface due to fast dissipation of heat into the bulk material. This yields gradient microstructures consisting of a hard martensitic surface layer and a pristine bulk microstructure that retains the mechanical properties of the untreated steel [45,195].

The laser-hardened microstructure generally consists of a hardened top layer (typically extending 200-500 μm) which weakens progressively in favor of a combination of ferrite and pearlite as the distance from the surface increases [142]. Many studies have investigated the corrosion behavior after laser hardening [12,45,158,196–202]. Almost all these studies report an improvement in corrosion resistance compared to base material. However, these studies just focus on corrosion behavior at the surface of steel neglecting the effect of gradient microstructure. Due to the lack of proper method to assess corrosion behavior of gradient microstructure, it is still unclear whether the top layer or the microstructure of hardened zone, or the combination of both is producing improved corrosion resistance.

A depth-wise analysis of corrosion behavior would settle this question once and for all. It would also provide additional information on how gradient microstructure react to electrochemical attack enabling us to predict the behavior of the sub-surface material under accidental exposure to corrosive environment due to some external damage to the surface such as scratching or indentation.

In this section, a novel, yet simple method to evaluate the corrosion resistance of laser-hardened steel as a function of the gradient microstructure is proposed. The corrosion behavior at different depths from the specimen surface is investigated by sequentially removing 30 μm thick layers from the surface via mechanical polishing. The method is demonstrated using 50CrMo4 steel as a reference material. 50CrMo4 steel is a chromoly steel which is generally susceptible to corrosion because of the relatively low Cr content [203,204]. Unlike stainless steel—which develops a corrosion-resistant, Cr-rich (10 – 30 %) passive layer upon laser treatment—chromoly steel has insufficient Cr content (0 – 9%) to produce a dense passivation layer [205]. Therefore, use of this steel can clearly reveal the effect of laser-induced microstructure on corrosion resistance.

The corrosion behavior of the chromoly steel at different depths from the sample surface is investigated by sequentially removing 30 μm thick layers from the surface via mechanical polishing. By correlating the depth-wise corrosion behavior to the measured microstructure, it is found that the top-layer exhibits higher corrosion resistance than the sub-surface layer. This result is surprising given that some microstructural changes occur at the sub-surface region as well which do not seem to produce any improvement in corrosion resistance than base material.

The results provide better insights into the role of the laser-induced microstructure engineering on the corrosion behavior of chromoly steel. The experimental methods presented in this work can be used to study the corrosion behavior of other alloys with gradient microstructures.

6.2 Experimental procedure

6.2.1 Material

50CrMo4 steel of dimension $10 \times 10 \times 6 \text{ mm}^3$ was used for the corrosion experiments. The details of this steel are already presented in Chapter 3. All specimens were ground progressively using SiC paper up to P2000 grit finish before performing laser treatment.

6.2.2 Laser processing parameters

The polished specimens were irradiated with YLR-150/1500-QCW fiber laser along the whole area following the scheme as shown in Figure 6.1. A defocus distance of about 10 mm was maintained for all laser experiments and all experiments were carried out under argon gas protection with the flow rate of 15 L/min. A series of laser hardened tracks were made to determine the best parameters for surface hardening. Based on the surface morphology and depth of hardening obtained, a power density of $1.02 \times 10^5 \text{ W/cm}^2$, and the process speed of 50 mm/s was employed to prepare three specimens (with same parameters) for corrosion studies. The entire surface area was irradiated using a line scanning mode with an overlap ratio of 42%.

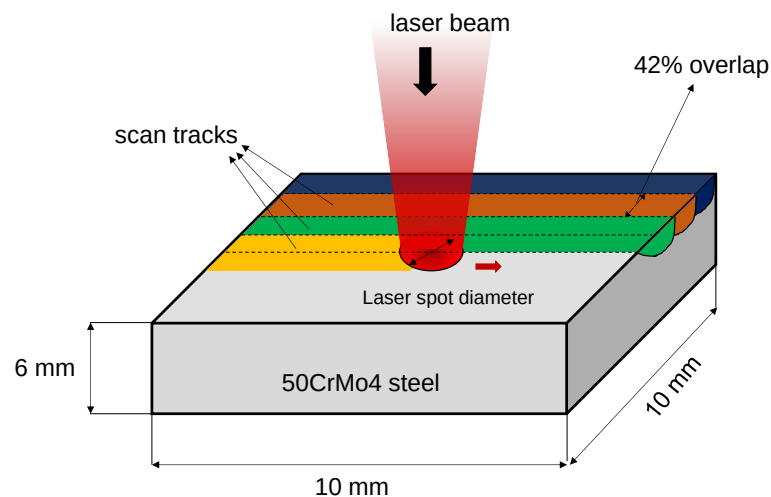


Figure 6.1: Schematic drawing showing laser surface treatment.

6.2.3 Characterization

The laser treated samples were characterized using standard metallography techniques. The cross-sections were mechanically ground and polished using process as described in Section 3.3.1. Metallographic inspections of the cross-sections were performed using a light microscope (Carl Zeiss AxioCAM), a confocal microscope (VK-X200 Keyence Corp.) and a scanning electron microscope (JEOL JSM7600F SEM) equipped with EDS (INCA X-Stream) and EBSD system (Oxford INCA systems).

The hardness measurements were made using an Agilent G200 nanoindenter equipped with a Berkovich indenter tip. The surface approach velocity and depth limit were set at 10 nm/s and 2000 nm, respectively. The average hardness for each point was measured using a depth range of 1000 to 1800 nm where the hardness values were more stable.

6.2.4 Electrochemical corrosion tests

A potentiostat/galvanostat (Model Reference 600, Gamry Instruments) interfaced with the analysis software (Echem AnalystTM, v.6.32) was used for all electrochemical corrosion tests. Prior to the corrosion test, the as-treated specimen was encapsulated in a high edge retention epoxy resin with only the laser treated surface exposed. The specimen was dried with both compressed and hot air and stored in a dry box at 40% relative humidity for an hour before corrosion tests were executed.

The tests were performed using a three-electrode cell equipped with a silver/silver chloride (Ag/AgCl) reference electrode and a platinum (Pt) mesh as counter electrode. The corrosion behavior at pre-determined depths of the laser treated surface was investigated via potentiodynamic polarization (PDP) curves at a sweeping rate of 1 mV/s in a three-electrode cell. Ag/AgCl electrode was used as a reference electrode and Pt mesh as counter electrode. The electrolyte, 3.5 wt.% NaCl solution, was purged with nitrogen gas for 30 minutes and after the sample was submerged into it, the gas was maintained at the headspace. For all electrochemical investigations, the

surface area exposed to the electrolyte, was 1 cm^2 . All electrolytes were prepared from analytical grade chemicals dissolved in ultrapure water. All measurements were repeated three times.

6.2.5 Serial sectioning technique

To study corrosion behavior at sub-surface, a constant thickness of $30 \pm 5 \text{ }\mu\text{m}$ was successively removed from the laser treated surface (Figure 6.2(a)). After the removal, corrosion test was performed at each depth. A depth of $30 \text{ }\mu\text{m}$ was chosen with an aim to remove any corrosion damage (e.g. pitting) from the material surface which may have been induced during the preceding corrosion test.

Careful polishing using $9 \text{ }\mu\text{m}$ and $1 \text{ }\mu\text{m}$ diamond suspensions and $0.04 \text{ }\mu\text{m}$ colloidal silica suspension was employed to remove the layer. To control the depth removed, an indent mark was created on the steel surface using a

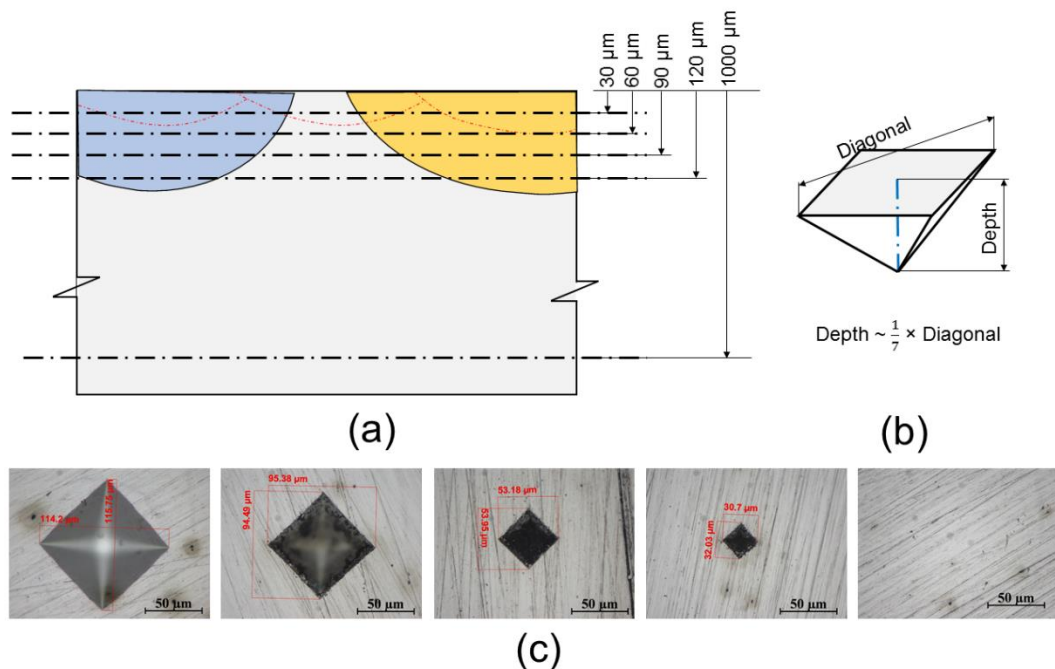


Figure 6.2: (a) Illustration showing surface layer removal across the laser affected region; (b) Schematic of the surface indent made by Vickers indenter; and (c) Micrographs showing progressive depth removal with reduction in indent size at the surface.

Vickers indenter at 2 kgf load and 15 s dwell time. The indenter creates a small inverted pyramid shaped pit on the surface whose depth was found to be about 1/7th of the diagonal of the square base at the surface (Figure 6.2(b)). For example, if the length of diagonal is 70 μm , the indent reaches a depth of 10 μm into the material.

After that, the specimen was mechanically polished until the indent was no longer visible. The process was repeated a few times until a depth of 30 μm was removed (Figure 6.2(c)). The method provided a simple way to study how the corrosion resistance of a laser-hardened chromoly steel changes as a function of the laser-induced microstructure.

6.3 Results

6.3.1 Laser treated surface before corrosion test

Figure 6.3 shows the surface topography of the specimen after laser treatment. The parallel surface ripples stem from moving the laser across the entire sample surface. Such ripples are formed as a result of the melting and re-solidification of the irradiated metal [206] and are typical of welding and laser surface modification processes [135,207–209].

Figures 6.4 and 6.5 show the elemental composition obtained from EDS analysis. The surface exhibited presence of a thin layer of oxide. This suggests that argon gas could not prevent the surface oxidation completely. Two types of oxides formed at the surface – a thin scale all over the irradiated surface and small bulges dispersed randomly over the surface. Further analysis revealed the bulges to be rich in O, Mn, Si, Cr and Fe. They probably formed due to elemental segregation and conglomeration at the surface.

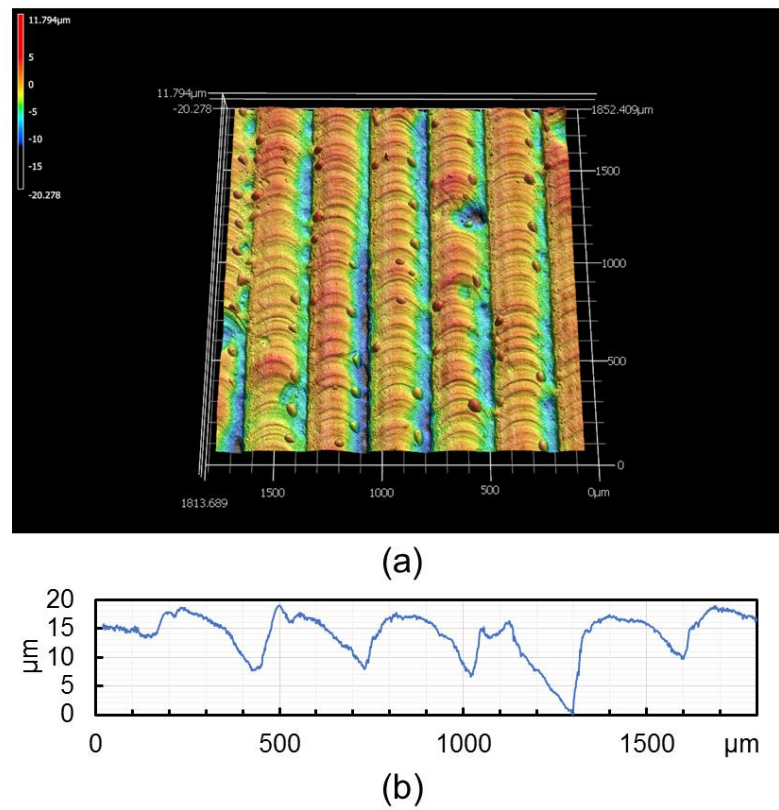


Figure 6.3: Surface morphology after laser surface treatment; (a) 3-D profile; and (b) 2-D profile.

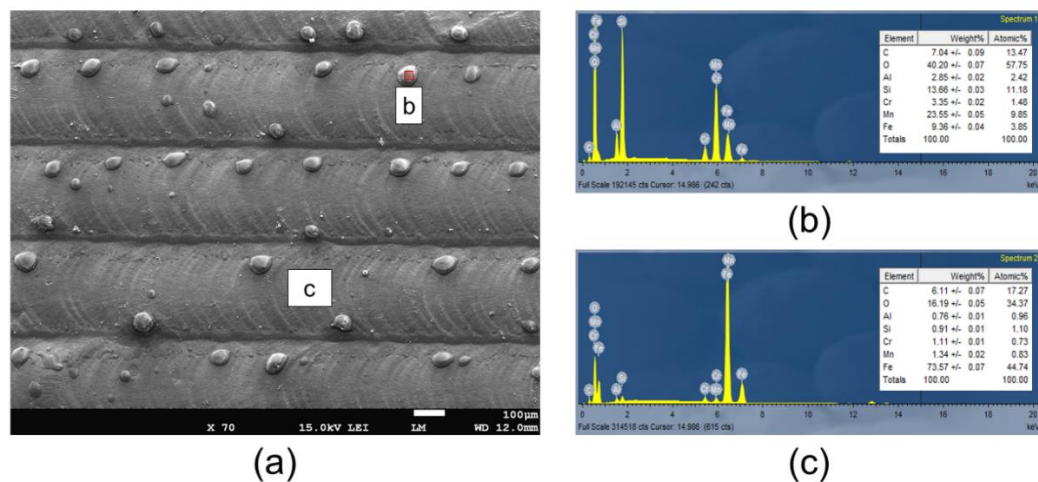


Figure 6.4: (a) SEM micrograph of laser treated surface; EDS results of (b) bumps; and (c) matrix region.

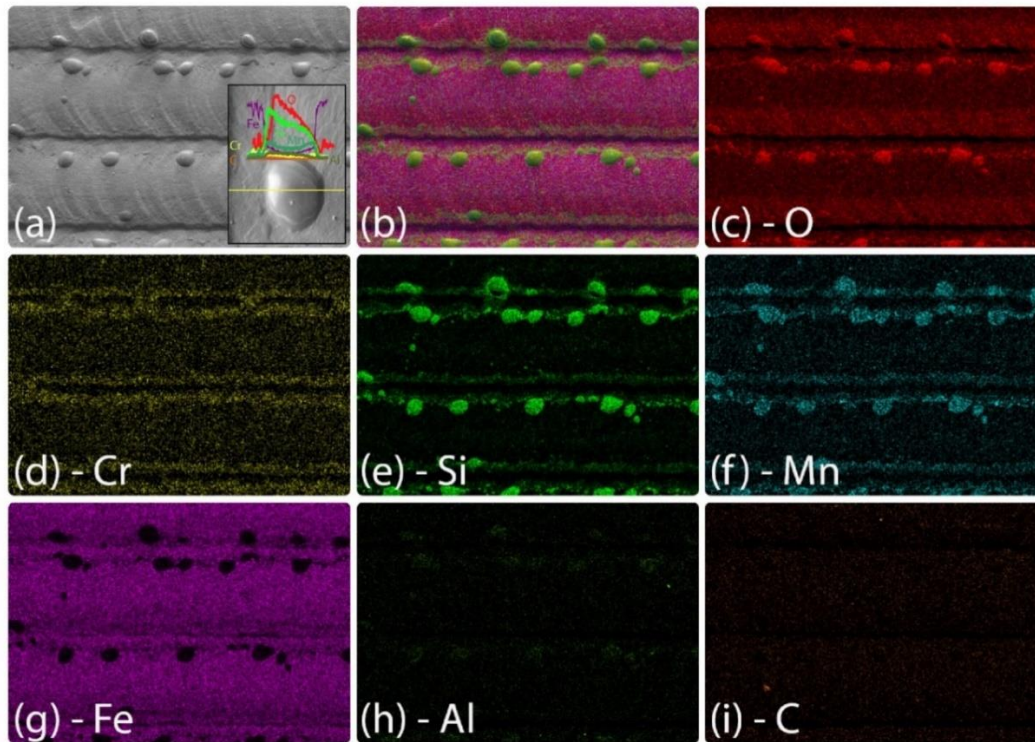


Figure 6.5: (a) SEM image (with globular bump in the inset); (b) Overlay image with all detected elements; Elemental map showing (c) oxygen; (d) chromium; (e) silicon; (f) manganese; (g) iron; (h) aluminum; and (i) carbon.

To investigate the microstructural changes brought about by laser treatment, further cross section metallographic studies were carried out. Similar microstructure as discussed in Section 4.3.3 was obtained and hence, the discussions are not repeated here. It is noteworthy to point out though that the heating from the laser had a decreasing effect along the depth and produced a gradient microstructure. Near the surface, the microstructure consisted of lath martensitic structure. The overlap during the laser scan could also be clearly observed. The overlapped area had a tempered martensitic structure.

The re-heating from the successive pass resulted in formation of mixed microstructure with tempered martensite, ferrite and spherical carbides in the sub-surface region. A clear demarcation between the laser affected zone and the base material could be observed. The laser affected depth was measured to be about 200 μm in depth for the condition used.

Figure 6.6 shows the EBSD map of the sample cross-section to a depth of around 470 μm . From this map it is clear that the laser-treatment induced a fine grain microstructure which extended to a depth of about $155 \pm 25 \mu\text{m}$ from the surface. Smaller elongated grains appeared in the base material at depths of about 350 - 470 μm . These features may have originated from the rolling and annealing processes during sample manufacturing. Figure 6.6(b) shows the average grain size distribution at different depths from the surface. It shows a similar profile for the regions between 0 – 120 μm , with a narrow spread between 1 – 7 μm . In contrast, the substrate region exhibited a wider spread ranging from 1 – 14 μm . Around 82% of the grains in laser treated region were less than 2.5 μm , as compared to 55% in the substrate region.

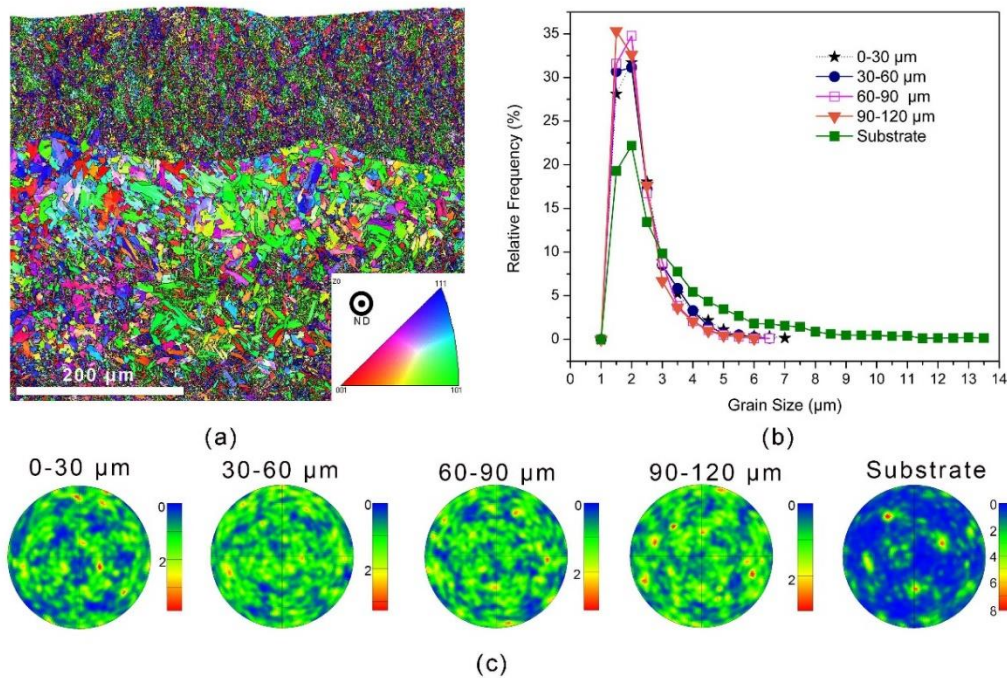


Figure 6.6: (a) Inverse Pole Figure (IPF) map of cross-section of a laser treated sample obtained from EBSD using 0.35 μm step size; and (b) grain size distribution at different depths.

The hardness profile correlated well with the microstructure obtained (Figure 6.7). Measurements were made along two directions: parallel to the surface (y-direction) and along the depth (z-direction) (Figure 6.7(a)). Surface of the specimen was taken as reference for measurements. The hardness profile in y direction fluctuates between 5 – 7 GPa with a lower hardness in the tempered region (Figure 6.7(b)). The hardness profile along the depth (z direction) shows a gradual variation in hardness going from a maximum of about 6.8 GPa near the surface to 5 GPa at ~100 μm to the bulk value of 3 GPa at ~200 μm (Figure 6.7(c)).

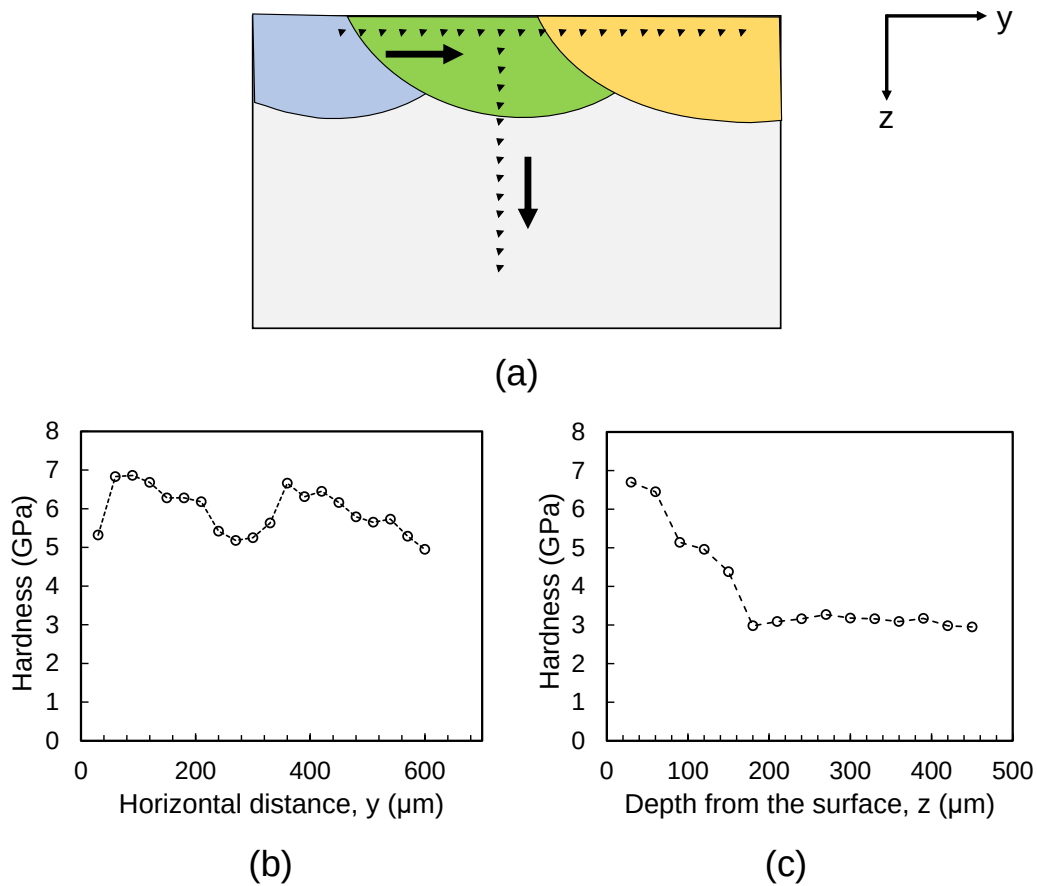


Figure 6.7: Hardness profile (a) schematics; (b) at 50 μm below the surface (y-direction); and (c) along the depth from the laser hardened surface (z-direction).

