

Surface structuring and functionalization of aluminium alloys using multimodal laser processing

By

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of PhD is entirely my own work, and that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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List of Publications

1. Cholkar, A., McCann, R., Perumal, G., Chatterjee, S., Swayne, M., Kinahan, D. and Brabazon, D., 2023. Advances in laser-based surface texturing for developing antifouling surfaces: a comprehensive review. *Applied Surface Science Advances*, 18, p.100513. <https://doi.org/10.1016/j.apsadv.2023.100513>
2. Cholkar, A., Chatterjee, S., Jose, F., O'Connor, R., McCarthy, É., Weston, N., Kinahan, D. and Brabazon, D., 2024. Parametric investigation of ultrashort pulsed laser surface texturing on aluminium alloy 7075 for hydrophobicity enhancement. *The International Journal of Advanced Manufacturing Technology*, pp.1-18 <https://doi.org/10.1007/s00170-024-12971-8>.
3. Cholkar, A., Chatterjee, S., C. Richards, McCarthy, É., Perumal, G., Regan, F., Kinahan, D., Brabazon, D., Biofouling and Corrosion Protection of Aluminum Alloys Through Ultrafast Laser Surface Texturing for Marine Applications. *Adv. Mater. Interfaces* 2024, 11, 2300835. <https://doi.org/10.1002/admi.202300835>
4. Cholkar, A., Chatterjee, S., Kumar, S., Sedaček, M., Podgornik, B., Kinahan, D., Brabazon, D.; 2024; “Combining ultrafast laser texturing and laser hardening to enhance surface durability by improving the hardness and wear performance”. *Adv. Eng. Mater.* 2024 2401183. <https://doi.org/10.1002/adem.202401183> .

Conference papers

1. Cholkar, A., Chatterjee, S., Kinahan, D., Brabazon, D., 2023. Ultrafast Laser Fabrication of Microchannels on Aluminium Alloy Substrate. SSP. <https://doi.org/10.4028/p-rjfp3>
2. Chatterjee, S., Cholkar, A.S., Kinahan, D., Brabazon, D. (2024). Fabrication of Periodic Textures at Micron Level on Silicone Membrane Using Femtosecond Laser. In: TMS 2024 153rd Annual Meeting & Exhibition Supplemental Proceedings. TMS 2024. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-031-50349-8_134
3. Chatterjee, S., Cholkar, A., Kinahan, D., & Brabazon, D (2023) Quality Assessment and Features of Microdrilled Holes in Aluminum Alloy Using Ultrafast Laser In: Broek, S. (eds) Light Metals 2023. TMS 2023. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-031-22532-1_53
4. Cholkar, A., McCann R., Kinahan, D., & Brabazon, D. (2022) Ultrafast laser-induced surface structuring of anti-fouling steel surfaces for biomedical applications. Paper presented at 17th International Manufacturing Science and Engineering Conference (MSEC2022) (online) June 27-July 1, 2022, West Lafayette, Indiana, USA. <https://doi.org/10.1115/MSEC2022-85249>
5. Cholkar, A., McCann R., Kinahan, D., & Brabazon, D. (2022) Fabrication of Anti-Icing Surface Structures on Aluminium Alloy for Aerospace Applications Paper presented at ESAFORM 2022. 25th International Conference on Material Forming, Braga Portugal. doi: <https://doi.org/10.4028/p-19ai96>

List of Poster presentations

1. Zehani, R., Pecault, I.T., Mincuzzi, G., Cholkar, A., Chatterjee, S., Kinahan, D. and Brabazon, D., 2024, June. Innovative laser manufacturing processes at nano scale within the NewSkin Open Innovation Test Bed. In *Laser Photonics for Advanced Manufacturing* (Vol. 13005, pp. 189-191). SPIE.
2. Cholkar, A., Chatterjee, S., Kinahan, D., & Brabazon, D (2023) Ultrafast laser texturing for enhancing anti-fouling and corrosion resistance in aluminum for Marine applications presented a poster at Waves of Change: Innovative Solutions for Water-Wise World in DCU Alpha, Dublin City University, Ireland.
3. Cholkar, A., Chatterjee, S., Kinahan, D., & Brabazon, D (2022) Ultrafast laser surface structuring of aluminum alloy for antifouling applications I-Form Gathering, Athlone Ireland, December 2022
4. Cholkar, A., McCann, R., Kinahan, D., & Brabazon, D (2022) Poster Presentation on Laser surface machining of aluminum for anti-icing applications at the International Conference on Material Science and Engineering and Smart Materials, Vienna Austria (Online) 12-13 November 2020.

ABSTRACT

This thesis explores advanced multimodal laser processing techniques to fabricate nano- and micro-scale structures on aluminum alloys, targeting the marine, aerospace, and automotive industries. Aluminum alloys are known for their physical and mechanical properties but are prone to degradation from fouling, corrosion, and wear. Conventional methods for mitigating these issues are insufficient, leading to the investigation of laser-based texturing as a more robust, environmentally friendly, and scalable alternative.

Chapter 2 reviews aluminum alloys as marine materials, the mechanisms of surface fouling, and traditional mitigation methods, alongside the principles of laser-based nano- and micro-fabrication techniques. Femtosecond and continuous wave (CW) fiber lasers were used to induce surface modifications that enhance antifouling, corrosion resistance, and wear performance.

Chapter 3 examines ultrafast laser texturing to increase hydrophobicity in aluminum alloy 7075. By optimizing parameters such as laser power and scan speed, the water contact angle was increased from 85° to 142° , showing a highly hydrophobic surface. Environmental aging further contributed to these improvements. In Chapter 4, five laser patterns were tested for biofouling and corrosion resistance. The star pattern texture reduced biofilm coverage by 79% and improved corrosion resistance by 25%.

Further, three optimized patterns were subjected to CW laser heat treatment, resulting in a 17.8% increase in microhardness and an 83% reduction in the friction coefficient. Amount of wear was reduced by 80% in the most hardened sample. Regression models were developed to fine-tune these characteristics, enhancing tribological performance.

This research highlights the potential of multimodal laser processing for creating robust and eco-friendly surface modifications on aluminum alloys, significantly improving their functional properties.

CHAPTER 1

1. INTRODUCTION

1.1.Motivation

This thesis presents the development of a novel approach to surface modification through multimodal laser material processing on commercial-grade aluminum alloy surface especially in parts susceptible to fouling, corrosion and wear and tear within engineering applications. The functionalization of surfaces is a crucial factor in a wide range of industrial applications, as it determines the resistance to various forms of surface fouling such as particle attachment, droplet adhesion, ice formation, microorganism proliferation, and wear and corrosion. The choice of material for a specific application depends on a variety of properties including mechanical, electrical, chemical, and physical attributes. However, the inherent properties of the material may not always be sufficient to address surface-related concerns, and thus, surface functionalization becomes a critical consideration in applications where the material is subjected to environmental exposure or fluidic interactions or interfaces with other surfaces. [1]. Surface functionalization potentially leads to enhancing the lifetime and quality of products, leading to improvements in material utilization, energy consumption, and cost-effectiveness. As a result, this research area has the potential to significantly increase the overall efficiency, quality, and durability of the end-products. By enhancing surface properties, it becomes possible to reduce material waste, lower energy requirements, and minimize the cost of production, while simultaneously improving the performance and longevity of the product. Thus, surface functionalization is a crucial area of research that offers the opportunity to drive innovation in a wide range of industrial applications and products. [2], [3].

Annually, billions of dollars are invested in the treatment of surfaces to improve their functionality and prevent surface fouling. For example, in the maritime industry, large sums of money are spent on antifouling treatments for the hulls of ships to prevent the buildup of unwanted materials such as algae and barnacles [4]. Moreover, a lot of money is spent on de-icing of aircraft parts [5]. The replacement and repair of moving parts such as bearings is common practice in the automobile industry as the materials wear over time [6], [7]. Furthermore, in the pharmaceutical and food processing industries, the attachment of proteins and other biomaterials on surfaces necessitates significant investment in cleaning and maintenance. However, these costs can be reduced if the surfaces made up of the same material have enhanced functionalized surface properties [8]–[14]. Physical-based techniques, such as lithography techniques, Vacuum casting, Ion etching, Hot embossing, additive manufacturing, plasma techniques can improve the wettability, corrosion

resistance, fouling resistance, and wear resistance of the material, ultimately leading to improved performance and reduced maintenance costs. Although these techniques are exceptionally suited for fabricating micro and nano patterns on surfaces, they are not considered rapid, cost-effective, or scalable manufacturing methods. Additionally, these processes often involve significant material wastage and the use of toxic substances, which further limits their practical application in industrial settings.

With recent developments in optic systems such as galvanometric scanners and advanced laser sources, the laser processing is the potential surface treatment which can be applied to the critical surfaces which are more susceptible to degradation within the applications. The time required to texture a surface depends on the material, the desired roughness level, and the laser system's output power. Therefore, laser material processing offers a highly effective and efficient alternative, addressing the scalability issues, minimizing material wastage, and avoiding the use of toxic substances. [15]–[24]. Special types of ultrafast pulsed laser systems and high-power continuous wave fiber lasers are used to make these surface structures which help in getting the above-mentioned properties. The use of laser material processing is one potential route toward further extending or enhancing the functionality of these materials for specific applications. Hence, this thesis aims to investigate the utilization of laser manufacturing techniques for the creation of micro and nano-scale textures on aluminum alloy surfaces and improve functional surface properties.

1.2. Research thesis and objectives

In this project, high-power solid-state femtosecond and continuous wave fiber lasers will be utilized to induce morphological modifications, thereby enhancing surface properties. The objective is to develop methodologies for fabricating high-quality, repeatable nano and microstructures that confer antifouling, corrosion-resistance, and wear-resistance characteristics, ultimately enhancing surface durability.

The research is structured into several key objectives:

1. Identification of a laser-based approach and the process parameter settings, and pattern design, capable of fabricating micron-sized structures on the surface of aluminum alloys in a highly effective and repeatable way.
2. Comprehensive characterization of the laser-processed substrate morphology and surface chemistry, providing insights into the mechanisms governing surface modification.
3. Exploration of potential routes for functionalization of the laser-textured aluminum alloy surfaces to further enhance their performance and utility in real-world applications .

4. Application of the fabricated nano and micro-structured surfaces for proof-of-concept assessments, including evaluations of antifouling, corrosion resistance, and wear performance.

1.3. Overview of work and thesis structure

This thesis is comprised of six chapters: Chapter 1 introduces this work and provides context for the following chapters.

Chapter 2 will provide an in-depth exploration of aluminum as a material in marine applications, focusing on surface fouling, its underlying mechanisms, and various strategies employed for fouling mitigation. The core theories and principles underlying different fabrication methods for functional surfaces will be discussed, drawing from established practices. Additionally, this chapter will delve into recent advancements in laser-based techniques for surface structuring and heat treatment, examining the mechanisms of laser-material interaction across different types of lasers. Various characterization methods to assess the functionality of laser-fabricated surfaces will be reviewed. Furthermore, the chapter will cover methodologies for effectively analyzing output data and utilizing it to optimize the overall manufacturing process. Chapter 3 presents an experimental investigation into the manufacturing of surface textures on an aluminum alloy (7075) surface using an advanced femtosecond laser surface texturing process, employing the design of experiments (DOE) approach. The influential factors including laser power, hatch distance, and scan speed of the femtosecond laser system were examined. Response surface optimization was utilized to determine the process parameters leading to the most hydrophobic surface. The study sheds light on the effects of different femtosecond laser process parameters on surface roughness, chemical composition, and surface wettability.

Chapter 4 investigates the potential of femtosecond laser processing to alter surface properties and achieve a superhydrophobic surface with marine anti-biofouling and corrosion resistance capabilities. Specifically, our focus is on modifying the wetting characteristics of aluminum alloy 7075 material. Chapter 5 suggests that the combination of continuous wave laser hardening and femtosecond laser texturing may enhance the mechanical properties of the surface, with a specific focus on improving wear resistance. The study investigates the influence of multimodal laser texturing by creating three different laser textures using femtosecond laser processing. Subsequently, varying parameters of laser hardening are applied to evaluate the hardness and wear resistance characteristics across the samples.

Chapter 6 concludes the thesis and presents an outlook as to where the output from this thesis can lead and what further work is needed in this research domain.

CHAPTER 2

2. LITERATURE REVIEW

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CHAPTER 2

2. LITERATURE REVIEW

This chapter will present a broad overview of aluminium material as marine materials, surface fouling, its mechanisms, and methods used to mitigate fouling, core theories, and principles of the different fabrication methods of functional surfaces that have been used for a long time. This chapter will focus more on micro and nano-structuring of different material surfaces using laser machining that uses an ultrafast pulsed laser system and its use in different industrial applications. The most recently used laser-based techniques for structuring and heat treatment of surfaces are discussed in this section and the mechanism of the laser-material interaction using the different types of lasers is reviewed. Also, the different characterization methods to determine the functionality of the laser-fabricated surfaces. Moreover, the methods of analyzing the output data presenting it effectively and using the same to optimize the overall manufacturing process are also discussed.

2.1. Aluminium alloy

Aluminum alloys are widely used materials known for their versatility, strength, and lightweight properties. They play a crucial role in various industries, including aerospace, automotive, marine, construction, and consumer electronics. Aluminum alloys, have been extensively used in marine applications due to their corrosion resistance and suitability for marine environments [25]. Wrought aluminium alloys are divided into 8 series depending on the mechanical properties and alloying elements as shown in Table 2.1.

Table 2.1 Aluminum alloy classification [26]

Series	Alloying element	Properties	Application
1000		Highly thermally conductive, highly ductile, and corrosion-resistant	Packaging and foil, roofing, cladding, low-strength corrosion resistant vessels and tanks
2000	Copper	Higher strength	Highly stressed parts, aerospace structural items, heavy duty forgings

3000	Manganese	Corrosion resistance and formability	Packaging, roofing and cladding, chemical drums and tanks 4000 Silicon process and food handling equipment
4000	Silicon	Good machinability and corrosion resistance and a moderate amount of strength	Filler metals, cylinder heads, engine blocks, valve bodies, architectural purposes
5000	Magnesium	Corrosion resistance	structural members, vessels and tanks, vehicles, rolling stock, marine applications, architectural application
6000	Magnesium and Silicon	Good strength, resistance to atmospheric corrosion, and are machinable	High-strength structural members, vehicles, rolling stock, marine applications, architectural application
7000	Zinc	High strength, good toughness, and fatigue and corrosion resistance	High-strength structural members, propellers, marine applications, heavy section aircraft forgings, military bridging, armor plate, heavy goods vehicle and rolling stock extrusions
8000	Other elements		Space applications, electric wires

These alloys are primarily appreciated for their excellent strength-to-weight ratio, corrosion resistance, and ease of fabrication, which collectively enhance the performance and durability of marine vessels and structures.

2.1.1. Strength-to-weight ratio

One of the most significant advantages of aluminum alloys in marine applications is their exceptional strength-to-weight ratio. Aluminum alloys, particularly those in the 6000 and 7000 series, are known for being strong yet lightweight. This property is crucial for marine vessels, where reducing weight can significantly improve fuel efficiency and increase speed [27]. For example, high-speed boats and yachts benefit from the lightweight nature of aluminum, which

allows them to achieve higher speeds and better maneuverability without compromising structural integrity [28].

2.1.2. Corrosion resistance

Corrosion resistance is another critical factor that makes aluminum alloys ideal for marine environments. The harsh conditions of saltwater and marine atmospheres can cause rapid deterioration of many materials. However, aluminum alloys form a natural oxide layer on their surface, which acts as a protective barrier against corrosion [29]. Alloys in the 7000 series, which contain magnesium, are particularly known for their superior resistance to seawater corrosion. This property reduces maintenance costs and extends the lifespan of marine structures and vessels, making aluminum alloys a cost-effective choice in the long term [30].

2.1.3. Fabrication and versatility

Aluminum alloys are also favored for their ease of fabrication. They can be easily cast, machined, and welded, allowing for the production of complex shapes and designs required in modern marine architecture. The ability to fabricate large, seamless sections can enhance the structural integrity and aesthetic appeal of marine vessels. Moreover, aluminum alloys are versatile and can be used in various applications, from hulls and superstructures of ships to offshore platforms and smaller components like masts and fittings [31].

2.1.4. Environmental and economic benefits

The use of aluminum alloys in marine applications also presents environmental and economic benefits. Aluminum is highly recyclable, and using recycled aluminum significantly reduces the energy required for production compared to primary aluminum. This characteristic aligns with the increasing emphasis on sustainability in the maritime industry. Economically, the durability and low maintenance requirements of aluminum alloys translate to reduced operational costs over the lifespan of marine vessels and structures [32].

Especially, Aluminum alloy 7075 is commonly used in marine applications due to its high strength and durability, but it is susceptible to corrosion in marine environments [33], [34]. Studies have shown that exposure to marine atmospheres accelerates the corrosion rate of 7075 alloy, leading to the formation of corrosion pits, intergranular cracks, and exfoliation of the matrix, ultimately deteriorating its tensile properties over time [35], [36]. Additionally, the corrosion behavior of 7075

alloy in sulfate-reducing bacteria (SRB) marine environments has been investigated, revealing that the presence of SRB in seawater can further accelerate the corrosion process, breaking down the protective film on the alloy surface and reducing its impedance significantly [27]. The root cause of the degradation of aluminum is surface fouling which is discussed in the next section.

2.2. Surface fouling

Surface fouling is a phenomenon that occurs in many industrial applications and negatively impacts the performance of engineering components and systems. It is characterized by the accumulation of unwanted materials on a solid surface due to adhesion between the fouling material and the surface. It mainly occurs in applications in fields such as marine [37]–[40], aerospace [41]–[44], energy sector [45]–[48], Medical [8], [49]–[51], pharmaceutical [52] and food industries [53]–[56]. The history of anti-fouling surfaces dates back to ancient times, when the Phoenician civilization used copper and lead coatings to coat wooden boats. With the expansion of industrialization and transportation in the late 19th and early 20th centuries, there was significant research on developing anti-fouling surface strategies [57], [58]. Many attempts have been made to manufacture hydrophobic surfaces using laser processing that plays a very important role in many applications, such as anti-biofouling, anti-corrosion, and anti-icing surfaces [59]. The ability to fabricate biomimetic surfaces with precise control over their wetting properties presents a plethora of opportunities for various applications, such as developing self-cleaning surfaces that exhibit antifouling characteristics, improving the efficacy of oil-water separation, and enhancing the performance of green energy systems like batteries and fuel cells [60].

Fouling is a time dependent, complex, and undesirable process with diverse mechanisms depending on the type of surface and foulant involved. Foulants can comprise macromolecules, bacteria, and/or suspended particles, and can be stationary or moving [38]. The types of fouling can be primarily classified in two categories: microfouling (<100 μm) and macrofouling (>100 μm). Another type of categorisation used is illustrated in the Figure 2.1.

