Laser Ablation of Paint From 2024-T3 Alclad Aluminum Alloy – Numerical Simulation and Experimental Characterization

by

Rahul Shah

A thesis submitted to the Faculty of Graduate and Postdoctoral Affairs in partial fulfillment of the requirements for the degree of

Master of Applied Science

in

Aerospace Engineering

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Carleton University
Ottawa, Ontario, Canada

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the Faculty of Graduate and Post-Doctoral Affairs
acceptance of the Thesis

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Submitted by Rahul Shah
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Master of Applied Science

_____________________________________
Dr. J. Laliberté, Thesis Supervisor

_____________________________________
Dr. R. Miller, Department Chair

Carleton University
2022
Abstract

Removal of paint from substrate material through laser ablation is a very promising and environmentally safe process as compared to chemical stripping and other processes. Potential thermomechanical damage of substrate material subjected to laser paint removal process plays a vital role in deciding the efficacy and the accuracy of a particular laser beam profile to be used. In the present research work, numerical simulation of thermomechanical behavior of substrate material (2024-T3 Alclad aluminum) with paint layer is developed subjected to laser heating with Gaussian (TEM$_{00}$) and Super-Gaussian (Top-Hat) beam profiles. It was observed that the Gaussian beam profile had the fastest stabilization time but produced higher thermal stresses on the surface of substrate material as compared to the Top-Hat beam profile. Moreover, the effects of various paint stripping processes (laser and chemical stripping) on the fatigue life and failure pattern of the substrate material (2024-T3 Alclad aluminum) were investigated through detailed statistical analysis and scanning electron microscope (SEM) analysis. It was observed that the differences in the mean fatigue life between laser and chemical stripped specimens were statistically insignificant. However, there was a distinct difference between the laser stripped and chemically stripped specimens with regard to final fracture zone. For the laser stripped specimen failure was brittle whereas for the chemically stripped specimens’ failure was ductile. In addition, surface roughness and surface microhardness measurement on the stripped surfaces were performed.
Acknowledgements

I would like to take this opportunity to express my gratitude to those who have helped me throughout the completion of my degree at Carleton University.

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Last but the most important, I would like to thank my parents and my wife for their continuous encouragement and their full support throughout this process.
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transverse Electromagnetic Modes</td>
</tr>
<tr>
<td>LASER</td>
<td>Light Amplification by Simulated Emission of Radiation</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>TEA</td>
<td>Transversely Excited Atmosphere</td>
</tr>
<tr>
<td>FAA</td>
<td>Federal Aviation Administration</td>
</tr>
<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
</tr>
<tr>
<td>PLA</td>
<td>Pulsed Laser Ablation</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LSO</td>
<td>Laser Safety Officer</td>
</tr>
<tr>
<td>ANSI</td>
<td>American National Standard Institute</td>
</tr>
<tr>
<td>NRL</td>
<td>Naval Research Laboratory</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Model</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl Methacrylate</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon Fibre Reinforced Plastic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerospace Materials Specifications</td>
</tr>
<tr>
<td>RCB</td>
<td>Randomized Complete Block</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>HSD</td>
<td>Honestly Significant Difference</td>
</tr>
<tr>
<td>LCVD</td>
<td>Laser Chemical Vapor Deposition</td>
</tr>
<tr>
<td>LPVD</td>
<td>Laser Physical Vapor Deposition</td>
</tr>
<tr>
<td>IEC</td>
<td>International Electrotechnical Commission</td>
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Chapter 1: Introduction

This chapter includes the motivations and objectives of the research work performed as well as an overview of each chapter.

1.1 Motivation

Although the aerospace industry is continuously developing better and better materials, this progress can be partly offset by aggressive environment [1]. Corrosion occurs in structures made of metals and metal alloys. Corrosion processes progress over time. Not detected and defined early enough and not properly repaired, corrosion changes can lead to disintegration of aircraft and loss of structural strength [2]. Corrosion prevention of lightweight aluminum alloy structures is done through various surface treatments such as cladding, anodizing etc. and layers of protective coatings. However, these coatings need to be removed periodically.

Removal of paint through laser ablation is a non-intrusive, solvent and abrasive media-free process for removing organic coatings from variety of substrates. It is very promising and environmentally safe process and has the potential to replace conventional paint stripping methods. The typical laser beam spatial profile used for this process is a fundamental mode Gaussian with transverse electromagnetic mode (TEM) of TEM\textsubscript{00}. However, there are many other higher order beam modes such as TEM\textsubscript{01}, TEM\textsubscript{10} and special beam profiles such as Super-Gaussian (Top-Hat) that can be used for the process. Potential thermomechanical damage of the substrate material subjected to laser paint removal process plays a vital role in deciding the efficacy and the accuracy of a particular beam 1
profile. A development of numerical simulation is required to evaluate the thermomechanical behavior of the substrate material subjected to laser heating. Moreover, the impact of the paint stripping process on the fatigue life of the substrate material is very important especially for lightweight aluminum alloys. A fatigue life assessment and subsequent fractography is required to evaluate the effect of laser paint stripping on the 2024-T3 Alclad substrate material subjected to various paint stripping processes (laser and chemical stripping). In addition, investigating the effect of paint stripping processes on the stripped surfaces of the substrate material with respect to the surface roughness and hardness is also very important.

1.2 Objectives

The purpose of this thesis is to evaluate the potential of higher order Gaussian beam profiles and other specialized beam profiles (Top-Hat) for the use in laser paint removal process by analyzing the thermomechanical behavior of substrate material through numerical simulation. Moreover, the fatigue life assessment of laser ablated 2024-T3 Alclad coupons is carried out with detailed statistical planning. Fractography analysis using SEM is also performed to understand the impact of various paint stripping processes (laser and chemical stripping) on the failure pattern of the coupons. In addition, the effect of various paint stripping methods on the substrate material with respect to the changes in surface roughness and hardness of the stripped surfaces is investigated through experimental tests.
1.3 Thesis Overview

This thesis is organized into five chapters; a description of each chapter is provided in this section.

**Chapter 1: Introduction** – The motivations and objectives of the research work performed as well as an overview of each chapter is provided.

**Chapter 2: Background, Application and Health and Safety of Laser** – This chapter provides the reader with a background information relevant to the topics covered in this thesis including: Types of lasers, Application of lasers, Environmental effects of lasers, and Health and safety issues related to use of lasers.

**Chapter 3: Laser-Matter Interaction and Mechanisms of Laser Ablation** – This chapter details the various mechanism behind laser ablation through literature review. First, information on how the laser material interaction takes place through laser heating of solid is provided along with the governing heat transfer equations. Then, detailed information on the ablation mechanisms in metal subjected to laser irradiation such as melting, melting and vaporization, and sublimation is provided. Finally, the laser ablation mechanisms in polymer are discussed.

**Chapter 4: Laser Beam Modes and Numerical Simulation of Thermomechanical behavior** – This chapter provides information on the transverse electromagnetic modes (TEM) of a laser beam. A mathematical representation of four
different possible beam modes (TEM$\text{}_00$, TEM$\text{}_01$, TEM$\text{}_11$ and Top-Hat) are developed and modeled in COMSOL Multiphysics and their potential use in the laser ablation process is discussed. Then, the heat transfer model presented in Chapter-3 is used to simulate the thermomechanical behavior of laser heating on the 2024-T3 Alclad substrate material with paint layer using TEM$\text{}_00$ and Top-Hat beams in COMSOL Multiphysics software. Finally, the results of the simulations are represented in terms of temperature distribution, heat affected zone (HAZ) and thermal stresses.

**Chapter 5: Experimental Characterization of Substrate Material** – This chapter describes the experimental testing performed on the laser stripped, chemically stripped and un-coated Al2024-T3 coupons to understand the effect of various paint stripping processes on the substrate material. First, the information on fatigue testing is presented with the details such as material, surface treatments, sample preparation and fatigue test set-up. Detailed statistical planning of fatigue tests is performed as per the ASTM STP 588 standard. Fatigue tests are conducted and the results of the same are summarized and discussed in terms of the statistical analysis (ANOVA), fatigue life and S-N curve. In addition, fractography analysis is performed using scanning electron microscope (SEM) to understand the impact of laser stripping on the failure pattern of the substrate material. Moreover, through thickness microhardness testing as per ASTM E384 is performed on all the strip scheme coupons to check the effect of laser heating on the surface hardness. Finally, surface roughness measurements are performed on the strip surfaces to check the effect of paint stripping on the substrate material.
Chapter 6: Conclusion and Recommendation (Future Work) – This chapter gives conclusive remarks based on the research work presented in the above mentioned chapters. Some areas still require more work to be performed to increase the understanding of underlying principles. Therefore, some future work encompassing additional testing and simulation work are recommended.

1.4 Summary of Contributions

Following technical and scientific contributions are made from the research work summarized in this thesis:

Published work:


Technical Contribution:

• Developed statistical planning of fatigue experiments and corresponding test matrix for fatigue testing.
• Developed detailed statistical analysis model for fatigue life evaluation.
• Developed numerical simulation with process and material parameters specific to Besnovo Technology Inc.
Chapter 2: Background, Applications and Health and Safety of Laser

Laser is one of the important innovations of 20th Century. As a versatile source of pure energy in a highly concentrated form, lasers have emerged as a key tool and research instrument with potential for applications in a variety of research and industrial fields. Laser ablation is the top-down process of removing material by focusing a laser beam onto a substrate. Ablation occurs when the material absorbs sufficient laser energy to be melted or vaporized. Before going into the details of laser ablation process, the basic introduction of laser systems and their application in various engineering fields is required. Moreover, worker health and safety is very important while working with lasers and therefore understanding the basic principles of laser safety is important.

2.1 Type of Lasers

The initial foundation of laser theory was laid by Einstein [3]. He predicted that the excited atoms could convert stored energy into light by process called stimulated emission. Subsequently, Kopfermann and Ladenburg [4] presented the first experimental confirmation of Einstein’s prediction. In 1960, Maiman [5] developed a ruby laser for the first time. This was followed by significant basic development of lasers from 1962 to 1968. Almost all the main types of lasers currently in use including semiconductor lasers, Nd-YAG lasers, CO₂ gas lasers, dye lasers and other gas lasers were invented in this era. Table 1 shows the list of different types of lasers available to date along with their construction and typical wavelength. In this chapter, however, Nd:YAG, Ti-Sapphire, Excimer and CO₂ lasers are analyzed because they are a versatile source of energy in a highly concentrated
form, being attractive tools and research instruments for a large variety of research and production fields, and for laser ablation particular.

**Table 1**: Types of lasers with their construction and typical wavelengths

<table>
<thead>
<tr>
<th>SR. No.</th>
<th>Laser</th>
<th>Type</th>
<th>Wavelength</th>
<th>CW or Pulsed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ArF, KrF, XeCl, XeF</td>
<td>Gas (excimer)</td>
<td>193 nm, 248 nm, 308 nm, 353 nm</td>
<td>ns</td>
</tr>
<tr>
<td>2</td>
<td>Dye</td>
<td>Liquid</td>
<td>400-1000 nm</td>
<td>CW, fs</td>
</tr>
<tr>
<td>3</td>
<td>Argon-ion</td>
<td>Gas</td>
<td>488 nm</td>
<td>CW</td>
</tr>
<tr>
<td>4</td>
<td>HeNe</td>
<td>Gas</td>
<td>632.8 nm</td>
<td>CW</td>
</tr>
<tr>
<td>5</td>
<td>AlGaNp, AlGaAs</td>
<td>Semiconductor</td>
<td>630-900 nm</td>
<td>CW, ms</td>
</tr>
<tr>
<td>6</td>
<td>Ti:Saph</td>
<td>Solid-state</td>
<td>650-1100 nm</td>
<td>CW, fs</td>
</tr>
<tr>
<td>7</td>
<td>Yb:YAG</td>
<td>Solid-state</td>
<td>1030 nm</td>
<td>CW, ps</td>
</tr>
<tr>
<td>8</td>
<td>Yb-glass</td>
<td>Fiber</td>
<td>1030 nm</td>
<td>CW, fs</td>
</tr>
<tr>
<td>9</td>
<td>Nd:YAG</td>
<td>Solid-state</td>
<td>1060 nm</td>
<td>CW, ps</td>
</tr>
<tr>
<td>10</td>
<td>Nd:glass</td>
<td>Fiber</td>
<td>1060 nm</td>
<td>CW, fs</td>
</tr>
<tr>
<td>11</td>
<td>InGaAs, InGaAsP</td>
<td>Semiconductor</td>
<td>1100-2000 nm</td>
<td>CW, ms</td>
</tr>
<tr>
<td>12</td>
<td>Cr:ZnSe</td>
<td>Solid-state</td>
<td>2200-2800 nm</td>
<td>CW, fs</td>
</tr>
<tr>
<td>13</td>
<td>CO2</td>
<td>Gas</td>
<td>10600 nm</td>
<td>CW, μs</td>
</tr>
</tbody>
</table>

2.1.1 **Nd:YAG Laser**

The crystal rods are a neodymium (Nd⁺⁺⁺)-doped YAG (yttrium aluminum garnett, \((Y₃Al₅O₁₂)_{13}\), YLF (yttrium lithium fluoride), YVO₄ (yttrium orthovanadate), or glass (SiBaRb, Ba(PO₃)₂, LaBBA, SiPbK, LaAlSi types) matrix. These materials have excellent thermal stability and properties (such as thermal conductivity) suitable for both short-pulse and continuous wave (CW) operation. The pumping of these lasers is done by arc lamps
(such as krypton or xenon lamps), or diode lasers. In the case of flashtube (F) pumping this is placed in one focus of an elliptical cylinder (cavity), the rod (R) being placed in the second focus. The flashtube is supplied by power supplies for high voltages, E (∼1,000 V) using capacitors, C and resistors, R as shown in Figure 1 [6] [7].

The spherical resonator (formed through two spherical mirrors, M1 and M2) in which the laser rod is placed, is the simplest to adjust but has the disadvantage that undesired transverse modes can easily start to oscillate. This means that the laser power is split up over several modes which are separated spatially from one another, and which cannot be focused to a common point as with longitudinal modes.