After establishing the microstructural changes brought by laser surface treatment, electrochemical corrosion tests were performed to evaluate the corrosion properties at different depths. The corrosion resistance at the surface was determined first, after which the surface layer was removed successively to various depths as described in Section 6.2.5 and corrosion tests were performed at each layer.

6.3.2 Corrosion test results

Figure 6.8 shows the potentiodynamic polarization curves obtained in 3.5 wt% NaCl solution for surfaces at different depths from the initial laser treated surface. Each curve indicates the anodic and cathodic behavior of the tested microstructure as well as its corrosion potential (E_{corr}). Hydrogen evolution dominates the cathodic region (left of E_{corr}), while the anodic region describes the material oxidation behavior (right of E_{corr}). A weak passive layer forms at all depths considered, evinced by the kink in the anodic region; this may be attributed to the minimal Cr content in 50CrMo4 steel (less than 1 wt.%).

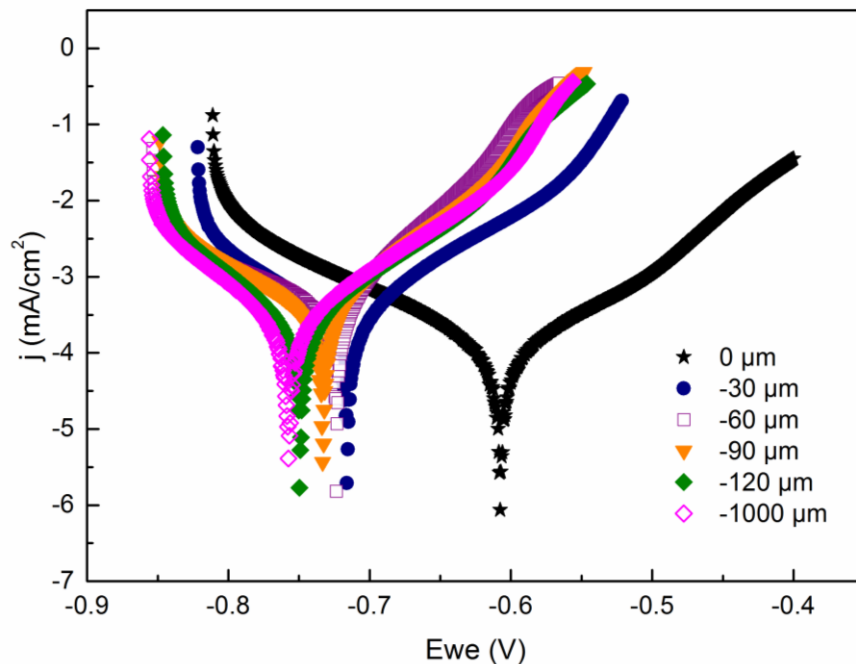


Figure 6.8: Potentiodynamic polarization curves obtained for surfaces at different depths from the laser treated surface in 3.5 wt.% NaCl at 298 K.

Table 6.1: E_{corr} , and j_{corr} values for laser treated 50CrMo4 steel at different depths from the surface in 3.5% NaCl solution.

Distance from laser treated surface (μm)	Average E_{corr} (mV)	Average j_{corr} ($\mu\text{A}/\text{cm}^2$)
0	-571 ± 50	0.087 ± 0.010
-30	-714 ± 3	0.261 ± 0.036
-60	-710 ± 20	0.405 ± 0.020
-90	-735 ± 2	0.256 ± 0.034
-120	-733 ± 5	0.419 ± 0.018
-1000	-753 ± 6	0.213 ± 0.004

E_{corr} reflects corrosion susceptibility of the material at its electrochemical equilibrium. j_{corr} —the current density at the corrosion potential—is proportional to the corrosion rate of the material [210–213]. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were determined from the potentiodynamic polarization curves. The results are shown in Table 6.1. The values of j_{corr} was obtained by extrapolating the linear portions of the cathodic and anodic regions of the potentiodynamic curves back to their intersection.

The data show that the laser treated surface was registered at much nobler potential than all other sub-surface conditions. The E_{corr} value reflects the equilibrium corrosion susceptibility of the bulk substrate. E_{corr} value of the initial laser treated surface (at a depth of 0 μm) was almost 100 – 150 mV nobler than all other sub-surface sections (at a depth of 30 μm and beyond). Beyond 30 μm depth, no significant changes in the E_{corr} value is recorded, indicating similar galvanic behavior. Notably, E_{corr} value of the bulk (-1000 μm from the surface) is 30 mV lower than that in the laser-affected zone (between 30 μm and 120 μm). The standard deviation (σ) in E_{corr} value of laser-treated surface (0 μm) was higher than other cases which is attributed to its higher surface roughness as unlike the former, the latter surfaces were polished.

Corrosion current densities (j_{corr}) reflected a similar trend as in corrosion potentials. At the surface, j_{corr} value was three to five times lower than sub-surface samples indicating lower corrosion rate. From $-30\text{ }\mu\text{m}$ to $-120\text{ }\mu\text{m}$ to the bulk substrate, j_{corr} , fluctuated between $0.2 - 0.4\text{ }\mu\text{A}/\text{cm}^2$.

Figure 6.9 shows some typical micrographs of the corroded surfaces. The tested surface revealed lots of pitting and corrosion products randomly distributed on the surface.

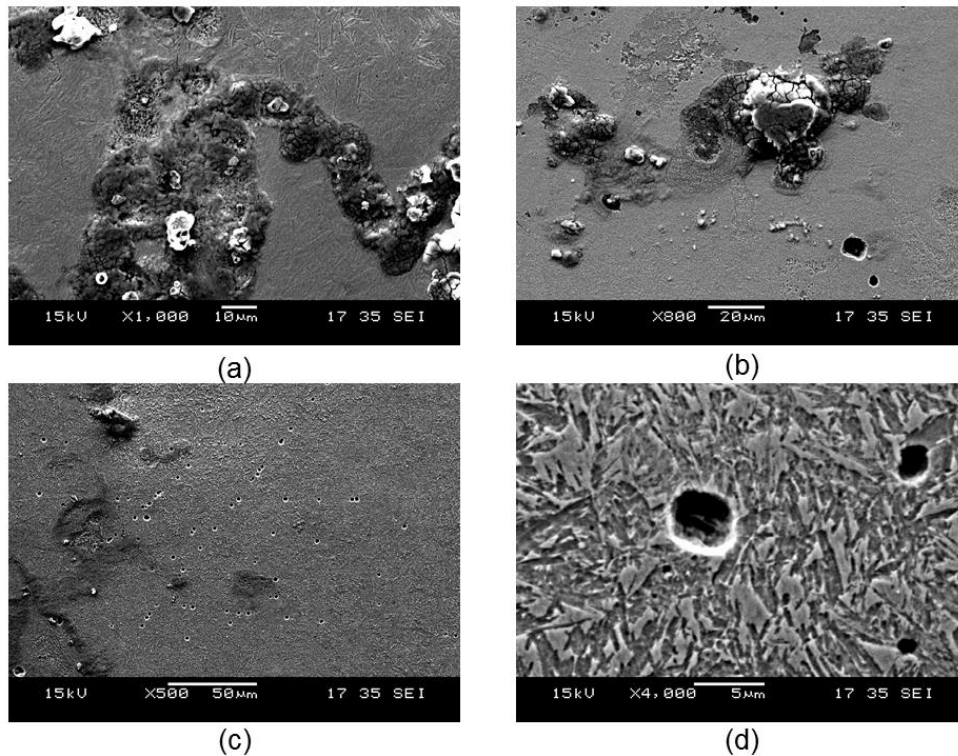


Figure 6.9: SEM micrograph of corroded surface showing (a) corrosion scales; (b) oxide scale and pits; (c) random minor pits; and (d) close-up of (c).

6.4 Discussion

The study investigates a complex problem of understanding the corrosion behavior of a material with a gradient microstructure. The gradient—induced by surface laser-hardening—consists of a combination of martensitic microstructure (near the surface) and mixed microstructure with tempered

martensite, ferrite, and spherical carbides (in the sub-surface region). One of the main challenges associated with this investigation is the ability to probe local corrosion properties as a function of this complex microstructure using standard electrochemical tests.

The solution is to use a simple, yet precise serial-sectioning method involving the mechanical polishing of a sample with a pre-existing indent until the indent is no longer visible on the surface. Depending on the indent size and depth, the removal of successive material layers can be performed with micrometer accuracy. Using this method, the corrosion resistance of the laser-treated 50CrMo4 steel microstructure at five different depths from the sample surface, evenly spaced by 30 μm , was assessed.

The study revealed that the corrosion potential and corrosion rate of the top surface are higher than the microstructure gradient portion of the material. This result suggests the elemental enrichment and formation of a protective oxide layer on the sample surface after laser-treatment which increases the corrosion resistance [202]. The change in elemental distribution is supported by the EDS analysis presented in Figure 6.4 and 6.5, which show an increase in Cr (1 to ~ 3 wt.%), Mn (1 to ~ 20 wt.%), and Si (1 to ~ 10 wt.%) at the surface. These findings allude to the possibility that laser-treated steel may behave similar to stainless steel albeit the significantly lower Cr content [214]. A more detailed analysis of the surface oxide layer by means of transmission electron microscopy and XPS may shed light onto its structure and composition.

Another exciting observation is that the recorded corrosion resistance is not a function of grain size or orientation distribution. Although grain refinement due to laser treatment extends to around 150-200 μm under the surface (see Figure 6.6) it did not yield benefits to the corrosion resistance of the material. Previous studies on different materials suggest improvement in corrosion resistance with grain refinement [215–217]. The current results seem to indicate negligible effect of grain refinement, probably due to the other overshadowing factors such as removal of protective layer, elemental enrichment and phase transition.

The findings reveal that the uniform removal of 30 μm of material from laser hardened surface will significantly increase the corrosion susceptibility (increase in E_{corr}) and reduce the corrosion rate (reduce I_{corr}) of the material in salt solution. This removal can be the result of intentional post-laser treatment finishing. In the event of unintentional material removal, such as a deep scratch, the galvanic coupling between the nobler laser hardened surface and the sub-surface will quicken failure of the material.

6.5 Summary

The corrosion behavior of laser surface hardened 50CrMo4 steel was studied in this chapter. The laser treatment produced a hardened structure at the surface with martensitic microstructure near the surface and mixed microstructure with tempered martensite, ferrite and spherical carbides in the sub-surface region. Electrochemical corrosion tests using 3.5% NaCl were performed at successive pre-defined depth intervals of 30 μm . The results reveal that the laser treated surface had very good corrosion resistance while it drops drastically after removal of the top surface layer. The improved corrosion resistance at the surface is attributed to formation of Cr-enriched oxide layer. Removal of this protective layer resulted in lower corrosion resistance at sub-surface layer. The study indicates that grain refinement during laser treatment has negligible effect on improving corrosion resistance of the steel.

Chapter 7: Methods to improve the effectivity of laser hardening process

Laser surface hardening suffers from challenges such as low energy absorption at the surface and surface decarburization. In this chapter, the various methods of improving the effectiveness of laser hardening process are explored. The first part studies the feasibility of underwater laser hardening. In the second part, decarburization during laser surface treatment is analyzed and methods to tackle the problem are discussed. An innovative approach of using gas during laser hardening is presented in the final section, which is proven to significantly improve the surface properties.

7.1 Underwater laser hardening

7.1.1 Introduction

Water assisted laser processing has been around since 1970s. Water is generally added on purpose to avoid redeposition of debris, to cool the material, to increase plasma pressure, to conduct light or even act as a chemical reagent during laser processing [218].

Underwater laser processing has been commercially implemented for various applications such as cleaning of electronic components [218–221], shock processing of metals [222–224] and other material processing in industries [225–229]. Most of these applications employ water as a medium to confine the mechanical impact of laser energy and induce shock waves or transport material. However, the cooling effect of water during laser processing is often undervalued. While water, mixed with organic chemicals and additives, is commonly used as coolant in heat treatment applications, it has rarely been used in laser surface hardening of steels.

During laser hardening, the fast dissipation of heat transforms the austenitized surface layer into hard martensite without affecting its bulk material properties. The surface hardness dictates the load bearing capacity and useful life of bearings. According to the literature, higher surface hardness usually results in the higher wear and corrosion resistance as well as longer fatigue life [68,230,231]. Therefore, there is a tendency to obtain superior surface hardness using various techniques. Since cooling rate after austenitization is one of the main factors determining the extent of martensitic transformation, it has a direct influence on hardness achieved at the surface.

Water, being easily available and having high specific heat, might have a beneficial cooling effect during the process producing very high quenching rate. Therefore, the effect of water layer during laser surface hardening process is investigated in this study. The underwater effects on hardening are analyzed based on surface morphology, microstructure, size and hardness of hardened layer and compared with results from conventional laser surface hardening. The study shows that water can increase surface hardness, but reduces the area of hardened zone.

7.1.2 Experimental methods

Three types of steels – 50CrMo4, AISI 1055 and AISI 52100 were used for this study. All the steels showed similar behavior during underwater laser hardening studies.

The Ytterbium based fiber laser from IPG Photonics (YLR-150/1500-QCW) was used for all experiments. Figure 7.1 shows a schematic diagram of underwater laser treatment. The specimen was completely submerged in water. The laser beam was delivered to the work surface by focusing the beam through a lens of 300 mm focal length and it produced a spot size of 0.5 mm diameter at the surface. The beam spot was traversed along the surface producing a single line tracks of 10 mm on the sample surface using a galvanometric scanner at various laser processing parameters as shown in Appendix B3.

For comparison purpose, experiments were also carried under argon gas protection with the flow rate of 15 L/min. For each of the processing parameters used, the experiments were repeated at least twice using same parameters to verify the reproducibility of the effect.

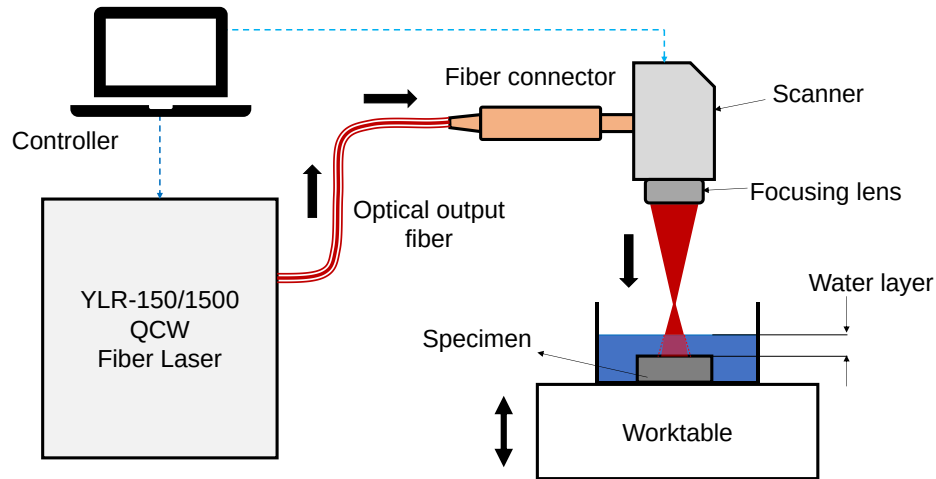


Figure 7.1: Schematic diagram of experimental setup.

After laser treatment, the surface morphology and cross section microstructure of the treated samples were studied using advanced microscopy. The depth and width of the laser affected zone was determined based on the optical micrographs obtained after etching with 2% nital solution with at least 5 measurements made at different cross-sections. Hardness measurements were performed using Vickers hardness indenter using 300 gf at the surface and 100 gf at cross section with 15 s dwell time. For surface hardness, at least 10 indents were made on the surface and the average value was taken.

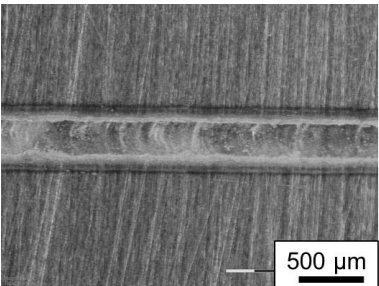
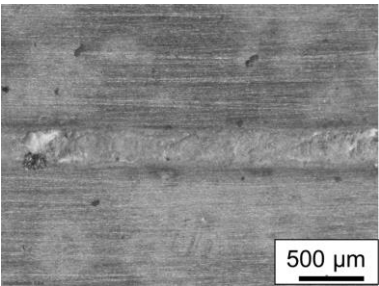
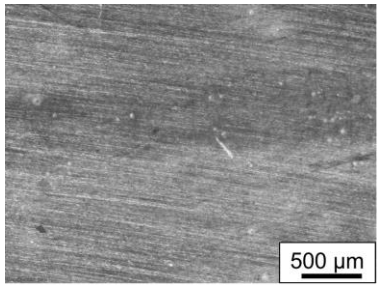
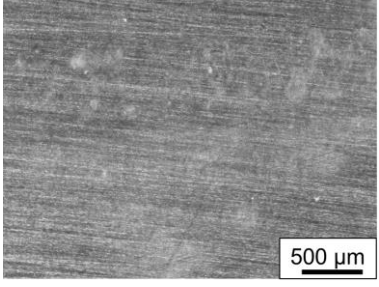
7.1.3 Results and Discussion

7.1.3.1 Surface morphology

All steels had similar surface morphology. Therefore, only the results from AISI 52100 are used for discussions here. Various levels of water layer thickness were used for the experiment (Appendix B3) and the results are summarized in Table 7.1. When the laser was turned on, the laser passed

through the water layer and irradiated the surface. A distinct hardened line could be seen for 1 mm thick water layer. However, only a faint black line was observed for 3 mm water layer. For 5 mm water layer, no observable effect was observed. Therefore, it was concluded that 5 mm water thickness did not produce any hardening effect. The result when the experiment was performed without any water layer is also added for easy comparison.

Table 7.1: Effect of water layer thickness on surface hardening (at 250 W power and 100 mm/s process speed).

Water layer thickness (mm)	Surface image	Remarks
0		Distinct hardened line
1		Distinct hardened line
3		Faint black line still observable with naked eye
5		No observable effect

The water layer above the specimen surface plays significant role during underwater laser treatment. Water acts like a shielding medium preventing the surface to come in contact with air. When the laser light is irradiated during the experiment, the water-air interface reflects part of the incident beam. Furthermore, the absorption of laser light in water attenuates the total beam energy striking the surface. The absorption depends on the thickness of water layer and absorption coefficient of water. Neglecting the reflection of beam by water, the absorption of laser beam by water is given by

$$A(z) = 1 - e^{-\alpha z} \quad (7.1)$$

where $A(z)$ is absorption at water depth z (cm) from the water-air interface (%) and α is absorptivity of water to laser beam. Takahashi et al. [232] measured the absorption coefficient of water to be 0.14 cm^{-1} for $1.06 \text{ }\mu\text{m}$ laser beam produced by a Q-switch Nd:YAG laser. Using this value, the theoretical laser power absorbed by water is only about 1.4% for 1 mm thickness and 13.1% for 10 mm thickness.

It is thus clear that very little amount of incident laser energy is lost due to absorption by water. However, the experimental results revealed no surface hardening effect for water layer of mere 5 mm. This can be explained by formation of plasma plume and water vapor cloud.

A bright plasma was observed during water submerged hardening experiments as shown in Figure 7.2. When the laser irradiates on the steel surface in air, the surface is heated up quickly to a high temperature and forms hardened structure on rapid cooling (see Figure 7.3(a)). In presence of water, evaporation forms vapor cloud over the surface. Zhang et al. [233] reported that a large water-vapor plume forms immediately above the surface when water layer is greater than 3 mm. The vapor cloud causes attenuation of energy reaching the surface.

In addition, when the water layer is thin, the laser energy is high enough to vaporize a small water channel along the beam path (see Figure 7.3(b))

delivering enough energy onto the surface [234]. However, when the water layer is thick, the plasma forming at the steel surface is confined by the water pressure. This results in no hardening effect at all (see Figure 7.3(c)).

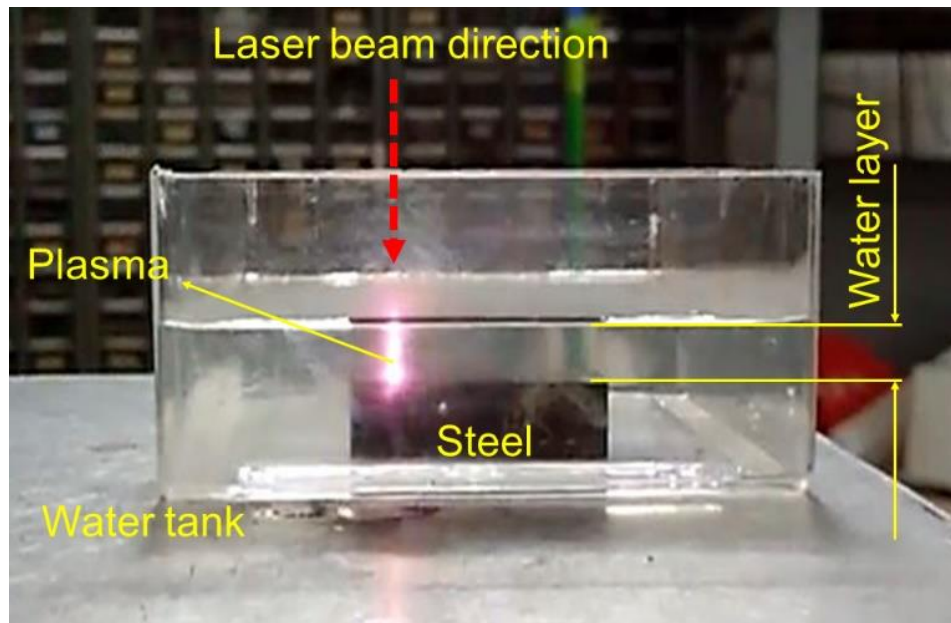


Figure 7.2: Image showing plasma formation during underwater laser hardening process.

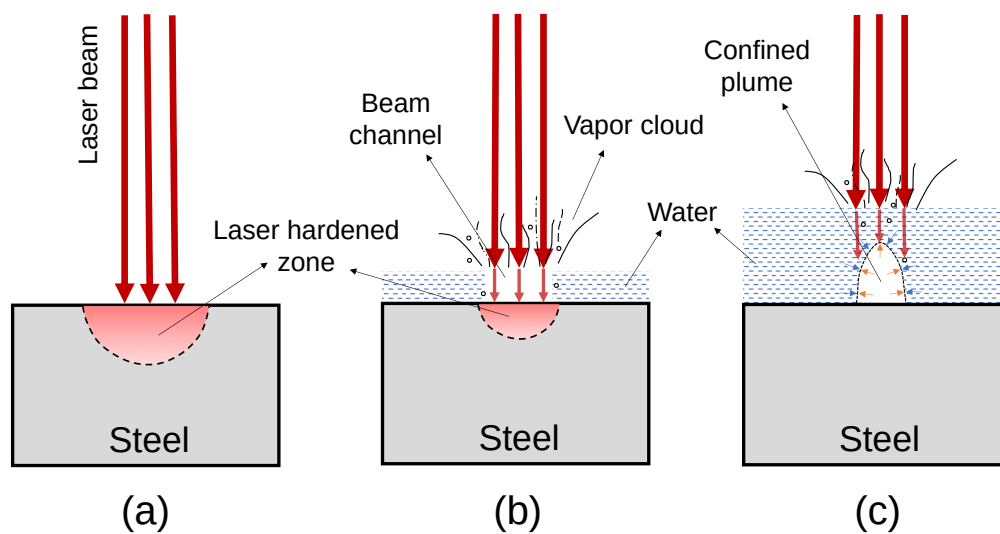


Figure 7.3: Illustration showing laser hardening process (a) in air; (b) with thin layer of water; and (c) with thick layer of water.