There are six mechanisms of fouling, these are: 1. colloidal, 2. scale, 3. chemical, 4. corrosion, 5. biofouling and 6. ice [61], [62]. Colloidal fouling, type 1, is a type of fouling that can be generated by organic or inorganic colloids. Fine particles with a size range of 1-1000 nm are involved. These colloids build up on membrane surfaces, reducing their performance. Fouling of this type is particularly common in reverse osmosis water filtration membranes. Aluminium silicate minerals, silica, iron oxides/hydroxides, and elemental sulphur are among the inorganic foulants found within various water sources [63].

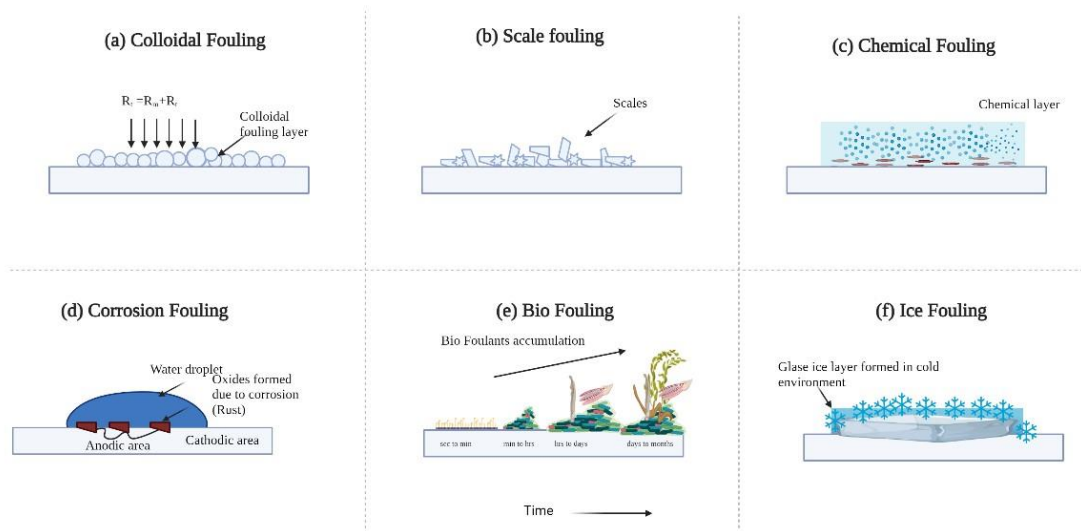


Figure 2.1. Schematics of the fouling processes of (a) colloidal, (b) scale, (c) chemical, (d) corrosion, (e) biological species and (f) ice formation

Another important type of fouling is scaling, type 2, is caused by inorganic salts and other particles in the fluid stream. This type of fouling increases the pressure drop in a heat exchanger and lowers the heat transfer between the fluid and the heat exchanger surface. Settling of the salts can occur with the fluid flow velocity falls below a critical level. This type of fouling occurs in heat exchangers of heating, ventilation, and air conditioning systems, and is one of the leading causes of system failure and inefficiency [64]. The foulants or scales are made up of calcium carbonate or calcium sulphate precipitations which are insoluble in fluids such as water. This type of fouling is also known as precipitation, crystallization, or sedimentation fouling [65].

Chemical fouling, type 3 is a fouling type whereby solid is deposited on a surface due to a chemical reaction. A common form of chemical fouling is the formation of asphaltenes as a fouling species in crude petroleum streams caused due to the oxidative condensation process [66]. When there is a lack of oxygen at high temperature it results in the formation of coke which has a high molecular mass. There are various parameters which affect the formation such as the temperature, velocity of the stream, composition of the feedstock, autoxidation, polymerization, and thermal decomposition, presence of oxygen, presence of sulphur and nitrogen and other impurities in the stream, material of the surface and presence of inorganic components and other environmental factors. These factors affect the rate of the chemical reactions taking place and hence also the magnitude of deposit formation [67].

In type 4, corrosion fouling, a chemical or electrochemical reaction occurs between the surface and its environment. The anode and the cathode are connected electrically both through the fluid and by some external metallic conductor [68]. Charge is transported by the electrons due to current flow in the external conductor and by the ionized species in the fluid. On removal from the fluid

and drying, the metal hydroxide loses its constituent fluid, and the remaining deposit consists of metal oxides. At the cathode, a electrochemical reaction occurs involving the reduction of oxygen dissolved in the fluid. These oxides and hydroxides constitute the fouling deposit [69]. This type of fouling occurs with time in applications such as marine applications including ships hulls, propellers and other parts of ships or boats which come in contact with sea water [70]. When corrosion is accelerated directly by the life activities of microorganisms or indirectly by their metabolites, it is termed as microbiologically influenced corrosion [71], and occurs in heat exchangers such as steam boilers, condensers and in the food industry [72].

Biofouling, type 5 refers to undesirable attachment of microorganisms at a phase transition interface (solid–liquid, gas–liquid or liquid–liquid), which might occur due to deposition, growth and metabolism of bacteria cells or flocs on the surface [73]. Biological fouling takes place in various stages such as surface conditioning by formation of a conditioning film, attachment of pioneer planktonic cells onto surfaces, formation of microcolonies by primary bio adhesion and subsequently development of mature biofilms which destroys the interaction of the surfaces with the fluids or other surfaces. It occurs due to diverse array of fouling organisms and has increased operational expenses and deleterious impacts however the extent of information on its causes is still lacking. Various organisms responsible for biofouling especially in medical and marine environments along with the size of the bio foulants are illustrated below in Figure 2.2.

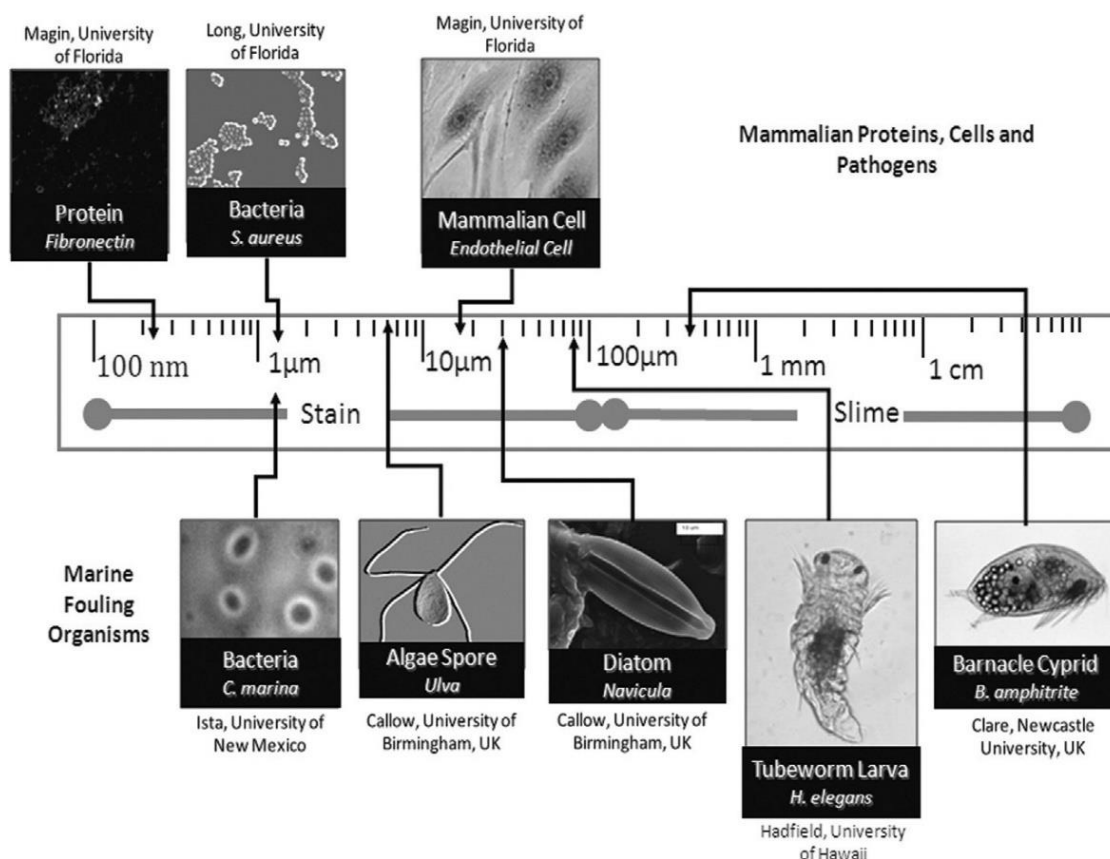


Figure 2.2 Illustration of different bio-foulants found in biomedical and marine environments. Cells and compounds relevant to biomedical applications are shown above the scale axis. Marine organisms are shown below the scale. Reproduced with permission from [74].

Other organic foulants include polysaccharides, proteins, and natural organic matter [75]. Fouling from such species especially occurs in low and high-pressure membranes which are used in bioreactors [76]. The economic costs associated with biofouling control have been estimated to range from \$1.5 to 3 billion per year [77]. The reduction of biofouling on the propeller and hull of a ship can significantly increase the resistance of the ship flow through the water [78].

Ice fouling, type 6, is one of the significant types of fouling in which ice is formed and accumulates on surfaces due to the low temperature and low pressure environmental conditions [79]. This occurs especially on airplane wings [80], power lines, wind turbines [45] and heat exchangers in cooling systems used in the food industry [81] due to the solidification of the fluids which come in contact with the surface at low temperature and pressure. Ice nucleation and growth which contaminates the surfaces, reduces the functional efficiency of these systems [82].

As fouling has been a problem for long time and directly affects the performance of many engineered systems, there is a need to develop surface manufacturing methods such that fouling can be prevented.

The further sections discuss various methods to mitigate fouling, and increase the life of the surface.

2.3. Fabrication methods for micro and nano structures

Various existing physical based methods suitable for production of functional surfaces are listed in Table 2.2 Various methods for the production of functional surfaces. Chemical and physical based techniques such as electrospinning [83], spray coating [84] and dip coating [85] are used for functionalization of large surface area.

Lithographic techniques are common approaches towards fabrication of highly structured surfaces. These approaches vary from the application of radiation to harden or soften photosensitive material, which is then removed via wet chemical approaches [86], imprint techniques utilising stamping for surface structuring, to beam lithographic approaches which rely on focused particle beams for material sputtering [87]. There are various lithographic techniques used such as photolithography [86], [88]–[94], electron beam lithography [95]–[100], ion beam lithography [87], [98], [101], soft lithography [102]–[104], nano-imprint lithography [105]–[109], colloidal lithography [110]–[114].

Conventional manufacturing approaches such as hot embossing and vacuum casting [115] have also been scaled to the nano- or micro-scale, and are suitable approaches for producing features for anti-fouling surfaces. Finally additive manufacturing approaches, often referred to as 3D printing, where parts can be fabricated in a layer wise manner, also offers the possibility for direct production of anti-fouling surface features [116].

Table 2.2 Various methods for the production of functional surfaces

Method	Description	Reference
Electrospinning	Production of synthetic filaments of the materials with the aid of electrostatic forces is known as electrospinning. This method is used in polymers materials.	[83]
Spray coating	Nanoparticles having hydrophobicity are sprayed onto hard and soft substrates	[84]
Dip Coating	In this process the substrate material is submerged in conformal coating, then taken out and allowed to drip dry.	[85]
Lithographic techniques	Photolithography	Uses light to transfer a geometric pattern from a photomask to a photosensitive chemical photoresist on the substrate. [86], [88]–[94]
	Electron beam lithography	Scanning focused beam of electrons to draw on a surface covered with an electron-sensitive film called a resist. It is capable to produce high precision 3 to 5 nm patterns. [95]–[100]
	Ion beam lithography	In this technique focused beam of ions in a patterned fashion across a surface to create very small structures. [87], [98], [101]
	Soft lithography	It uses PDMS as master template and can produce micro and nano patterns. [102]–[104]
	Nano-imprint lithography	Patterns are generated by mechanical deformation of imprint resist, cured by heat or UV light during the imprinting. [105]–[109]
	Colloidal lithography	In this method the colloidal crystals are used as a mask on the surface of the substrate used. [110]–[114]
Nano and Micro moulding	It is a fast fabrication method for transferring nanostructures on to a substrate made up of polymer. In this process a mould is created that has a cavity in the shape of the part desired.	[117], [118]
Vacuum casting	In this method, a mould is placed onto a PDMS sample and is completely covered in unsaturated polyester resin which contain glass fibres under vacuum conditions. This method is commonly used to reproduce the patterns.	[115], [119]–[121]
Reactive Ion etching	In this process the plasma is initiated in the system by applying a strong radio frequency electromagnetic field to the wafer platter, the positive ions tend to drift toward the wafer platter, where they collide with the samples to be	[122]–[126]

	etched. The ions react chemically with the materials on the surface of the samples and remove material in nanoscale.	
Hot embossing	Stamping of pattern into the polymer softened by increase in temperature above glass transition temperature.	[127]–[129]
Additive Manufacturing	Versatile and various micro or nano patterns can be manufactured using layer by layer addition of material.	[116], [130]–[132]

2.4. Laser surface modification

There are lot of advantages of using a laser for manufacturing and structuring of different surfaces according to the desired application. A LASER can be defined as a source of narrow beam of monochromatic coherent light which can be in infrared, ultraviolet or visible form which delivers energy. The laser can be essentially classified into two categories such as continuous wave laser and pulsed wave laser which are again classified into two categories according to their principles which are by using external switch or modulator applied to continuous wave laser beam or by using an internal modulation process.

Power variations can occur in continuous laser systems due to mode beating and other kinds of laser noises such as intensity noise, phase noise, frequency noise [133]. Therefore, the preference for pulsed laser systems over continuous laser systems. However, the performance of laser systems varies in different scenarios; while continuous laser systems may perform better in some material processing but pulsed laser sources have the advantage of finer control over the power density of the laser beam-surface interaction. This fine control over power density provides the potential for more precise control over the resulting surface modification.

Hence, pulsed laser systems are preferred over the continuous lasers. The pulsed laser systems are the laser in which the optical power appears in pulses of some period at some repetition rate. The first most important motivation for using pulsing devices is to obtain very high peak intensity so that large number of photons are released in short time. The second motivation is to produce a laser with very short pulse duration to probe the events to find out how the excited molecule behaves when it is exposed to the light. Chirped pulse amplification (CPA) is quite a recent method developed which is implemented in ultrafast lasers. This technique eliminates the nonlinear effects which occur in other ultrafast laser techniques by stretching the pulse prior to amplification, reducing its peak power. The compressed pulses generated by CPA have a well-defined spectral content and temporal duration, making them ideal for various applications that require precise control over the laser pulse properties. Moreover, this leads to reduction in size results in more compact laser systems which are more energy-efficient and cost-effective making them easier to integrate into various applications such as surgery, manufacturing, surface structuring, embossing, or writing etc. The quality of manufactured product by laser processing is high, this is because of the high accuracy and precision obtained during the process [134].

The earliest report on the application of short and ultrashort lasers in materials processing dates back to the early 1980s [135]. The development of chirped pulse amplification technique in 1985 to produce high energy ultrashort pulse width pulses has enabled the development of ultrashort pulse laser systems such as the femtosecond laser which has advantages such as delivering high

energy density at spatial and temporal scales of femtosecond lasers [136]. The first publication of the femtosecond laser being used was reported in 1991 [137]. This laser has proven its capability to be used in a number of laser micro/ nano machining applications, including biomedicine, photonics, and semiconductors. In these lasers it is possible to change the states and properties of materials through the interaction with them and they can be used to control materials for processing from micron to nanometre scales. Hence the femtosecond lasers can process almost any material with high quality and high precision and realize three-dimensional complex structure fabrication [21]. The general setup of femtosecond laser is as illustrated in Figure 2.3.

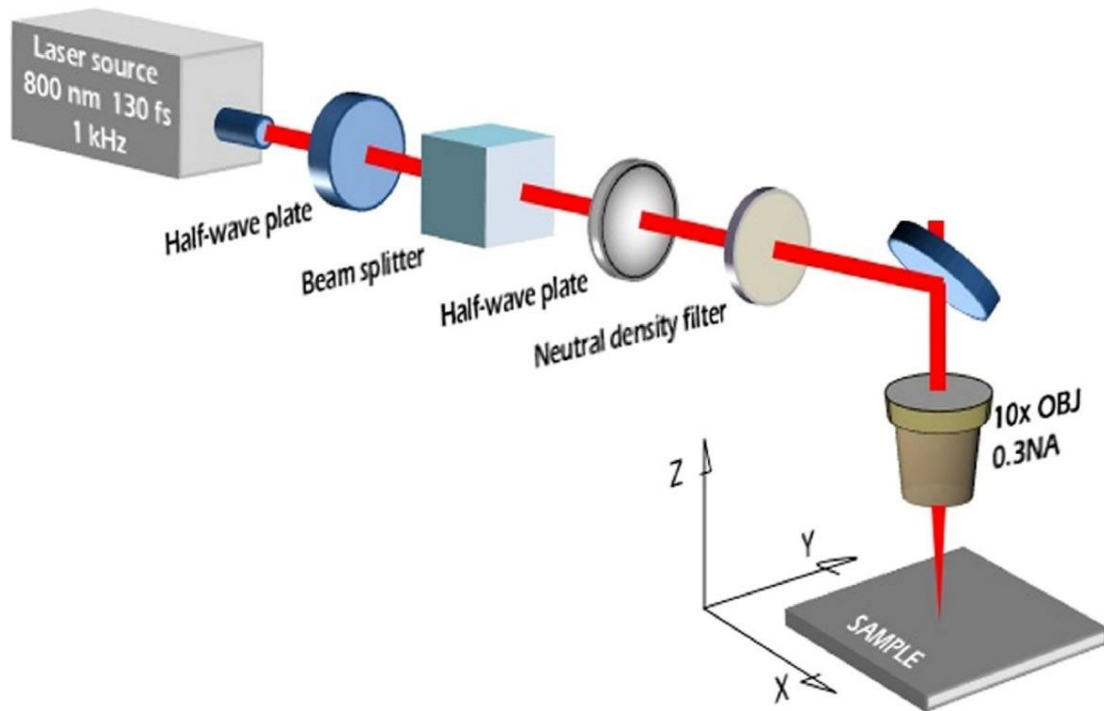


Figure 2.3 Typical ultrafast laser texturing setup [138]

By using laser structuring various artificial surface can be manufactured which involve surface property modifications which involves topography modification by patterning using thermal ablation which can generate micro or nano scale holes on the surface. The second is patterning by optical interference which is capable of manufacturing laser-induced periodic surface structure (LIPSS) which are artificial wavelength-scale surface structures. Patterning by surface hydrodynamic effects which involves spike formation, biomimicking the natural surfaces, artificial nano level hill and valley creation. This enhances the hydrophobicity or hydrophilicity of the particular surface. The laser ablation is also used for modification of the microstructure of the material which involves amorphization and crystallization and formation of novel phases such as processing of thin film shape memory alloys like nitinol. In some cases, the femtosecond laser surface structuring is also capable of modification of topology

and microstructure simultaneously [113]. Various types of laser sources used in laser texturing which are described in the literature are enlisted in the Table 2.3.