Nd:YAG and Nd-glass absorbs mostly in the bands between 0.5 and 0.8 μm, being excited the $^4F_{5/2}$ states (or higher states).
2.1.2 **Ti-Sapphire Laser**

These lasers (also known as Ti-Al$_2$O$_3$ lasers, titanium-sapphire lasers, or Ti-sapphs) are tunable lasers which emit red and near-infrared light in the range 650 - 1,100 nm and generate ultrashort pulses [8]. The lasing medium of a Ti-sapphire laser is a crystal of sapphire (Al$_2$O$_3$) that is doped with titanium ions. Usually, Ti-sapphire lasers are pumped with another laser with a wavelength of 514 - 532 nm such as Ar-ion lasers (514.5 nm) and frequency-doubled Nd-YAG, Nd-YLF, and Nd-YVO lasers (527 - 532 nm). Ti-sapphire lasers operate most efficiently at wavelengths near 800 nm.

Since the laser operation is based on the overlapping of two beams narrow focused in the case of cylindrical cross sections the system is very sensitive to the alignment of the optical devices and the mirrors which guides the pumping beam and must be mounted on rigid supports as shown in Figure 2 [6].

![Figure 1: Schematic of Nd:YAG laser ( [6] [7])](image)
2.1.3 Excimer Laser

The term excimer is formed by two short parts from ‘excited dimer’ (since a dimer refers to a molecule of two identical or similar parts). The excimer laser was first described by Basov et al. in 1970 using a xenon dimer (Xe2) excited by an electron beam to give stimulated emission at 172 nm wavelength [9]. A later improvement was the use of noble gas halides, originally XeBr, but also XeCl that was excited using a microwave discharge [10]. Figure 3 shows the schematics of Excimer laser [11].

The operation wavelength of an excimer laser depends on the molecules used and is usually in the ultraviolet as shown in Figure 4. For example, the wavelength is 193 nm for ArF laser, 248 nm for KrF, 308 nm for XeCl, and 351 nm for XeF, the pulse energy being in the range several to tens of mJ, while the relative power is in the range 50 - 100 mW.
Figure 3: Schematics of Excimer laser ([11]).

Figure 4: Lasing wavelength (lower scale) and corresponding photon energy (upper scale) of the different Excimer lasers ([11]).
2.1.4 CO₂ Laser

The carbon dioxide (CO₂) laser was the first high-powered infrared laser developed [12]. In the case of CO₂ laser the gain medium is a gas mixture consisting mainly of CO₂, helium (He), and nitrogen (N₂) in proportion to CO₂: N₂: He = 1 : 1 : 6. The N₂ molecules are excited by an electric discharge into a metastable vibrational level. The excitation energy is transferred to the CO₂ molecules from the energetic band 00₀¹ by collision processes: CO₂ (0₀₀₀) + e⁻ → CO₂ (0₀₀₁) + e⁻ or by resonant transfer of excitation between N₂ (v=1) and CO₂ (0₀₀₀): CO₂ (0₀₀₀) + N₂ (v=1) → CO₂ (0₀₀₁) + N₂ (v=0) – 18 cm⁻¹.

Concerning the construction principle, there are several types of CO₂ lasers: lasers with longitudinal and transverse gas flows, locked lasers, guided wave lasers, lasers with transversely excitation, lasers with excitation produced by gas-dynamic processes, lasers pumped by optical methods and by chemical reactions etc. Figure 5 shows the schematic of CO₂ laser with longitudinally flow of the gas mixture. Due to practical limits in the length of the laser cavity, commercial continuous wave (CW) CO₂ lasers in the 500 W - 1,000 W range use a folded-tube configuration and axial flow conditions. Pulsed operation is triggered in transversely excited atmospheric-pressure (TEA) lasers, where the discharge is applied transverse to the optical axis. After an elapsed time of ms a strong spike pulse of width 100 - 200 ns is emitted, followed by a longer and lower-amplitude tail that lasts for 10 ms.
2.2 Applications of Lasers

In the early years of their development, lasers were regarded by skeptics as “a solution looking for a problem”. More and more “problems” were found, and lasers have become an important part of the science and technology of our time, with applications ranging from medical to military. Lasers have been used in distance and velocity measurements, holography, printers, bar coding, CD/DVD/BluRay players, surgery, and many other areas for many years now, and such “everyday” applications will not be touched upon here. In this section, instead, we will briefly discuss the application of laser related to material processing.

2.2.1 Laser Drilling

Laser drilling is both a widely used industrial process and an active research area. Due to the noncontact nature of laser drilling, holes can be drilled in traditionally hard-to-machine materials without any tool wear issues. High-strength and brittle materials are challenging to machine conventionally, however, laser drilling of high-strength superalloys and brittle
ceramics is routinely done in the aerospace and microelectronic industries. All classes of materials can be laser drilled [13].

Laser drilling involves a stationary laser beam that uses its high-power density to melt or vaporize material from the workpiece. In principle, laser drilling is governed by an energy balance (Figure 6) between the irradiating energy from the laser beam and the conduction heat into the workpiece, the energy losses to the environment, and the energy required for a phase change in the workpiece [14]. Energy losses occur for a number of different reasons, some of which are: (i) when the material is being heated above the required temperature for melting, (ii) plasma formation, (iii) the low absorptivity of the material, (iv) the convection of heat due to the use of gas jet, and so on. However, the advantages ensuing from the use of laser drilling instead of mechanical drilling have to do with (i) its thermal nature (which does not depend on the mechanical properties of the workpiece), (ii) the higher accuracies achieved and (iii) the higher machining rates. The main limitations of the process comprise its inability to produce stepped diameter holes and the lack of accurate depth control.
Laser drilling can be carried out in a number of ways including single pulse drilling, percussion drilling, trepanning and helical drilling. Trepanning and helical drilling usually provide higher quality holes at the cost of drilling time. While percussion drilling provides the advantages of higher drilling speed, the quality of the holes is usually poorer than trepanning. Figure 7 shows the different style of laser drilling.

2.2.2 Laser Cutting

Laser cutting is a process based on the removal of material by heating and cutting the part following a determined trajectory. Heating is achieved by focusing a laser beam on the
surface of the part. In the laser cutting process, most of the lasers used are CO$_2$ or solid state lasers (Nd:YAG, fibre or disc lasers) [16]. The use of either type introduces strong variations in the machine and in the process itself. Once the beam has been generated, regardless of the type of laser, it must be guided to a cutting head. The cutting head has a lens system that focuses the beam at a point whose size is usually less than 0.2 mm in diameter. This focusing of the beam can achieve very high energy densities, with a typical value of about $1.4 \times 10^{10}$ W/m$^2$. Figure 8 (a) shows a laser cutting operation of a stainless steel sheet and Figure 8 (b) shows a schematic of a cutting head.

Figure 8: (a) Laser cutting operation of stainless steel sheet, (b) Schematic of a cutting head ( [17])
Figure 9: Striations on the cut face of a piece of stainless steel cut with 3-kW laser power at speed of 1.5 m min$^{-1}$. ([18])

At the same time, a gas flow is injected coaxially into the laser beam. Depending on the material, the gas may have different functions. In general, the optimum parameters are the minimum power and higher cutting speed to achieve the highest cutting quality. Laser cutting has many advantages over the conventional cutting methods due to its precision of operation, non-frictional processing, and operational cost. The localized heat generation during the laser cutting process minimizes the heat losses from the region, which is irradiated by a laser beam.

2.2.3 Laser Surface Treatment

The laser has some unique properties for surface heating. Typically, the electromagnetic radiation of a laser beam is absorbed within the first few atomic layers for opaque materials, such as metals, and there are no associated hot gas jets or eddy currents and there is even no radiation spillage outside the optically defined beam area. In fact, the applied energy
can be placed precisely on the surface only where it is needed. Thus, it is a true surface heater and a unique tool for surface engineering. The use of laser in surface treatment include: surface heating or laser heat treatment, surface cladding, surface texturing, plating by laser chemical vapour deposition (LCVD), laser physical vapour deposition (LPVD), etc. In this section, we will briefly discuss about these applications.

2.2.3.1 Laser Heat Treatment

The initial goal of laser heat treatment [19] was selective surface hardening for wear reduction; it is now also used to change metallurgical and mechanical properties. Laser heat treatment is used on titanium, some aluminum alloys, steels with sufficient carbon content to allow hardening and cast irons with a pearlite structure. As the laser beam moves over an area of the metal surface, the temperature starts to rise and thermal energy is conducted into the metal component. Temperatures must rise to values that are more than the critical transformation temperature but less than the melt temperature. After the beam has passed, cooling occurs by quenching from the bulk of the material which has hardly been heated by this fast surface heating process. Figure 10 shows the experimental arrangement of laser heat treatment.

2.2.3.2 Laser Cladding

The aim of most cladding operations is to overlay one metal with another to form a sound interfacial bond or weld without diluting the cladding metal with substrate material. In this situation dilution is generally considered to be contamination of the cladding which degrades its mechanical or corrosion-resistance properties. The advantage of the laser is its ability to heat and clad in specified areas alone.
Figure 10: Experimental arrangement of laser heat treatment ([7])

Figure 11: Arrangement of laser cladding by the blow-powder technique ([7])
Among the laser cladding routes are those which melt preplaced powder [20], or blown powder [21] (Figure 11), those which decompose vapour by pyrolysis [20], or photolysis [22] as in LCVD, those which are based upon local vaporisation as in laser physical vapour deposition or sputtering and those which are based on enhanced electroplating or cementation.

2.2.3.3 Laser Surface Texturing

The rolls in temper mills are textured to dull the surface of sheet steels, which improves the grip in a press and the flow of paint on the final surface. There are several techniques for doing this [23] [24]. The conventional technique is to shot-blast the surface. This, however, gives a random roughness which exhibits a waviness in the finished paint surface. This can be avoided by a regular patterned roughness. The pattern can be placed using laser (either CO$_2$ or Nd:YAG). The roughness must be higher than approximately 1 μm for press formability and the waviness should be as low as possible. The Nd:YAG laser does not give sufficiently consistent high-quality spots owing to the variations within the YAG rod. The electron beam method requires a vacuum chamber and special cleaning of the roll prior to work. On the whole, the CO$_2$ laser technique is preferred over Nd:YAG laser when a comparison is made with respect to the consistency of high-quality spots [24].

2.2.3.4 Laser Chemical Vapour Deposition (LCVD)

Blowing thermally sensitive vapour onto a laser-generated hot spot can cause a deposit to be formed by pyrolysis. The rate of deposition is controlled by chemical reaction rates (Arrhenius equation) up to certain deposition rates dependent on the surface temperature; above these temperatures the process is controlled by mass transport. Alternatively, the
vapour could be directly broken by the photons in a process of photolysis. This is particularly relevant to processing with the excimer laser. Leon et al. [25] [26] have deposited SiO$_2$ in this manner.

### 2.2.3.5 Laser Physical Vapour Deposition (LCVD)

The laser beam can be directed onto a target situated in a vacuum chamber. The target evaporates and the vapour condenses on the substrate among other areas. This process has the advantage of extreme cleanliness in the heating technique. It is possible using an excimer laser pulse to ablate the surface of the target, resulting in a deposit on the substrate which is of the same composition as the target material with no difference due to vapour pressures. Such a process has been described for the deposition of superconducting alloys [27], calcium hydroxyapatite for medical implants [28] and TiN on hydrogen-terminated silicon [29].

### 2.2.4 Laser Additive Manufacturing

The laser is seen as playing a pivotal role in the growth of additive manufacturing (AM) systems and metal AM, recently. It is at the “heart” of metal AM technology, and its developments in terms of power, efficiency, beam quality, and reliability boosted the growth and application of metal AM systems globally. The laser metal AM approaches involve “powder or wire-fed” or laser metal deposition and “powder bed” or selective laser melting [30]. Of the many laser sources that have been discovered over the years, the carbon dioxide (CO$_2$) and the flashlamp and diode-pumped neodymium-doped yttrium-aluminum-garnet (Nd:YAG) lasers have dominated metal AM from about the late 1980s
to early 2000s. Since then, fibre, disk, and diode lasers have become the lasers of choice for these applications, primarily because of their overall efficiency (around 30 - 40%), fibre beam delivery, and general robustness, which have considerably simplified and improved processing [7].

2.2.5 Pulsed Laser Ablation (PLA)

The laser ablation process can be used in a wide range of particular applications in which mass removal of laser irradiated materials is the essence of the final required process. Even more than previously mentioned cutting and welding processes, physical mechanisms involved in laser ablation are extremely complex [31] depending on the particular ablation technique considered (molten material ablation, vaporization phase ablation, sublimation techniques, non-thermal ablation, etc.). Quality control in laser ablation implies surface final state characterization, including, if possible, estimation of ablated mass, walls morphology in ablation fronts and layer behavior in multilayer laser ablation. That is also the case in laser cleaning [32], and other process as laser lithography and surface modification [33] very well known in the frame of micromachining techniques. The focus of this thesis is the PLA process and Chapter 3 provides detailed information on PLA, its mechanisms and its application for paint removal.

2.3 Laser Health and Safety

All energy is dangerous, and the laser is no exception. It poses an unfamiliar hazard in the form of an optical beam. The main dangers from the laser are: damage to the eye; damage to skin; electrical hazards; and hazards from fumes/vapours.
These risks can be minimized by following standards which have been laid down by various authorities. Most countries have their own set of standards, but recently the laser community has started coming together on a single set of principles. The Technical Committee No. 76 of the International Electrotechnical Commission (IEC) drew up the basic standard from which most others have developed; this is IEC 825-1 (1993), the original version was written in 1984 and amended in 1990. This covers manufacturers and users and applies to both lasers and LEDs.

The European Committee for Electrotechnical Standardization (CENELEC) adopted the IEC 825 standard in 1992 as European Norm EN 60825. EN 60825-1 [34], which is identical to IEC 825-1, was approved in 1994 and amended in 1996 and in 2001 [35]. In the USA the American National Standards Institute (ANSI) issued ANSI Z136.1-1993 [36]. This differs from IEC requirements primarily in labelling, class 1 limits, interlocks, measurement criteria and collateral radiation.

These standards give guidance and rules concerning engineering controls, advice on personal protective equipment, administrative and procedural controls, and special controls. Class 4 laser installations, in which category nearly all material processing systems fall, should also have a laser safety officer (LSO), who should see that these guidelines are observed. He or she is also responsible for evaluating laser hazards and establishing appropriate control measures.
2.3.1 The Safety Limits

There are two types of problems with radiation falling on the eye. There is potential damage to the retina at the back of the eye and potential damage to the cornea at the front of the eye. Radiation which falls on the retina will be focused by the eye’s lens to give an amplification of the power density by a factor of around 105. This means that lasers with wavelengths in the visible or near-visible waveband (Ar, He - Ne, Nd:YAG, Nd:glass) are far more dangerous than those with wavelengths outside that band (CO₂, excimer, Er:YAG). Safe exposure limits have been found by experiment and they are listed as the maximum permissible exposure (MPE) levels. These levels are plotted in Figure 12(a) and Figure 12(b) for retinal and corneal damage. For example, a 1 mW He-Ne laser with a 3 mm diameter beam would have a power density in the beam of \( \frac{0.001 \times 4}{3.14 \times 0.3 \times 0.3} = 0.014 \text{ W cm}^{-2} \). On the retina, this would be amplified by 100,000 to be \( 0.014 \times 10^5 \text{ W cm}^{-2} = 1,400 \text{ W cm}^{-2} \). A blink reflex at this level would only allow a 0.25 s exposure, which is the MPE level for a class 2 laser.