Therefore, it is possible that the attenuation by water-vapor plume resulted in no hardening effect in case of 5 mm water layer even though very little of the laser beam is absorbed by the water layer. The explanation is consistent with our result obtained as there was only a faint line at the surface when water layer was 3 mm and no observable change when water layer was 5 mm. Therefore, only the underwater hardening studies with 1 mm water layer thickness is pursued in rest of the analysis.

Investigations were performed to study the effect of process speed on hardened surface morphology. Figure 7.4(a) and (b) shows the hardened track at different process speeds when treated in presence of 1 mm thick water layer. At slow process speed, the hardened line was found to be zigzag and random. Distinctly separated parts in the laser hardened line were observed particularly at slow speed under water, as shown in Figure 7.4(a). No such interruptions were found at high speed which produced a uniform single hardened line.

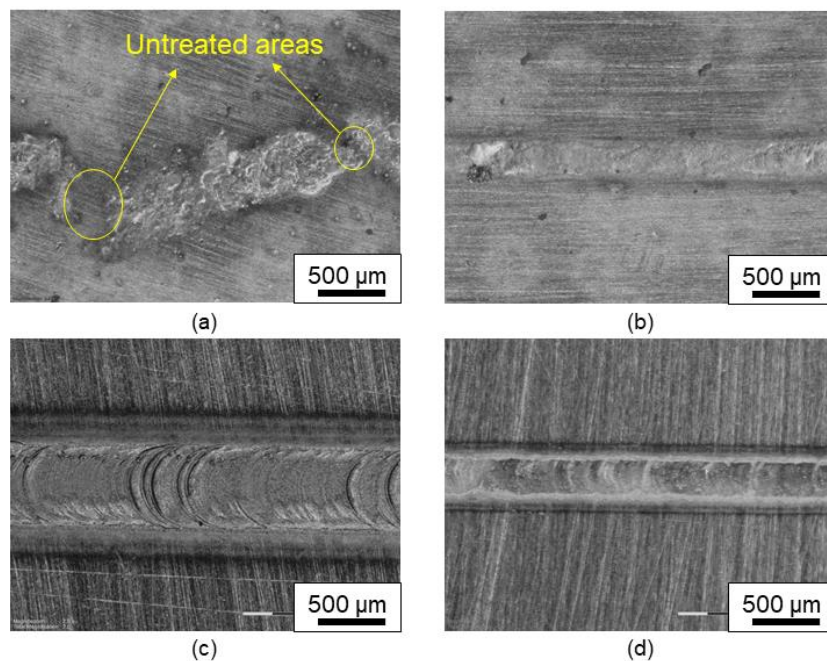


Figure 7.4: Stereo-images of laser hardened lines during (a,b) underwater laser processing; and (c,d) argon gas protection. Process speed was 10 mm/s for (a) and (c), and 100 mm/s for (b) and (d). A constant power of 250W was used for all experiments.

Figure 7.4(c) and (d) shows the hardened track under argon protection using same power for comparison. The hardened track was straight, but the width was larger for slow process speed than for fast speed due to longer interaction time [142].

When the laser beam irradiates the metal underneath, its surface temperature increases rapidly. The heat from the metal surface is absorbed by the water in contact with the surface. During slow process speed, there is enough time for the heat from the base metal to be absorbed by water which results in the convective motion of the water. In addition, the shock wave produced by formation of vapor bubbles in water disturbs the molecules [227]. The combined effect produces random motion of water and diffracts laser beam in random directions producing zigzag hardened track (see Figure 7.5(a)).

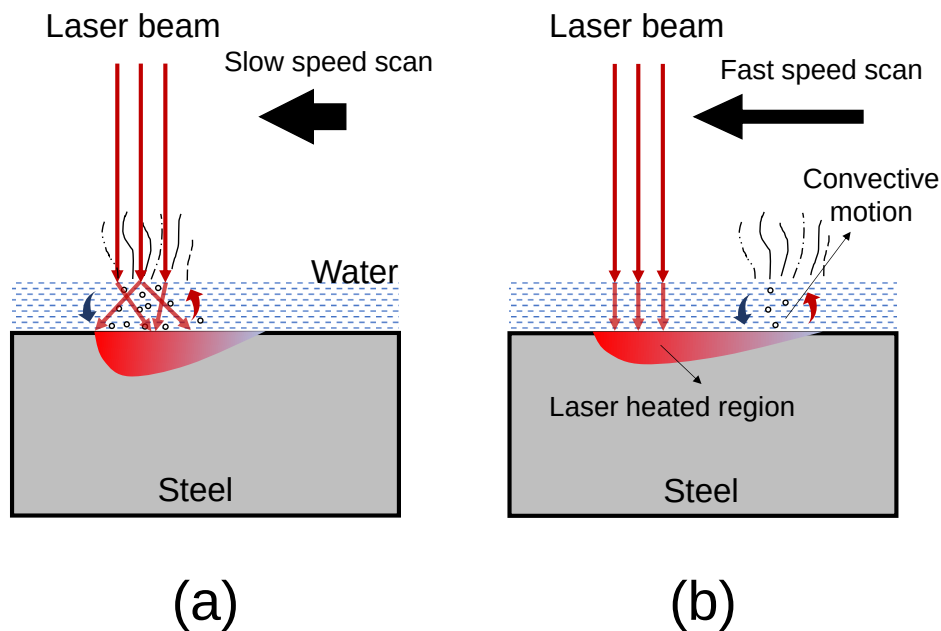


Figure 7.5: Schematic diagram showing (a) convective motion of water and vapor formation above the irradiated area during slow process speed, and (b) absence of any disturbance in water above the irradiated area during fast process speed.

On the contrary, during fast processing, the fast-moving laser heat source coupled with high specific heat capacity of the water results in time lag between the heat transfer from surface to water. Therefore, the water molecules near the laser irradiated area are undisturbed during the process producing a straight hardened line (see Figure 7.5(b)).

SEM and EDS analysis were carried out in order to study the chemical and morphological changes occurring at the surface. Figure 7.6 reveals typical phases formed at the surface using 10 mm/s and 100 mm/s scanning speeds. At 10 mm/s speed, the width of hardened track was non-uniform for reasons discussed above (Figure 7.6(a)). The hardened track width at 100 mm/s speed was smaller than at 10 mm/s speed (Figure 7.6(c)); but had a uniform width.

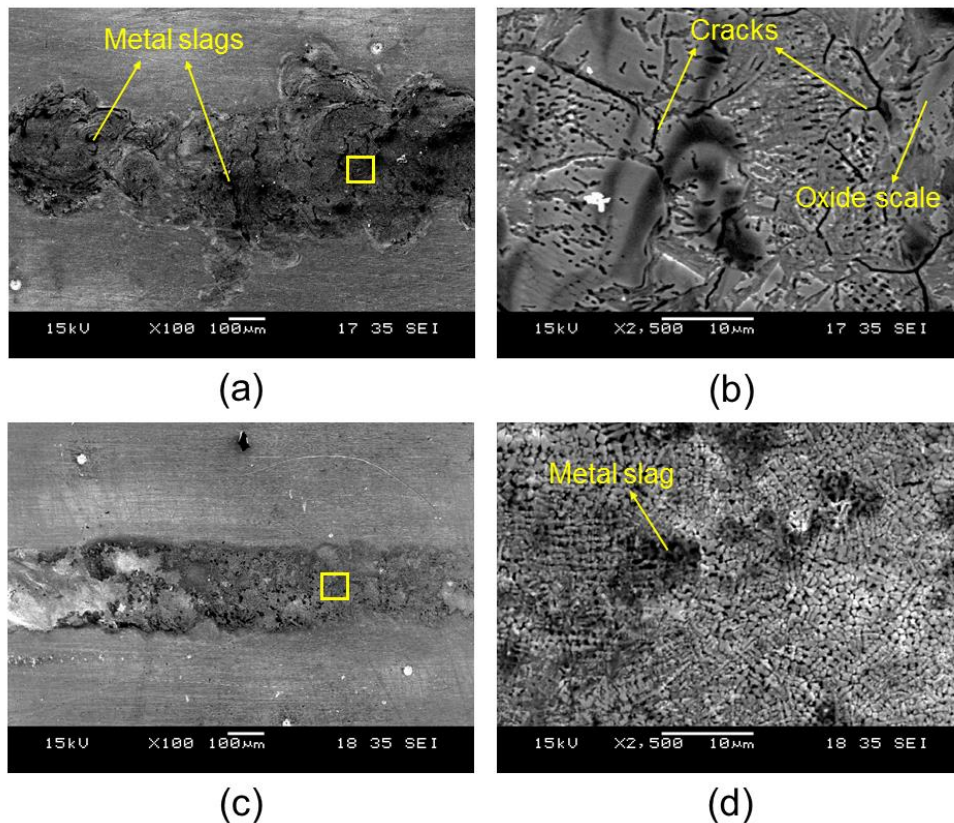


Figure 7.6: SEM image showing (a) surface morphology at 10 mm/s speed; (b) blow-up of a square area in (a); (c) surface morphology at 100 mm/s speed; and (d) blow-up of a square area in (c). A constant power of 250 W was used for both cases.

High magnification images revealed presence of a thin layer of surface oxide at both speeds. Interestingly, the oxides at 10 mm/s speed were lumped and somewhat detached from the surface (Figure 7.6(b)). Some cracks were also observed on the oxide scales. Contrary to this, the oxide scale at 100 mm/s speed was uniformly spread over the surface without any visible cracking (Figure 7.6(d)).

The presence of oxide layer suggests that surface oxidation could not be prevented completely even though water acts as shield from air. EDS analysis identified the black phase as metal slag rich in oxygen, silicon, chromium and manganese. These elements segregate from the base material during laser heating process [133]. The slag was randomly distributed in the laser treated area at slow speed due to movement of water. At fast speed, the interaction time is not long enough for agglomeration of surface oxides.

Figure 7.7 shows surface profiles of laser hardened lines obtained from confocal microscope. The laser treated area appeared to be raised slightly compared to the base surface. At 10 mm/s speed, the hardened line in underwater condition had a raised hump of about 5 μm height from the surface (Figure 7.7(a)). On the contrary, the hardened line at 100 mm/s speed in underwater condition did not reveal a significant raise in surface height (Figure 7.7(b)). Similar results were obtained for argon protected cases where a slightly raised hump (about 3 μm) was observed at 10 mm/s speed (Figure 7.7(c)) and no increase in surface height was found at 100 mm/s speed (Figure 7.7(d)).

The formation of surface hump at slow speed in underwater condition is attributed to the presence of oxide scale as discussed above. A thick layer of surface oxides forms at slow speed than at fast speed. Therefore, it manifests itself as raised surface under confocal microscope. Interestingly, the underwater treated cases revealed higher raise in surface profile than argon protected cases under same speed. This is because argon gas protection minimizes the formation of surface oxides.

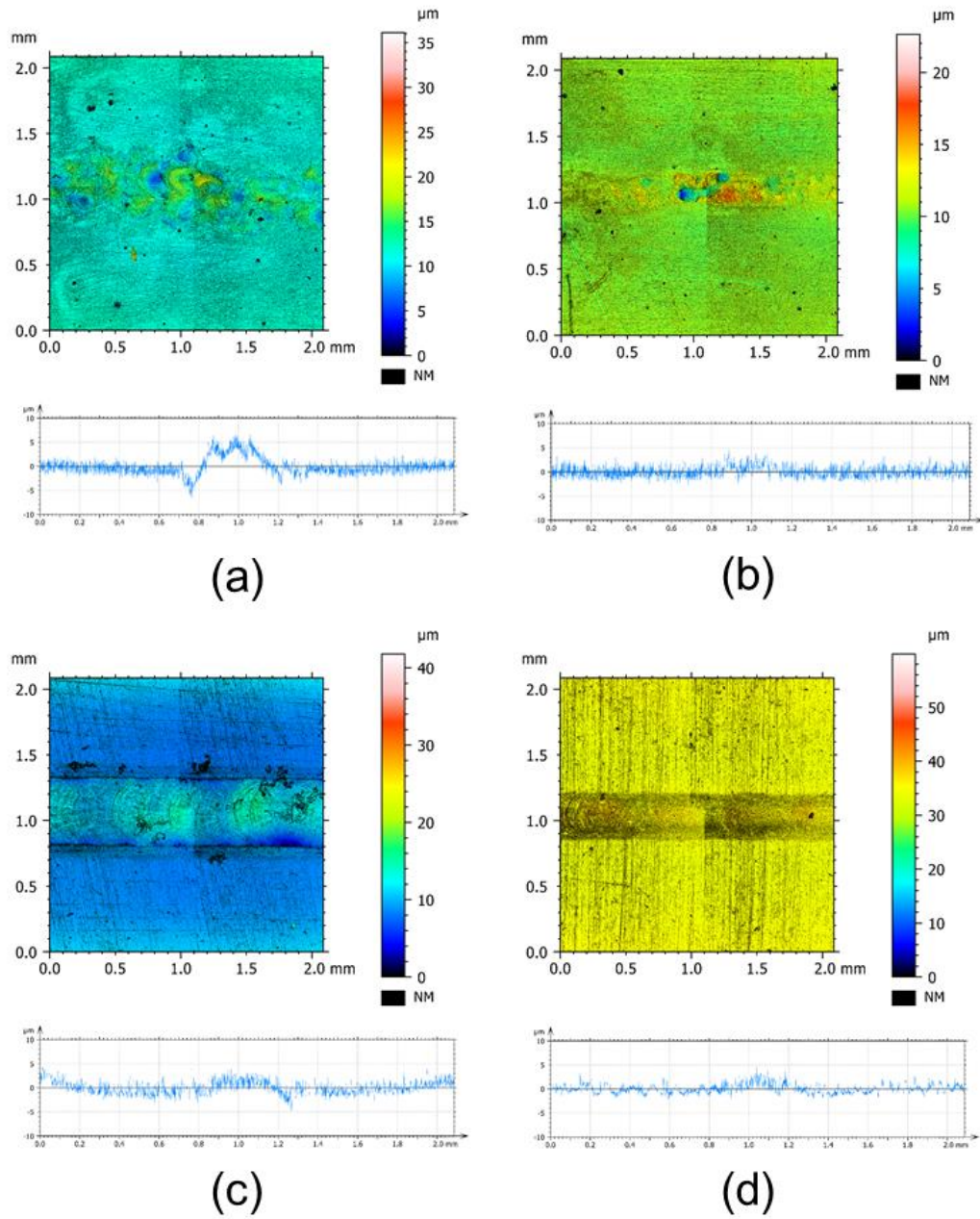


Figure 7.7: Surface topographies and line scans obtained from confocal microscope in (a,b) underwater condition and (c,d) argon protected condition at (a,c) 10 mm/s speed; and (b,d) 100 mm/s speed.

7.1.3.2 Cross-section microstructure

In order to study the microstructure of laser affected zone, cross-section metallographic studies were performed. Figure 7.8 shows a typical cross

section microstructure of laser hardened line which was processed in underwater condition at 250 W power and 10 mm/s process speed. The laser affected zone is crescent shaped with clearly distinct microstructure in the laser hardened zone compared to the base microstructure.

The base microstructure of the steel consists of spheroidized cementite particles uniformly distributed over the whole matrix (Figure 7.8(d)). After laser treatment, the spherical carbide particles are completely dissolved in the matrix due to rise of temperature above austenitization temperature. The laser heated area cools rapidly due to the bulk material being at sufficiently lower temperature ("self-quenching" effect). This produces hard martensitic structure as shown in Figure 7.8(a).

A closer observation of the laser treated area reveals the presence of multiple cracks near the surface as shown in Figure 7.8 (c). Owing to the higher carbon content in 52100 steel (about 1 wt%), these cracks must have formed due to the internal stresses developed during quenching [128]. A mixed microstructure existed in the heat affected zone as shown in Figure 7.8(d). In this region, the temperature is not high enough to dissolve carbide particles completely due to decreasing effect of laser heating.

Figure 7.9 shows the variation in laser affected area with change in process speed in both argon protection and underwater condition. The solid line and the dotted line represent the case for argon protected condition and underwater condition respectively. Both depth and width in water submerged condition are significantly lower than argon protected condition. In all cases with argon gas protection, both laser-affected depth and width reduced with increase in speed. Interestingly, the underwater treated specimens did not show much variation in depth and width up to a speed of 75 mm/s. Laser hardening at slower speeds under water showed lots of variation in measurements as indicated by the large error bars.

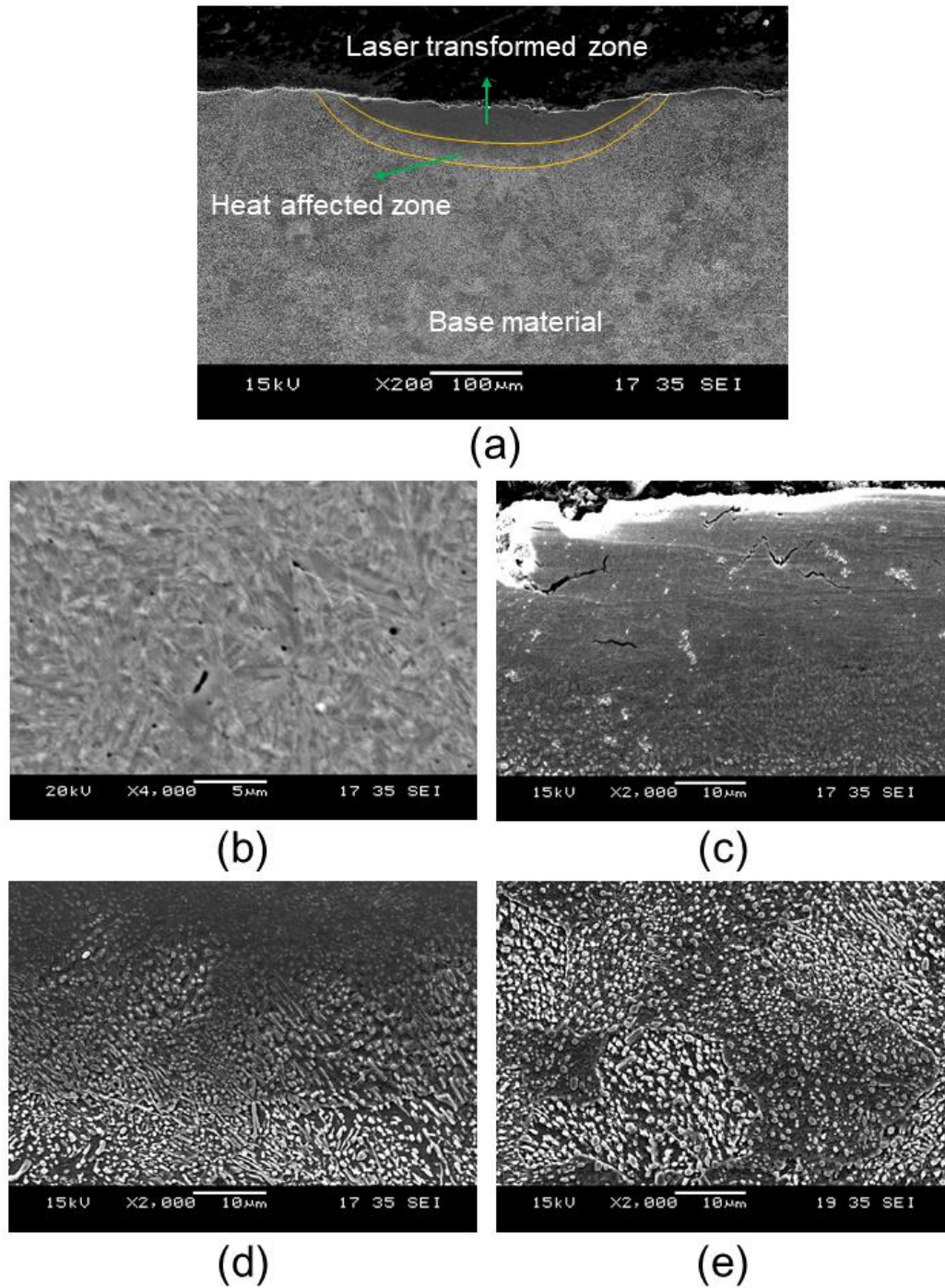


Figure 7.8: Micrographs showing laser affected region during under-water hardening. (a) Martensitic structure in laser transformed zone; (b) quenching cracks near the surface; (c) heat affected zone with mixed microstructure; and (d) base microstructure with spheroidized cementite particles uniformly distributed over the matrix.

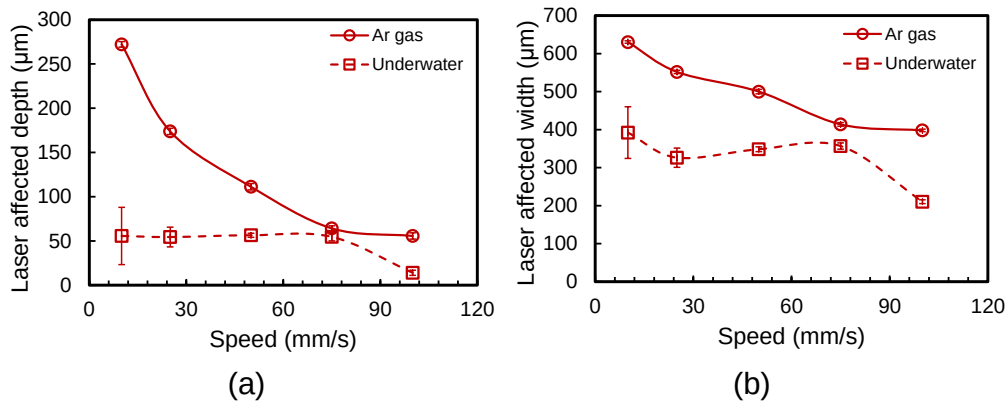


Figure 7.9: Graphs showing variation in laser affected (a) depth, and (b) width for water submerged and Argon protected conditions.

The presence of water near the surface carries the heat away more efficiently from the source of generation. With water acting as cooling agent, a huge portion of the heat generated by laser irradiation on the metal surface is dissipated by water. Therefore, the laser affected region is smaller for underwater treated condition than for argon gas protected case.

On the other hand, the change in size of laser affected region with variation in speed can be attributed to the interaction time available for austenitization. Increase in speed of the process reduces the interaction time. At very fast speed, short interaction time to austenitize the surface results in a small laser affected area. On the other hand, the total interaction time is longer at slow speed of operation which provides enough time for laser to austenitize a larger area.

Especially during underwater processing, the laser affected region remains almost constant at medium speeds. This suggests that there exists a threshold laser energy to produce significant change in laser affected area based on other parameters including water-level and process speed for effective coupling.

As mentioned earlier, a large variation in the size of laser affected area is found at slow speeds in underwater condition. This is due to the random diffraction of water during slow speed processing (as discussed in Section 7.1.3.1). The laser affected area will be significantly different when evaluated from the interrupted part of the line and from the central part of the line (Figure 7.4(a)). This also resulted in a large standard deviation in the measurements.

7.1.3.3 Microhardness variation

Figure 7.10 compares the hardness variation along the depth from the surface for under-water hardened and argon gas protection hardened specimens at 10 mm/s speed. The microhardness values obtained verifies the occurrence of martensitic transformation in the surface of steel.

As can be seen, the hardness of the laser treated region is higher in comparison to the original specimen (untreated one). The water submerged specimen exhibited even higher hardness than argon protected specimen with maximum value reaching about 900 HV. However, it is to be noted that the hardened depth during submerged condition is very shallow (just about 50-70 μm) compared to argon protected specimens.

Higher microhardness is attributed to the rapid phase transformation as well as substantial fragmentation of the structure resulting in greater contribution of grain boundaries. The presence of water layer further enhances the cooling rate at the surface. This results in additional heat dissipation at the surface and high temperature gradient [235]. The fast cooling, thus increases hardness at the surface, but limits the depth of heat penetration.

Moreover, from Figure 7.11, it is found that the surface hardness values of underwater treated specimens were higher than argon protected cases irrespective of process speed used. This suggests that for the range of process speed used, it has less effect on surface hardness, but significantly changes the depth and width of hardened region.