Table 2.3 Classification of wavelength for various laser types

Types of lasers	Wavelength (nm)
Diode pumped	1030
Excimer	193-351
Nd:YAG	1064
CO ₂	10600
Fibre	1064

2.5. Laser- material interaction

The different materials interact with the laser in different way. Laser interaction with different materials has gained considerable research interest in both academics and industry. It depends on both the material properties as well as the type of laser and the environment such as in air or vacuum where the interaction takes place[139]. The pulse width is a major classification of the laser which influences the laser- material interaction (ablation). The ablation of different solids using different lasers [140]. Different lasers interact with materials in different way. In this project we are focusing on the ultrafast laser and continuous wave laser system.

2.5.1. Continuous wave laser- matter interaction

In the continuous wave laser, the emission occurs in a single resonator mode. In theory, free electrons are accelerated by the applied electromagnetic field and collide with the lattice, thereby transferring energy into the material The physical phenomena continuous wave laser matter interaction is shown in [141]. Figure 2.4

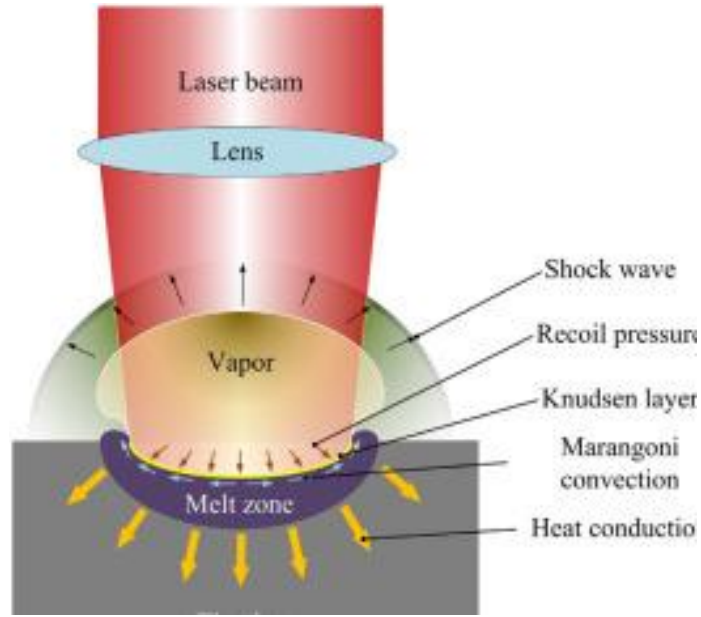


Figure 2.4 Physical phenomena continuous wave laser matter interaction [80]

In the continuous mode of the laser the interaction of the laser beam with the material is determined by power density, time of irradiation and energy density [142].

Power density (q_p): Power density is defined as the ratio of laser output power to the laser spot area. It is generally expressed as in the equation (1).

$$q_p = \frac{P_L}{A_s} \quad (1)$$

Where P_L is the laser output power and A_s is spot area.

Interaction time (t_i): It is defined as the time, in which a particular point is exposed to the laser beam while the laser beam is moving. It is the ratio of the beam diameter in direction of travel to the travelling speed or scan velocity.

$$t_i = \frac{d}{v} \quad (2)$$

Where d is the spot diameter and v are the scan velocity.

Energy delivered (E_{SP}): The energy delivered to any specific point on the surface of the material is called the specific point energy

$$E_{SP} = q_p t_i A_s$$

Where q_p is power density, t_i is the interaction time and A_s spot area.

These types of laser system create melt pool or penetration in the material and it occurs in three modes which is conduction mode, transition mode and keyhole mode. This can be observed by increasing the power density with a constant interaction time [143]. In the conduction mode very, less vaporization occurs and in keyhole mode the power density is high enough not only to vaporize material but also to open a hole. The transition mode lies between these two modes in which penetration depth upto 1 mm can be achieved. Controlled penetration depth in the material can be achieved by changing the process parameters.

2.5.2. Ultrafast laser-matter Interaction

Pulsed laser systems are categorised between two types **short laser systems** which are in the microsecond and nanosecond range and **ultrashort laser systems** which are in picosecond and femtosecond range [144]. The industrial term **ultrafast lasers** is defined as laser systems emitting ultrashort pulses. This means these laser systems are capable of generating light pulses with pulse duration within range of 100 femtosecond to 100 picoseconds. The typical pulse repetition rates of ultrafast lasers are of the order of megahertz or even gigahertz range [135].

Pulsed laser-material interaction can be separated in three groups as shown in Figure 2.5. The initial ultrafast processes occur in response to the electronic excitation (yellow) because of nonlinear multiphoton absorption process. , secondly the energy transfer from the excited electrons to atomic vibrations (green) occurs within picosecond ranges, The nonlinear photoionization processes (multiphoton or tunnelling) dominate the absorption of ultrashort laser pulses with durations of tens of femtoseconds (fs). The material ablation occurs in three steps within the femtosecond to pico-second range, shown within yellow boxes in Figure 2.5. First the absorption of light due to inverse Bremsstrahlung takes place in the outer layer. Then the electron thermal wave propagates by fast energy relaxation within the electron subsystem. Finally, electron-lattice relaxation occurs owing to electron-phonon coupling [145].

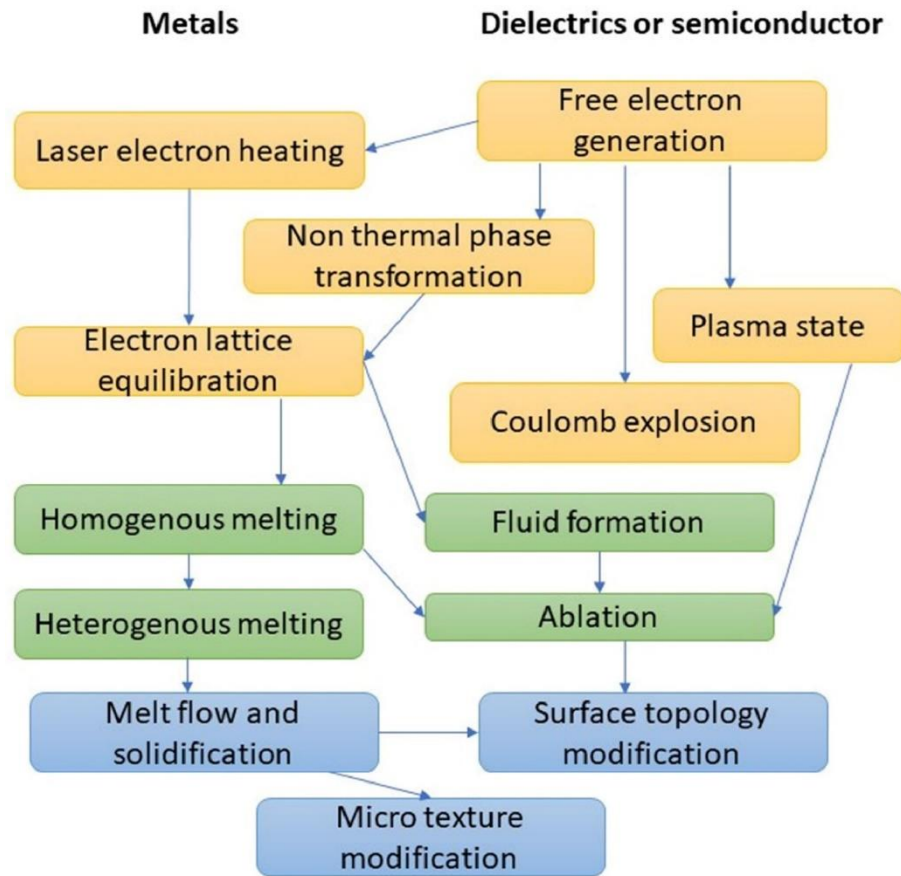


Figure 2.5 Energy dissipation and phase transformations following the excitation of a material by an ultrashort laser pulse

On other hand in the short laser pulses the ablation in this case nanosecond laser ablation represented in Figure 2.5 (turquoise), occurs due to absorption of laser energy, which is conducted in form of heat flux, melted, evaporated, or formed into plasma in the material depending on the temperature reached. The ablation mechanism depends on pulse duration and pulse energy. The depth of cut, ability to machine, and quality of produced surface features is also affected by the wavelength of the light [146], [86].

As the laser matter interaction depends on the process parameters, the next section discusses about the key process parameters in laser processing explained in the literature.

2.6. Key process parameters in laser processing

Process parameters are the input or in process parameters which directly or indirectly affect the quality of the material produced. These process parameters are very important as they affect the processing of material. Some process parameters for laser structuring summarized in the literature are as follows.

2.6.1. Laser pulse duration

It is one of the most important parameters in quality consideration of laser micro or nano machining or surface structuring. This is because long and short laser pulses in the range of millisecond to nanosecond pulse lengths are described by thermal ablation which is dominated by heat conduction, melting, evaporation, and plasma formation. If the pulse length is longer than the relaxation time the energy absorbed by the material is conducted away from the source as heat, this will produce a temperature field in the work piece known as the heat affected zone (HAZ)[147]. This will produce a melt pool around the heat source application location [148]. The extreme pressure and temperatures caused by the ultra-short pulse build up and accelerate the ionized material to extremely high velocities. Due to the short timescale continuous evaporation of the material does not occur, instead the material is transferred into an overheated liquid state. This high

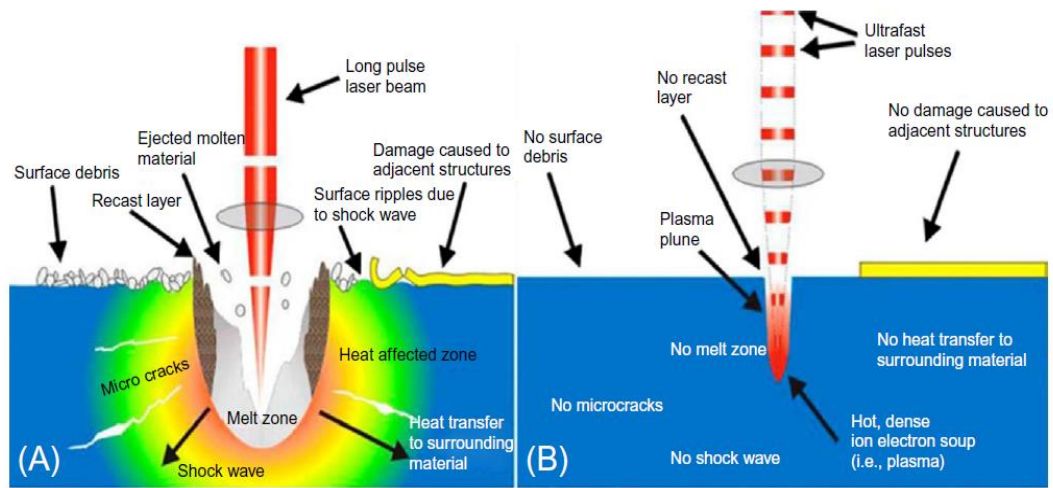


Figure 2.6 (a) Long and (b) short pulse laser ablation [90].

pressure overheated liquid merges into a mixture of vapour and liquid droplets causing a rapid expansion of the material removing it from the ablated area [149]. The femtosecond laser processing is named as cold processing as the laser power appears off before electrons transferring energy to lattice. The HAZ is approximately in range of 10 nm. A comparison of the ablation by long pulse such as micro or nanosecond width and ultrashort pulse width lasers such as femtosecond laser is shown in Figure 2.6.

There are other in process parameters such as laser fluence, pulse repetition rate or frequency, beam scan speed, polarization, beam profile, depth of focus. All these parameters affect the quality and type of the textures formed and its dimensional accuracy and hence quality of the topology. In the study reported by Yang et al, the laser fluence was varied and laser polishing was conducted on titanium alloy and the SEM and surface roughness was reported that the stronger the laser fluence,

the greater is the variation of surface roughness [150]. The comparison of different laser systems is illustrated in the Figure 2.7.

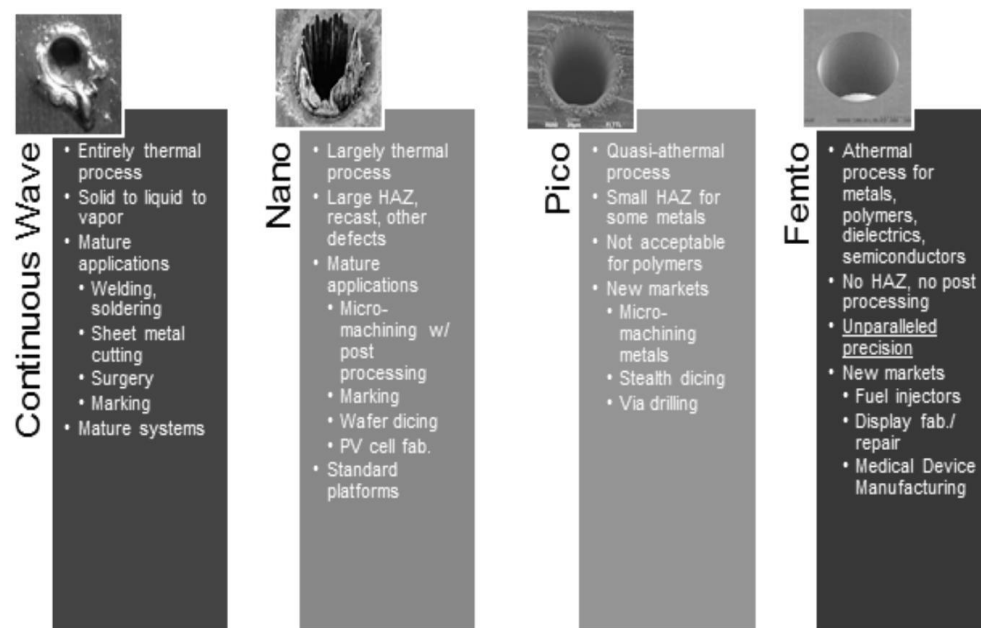


Figure 2.7 Assessment of hole quality and potential applications of laser systems with varying pulse durations [151]

2.6.2. Laser fluence

The ablation depth is directly dependent on the laser fluence which is the energy supplied per unit area. The area is determined by the diameter of the laser beam which is dependent on the laser beam profile. The fluence is one of the key parameters and was found to be universal. The fluence can be calculated by following formula.

$$F = \frac{\text{pulse energy}}{\text{area of the beam}}$$

To support this various microgrooves were manufactured on aluminum samples by femtosecond laser with different magnitude of laser fluence and analysis on the surface morphology was conducted using SEM and 3D laser confocal microscopy were recorded also its effect on the super wicking properties was done in the study [152]. Also in another study by Yang et al the laser fluence was varied and laser polishing was conducted on titanium alloy and the SEM and surface roughness was reported that the stronger the laser fluence, the greater is the variation of surface roughness [150].

2.6.3. Wavelength

In most of the cases in application of micro or nanomachining or structuring the wavelength is non variable parameters however it is important from functioning of the laser. Different wavelength of lasers is used for different materials and different purposes as different materials have different absorptivity as shown in Figure 2.8. Femtosecond lasers with different centre wavelengths are available in the market. The wavelength is an important parameter which is to be considered before the processing specific type of materials. A study was conducted to see the influence of variation of laser wavelength on the micro machining attributes. In this study two wavelength lasers were used one with 355 nm and other with 532 nm wavelength. It was reported that the crater depth which is the micromachining attribute, increment declinations of 355 nm are more evident than 532 nm wavelength operation [153].

Figure 2.9 shows the effect of wavelength on the absorptivity of different materials such as

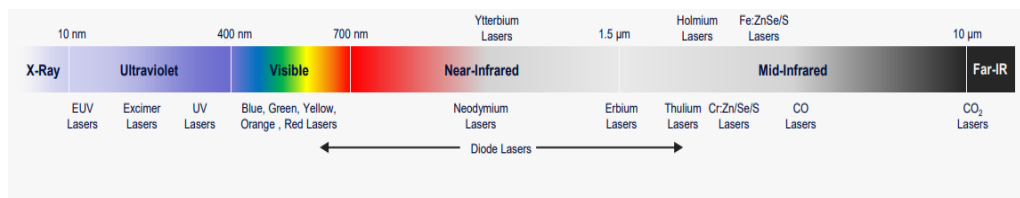


Figure 2.8 Wavelengths of commercially available laser systems [153]

aluminium, gold, silver, copper, molybdenum, iron, and steel.

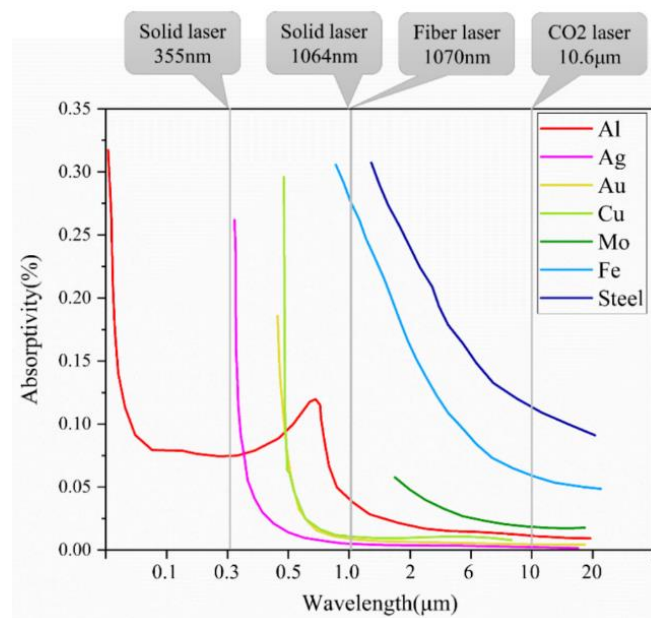


Figure 2.9 Absorptivity of metals with respect to wavelength [107].

2.6.4. Pulse repetition rate (Frequency)

Pulse repetition rate or frequency is defined as “the number of emitted pulses per second, or more precisely the inverse temporal pulse spacing [154] and is a key parameter as it leads to fast and localized energy deposition, and minimal thermal load to the workpiece and also ensures high accuracy and precision of the machining process at increased processing speed. In the research by Schille et al a study was conducted on the different type of ultrashort pulse laser systems supplying high average laser power were applied in order to investigate the influence of the laser parameters on machining qualities on copper. This was obtained by irradiating at different frequencies and then were evaluated by means of surface roughness measurements and scanning electron microscope micrograph analysis. The result showed that the removal rate increased with the higher repetition rate to a maximum at 6.44 MHz [155].

2.6.5. Beam scanning speed

It is the speed at which the material is ablated by the laser and is measured in mm/s and is one of the key parameters for quality of micro/ nano structures produced by laser ablation. In recent research, an investigation was conducted to find out the influence of laser parameters on the ablation in ultrafast surface structuring. In this an array of rectangular cavities were manufactured on solid copper material. In this, the laser beam scanning speed has been varied in order to reach maximum material removal rate. The results show that a high number of pulses per spot is achieved because of the high pulse overlap. Therefore, the ablation threshold decreases drastically, and the total ablated depth increases. And on other hand at high scan speed the ablation threshold increases due to the accumulation effect which causes a small ablation depth [156].