![Diagram of retinal power density and time](image)
There are also MPE levels for skin damage. These are far less severe than for the eye and so are essentially irrelevant. The laser is capable of penetrating the body at speeds as fast as that for steel and so the focused beam needs to be seriously respected. Without meaning to trivialize the problem with skin effects, the damage done is usually blistering or cutting, neither is pleasant but the wound is clean and will heal - unlike some eye damage.

2.3.2 Laser Classification

Lasers are classified in EN 60825-1:2001 and ANSI Z136.1:2007 according to their relative hazard. All lasers of interest to material processing will be classified as class 4, except some which are totally built into a machine in which there is no human access possible without the machine being switched off. Table 2 [37] provides summary of the classification, based on accessible emission limits.
Table 2: Classification of laser and LED Sources

<table>
<thead>
<tr>
<th>Class</th>
<th>Definition</th>
<th>Warning Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Intrinsically safe for continuous viewing</td>
<td>None</td>
</tr>
<tr>
<td>1M</td>
<td>Low risk to eyes. No risk to skin. Safe, provided binoculars, etc., are not used for viewing.</td>
<td>Laser radiation. Do not view directly with optical instruments</td>
</tr>
<tr>
<td>2</td>
<td>Low risk to the eyes. No risk to the skin. Visible radiation in which protection is by blink reflex (0.25 s), &lt;1 mW continuous wave (CW) laser.</td>
<td>Do not stare into the beam</td>
</tr>
<tr>
<td>2M</td>
<td>Low risk to the eyes. No risk to the skin. Same as class 2 except binoculars and telescopes are not to be used.</td>
<td>Do not stare into the beam</td>
</tr>
<tr>
<td>3R</td>
<td>Low risk to eyes. Low risk to skin. Protection by blink reflex and beam size.</td>
<td>0.4-1.4-mm wavelengths: “avoid direct Eye “exposure”. Other wavelengths: “Avoid exposure to the beam”.</td>
</tr>
<tr>
<td>3B</td>
<td>Medium risk to the eyes. Low risk to the skin.</td>
<td>Avoid exposure to the beam.</td>
</tr>
<tr>
<td>4</td>
<td>High risk to the eyes and skin. May cause a fire. Standard safety precautions must be observed</td>
<td>Avoid eye or skin exposure.</td>
</tr>
</tbody>
</table>
Chapter 3: Laser-Matter Interaction and Mechanisms of Laser Ablation

Ablation is a combination of both vaporization and melt expulsion as represented in Figure 13. When a focused beam of laser radiation strikes a surface, the electrons present in the substrate are excited by laser photons [38]. This excitation results in the generation of heat as the photon energy is absorbed, which is consistent with Beer Lambert's law [39] [38]. Beer Lambert’s law states that the amount of light absorbed is dependent on the thickness of the materials and intensities of the light source. The heating causes melting and/or vaporization of the material, thus resulting in the removal of macroscopic materials from the substrate. The transition from solid to gas results in the formation of a plasma plume.

![Figure 13: The mechanism at laser-material interface (40)](image-url)
The phase transition takes place in a series of steps. The initial heat produced by the absorption of the laser photons results in the formation of a melt pool at the laser-substrate interaction zone. Section 3.2 describes the heat transfer mechanism at this state. The temperature further increases due to additional incoming laser pulses and the melt pool reaches the vaporization state [41]. High pressure is created during vaporization, which is also called the “recoil pressure”, which pushes molten materials from the pool where it is ejected [42]. The ejected material is a concern due to its redeposition on the substrate or on the interaction zone [43] [44]. By further increasing the temperature at the laser-substrate interaction zone, the liquid attains an explosive liquid vapor phase transition stage [45] [46]. This mechanism is commonly seen during ablation using long pulsed lasers and may be referred to as a “burst”. In this mechanism, the dynamics of the fluid phase and the vapor conditions are quite complex, and the re-solidification of the molten material also results in geometric changes in the ablated features. Section 3.3 presents the heat transfer mechanism at this state.

These various mechanisms are all dependent on the specific combination of light and material properties. As a result, it is essential to consider certain important phenomena while studying the laser-material interaction. These phenomena include the type and magnitude of light energy absorption and the time scale of the laser pulse. At normal intensities, the absorption is linear and follows Beer Lambert’s law. This implies that the electrons excited due to the photon absorption transfer the heat to the lattice, thereby resulting in melting and vaporization. However, the extreme intensity of the laser pulse in the ultrashort time frame (picosecond and femtosecond) results in inaccurate predictions
under classical heat transfer conditions. At ultrashort timescales, the absorption becomes nonlinear and becomes intensity dependent [40]. The bound electrons of the material can be directly ionized by large absorption coefficient and due to high intensities. This thesis focuses only on the laser ablation mechanisms at normal intensities and the mechanism at the ultrashort regime is out of the focus of this thesis.

3.1 Laser Heating of Solids

The beam from a materials processing laser can carry considerable energy, and the low divergence of that beam allows the energy to be concentrated in a small area. If we allow such a beam to impinge on a surface, some light will be reflected, some will be absorbed, and some may be transmitted. With a metal target, almost all the light will be reflected, a little will be absorbed, and none will be transmitted. However, for heating the material, a lot of light needs to be absorbed. One way to do this is to cover the highly reflective metal surface with an absorbing dielectric coating that heats up and transfers the heat to the metal [47]. This works except that the coatings tend to change their properties at heat-treating temperatures, affecting the coupling.

Another approach is to use a plane-polarized beam that is incident on the surface at Brewster's angle, maximizing the coupling. This eliminates the need for, and variability of, coatings but makes it difficult to treat curved surfaces. For the 10.6 μm light emitted by CO₂ lasers, Brewster's angle is about 89°, which is very unwieldy. The angle for 1.06 μm light is shallower, making this a more attractive approach for high-power Nd:YAG lasers, except that they are hard to polarize. The presence of any films on the surface of the metal
will radically alter the optical properties [48], so this method also has problems of repeatability. The most typical regimes of laser heating of metals are such conditions that no compound of any kind is formed as an effect of laser irradiation, and no intense vaporization or plasma generation occurs close to the surface. In other words, our reference term is the low-intensity laser irradiation of metals in inert gases.

Whatever method is used, the lasers only heat the surface of metals. All subsurface heating is accomplished by conduction. Let us assume that the metallic sample is a homogeneous and isotropic medium. We shall consider the surface influence only through the changes in absorptivity. Volume defects and impurities shall be ignored. Then in the case of a semi-infinite solid, the heat action of the laser radiation can be described in terms of the variable temperature, T (x, y, z, t) at any particular point of the sample, and at specific moments in time. This quantities obey the heat conduction equation given below:

\[
\rho C_p \frac{\partial T}{\partial t} = K_T \nabla^2 T + A_V I(x, y, z, t)
\]  

(3.1)

where \( \rho, C_p, K_T \) are the density, the specific heat and the heat conductivity of the metal, respectively, and \( A_v \) is the fraction of the radiation energy absorbed into the sample per unit time and unit volume of metal. The temperature dependence of the thermophysical parameters \( \rho, C_p, K_T \) and of the optical parameter, \( A_v \), of the metal sample makes Equation 3.1 non-linear, so that its analytical solution is available only in a quite limited number of
cases. The general non-linear heat conduction equation taking into account the above-mentioned variation is obtain as below [49] [50].

$$\rho(T)C_p(T) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( K_T(T) \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_T(T) \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial Z} \left( K_T(T) \frac{\partial T}{\partial Z} \right)$$

(3.2)

With boundary and initial condition as:

$$K_T(T) \frac{\partial T}{\partial Z} \bigg|_{Z=0} = -A(T)I(r, t)$$

(3.3)

$$T(\pm\infty, y, z, t) = T(x, \pm\infty, z, t) = T(x, y, \pm\infty, t) = T(x, y, z, 0) = T_0$$

(3.4)

Here $T_0$ is the initial temperature which in the above calculations assumed to be $T_0 = 0$. The analytical solution of Equation 3.1 can be obtained by various methods such as separation of variable method, Fourier transformation, and Laplace transformation [51].

3.2 Laser Melting of Metals (Formation of a Melt Pool)

If the heating process continues, and if enough heat is transferred and the temperature is raised locally, the solid being heated will change its state. Most materials will melt (graphite vaporizes; most polymers decompose). A molten metal surface interacts with light much like a solid one. Liquid semiconductors have large numbers of free electrons, so they behave like metals. Absorption for metals increases when they melt because the degree of disorder in the material has increased, causing more interaction between atomic vibrations and electrons. Reflectivity drops from over 90% to about 50% for common
metals. This is fortunate because it is impractical to apply an absorbing coating to a liquid. Consider a scheme for the laser heating of a solid (metal) in the presence of a liquid phase as shown in Figure 14 [51]. $T_2$ is the temperature in the solid, and the front surface at $Z = 0$ first warms up to the melting point $T_m$ (above ambient temperature), and then begins to move to the right. $S$ denotes its position as a function of time. When $S = \ell$, the process is over, and we call this time $t_f$. We denote by $t_m$ the time at which the front surface begins to melt. Subscript 1 now refers to the molten state, whereas subscript 2 is still the solid state. Assuming that the intensity of the incident laser radiation is constant, $I(t) = I_0$, without taking into consideration, for the time being, the vaporization and sputtering phenomena, laser heating of the sample up to the melting point $T_m$ and beyond is usually described by the following equation system, with initial and boundary conditions:

\[ \text{Figure 14: Schematic of laser heating of solid (metal) in the presence of a liquid phase (~[51])} \]
\[
\frac{\partial^2 T_2}{\partial Z^2} - \frac{1}{K_2} \frac{\partial T_2}{\partial t} = 0 \text{ for } 0 \leq t \leq t_f (Solid) 
\]
(3.5)

\[
\frac{\partial^2 T_1}{\partial Z^2} - \frac{1}{K_1} \frac{\partial T_1}{\partial t} = 0 \text{ for } t_m \leq t \leq t_f (Liquid) 
\]
(3.6)

The boundary conditions are:

\[
K_2 \frac{\partial T_2}{\partial Z} \bigg|_{Z=0} = -I_0 \text{ for } 0 \leq t \leq t_m 
\]
(3.7)

\[
K_1 \frac{\partial T_1}{\partial Z} \bigg|_{Z=0} = -I_0 \text{ for } 0 \leq t \leq t_f 
\]
(3.8)

\[
K_1 \frac{\partial T_1}{\partial Z} \bigg|_{Z=S} - K_2 \frac{\partial T_2}{\partial Z} \bigg|_{Z=S} = \rho L \frac{dS}{dt} \text{ for } t_m \leq t \leq t_f 
\]
(3.9)

\[
K_2 \frac{\partial T_2}{\partial Z} \bigg|_{Z=\ell} = 0 \text{ for } 0 \leq t \leq t_f 
\]
(3.10)

\[
T_2 \big|_{Z=S} = T_1 \big|_{Z=S} = T_m \text{ for } t_m \leq t \leq t_f 
\]
(3.11)

The initial conditions are:

\[
T_2(Z, 0) = T_{20} \text{ and } S|_{t=t_{st_m}} = 0 
\]
(3.12)

The above boundary conditions are non-linear and a solution in an analytical form is very difficult. This is due to the presence of the moving boundary and appears in the second boundary condition, which states that the boundary moves at a rate \(dS/dt\) determined by a balance between the heat of melting \(L\), the heat input \(I_0\), and the heat flow by thermal conduction. One relationship must hold for this problem, however, which follows energy balance – The total energy put in per unit area is \(I_0 t_f\) and, since the material is simply heated to \(T_m\) and melted, this energy goes solely to those processes:

\[
I_0 t_f = \rho (L + C_p T_m) 
\]
(3.13)
3.3 Laser Melting and Vaporization (Explosive Liquid Vapor Phase) of Metals

Consider the case of a slab material, insulated on the surfaces, subjected to uniform and continuous irradiation as shown in Figure 15 [51]. It is assumed that the melt is fully retained until it reaches the vaporization temperature, where it disappears. Here $S_2$ is the position of the liquid–vapor interface and $S_1$ the position of the solid–liquid interface. This problem has been solved numerically at NRL [52], and we shall show sonic results. The assumptions are that in each phase, the thermal properties are independent of temperature.

![Figure 15: Melting and vaporization, with fully retained liquid (51)](image)

Note that when $I_0 \to 0$ and $I_0 \to \infty$, we obtain certain simple limits. For $I_0 \to 0$ no vaporization can take place, the melting is small, and we approach to fully ablated limit. On the other hand, as $I_0 \to \infty$, all the liquid should be vaporized by $f$, the time the back surface melts.

\[
I_0 t_f = \rho \ell [L + (T_m - T_0)C_{solid} + (T_V - T_m)C_{Liquid} + L_V] \text{ for } I_0 \to \infty \tag{3.14}
\]

\[
I_0 t_f = \rho \ell [L + (T_m - T_0)C_{solid}] \text{ for } I_0 \to 0 \tag{3.15}
\]
Where, $L_v$ is the latent heat of vaporization.

Vaporization of the metal proceeds from a liquid phase. A recoil, reactive pulse of vapors is therefore acting upon the melted layer, and the existence of a vapor gradient acting from the center to the spot periphery leads to supplementary removal of metal from the irradiation spot [53]. These effects provide an interpretation for the deposition of substance on the borders of the crater, well visible in Figure 16 [54]. Metal vaporization is generally accompanied by plasma ignition in vapors, which facilitates the visual identification of the moment when vaporization damage starts and eliminates the need for a thorough analysis of the sample's surface.

**Figure 16:** (a) Photograph of a crater formed in the irradiation zone on the surface of a Gold sample.

(b) A transverse section across the crater formed in the irradiation zone ([54])
Vaporization damage causes the formation of a crater in the zone of action of the laser radiation. A typical photograph of such a crater is given in Figure 16 [54], along with a cross section of the irradiation zone. However, as in the case of melting, damage by vaporization \((I = I_v)\) can occur—depending on the material purity and the degree of processing of its surface—either in point-like, localized zones, or simultaneously, over the whole irradiation spot.