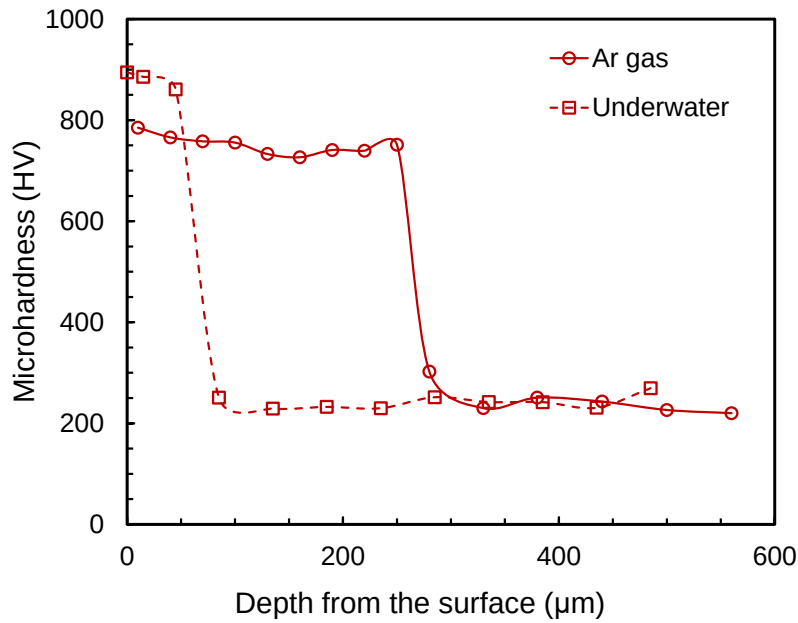


Figure 7.10: Graph comparing the hardness variation along the depth for water submerged and Argon gas protected conditions. The power and process speed used was 250 W and 25 mm/s for both cases.

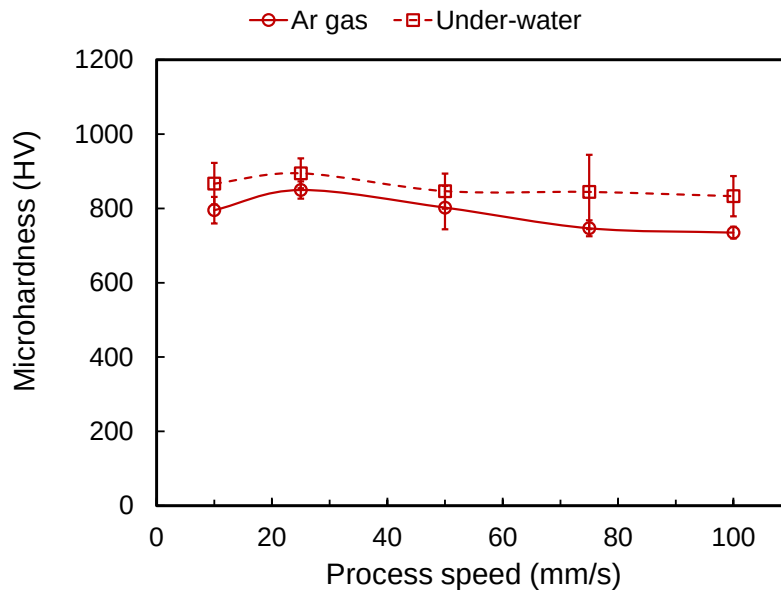


Figure 7.11: Variation of surface hardness with process speed.

The study thus shows that underwater laser hardening can produce higher hardness at the surface than conventional hardening process; but the laser affected area is significantly diminished due to dissipation of heat in water. Especially at slow process speeds, the hardened line is inconsistent with lots

of interruptions due to random diffraction of laser beam by water movement. One possible solution to this could be to use a running water than stagnant water.

7.2 Decarburization during laser hardening

7.2.1 Introduction

Decarburization is a well-known surface degradation process involving the loss of near-surface carbon from steel during exposure in air at elevated temperatures. It usually occurs at temperature above 700°C i.e. austenite phase region whereby the carbon atoms diffuse from the surface of the metal. As a result of near-surface carbon loss, the surface of the steel has a lower strength, lower fatigue resistance and higher wear rate [236]. The problem has been prevalent during high temperature heat treatments carried out in industrial operations such as rolling and forging. During furnace heating, the chemical potential of carbon in the atmosphere may be lower than that in the steel being heat treated [237]. Therefore, carbon from steel interact with the furnace atmosphere and are removed as a gaseous phase.

Unlike in conventional heat treatment, laser surface treatment produces a rapid heating condition at the surface characterized by high heating and short austenitization periods. Despite the short interaction time, there is a chance of carbon loss from the surface. Some studies have mentioned the possibility of decarburization after laser surface treatment as one of the reasons for degraded surface mechanical properties [158,238,239]. However, an elaborative investigation on quantifying the decarburization during laser surface treatment is still missing. In this section, the decarburization during laser hardening and counter-measures to induce superior surface properties by carburization is studied.

7.2.2 Quantifying decarburization

Quantifying the decarburization during laser surface treatment is a challenging task. Even in conventional heat treatment, there exists a lot of variation in measuring the depth of decarburized layer. Some measure the greatest depth of total carbon loss (free-ferrite depth, or FFD) while others define decarburization depth as the greatest depth location in the interior where the bulk carbon content is reached i.e. both FFD and partial loss of carbon depth. The ASTM E1077-14 [240] standard defines all these terms commonly used in industries and depicts the test methods to estimate the depth of decarburization of steel. According to the standard, the decarburization depth can be measured by measuring surface hardness, microscopic etching method or by chemical analysis depending the level of accuracy desired. For general industrial purpose, a simple qualitative screening approach by hardness measurement is suggested in [241].

As for the laser treated surface, the decarburization depth can be tricky to determine. The short thermal cycle during laser surface treatment produces non-equilibrium phases in a thin layer of the surface. Hardness measurements is difficult in such case and it might not accurately gauge the decarburized depth. Therefore, a simple mathematical model based on 1-D diffusional equation is developed to predict the decarburization depth during laser hardening.

7.2.3 Analytical Modelling

During laser surface treatment, the temperature at the surface can reach to very high temperature well above austenitization temperature. At such high temperature, the carbon can diffuse in or out of the metal surface depending on the interaction time and atmospheric condition [8]. One of the important processes controlling decarburization is the environmental reaction at the surface that causes carbon to be removed from the surface of the steel. The carbon potential between the material and the atmosphere is the driving force. Another is the rate at which carbon diffuses from the interior to the surface of

the steel. One of the most important reaction during carburization/ decarburization is [242]



The relationship between the gaseous components and the carbon in solution of austenite is described by fundamental law of mass action. It defines an equilibrium constant K which is given as

$$K = \frac{P_{CO}^2}{f_c * wt\%C * P_{CO_2}} \quad (7.3)$$

where, P_{CO} and P_{CO_2} are the partial pressures of CO and CO₂ respectively and f_c is the activity coefficient of carbon.

The equilibrium constant, K , is a function of temperature, T (expressed in Kelvin) and is given by

$$\log K = -\frac{8918}{T} + 9.1148 \quad (7.4)$$

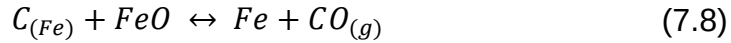
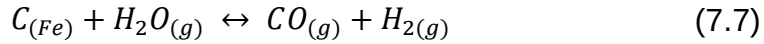
Knowing the partial pressure of the CO₂ and the CO, the equilibrium weight percent of carbon on steel at the given processing temperature can be predicted by rearranging equation (7.3)

$$wt\%C = \frac{1}{K f_c} \frac{P_{CO}^2}{P_{CO_2}} \quad (7.5)$$

If the partial pressure of CO exceeds the partial pressure required to maintain a given carbon content, the reaction represented above goes from right to left causing surface carburization until a new equilibrium is reached. On the other hand, if the CO₂ partial pressure is high relative to CO content, the surface will be decarburized i.e. the reaction proceeds from left to right. The above equation also requires determination of activity coefficient f_c which is a function of temperature and the composition of austenite. According to Harvey [242], f_c for Fe-Si-C system can be calculated by using following equation:

$$\log f_c = \frac{2300}{T} - 2.24 + \frac{179 + 8.9 \text{ wt}\%Si}{T} \text{wt}\%C + \left(\frac{62.5}{T} + 0.041 \right) \text{wt}\%Si \quad (7.6)$$

The preceding equations can be used to calculate the equilibrium weight percent of C in the steel surface during carburization/decarburization. Apart from equation (7.2), other reactions such as reaction of carbon with water vapor and iron oxides may also occur at the surface [243], given as



These are not considered in the analysis. It is to be noted that decarburization is a complex process and a much higher CO than CO₂ content is required for carburizing [244].

The decarburization process is governed by Fick's Law of Diffusion according to which the net flux of carbon diffuses from a higher concentration to a lower concentration region given by

$$J = -D \frac{\delta C}{\delta x} \quad (7.9)$$

where J is the diffusion flux per unit cross section area per unit time, D is the diffusion coefficient and $\frac{\delta C}{\delta x}$ is the concentration gradient. The diffusivity of an element can be determined by the Arrhenius reaction equation

$$D = D_0 \exp\left(\frac{E_a}{RT}\right) \quad (7.10)$$

where, D_0 is the pre-exponential factor (cm²/s), E_a is the activation energy for diffusion (J/mol), $R = 8.314$ J/(mol K) and T is the absolute temperature in Kelvin.

It is noteworthy to point out that the Fick's first law alone cannot model the carburization/decarburization process, as the diffusion flux keeps on changing

with time and the concentration gradient. For the time transient decarburization modelling, Fick's second law is used which is given as

$$\frac{\delta C_x}{\delta t} = D \frac{\delta^2 C_x}{\delta x^2} \quad (7.11)$$

where, C_x is the concentration at distance x from the surface, and t is the time. The average carbon diffusivity (cm^2/s) for most steel can be approximated by

$$D_c^\gamma = 0.12 \exp - \frac{32000}{RT} \quad (7.12)$$

For modelling, Van-Ostrand-Dewey solution to Fick's second law was used which can be defined as

$$\frac{C_x - C_s}{C_0 - C_s} = \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (7.13)$$

where C_s is the surface concentration of carbon and C_0 is the initial carbon level in steel.

The carbon content profile along the depth was generated using ThermoCalc DICTRA software. The solution yields the carbon concentration profiles at every step of the simulation. In order to validate the model, the decarburized depth during normal heat treatment of AISI 1055 steel was studied first. A 1055 steel specimen was heated in a box furnace at 860°C for 20 min and cooled in open air. Hardness measurements were made on the cross-section of heat treated sample to estimate the decarburization depth. The predicted depth and experimentally measured depth were found to match perfectly validating the accuracy of the model (see Figure 7.12).

After validating the model, the model was used to predict the decarburization depth for laser treated specimen. It predicted a decarburization depth of about $65 \mu\text{m}$ for a surface treated with 250 W laser and 10 mm/s process speed (see Figure 7.13). The loss of carbon is strongly dependent on the distance from the surface, as expected.

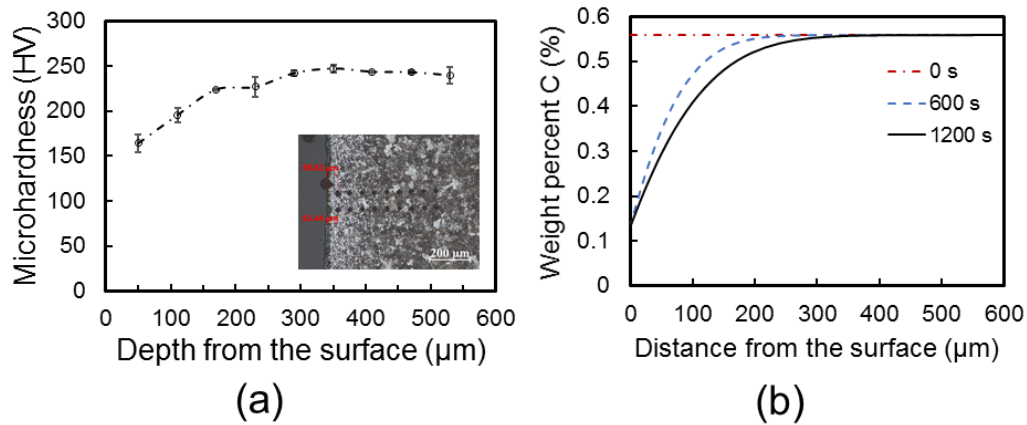


Figure 7.12: Decarburization during furnace heating of AISI 1055 steel – (a) decrease in hardness near the surface (inset shows micrograph of decarburized surface); and (b) loss of carbon content in the near-surface region obtained from Thermo-Calc DICTRA modelling.

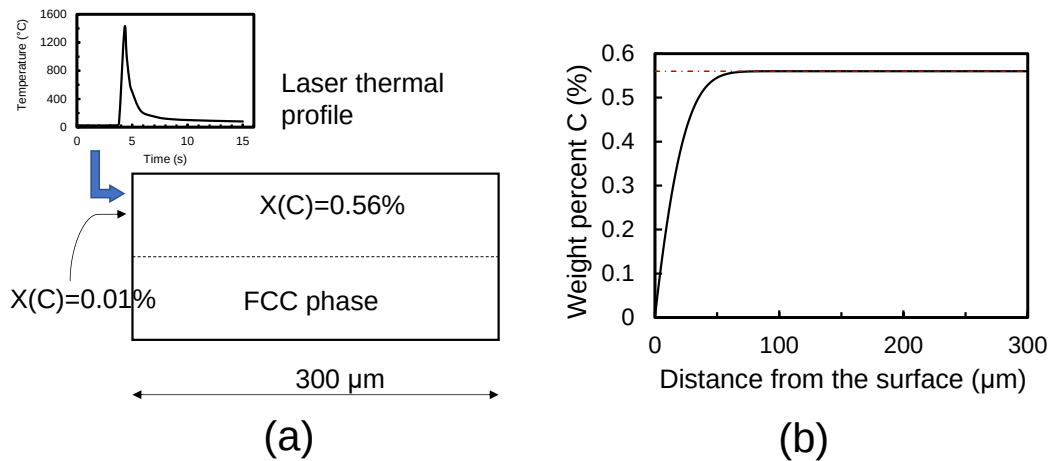


Figure 7.13: Decarburization during laser hardening of AISI 1055 steel at 250 W power and 10 mm/s process speed – (a) one dimensional model used; and (b) carbon profile in the near surface region showing decarburization.

The peak temperature reached during laser treatment, albeit for a short time, also has a big effect on decarburization depth as shown in Figure 7.14. A very small decarburization depth is obtained for low temperature which increases exponentially with increase in peak temperature. However, the

decarburization should not keep on increasing continuously as at higher temperature, the surface has higher chances of evaporation and ablation.

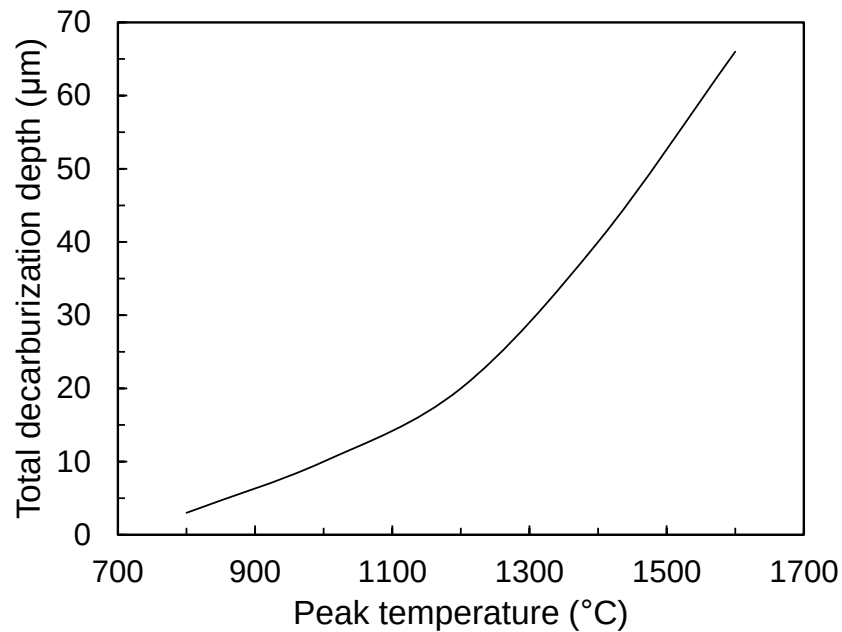


Figure 7.14: Variation of decarburization depth with peak temperature during laser surface processing.

7.3 Laser carburizing using surface coatings

7.3.1 Introduction

Since decarburization is detrimental for surface properties of steel, investigations were carried out to explore the possibility of preventing decarburization. Previous studies have found that graphite coating during laser surface hardening of steels introduced substantial amount of carbon into the steel [245–248]. The introduction of carbon into the substrate can be beneficial, not only for preventing decarburization, but also to induce wear resistant properties at the surfaces [246]. In addition, the coating also serves as a couplant for laser beam absorption by the substrate [37,58,131,249,250]. Therefore, studies were performed to evaluate the possibility of laser carburizing.

7.3.2 Graphite as surface coating

Commercial graphite spray was used to pre-coat a 52100 steel sample with graphite before performing the laser test. The details of experimental parameters used can be found in Appendix B3. The spray was an aerosol of graphite particles (in the range of 3 – 50 μm) and alcohol. On spraying it over the cold metal substrate, the alcohol evaporated leaving behind a thin layer of graphite over the surface as shown in Figure 7.15. The laser heating burnt off the graphite from the irradiated area inducing some carbon into the substrate by surface alloying.

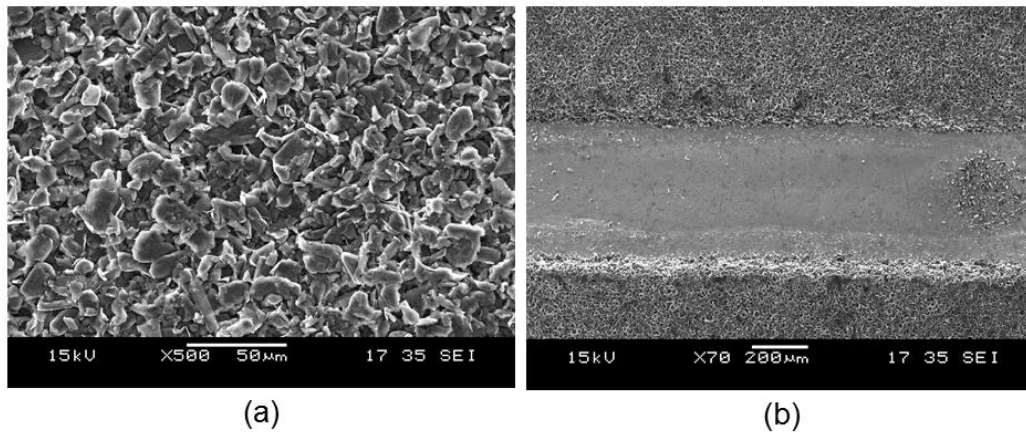


Figure 7.15: (a) Graphite flakes covering the surface; and (b) Laser scan line over the graphite coated surface.

Figure 7.16 shows a typical microstructure of the carburized region just beneath the surface. The microstructure had cast iron like dendritic structure which verifies the diffusion of carbon into the substrate during melting and solidification of the layer. The higher absorption of laser energy due to graphite coating must have increased the surface temperature beyond the melting point. Carbon can diffuse easily in the liquid which on subsequent solidification forms cast iron like microstructure. However, this resulted in lower hardness than in uncoated specimen zone as shown in Figure 7.17. A maximum hardness of about 900 HV was recorded in the hardened region just beneath this remelted zone which can be attributed to the higher carbon content due to solid state carbon diffusion [248].

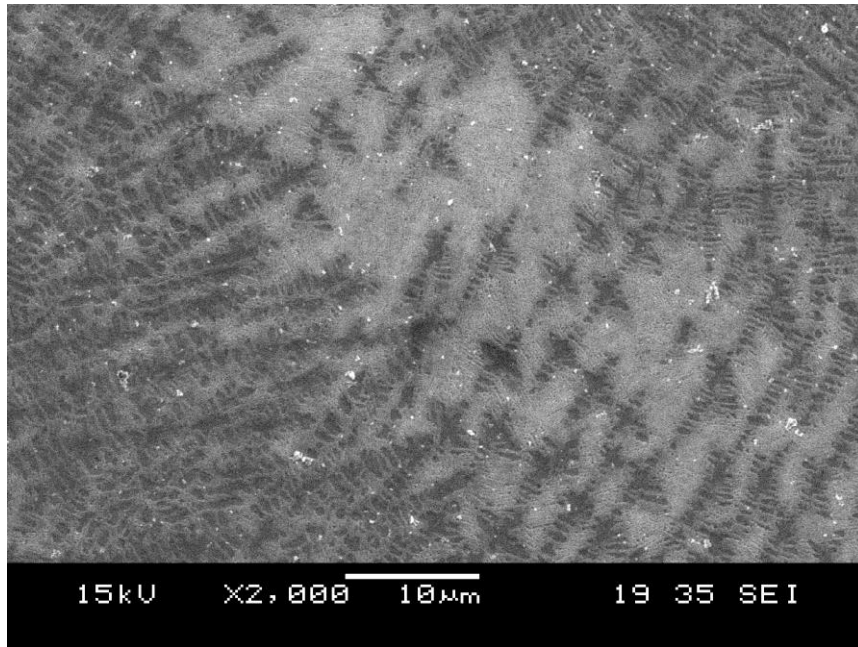


Figure 7.16: Cast iron like microstructure formed after carburizing the surface with graphite.

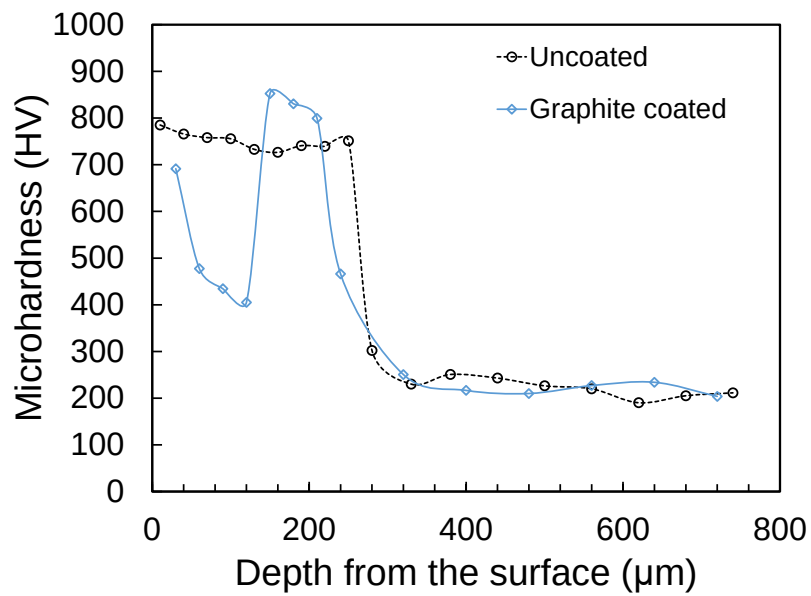


Figure 7.17: Microhardness profile along the depth for uncoated and graphite carburized surfaces.

The graphite carburizing experiments were attempted for other steels as well. Figure 7.18 shows the typical microstructure of different steels after

performing graphite induced laser carburizing with same laser parameters. A slight volume expansion occurred for all cases owing to the formation of martensite and diffusion of carbon into the steel. Large number of severe cracks and porosity appeared for AISI 1020 and AISI 1055 steels. These steels have lower amount of carbon (0.20 wt% and 0.56 wt% respectively). Therefore, higher amount of carbon could diffuse into the surface which forms a hypereutectic solidification structure. This structure is very brittle and results in cracking due to high thermal stress generated during cooling [246]. Some pores might also form during the rapid solidification process due to entrapment of gases. On the other hand, the cracking was limited to the top region in case of 50CrMo4 and AISI 52100 steels. This can be attributed to the presence of higher amount of carbides and alloying elements in these steels [31] which limit the carbon diffusion to a shallow depth.