2.6.6. Polarization

Polarization is defined as direction of the electric field oscillation of a laser beam and is an important parameter as the main impact of polarisation effects can be seen in laser processing of metals, where the actual angle of incidence can be high (70° to 80°), since the beam strikes and is absorbed by the inclined cut surface during the process and not by the original face of the workpiece. In a recent research paper the experimental investigation is conducted on femtosecond laser structuring with continuous spatial evolution of polarization and fluence distribution in the focal plane [157]. There are two types of polarization linear polarization and circular or radial polarization. Linear polarization creates elliptical shape of the column bases as seen in the research by Nivas et al [157]. Circular polarization leads to circular shape of the column bases [158], [159].

2.6.7. Beam Profile

Beam profile provides the data on the beam spatial characteristics such as size, position, shape, propagation, and mode structure. This information is key not only for maintaining the optimum system performance, but also for achieving the process-specific beam parameters. The laser beam spatial intensity profile of the beam, which is the power density distribution in the plane perpendicular to the beam propagation direction is an important characteristic. Normally, there are two types of beam profiles Gaussian and Top-hat profiles. This mostly affect the submicrometric alignment accuracy of the structure [160], [161].

2.6.8. Depth of focus

Depth of focus also referred to as depth of field can be defined as the allowable distance from the point of best focus (smallest spot size), which produces an acceptable spot size. A general expression for depth of focus is given as follows [162].

$$d = \pm \frac{\pi\sqrt{\rho^2 - 1}\omega_o^2}{\lambda C}$$

Where ρ is the allowable spot size variation, ω_o is focused spot radius, C is a factor that accounts for higher order modes [163]. The depth of focus is a parameter which affects the operation flexibility and quality of laser micromachining.

2.6.9. Effect of environment of ablation

Femtosecond micro and nano machining can be done in ambient atmospheric conditions since it is a cold working process. However, it should be done in low dust and low humid place. The humidity significantly affects the quality of ablation and dust can cause contamination. However, for some material vacuum atmosphere is required. In a study by Dou et al ablation rates of Al-Mg alloy were studied in air and vacuum for laser ablation. It is reported that the ablation rate in vacuum is much higher than that in air. The researcher suggests that this was because of the oxidation effects and strong defocusing effects associated with the non-equilibrium ionization of air. Also, the quality ablation in the SEM images are distinct [164]. On other hand the generation of vacuum system is very expensive and requires additional instruments such as vacuum generation pumps etc.

The next section discusses about different types of material processing techniques using different types of laser system used industrially and in research.

2.7. Laser material processing techniques

Three important ultrafast laser processing techniques which appear in the literature and are used to manufacture functional surfaces are direct laser interferences patterning (DLIP), direct laser writing (DLW) and Optical wavefront shaping (OWS).

2.7.1. Direct laser interference patterning

Direct Laser Interference Patterning (DLIP) incorporates multiple overlapping laser beams to produce an interference pattern as shown in Figure 2.10. This process produces periodic micro-nano structures on the surface of the material with the structures corresponding to the amplitude distribution of the interference pattern [165]. The polarization, number of beams and laser fluence all contribute to the distribution and size of the final texture produced [166]. DLIP is a highly suitable approach for high throughput processing due to its ability to process sub-millimetre scale areas with a single pulse, and fast processing speeds of up to $0.9\text{m}^2/\text{min}$ as shown in the research by [167]. LIPSS is also commonly formed during the DLIP process producing higher order structures on the surface [168]. The effect of altering process parameters on the homogeneity of DLIP processed structures on Ti6Al4V using a nanosecond Nd: YLF laser was investigated. The authors reported that hatching distance is the most significant parameter for the surface homogeneity. with a relevant importance on the large periodic modulation, it shows that the hatching distance must be a multiple of the interference spatial period and must be smaller than the laser beam diameter. Higher pulse to pulse overlaps also showed the highest texture homogeneity with the overlap having a strong influence on the structural depth of the line pattern. This increase homogeneity has been seen to increase the water contact angle and antifouling properties. Figure 2.10 shows the working principle of the DLIP process. In the Fig. 7., ω is the beam diameter, Λ is laser intensity profile/ ablated structure period, θ is beams intersection angle, d is the distance between the laser spots, OVP is the spot overlap; v is the samples' translation speed; R_{oth} is the radius of ablated area and h is ablated structure depth [169].

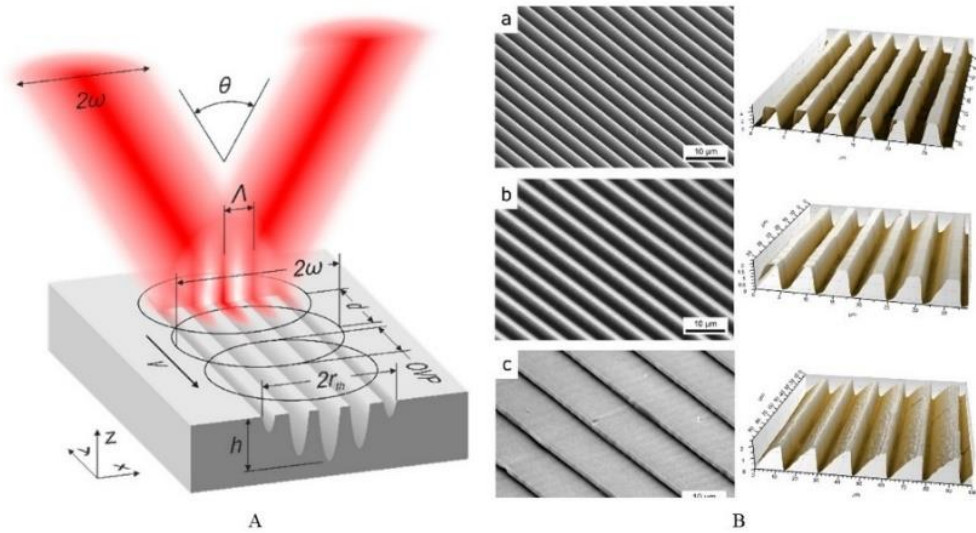


Figure 2.10 A. Model of direct laser interference patterning (DLIP) , B, SEM micrographs (left) and confocal topography (right) of the structured polyimide foils using DLIPS. [170], [171]

2.7.2. Direct laser writing

Direct laser writing (DLW) is one of the most common laser texturing methods. An example of the setup for DLW is shown in Figure 2.11. The relative ease of DLW processing and simpler equipment compared to other techniques is well noted [172]. DLW has been used to produce a plethora of different 3D micro structure on a large variety of materials [173]. Even with its excellent texturing ability DLW is hindered by its low through-put processing minimizing its efficiency in large scale processing. To combat this issue DLW has more recently been combined with the other laser texturing method such as LIPPS or DLIP.

Nanosecond DLW to produce a microcell pattern with a width of $50\mu\text{m}$ on TiAl6V4 followed by the use of picosecond DLIP to create micropillars within the larger microcells at a width of $2.6\mu\text{m}$ this produces a hierarchical micro-nano structure on the surface of the material increase in water contact angle (WCA) to a value over 110° [174]. Also, DLW method to fabricating super hydrophobic steel surfaces using a two-step process of water confined nanosecond laser texturing in combination with an immersion in chlorosilane solution to hydrophobize the textured surface. The submerging of the steel specimen in deionized water confines the laser pulse induced plasma increase the texturing effect of the laser allowing for a higher throughput process. This process produces super hydrophobic micro-nano scale textures on the surface of the steel. The effect of different laser power on the final water specific contact angle (WSCA) was investigated and showed a sharp increase in WSCA from 0 to $0.2\text{GW}/\text{cm}^2$ where the WSCA was 155° [175].

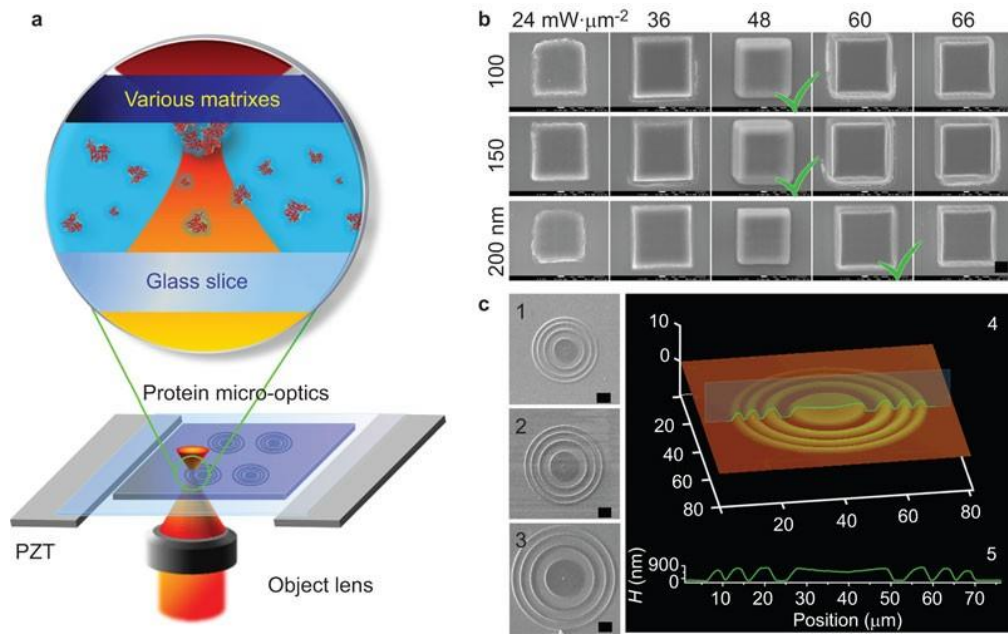


Figure 2.11 (a) Direct laser writing process, (b) SEM images showing topography influenced, and (c) SEM images of glass cover slips and AFM characterization exhibiting 3D morphology [176]

2.7.3. Optical wavefront shaping

Optical wavefront shaping is the type of generating surface structures on the materials by splitting laser beam using spatial light modulator (SLM) as seen in Figure 2.12. A spatial light modulator is a tool that alters the polarization, amplitude, or phase of light waves. It often uses liquid crystals that are directly and precisely controlled by voltage. This allows for high resolution, high speed reflective or transmissive phase modulation with individually addressable pixels to control beam form, focus location, and even intensity distribution.. The diffractive multi-beam patterns are modulated in real time by computer generated holograms. The patterns are generated at high throughput according to research by Kuang et al. Using this technique complex structures can be formed on the large surface area [177].

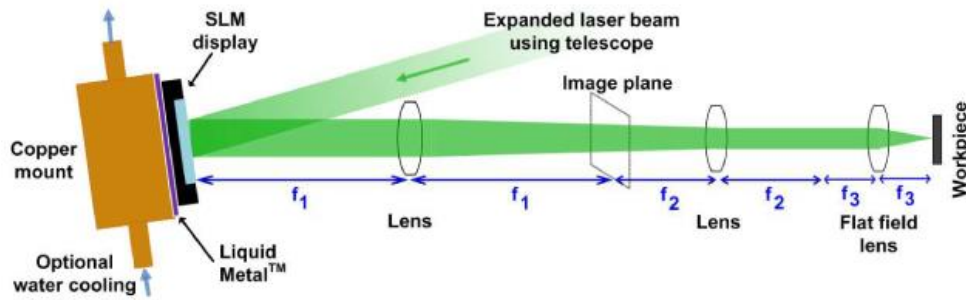


Figure 2.12 Setup for laser machining using optical wavefront shaping using spatial light modulator [178]

This shaping method can be used to laser process thin foil materials and is capable to produce high aspect ratio surface structures. One of the recent research by Sun et al shows use of this technique to fabricate microporous arrays for oil–water separation application [179]. This process is also used to generate micro channels in the transparent polymer materials recently [180]. SLM has a great potential in multi-beam laser micromachining for speeding up the processing rate. However, this process is quite novel and under development and is in the initial phase.

2.7.4. Laser surface heat treatment and hardening

Laser heat treatment is one of the most versatile and industrially accepted process and is mainly used for surface hardening of the metallic materials. This is the cleanest process as laser hardening is achieved with negligible contamination and this process is easiest process as it does not require vacuum environments. Moreover, the energy requirement for laser is less than the case hardening process which is done in heating chambers [181].

In laser surface hardening, fluxes generated by lasers are most suitable to heat the surface layer to authentication levels without affecting the bulk temperature of the sample. The self-quenching in air eliminates need of external quenching and hard martensitic alloy is achieved on the surface. This improves the wear resistance and enhanced tribological properties [182]. The Figure 2.13 illustrates the laser surface hardening using continuous wave laser.

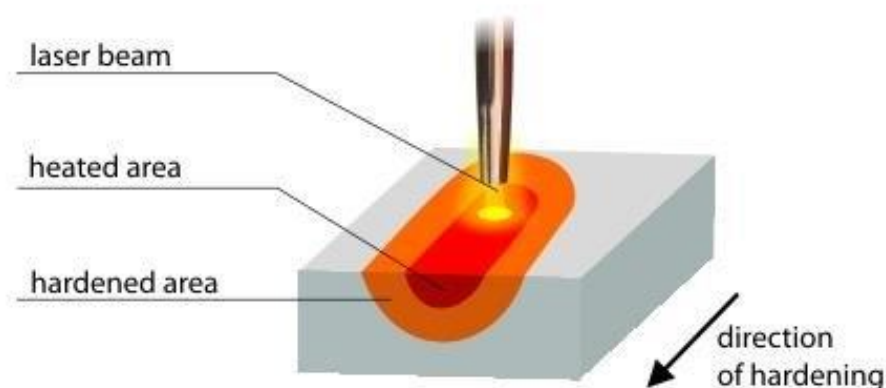


Figure 2.13 Schematic of laser surface hardening [183]

Continuous lasers are also used for laser surface alloying in order to get enhanced surface performance for wear and corrosion resistance [184]. Another work is conducted on the tool steel AISI H13 using fibre laser to improve the hardness and it improved it by 112% as reported. There is almost no study of laser hardening of aluminium and aluminium alloys as aluminium has high reflectivity and it absorbs very less amount of energy, however combining this technique along with laser patterning technique can be done in order to laser harden aluminium.

2.8. Functional surfaces

There are various micro or nano topographic structures found in the nature which inherit functional properties such as antifouling, antibacterial, self-cleaning and water or ice repellent. These topographic structures can be replicated onto another material using the femtosecond micro or nano machining or structuring. This strategy is nontoxic and eco-friendly strategy to prevent fouling on surfaces.

2.8.1. Biomimetic micro-scaled surfaces

There is nature inspired strategies in which the surfaces are designed by replicating the surface topology of that of some biological organism which can be termed as biomimetic surfaces. Other strategies are controllable periodic structures which are repetitive structures which are fabricated using laser irradiation, laser induced graphene coating formation, and foam nano structuring.

Anti-biofouling approaches are found in the natural surfaces of different organisms. In the ambient environment plants such as rice leaves and insects employ these controls. In the marine environment plants, corals, and fish, crabs employ the physical and chemical controls of anti-fouling. Some of interesting surfaces are lotus leaves, taro leaves and shark skin which have property to prevent bacterial adhesion and cell attachment due to the presence of micro and nano superhydrophobic structures and surface patterns which are present on them naturally. These structures affect the wettability and adhesive properties of the surface which are function of the fouling resistance [185].

The self-cleaning behaviour is studied which is the effect of the micro and nano structures naturally present on the skin of the lotus leaf [186], rose petal [187]. Furthermore, bacterial adhesion reduction was also studied on lotus leaf-inspired hierarchical, fluorinated polypropylene surfaces which were manufactured using reactive ion etching (RIE) treatments and it has been reported that best anti-biofouling results were obtained from fluorine reactive ion etched samples that created lotus leaf-like hierarchical structures consisting of microstructures and nanofibrils [188]. Furthermore, there is an ongoing research conducted on bioinspired self-cleaning and low drag micro/nanopatterned surfaces in mediums such as water, oil, and air flow based on the rice and butterfly wing which potentially prevents the colonization of microorganisms leading to biofouling [89]. Moreover, the research is focused on the anti-fouling properties of microstructure surfaces rice leaves and butterfly wings. Their study was focused on the anti-biofouling of *E. coli* microorganisms and have reported anti-inorganic fouling results from wash experiments using SiC simulated dirt particles [88]. Measurements and imaging were done using light microscopy and SEM. Contaminant removal was reported to be 95% using the rice leaf pattern. The antifouling surface structures seen in various natural surface which are illustrated in Figure 2.14.

More interestingly, the gecko foot has some advanced surface properties such as antibacterial and self-cleaning [128]. The micro and nano structure of the skin exhibited ultralow adhesion with contaminating particles. The focus of the study was to investigate some of the associated properties/functions of this outer skin layer with a focus on solid and liquid contamination and it was found that gecko skin provides a unique topographical template for multifunctional man-made designs which may potentially aid in areas as diverse as self-cleaning surfaces [189].

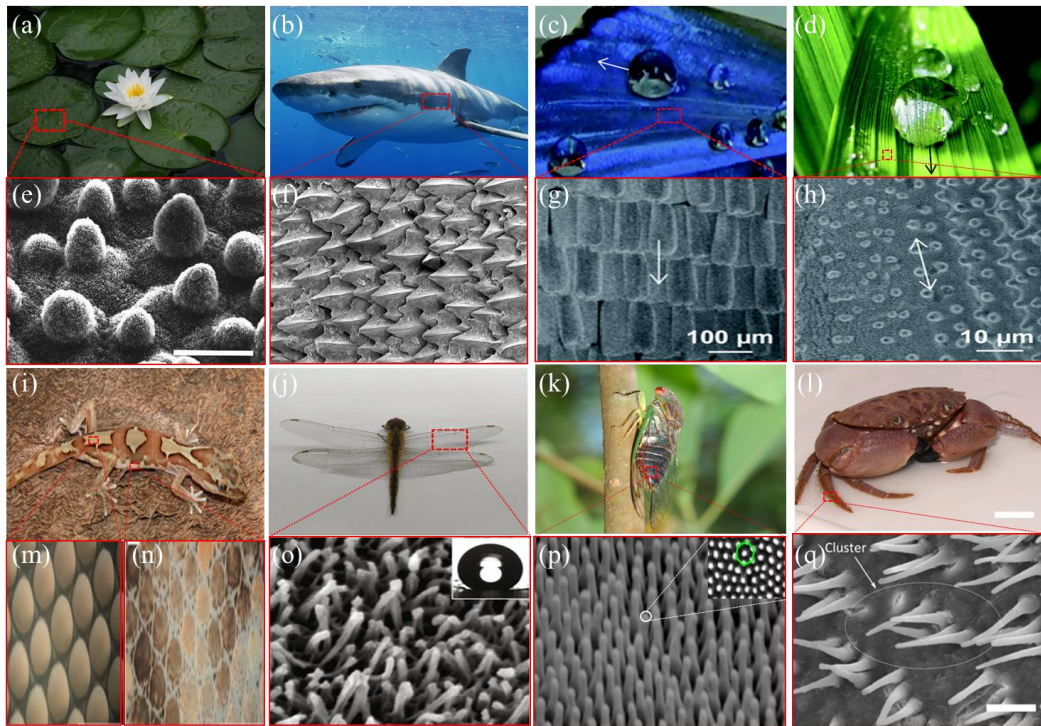


Figure 2.14 Examples of bioinspired antifouling surfaces from different organisms such as (a) lotus leaf, (b) shark skin (c) butterfly wings, (d) rice leaf, (e-h) corresponding SEM images of the above examples, (i) geko (*Lucasium steindachneri*) (j) dragonfly of *Pantala flavescens* Fabricius (k) *Psaltoda claripennis* cicadae (l) marine decapod crab (*M. Hardwicke*), (m-q) respective high magnification images of i, j, k and l. [190]–[194]

The skin of the sharks is very intriguing three-dimensional rib patterns in their experimental study in oil flow channel optimization. The results show that shark skin reduced the drag significantly which also reduced the fouling which can be patterned onto different surfaces [191]. To support this a computational fluid dynamics study was conducted by researchers on a ship hull surface design. In their work, a comparison of surfaces one with biomimetic shark skin and another without showed that the hull with the biomimetic shark skin has better total drag coefficient with a reduction of about 9.5% compared to the original hull. Drag reduction results from improved fouling resistance. The antifouling and friction reduction performance was also evaluated, and the results show that a remarkable improvement of 13% was observed in fouling resistance and wettability as compared to the surface without the biomimetic shark skin. This was conducted using SEM analysis of the algae formation on the surface [192].