### 3.4 Laser Ablation Through Sublimation

Sublimation is a physical process in which a solid directly converts into a gaseous (vapor) state without going through a liquid state [51]. The latent heat of sublimation at a particular temperature is the amount of heat required to convert a unit mass of solid into gas. A generally accepted theoretical model of ablation through sublimation is based on the Hertz-Knudsen equation which considers penetration of laser radiation into the target and the attenuation of the laser beam in the laser-induced plume [55]. The one-dimensional non-stationary heat conduction equation is expressed as below:

\[
\rho \left( C_p + L_m \delta(T - T_m) \right) \left( \frac{\partial T}{\partial t} - u(T_s) \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \lambda \frac{\partial T}{\partial x} + I(t) \alpha e^{-\alpha x} \tag{3.16}
\]

With the boundary and initial conditions as:

\[
T(x, 0) = T_0, T(0, t) = T_s(t), \lambda \frac{\partial T}{\partial x} \bigg|_{x=0} = \rho L_V u(T_s) \tag{3.17}
\]
Where, $\rho$, $C_p$, $\lambda$ and $\alpha$ are the mass density, the heat capacity, the thermal conductivity and the absorption coefficient of the target material; $I(t)$ is the absorbed laser intensity; $L_m$ and $L_v$ are the latent heat for melting and evaporation; $T_m$ is the melting temperature. The term $L_m\delta(T-T_m)$ allows to take into consideration melting in the target. The rate of evaporation is determined by the relation:

$$u(T_S) = m\Psi(T_S)/\rho$$

(3.18)

Where, $\Psi(T_S)$ is the flux of particles from the surface which is determined from the Hertz-Knudsen equation as:

$$\Psi(T_S) = \frac{1}{4}n_Su_T(1 - \beta) = \frac{P_S(T_S)}{\sqrt{2\pi mkT_S}}(1 - \beta)$$

(3.19)

Here "$m$" is the atomic mass; "$k$" is the Boltzmann constant; $n_S$ and $P_S$ are number density and pressure of the saturated gas under temperature $T_S$; $u_T = \sqrt{8kT_S/(\pi m)}$ is the average thermal velocity of evaporating particles; $\beta = 0.163$ is the fraction of the evaporated particles returning to the target surface. To determine the saturation pressure, the Clausius–Clapeyron equation is used [56]:

$$P_S(T_S) = P_b\exp\left(\frac{mL_v}{K}\left(\frac{1}{T_b} - \frac{1}{T_S}\right)\right)$$

(3.20)
Where, $T_b$ is the boiling temperature under pressure $P_b$. Note that the parameters $T_b$ and $P_b$ do not represent the boiling vaporization mechanism and are used only as normalizing values. From Equation 3.19 and 3.20, the velocity of the surface recession is determined by the Hertz–Knudsen equation coupled with the Clausius–Clapeyron equation is expressed as below:

$$u(T_S) = F \frac{P_b}{\rho} \sqrt{\frac{m}{2\pi k T_S}} \exp \left[ \frac{L_v}{k} \left( \frac{1}{T_b} - \frac{1}{T_S} \right) \right]$$  

(3.21)

Equation 3.21 gives the material removal rate through evaporation of a solid surface illuminated by laser.

### 3.5 Laser Ablation of Polymers

Processes of polymer breakdown when exposed to laser radiation, as a component of laser ablation, have certain features that differ from the breakdown of other materials such as metals or semiconductors. The kinetics and mechanisms of laser breakdown of polymers may vary widely depending on the chemical structure of the polymer. This creates certain difficulties in studying the breakdown process [58]. Laser ablation of polymers was first reported by Srinivasan and Mayne-Banton [57] and Kawamura et al. [60] in 1982. It was proposed in [58] that all polymers should be divided into the following groups according to their behavior in a laser beam: Group A, consisting of polymers that melt and splatter; Group B, consisting of polymers that form a layer of char on the surface; and Group C, consisting of polymers that transform into the gaseous state without any residue. These
three classes represent the behavior of all known types of polymers when exposed to a laser beam. In certain cases, however, it is necessary to consider ignition, which has an additional destructive effect on polymers.

In Group A we find mainly thermoplastic polymers such as Polyethylene, Polypropylene, Polyethylene succinate, Nylon, Kapton, Polystyrene, Polymethyl Methacrylate (PMMA), etc. In [59] [60] [61], the behavior of thermoplastic polymers in a field of laser radiation was studied in the example of PMMA and polystyrene (PS). It was established that within the specimen, in the surface layers, the breakdown proceeds along the boundaries of supramolecular structures; as a result, a cloud appears over the surface, containing solid, liquid, and gaseous products. The cloud shields the specimen by absorbing part of the radiation.

**Figure 17:** Schematic representation of breakdown zones in thermoplastics when exposed to infrared laser radiation at 10.6 μm: $T_g$, $T_s$, $T_d$, and $T_f$ are the glass transition temperature, the softening point, the decomposition temperature, and the temperature of the breakdown front, respectively ( [61] )
Zones of breakdown of the specimen across its section, which are important for an understanding of the process, are shown in Figure 17. Where, Zone: I) solid polymer, in which the temperature distribution follows an exponential law; Zone: II) polymer in the high-elastic state; Zone: III) liquidlike molten polymer (in this region, when the temperature is raised, pyrolysis takes place); Zone: IV) extremely fine drops formed as a result of fragmentation of molten polymer; Zone: V) gaseous state of decomposition products. Zones IV and V can be distinguished only by analyzing the composition of the products of these zones. It can be seen from Figure 17 that for Group A polymers, we can clearly distinguish zones of breakdown, and even determine their widths.

Group B polymers are those that form a char layer when exposed to a laser beam. These are generally thermosetting aromatic polymers (polybenzimidazole, polycyanurates, polyphenylenes, etc.), and certain thermoplastics that are capable of cross-linking when heated (polyphenylene oxide, polyphenylquinoxaline, polyarylate, etc.), these polymers subsequently behaving in the same manner as thermosetting plastics - i.e., they form a char layer in a laser beam. Group B polymers usually do not melt when irradiated (their cross-linking temperature is below or close to the softening point). For such polymers, along with the formation of a char layer, the processes of breakdown and cross-linking may be accompanied by ablation of oligomeric products from the surface. The behavior of Group B polymers can be followed in Figure 17. When they are exposed to laser radiation, zones II, III, and IV are either completely absent or are considerably narrowed, and the transition through their temperatures takes place within very short intervals of time.
The third group of polymers (Group C) consists of polymers that ablate without any residue. The mechanism of such a process may be depolymerization, complete breakdown to gaseous products, or carry off of the polymer in the form of individual fragments of the chain (oligomers) and precipitation of these fragments on cold surfaces close to the point of laser application.

3.5.1 Ablation Mechanisms of Polymers

Ablation of polymers occurs by either photothermal, photochemical, photophysical or the combination these processes which are described by various models. In photothermal process, the electronic excitation is thermalized on a picosecond (ps) timescale that then results in thermal bond breaking [62] [63]. In photochemical process, electronic excitation results in direct bond breaking [64] [65]. The photophysical process involves both thermal and non-thermal processes. Two independent channels of bond breaking [66] [67] or different bond breaking energies for ground-state and electronically excited-state chromophores are applied in this model. It is most adequate for short laser pulses in the picosecond and femtosecond timescales [68].

A new coarse-grained chemical reaction model (CGCRM) has been proposed by Garrison and coworkers [69] [70]. In this model a kinetic Monte Carlo approach that includes a probabilistic element is used to predict when reaction occurs. The CGCRM uses known chemical reactions along with their probabilities and exothermicities for a specific material to estimate the effect of chemical reaction on the ablation process. Mechanical stresses and pressure are dominant for very short pulses in the stress confinement regime and can
initiate ablation by a mechanical breakdown of the polymer in the case of pure heating. For longer pulse lengths, the ejection process is mainly thermally activated. This can be well described with thermal models based on thermally activated bond breaking processes. The presence of small molecules and gaseous products cannot be accounted for by a purely thermal mechanism. A modeling of the photoablation channels requires a two-step ablation model, which incorporates the effect of photolysis of the polymer and the creation of new species, that is then followed by a thermally activated removal step.

Although laser ablation of polymers has been researched for the past two decades, there are still several challenges that have yet to be addressed. For instance, there are several models and simulations that try to explain ablation mechanism at the laser-material interaction zone that results in the etching of the material. These models tend to explain the physics phenomenon such as absorption, reflectivity, optical excitation, thermal and chemical reactions to refer to the ablation occurring at the laser-material interaction. However, it is difficult for a systematic way to explain the ablation mechanism of these phenomena. Some models assume the ablation occurs purely due to thermal reactions occurring due to laser irradiation while other models suggest chemical reactions are dominant. A single model cannot explain the ablation in different materials because the mechanism of ablation depends on the type of laser and the materials properties [40].
Chapter 4: Laser Beam Modes and Numerical Simulation of Thermomechanical Behavior

As discussed in the previous sections, laser ablation or laser material processing offer high energy concentrations, a variety of temporal and spatial distributions and fast processing times. To maximize these advantages, the study of the final quality of the processed materials is essential. The quality of the processed materials is highly influenced by various laser parameters, including laser power, moving speed, beam radius, and beam shape. Moreover, high local heating and cooling rates during the laser processing results in high thermal stress field in the treated region which may affect long term mechanical performance. The optimal processing of laser power and moving speed has been the focus of considerable interest. A growing body of theoretical and experimental work has also explored the spatial structure of the laser beam modes in the areas of modern optics and laser physics [71] [72] [73]. However, one area that has received little quantitative attention is the effects of laser beam spatial distribution or modes on the thermomechanical behavior of the substrate material.

Considerable research studies were carried out to examine laser heating of surfaces and thermal stress formation. Analytical solution for laser pulse heating and thermal stress field developed was investigated by Yilbas and Aqeeli [74]. They demonstrated that internal energy gain dominated the conduction losses from the surface vicinity and the thermal stress levels attained high values in the surface region, which was compressive. Yao Lu et al. [75] developed a theoretical model of nanosecond laser removal of the paint layer on a
ferrous (Fe) substrate. The model predicted the theoretical cleaning and damage threshold based on the mechanism of thermal stress. Figure 18 and Figure 19 shows the results of the theoretical model. Plastic deformation during laser heating of a metal plate was studied by Chen et al. [76]. They showed that the plastic zone outspreaded gradually and crossed the depth of the metal plate. Laser heating of aluminum surfaces and thermal stress analysis was carried out by Yilbas et al. [77]. They demonstrated that the high heating and cooling rates resulted in high von Mises stress levels in the surface region. The residual stress analysis for laser treated Inconel 718 nickel-base superalloy was carried out by Liu et al. [78]. They indicated that the residual thermal stress was unevenly distributed in the treated workpiece, which was influenced by the recrystallization during solution annealing treatment.

Laser multi-beam heating of moving steel sheet and thermal stress analysis was carried out by Shuja and Yilbas [79]. Figure 20 shows their FEM model. Their findings revealed that presence of multi-spots at the surface modified temperature and stress fields in the heated region, which was more pronounced with increasing intensity at their radiated spots. Figure 21 and Figure 22 summarize their results in terms of temperature and von Mises stress distribution in steel plate. Laser heating of sheet metals and thermal stress development in their radiated region was studied by Khan et al. [80]. They demonstrated increasing laser scanning speed reduced temperature in the region away from the center of the laser heat source. In addition, the stress components were compressive in the region close to the source; however, it became tensile in the region away from the heat source. The stress measurements of laser-processed carbon fibre reinforced plastics (CFRP) were
carried out by Muramatsu et al. [81]. They showed that the stress levels changed in their radiated regions when the laser treatment parameters changed.

Figure 18: Temperature Vs laser fluence of (a) paint layer (b) substrate ([75])

Figure 19: Thermal stress Vs laser fluence of (a) paint layer (b) substrate ([75])
Figure 20: Model of laser heating of steel plate ( [79] )

Figure 21: Temperature contour for laser heating of steel plate ( [79] )

Figure 22: von Mises stress contours for laser heating of steel plate ( [79] )
While most studies of laser-material interaction modeling have adapted a Gaussian laser beam shape for simplicity [82] [83] [84] [85], one often finds several different laser beam shapes, called Transverse Electromagnetic (TEM) modes [86], in real applications. Figure 23 shows the heat source distribution of various transverse electromagnetic modes. This is because of the following reasons. First, even in an accurately aligned cavity, some waves travel off-axis as they bounce back and forth, due to the effects of diffraction [87] [88]. Second, there is considerable scattering loss that results from scratches on the reflective surface. Therefore, the effect of different TEM modes on the substrate material needs to be evaluated. In the present research work, four different beam shapes namely TEM\(_{00}\), TEM\(_{01}\), TEM\(_{11}\), and Top-hat are considered and their temporal distribution is studied. These beam shapes have been chosen due to their popularity as commercially available lasers.

![Power density profile across diameter of beam](image)

**Figure 23:** Heat source distribution of various transverse electromagnetic modes (89)

The general formula of TEM modes proposed by Enderlein and Pampaloni [90] are modified for all cases to have the same laser power since the definition of the beam radius is different for each case. Out of the four different laser beam modes, the gaussian (TEM\(_{00}\)) and super-gaussian (Top-Hat) were then selected and their effect on the thermomechanical
behavior of the substrate material is evaluated and compared by simulating laser-material interaction in COMSOL Multiphysics commercial finite element package.

4.1 Mathematical Model of Various Laser Beam Modes

4.1.1 Fundamental Gaussian Beam Mode (TEM$_{00}$)

By solving the Paraxial Helmholtz equation [91] [87], the complex amplitude $U(r)$ of the Gaussian Beam is expressed as:

$$U(r) = A_0 \frac{W_0}{W(Z)} \exp\left[\frac{-\rho^2}{W(Z)^2}\right] \exp\left[-jkz - jk \frac{\rho^2}{2R(Z)} + j\xi(Z)\right]$$  \hspace{1cm} (4.1)

Where,

$$W(Z) = W_0 \sqrt{1 + \left(\frac{Z}{Z_0}\right)^2} \quad \text{Beam waist radius at distance "Z".}$$

$$R(Z) = Z \left[1 + \left(\frac{Z_0}{Z}\right)^2\right] \quad \text{Raileigh range}$$

$$W_0 = \sqrt{\frac{\lambda Z_0}{\pi}} \quad \text{Beam waist radius}$$

$$\xi(Z) = \tan^{-1}\left(\frac{Z}{Z_0}\right)$$

The optical Intensity $I(r) = U(r)^2$ of the Gaussian Beam is a function of the axial and radial positions, $Z$ and $\rho = \sqrt{x^2 + y^2}$, respectively and it is expressed as:
The optical intensity \( I(r) \) of a Gaussian Beam in terms of the laser power \( P \) is expressed as:

\[
I(\rho, Z) = \frac{2P}{\pi W(Z)^2} \exp\left[-\frac{2\rho^2}{W(Z)^2}\right]
\]  

(4.2)

Figure 23 shows the normalised Gaussian Beam intensity as a function of radial distance \( \rho \) at different axial distances \( Z \). Equation (4.3) is the mathematical expression for TEM\(_{00}\) Gaussian Beam profile. Figure 24(a) shows the Gaussian Beam profile generated in COMSOL based on Equation (4.3).