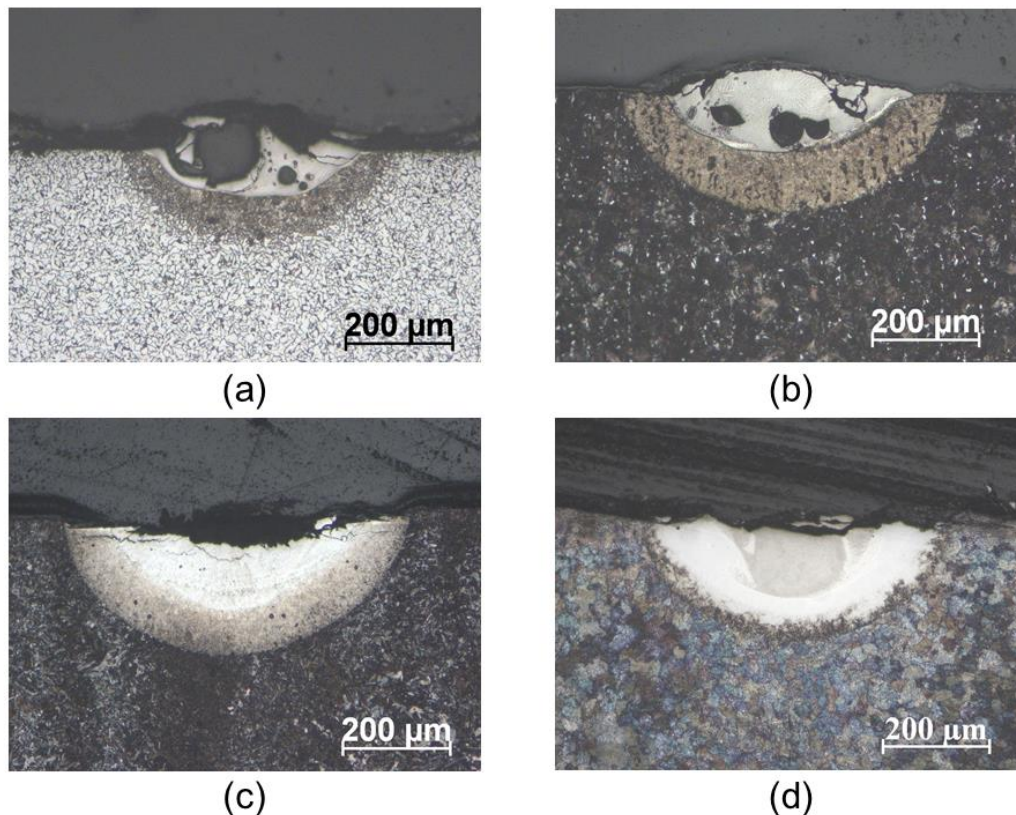


Figure 7.18: Graphite coated laser carburized microstructure of different steels - (a) AISI 1020; (b) AISI 1055; (c) 50CrMo4; and (d) AISI 52100.

The investigation therefore, demonstrates that graphite coating can induce carburization on the surface of steel. However, the process has many limitations. One of the major drawbacks of using graphite powder is its difficulty in obtaining a uniformly covered surface. Woo et al. [247] highlighted the significance of graphite coating thickness in laser hardening and suggested to use an optimum thickness to obtain uniform hardened layer dimension. They found the optimum value using linear regression and neural network model. However, controlling the layer thickness of graphite is very challenging as it requires meticulous application of the graphite layer on the surface. This renders less controllability to the carburizing process and depending on the amount of graphite and the laser parameters, may result in lower hardness, cracking and porosity.

7.3.3 Carbon nanotubes as surface coating

Carbon nanotube (CNT) fibers were utilized as surface coating in the next series of studies. With the recent development of nanotechnology, nano-structured materials such as WC-Co [251], nano-sized alumina [252] and CNTs [253] present excellent opportunity to be used as thin coating on the metal surface to produce different microstructure than that of bulk metal. The carburization depends on the carbon potential available at the surface. Compared to graphite, CNTs could be more uniformly coated on the surface which can increase the carbon potential significantly. Furthermore, the nano-sized structure of CNT might be more favorable for easy dissolution of carbon during laser heating. Therefore, studies were performed to investigate the laser surface carburizing using CNTs as source of carbon.

A multiwalled CNT was used as coating on the steel substrate. Since CNTs tend to agglomerate due to their hydrophobic nature [254], it was first mechanically crushed and mixed with ethanol. The mixture was then ultrasonicated for 2 hours to make a homogeneous slurry. This slurry was uniformly applied over the steel surface and left to dry in air. Laser treatment were performed on the CNT coated surface as before using fiber laser. The different laser parameters used are shown in Appendix B3. Figure 7.19 shows

the surface of the substrate with CNT coating before and after laser treatment. The mesh of carbon nanotube fiber bundles can be clearly seen before laser treatment which completely burns out due to heating from the laser.

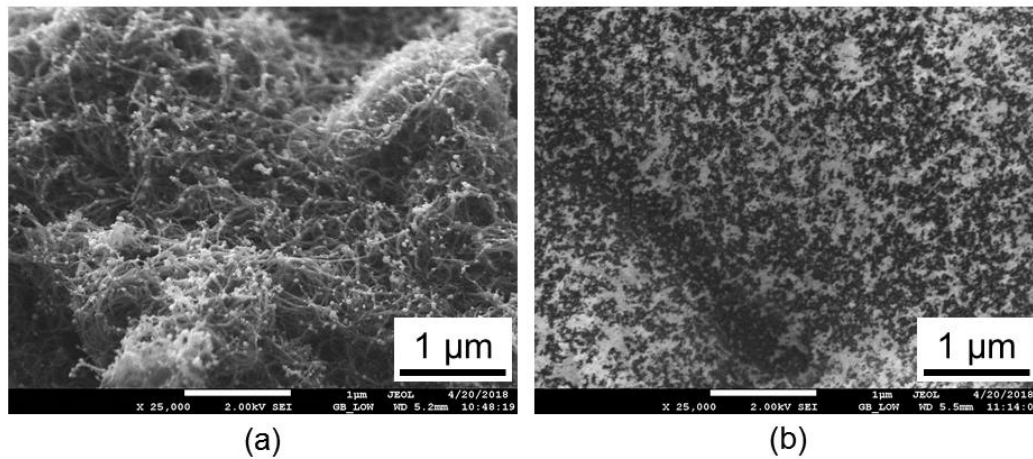


Figure 7.19: (a) Carbon nanotube (CNT) fibers on the surface; and (b) CNT remains after laser treatment.

The carbon from the CNTs diffuse into the molten surface due to higher carbon potential at the surface than in the steel. This forms a cellular solidification microstructure near the surface with depth ranging from 36 μm to 105 μm depending on the laser parameters used. A typical microstructure is shown in Figure 7.20.

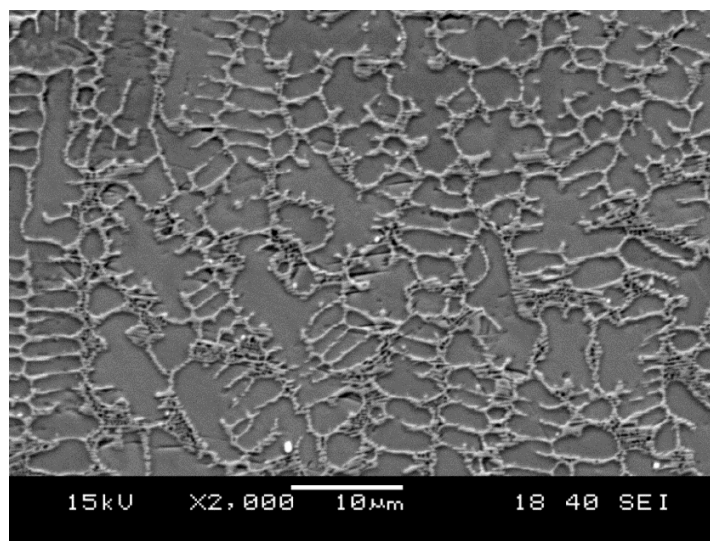


Figure 7.20: Cellular dendritic structure observed in CNT carburized region.

The solidification structure is primarily determined by solidification gradient, G and velocity of solid-liquid interface, R . The values of G and R varies continuously from the boundary to the laser irradiated center; therefore, the solidification mode changes from a planar mode near the fusion boundary to cellular, dendritic and equiaxed near the surface.

The cellular dendritic structure is identified as eutectic carbides in austenite/ledeburite matrix which form due to the alloying of molten layer with carbon. Similar results have been observed by Katsamas and Haidemenopoulos [248] using graphite slurry which they attributed to diffusion of excessive amount of carbon into the steel leading to compositions exceeding the eutectic (4.3 wt%). However, unlike in graphite carburizing, it is noteworthy to point out that the cracking and porosity were almost absent in this case. This is probably due to uniformity of CNT layer thickness on the substrate. Compared to graphite coating, CNT coating can be uniformly applied on the surface owing to their smaller dimension and larger surface area which results in more carbon contacting with the surface (see Figure 7.21). This leads to lower chance of carbon accumulation at the surface during laser heating and hence, a better inflow of carbon into the steel with its content below solubility limit than in graphite carburization.

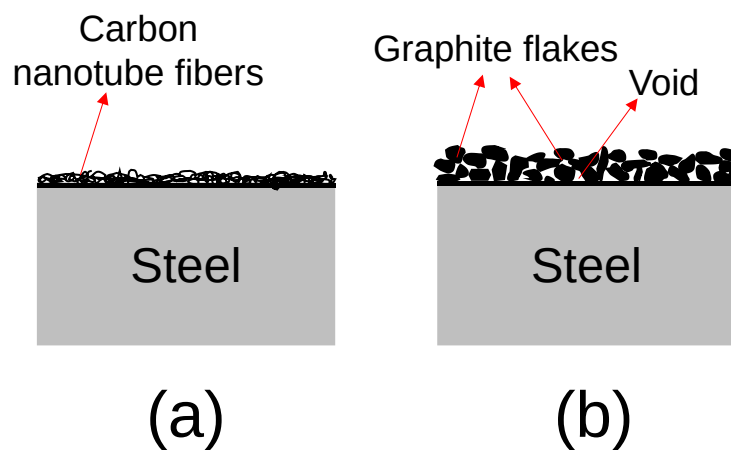


Figure 7.21: Schematic diagram showing less voids in CNT coated surface (a) than in graphite coated surface (b).

The microhardness measurements made on the specimens correlated well with the metallographic observations. The hardening mechanism is different in the melt carburized region and the hardened region. In the carburized zone, the iron carbide precipitates withdraw carbon from the original melt during their formation [255]. The lowering of carbon in the matrix results in formation of retained austenite which has lower hardness than the eutectic carbides. In the regions where there was substantial volume of carbides, hardness as high as 1157 HV could be achieved, while the hardness in the matrix varied from 560 HV to 852 HV depending on the amount of carbides present. The hardness in the hardened zone was determined by the hardness of the martensite formed. It had hardness as high as 950 HV near the fusion boundary with hardness gradually decreasing along the depth until base metal was reached. Without any carburization, the conventional laser hardening produced maximum hardness of about 821 HV. The higher hardness obtained also indicates the increase in carbon content of the steel surface.

Although CNT coated laser carburizing showed significant improvement compared to graphite coated specimen in terms of crack prevention and surface improvement, the challenge still lies in applying the coat on the surface. The graphite spray or CNT coating generally does not adhere to the substrate and some binders need to be used. At critical speeds during laser hardening, these binders evaporate. In addition, shrouding gas from nozzle might blow the coat away. Moreover, applying the uniform coat over the surface can be a tedious task when the shape of the component is complex. Gas assisted laser carburizing can overcome all these limitations with additional advantage of controlling carburization rate. By controlling the gas flow rate and the concentration of gas in contact with the surface, desired carburization with superior material properties can be obtained which is discussed in the next section.

7.4 Gas assisted laser hardening

7.4.1 Introduction

Conventional gas carburizing has been well established in industries for case hardening of various machine components. The technique uses a mixture of gases in a high temperature furnace which results in diffusion of carbon into the substrate (see Section 2.4.5.5). Since the hardening process in such case depends on the composition, function and control of furnace atmosphere [256], it is considered more flexible than pack carburizing which uses a solid compound. Similar to carburizing, nitriding and carbonitriding are also frequently used in manufacturing of airplanes, automobile parts, bearings, textile machinery, and turbine systems [257]. However, the need for a high temperature furnace and precise control of furnace atmosphere makes it time consuming and expensive.

Gas assisted laser carburizing combines the advantages of both gas carburization and laser as a heat source removing the need for expensive furnaces and their control. The use of gas as carburizing source provides more uniformity and controllability to the process than using a surface coating. In most of the previous studies, the gas assisted laser hardening is performed in two steps – first carburizing or nitriding the surface in a high temperature furnace and second, irradiating the carburized surface with laser. Kulka et al. [84] obtained hardness as high as 820 HV in re-melted and heat affected zone of 15CrNi6 low carbon steel using two step borocarburing and laser heat treatment process. Panfil et al. [85] performed laser heat treatment on gas-nitrided 42CrMo4 steel to improve the mechanical properties and found a significant increase in surface hardness (about 11.87 GPa). Similarly, Sola et al. [258] proposed a double step surface treatment combining low pressure gas carburizing and laser quenching to improve the surface hardness, hardening depth thickness and mechanical properties of C20 steel.

Extensive studies on one-step laser induced gas nitriding of various metals have been conducted by Peter Schaaf [259]. He used short pulsed lasers to

irradiate metal surfaces in nitriding atmosphere and found a large amount of nitrogen entering the metal substrate by diffusion. Yilbas et al. [260] also reported the formation of nitride species on H13 tool steel substrate during laser nitriding using co-axially supplied nitrogen gas at a high pressure of 600 kPa. The studies thus indicate the possibility to directly introduce an alloying element into the steel substrate by using laser irradiation in presence of suitable source gas. However, very limited studies on direct laser carburizing of steel using a carburizing atmosphere has been reported in the literature.

Considering the advantages of using gas for carburizing than using a surface coating, the laser assisted gas carburization of different steels is explored in this section. The preliminary study investigated the effect of various carbon rich gases such as CO_2 and propane (C_3H_8) on surface hardening. On identifying the carburizing potential of propane, further detailed studies were performed on propane carburized specimens.

7.4.2 Experimental Setup

The experimental setup for the laser gas carburizing is shown in Figure 7.22. All four kinds of steels, AISI 1020, AISI 1055, 50CrMo4 and AISI 52100, were used for the study. The details of these steels can be found in Chapter 3. At first, trial experiments were performed in open air with gas being supplied at the irradiated surface using a nozzle. It was found that it was not very effective in preventing surface oxidation. On the other hand, only the flow rate could be controlled by using nozzle and with flammable gas such as propane, there's always a risk of fire hazards. Therefore, a special chamber was designed in-house to perform the controlled experiment.

The chamber is shown in Figure 7.23. The chamber has dimensions of 120 x 120 x 12 mm³ with a laser transparent laser window at the top. The laser beam enters the chamber from this window. It also has a vacuum gauge and a pressure gauge fitted to measure the vacuum pressure and gauge pressure inside the chamber during operation. The chamber is properly sealed to prevent any leakage of air. It has an inlet and an outlet for gas to flow in and

out respectively. Two valves V1 and V2 are connected at the either side to control the flow of the gas. The inlet side is connected to a gas cylinder while the outlet is connected to a vacuum pump.

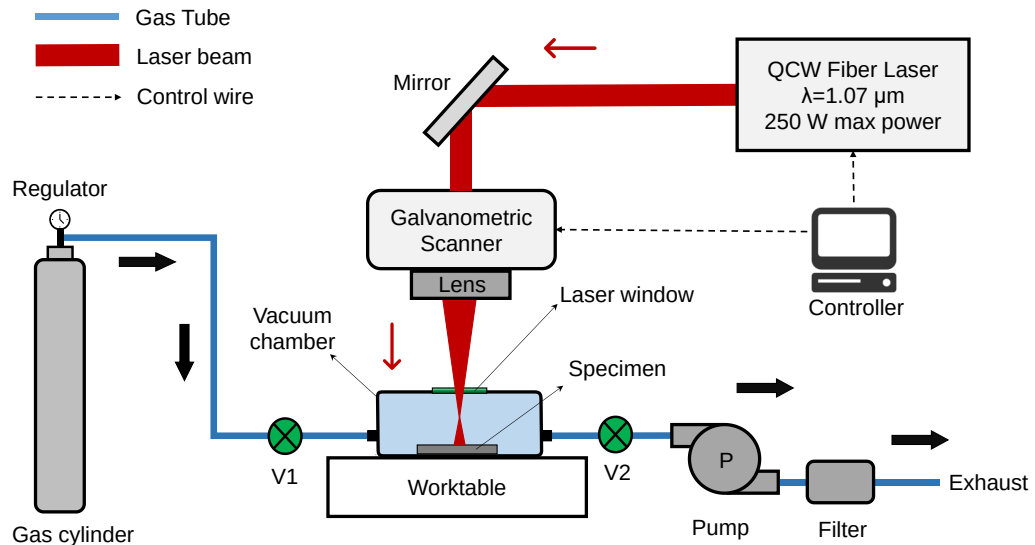


Figure 7.22: Experimental setup for gas assisted laser hardening experiments.

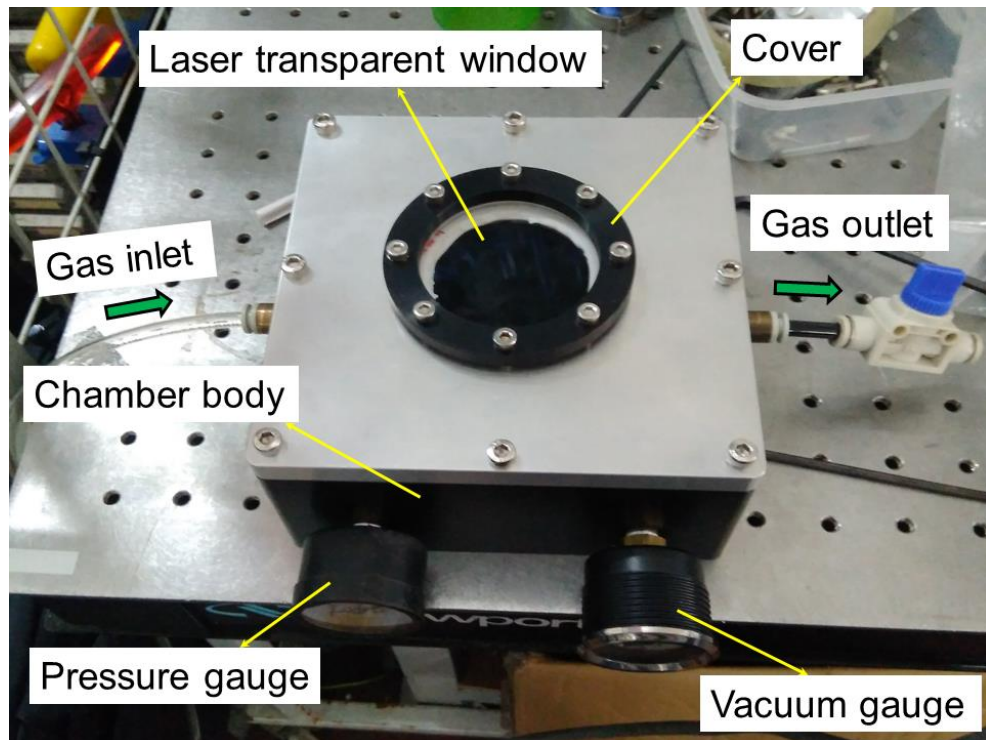


Figure 7.23: Chamber designed for gas assisted laser hardening.

The air inside the chamber must be evacuated first before filling it with the gas. For this purpose, valve V1 is closed and with valve V2 open, the vacuum pump is turned on. The pump sucks all the air out of the chamber. After the vacuum pressure reaches -90 kPa, valve V2 is closed and the pump is turned off. Then, the gas is released from the gas cylinder and valve V1 is opened.

The gas fills the chamber and when the pressure reaches atmospheric pressure, valve V1 is closed. This way, the chamber is filled with the carburizing gas. By controlling the pressure inside the chamber, desired level of gas concentration can be maintained in the chamber. Finally, the laser is turned on which passes through the laser window and heats up the specimen inside the chamber.

The experiments were performed using different laser processing parameters (Appendix B3) to investigate the effect of gas used. For each parameter used, the experiment was repeated at least twice.

7.4.3 Results and Analysis

Figure 7.24 summarizes the effect of various gases on surface hardening of different steels used in this study. The average hardness values of as-received materials are also shown for reference. As expected, the average hardness after laser treatment is higher for all specimens compared to the base material hardness. Furthermore, the hardness of laser treated surface in air and argon gas protection are almost similar for all steels which corroborates the inert nature of argon. The slight difference in the measured values could be due to surface oxidation during laser treatment in air.

Interestingly, a slightly lower average hardness was recorded for laser hardening under CO₂ gas protection. On the other hand, ultra-high hardness was achieved with laser hardening in propane gas. Therefore, the structural changes in laser treated surface under protection of CO₂ and propane were investigated further.

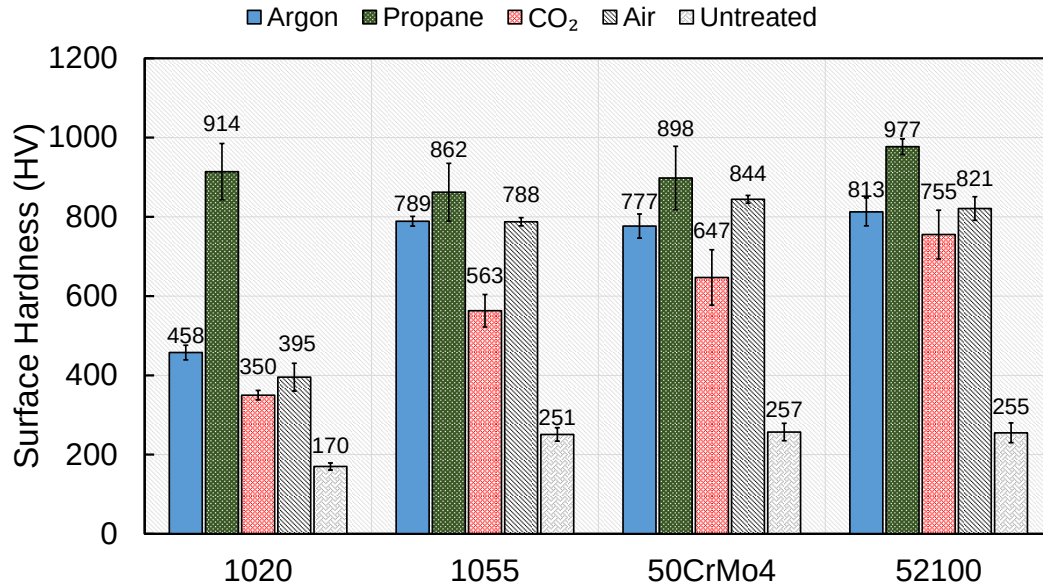


Figure 7.24: Comparison of average surface hardness of various steels treated with different gases.

7.4.3.1 CO₂ gas carburizing

Cross-section metallographic studies were performed to investigate the reason behind lower hardness in specimen treated in CO₂ atmosphere. Figure 7.25 shows a typical microstructure of AISI 1055 steel obtained near the laser treated surface. High magnification electron imaging revealed the top surface to consist of lath martensite up to a depth of about 80 μm . The microstructure gradually changed to mixed and plate martensite in the sub-surface hardened zone due to rapid phase transformation. Lath martensite is associated with lower carbon content in steel which form during rapid quenching process [52]. This indicates the possibility of carbon loss from the surface during laser treatment in CO₂ atmosphere.

Microhardness measurements were made on the cross section to verify the carbon loss. A typical hardness profile along the depth is shown in Figure 7.26. The profile correlated well with the microstructure obtained. The hardness near the surface was about 500 HV, typical of the martensitic hardness achieved by phase transformation of low carbon steels [261]. It increased to about 710 HV at about 100 μm below the surface and gradually decreased to base material hardness due to decreasing effect of laser heating.