Moreover, in a recent study proposed biomimetic strategies and identified microstructures on the different marine shells such as *Dosinia japonica*, *Gafrarium pectinatum* and *Mimachlamys nobilis* which possess some antifouling properties. The researchers conducted antifouling trials on the replicated surface patterns on the polymer by measuring the chlorophyll-a content at different contact angles. The produced surfaces produced good fouling resistance. A lot of research has been

conducted till now on biomimetic structure however it is still not complete as the replication of these structure on large surfaces is extremely costly. Studies need to be conducted for cost effective microstructures replication on large surfaces irrespective of their material which would increase the fouling resistance properties of the surfaces. The following section discusses some of important laser based micro and nano texturing techniques already being used in labs and industry [193]. In our this project we do not specifically target to produce any biomimetic surface however in the later sections the star pattern resembles the shark skin as shown in Figure 2.14 b.

2.8.2. Hierarchical structures

Hierarchical textures are micron scaled textures formed on the solid material surfaces. They also contain certain sub-micron features which enhance their fouling resistance. There are various artificial hierarchical textures which have the capacity to prevent adhesion and accumulation of particles. These are periodic in nature and can be fabricated easily onto the different material surfaces. In recent study, conducted by Sun *et al.* by fabricating controlled periodic structures on AISI304 stainless steel substrate using picosecond laser system, and their anti-biofouling performance was examined by submersion of the substrate for five weeks in summertime [134]. A 50% decrease of the average microbe attachment was obtained (see Figure 2.15).

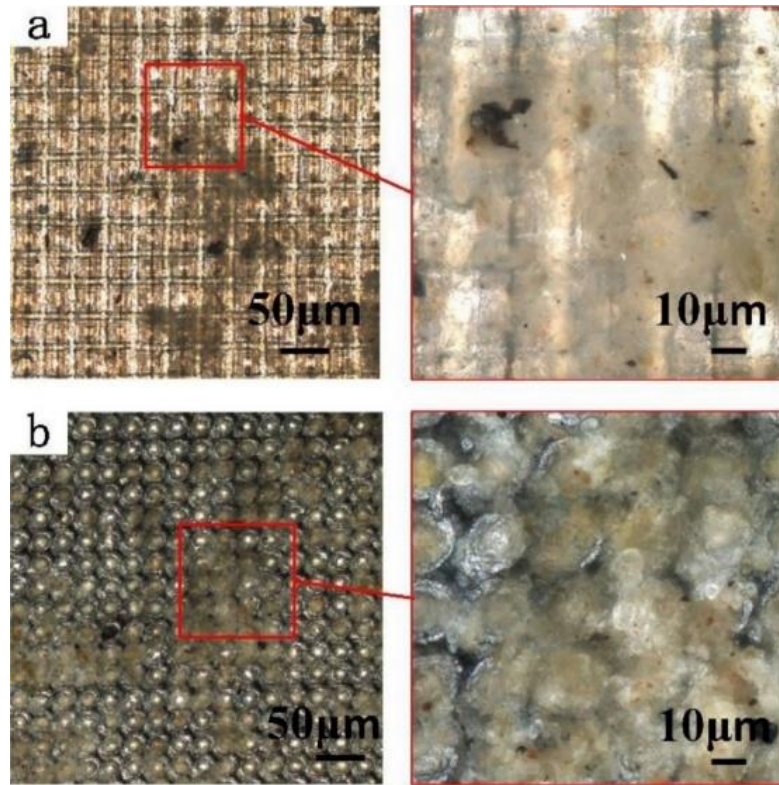


Figure 2.15 Comparison of micro groove and pit patterns formed by controllable periodic structures using femtosecond laser (a) SHS with micro-groove pattern and (b) SHS with micro-pit pattern [195]

In another recent research by Tuo et al, superamphiphobic surfaces were developed on the 304 stainless steel and 6061 aluminium alloy surfaces using ultraviolet laser texturing and then coating with PTFE/FS-61 on the rough structures made by laser. The findings show that the surfaces exhibit excellent repellence to liquids such as water and oil. Moreover anti-fouling and drag reduction properties were also being reported [196]. These types of structures are useful when the fouling is at macro scale such as colloidal, scale, corrosion and ice fouling however micro-scale fouling is not much affected because of these structures such as biofouling which includes bacterial adhesion, protein adhesion or chemical fouling [197].

2.8.3. Nano scaled laser induced periodic surface structures

Laser induced periodic structures also known as LIPSS are the self-organized nano scaled structures produced by the laser irradiation of a material surface. LIPSS produces periodic ripple textures on the surface of the material with a spatial period (Λ). LIPSS are then broken down into two further categories based on the spatial period these are low spatial frequency LIPSS (LSFL) where the spatial period is roughly equal to the wavelength of the incident laser sources $\Lambda \sim \lambda$ and

high spatial frequency LIPSS (HSFL) where $\Lambda \sim \lambda/3$ [198]. Due to the larger HAZ and less precise nature of short laser pulses only HSFL has been successfully synthesized using ultrashort pulse lasers [199]. The mechanism for the formation of LIPSS is still under consideration but the most widely accepted being Sipes theory which is based on the interference of the incident laser radiation with surface electromagnetic waves that are generated by scattering on the surface roughness [200]. The wavelength scale of the LIPSS texture makes it an ideal choice for the creation of ordered micro-nano structures which increase antifouling and hydrophobic behaviour [201].

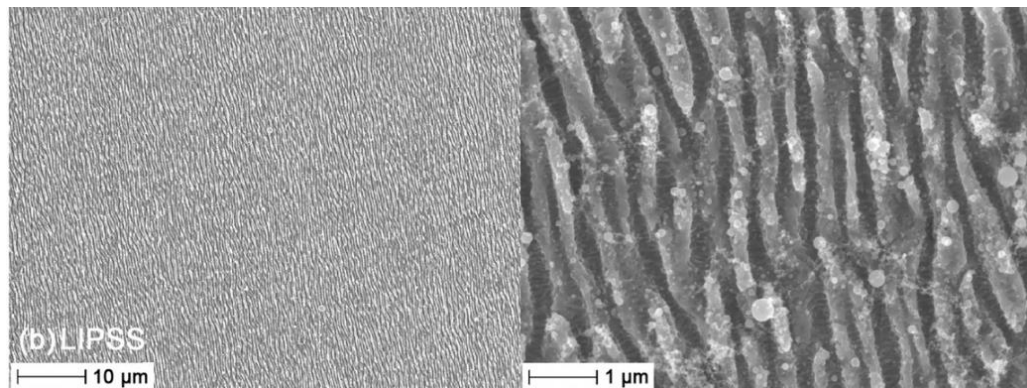


Figure 2.16 SEM image of laser induced periodic surface structures to enhance antifouling properties at (a) low and (b) high magnification

The antifouling ability was tested for femtosecond laser produced periodic nanostructures by Epperlein et al, using the technique of purposefully colonizing with bacteria to investigate their adhesion ability [140]. *E. coli* and *S. aureus* were used to purposefully colonize the laser textured area. Here in this study it is reported that the femtosecond laser processing technique was able to be applied to control bacterial colonization [202].

Another study on laser surface texturing of titanium as a method to reduce the adhesion of *Staphylococcus aureus* and biofilm formation was conducted in which LIPSS-produced nanoscale structures were formed using femtosecond laser processing shown in Figure 2.16. Due to laser irradiation, it formed nanostructures such as nanometric level periodic surface structures and nanopillars. The assessment of antifouling ability was conducted using fluorescence microscopy image analysis of *S. aureus* 48 h after bacterial cell seeding. The results depict that the average fraction of surface area covered by bacteria on laser treated surface was 7 % whereas the average fraction of surface area covered by the same bacteria on a polished sample was 25%. This shows that the bacterial adhesion was reduced by 18%. This was because the features made by laser irradiation were slightly smaller than the bacteria size and denser. This study also reported a reduction in the tendency to form biofilms [203].

2.9. Characterization

2.9.1. Wettability

Wettability is the ability to the surface to become wet. Wettability of a given surface is characterized by the static contact angle (CA) which is the visually measurable angle between the tangent to the liquid–vapor interface and the solid surface at the three-phase contact line. Generally, the contact angle is measured from the liquid side. It has defined by young’s equation as given.

$$\cos\theta_{Youngs} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}$$

Where θ_{Youngs} is the Youngs contact angle γ_{SV} and γ_{SL} are the solid- vapor and solid- liquid interfacial tension. From the Young’s equation, it is understood that a solid surface with high surface energy shows lower contact angle and solid surface with low surface energy shows higher contact angle. This contact angle is static contact angle as illustrated in Figure 2.17.[204],[205].

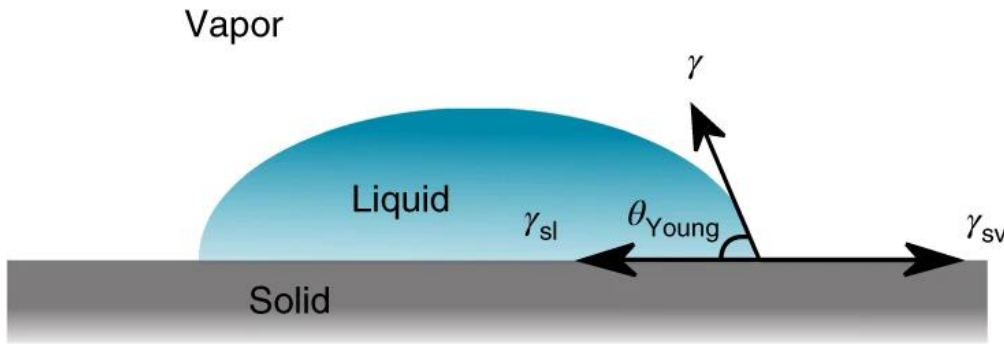


Figure 2.17 Illustration of water contact angle measurement [204]

There are two methods for measuring the wettability of the surface – direct and indirect methods. The direct method involves two methods namely sessile drop goniometry and tilting plate method.

Sessile-drop goniometry is a technique used in the procedure to measure contact angles or wettability of the surface. It is carried out by filming a water drop on a solid surface and using a fitting technique to extract the contact angle from the video which is converted to frames images.

Based on the contact angle measurements, the surface is termed as hydrophilic superhydrophilic, transition, hydrophobic and superhydrophobic (ultra-hydrophobic) surface. The schematic diagram shown in Fig. helps to feature the four different wetting behaviors of the surface such as super-hydrophilic, hydrophilic, hydrophobic and super-hydrophobic nature of the surfaces.

When the water contact angle is less than 10° the surface is called as superhydrophilic, the contact angle is less than 90° the surface is called as hydrophilic, contact angle is more than 90° the surface is called as hydrophobic and the contact angle is more than 150° the surface is called as superhydrophobic as illustrated in Figure 2.18 [59], [206].

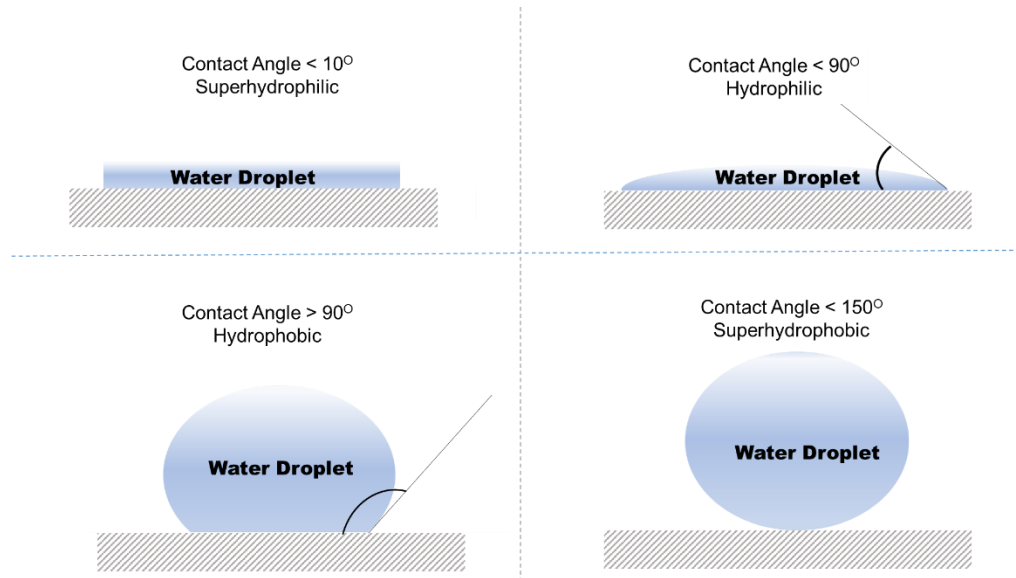


Figure 2.18 Different types of wetting behaviours

In some cases the sliding contact angle is also characterized by measuring the angle from the leading edge and the trailing edge of a distorted drop on an inclined plane when the drop starts sliding as the plate is tilted at certain angle [207], [208].

The indirect method to measure wettability is Wilhelmy plate method where the surface in the form of a thin plate is dipped vertically into water, and the contact angle is determined from the measured force. The change in the force is a combination of buoyancy and the force of wetting. This method is rarely used for wettability measurements as there is no visual feedback to help detect how wetting occurs [209].

The surface roughness is one of the key parameters which changes the wettability of the surface. The surface roughness impacts the apparent contact angle θ , which is often different from the one expected from the young's equation. For this there are two models developed by scientists. Wenzel model and Cassie baxter model as illustrated in the diagram Figure 2.19.

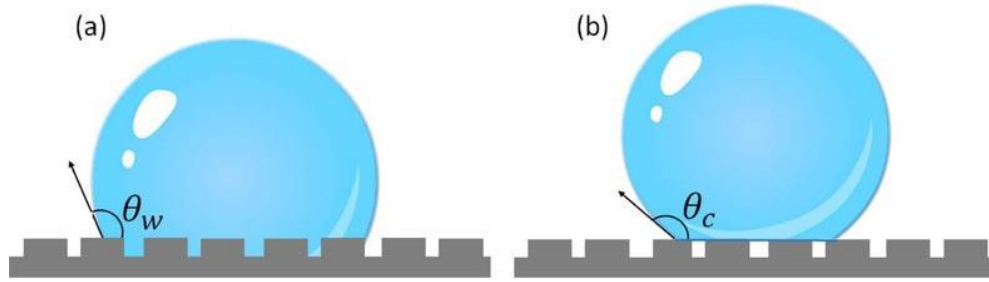


Figure 2.19 Schematic of water droplet on a rough surface (a) Wenzel state ,(b) Cassie Baxter state

A droplet on a rough surface spread until it reaches an equilibrium state characterized by Wenzel equation.

$$\cos\theta_w = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma}$$

Where θ_w is the contact angle by Wenzel method γ_{SV} and γ_{SL} are the solid- vapor and solid- liquid interfacial tension and r is the surface roughness factor.

This equation states that the originally hydrophilic surface will become more hydrophilic and originally hydrophobic more hydrophobic with the increase in surface roughness [210]. In other theory, Cassie-Baxter equation describes rough surface, which is able to trap air between. surface features when a droplet is deposited on the surface.

$$\cos\theta_c = f(1 + \cos\theta) - 1$$

Where θ_c is the contact angle by Cassie Baxter method, f is the fraction of the solid surface that is in contact with the liquid.

There are various surface modification methods as described in above sections which are capable of changing the surface roughness which affects the surface wettability. By optimal design of nano and microstructures is possible to repel different liquids without additional chemical treatment.

2.9.2. Surface roughness

Surface roughness can be characterized by different mechanical, electronic and optical methods. Ultrafast lasers are used especially used to modify the surface attributes at nano and micro scales. To detect the surface nano and micro roughness surface profilers such as stylus profilers which is stylus and probe which is attached to the electro-mechanical sensors. This probe physically moves along the surface at specific distance at specified contact force in order to acquire the surface

heights. The range of measurements lie between 10 nanometres to 1 millimetre. Generally, these techniques use Taylor -Hobson method for measurement of surface roughness.

In recent times the non-destructive 3d optical profilers are also used which use white light or laser interferometry to detect the change in the topology or depth. These techniques are quite precise and repeatable.

Also, atomic force microscope is used to measure the roughness of nano and sub nano ranges. In this technique information is gathered by "feeling" or "touching" the surface with a mechanical probe. One of the advantages of AFM in the study of surface properties is the ability to quantify both surface morphology and surface interactions with a single instrument. This technique is considered to be destructive technique but at nano scale also it can be negligible. However this technique is quite popular for small area nano level roughness detection [211].

In almost every instrument used for surface roughness the quantification of surface roughness is given by surface roughness metrics or attributes. According to ISO 25178 standard there are seven different standard surface roughness metrics for 3D areal measurement: S_a , S_q , S_{sk} , S_{ku} , S_p , S_v , and S_z . The 2D profile measurements are represented by roughness metrics: R_a , R_q , R_{sk} , R_{ku} , R_p , R_v , and R_z as shown in Table 2.4 .

Table 2.4 Roughness attributes and its definition

Roughness attribute	Definition
S_a / R_a	Arithmetical mean height
S_q / R_q	Root mean square of height
S_{sk} / R_{sk}	Skewness
S_{ku} / R_{ku}	Kurtosis
S_p / R_p	Maximum peak height
S_v / R_v	Maximum pit depth
S_z / R_z	Maximum height

2.9.3. Surface chemistry characterization

The measurements of amount of elements present on the surface and their analysis of physical and chemical properties is conducted by various techniques. Some of the techniques are listed below.

XPS (X-ray Photoelectron Spectroscopy)

In this technique quantitative elemental, chemical state and functional group information from the surface of materials is conducted. The sample is irradiated with monochromatic x-rays which stimulate emission of core level electrons from atoms within the surface. In this technique, the kinetic energy of these photoelectrons is measured in an electron spectrometer and used to identify the elements present on the surface [212].