### 4.1.2 Higher Order Gaussian Beam Mode (TEM\(_{01}\))

The Gaussian beam is not the only beam-like solution of a Paraxial Helmholtz equation [88][86]. Of particular interest are solutions that exhibit non-Gaussian intensity distributions but share the wave fronts of the Gaussian Beam [91][87]. These solutions are called the Hermite Polynomial or Hermite-Gaussian functions and is expressed as:

\[
U_{lm}(x, y, z) = |A_{lm}| \left[\frac{W_0}{W(Z)}\right] G_l \left[\frac{\sqrt{2X}}{W(Z)}\right] G_m \left[\frac{\sqrt{2Y}}{W(Z)}\right] \exp\left[-jkz - jk\frac{x^2+y^2}{2R(Z)} + j(l+m+1)\xi(Z)\right]
\]  

(4.4)
Where,

\[ G_l(u) = H_l(u) \exp\left(\frac{-u^2}{2}\right), l = 0, 1, 2, ... \]

Equation (4.4) is known as the Hermite-Gaussian function of order “l” and \( A_{l,m} \) is a constant. Since \( H_0(u) = 1 \), the Hermite-Gaussian function of order “0” is simply the fundamental Gaussian function. Continuing to higher order, \( G_1(u) = 2u\exp(-u^2/2) \) is an odd function, \( G_2(u) = (4u^2 - 2)\exp(-u^2/2) \) is even, \( G_3(u) = (8u^3 - 12u)\exp(-u^2/2) \) is odd and so on. These functions are displayed schematically in Figure 24.

The optical intensity \( I(r) \) of HG\(_{l,m}\) order Hermite-Gaussian Beam is expressed as:

\[
I_{l,m}(x, y, z) = \left| A_{l,m} \right|^2 \left[ \frac{W_0}{W(z)} \right]^2 G_l^2 \left[ \frac{\sqrt{2X}}{W(z)} \right] G_m^2 \left[ \frac{\sqrt{2Y}}{W(z)} \right] \quad (4.5)
\]

For HG\(_{01}\) = TEM\(_{01}\); For \( l = 0 \), \( G_l = G_0(u) = \exp(-u^2/2) \) and for \( m = 1 \), \( G_m = G_1(u) = 2v\exp(-v^2/2) \) and for \( Z = 0 \); \( W(Z) = W_0 \). Hence, equation (4.5) will be expressed as:

\[
I_{l,m}(x, y, z) = \frac{2P}{\pi W(z)^2} \left[ \frac{\sqrt{2X}}{W(z)} \right] \left( \exp\left[\frac{-x^2}{2}\right] \right)^2 \left[ \frac{4Y^2}{W(z)^2} \right] \left( \exp\left[\frac{-y^2}{W(z)^2}\right] \right)^2 \quad (4.6)
\]

Equation (4.6) is the mathematical expression for TEM\(_{01}\) Beam profile. Figure 24(b) shows the TEM\(_{01}\) Higher-order Gaussian Beam profile generated in COMSOL.
4.1.3 Higher Order Gaussian Beam Mode (TEM$_{11}$)

For HG$_{11} = $ TEM$_{11}$; For $l = 1$, $G_l = G_l(u) = 2u \exp(-u^2/2)$; for $m = 1$, $G_m = G_1(u) = 2v \exp(-v^2/2)$. Hence, equation (4.5) will be expressed as:

$$I_{l,m}(x, y, z) = \frac{P}{2 \pi w(Z)^2} \left[ \frac{8x^2}{w(Z)^2} \right] \exp \left( -\frac{2x^2}{w(Z)^2} \right) \left[ \frac{8y^2}{w(Z)^2} \right] \exp \left( -\frac{2y^2}{w(Z)^2} \right)$$ (4.7)

Equation (4.7) is the mathematical expression for TEM$_{11}$ Beam profile. Figure 24(c) illustrates the dependence of the intensity on the normalized transverse distances $u = \frac{\sqrt{2x}}{w(Z)}$ and $v = \frac{\sqrt{2y}}{w(Z)}$ for several values of “l” and “m”. Figure 24(c) shows the TEM$_{11}$ Higher-order Gaussian Beam profile generated in COMSOL based on equation (4.7).

4.1.4 Super-Gaussian (Top-Hat) Beam Profile

The heat generated by a super-Gaussian profile (i.e., a smoothed Top-Hat profile) of transverse optical intensity of order “n” [91] [92] can be given as:

$$Q(r) = Q_0 \exp \left[ -2 \left( \frac{r}{w_0} \right)^n \right]$$ (4.8)

Where, $Q_0$ is the peak intensity, $w_0$ is the beam radius over the incident surface, and $r$ is the radial distance from the propagation axis. A conventional Gaussian profile results from a super-Gaussian one of order two; the higher the order, the steeper the edges of the profile [93]. A super-Gaussian intensity profile of “order 20” was implemented [94] [95] as shown.
in Figure 24(d), based on actual data acquisition via beam profiler [101]. Under this assumption and for “P” denoting the operating power, the peak intensity in Equation (4.8) approaches:

\[ Q_0 = \frac{P}{\pi W_0^2} \]  

(4.9)

With \( x_0 \) and \( y_0 \) being the coordinates of the starting point of the beam path, a heat source was implemented in a Cartesian coordinate system, hence Equation (4.8) yielding:

\[ Q(x, y) = \frac{P}{\pi W_0^2} \exp \left( \frac{-2[(x-x_0)^2 + (y-y_0)^2]}{W_0^2} \right) \]  

(4.10)

Equation (4.10) is the mathematical expression for Top-Hat Beam profile. Figure 24(d) shows the Top-Hat (Super-Gaussian) Beam profile generated in COMSOL based on equation (4.8):

(a)
Figure 24: Beam profile in COMSOL for beam waist radius $W_0 = 1.5$mm, (a) TEM$_{00}$ (b) TEM$_{01}$ (c) TEM$_{11}$ (d) Top-Hat (Super-Gaussian beam)
4.2 Mathematical Model of Heat Transfer and Thermal Stresses

4.2.1 Model for Heat Transfer Analysis

The heat transfer mechanism of a solid irradiated by a laser beam was discussed in detail in Section 3.2 of this thesis. Accordingly, the governing heat conduction in the solid is defined by following equation:

\[ \rho C_p \frac{\partial T}{\partial t} = K_T \nabla^2 T + A_v I(x, y, z, t) \]  \hspace{1cm} (4.11)

Where, \( \rho \) is the density, \( C_p \) is the heat capacity, \( T \) is the temperature, \( K_T \) is the thermal conductivity, \( A_v \) is the absorption coefficient and \( I(x, y, z, t) \) is the optical intensity of a laser beam. The term \( A_v I(x, y, z, t) \) represent the laser heat generation. If we include the terms for the heat dissipated by convection and radiation [96], equation (4.1) takes the form as below:

\[ \rho C_p \frac{\partial T}{\partial t} - K_T \nabla^2 T = A_v I(x, y, z, t) + \frac{h_{\text{trans}}}{dA} (T_{\text{ext}} - T) + \varepsilon \sigma (T_{\text{amb}}^4 - T^4) \]  \hspace{1cm} (4.12)

Where, \( h_{\text{trans}} \) is the heat transfer coefficient, \( \varepsilon \) is the emissivity, \( \sigma \) is the Stefan-Boltzman constant. Taking into consideration the temperature dependence of the thermophysical parameters \( \rho, C_p, K_T \) and of the optical parameter, \( A_v \), of the metal sample makes equation (4.11) non-linear. The general non-linear heat conduction equation taking into account the above-mentioned variation is obtained as below:
\[ \rho(T)C_p(T) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( K_T(T) \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_T(T) \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_T(T) \frac{\partial T}{\partial z} \right) \]  

(4.13)

With boundary and initial condition as:

\[ K_T(T) \frac{\partial T}{\partial Z_{z=0}} = -A_v(T) I(r, t) \]

\[ T(\pm\infty, y, z, t) = T(x, \pm\infty, z, t) = T(x, y, \pm\infty, t) = T(x, y, z, 0) = T_0 \]

Here \( T_0 \) is the initial temperature which is assumed to be the ambient temperature. The described model is applicable if there is no phase transition or other substantial surface changes i.e. for temperature profile remains below the melting point. At present we are only interested in thermomechanical behavior of laser heating of a substrate with paint material. Therefore, we shall apply the above assumptions and use the heat transfer equation in our numerical simulation.

### 4.2.2 Material Model for Thermal Stress Analysis

Assuming the elastic behavior, the increment in Cauchy stress (\( \Delta T \)) over an incremental time \( \Delta t \) is given as a linear isotropic function of the spatial elastic rate of deformation \( D^e \).

The following evolution equation can be written [75] [97]:

\[ \Delta T = \mathcal{L}^e [D^e \Delta t - \varepsilon^{th}] \]  

(4.14)
Where, \( \mathcal{L}^e \) is the elastic isotropic moduli and \( \varepsilon^{th} \) is the strain vector defined as follow:

\[
\varepsilon^{th} = \alpha_e \Delta T = \alpha_e (T - T_{ref})
\]  

(4.15)

where \( \Delta T \) represents the temperature rise at a point \((x, y, z)\) at time \(t\) with respect to that at \(t = 0\) corresponding to a stress-free condition, and \(T_{ref}\) is the reference temperature at \(t = 0\). When \( \alpha_e \) is a function of temperature, then Equation (4.15) becomes:

\[
\varepsilon^{th} = \int_{T_{ref}}^{T} \alpha_e(T) \, dT
\]  

(4.16)

Since there is no surface traction involved in the problem under consideration, the corresponding initial and boundary conditions can be written as:

Initial Condition:
At time \(t = 0\), the substrate material is free from any stress i.e. At \(t = 0 \rightarrow \sigma_{\text{Surface}} = 0\)

Boundary conditions:
The surface of the substrate material is considered to be free to expand and there are no forces acting at the surface at any time of the heating process (stress free surface), i.e.
At \(x = 0\) (at the surface) \(\rightarrow \sigma_{\text{Surface}} = 0\)
And at the far distance away from the irradiated region, the substrate material is free from any stresses at any time of the heating process (stress-free body at infinity) i.e.
At \(x = y = z = \infty \rightarrow \sigma = 0\)
4.2.3 Beer-Lambert Law of Energy Absorption by Paint Layer

The process of a plate of homogeneous and isotropic material absorbing a monochromatic and parallel laser beam of incident power density $I_0$ can be described by the Beer-Lambert Law [98]:

$$I = I_0 e^{-A_V Z}$$

(4.17)

where $I$ is the depth dependent laser intensity and $I_0$ is the surface laser intensity of different laser beam modes as defined in section 4.1 and $A_V$ is the spectral linear absorption coefficient (cm$^{-1}$) of the material at laser wavelength.

4.3 Material Properties for Numerical Simulation

4.3.1 Epoxy Paint Coating

In the present research, epoxy paint is used as it is widely used in industry because of its excellent chemical and water resistance and good adhesion to aluminum alloy. Moreover, it is a standard aerospace paint material whose mechanical and thermal properties are well documented in the literature [99] [100] [101] and tabulated here in Table 3. FTIR spectroscopy of epoxy paint was carried out [102] to measure the absorption coefficient ($A_V$) and the value comes out to be 14.9x10^2 (cm$^{-1}$).
Table 3: Thermal properties of epoxy paint

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Heat ($C_p$)</td>
<td>1180</td>
<td>J/(kg*K)</td>
</tr>
<tr>
<td>Thermal Conductivity ($K$)</td>
<td>0.2</td>
<td>W/(m*K)</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion ($\alpha I$)</td>
<td>$55 \times 10^{-6}$</td>
<td>[1/K]</td>
</tr>
<tr>
<td>Density ($\rho$)</td>
<td>1800</td>
<td>Kg/m$^3$</td>
</tr>
<tr>
<td>Absorption Coefficient ($A_V$) at 10.6μm Wavelength</td>
<td>$14.9 \times 10^2$</td>
<td>(cm$^{-1}$)</td>
</tr>
</tbody>
</table>

4.3.2 2024-T3 Alclad Substrate Laminate

The material specifications of Alclad 2024-T3 are as per the AMS 4041T standard [103]. The mechanical tests are performed and the mechanical properties of Alclad 2024-T3 are derived in the FAA technical report CT-93/43 [104]. These properties are tabulated in Table 4 and the temperature dependant thermal properties are tabulated in Table 5.