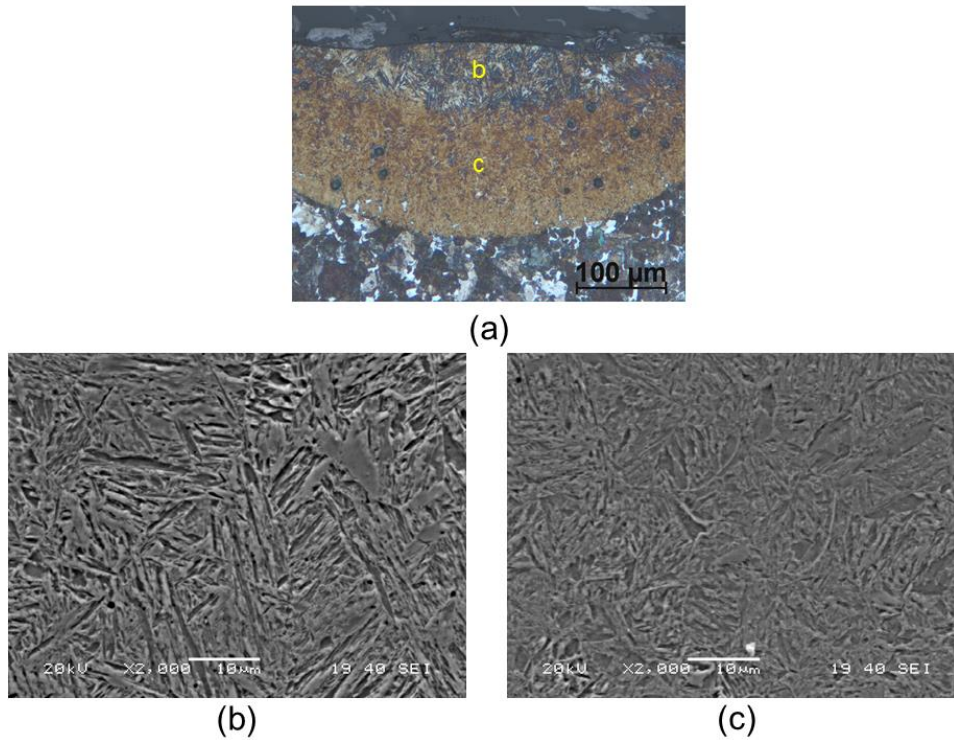


Figure 7.25: Microstructure obtained after laser treatment under CO_2 atmosphere – (a) laser affected area; (b) lath martensite observed near the surface (marked as region b in (a)); and (c) mixed martensitic structure obtained in the laser hardened zone (marked as region c in (a)).

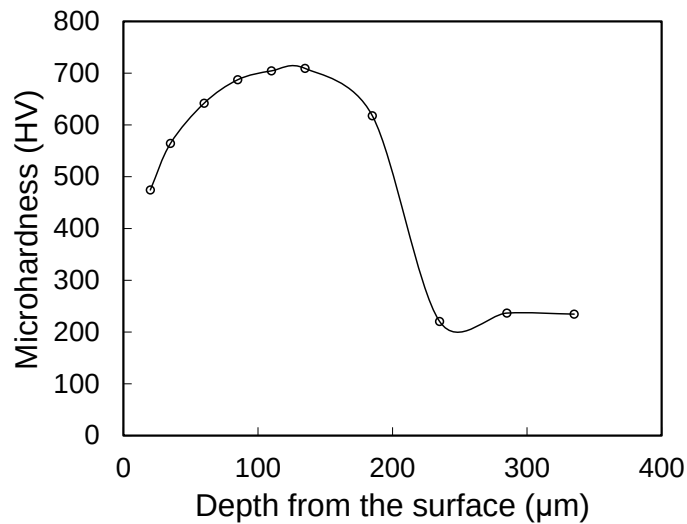


Figure 7.26: Microhardness variation along the depth for specimen treated in CO_2 atmosphere.

The results, thus, suggest the possible decarburization of the surface when laser treated in CO_2 atmosphere. During conventional gas carburization, the

carbon can diffuse in or out of the steel depending on the carbon potential of the atmosphere [262]. Therefore, the gas composition needs to be regularly monitored during the process. The fast heating and cooling during laser treatment in CO₂ atmosphere might induce decarburizing effect [263], which could have led to lower surface hardness.

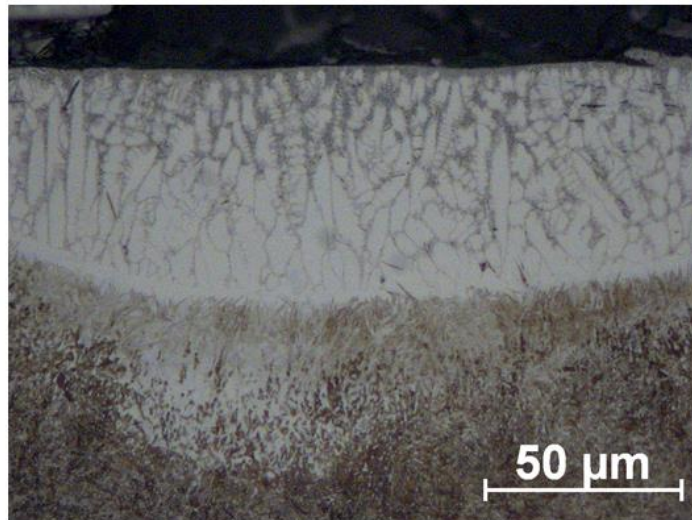
Similar effect was observed for AISI 1020 steel and 50CrMo4 steel with lower hardness near the surface and higher hardness in the sub-surface region. The decrease in hardness was lower for AISI 1020 steel as it already has low initial carbon content. Compared to these steels, AISI 52100 showed very little change in surface hardness even under CO₂ gas protected laser treatment. This is surprising given that this steel has highest carbon content (about 1 wt%). The possible reason could be the presence of other alloying elements which tends to slow down the outward diffusion of carbon during fast laser heating [31,144,264,265].

7.4.3.2 Propane gas carburizing

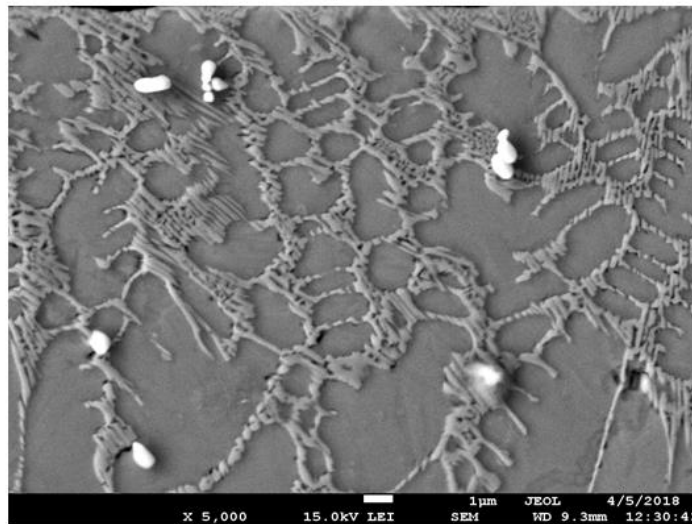
Superior hardness was obtained for all steels treated in propane atmosphere as shown in Figure 7.24. Therefore, the structural changes occurring during propane gas carburizing were analyzed in detail. Corresponding to the similar hardness obtained, all steels showed similar microstructural changes near the surface. Figure 7.27 shows a typical micrograph of laser treated steel in propane atmosphere. Three distinct zones could be clearly observed – a carburized layer (CL) near the surface, an unetched thin white band and a laser hardened zone (LHZ).

The depth of CL varied from 20-100 µm depending on the laser parameters used. For the same parameters, the depth was almost same in all steels. The microstructure observed in this region had cast iron like structure similar to that found in laser treatment with CNT coating (see Figure 7.20). It consisted of transformed ledeburite ($\gamma + \text{Fe}_3\text{C}$) matrix with dendrites of cementite eutectic. Dendrites form due to cooling of the liquid phase during non-equilibrium solidification. Depending on the laser intensity and available carbon at the surface, the microstructure varied along the depth with

hypereutectic structure occurring at the top (for highly carburized specimen) and gradually transforming to eutectic and hypoeutectic microstructure.



(a)



(b)

Figure 7.27: Typical microstructure obtained during propane assisted laser carburizing – (a) carburized layer and hardened zone; and (b) close-up of carburized layer showing eutectic carbides in transformed ledeburite matrix.

A thin lightly etched band existed in the interface between CL and LHZ with large plate martensite just beneath the band. According to the literature, this indicates excessively high carbon potential leading to solid state diffusion of carbon into the matrix [248]. The LHZ was somewhat larger than the CL with maximum depth of up to 250 μm for highest laser intensity used. The LHZ had martensitic structure with microstructure varying gradually along the depth (see Figure 7.28). It consisted of plate martensite near the CL. On further moving away from the surface, a mixed microstructure consisting of martensite, bainite and undissolved carbides formed.

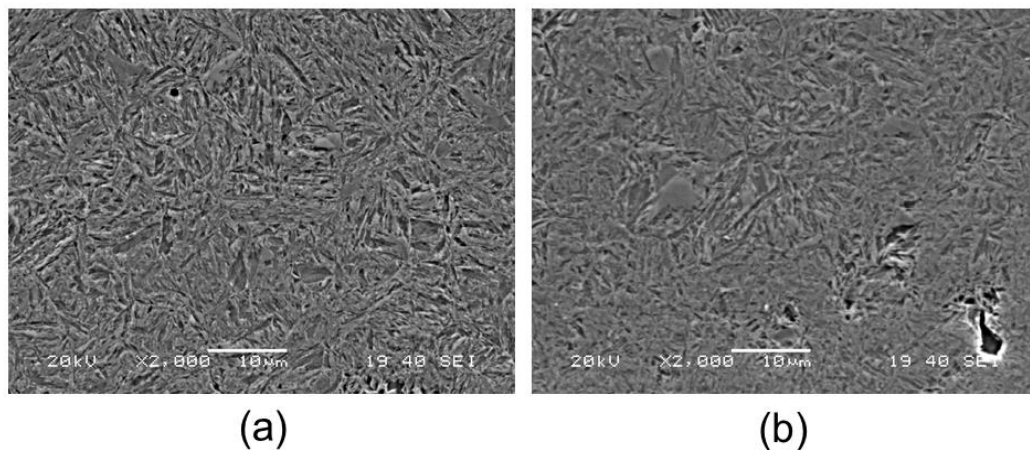


Figure 7.28: Varying microstructure in the laser hardened zone – (a) plate martensite near the CL; and (b) mixed microstructure near the substrate.

The strongly carburized microstructure of remelted layer suggests considerable reaction and influx of carbon into steel surface during laser processing. A heterogeneous microstructure from top to the inside of the surface is because of different carbon concentration, temperature gradients and the non-uniform cooling rates along the depth.

The carbon influx during the process is affected by the amount of carbon available at the surface which could possibly be controlled by altering the concentration of propane in the chamber. Therefore, further studies were carried out by varying the gas concentration in the chamber and the results are shown in Figure 7.29. A fully hypereutectic microstructure was observed for high concentration of propane. The microstructure changed to eutectic and

hypoeutectic structure with lowering of the propane concentration. This indicates the possibility of controlling carburization by controlling the gas concentration in the chamber.

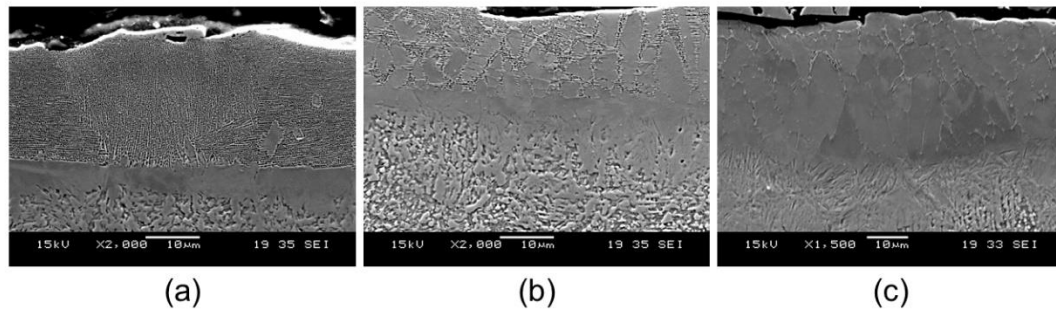


Figure 7.29: Cross section microstructure of carburized layer treated with varying concentration of propane – (a) high concentration; (b) medium concentration; and (c) low concentration.

EBSD was used to identify the new phases formed during the surface carburization. Figure 7.30 shows the EBSD maps of a typical carburized microstructure near the surface. Three different phases were identified – carbides (Fe_3C), austenite (FCC Fe) and martensite (BCT Fe). The top surface basically consisted of austenitic matrix with dendrites of carbides precipitating out. The carbide phases were clustered near the surface and its quantity decreased along the depth.

Random misorientation profiles drawn in the carburized region revealed that the grain misorientation was very small (maximum of about 3°). A typical profile is shown in Figure 7.31(a). This suggests the formation of large austenitic grain during the process. Beneath this heavily carburized region, martensitic phase formed as can be seen in Figure 7.30(c). The martensite phase had fine grains and a typical misorientation profile is shown in Figure 7.31(b). For comparison, the inverse pole figure map of base microstructure is also shown in Figure 7.30(d).

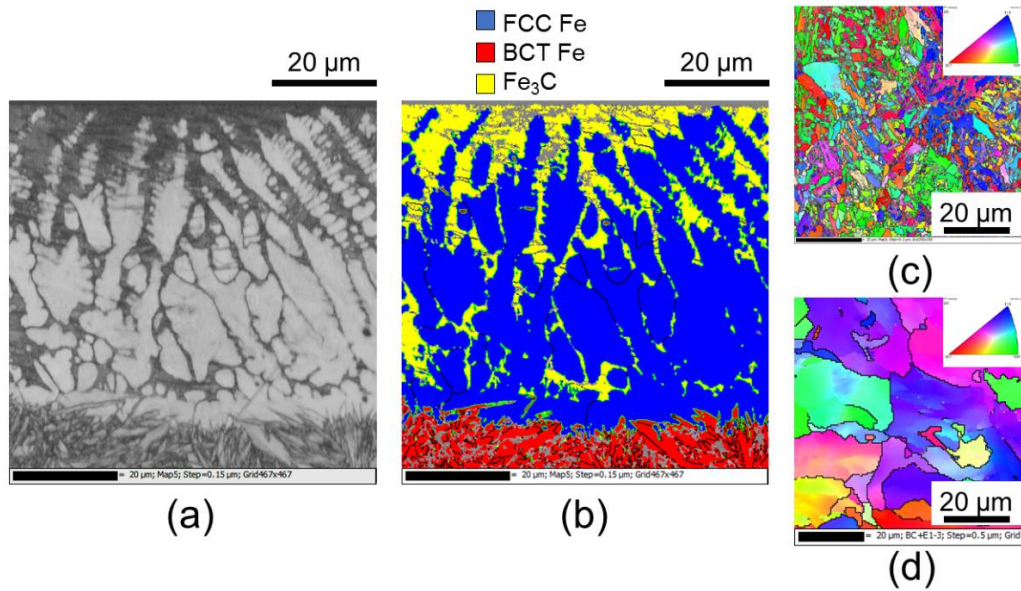


Figure 7.30: EBSD map of the laser treated area – (a) band contrast map; (b) phase map showing FCC (blue), BCT (red) and Fe₃C phase (yellow); (c) inverse pole figure (IPF) map of laser hardened zone; and (d) IPF map of base microstructure.

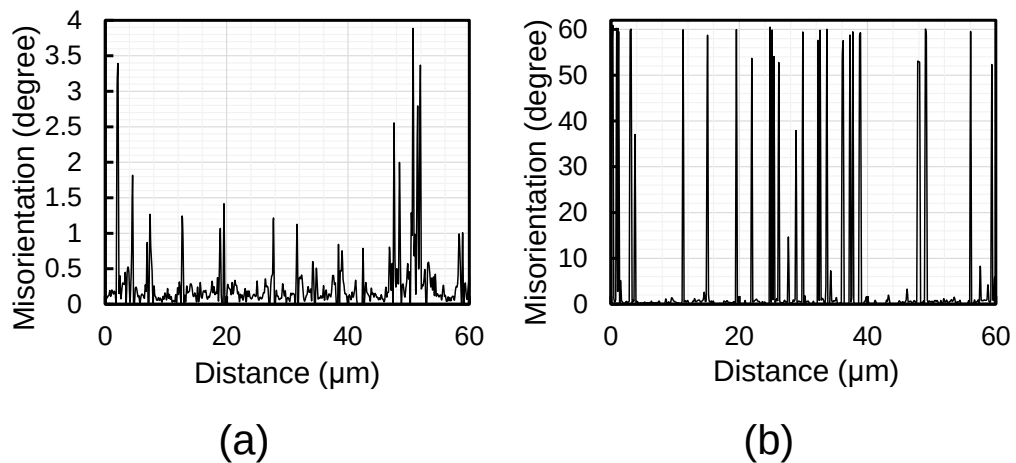


Figure 7.31: Typical misorientation profile along (a) carburized layer; and (b) laser hardened zone.

It is thus, clear that the ultrahigh surface hardness was achieved due to the formation of carburized layer near the surface. The hardness was further studied by making several nanoindents in the cross-section microstructure of the specimen. In order to confine the indent within a particular feature, a small

penetration depth of just 600 nm was used. This produced indents of about 4 μm size. The indents were made on a polished surface and the specimen was later etched with 2% nital to reveal the exact location.

Figure 7.32 shows a series of indentations made on the cross-section microstructure with the corresponding hardness values. The nanohardness values reported are the average values taken within the depth limits of 250 to 550 nm where the hardness was stable. It can be seen that the eutectic structure had very high hardness. The hardness was lower for the austenite matrix while the LHZ also had very high hardness due to presence of martensite in this region.

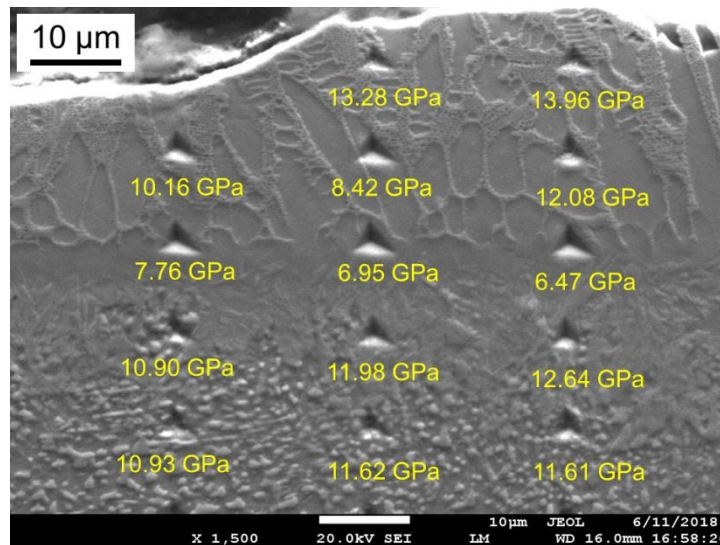


Figure 7.32: Nano-indentations made on the cross-section microstructure of the laser treated steel.

Figure 7.33 summarizes the hardness profile obtained at different concentration of propane. Compared to the hardness in air treated specimen, the hardness was higher in specimens treated in propane gas. Surface hardness as high as 13 GPa was obtained. All the specimens in propane gas showed similar trend with very high hardness near the surface and in the LHZ until gradually decreasing to base microstructure hardness. The hardness in the subsurface region at the depth of about 40 μm plummeted to about 7 GPa corresponding to the formation of austenitic ring in this region.

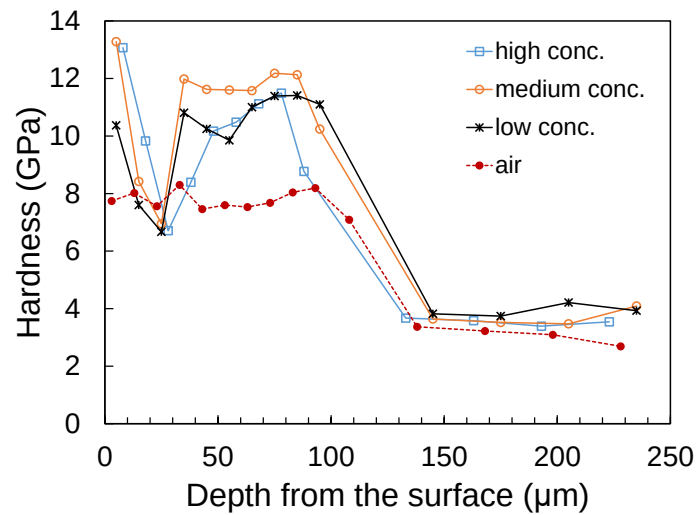


Figure 7.33: Variation of nano-hardness along the depth for samples treated with different concentration of propane. The lower hardness in the sub-surface region corresponding to the lightly etched retained austenite band.

The hardness measurements correlate with the microstructure observed. The higher hardness near the surface is attributed to the formation of eutectic structure due to alloying with carbon. The carbon diffusion decreases with increase in depth. In the CL, the gradient in carbon content in the eutectic causes decrease in hardness with increase in depth. A lower hardness is measured for the unetched band which is due to the change in microstructure from eutectic to eutectoid.

In the LHZ, however, the martensitic transformation leads to high hardness. The hardness of martensite is dictated by the amount of carbon present in original austenite. When the carbon content is too high, some austenite might be retained even during fast cooling. This could be the reason why a slightly lower hardness was observed in the LHZ for high concentration than for medium concentration.

The surface carburization using propane was realized in other steels as well and all of them were found to have a CL at the surface (Figure 7.34). However, the volume of eutectic dendritic morphology was different for different steels

with AISI 1020 steel having large amount of carbide dendrites and AISI 52100 having the least. This can be attributed to the chemical composition of the specimen.

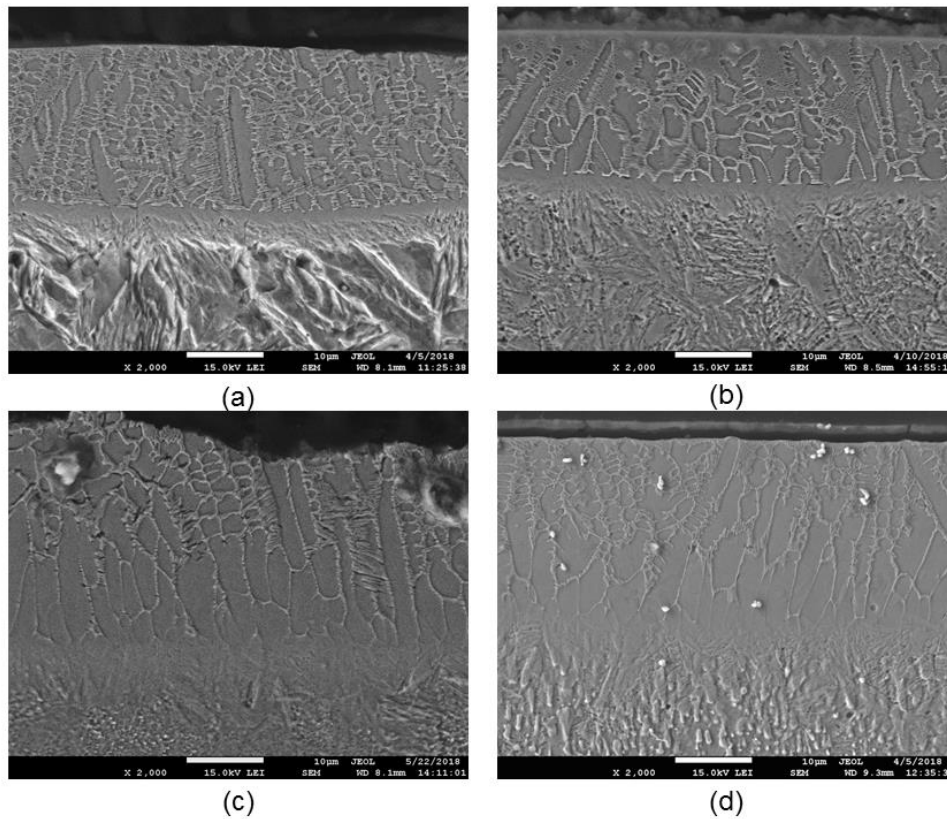


Figure 7.34: Near surface microstructure during propane assisted laser hardening of different steels showing varying volume fraction of eutectic carbides – (a) 1020 steel; (b) 1055 steel; (c) 50CrMo4 steel; and (d) 52100 steel.