SEM/EDX (Scanning Electron Microscopy / Energy Dispersive Analysis)

The scanning electron microscopy is a technique in which a beam of electrons is produced by an electron gun. This beam is concentrated on the sample which is placed at the focus. The beam hits the sample, electrons and X-rays are ejected from the sample. These back scattered electrons and X-rays are detected by the detectors which are placed at the angle. Using this technique microstructural analysis, fault diagnosis, imaging can be conducted.

Moreover, the energy dispersive x-ray spectroscopy technique involves raster scanning a coherent focused probe across the object while recording the resulting x-ray emission spectra at each probe position. An elemental map is then created using this spectrum [213], [214]. However, this technique is not very accurate method as there are many limitations for using this technique and it can just provide an indicative elemental composition on the surface.

XRD (X-Ray Diffraction)

X-ray diffraction spectroscopy is a non-destructive approach for characterizing crystalline materials. In this technique sample is irradiated with a beam of monochromatic x-rays over a variable incident angle range. Interaction with atoms in the sample results in diffracted x-rays when the Bragg equation is satisfied. It gives information on structures, phases, preferred crystal orientations (texture), and other structural data such as average grain size, crystallinity, strain, and crystal defects.

The constructive interference of a monochromatic beam of X-rays dispersed at certain angles from each pair of lattice planes in a sample produces X-ray diffraction peaks. The distribution of atoms inside the lattice determines peak intensities. These peaks help to determine the elemental composition. The technique uniquely provides phase identification along with phase quantification, % crystallinity, crystallite size and unit cell size [215].

FTIR (Fourier Transform Infrared Analysis)

Fourier transform infrared spectroscopy analysis provides comprehensive information on compound bond structures. The absorption of infrared light caused by the vibrational and rotational properties of dipolar chemical molecules is the basis for FTIR. The arrangement and strength of

chemical bonds within a molecule have a direct effect on the molecule's characteristic modes of vibration and vibrational bond frequencies, resulting in the formation of a series of distinct mid-infrared absorption bands (4000-400 cm^{-1}) that can be used to characterize and quantify individual compounds.

Raman Spectroscopy

In this method a non-contact method providing information on chemical bonds and molecular structure. It offers molecule-specific information, which is a distinct advantage over commonly used detection schemes [216].

2.9.4. Characterization of surface fouling properties

In general, there exist numerous techniques to evaluate the fouling properties of surfaces. The majority of fouling characterisation methods employ self-made laboratory experiments that are tailored to the specific application of the material. At first, a significant number of works measure the hydrophobicity and icing characteristics of newly developed metal surfaces using contact angle measurements. Contact Angle Hysteresis (CAH) was utilized to measure wetting phenomena and fluid-metallic surface interactions [217]. Furthermore, the phenomenon of freezing effect or ice adhesion is commonly evaluated by the experimental arrangement depicted in the **Figure 2.20** (a)-(c). The calculations involved determining the icing delay time and the contact interaction time in relation to the anti-icing or freezing qualities of the surface. In order to assess the strength of ice adhesion, many methods were employed, including the peak force method, centrifugal force method, tensile force method [218].

In general, biocorrosion was characterized using the conventional method of weight loss and electrochemical characterization. Electrochemical characterization consists of tests such as open circuit potential (OCP), Potentio-dynamic polarization (PDP), and linear polarization experiments utilizing a three-electrode setup shown in **Figure 2.20** (d). Electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) studies were also used to passivation or oxide layer on the metallic surface [219]. These approaches were utilized to quantify the ice adhesion strength which evaluates the anti-freezing capability of the metallic surface. Few common in-vitro methods for biological assays include growth inhibition studies using absorbance measurements, colony forming unit (CFU) counting using ImageJ, live/dead bacteria staining tests using fluorescence microscopy, and morphological analysis using scanning electron microscopy (SEM). In summary, all these assays offer initial evaluations for the overall integrity of the prepared surfaces before applying their real-time utilization.

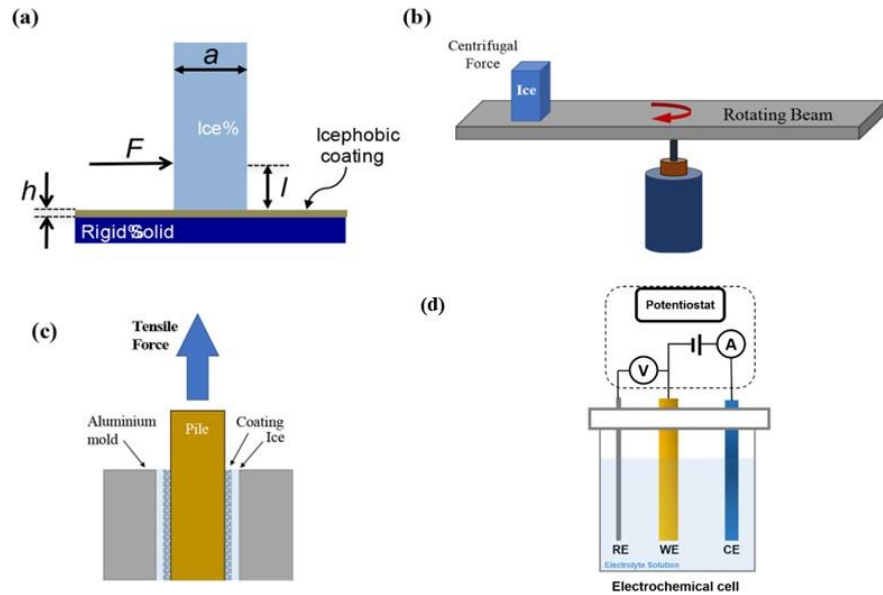


Figure 2.20 Illustrations of experimental methodologies used to assess ice adhesion (a) Cuvette-encased ice column: This approach involves measuring the shear stress required to detach an ice column that is encased in a cuvette from the surface; (b) Centrifugal for method: In this method, induced shear stress at the ice-coating interface is measured by subjecting the system to centrifugal forces; (c) Tensile force method: This technique utilizes a tensile machine to induce shear stress at the interface, evaluating the adhesion of ice to the coating; (d) 3 electrode electrochemical setup to test corrosion Reproduced with permission [220],[218]

2.9.5. Surface mechanical characterization

Micro Hardness

Mechanical properties such as hardness and modulus of elasticity define the strength of the material at structure level. In certain application where these properties are very important such as machine tooling industry. Mechanical properties such as hardness and modulus of elasticity can be detected using various destructive and pseudo destructive techniques such as micro hardness testing, nano indentation. Vickers hardness test is one of the most easiest test carried out which estimates the hardness based on basic principle which is to observe a material's ability to resist plastic deformation from a standard source [221].

For more accurate and precise at small scales nano indentation is used for experimental studies of fundamental materials physics. Using this technique, it is very easy to measure the most important mechanical properties hardness, elastic modulus, creep and residual stresses. The key components

in a nanoindentation test are the material, the sensors and actuators used to apply and measure the mechanical loading and indenter displacement, and the indenter tip which is at nano scale [222].

Wear Resistance

The safety, stability, and longevity of engineering devices are intricately tied to the tribological performance of their moving components, particularly in the challenging environment of seawater, on higher altitudes, or in engine parts. Therefore, it is crucial to improve the tribological performance of these moving parts to ensure their reliable operation. There are various ways to test the wear resistance properties such as the sliding wear test, rotary wear test setups as illustrated in Figure 2.21.

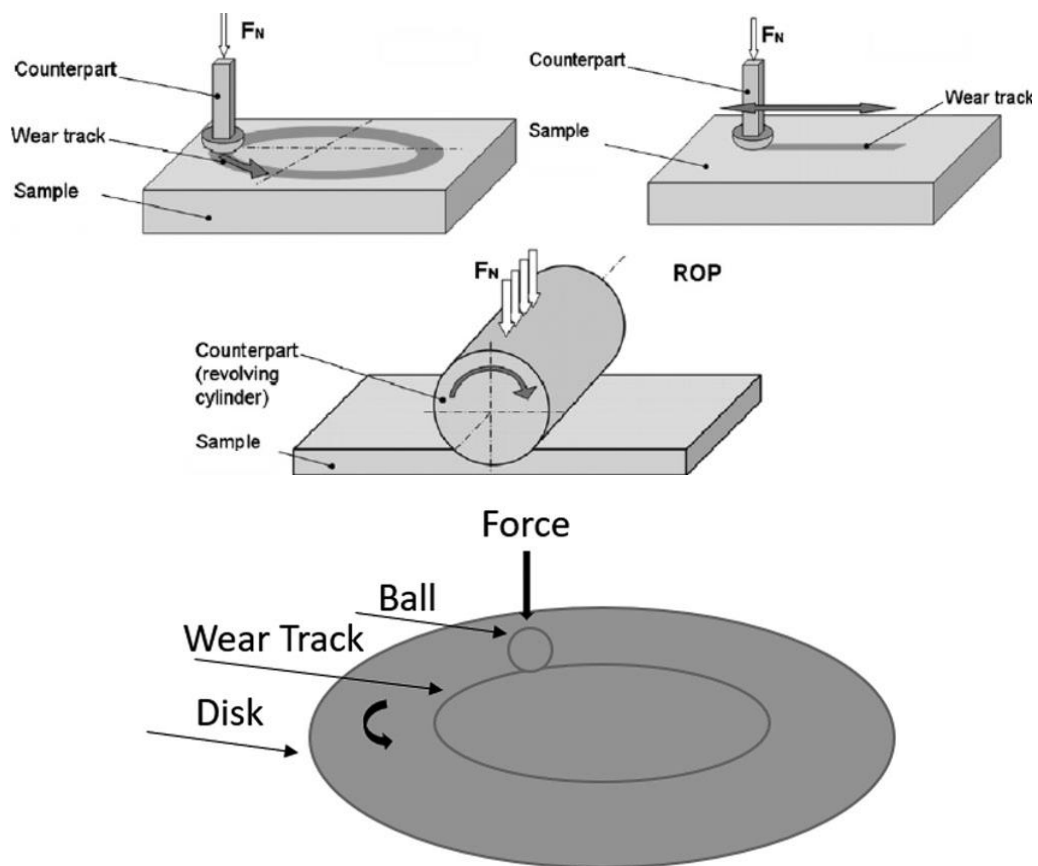


Figure 2.21 Schematic illustration of wear testing setup

Material wear processes encompass a range of mechanisms, including abrasion, fretting, adhesion, fatigue, oxidation, and other tribo-chemical reactions [223]–[226]. Wear-resistant materials have been developed or tailored to mitigate material damage or loss caused by wear. Typically, wear processes are categorized into three states: low, mild, and severe wear states [151].

2.10. Summary

Physical and chemical material surface functionalization approaches involve lithographic techniques, including radiation application, imprint techniques, and beam lithography, have been frequently utilized for crafting intricately structured surfaces. Conventional manufacturing approaches such as hot embossing and vacuum casting have also been scaled to nano- or micro-scale, offering suitable methods for producing features for anti-fouling surfaces. Additionally, additive manufacturing approaches, often referred to as 3D printing, provide the possibility for the direct production of anti-fouling surface features. The chemical techniques involve electropolishing, acid dipping, electrodeposition (pulse current deposition), chemical vapor deposition and Sol-gel coating, painting.

However, different methodologies for surface structuring offer unique advantages and limitations, depending on the application and available laser sources. Fabricating micro and nanostructures using lasers on various materials like metals, polymers, and composites is widely studied in the scientific community. Despite the challenges presented by highly reflective aluminum alloys, ultrashort pulse lasers by virtue of its controlled laser material interaction can create precise nano and microstructures with advanced techniques. Identifying and optimizing laser and processing parameters is crucial to enhance laser-induced micro- and nanostructures for surface functionality. Exploring hydrophobic surfaces is crucial for scientific and industrial uses, remains a significant research focus. However, consistently improving hydrophobic surfaces through laser texturing is still a challenge. Adjusting laser and processing parameters is vital in forming highly repeatable micro- and nanostructures with desired wettability properties. This study aims to address the gaps by concentrating on creating hydrophobic surfaces using laser technology precisely.

Surface texture significantly impacts biofouling mitigation and corrosion rates especially in marine environments. Different scan patterns produce unique surface textures that need evaluation for their effectiveness in reducing biofouling and corrosion rates. Identifying and comparing the best texture patterns is essential for advancing surface functionalization understanding. Exploring the effects of various scan patterns on biofilm formation and corrosion resistance would fills the gap in current research.

Wear resistance is another critical aspect where the combination of laser surface structuring and laser surface hardening can make a significant impact. Aluminum alloys, widely used in marine, aerospace, and automotive sectors, often face challenges related to surface wear resistance, which limits their application in high-friction environments. Research on enhancing wear resistance through laser surface hardening is limited, particularly for aluminum due to its inherent high reflectivity.

Integrating laser surface structuring with laser surface hardening offers a synergistic approach to enhance wear resistance due to hardening. The laser structuring process creates micro- and nano-textures on the surface, which can help in reducing friction and wear. Concurrently, laser surface hardening improves the material's hardness and resistance to mechanical wear. This combined approach results in surfaces that not only exhibit superior hydrophobicity and corrosion resistance but also possess significantly enhanced wear resistance and hence durability is increased.

This literature review highlights the potential of ultrafast laser processing in enhancing the surface properties of aluminum alloys, particularly in achieving high hydrophobicity, resistance to biofouling and corrosion, and improved wear resistance. The review identifies a significant gap in the current understanding of how different scan patterns and process parameters influence these properties. By addressing these gaps, this study aims to contribute valuable insights into the optimization of laser processing parameters, ultimately leading to the development of more efficient and durable materials for various applications. The Figure 2.22 shows an overview of the three working chapters and the experiments and tasks conducted.

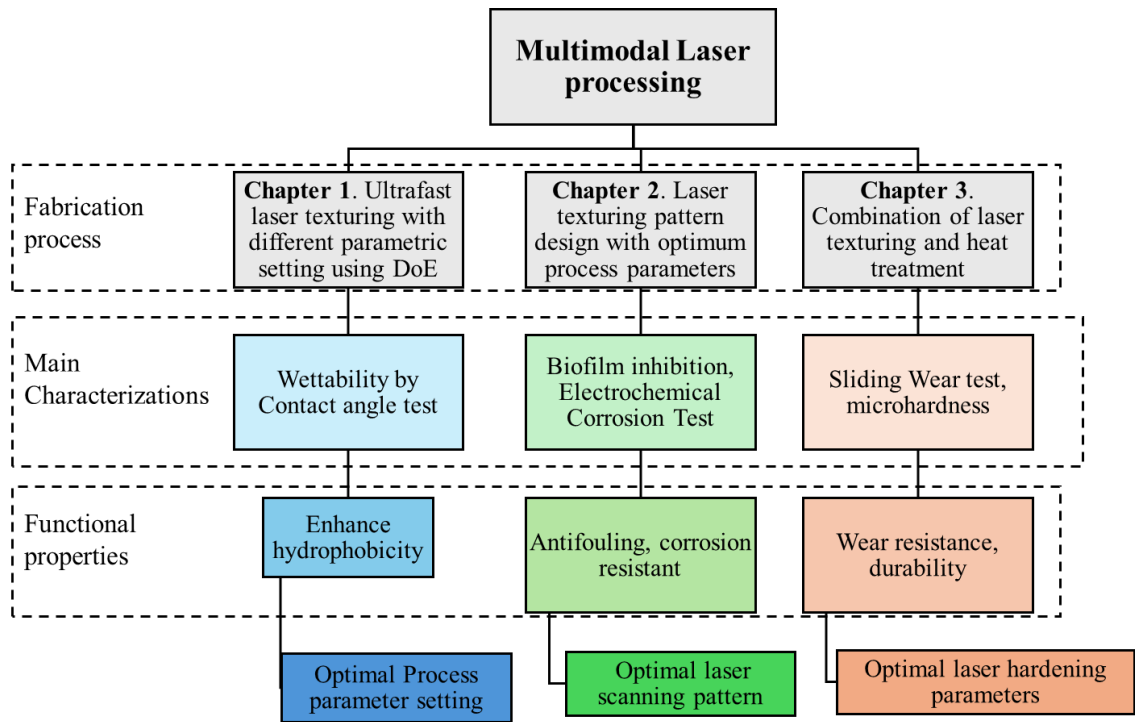


Figure 2.22 Schematic of multimodal laser surface structuring process development

CHAPTER 3

Hydrophobicity enhancement using laser surface texturing

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CHAPTER 3

3. HYDROPHOBICITY ENHANCEMENT USING LASER SURFACE TEXTURING

3.1. Introduction

Aluminium and aluminium alloys, especially the 6000 and 7000 series, are ubiquitous materials in the marine, aerospace, energy, medical, pharmaceutical, and food industries. This is because of their excellent physical and mechanical properties such as a high strength-to-weight ratio, strong corrosion resistance, and low cost [227]. In this wide range of applications, aluminium alloys come in contact with many fluids which contain foulants that can degrade the surface and other characteristic properties such as corrosion resistance, adhesion, and wear resistance over time [228]–[230]. In order to prevent or reduce this, surface modification of aluminium is required by developing a well-defined surface texture. This can be achieved using a technique that is non-toxic, cost-effective, robust, and environmentally friendly [231].

Surface topography and chemistry play an important role in various applications where the surfaces come into contact with different fluids. Enhanced surface functions can be achieved by controlling these surface properties, which in turn control the extent of the surface hydrophobicity or hydrophilicity [232]. The surface topology can be modified using many existing chemical and physical-based techniques to obtain hydrophobic or even superhydrophobic surfaces on aluminium surfaces. Chemical etching [233], chemical vapor deposition [234], self-assembled monolayer formation [235], spray coating [236], dip coating [237], and sol-gel process [238] are some of the chemical-based techniques which are used traditionally. Physical texturing processes include lithography [239], electrospinning [240], plasma techniques [241], additive manufacturing [242], and electrochemical machining [243], [244]. However, laser-based nano and micro texturing methods have been used to produce textures on aluminium and aluminium alloys to change the wetting properties of their surfaces effectively. These laser-based manufacturing processes are capable of creating complex, precise, and consistent patterns with high dimensional resolution [19], [245], [246].

A number of studies have been conducted on the production of hydrophobic aluminium alloy surfaces through pulsed laser processing, as reported by various researchers including Ahuir-Torres et al [245], Cardoso et al [246], Milles et al [247], Rukosuyev et al [248], and Jagdheesh et al [249]. The texture induced by pulsed laser on different surfaces offers advantages such as friction reduction between two surfaces, reduced drag, corrosion prevention by repelling water, as well as resistance to dirt and other particles, making them self-cleaning surfaces [250]–[253].

Consequently, such surfaces are easier to maintain and demonstrate increased resistance to fouling [254].