Table 4: Mechanical properties of 2024-T3 Alclad

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1265</td>
<td>Kg/m$^3$</td>
</tr>
<tr>
<td>Tensile Yield Strength</td>
<td>373.69</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile Ultimate Strength</td>
<td>458.50</td>
<td>MPa</td>
</tr>
<tr>
<td>Modulus</td>
<td>61.36</td>
<td>GPa</td>
</tr>
</tbody>
</table>
**Table 5:** Temperature dependent thermal properties of 2024-T3 Alclad

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Cp [J/(Kg*K)]</th>
<th>K [W/(m*K)]</th>
<th>α [1/Kx10^{-5}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>470</td>
<td>164</td>
<td>1.4</td>
</tr>
<tr>
<td>400</td>
<td>484</td>
<td>182</td>
<td>2.3</td>
</tr>
<tr>
<td>500</td>
<td>521</td>
<td>194</td>
<td>2.45</td>
</tr>
<tr>
<td>600</td>
<td>607</td>
<td>202</td>
<td>2.52</td>
</tr>
<tr>
<td>700</td>
<td>773</td>
<td>210</td>
<td>2.56</td>
</tr>
<tr>
<td>770</td>
<td>800</td>
<td>220</td>
<td>2.66</td>
</tr>
</tbody>
</table>

### 4.4 Properties of TEA CO₂ Laser for Numerical Simulations

Compared to other lasers, TEA CO₂ laser has a distinct advantage in terms of high efficiency, high peak power and higher absorption coefficient [105] for most of the paints. The higher absorption of CO₂ laser energy by the epoxy paints makes this the ideal choice for paint stripping. Therefore, in this research work TEA CO₂ lasers have been used for the numerical simulation and the properties of which are listed in Table 6 and Figure 25 shows the pulse generation using analytical function with periodic excitation in COMSOL. The simulation is run for total 10 milliseconds.
Table 6: Properties of TEA CO$_2$ laser

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength ($\lambda$)</td>
<td>10.6</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Laser Power ($W$)</td>
<td>2000</td>
<td>Watt</td>
</tr>
<tr>
<td>Pulsed Width</td>
<td>200</td>
<td>Microseconds ($\mu$s)</td>
</tr>
<tr>
<td>Beam Waist Radius ($W_0$)</td>
<td>1.5</td>
<td>mm</td>
</tr>
</tbody>
</table>

Figure 25: Analytic function in COMSOL to depict pulse train

4.5 Modeling in COMSOL

Two different finite element models were prepared for the numerical simulation of thermomechanical behavior of laser heating: one model is a 2D model with 2024-T3 Alclad as a substrate material for analyzing the heat affected zone (HAZ). The other model is a 3D model with 2024-T3 Alclad as a substrate material for analyzing temperature and
thermal stress distribution. For both models, the paint coating on the substrate material was epoxy paint.

COMSOL Multiphysics is used for modeling of laser heating and subsequent thermo-mechanical behavior of a substrate with paint material. COMSOL has a unique capability to model very thin layered material via “Layered Shell” interface. The “Heat Transfer in Layered Shell” interface is used for generating laser heat source and simulating heat transfer as per Equation (4.13). A two-dimensional square plate with dimension: 100 mm (L) x 100 mm (W) is modeled. For the model with alclad 2024-T3 Alclad as a substrate material, the thickness of the plate is defined by bottom layer of Al2024-T3 (0.82 mm thickness), then a layer of aluminum cladding (38.1 μm thickness) and the top layer of epoxy paint (80 μm thickness) with the total thickness of 0.9381 mm. The following boundary condition adopted for heat transfer in COMSOL: Inward heat flux applied at the top surface, heat dissipated by convection and radiation at the top surface and the edges are insulated. Layered cross section preview for 2024-T3 Alclad substrate with epoxy paint layer is shown in Figure 26 and Figure 27 shows the meshed geometry in COMSOL. The multi-physics capacity of COMSOL is used for running multiple physics together. Here we run the model for coupled “Heat Transfer in Layered Shell” and “Structural Mechanics” physics to get the deformation, stresses, and temperature distribution.
Figure 26: Layered cross-section preview - 2024-T3 Al clad with epoxy paint

Figure 27: Meshed geometry in COMSOL
4.6 Simulation Results and Discussion

Transient time-dependent coupled Heat Transfer and Thermal Stress analysis was performed in COMSOL with the above-mentioned material properties, pulsed laser properties and specified initial and boundary conditions. The results of the simulation are summarized in the following section in terms of temperature distribution, surface thermal stresses, through thickness stresses and heat affected zone (HAZ) for both the Gaussian and Top-Hat beam profiles.

4.6.1 2024-T3 Alclad with epoxy Paint

Narsollahi et al. [72] studied the effect of heat affected zone for the laser drilling of hole in silicon nitride. They compared the Heat Affected Zone (HAZ) for Gaussian and Top-Hat beams. Figure 28 shows the comparison of HAZ. It is evident that the fluence of the tail of the Gaussian beam is lower than the ablation threshold and it is sufficient only to heat the surrounding surface without any ablation. In contrast, the fluence of the Top-Hat beam can be tailored at the beam spot and thus can be maintained above the ablation threshold to minimize the size of the HAZ. Figure 29 and Figure 30 shows the HAZ in the Alclad Al2024-T3 without epoxy paint for the laser heating with Gaussian and Top-Hat beam profile. Note that for the Top-Hat beam, the temperature immediately surrounding the beam spot is 310 K whereas for the Gaussian beam, the temperature surrounding the beam spot is 330 K. Also, note that the HAZ inside the substrate material reaches a greater depth in the case of the Gaussian beam as compared to the case of Top-Hat beam.
Figure 28: Effect of (a) Gaussian and (b) Top-Hat beams on HAZ (72)

Figure 31, Figure 32, Figure 35 and Figure 36 shows the temperature distribution at the surface of the epoxy paint for the Gaussian and Top-Hat beam profile respectively. Note that after 10 milliseconds, the surface temperature is 400 K in case of Gaussian beam pulse and 320 K in case of Top-Hat beam pulse. This is the evident that Gaussian beam has the fastest stabilized time as compared to the Top-Hat beam. Figure 33, Figure 34, Figure 37 and Figure 38 shows the surface von Mises stresses both as an absolute value and as a percentage of yield strength of Al clad Al2024-T3 for the Gaussian and the Top-Hat beam profiles. Note that the thermal stresses are highest at the surface and decreases through the thickness of the laminate. Also, the value of surface thermal stress for the Gaussian beam pulse is 30 MPa (8% of the yield strength) whereas for the Top-Hat beam pulse the value is 8 MPa (2% of the yield strength) after 10 milliseconds. This is evident that the Top-hat beam profile generates less thermal stress on the surface and into the substrate material as compared to the Gaussian beam profile.
Figure 29: Effect on HAZ for 2024-T3 Alclad substrate: (a) Gaussian (b) Top-Hat beam
Figure 30: Contour plot of effect on HAZ - 2024-T3 Alclad substrate: (a) Gaussian (b) Top-Hat beam
Figure 31: Temperature distribution – 2024-T3 Al clad – Gaussian Beam: (a) 2 millisecond (b) 4 millisecond
Figure 32: Temperature distribution – 2024-T3 Al clad – Gaussian Beam: (a) 7 millisecond (b) 10 millisecond (Inset: distribution around the laser spot)
Figure 33: Surface von Mises stress distribution at 7 millisecond – 2024-T3 Alclad – Gaussian beam:

(a) absolute value (MPa) (b) percentage of Yield Strength (%)
Figure 34: Surface von Mises stress distribution at 10 millisecond – 2024-T3 Alclad – Gaussian beam:

(a) absolute value (MPa) (b) percentage of Yield Strength (%)
Figure 35: Temperature distribution – 2024-T3 Alclad – Top-Hat beam: (a) 2 millisecond (b) 4 millisecond
Figure 36: Temperature distribution – 2024-T3 Al clad – Top-Hat beam: (a) 7 millisecond (b) 10 millisecond (Inset: distribution around the laser spot)
Figure 37: Surface von Mises stress distribution at 7 millisecond – 2024-T3 Alclad – Top-Hat beam:

(a) absolute value (MPa) (b) percentage of Yield Strength (%)
Figure 38: Surface von Mises stress distribution at 10 millisecond – 2024-T3 Alclad – Top-Hat beam:

(a) absolute value (MPa) (b) percentage of Yield Strength (%)
Chapter 5: Experimental Characterization of Substrate Material

Most of the work on laser ablation for paint removal has been focused on effectiveness in terms of cleanliness and removal rate, with examination of the effects of laser parameters, like laser power density, scanning speed and pulse width to achieve a high degree of cleanliness with a good removal rate. Though such studies have a potentially high industrial value, it is also important to understand the effect of laser paint removal on the underlying substrate before one can replace existing paint removal methods. A limited number of studies focused on the possible effects of laser ablation on the underlying substrate [106] [107] [108], and these studies raised a number of possibilities related to near surface melting: reduction in surface roughness resulting in reduced subsequent coating adhesion and degradation of fatigue performance due to near surface tensile residual stress introduced during melting and re-solidification.

The influence of laser paint removal process on metal substrate has also been studied [109] [110] [111]. For instance, Shamsujjoha M et al. [112] [113] used a 1064 nm Nd:YAG nanosecond laser pulse to remove the red epoxy paint from a high strength steel used in shipbuilding. The effects of laser parameters on surface roughness, microstructure, hardness, repainting adhesion, residual stress state and fatigue properties of the underlying substrate material (carbon steel) were studied. The results showed that the underlying metal substrate was melted and re-solidified. The melting depth was 1–5 μm. The surface appearance had visibly changed. The adhesion of the repainted samples subjected to laser ablation coating removal (LACR) was comparable or even superior to that of the abrasive blasted and repainted samples. The residual stress was typically $242 \pm 63$ MPa in tension.
and confined to the shallow depth of ~35 μm. Fatigue tests confirmed that the LACR-treated samples performed just as well as abrasive blasted samples. Guodong Zhu et al. [114] used an Nd: YAG laser with 1064 nm wavelength to remove BMS10-11 paints from the surface of the Boeing series aircraft skins. The effects of laser energy density on the surface depainting effect, surface morphology, friction and wear properties, microhardness and residual stress and corrosion performance were investigated. The results showed that after laser depainting, the aircraft skin surface produced a certain plastic deformation and hardened, increasing the residual tensile stress. Pantelakis et al. [108] conducted a detailed study on the effect of paint stripping processes, including laser radiation and plasma etching, on the mechanical behavior of the widely used structural aluminium alloy 2024-T351. The mechanical properties studied were tensile properties, fracture toughness and fatigue life. It was found that although there appears to be no significant effect on yield strength and ultimate tensile strength, the tensile ductility and fracture toughness degrade considerably. On the other hand, fatigue life was extended, but no experimental explanation was offered for the observed behaviour.

Alclad sheets are formed from high-purity aluminum surface layers metallurgically bonded (rolled onto) to high-strength aluminum alloy core material and are very common for its high corrosion resistance. However, the effect of laser paint removal process on 2024-T3 Alclad substrate is not studied so far. The aim of the present research is to study in detail the effects of laser ablation of paint on the fatigue life, failure pattern, surface topology and surface hardness of 2024-T3 Alclad substrate by performing various experimental tests.
5.1 Fatigue Testing and Fatigue Life Evaluation

Fatigue is a localized damage process produced by cyclic loading, consisting of crack nucleation, propagation, and final failure. The fatigue failure of a material is dependent on the interaction of a large stress with critical flaws or discontinuities. Since fatigue cracks almost always nucleate at a free surface, any surface condition and treatment can have significant effect on fatigue life [115]. At low applied stresses or high cycle fatigue, the crack nucleation and early (short) crack growth period dominates the fatigue life and, therefore, factors such as surface finish and treatment become even more influential [116] [117] [118]. The presence of a clad/anodized layer and residual stresses has proven to be the controlling factors for crack nucleation of aluminum alloys [119]. Therefore, the exposure of the metal surface to laser treatment could override, suppress or enhance detrimental surface conditions.

The importance of fatigue in aerospace structural design suggests the need for addressing the effect of the novel de-coating method (such as laser stripping) on fatigue behavior. During the normal lifespan of an aircraft, many cycles of de-painting and re-painting steps are performed to prevent corrosion or any surface deterioration and to enable necessary inspections for cracks and other surface damage [120]. It is imperative to determine the effects of any potential paint stripping method on mechanical properties, in particular, the fatigue behavior of substrate material because the danger it poses to aircraft which is outlined in FAA AC 25.571 [121] in terms of fatigue damage tolerance.
5.1.1 Test Equipment and Specimen Geometry

An MTS uniaxial load frame with the capacity of 15 kN was used to perform fatigue testing. The experimental/fatigue test set up is shown in Figure 39(a). The dimensions of the fatigue test coupons were selected as per SAE 4872A standard [122] with double sided shallow U-notches as shown in Figure 39(b). The stress concentration factor with the notched geometry is calculated by referring to Paterson’s stress concentration factors by Pilkey [123] and found to be equal to $K_t = 1.4$. The specimen design was modified from the SAE standard to ensure consistent and repeatable initiation and propagation of fatigue cracks. Total of five coupons at each stress level for each strip schemes are tested.

![Figure 39: (a) Fatigue test set up with MTS uniaxial load frame (b) Geometry of notched coupon for the fatigue test (all dimensions are in mm)](image-url)
5.1.2 Material Specifications and Preparation of Test Coupons

Section 5.4 in SAE 4872A standard [122] dictates the use of 2024-T3 Alclad alloy with un-coated thickness of 0.82 mm including cladding for performing fatigue testing. The material specifications of 2024-T3 Alclad are as per AMS 4041T standard [103] and according to this, the cladding thickness adopted is 38.1 μm. The paint system is according to ANNEX A of SAE 4872A standard which consists of a layer of MIL-P-23377 epoxy primer and a layer of MIL-C-85285 polyurethane enamel. Figure 40 shows the schematic of fatigue test coupons with layers of coatings and cladding. Stripping of paint was performed following the requirements listed in Section 4.0 of SAE4872A standard. First, 1000 mm (L) × 600 mm (W) 2024-T3 Alclad panels were prepared and applied with a paint system. Then the panels are stripped such that on one side of the panel, full stripping is achieved by removing both the paint and primer layers and on the other side of the panel, only paint is removed keeping the primer layer (Figure 42 (b)). Four different type of paint
stripping processes were adopted to prepare the stripped specimens, namely, chemical stripping (“Scheme D”), moderate laser stripping (“Scheme A”), aggressive laser stripping (“Scheme B”), light laser stripping (“Scheme C”) and uncoated-unstripped (“Scheme E”). Finally, the fatigue coupons with the dimensions according to Figure 40 were waterjet cut and then machined and polished to the required dimensions and surface finish. Figure 41 shows final fatigue coupons with different stripping schemes. TEA CO₂ laser with the wavelength of 10.6 μm [124] is used for laser stripping. Note that the laser travel direction was in the rolling direction. Figure 42 (a) shows the laser lab set up used for the stripping. Laser parameters such as beam power, beam radius and moving speed were varied to create the aggressive, moderate and light levels of laser stripping.