Since all the steels were treated under same condition, the carbon potential of the atmosphere must be the same. However, plain carbon steels possess only Fe and C and hence carbon can easily diffuse into the substrate without much barrier. The higher amount of carbon diffusing into the substrate can exceed the eutectic composition (4.3 wt%) and during rapid cooling, excess C precipitates as primary cementite eutectic. The hypereutectic microstructure appearing near the surface of plain carbon steel supports this phenomenon as more carbon diffuses into the substrate from the surface and form larger volume fraction of cementite eutectic.

On the other hand, 50CrMo4 and AISI 52100 steels consists of alloying elements such as Cr and Mn. According to literature, presence of alloying elements increases the energy required for carbon to diffuse into the matrix [266]. Furthermore, higher amount of carbon in the matrix itself reduces the carbon potential difference between the substrate and the carburizing atmosphere. As a result, a lower volume fraction of cementite eutectic is formed on rapid cooling.

7.4.4 Discussion

When the laser is irradiated on a surface, the surface absorbs the beam energy and heats up quickly. The heat from the surface pyrolyzes the surrounding gas resulting in its decomposition. Unlike in conventional gas carburizing, the laser hardening process is very fast with limited time for gas to decompose. In addition, the short dwell time above austenitization temperature provides less time for carbon to diffuse into the substrate. Thus, the possibility of achieving required carbon potential at the surface and the desired carburization depth is a challenge.

The solution could be to use a carburizing gas with significant carbon content which is enough to produce required carbon potential during fast laser beam interaction. Propane fits this requirement very well. Compared to the conventional natural gas used in furnace gas carburizing, the molecules of propane inherently contain a higher C/H atoms ratio, which enables a greater number of carbon atoms to be supplied to the substrate in a short time. Furthermore, Olga et al. [262] reported to achieve an equivalent atmosphere carbon potential using four times lower flow of propane over conventional natural gas enrichment. Therefore, propane provides a low-cost alternative to endothermic carburizing atmospheres with more energy utilization.

Under intense laser heating, propane pyrolyzes to form carbon and methane according the following reaction [267]



The decomposition reaction quickly raises the carbon concentration in the atmosphere. Such high carburizing atmosphere coupled with high temperature of steel surface provides a perfect condition for carbon to react with the surface.

Figure 7.35 shows the schematic of the carbon transfer mechanism during the laser assisted gas carburizing process. It involves three main steps - mass transfer from the gas to the steel surface, reactions at the surface and diffusion of carbon into the steel. The laser heating provides enough carbon at the surface by decomposition of propane. Higher the heating effect of the laser, larger is the carbon potential of the atmosphere. The transfer of carbon from gas to the steel surface is proportional to the difference between carbon potential of the atmosphere (C_p) and the carbon at the surface (C_s).

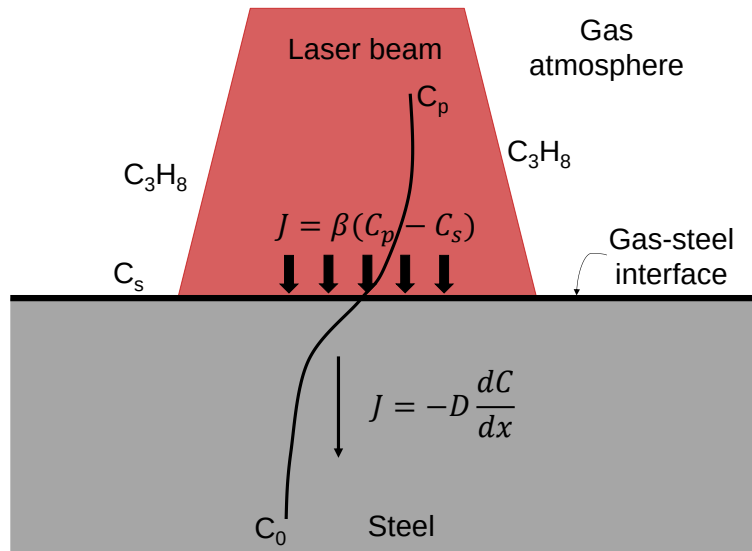


Figure 7.35: Schematic diagram showing the mechanism of carbon diffusion in steel during laser treatment.

By introducing a controlling factor called mass transfer coefficient (β), the flux of carbon uptake (J) by the steel surface can be defined as

$$J = \beta(C_p - C_s) \quad (7.15)$$

Inside the steel, the process is primarily controlled by Fick's law of diffusion, similar to decarburization process as discussed above, albeit in opposite

direction. The coefficient of carbon diffusion in austenite (D) is the controlling factor for carbon diffusion inside steel. The maximum carburizing rate requires the carbon transfer from atmosphere to be equal to or greater than the carbon diffusion rate in steel. Thus, the whole process is diffusion controlled which depends on the laser processing parameters, carbon potential of the atmosphere and the material properties.

The carburization inside the steel occurs either by surface alloying mechanism or by solid state diffusion [248]. The near surface region which melt due to laser heating permits more amount of carbon to be absorbed quickly by surface alloying mechanism [268,269]. As the carbon content in the steel increases, various phases appear on rapid solidification of the melted zone. The maximum equilibrium solubility of carbon in austenite is about 2.14 wt%. The fast uptake of carbon during the carburizing process increases the carbon content in steel to more than this value which results in formation of austenite dendrites and eutectic carbides on solidification. The austenite is retained during solidification due to lowering of M_s temperature caused by carbon [35]. With increasing carbon content, the proportion of eutectic present on solidification increases at the expense of austenite until it becomes fully eutectic at ~4.3 wt%. At even higher laser power density, the carbon content exceeds the eutectic composition leading to the formation of hypereutectic structures as shown in Figure 7.36.

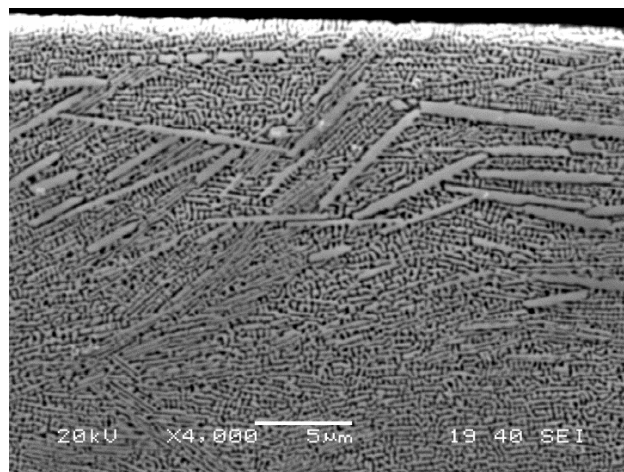


Figure 7.36: Near surface hypereutectic microstructure obtained under higher laser power density.

The eutectic phase increases the bulk hardness of the microstructure by virtue of their own very high hardness and their substantial volume fraction [255]. That's why the hardness in the solidified microstructure decreases gradually along the depth with decreasing proportion of eutectic in the matrix as observed in Figure 7.27 and Figure 7.34. The hardness reaches lowest value in the light unetched region which is identified as the ring of retained austenite (see Figure 7.37). The carbon content in this zone was high enough to stop complete martensite transformation on rapid solidification and forms retained austenite. The hardness in this region is still higher than the base microstructure due to formation of fine microstructure.

The retained austenite band forms due to planar solidification. The constitutional segregation must not occur for planar solidification front to be present. This is expressed as

$$\frac{G}{R} \geq \frac{mC_0}{D} \left(\frac{1 - k_0}{k_0} \right) \quad (7.16)$$

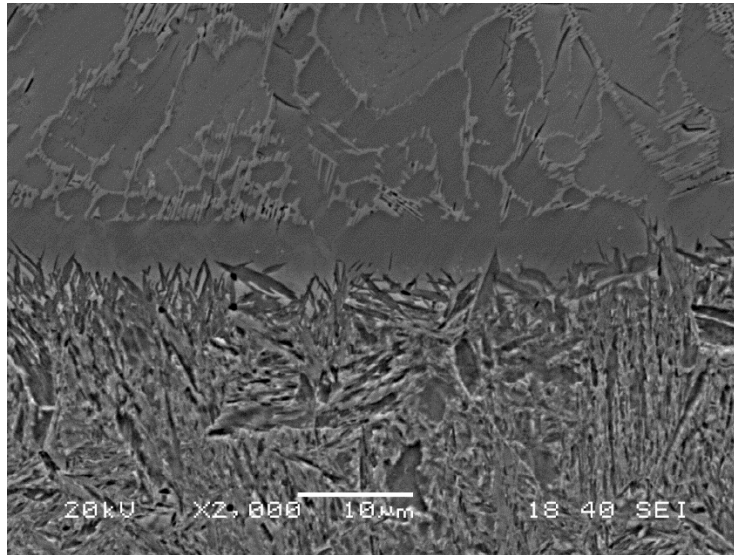


Figure 7.37: Micrograph showing the unetched boundary between the carburized layer and the hardened zone. The carburized layer shows the eutectic carbides while plate martensite can be seen in the hardened zone.

where G is the temperature gradient in the liquid, R is the velocity of the solid/liquid interface (solidification rate), m is the slope of the liquidus, C_0 is the initial solute concentration, D is the diffusivity of carbon in liquid steel and k_0 is the ratio of the solute concentration in the solid to solute concentration in the liquid.

The influence of G and R on solidification morphology is illustrated in Figure 7.38. Laser surface processing produces melted region that solidifies at different G/R ratios, hence producing different solidification morphology. At the bottom and sides of the melt zone, extremely high values of G/R can occur. As the laser beam moves away, melting immediately stops, but freezing does not start instantaneously. Thus, solidification rate becomes almost zero for a very short time making G/R almost infinite. As a result, the planar solidification forms a featureless ring of austenite between the fusion zone and the hardened zone.

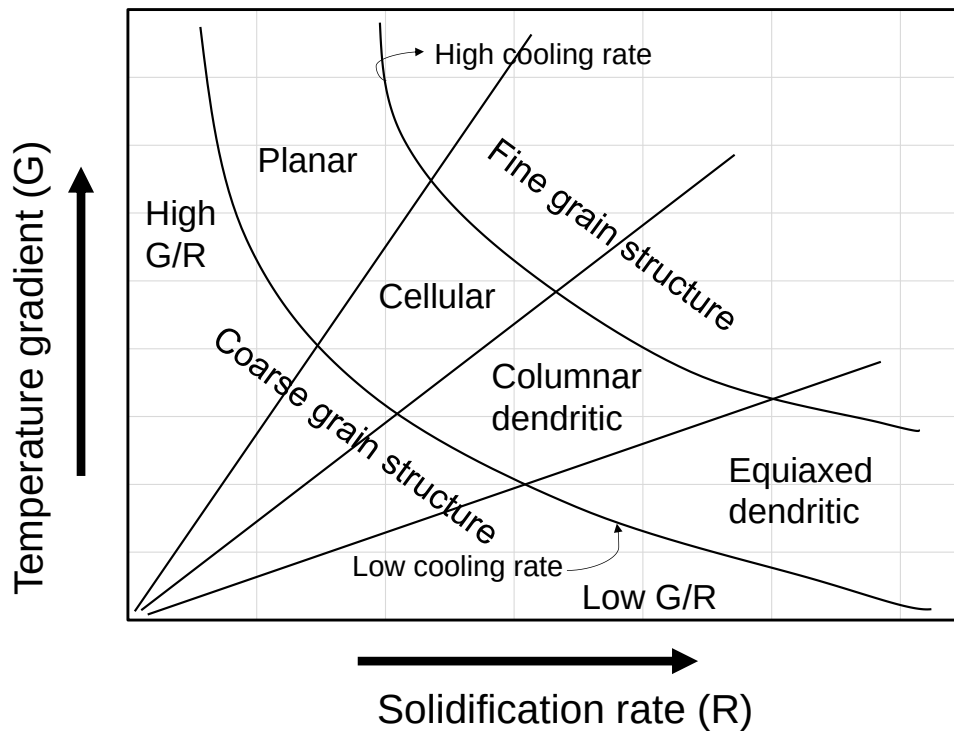


Figure 7.38: Diagram showing the influence of temperature gradient and the solidification rate on mode of solidification and grain size [270].

According to Coriell and Sekerka, the planar solid front morphology will stabilize when

$$\frac{G}{R} \geq \frac{\Delta T_0}{D} \quad (7.17)$$

where, ΔT_0 is the temperature interval between liquidus and solidus.

The ratio on the right of equation (7.17) was calculated assuming the values of ΔT_0 and D to be 391 K and 10^{-2} mm²/s respectively and found to be 39100 Ks/mm². The approximate value of G/R can be obtained by considering a simplified geometry of the fusion pool during laser heating as shown in Figure 7.39. The average temperature gradient, G is assumed as the ratio of difference between boiling point (assumed to reach at the top of melt zone) and solidus temperature (at the bottom of the melt zone) to the depth of melt zone. For conduction limited melt zones, the width of melt pool can be considered same as the laser beam diameter [271]. The average solidification rate, R , for the entire fusion pool is then approximated as the rate of change of melt pool depth given simply by the ratio of melt pool depth and the freezing time.

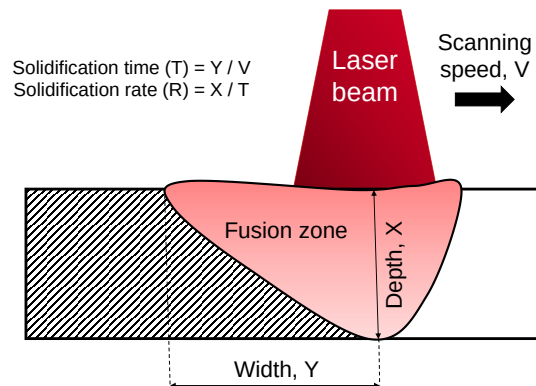


Figure 7.39: Schematic diagram showing simplified model for determining average solidification rate.

From above approximation, the value of G/R was found to be 13720 Ks/mm^2 which is smaller than $\Delta T_0/D$ value obtained above. This implies that planar morphology does not stabilize in the solidified region and cellular and dendritic grow appears.

This is also supported by equation (7.16) which states the lower probability of planar solidification front being stable as carbon content increases. As discussed above, the carbon content gradually increases from the bottom of the melt zone towards the surface. Thus, cellular and dendritic morphology starts appearing in these regions. At the melt zone center near the surface, the solidification rate is very fast and temperature gradient is small. This favors the formation of equiaxed dendritic morphology as observed in our results.

The presence of austenite ring in the microstructure indicates the maximum carbon content to be about 2.14 wt% in the bottom of carburized layer. Just beneath the austenite ring, plate martensitic layer appeared. The high hardness of this martensite suggests carbon enrichment. The carburization mechanism is different in this case than surface alloying as it involves austenitization of the substrate and solid-state diffusion of carbon in austenite. Despite the short heating time imposed by the laser beam, the carbon can still penetrate through the austenite.

However, it is to be noted that the carbon content in this zone must be lower than 2.14 wt% and should decrease with distance from the surface. The process is dictated by diffusion and is just reverse of the decarburization process described in Section 7.2.3. The solid-state carbon diffusion has also been verified by Katsamas and Heidemenopoulos using simple one-dimensional kinematic simulations [248]. However, compared to shallow carburizing depth predicted by their model, a large carburized depth up to 100 μm were achieved in our experiments as seen from high hardness measured in gas carburized samples. Further kinematic modelling is recommended to optimize the process and identify appropriate process conditions to achieve desired carburization depths.

Although cracking during propane assisted hardening was not severe as in surface coated specimen, some cracks still formed in the hardened surface. A typical cracking across the structure is shown in Figure 7.40(a). The cracks predominantly appeared at the hypereutectic structure. The reason was attributed to the thermal stresses induced during the solidification [272].

When the carburized layer solidifies, the surface and sub-surface layers contract at different rates. Compared to the surface, the interior cools faster due to lower heating rate and rapid heat dissipation to the bulk. The difference in cooling rate results in tensile stresses near the surface. Owing to the low yield strength at high temperature, plastic flow of the material counterbalances the tensile stress. When the tensile strain exceeds the fracture strain of the surface microstructure, cracking starts. The carbide lamellae subjected to high tensile strain are thus vulnerable to cracking due to their lower fracture strain. The effect becomes more pronounced when the higher amount of carbon enters the steel.

Some cracks existed in the martensitic phase as well (see Figure 7.40(b)). These cracks generally appeared when the laser parameters were controlled such that it produced martensitic phase at the surface with no eutectic phases. In contrast to straight cracks in hypereutectic structure, the cracks in martensite were zigzag.

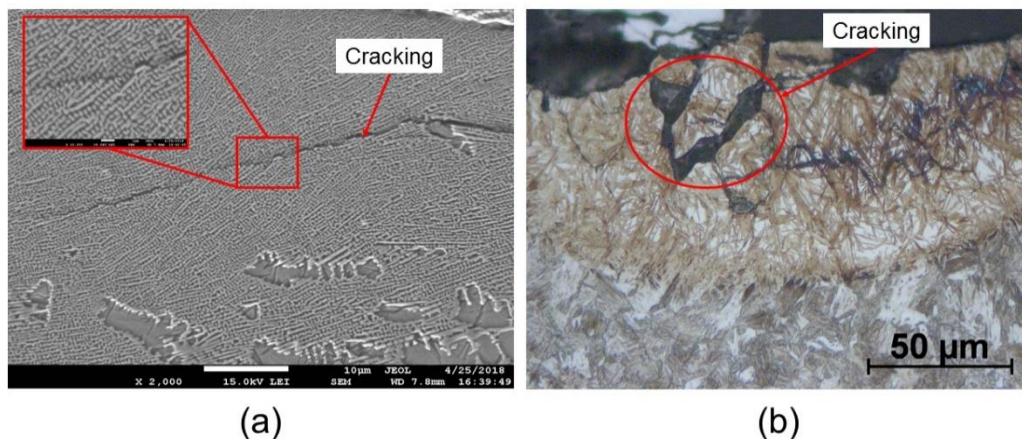


Figure 7.40: (a) Eutectic microstructure near the surface with straight line cracking; and (b) Cracking in martensite region.

These cracks might have originated due to presence of diffusional hydrogen in steel. The hydrogen from propane gas can diffuse into the steel during austenitization owing to the high solubility of hydrogen in austenite. On the other hand, the low diffusion rate of hydrogen in austenite renders the atom immobile making austenite as an effective trap [273]. However, the transformation of austenite to brittle martensite releases the hydrogen atoms which gradually recombine inside steel to form hydrogen molecules, creating internal pressure and cracking.

In this sense, the microstructure with austenite and eutectic carbides seem to be most suitable. The processing parameters should be optimized to achieve such microstructure with crack free structure and high hardness. Moreover, the ingress of hydrogen at the laser heated surface can be minimized by using a controlled flow of gas and preheating the specimen prior to the treatment although further studies are required to verify its effectiveness.

7.5 Summary

This chapter investigated various methods to improve the effectivity of laser surface hardening process. The feasibility of using water, graphite coating, carbon nanotubes (CNTs) coating and various gases are explored with an aim to achieve superior surface properties of steel during laser surface processing. The main conclusions are summarized below:

1. Underwater laser hardening studies showed that water can increase surface hardness, but reduces the area of hardened zone. The surface hardening effect is virtually absent for a thick water layer thickness (>5 mm) above the metal surface. The thick layer attenuates the laser energy arriving at the surface due to shielding effect by water vapor plasma. A significantly smaller hardened area with superior surface hardness is obtained for a thin water layer thickness (1 mm) than those of conventional laser hardening. The higher hardness is attributed to the water acts as cooling agent and produces higher cooling rate during the process.

2. Despite the fast heating during laser surface treatment, decarburization can occur in steel surface. Depending on the time and temperature of the laser interaction with the surface, the affected depth can reach up to 65 μm and can go even higher.
3. Graphite coating can prevent surface decarburization and in addition, improve laser beam absorption at the surface. However, the non-uniformity of the coating layer compounded by a massive carbon influx into the substrate often produce excessive surface melting, cracking and porosity. Use of carbon nanotubes as surface coating improves the surface quality in terms of crack prevention and carburization, but the challenge still lies in applying a uniform coat on the surface.
4. A one-step gas assisted laser surface hardening can be the best solution to have a controllable hardening process. A special chamber with a laser window was fabricated to study the gas assisted laser hardening process. Preliminary investigations with different gases revealed that propane can produce an ultrahigh surface hardness. Hardness as high as 900 HV was obtained even for low carbon AISI 1020 steel. Further investigations found that propane produces a carburized surface layer due to diffusion of carbon into the surface during laser heating. The carburized layer consisted of eutectic carbides and austenite matrix. The surface microstructure and properties can be modulated by carefully controlling the operating parameters.

Chapter 8: Conclusions and Recommendations

This chapter presents a summary of major findings in this thesis, the significance of the results obtained and finally, suggests some recommendations for future work.

8.1 Summary and conclusions

Laser surface hardening carries immense potential for industrial application as a selective hardening tool to improve the mechanical properties of surface of machine components such as bearings, gears and camshafts. This thesis investigated various aspects of laser surface hardening of bearing steels with an aim to elaborate the underlying mechanism and improve surface properties. The main findings from the study are summarized below.

First, the fundamental understanding of surface hardening and the microstructural changes in hardened steel was elucidated by performing laser hardening using continuous wave fiber laser. The laser treatment produced a hard outer case owing to the martensitic transformation due to rapid heating and cooling while virtually leaving the bulk material unaffected. Maximum hardness as high as 844 HV was achieved for 50CrMo4 steel near the surface with the depth of hardening depending on the operating parameters used. Table 8.1 shows the maximum hardness achieved for each steels used in this study and the respective hardness of their base material. The high hardness achieved was attributed to the combined effect of various hardening mechanisms including dislocation hardening, solid solution strengthening, grain boundary hardening and precipitation hardening. A gradient microstructure developed along the depth due to different heating and cooling rate. It was found that the size of the laser affected zone depends on the austenitization temperature reached and the distribution of carbon content in the austenitic matrix.

Table 8.1: Summary of hardness values measured for different steels after laser hardening using CW laser beam.

Steel	Maximum hardness (HV)	Base material hardness (HV)
AISI 1020	395 ± 35	170 ± 9
AISI 1055	788 ± 10	251 ± 17
AISI 4150 (50CrMo4)	844 ± 10	257 ± 22
AISI 52100	821 ± 30	255 ± 25

After scrutinizing the response of steel to fast laser heating, further studies were carried out to investigate the influence of operating parameters. Beam spot size affected the hardened depth and width; however, the maximum hardness at the center of the beam spot did not change. Similarly, a large laser hardened area was obtained for slow process speed and high power. The laser power had lower effect on hardness than the process speed given that it was sufficient to ensure heating to austenitization temperature. Further increase in power resulted in surface melting and distortion. Moreover, presence of oxide layer on the surface improved the surface absorptivity to laser which increased the laser affected volume, however the surface hardness might decrease due to the possibility of decarburization. Overlapping of hardened tracks was found to produce a tempered microstructure in the overlap zone which had lower hardness than the hardened structure. The parametric study, thus provided a foundation for understanding the individual effects of various operating parameters which can be a significant input for designing the laser hardening system for real industrial application.

The feasibility of hardening using pulsed lasers was also explored. Under proper condition, millisecond laser could produce a peak surface hardness and hardening depth of same magnitude as continuous wave laser using about 9 times lower power than continuous wave laser. Similarly, nanosecond laser produced very shallow hardening depth (about 50 – 80 μm) due to insufficient heating by short pulses. Further attempts were made to exploit the

femtosecond laser ablation for surface cleaning and damage layer removal. The ablation threshold of bearing steel was determined first and calculated to be 0.142 J/cm^2 . By operating the femtosecond laser at fluence value slightly above the ablation threshold, the damaged surface layer was effectively removed.

Corrosion behavior of laser hardened surface is an important factor determining its suitability in real application. While lots of studies can be found on corrosion studies of laser hardened surface, no attention is paid to the corrosion properties of gradient microstructure produced by laser heating which might be exposed to the corrosive atmosphere during post-laser finishing treatment or operational hazards. The layer-by-layer electrochemical corrosion studies using 3.5% NaCl solution revealed that the laser treated surface had very good corrosion resistance while it dropped drastically after removal of the top surface layer. The improved corrosion resistance at the surface was attributed to the formation of Cr-enriched oxide layer and phase transformation due to laser treatment. Removal of this protective layer and formation of tempered martensite resulted in lower corrosion resistance at sub-surface layer. Furthermore, grain refinement was found to have negligible effect on improving corrosion resistance of steel.