In recent years, the field of laser technology has experienced remarkable advancements, driven by extensive research and development endeavours. These efforts have led to notable breakthroughs, particularly in the domain of pulse durations. The continuous improvement in laser systems has successfully pushed the boundaries, resulting in pulse durations that now reach the femtosecond scale (10^{-15} seconds) [21]. Femtosecond (fs) laser surface texturing has numerous advantages such as the production of highly precise textures due to the reduced heat-affected zone compared to laser processing with higher pulse widths because of non-linear photon absorption, as observed by Valette et al [255] and Malinauskas et al [15]. The laser process parameters, including laser power [256], pulse repetition rate [257], scan speed, and hatch distance [150], can be adjusted to easily control the surface structures created by laser processing. The surface roughness and profile attributes of laser-structured surfaces can be tailored using femtosecond laser processing, as demonstrated in the early experiments conducted by and Martínez-Calderon et al [258].

The achievement of hydrophobic and superhydrophobic properties on surfaces can be attributed to various factors, such as the low surface energy resulting from specialized tailored morphology, as reported by Tang et al [259]. Surface textures consisting of repetitive patterns create an air boundary between the material surface, leading to low adhesion between fluid drops and the surface interface. Consequently, this alters the surface's wetting properties, as discussed by Long et al [260]. The wetting properties, especially on aluminium alloys, tend to change over time, and it is recommended to measure these properties once the surface textures have stabilized after environmental aging. For aluminium alloy, this stability is typically achieved between 45 and 60 days after laser processing. The duration may also depend on the complexity of the surface structures, as noted by Milles [254]. Contact angle measurements are commonly used to assess surface wettability, which involves the dispensing of a water droplet onto the surface and measuring the angles between the solid-liquid-gas interfaces [205]. Over the past years, several researchers have worked on understanding the effect of different laser process parameters separately [261]–[264], however the investigation of the correlation of the laser process parameters and surface properties such as surface roughness and wettability especially on aluminium alloy 7075 requires further research to provide sufficient fundamental understanding to create tailored surfaces and identify the best laser processing settings [265], [266]. To understand the effect of the input laser parameters and determine the correlation with the wettability process responses such as contact angle, a design of experiment layout is often used to relate the process inputs and output responses [267].

Table 3.1 Literature Summary Table

Authors	Summary	References
Ahuir-Torres et al	Picosecond laser texturing of AA2024-T3 altered wettability from hydrophilic to hydrophobic with varying patterns but did not affect corrosion behaviour in the study. The effect of specific process parameter is not discussed.	[245]
Cardoso et al	Study on laser-textured Al2024 plates using a Yb-doped fiber nano-second laser was conducted. These textured surfaces were assessed for wettability properties evolution. Influence of laser parameters and ambient conditions on surface properties are studied.	[246]
Milles et al	Laser processing of pure aluminum plates is done using 200 ns Ytterbium fiber laser. Determination of wettability behaviors as a function of temperature. Comprehensive assessments needed for tuning process parameters.	[247]
Rukosuyev et al	Superhydrophobic hierarchical structures were successfully fabricated in a single step using femtosecond laser ablation on Austenitic stainless steel 316L. Surface penetration leads to hydrophobic property degradation. Hydrostatic pressure can cause loss of hydrophobic properties.	[248]
Jagdheesh et al	Micro channels and pillars were fabricated by a nanosecond laser source on pure aluminum thin foil of 100 μm . In this study transition of wetting properties is studied however only one set of process parameters are used.	[249]
Martínez-Calderon et al	Surface patterns with different geometries and distributions were fabricated by femtosecond and nano level LIPSS were produced. Only the different texture study was conducted by varying spot size.	[258]

Basset et al	Nanometric scaled textures were fabricated on a pre-polished stainless steel 316L surface and effects of the environment are studied.	[261]
Florian et al	Laser processing is done on 16MnCr5 alloy steel surface using a femtosecond pulsed fibre laser system. The effect of interline spacing and number of scans are studied in this research.	[263]
Yilbas et al	Controlled ablation results in micro/nano texturing of the surface which fabricated superhydrophobic surface on the alumina surface using a femtosecond laser source.	[268]

In the past literature, a lot of research has been conducted on the modification of morphology using different types of laser systems on different materials for various applications however the effect of process parameters in femtosecond laser processing to develop highly hydrophobic surfaces on aluminium remains largely unexplored.

In this chapter, an experimental study of the manufacturing of surface textures on an aluminium alloy (7075) surface employing an advanced femtosecond laser surface texturing process using the design of experiments approach is presented. Surface height roughness (Sz) and spatial roughness (Sa) profile parameters, surface profile aspect ratio (Str), and contact angle were measured as output responses. The influential factors such as laser power, hatch distance, and scan speed of the femtosecond laser system are examined in this chapter. The process parameters resulting in the most hydrophobic surface were determined using response surface optimization. Relatively little is known about how the different femtosecond laser process parameters affect the surface roughness and chemical composition, and surface wettability. The findings underscore the importance of the interplay between laser power, hatch distance, and scan speed in achieving optimal hydrophobicity. This represents a noteworthy advancement, as it not only establishes a correlation between process parameters and surface properties but also elucidates the significance of these parameters in determining the effectiveness of the manufactured surfaces in resisting water contact. This study was targeted to fill this gap of knowledge and develop an understanding of the main reasons and phenomena behind these effects which can further enhance the development of antifouling and corrosion resistance surfaces, especially for marine applications.

3.2. Materials and methods

3.2.1. Materials

Aluminium alloy 7075-T651 with the chemical composition of 0.1% Si, 0.22% Fe, 1.5% Cu, 0.17% Mn, 2.8% Mg, 0.21%, 5.8% Zn, 0.03% Ti, and Al Balance, supplied by Impact Ireland Metals Ltd and was thermally treated to stress-relieve by stretching and artificially aged. The primary alloying element in this aluminium alloy is zinc which makes the material highly ductile, with excellent mechanical properties such as a yield strength of 507 MPa, ultimate tensile strength of 574 MPa, and hardness of 171 HB. The surface roughness of the as-received samples was $S_a = 492$ nm as measured using a Bruker Contour GT-X Profilometer. The test samples were sliced to the dimensions of 80×80 mm with a thickness of 2 mm. The surface of the samples was cleaned using isopropyl alcohol before laser processing to clean away any dust particles or other contaminants. The spectral absorbance of the laser light at 1030 nm wavelength (the laser wavelength used in this study) for aluminium alloy 7075 is 0.7 at room temperature as reported by El-Hameed et. al [269].

3.2.2. Experimental process

The laser surface texturing was conducted using a high-energy industrial ultrafast femtosecond laser source (NKT Origami XP). This laser provides a stable, low noise, pulsed beam with an average wavelength of 1030 nm, a pulse duration <370 fs, average power of 4 W, and a maximum repetition rate of 1 MHz. An integrated galvanometer beam scanner (FOCUSSHIFTER-15, RAYLASE GmbH) was used to control the scanning of the laser beam over the sample surface. The beam was focused on the sample surface using an F-theta lens with a working distance of 219 mm from the lens. The experimental setup and scan pattern used are shown in Figure 3.1(a).

The beam has a Gaussian profile with a diameter ($1/e^2$) of 51.2 μm at the focal position, as measured with a CMOS camera beam profiler (Figure 0.1).

The pulse fluence was calculated as follows:

$$Fluence = \frac{Average\ Power\ (W)}{Repetition\ rate\ (Hz) \times Beam\ area\ (cm^2)} \times 100$$

The pulse overlap can be calculated as follows:

$$Overlap = \frac{\phi - (Repetition\ rate\ (Hz) \times scan\ speed\ (mm))}{\phi} \times 100$$

Where ϕ is the beam diameter in (mm). The samples were mounted and fixed on 4 axes positioning stage 225P from Aerotech Inc, which was used to set the laser beam focus at the sample surface.

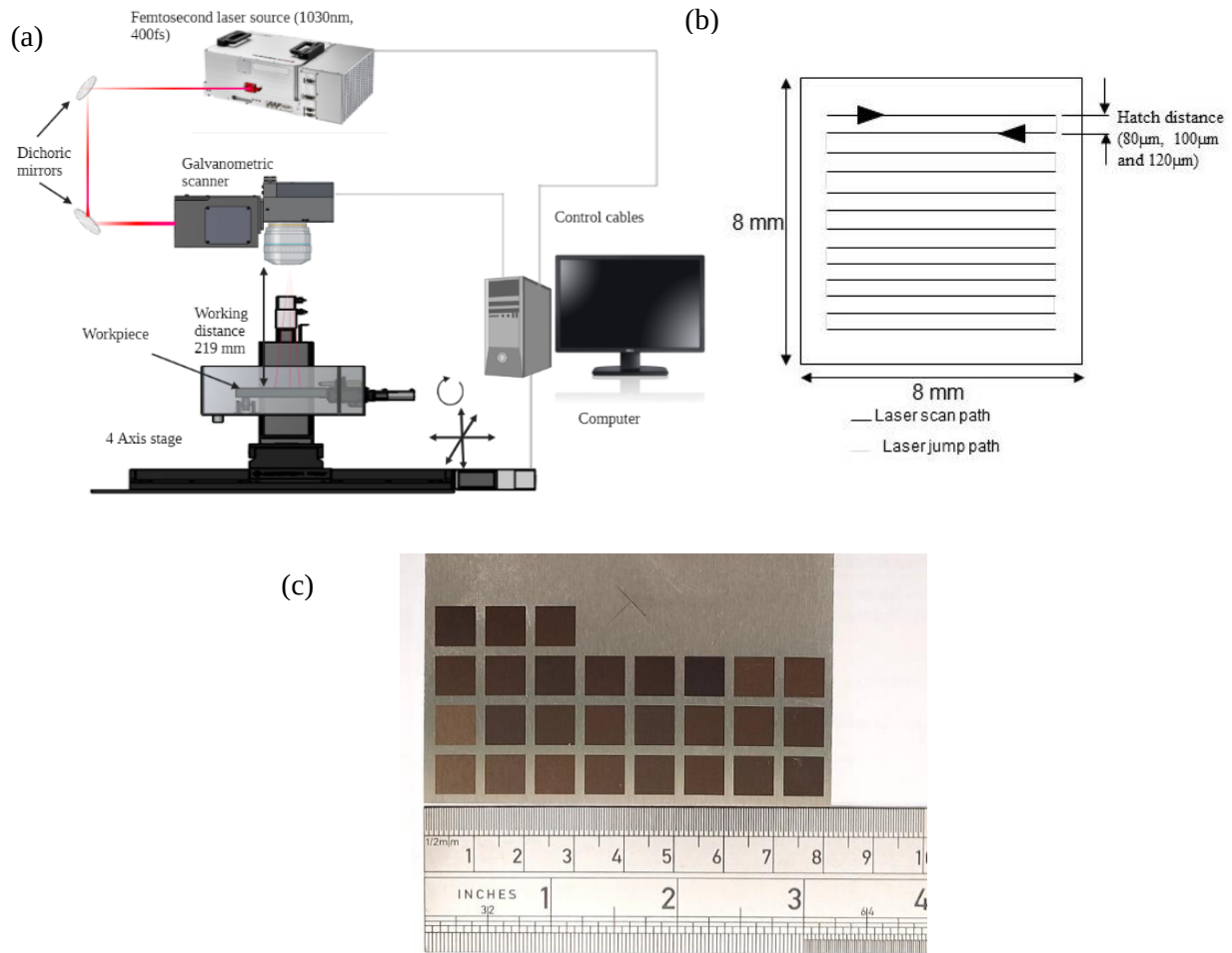


Figure 3.1 Schematics of (a) laser surface texturing setup and (b) the laser scanning raster pattern, (c) Actual sample image after laser treatment

A bidirectional scanning strategy was employed for manufacturing surface textures as shown in Figure 3.1(b). The surface texturing was conducted over areas of 8 mm × 8 mm at different positions on the sample with different process parameter settings. The laser processing was conducted in the atmospheric environment at a room temperature of 20° C and humidity of 75%. The samples were cleaned with isopropyl alcohol after laser texturing to remove the dust particles and then stored in an airtight petri dish in a clean environment for ageing for 60 days.

3.2.3. Experimental design

A full factorial Design of Experiment (DoE) model of 3^3 (three factors at three levels) was developed in order to investigate the effect of the input processing parameters on the output characteristics. The input parameters were the laser power, the scanning speed, and the hatch distance, see Table 3.3 . A preliminary test was conducted and carried out to identify the most

significant processing parameters and their level of significance for process optimisation. The parameters were selected based on the pilot tests and near to matching with the previous literature [270].

Table 3.1 The design of experiments (L27) laser process parameters and levels examined.

Parameter	Unit	Level 1	Level 2	Level 3
A Laser Power (P)	W	3	3.5	4
B Hatch Distance (h)	mm	0.08	0.1	0.12
C Scan speed (v)	mm/s	3	4	5

The pulse repetition rate was fixed at 100 kHz. The laser power was varied between 3, 3.5, and 4 W, the scan speed was varied between 3, 4, and 5 mm/s and the hatch distance were varied between 0.08 mm, 0.1 mm, and 0.12 μm . The scanning pattern was raster scanned parallel lines (using a bidirectional scan strategy) with the noted process parameters. The fluence was calculated with varying the average power. As there were three powers used the calculated fluences were 2.914, 3.4 and 3.886 J/cm^2 . As there were three scan speeds the pulse overlaps were 4.85%, 6.81% and 8.75%. Laser texturing is contingent upon the attainment of a specific fluence of the laser that surpasses the ablation threshold value inherent to the material under consideration. During the preliminary experimental phase, optimal textural outcomes were observed when the laser power was configured to exceed 3W. Given the maximum power setting of 4W in the employed laser system, power levels within the range of 3W to 4W were systematically investigated. The hatch distance range was selected based on the diameter of the laser beam spot, as this parameter has a direct impact on the resolution and quality of the resulting processed features. Similarly, the scan speed was selected based on pilot tests conducted with the laser setup and material. Table 3.2 shows the experimental parametric settings for each of the 27 laser-fabricated samples. Each sample was manufactured and tested 3 times in order to examine the repeatability of the results. Therefore 81 samples were manufactured and characterized.

Table 3.2 Full listing of the process parameters and associated levels investigated for each sample.

Sample	Laser Power (W)	Hatch Distance (mm)	Scan Speed (mm/s)
1	3	0.08	3
2	3	0.08	4
3	3	0.08	5
4	3	0.1	3
5	3	0.1	4
6	3	0.1	5
7	3	0.12	3
8	3	0.12	4
9	3	0.12	5
10	3.5	0.08	3
11	3.5	0.08	4
12	3.5	0.08	5
13	3.5	0.1	3
14	3.5	0.1	4
15	3.5	0.1	5
16	3.5	0.12	3
17	3.5	0.12	4
18	3.5	0.12	5
19	4	0.08	3
20	4	0.08	4
21	4	0.08	5
22	4	0.1	3
23	4	0.1	4
24	4	0.1	5
25	4	0.12	3
26	4	0.12	4
27	4	0.12	5

Response surface method (RSM) of experimental design is a set of mathematical and statistical techniques that is useful for modeling and predicting the output response. This was conducted to explore the relationship between the input laser process parameter factors and the responses of Sa, Sz, and Str, as defined in the introduction section, the surface composition, and the water contact angle. The response data obtained from the experiments underwent analysis using Design-Expert 13 and Minitab 18 software. Only models with high significance, and no significant lack of fit in the data, are presented in the results section. The surface response equations expressed the actual

factors and levels of process parameters and included coefficients accounting for the actual units of each parameter.

3.2.4. Surface Characterization

Surface Morphology

The laser-treated surfaces were evaluated using scanning electron microscopy (SEM), EVO LS15 (Zeiss) with LaB6 filament, an accelerating voltage of 10 kV, and a beam current intensity of 25 pA.

Surface Roughness

The different surface roughness attributes such as arithmetical mean height (S_a), maximum height (S_z), and aspect ratio (S_{tr}) were investigated as areal parameters of the surface roughness. S_{tr} , surface texture aspect ratio, is defined as the ratio of the average width of the surface features to the average height of the surface features. These are considered in this study as per ISO 25178-2 (2021) [271]. These were characterized using a 3D Bruker Contour GT-X Profilometer (Billerica, MA, USA). The measurements were made using a 5X lens focusing on a 1 mm² surface area. The acquired data was analysed using Bruker Vision 64® software. The results were plotted considering the average and the standard deviation calculated on the basis of the three experiments carried out for each set of processing conditions.

Wettability

Prior to the wettability test, the samples were carefully prepared by drying and cleaning using compressed air to remove any debris or contaminants. The static water contact angle measurements were performed using a FTA200 Dynamic Contact Angle Analyser. The sessile drop profile was measured using the non-spherical liquid–vapor curve fit method within the FTA 200 software. These measurements were conducted at ambient conditions (16 °C and 86% relative humidity). For the measurements, approximately 10-18 µl volume of deionized water was used for each measurement. The average static contact angle is reported in this study with (n=3). The experiment was performed on three separate samples, with each instance using the same model to ensure reproducibility. The contact angle test was conducted on the samples on day 1 of the laser texturing and after 60 days of environmental aging as the surface textures were thermodynamically stabilized.

Surface elemental composition

The surface chemistry of the irradiated materials was analysed by X- Ray photoelectron spectroscopy (XPS). In this study, Scienta Omicron XPS system equipped with a monochromatic Al K α X-ray source (operated at 240W and 8 kV) at base pressure setup at 6×10^{-7} Pa with a 128 channel Argus CU detector was employed. The kinetic energy of the photoelectrons was determined using an analyser with a pass energy of 100 eV to survey and 50eV for high-resolution

spectra. The take-off angle between sample's surface normal and the electron optical axis of the spectrometer was 0°. Spectra were referenced to the C1s peak of aliphatic carbon at a binding energy of 284.8 eV. CasaXPS software (Casa Software Ltd., UK) was used to analyze the results using satellite subtraction procedure. Quantitative elemental compositions were determined from peak areas using this method.

3.3. Results

3.3.1. Design of experiment results

In this experimental design, the effects of laser power, hatch distance, and scan speed on surface roughness and contact angle were investigated. From the previous literature as both height roughness parameters and spatial roughness parameters influences the hydrophobicity therefore Sa, Sz and Str are characterized for RSM modelling. The response variables were measured using a 3D profilometer and a goniometer, respectively. The initial samples were not subjected to any mechanical or chemical treatment and had an average surface roughness Sa of $0.5 \pm 0.005 \mu\text{m}$, maximum height roughness of $6.82 \pm 3.36 \mu\text{m}$, and a texture aspect ratio of 0.06 ± 0.01 . To ensure reproducibility and repeatability, measurements were conducted on three different samples with the same process parameters. Table 3.3 shows the resulting average surface profile values measured for surface roughness attributes Sa, Sz, Str, and contact angle. Samples 1 and 22 (green highlight) show the high contact angles and another is selected as a central value recorded, and samples 12 and 17 (orange highlight) show the low recorded contact angle measurements with another central value. These samples were analysed using SEM and XPS.

Table 3.3 Resulting average surface profile values measured for surface roughness attributes Sa, Sz, Str and contact angles.