Figure 41: Test coupons with five different strip schemes after paint stripping
Figure 42: (a) Laser set up for stripping the paint. Scanning Electron Microscope (SEM) image showing (b) thickness of cladding on strip side (c) thickness of cladding and primer on the primed side
5.1.3 Design of Experiment – ASTM STP 588

It is very important to design an effective fatigue test program that not only accomplishes the major test objectives but also satisfies the specific test constraints involved [125] [126]. The fatigue experiments with statistically designed organizational structure is important and mandatory for test program with time and cost constraints. There are certain design of experiments fundamentals which must appear in planning and conduct of any competent experimental program. ASTM STP 588 [127] standard is referred to follow these fundamentals and to illustrate its application and importance on the fatigue testing conducted on stripped coupons. First, a well-designed experiment has a clearly organizational structure. Second, well-defined experiments employ clearly defined experimental units which are not only structured appropriately in blocks (planned groups), but upon which the desired treatments are applied following the procedure known as mechanical randomization. Third, carefully selected treatment levels and treatment combinations are employed such that the desired treatment effect estimates are not confounded with nuisance variables [128]. Finally, it was ensured that this experiment employed sufficient replication that is, provided sufficient specimens to ensure reasonably precise estimates of the desired treatment effects. Table 7 Shows the Randomised Complete Block (RCB) [126] organizational structure adopted for our fatigue testing program. In total, 75 coupons are tested at different stress levels (5 coupons per stress level for each strip scheme).
5.1.4 Fatigue Test Parameters

As per the SAE 4872A [122] standard, it is suggested to conduct fatigue testing under constant amplitude loading at a test frequency of 10 Hz with a stress ratio R=0.1 and at a minimum of three different maximum stress levels. The maximum stress level suggested for the un-notched coupons in the range of 200 to 350 MPa with the aim of producing failures of the control coupons at lives between $10^4$ and $5 \times 10^5$ cycles. For the notched specimens, material S-N curve for un-cladded Al2024-T3 alloy from the MIL-HDBK-5H [129] is referred for initial planning guidance. Figure 3.2.3.1.8(f) from the handbook is referred and three different stress levels namely High Stress, Moderate Stress and Low Stress are selected for current fatigue test program. Also, for the fatigue test program, the tests are conducted at a frequency of 20 Hz instead of 10 Hz as suggested by SAE 4872A.

<table>
<thead>
<tr>
<th>Block1</th>
<th>Treatment 1</th>
<th>Treatment 2</th>
<th>Treatment 3</th>
<th>Treatment 4</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block2</td>
<td>3(4)</td>
<td>2(5)</td>
<td>1(2)</td>
<td>4(1)</td>
<td>5(3)</td>
</tr>
<tr>
<td>Block3</td>
<td>7(5)</td>
<td>6(2)</td>
<td>10(1)</td>
<td>8(4)</td>
<td>9(3)</td>
</tr>
<tr>
<td>Block4</td>
<td>14(2)</td>
<td>11(3)</td>
<td>13(4)</td>
<td>12(1)</td>
<td>15(5)</td>
</tr>
<tr>
<td>Block5</td>
<td>19(2)</td>
<td>20(5)</td>
<td>18(4)</td>
<td>16(1)</td>
<td>17(3)</td>
</tr>
<tr>
<td>Block5</td>
<td>21(4)</td>
<td>23(2)</td>
<td>25(3)</td>
<td>22(1)</td>
<td>24(5)</td>
</tr>
</tbody>
</table>

* Random assignment of time order of test within each block (i).
* Total 25 number of specimens are tested for each stress level.
* The RCB organizational Structure as above is followed for each stress level testing
5.1.5 Fatigue Test Results and Statistical Analysis

The fatigue test results are summarized in Table 8 in terms of mean values and standard deviation for each strip schemes at three different stress levels. Data is used for detailed statistical analysis. A formal outlier test is performed on the fatigue test results to identify and remove any outliers. An outlier is an observation that appears to deviate markedly from other observations in the sample population [128]. If it can be determined that an outlying point is in fact erroneous, then the outlying value should be removed from further analysis. However, in some cases, it may not be possible to determine if an outlying value is bad data. Therefore, one does not want to simply delete the outlying observation and one may want to consider the use of robust statistical analysis techniques [130] [125]. Grubb’s outlier test [128] is performed on the fatigue test results and it is found that no outlier is detected in the test data.

The significance of strip schemes on the fatigue life of specimens are checked by performing one-way analysis of variance (ANOVA). A two-way ANOVA is also performed to check the interaction effect of the strip schemes and the stress levels on the fatigue life of specimens [131] [132]. With respect to ANOVA, fatigue life of the coupons is considered as a dependent variable and the strip schemes and stress levels are considered as the independent variables. Thus, the one-way ANOVA tells us whether there are statistically significant differences between the means of three or more independent groups or variables. According to the ANOVA hypothesis, all the means are equal, and the alternate hypothesis is that not all the means are equal and that at least one mean is different from the rest [125]. However, if the null hypothesis is rejected, the ANOVA test does not
### Table 8: Descriptive statistics of ANOVA

<table>
<thead>
<tr>
<th>Strip Schemes</th>
<th>Stress Level</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Nos. of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme A</td>
<td>High Stress</td>
<td>4.852</td>
<td>0.049</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.507</td>
<td>0.073</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.182</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.181</td>
<td>0.271</td>
<td>13</td>
</tr>
<tr>
<td>Scheme B</td>
<td>High Stress</td>
<td>4.889</td>
<td>0.025</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.406</td>
<td>0.152</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.156</td>
<td>0.082</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.15</td>
<td>0.237</td>
<td>15</td>
</tr>
<tr>
<td>Scheme C</td>
<td>High Stress</td>
<td>4.883</td>
<td>0.052</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.471</td>
<td>0.116</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.132</td>
<td>0.109</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.162</td>
<td>0.264</td>
<td>15</td>
</tr>
<tr>
<td>Scheme D</td>
<td>High Stress</td>
<td>4.9</td>
<td>0.041</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.494</td>
<td>0.105</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.104</td>
<td>0.073</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.166</td>
<td>0.265</td>
<td>15</td>
</tr>
<tr>
<td>Scheme E</td>
<td>High Stress</td>
<td>4.896</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.399</td>
<td>0.044</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.12</td>
<td>0.043</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.139</td>
<td>0.217</td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td>High Stress</td>
<td>4.886</td>
<td>0.044</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Low Stress</td>
<td>5.453</td>
<td>0.106</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Moderate Stress</td>
<td>5.139</td>
<td>0.072</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5.159</td>
<td>0.244</td>
<td>73</td>
</tr>
</tbody>
</table>
tell which specific means are different from the others. Therefore, post hoc analysis such as Tukey HSD test is performed to determine whether the difference in the means are statistically significant or not and if they are, then which specific means are different from others [133] [134]. The IBM SPSS Statistics software tool is used to perform the statistical analyses outlined in this thesis [135]. The formal outlier test and the ANOVA is performed assuming the log normal distribution of data. The homogeneity of variances, the most important assumption for ANOVA, is confirmed by performing Levene’s test on the fatigue test data [136]. Table 9 shows the summary of one-way ANOVA for the moderate stress, low stress, and high stress level test data respectively. Table 10 shows the summary of two-way ANOVA with the interaction effect of the strip schemes and the stress level. Summary of Tukey HSD post hoc analysis with multiple comparison between various strip schemes is shown in Table 11. Section 5.1.7 of this thesis discusses results of these statistical analysis results.

5.1.6 Fatigue Life S-N Curves

The S-N curves are generated by plotting the average values of fatigue log life on X-axis and normalized maximum stress levels on Y-axis as shown in Figure 43 and curve fitting is performed by taking a second degree of polynomial using regression analysis according to ASTM E739 standard [137].
<table>
<thead>
<tr>
<th></th>
<th>Sum of Squares</th>
<th>Degree of Freedom (Df)</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Moderate Stress Level Test Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between Groups</td>
<td>0.019</td>
<td>4</td>
<td>0.005</td>
<td>0.882</td>
<td>0.492</td>
</tr>
<tr>
<td>Within Groups</td>
<td>0.108</td>
<td>20</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.127</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Low Stress Level Test Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between Groups</td>
<td>0.047</td>
<td>4</td>
<td>0.012</td>
<td>1.042</td>
<td>0.412</td>
</tr>
<tr>
<td>Within Groups</td>
<td>0.215</td>
<td>19</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.262</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>High Stress Level Test Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between Groups</td>
<td>0.006</td>
<td>4</td>
<td>0.002</td>
<td>0.757</td>
<td>0.566</td>
</tr>
<tr>
<td>Within Groups</td>
<td>0.038</td>
<td>19</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.045</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 10: Two-Way ANOVA between-subjects effects

<table>
<thead>
<tr>
<th>Source</th>
<th>Type III Sum of Squares</th>
<th>Degree of Freedom (df)</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Sig.</th>
<th>Partial Eta Squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected Model</td>
<td>3.958(^a)</td>
<td>14</td>
<td>0.283</td>
<td>45.324</td>
<td>0.000</td>
<td>0.916</td>
</tr>
<tr>
<td>Intercept</td>
<td>1932.489</td>
<td>1</td>
<td>1932.489</td>
<td>309780.234</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Strip Scheme</td>
<td>0.014</td>
<td>4</td>
<td>0.004</td>
<td>0.571</td>
<td>0.684</td>
<td>0.038</td>
</tr>
<tr>
<td>Stress Level</td>
<td>3.903</td>
<td>2</td>
<td>1.951</td>
<td>312.822</td>
<td>0.000</td>
<td>0.915</td>
</tr>
<tr>
<td>Strip Scheme * Stress Level</td>
<td>0.057</td>
<td>8</td>
<td>0.007</td>
<td>1.144</td>
<td>0.349</td>
<td>0.136</td>
</tr>
<tr>
<td>Error</td>
<td>0.362</td>
<td>58</td>
<td>0.006</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1947.555</td>
<td>73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>4.320</td>
<td>72</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) R Squared = .916 (Adjusted R Squared = .896)
Figure 43: S-N curve of fatigue life for all strip scheme coupons

5.2 Fractography

Analysis of fractured surfaces of failed specimens is very important as it reveals the failure characteristics of the material and how it behaved under fatigue loading and crack propagation. Fatigue in metallic materials typically develops under three stages which are crack nucleation, crack propagation, and failure [138]. Crack nucleation is the spark of the fatigue mechanism. For example, some of the manufacturing processes such as machining leave tool traces or scars on the material surfaces and create crack nucleation sites. Crack nucleation generally starts at plastic strain accumulation regions such as sharp notches, scratches, nonmetallic inclusions or crack-like defects [139][119]. In the crack propagation stage, cyclic loading creates striations on the fracture surface which each indicate a period of crack propagation.
### Table 11: Tukey HSD multiple comparison

<table>
<thead>
<tr>
<th>(I) Strip Schemes</th>
<th>(J) Strip Schemes</th>
<th>Mean Difference (I-J)</th>
<th>Std. Error</th>
<th>Sig.</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower Bound</td>
</tr>
<tr>
<td>Scheme A</td>
<td>Scheme B</td>
<td>0.030</td>
<td>0.0299</td>
<td>0.845</td>
<td>-0.053</td>
</tr>
<tr>
<td></td>
<td>Scheme C</td>
<td>0.018</td>
<td>0.0299</td>
<td>0.970</td>
<td>-0.065</td>
</tr>
<tr>
<td></td>
<td>Scheme D</td>
<td>0.014</td>
<td>0.0299</td>
<td>0.988</td>
<td>-0.069</td>
</tr>
<tr>
<td></td>
<td>Scheme E</td>
<td>0.042</td>
<td>0.0299</td>
<td>0.625</td>
<td>-0.042</td>
</tr>
<tr>
<td>Scheme B</td>
<td>Scheme A</td>
<td>-0.030</td>
<td>0.0299</td>
<td>0.845</td>
<td>-0.114</td>
</tr>
<tr>
<td></td>
<td>Scheme C</td>
<td>-0.011</td>
<td>0.0288</td>
<td>0.994</td>
<td>-0.092</td>
</tr>
<tr>
<td></td>
<td>Scheme D</td>
<td>-0.015</td>
<td>0.0288</td>
<td>0.982</td>
<td>-0.096</td>
</tr>
<tr>
<td></td>
<td>Scheme E</td>
<td>0.011</td>
<td>0.0288</td>
<td>0.994</td>
<td>-0.069</td>
</tr>
<tr>
<td>Scheme C</td>
<td>Scheme A</td>
<td>-0.018</td>
<td>0.0299</td>
<td>0.970</td>
<td>-0.103</td>
</tr>
<tr>
<td></td>
<td>Scheme B</td>
<td>0.011</td>
<td>0.0288</td>
<td>0.994</td>
<td>-0.069</td>
</tr>
<tr>
<td></td>
<td>Scheme D</td>
<td>-0.004</td>
<td>0.0288</td>
<td>1.000</td>
<td>-0.085</td>
</tr>
<tr>
<td></td>
<td>Scheme E</td>
<td>0.023</td>
<td>0.0288</td>
<td>0.927</td>
<td>-0.057</td>
</tr>
<tr>
<td>Scheme D</td>
<td>Scheme A</td>
<td>-0.014</td>
<td>0.0299</td>
<td>0.988</td>
<td>-0.099</td>
</tr>
<tr>
<td></td>
<td>Scheme B</td>
<td>0.015</td>
<td>0.0288</td>
<td>0.982</td>
<td>-0.065</td>
</tr>
<tr>
<td></td>
<td>Scheme C</td>
<td>0.004</td>
<td>0.0288</td>
<td>1.000</td>
<td>-0.077</td>
</tr>
<tr>
<td></td>
<td>Scheme E</td>
<td>0.027</td>
<td>0.0288</td>
<td>0.877</td>
<td>-0.053</td>
</tr>
<tr>
<td>Scheme E</td>
<td>Scheme A</td>
<td>-0.042</td>
<td>0.0299</td>
<td>0.625</td>
<td>-0.126</td>
</tr>
<tr>
<td></td>
<td>Scheme B</td>
<td>-0.011</td>
<td>0.0288</td>
<td>0.994</td>
<td>-0.092</td>
</tr>
<tr>
<td></td>
<td>Scheme C</td>
<td>-0.023</td>
<td>0.0288</td>
<td>0.927</td>
<td>-0.104</td>
</tr>
<tr>
<td></td>
<td>Scheme D</td>
<td>-0.027</td>
<td>0.0288</td>
<td>0.877</td>
<td>-0.108</td>
</tr>
</tbody>
</table>

Based on observed means.

The error term is Mean Square (Error) = .006.
Striation width increases with increasing maximum stress level indicating faster growth per cycle. Finally, in the failure stage, the remaining undamaged cross-sectional area of the material cannot bear the acted loads and the material ruptures. Failure surface shows either ductile or brittle fracture characteristics depending on the material from this stage [115]. Generally, this stage passes very fast, and rupture occurs suddenly. In ductile fracture, plastic deformation takes place, and the failure is procrastinated for a while. However, failure is seen without plastic deformation in brittle fracture [140].