In the next step, new methods were explored to improve the effectivity of the hardening process. On identifying the significance of surface absorptivity and cooling rate, feasibility of using water as surface absorbent was examined. It was soon realized that a thick layer of water over the surface produced a shielding effect and absorbed most of the incident laser energy. This resulted in shallow hardening depth and width. The study indicated the possibility of improving surface hardness due to additional rapid quenching by water, but care must be taken to minimize the attenuation of laser energy by water layer.

Further investigations were made using graphite as surface coating to achieve superior surface properties by laser surface processing. The graphite coating had two-fold benefits – it prevented surface decarburization and improved laser beam absorption at the surface. However, the difficulty in applying a

uniform coating layer compounded by a massive carbon influx into the substrate due to heating from laser resulted in excessive surface melting, cracking and pores in the steel. In an attempt to control the carburization, carbon nanotubes (CNTs) were utilized as surface coatings as it had finer structure and could produce more uniform thickness than graphite coating. This resulted in a uniform carburized layer near the surfaces. However, the CNT coatings did not adhere to the substrate and might be blown away during the processing.

Using gas as a carburizing source provided better controllability than using a solid coating. In this sense, gas assisted laser hardening seemed to be the best method to improve effectivity of laser surface treatment. A special chamber was designed to perform the experiments which provided a better control of gas flow and concentration. The chamber had gauges to monitor the pressure inside the chamber and a laser window for laser beam to pass inside the chamber. Initially, different gases such as argon, CO₂ and propane were utilized to study their effects on surface hardness. It was found that argon did not bring any significant change in surface hardness while CO₂ had an inverse effect with slight reduction in surface hardness. The reduction in surface hardness under CO₂ was attributed to the decarburizing effect of the gas.

Propane gas produced an ultra-high hardness for all steel samples with hardness reaching as high as 900 HV. The high hardness resulted from the formation of a carburized layer near the surface due to the influx of carbon during laser heating. Further analysis of the carburized region showed that it consisted of eutectic carbides, transformed ledeburite and retained austenite. An unetched band appeared between the heavily carburized region and the hardened region which was identified as retained austenite. The hardened zone beneath the carburized layer also recorded high hardness values owing to the solid-state diffusion of carbon into the matrix. The diffusion of carbon into the steel and the corresponding microstructure obtained was found to vary with change in concentration of propane in the chamber. Therefore, it was

concluded that the surface microstructure can be modulated by controlling the operating parameters and the gas concentration.

8.2 Major contributions

1. Better understanding of the microstructural changes and mechanism of hardening

The non-equilibrium microstructural changes occurring during fast laser heating was studied by microstructural analysis and analytical modelling. The study helped to further enrich our knowledge on basic understanding of the theory which can pave way to optimize the process.

2. Corrosion studies of laser hardened gradient microstructure

The sub-surface of hardened component might be exposed to corrosive atmosphere during operation due to unintentional scratching or due to post-laser finishing operations. However, little attention is paid in literature regarding the corrosion properties of sub-surface layer. The current study carried out a systematic layer-by-layer corrosion study of laser hardened microstructure by successive removal of material. It was found that the surface had better corrosion resistance than the sub-surface layer while grain refinement had very negligible effect on corrosion resistance. The knowledge can be useful in developing innovative methods to produce a dense passivating oxide layer on the surface during the hardening process.

3. Gas-assisted laser hardening

Although graphite is widely used as surface coating to absorb more laser energy, the excessive influx of carbon and non-uniform coat layer results in embrittlement and deterioration of steel surface. Our studies on gas-assisted laser hardening exhibited the possibility of utilizing a gas to achieve superior hardness on the surface with much better controllability. An inhouse designed chamber was used for this purpose which allows the control of gas pressure

and the flow rate. By careful control of the gas concentration and the operating parameters, the method can be applied in industries for hardening of steels that cannot be hardened by any other techniques. Furthermore, the gas assisted laser processing opens new opportunities to employ novel laser alloying technique to modify the surface properties.

4. Application of ultrashort laser pulse ablation for surface cleaning

The study of surface treatment using ultrashort pulse laser revealed the ablation effect which can be beneficial for surface cleaning applications. The method can be useful for cleaning in remanufacturing and repair process. In addition, the smooth surface morphology produced by the ablation can be beneficial for wettability, tribology and other surface engineering applications.

8.3 Recommendations for future work

The research explored the basic mechanism during laser hardening and material response during the process. It also exhibited the new methods of improving surface hardening by using gas. The research can be further expanded in following directions.

1. Overlapping studies

Generally, the component to be hardened is larger in size than the size of the laser beam. Thus, multiple scan tracks are used to harden the whole surface. However, the overlapping during multi-track hardening results in tempering of the previously hardened track, producing a non-uniform hardness profile and case depths. The problem becomes even more complicated for components with complex geometry like bolt or camshaft. Therefore, the hardening process needs to be modified to address these issues. One method could be to adjust beam spot size according to the geometry of the component using automation and machine programming. The numerical modelling can be carried out to optimize the laser processing path with an aim to achieve uniform hardened surface. Further studies are recommended in this direction.

On the other hand, the non-uniform hardness produced during overlap scanning might be beneficial for some specific applications (like tribology) where a combination of both load bearing capacity and material toughness is required at the surface (see Figure 8.1). Preliminary studies have shown that the change in hardness can be modulated by the extent of overlapping of the scan tracks [274]. Thus, it is possible to achieve the surface with series of hard and soft tracks. The hardened wear resistant tracks can retain the load bearing capacity of the surface while the softened tracks might be removed during operating creating pockets for storage of lubricant or trapping contaminant. Further investigations can be pursued in this direction to generate engineering value out of this challenge.

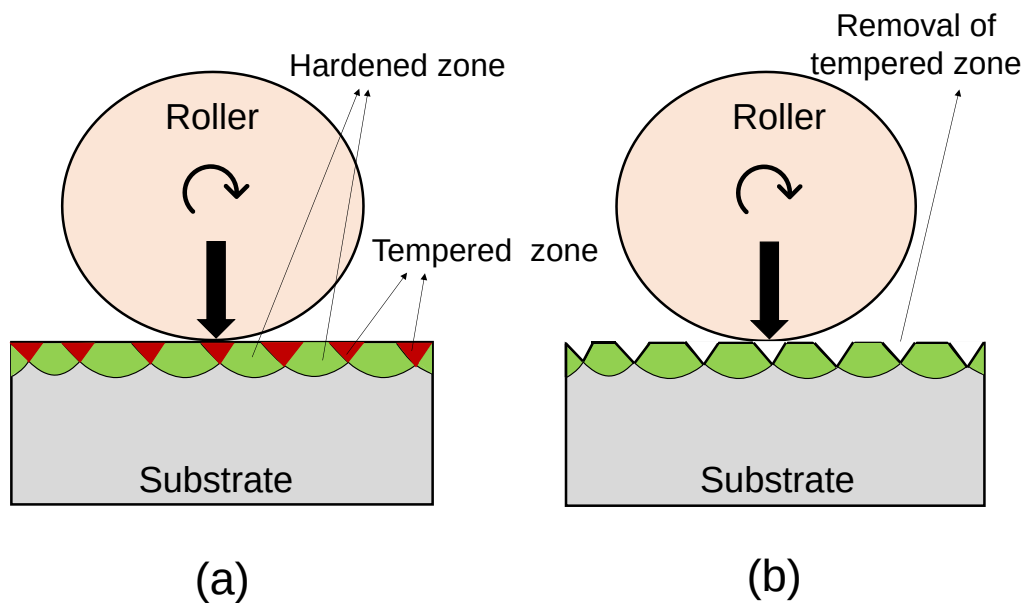


Figure 8.1: Illustration showing the potential application of non-uniform surface hardness produced by overlapping scan tracks – (a) initial condition; and (b) after wear-in period.

2. Gas-assisted laser carburizing

The current study established the mechanism of gas assisted laser hardening mechanism and exhibited its controllability. As pointed out, depending on the

amount of carbon diffused into the steel, different microstructure can be obtained. The next step could be to optimize the process parameters to achieve the desired microstructure and hardness at the surface.

There are also some challenges to be addressed. With fast laser heating, the controlling can become more complicated as long-time operation of the laser can result in higher residual methane in the chamber which has tendency to form graphite precipitates by sooting [262]. Moreover, the presence of hydrogen in the chamber may induce hydrogen assisted cracking on the steel as hydrogen can be introduced into steel during laser treatment [275]. The problem might be solved by using proper gas flow rate to purge out residual methane or by supplying some other purge gas into the chamber. A detailed investigation can be performed to have a clear understanding of the phenomenon. Furthermore, different types of gases and steels can be studied using the designed chamber to further understand the underlying physics.

3. Laser cleaning based on ablation

The ablation studies of ultrashort pulse lasers showed the potential of using short pulsed lasers to control the material removal and achieve the surface with desired properties. However, the real application will still require further parametric study and deeper understanding of the process. This can be further explored.

Appendix A: List of common terminologies

Ablation - direct removal of material at the surface by laser beam

Beam spot size – diameter of the beam spot at the surface of the specimen

Bead overlap – percentage of overlapping of melted spot at the surface formed due to rapid heating by single laser pulse

Carburization – process of introducing carbon to the steel surface from external atmosphere

Corrosion – process of eroding of material from the surface by chemical reaction during exposure to electrochemically reactive atmosphere

Decarburization – process of removal of carbon from the steel surface

Defocus position – out of focus plane perpendicular to the beam travel direction during laser experiments

Energy density - measurement of energy per unit area of spot size, usually expressed as Joules per square centimeter (J/cm^2) or Joules per square millimeter (J/mm^2); also known as fluence (especially for pulsed lasers)

Laser – a device that generates an intense beam of coherent monochromatic light by stimulated emission of photons from excited atoms or molecules; unless otherwise indicated by the context, the term “laser” and “laser beam” has been used interchangeably in the text.

Laser affected depth – maximum depth in the cross-section of laser-hardened surface (along the center spot of laser beam) observed after etching the specimen with 2% nital solution

Laser affected width – length of the hardened track formed at the surface by laser beam irradiation

Laser surface hardening / laser hardening – surface heat treatment process in which a laser beam rapidly heats and cools a metal surface forming a hard surface layer; can occur with or without melting of the surface

Laser transformation hardening – surface heat treatment process in which a laser beam heats the surface of a metal and then let it cool down rapidly in surrounding air forming a hard surface without any melting of the surface

Melting – process of becoming liquefied by heating; generally avoided in laser transformation hardening

Peak power - highest power in each pulse (for pulsed laser only)

Power density - measurement of power per unit area of spot size, usually expressed as Watts per square centimeter (W/cm^2) or Watts per square millimeters (W/mm^2); also known as intensity, irradiance, and radiance

Process speed – rate of change of distance travelled by the laser beam during hardening process; expressed as millimeter per second (mm/s)

Pulse duration – total amount of time that a pulse is emitted (for pulsed laser only); also known as pulse width

Remelted layer – a thin layer of the surface that melted during heating by laser beam and solidified later after laser beam moved away

Repetition rate – number of pulses per second; expressed in Hertz (Hz); also called as frequency

Ripples – undulating feature at the surface with repetitive periodic pattern

Appendix B: Laser processing parameters

B1. Operating parameters in hardening of 50CrMo4 steel (Chapter 4)

Laser system: YLR-150/1500-QCW (IPG Photonics)

Material : 50CrMo4 steel

Operated in continuous wave mode and single line tracks of 10 mm length drawn on specimen surface

Experiment 1: Varying defocus distance

S.N.	Power (W)	Speed (mm/s)	Defocus (mm)
1	230	10	0
2			2
3			4
4			6
5			8
6			10
7			12
8			14
9			16
10			18
11			20

Experiment 2: Speed and power variation

S.N.	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	230	0.5	10	Specimen 1 used for detailed metallographic analyses
2			25	
3			50	
4			75	
5			100	
6	200	0.5	10	
7			25	
8			50	
9			75	
10			100	
11	150	0.5	10	
12			25	
13			50	
14			75	
15			100	

Experiment 3: Different surface condition

S.N.	Surface condition	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	Surface polished to P1200 grit finish	230	0.5	10	Specimen 1 and 6 used for detailed metallography and hardness analyses
2				25	
3				50	
4				75	
5				100	
6	Surface oxidized by heating at high temperature in air	230	0.5	10	
7				25	
8				50	
9				75	
10				100	

Experiment 4: Overlap studies

S.N.	Power (W)	Speed (mm/s)	Spot size (mm)	Overlap (%)	Remarks
1	230	10	0.5	0	
2				33.33	
3				66.66	

Experiment 5: Initial microstructure

S.N.	Initial condition	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	As-received	230	0.5	10	Specimens 1, 6 and 11 used for detailed metallography and hardness analyses
2				25	
3				50	
4				75	
5				100	
6	Normalized	230	0.5	10	
7				25	
8				50	
9				75	
10				100	
11	Water-quenched	230	0.5	10	
12				25	
13				50	
14				75	
15				100	

B2: Experiments conditions used in different pulsed lasers (Chapter 5)

Experiment 1: Millisecond laser

Laser system: YLR-150/1500-QCW (operated in pulsed mode)

Material : AISI 1055 steel

Single line tracks drawn on the specimen surface

S. N.	Pulse duration (ms)	Pulse energy (J)	Average power (W)	Speed (mm/s)	Spot size (mm)	Frequency (Hz)
1	10	15.00	150.0	2	0.5	10
2	10	12.40	12.4	2		
3	10	9.30	93.0	2		
4	10	6.00	60.0	2		
5	10	2.70	27.0	2		
6	10	1.07	10.7	2		
7	10	2.70	27.0	0.5		
8	10	2.70	27.0	1		
9	10	2.70	27.0	5		
10	5	1.35	13.5	2		
12	15	4.05	40.5	2		
13	20	5.40	54.0	2		

Experiment 2: Nanosecond laser

Laser system : Nd:YAG pulsed laser system

Wavelength : 1.06 μm

Pulse duration : 220 ns

Frequency : 500 kHz

Beam spot : 120 μm

Material : 50CrMo4 steel

Appendix B: Laser processing parameters

S. N.	Average power (W)	Process speed (mm/s)	Spot size (μm)	Overlap rate (%)	Power density (W/cm^2)
1	30	200	120	50	2.65×10^5
2	60	200	120	50	5.31×10^5
3	90	200	120	50	7.96×10^5

Experiment 3: Femtosecond laser

Laser system : Quantronix Integra C-1.0

Wavelength : 790 nm

Pulse duration : 130 fs

Frequency : 1 kHz

Beam spot : 26.48 μm

Material : AISI 52100 steel

Surface treated using 5,10,50,100 and 500 laser shots for different pulse energies as shown below

S.N.	Pulse Energy (μJ)	Peak fluence (J/cm^2)	Remarks
1	3.10	0.281453	
2	3.50	0.317769	
3	4.70	0.426719	
5	6.80	0.617381	
6	9.30	0.844359	
7	13.70	1.243841	
8	19.00	1.725034	
9	22.50	2.042804	
10	46.00	4.176399	
12	53.50	4.857334	
13	94.00	8.534381	

B3: Experimental conditions used for different treatments (Chapter 7)

Experiment 1: Underwater laser treatments

Laser system: YLR-150/1500-QCW

Wavelength : 1.07 μm

Material : AISI 52100

Single line tracks drawn at varying speed and power

Trials 1: Water layer thickness varied

S.N.	Power (W)	Speed (mm/s)	Spot size (mm)	Water layer thickness (mm)	Remarks
1	250	100	0.5	0	Ar protection
2				1	
3				3	
4				5	

Trials 2: Speed variation with 1 mm water layer

S.N.	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	250	0.5	10	Specimen 1 and 5 used for surface and microstructure analyses
2			25	
3			50	
4			75	
5			100	

Trials 3: Speed variation with argon gas protection

S.N.	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	250	0.5	10	
2			25	
3			50	
4			75	
5			100	

Experiment 2: Graphite as surface coating

Laser system: YLR-150/1500-QCW

Material : AISI 52100

Aerosol of graphite particles (3-50 μm) and alcohol manually sprayed on the surface

Single line track of 10 mm length drawn on the surface in open atmosphere

S.N.	Power (W)	Spot size (mm)	Speed (mm/s)	Remarks
1	250	0.5	10	Specimen 1 used for detailed analyses
2			25	
3			50	
4			75	
5			100	

Experiment 3: Carbon nanotubes as surface coating

Laser system: YLR-150/1500-QCW

Material : AISI 52100

Multiwalled CNT used as coating on the steel substrate

Single line track of 10 mm length drawn on the surface in open atmosphere

S.N.	Power (W)	Spot size (mm)	Speed	Remarks
1	250	0.5	10	Specimen 1 used for detailed analyses
2			25	
3			50	
4			75	
5			100	

Experiment 4: Gas assisted laser hardening

Laser system: YLR-150/1500-QCW (operated in continuous mode)

Materials : AISI 1020, AISI 1055, 50CrMo4 and AISI 52100

Gas used : Argon, Propane, CO₂ and air

Special chamber used for the experiment

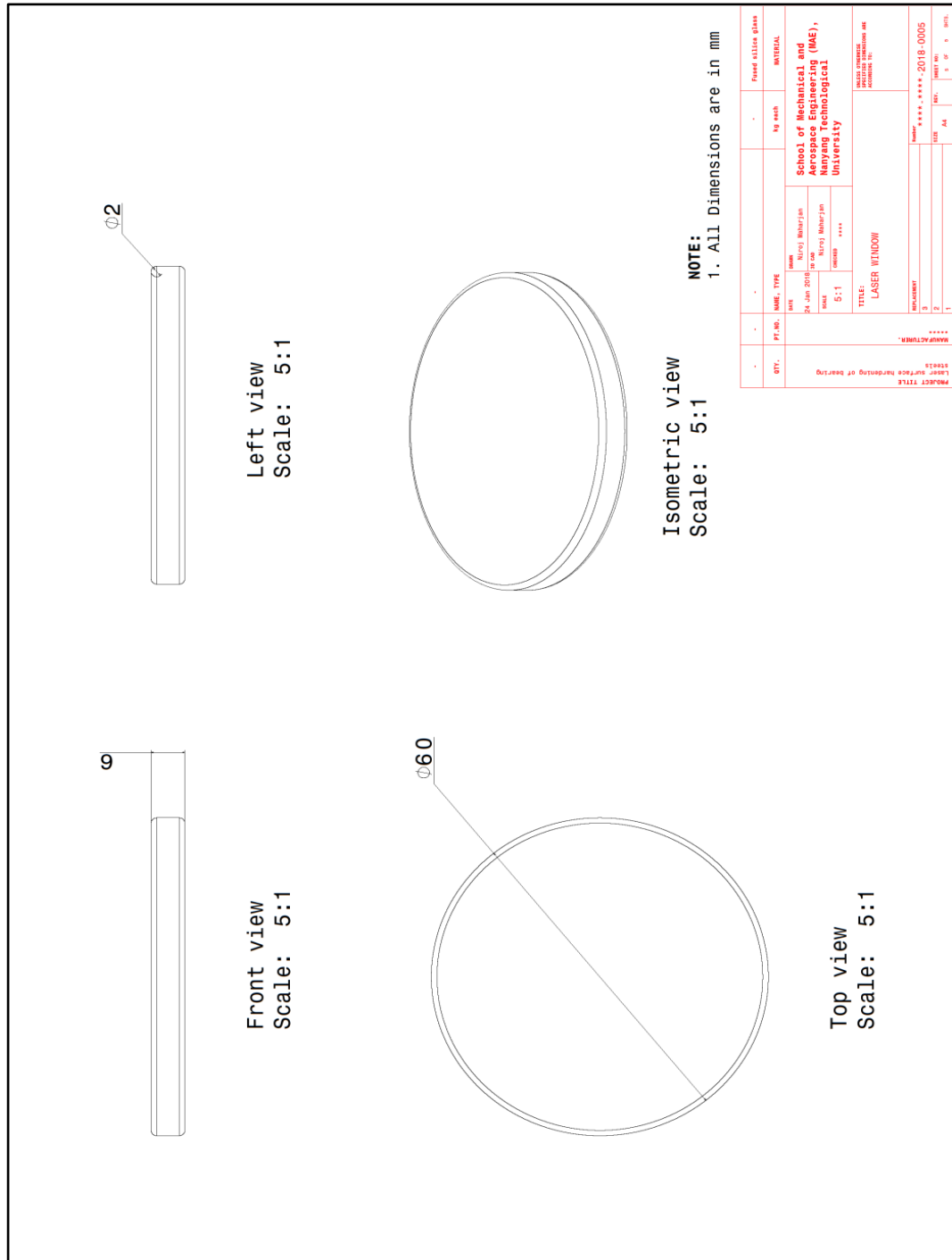
Trial 1: Varying speed

S.N.	Power (W)	Spot size (mm)	Gas used	Speed (mm/s)	Remarks
1	250	0.5	Air	10	Specimen 1 used for detailed analyses
2				25	
3				50	
4				75	
5				100	
6	250	0.5	Argon	10	Specimen 6 used for detailed analyses
7				25	
8				50	
9				75	
10				100	
11	250	0.5	CO ₂	10	Specimen 11 used for detailed analyses
12				25	
13				50	
14				75	
15				100	
16	250	0.5	Propane	10	Specimen 16 used for detailed analyses
17				25	
18				50	
19				75	
20				100	

Trial 2: Varying concentration

S.N.	Power (W)	Spot size (mm)	Speed (mm/s)	Gas used	Concentration in the chamber	Remarks
1	250	0.5	10	Propane	Low	
2					High	
3					medium	

C5. Laser window



List of Publications

Journal Papers

1. N. Maharjan, W. Zhou, Y. Zhou, Y.C. Guan, and N. Wu, "Comparative study of laser surface hardening using continuous laser and pulsed lasers with ms, ns, ps and fs pulse duration," *Surface & Coatings Technology*, vol. 366 (pp311-320), 2019.
2. N. Maharjan, W. Zhou, Y. Zhou, and N. Wu, "Underwater laser hardening of bearing steels," *Journal of Manufacturing Processes*, 2018. [under review]
3. N. Maharjan, W. Zhou, Y. Zhou, and N. Wu, "Laser Surface Hardening of AISI 1055 steel in water-submerged condition," *Surface Review and Letters*, 2018.
4. N. Maharjan, W. Zhou, Y. Zhou, and N. Wu, "Decarburization during laser surface processing of steel," *Applied Physics A: Materials Science & Processing*, vol. 124(10) (pp. 682), 2018.
5. N. Maharjan, W. Zhou, Y. Zhou, and Y. C. Guan, "Ablation morphology and ablation threshold of Ti-6Al-4V alloy during femtosecond laser processing," *Applied Physics A: Materials Science & Processing*, vol. 124 (8) (pp. 519), 2018.
6. N. Maharjan, W. Zhou, and Y. Zhou, "Surface ablation of 52100 bearing steel under femtosecond laser irradiation," *Surface Review & Letters*, (p1850227), 2018.
7. N. Maharjan, W. Zhou, H. Zheng, and N. Wu, "Surface Cleaning of a Titanium Alloy using Femtosecond Laser Pulses," *Lasers in Engineering*, 2018. [accepted, in press] *
8. G. Yan, A. Crivoi, Y. Sun, N. Maharjan, X. Song, F. Li, and M. J. Tan, "An Arrhenius equation-based model to predict the residual stress relief of post weld heat treatment of Ti-6Al-4V plate," *Journal of Manufacturing Processes*, vol. 32 (pp. 763–772), 2018. *

Conference Papers

1. N. Maharjan, W. Zhou, Y. Zhou, and N. Wu, "Influence of operating parameters on morphology of laser hardened surfaces," in Proc. SPIE 10525, *High-Power Laser Materials Processing: Applications, Diagnostics, and Systems VII*, 10525M, 2018.
2. N. Maharjan, W. Zhou, Y. Zhou, and Y. C. Guan, "Femtosecond laser cleaning for aerospace manufacturing and remanufacturing," in *Conference on Lasers and Electro-Optics Pacific Rim (CLEO-PR)*, IEEE (pp. 1-4), 2017. *
3. N. Maharjan, W. Zhou, and Y. Zhou, "Microstructural study of bearing material failure due to rolling contact fatigue in wind turbine gearbox," in *Proceedings of the International Symposium on Current Research in Hydraulic Turbines*, (p. 8), 2016. *

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