5.2.1 Analysis and Results

In the present research work, Scanning Electron Microscope (SEM) is used to perform the fractography on all five strip scheme specimens. The specific SEM used was a Tescan Vega II XMU-SEM shown in Figure 44. The microscope is equipped with an Oxford X-ray detection system (INCA NES), a turbomolecular and rotary force vacuum pump, and four lenses capable of 10 nm resolution, a maximum magnification of 500 kx, and accelerating voltages from 0.2 kV to 30 kV. Figure 45 to Figure 51 shows the results of fractography analysis of fatigue coupons in terms of the failure pattern.
**Figure 44:** Tescan Vega II XMU-SEM used for fractography
Figure 45: SEM images of crack propagation region with clearly visible fatigue striations
Figure 46: Ultimate brittle failure region with clearly visible cleavage cracks for strip scheme-A specimens: (a) Specimen-1, (b) Specimen-2
**Figure 47:** Ultimate brittle failure region with clearly visible cleavage cracks for strip scheme B specimens

**Figure 48:** Ultimate brittle failure region with clearly visible cleavage cracks for strip scheme C specimens
Figure 49: Ultimate failure region with ductile dimples for strip scheme D - Specimen-1

Figure 50: Ultimate failure region with intergranular cracks for strip scheme E - Specimen-1
5.3 Surface Roughness Measurement

Surface characterization after the paint removal process is very important. Possible alteration of the surface topology (roughness) of the substrate material after the paint stripping is a concern and could detrimentally affect subsequent coating adhesion and prevent meeting recoating specifications. Moreover, roughness could also be connected to fatigue crack propagation theory. Smoother surfaces have fewer crack propagation sites.

5.3.1 Testing and Results

In this section, surface roughness measurements are taken on all the five strip scheme coupons. Figure 52 Dektak 150 surface profiler by Veeco® with the stylus tip radius of 12.5 μm used for the surface roughness measurements with traverse length of 5 mm. 10 random locations on the strip side for each sample are selected for taking the readings.
Figure 54 to Figure 56 shows the representative line traces of surface topology while measuring the surface roughness. Figure 53 shows the average value of surface roughness in terms of $Ra \, (\mu m)$ for various strip schemes specimens.

**Figure 52:** Dektak 150 stylus profilometer for surface roughness measurement

**Figure 53:** Average value of surface roughness, $Ra \, (\mu m)$ for various strip schemes
Figure 54: Representative line traces of surface topology: (a) scheme-A (b) scheme-B
Figure 55: Representative line traces of surface topology: (a) scheme-C (b) scheme-D
5.4 Surface Microhardness Measurement

To study the effect of paint stripping on the hardness of the substrate material, microhardness measurements are performed. Hardness of the stripped surfaces may be connected to thermal stresses and Heat Affected Zone (HAZ). Preliminary tests are conducted on all the five strip scheme samples to measure the Vickers hardness of the substrate material.

5.4.1 Testing and Results

Material for the microhardness testing is first cold mounted using the epoxy resin and hardener system. For this, Epothin-2 epoxy mounting system by Buehler® is used. The samples were then polished by hand using wet sandpaper in the following order: 180 grit, 101
240 grit, 320 grit, 400 grit, 600 grit and 1200 grit. Then, the Buehler Automet 300 machine is used for polishing the samples with 3 μm polycrystalline diamond suspension and finally with 0.01 μm colloidal silica suspension. After achieving the final polishing, the samples are then cleaned in the Ultrasonic cleaning bath at 50°C for 5 minutes. Figure 58 shows the apparatus used for Ultrasonic cleaning bath. All the five strip scheme samples are prepared in this way.

**Figure 57:** Apparatus for the Vickers hardness testing

**Figure 58:** Ultrasonic bath for cleaning the samples after polishing
After the sample preparation, Vickers microhardness measurements are taken as per ASTM E92 standard [141] at various depths through the thickness of sample. A diamond pyramid indenter with an apical angle of 136°, and indentation load of 200 gf (gram force) is used. Figure 57 shows the apparatus used for conducting Vickers hardness testing. Due to the size of the microhardness indentations, reliable microhardness measurements are only obtained for depths of 60 μm or more. Therefore, Vickers microhardness values from cross-sectioned samples were obtained at a depth of 100 μm from the stripped surface, middle (bulk material), and approximately 100 μm from the primed/un-stripped surface regions of the specimen. In total, 6 readings are taken through the thickness of the sample (one data point on the stripped surface, 4 data points in the bulk material and one data point on the primed/back surface). The reason for taking the measurements at a finite depth is that the indentation has a finite size and the volume of material, which interacts with the indenter, is even larger. It is standard practice to obtain hardness data at a distance no less than 2.5 times the linear dimension of the indentation from the surface, to avoid edge effects. Figure 59 below shows the results of preliminary microhardness measurements. Please note that the results are presented in such a way that they are divided in three zones, namely, stripped surface zone, bulk material zone and primed/un-stripped zone for comparison.
5.5 Discussion of Experimental Results

5.5.1 Fatigue Life Evaluation

From the S-N curve presented in Figure 43, it is observed that at low stress level (high cycles), the fatigue life of aggressive laser scheme (Scheme-B) is lower than the light laser scheme (Scheme-C). Also, at the low stress level, the fatigue life of chemical strip scheme (Scheme-D), is higher than both the aggressive and light laser schemes. This may be because of the fact that at low stress level, even the small surface defects due to the laser plays a major role and may reduce the fatigue life. On the other hand, it is observed that at high stress level (low cycles), the fatigue life of aggressive laser, light laser and chemical strip specimens are almost the same since the effects of small surface defects are reduced at high load.
The one-way ANOVA results presented in Table 9 shows that the “p” value (significance level) for all the three stress levels is greater than 0.05, which means that we can accept the null hypothesis that all the means are equal. However, at the same time, we do not have enough evidence to reject the alternate hypothesis that not all means are equal. Therefore, we need to examine the Tukey HSD multiple comparison results presented in Table 11 to check if the difference in the means is statistically significant or not. The results of Tukey HSD post hoc analysis reveals that the differences in means of fatigue life between all the strip schemes are not statistically significant.

The two-way ANOVA results presented in Table 10 reveals that the “p” value for the main effects (strip schemes) is 0.684 and for the interaction effects (strip schemes and stress levels) is 0.349 which both are greater than 0.05, the significance level. This indicates that the response mean for the level of one factor (say strip schemes) does not depend on the value of the other factor level (say stress levels) and that the interaction effects are not statistically significant.

5.5.2 Failure Pattern

From the fractographic analysis results presented in Section 5.2, it is observed that the crack propagation zone for all the specimens is very distinctive with clearly visible fatigue crack striations as shown in Figure 45. Each striation displays a time interval which crack propagation happened and all the five strip scheme coupons have similar behavior with respect to the initiation and propagation zone. However, there is a distinct difference between the laser stripped, chemically stripped and un-coated specimens with regard to the
final fracture zone. Figure 46 shows the fracture surface of strip scheme A (moderate laser) specimens in the final fracture zone. We can see clearly visible cleavage cracks with necking which are the sign of brittle-ductile failure. Similarly, Figure 47 and Figure 48 shows the fracture surface of strip scheme B (aggressive laser) and strip scheme C (light laser) specimens in the final fracture zone with the clear sign of brittle-ductile failure. Also, it is observed that the necking is present, and it stopped before the brittle failure and the rupture occurred suddenly.

On the other side, for the chemically stripped (Scheme D) and un-coated (Scheme E) specimens, the ductile fracture was observed in the final fracture zone with intergranular cracks and ductile dimples as shown in Figure 49, Figure 50 and Figure 51. Notice that the necking continues until the final failure.

5.5.3 Surface Roughness

Figure 53 shows the average value of surface roughness measurements in terms of Ra (μm) for various strip schemes specimens. The limit specified by Section 5.9 of SAE4872A [122] is 3.2 μm and all the strip scheme specimens satisfy this limit. Also, Figure 54, Figure 55, and Figure 56 shows the representative line traces of surface topology while measuring the surface roughness. There is a distinct appearance in the details of the profilometry traces. Note that the chemically stripped sample shows a level of fine-scale (smooth) roughness that is not apparent in the laser treated surface. This might be corelated to the higher fatigue life of chemical stripped (Scheme-D) specimens at low stress level compared to the moderate, aggressive, and light laser stripped (Scheme-B, A & C) specimens.
5.5.4 Surface Microhardness

Figure 59 shows the results of preliminary microhardness tests conducted. It can be noticed that for Scheme-A (moderate laser stripped) and Scheme-B (aggressive laser stripped) samples, hardness is reduced drastically on the stripped surface (100 μm from top) as compared to the hardness in the bulk material. This might be due to the application of aggressive/moderate laser stripping, which changes the microstructure due to localized heating and cooling. Although, we cannot draw a solid conclusion knowing the fact that, due to the size of microhardness indentation, the measurements are taken only at depth >70 μm and near surface hardness data is not available. Nanoindentation hardness tests through the cross-section of a sample may be a suitable alternative.
Chapter 6: Conclusions and Recommendations

In this research, laser paint removal from 2024-T3 Alclad substrate material was characterized by numerical simulation and experimental tests. The potential of higher order Gaussian beam profiles and other specialized beam profile (Top-Hat) for laser paint removal process is investigated by evaluating the thermomechanical behavior of substrate material through numerical simulation. Moreover, the fatigue life of laser ablated 2024-T3 Alclad coupons is characterized and fractography is performed to understand the impact of various stripping schemes on the failure pattern of the material. In addition, the effect of laser paint stripping on the substrate material with respect to the changes in surface roughness and hardness of the stripped surface is investigated through experimental tests. The conclusions of the research are summarized in the following section.

6.1 Effect on thermomechanical behavior

A numerical simulation for laser heating of 2024-T3 Alclad substrate material with a layer of epoxy paint was performed as outlined in Chapter-4 with two different beam profiles: Gaussian and Top-Hat. A comparison of these two beam profiles was made by evaluating the thermomechanical behavior of substrate material with respect to temperature distribution, heat affected zone (HAZ) and thermal stresses generated. Following observations can be made from these results:

- For the Top-Hat beam profile, the heat affected zone (HAZ) on the surface was smaller compared to the Gaussian beam profile. Meaning that the temperature immediately surrounding the laser spot was lesser for Top-Hat than the Gaussian beam profile.
• Also, in the case of the Gaussian beam, the HAZ inside the substrate material is deeper than with the case of Top-Hat beam profile. Meaning that the heating due to the laser irradiation reached at higher depth in the substrate material with Gaussian beam as compared to the Top-Hat beam profile.

• The Gaussian beam profile had the fastest stabilized time meaning that the temperature on the surface of the substrate material increases faster as compared to the Top-Hat beam profile.

• Thermal stresses generated on the surface were higher in case of the Gaussian beam as compared to the Top-Hat beam profile.

6.2 Effect on Fatigue Life and Failure Pattern

The fatigue life evaluation of all the five strip scheme coupons were performed according to the detailed test plan and test matrix outlined in Sections 5.1.1 to 5.1.6. A detailed statistical analysis of the test data was performed by One-way and Two-way ANOVA and a Tukey HSD post hoc analysis. Finally, the S-N curve of fatigue life was developed. Moreover, the fractography was performed as outlined in Section 5.2. Detailed discussion on these results were presented in Section 5.5.1 and 5.5.2 and following observations can be made:

• The one-way ANOVA result shows that the “p” value (significance level) for all the three stress levels is greater than 0.05, which means that we can accept the null hypothesis that all the means are equal.
• The results of Tukey HSD post hoc analysis give concrete evidence that the differences in means of fatigue life between all the strip schemes are not statistically significant.

• The two-way ANOVA result gives the significance of interaction effect between strip schemes and stress levels. It reveals that the “p” value for the main effects (strip schemes) is 0.684 and for the interaction effects (strip schemes and stress levels) is 0.349 which both are greater than 0.05, the significance level. It means that the response mean for the level of one factor (say strip schemes) does not depend on the value of the other factor level (say stress levels) and that the interaction effects are not statistically significant.

• The fracture surface of all the laser stripped specimens (Scheme-A, B and C) have clearly visible cleavage cracks in the final fracture zone with the necking which are the sign of brittle-ductile failure. The necking stopped before the brittle failure and the rupture occurred suddenly.

• On the other side, for the chemically stripped (Scheme D) and un-coated (Scheme E) specimens, the ductile fracture was observed in the final fracture zone with intergranular cracks and ductile dimples. Also, the necking continues until final failure.

6.3 Effect on Surface Roughness

Surface roughness of the stripped side for all the five strip scheme specimens were measured as outlined in Section 5.3. Discussion on these test results were presented in Section 5.5.3 and following observations can be made:
• All the five strip scheme specimens satisfy the limit of average surface roughness specified by Section 5.9 of SAE4872A standard which is 3.2 μm.

• However, there was a distinct appearance in the details of the profilometry traces. The chemically stripped sample showed a level of fine-scale (smooth) roughness that was not apparent in the laser treated surface.

6.4 Effect on Surface Hardness

The effect of paint stripping on the hardness of substrate material for all the five strip scheme specimens were evaluated by performing preliminary microhardness tests as outlined in Section 5.4. Discussion on these test results were presented in Section 5.5.4 and following observations can be made:

• For Scheme-A (moderate laser stripped) and Scheme-B (aggressive laser stripped) samples, hardness was reduced drastically on the stripped surface (100 μm from top) as compared to the hardness in the bulk material. However, this is based on preliminary tests only and more data is needed to prove this.

6.5 Recommendation (Future Work)

In the present research work, numerical simulation for the thermomechanical behavior of substrate material was developed only with respect to laser heating of solids. It was assumed that no phase transition or other substantial surface changes occurs i.e. temperature profile remains below the melting point of the paint layer. However, to understand the true thermomechanical behavior of the substrate material, a numerical simulation depicting the complete paint removal along with the laser heating is required.
Moreover, the presence of residual stresses due to the paint stripping process can have significant effect on the fatigue life. Therefore, it is recommended to perform X-Ray diffraction (XRD) analysis to directly measure the residual stresses and to adjust the S-N curve presented in this thesis accordingly. Also, in the present research work, microhardness testing was adopted for measuring the surface hardness of the paint stripped surfaces. As noted, due to the size of microhardness indentation, the measurements were taken only at depth >60 μm and near surface hardness testing was not possible. Therefore, it is recommended to use nanoindentation hardness tests through the cross-section of a sample to determine the near surface hardness data. It is also imperative to check the effect of any surface treatment such as anodizing, as well as other coating methods such as conversion coating on the substrate material.
References