Sample number	Responses			
	Sa (μm)	Sz (μm)	Str	Contact Angle (deg)
1	0.87 ± 0.075	19.4 ± 2.12	0.042 ± 0.001	141.51 ± 0.18
2	0.88 ± 0.023	17.1 ± 1.24	0.037 ± 0.00033	139.31 ± 0.63
3	0.85 ± 0.078	13.9 ± 0.40	0.042 ± 0.00088	132.39 ± 3.04
4	0.72 ± 0.064	16.7 ± 6.64	0.034 ± 0.00267	135.39 ± 2.26
5	0.72 ± 0.047	17.0 ± 3.98	0.052 ± 0.00033	137.52 ± 0.65
6	0.7 ± 0.036	8.2 ± 1.44	0.038 ± 0.00252	134.23 ± 1.97
7	1.86 ± 0.19	19.7 ± 3.8	0.04 ± 0.00186	136.12 ± 3.25
8	1.72 ± 0.67	13.8 ± 2.94	0.047 ± 0.00067	135.15 ± 1.13
9	1.04 ± 0.33	15 ± 9.37	0.05 ± 0.00267	136.95 ± 0.48
10	2.17 ± 0.62	20.8 ± 1.44	0.033 ± 0.001	108.25 ± 2.55
11	2.48 ± 0.59	20.3 ± 1.74	0.045 ± 0	133.54 ± 2.73

12	1.57±0.57	17.3±0.22	0.056±0.002	100.12±1.6
13	1.47±0.09	16.93±7.57	0.051±0.00167	136.19±0.6
14	1.23±0.19	13.3±0.49	0.043±0.001	130.53±2.69
15	1.1±0.06	12.8±6.83	0.055±0.00167	140.85±2.58
16	1.61±0.58	20.3±6.93	0.031±0.00033	130.71±3.07
17	1.51±0.47	23.1±5.76	0.036±0	123.14±0.24
18	1.27±0.58	15.8±2.35	0.042±0.00033	119.31±2.68
19	2.49±0.051	23.3±4.89	0.04±0.004	129.41±1.98
20	2.29±0.08	20.1±4.52	0.053±0.002	121.3±0.84
21	1.77±0.57	18.9±2.33	0.053±0.00058	136.17±0.16
22	2.32±0.40	25.2±7.38	0.053±0.00208	138.45±1.64
23	1.25±0.013	20.4±2.74	0.043±0.00067	135.74±1.55
24	0.91±0.036	16.53±4.24	0.041±0	135.89±1.15
25	2.47±0.59	22.9±0.58	0.028±0	134.92±1.08
26	2.53±0.45	22.3±0.19	0.041±0.00033	134.66±2.19
27	2.16±0.47	21.0±0.065	0.035±0.00067	138.16±0.24

3.3.2. Input-output correlation

To investigate potential correlations between input process parameters and the corresponding responses, Pearson correlation coefficients were employed. To gain insights into the strength and direction of correlations between multiple variables, we utilized a heat map of Pearson correlations coefficient as shown in Figure 3.2 . The heat map shows the correlation of the input process parameters and the response variables. A negative r value indicates an inverse relation.

	<i>P</i>	<i>h</i>	<i>v</i>	<i>CA</i>	<i>Sa</i>	<i>Sz</i>	<i>Str</i>
<i>P</i>	1						
<i>h</i>	0	1					
<i>v</i>	0	0	1				
<i>CA</i>	-0.1097	0.2174	-0.0774	1			
<i>Sa</i>	0.5043	0.1101	-0.3065	-0.1241	1		
<i>Sz</i>	0.4576	0.0264	-0.4232	-0.0272	0.4449	1	
<i>Str</i>	0.3468	-0.2816	0.3086	-0.1493	0.0066	0.1207	1

Figure 3.2 Pearson correlation heat map of input parameters (laser power, hatch distance, and scan speed) and output responses (contact angle, Sa, Sz, and Str).

3.3.3. Significance analysis

Design Expert 13 DOE software was employed to analyze the output data and develop models that describe the relationship between the processing parameters and the resulting responses. The ANOVA tables and details are provided in the supplementary information. Four statistically

significant model equations were derived from the recorded responses, which describe the effects on the contact angle (a measure of wetting behavior), surface mean height, surface maximum height (based on the difference between the height of peaks and depth of valleys across the surface area), and the texture aspect ratio (which relates to the uniformity of the surface texture). The results of the ANOVA analyses for these models are presented in Table 3.4 .

Table 3.4 Goodness of fit statistical measures for the developed models

Response	Degree of freedom	R²	Adequate precision
Arithmetic mean height (Sa)	12	0.80	15.29
Maximum height (Sz)	9	0.75	9.5
Texture aspect ratio (Str)	16	0.87	14.36
Contact Angle (CA)	20	0.91	25.22

The R² values for all the models were greater than 0.75 which shows that the models were significant. Moreover, it can be seen from this table that adequate precision for all the models is greater than 9. If the ratio surpasses 4, the model equations are regarded as having attained a satisfactory level of precision [272], [273].

3.3.4. Effect of laser surface texturing on height roughness parameters (Sa, Sz)

The surface roughness measurements were done using 3D optical profilometer that uses white light interferometry and measures the roughness height attributes as per ISO 25178-2 (2008) [271]. Figure 3.3 shows the surface morphology change after laser texturing, as observed on 3D profilometer.

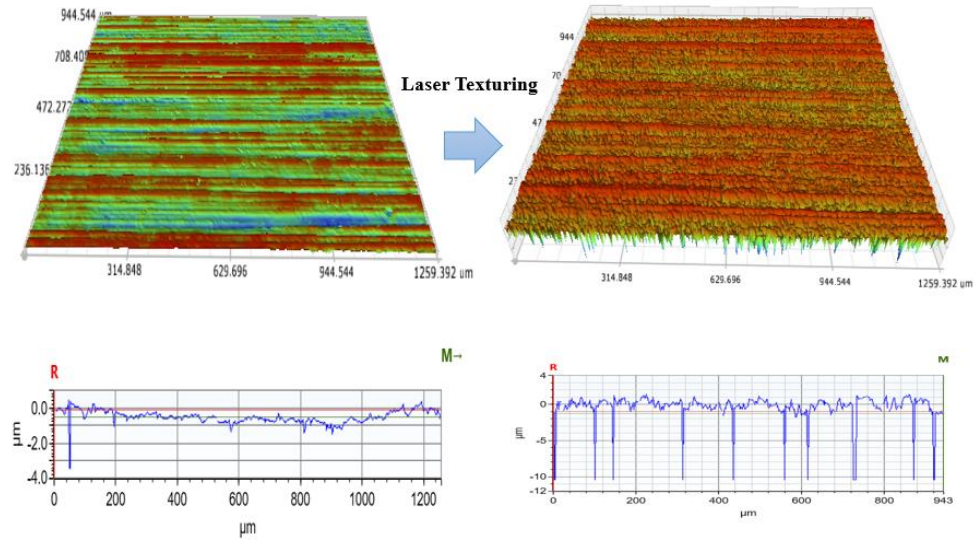


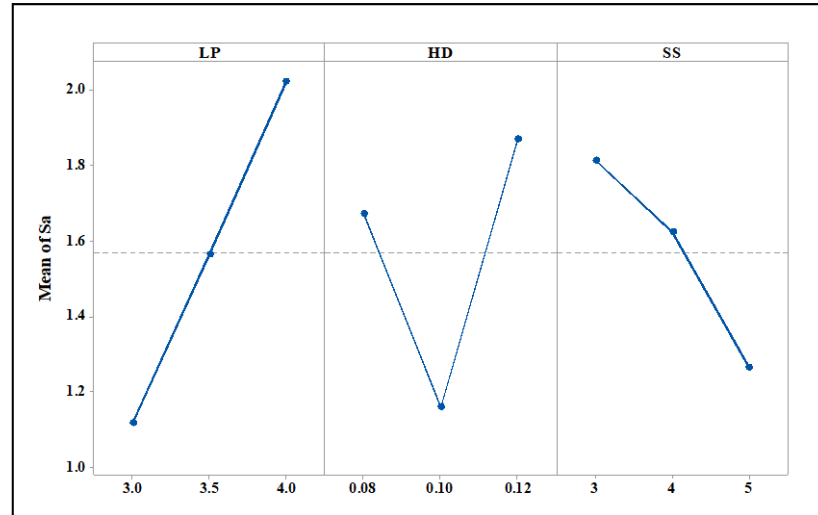
Figure 3.3 Change in surface morphology after laser surface texturing as observed on the 3D optical profilometer of Sample 1.

ANOVA analysis through the DoE softwares Minitab and Design Expert was conducted in which two significant mathematical models were discovered. These models indicate the features associated with the surface height roughness of the samples with respect to the laser process parameters selected. The regression equation derived for S_a and S_z were as follows.

$$\begin{aligned} S_a &= -38.5008 + 12.6472 P + 336.749 h + 8.9592 v - 131.962 Ph - 1.8307 Pv - \\ &\quad 87.0903 hv + 561.985 h^2 + 9.7049 Phv + 2.93506 P^2h + 69.1836 Ph^2v \quad (1) \\ S_z &= -4035.03 + 2442.32 P + 83961.4 h - 5.7796 v - 50444.4 Ph + 0.6444 Pv + \\ &\quad 9.7222 hv - 355.4 P^2 - 420347h^2 + 7341.11P^2h + 252194 Ph^2 - 36666.7 * P^2h^2 \quad (2) \end{aligned}$$

Where P is the laser power measured in W, h is the hatching distance measured in mm, and v is the laser scan speed measured in mm/s. The mean effect plots in Figure 3.4 and response surface graphs in Figure 3.4 were generated by applying the model equations (1) and (2) for surface roughness parameters S_a and S_z , as shown in the above section.

(a)



(b)

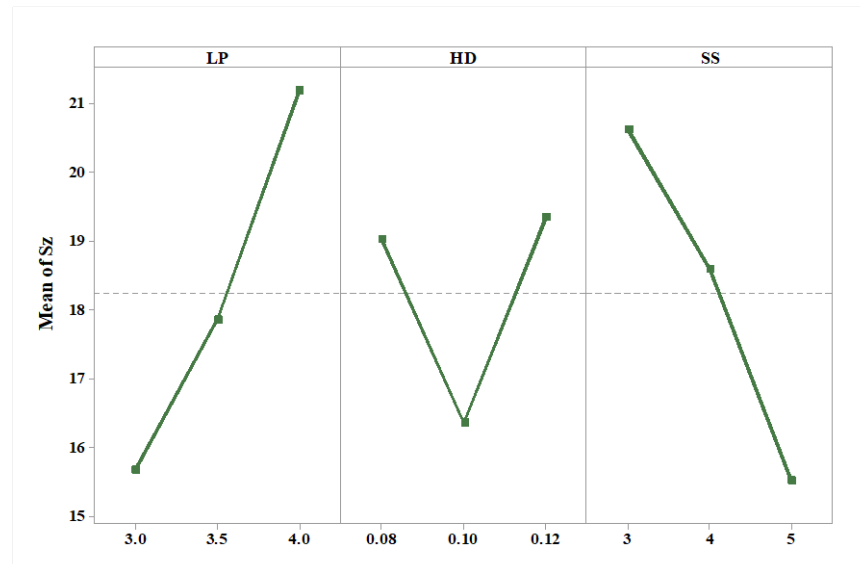


Figure 3.4 Main effect plots for (a) the arithmetic mean surface roughness (Sa) and (b) the maximum height roughness (Sz); showing the effects of the input processing parameters of LP- laser power, HD- hatch distance and SS- scan speed.

Laser power was identified as the most influential parameter on the height roughness parameters, with a direct relationship to the laser energy density. These findings are consistent with the results previously reported by Zang et al [38]. Laser scan speed was found to be the second most influential parameter and Sa values shows a declining trend with increase in scan speed. However, changes in hatch distance were found to greatly impact the mean roughness (Sa) of the surface. An increasing trend in arithmetic mean roughness (Sa) was observed with increasing laser power. The mean of Sa decreased with an increase in hatch distance from 0.08 to 0.1 mm, but the trend changed drastically between 0.1 and 0.12 mm. An increasing trend was observed.

A similar trend of mean of Sa was observed in the literature by Wang et al. [39]. The Sa value was observed to rise with the increase in laser power from 3 W to 4 W, as shown in Figure 3.5(a). Furthermore, the hatch distance was determined to be another crucial factor in getting higher Sa values at hatch distances of 0.08- and 0.12 mm, while lower Sa values were observed for hatch distances close to 0.1 mm. Figure 3.5(b) showed that there is a linear correlation between increasing laser power and Sz values, and the Sz values indicated a decrease in Sz with an increase in laser scan speed. The agreement of this model with the experimental results was evaluated with the aid of a normal plot of the residuals and a plot of the predicted vs actual values (see supplementary information). It can be seen from these graphs that deviations from the model are approximately normal and there are no significant outliers in either dataset.

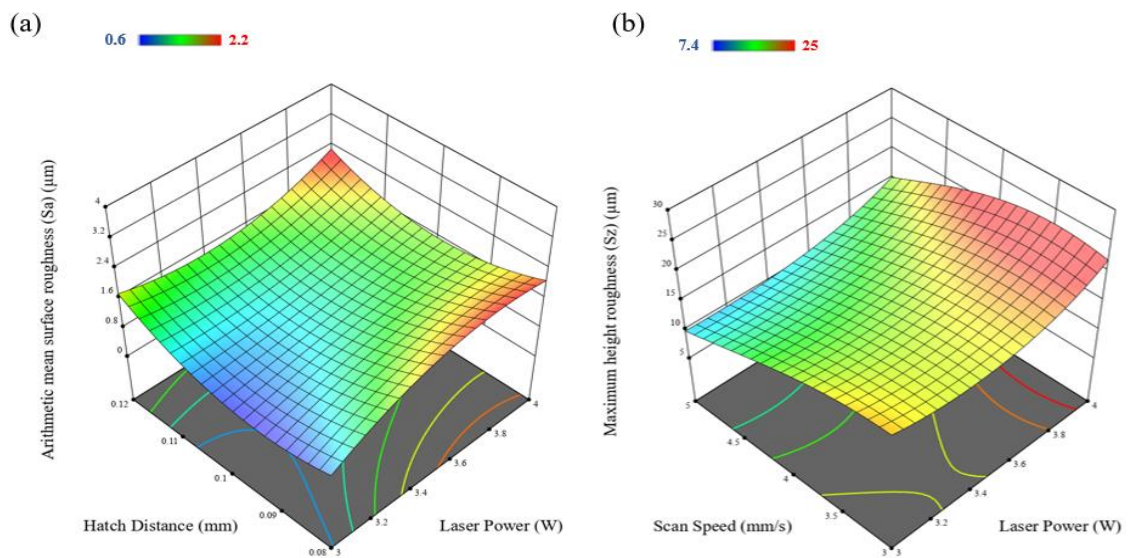


Figure 3.5 Response graphs showing the effect of the input processing parameters on the output measured surface roughness (a) arithmetic mean surface roughness (Sa) and (b) the maximum height roughness (Sz).

3.3.5. Effect of laser surface texturing on spatial roughness parameters

Texture uniformity is an important response parameter in laser surface texturing because it is a measure of how consistent the surface structures are across the entire surface. A uniform surface texture will have a consistent pattern of peaks and valleys, with similar shapes and sizes, resulting in a more reliable and consistent behaviour when the surface comes into contact with different fluids. The regression equation for Str is as follows:

$$\begin{aligned} \text{Str} = & 6.4377 - 3.8912 P - 25.568 h + 4.7648 v + 1.1947 Ph - 67.0004 hv + \\ & 0.85492 P^2 - 0.6534 v^2 - 0.4969 P^2 v - 31.9142 Ph^2 + 0.2717 P v^2 + 194.46 h^2 v + \\ & 6.2146 P^2 h v - 0.0085 P^2 v^2 + 105.808 Ph^2 v - 0.5173 Ph v^2 - 42.4881 P^2 h^2 v \end{aligned} \quad (3)$$

Where P is the laser power measured in W, h is hatching distance measured in mm and v is the laser scan speed measured in mm/s.

The mean effect plot and response surface 3d plot is illustrated in Figure 3.6. These plots were generated by applying the model equation (3) for surface texture aspect ratio (Str).

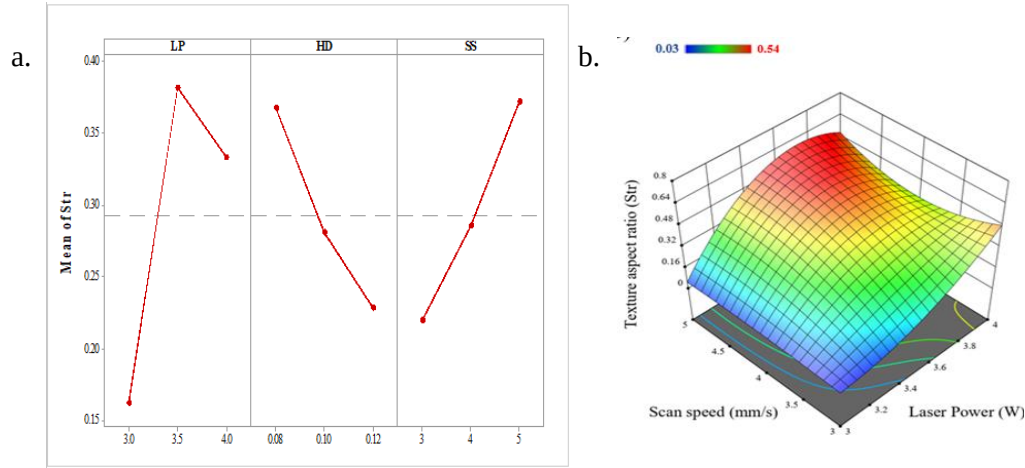


Figure 3.6 (a) Main effect plot for texture aspect ratio surface roughness (Str) showing the effect of the input processing parameter such as LP- laser power, HD- hatch distance and SS- scan speed, and (b) 3D response surface plots for Str.

As the size of the laser spot is smaller than the step-over distance, the laser will only affect discrete areas of the material during each pass, resulting in a pattern of parallel lines with un-affected gaps between them. This observation is consistent with the principles of laser-material interaction, where the size and shape of the laser spot and the scan path determine the spatial distribution and extent of the laser affected area on the surface. From the mean effect plots illustrated in Figure 3.6(a), laser power and laser scan speed are the significant laser process parameters affecting the texture aspect ratio. When the laser power is increased, more energy is delivered to the material surface, causing more melting and evaporation, and resulting in a greater degree of surface roughness. This leads to an increase in the height component of the surface roughness, which results in an increase in the texture aspect ratio. The linear increasing relationship can be seen in the mean of Str with increasing scan speed.

This trend can be observed in the 3D response surface plot shown in Figure 3.6(b). Higher Str value is seen when the laser power is 4 W and scan speed is 5 mm/s, and lower Str value is shown at 3 W power and 3 mm/s.

The model's compatibility with experimental results was assessed using a normal plot of residuals and a predicted vs actual values plot (*refer to supplementary information* Figure 0.11). The analysis indicated that any deviations from the model followed an approximately normal distribution, and there were no noteworthy outliers observed in the data.

3.3.6. Effect of laser surface texturing on wettability

The contact angle serves as a quantitative assessment of the surface wetting characteristics, whereby a higher contact angle signifies a hydrophobic surface that repels water, while a lower contact angle indicates a hydrophilic surface that attracts water. In the instance of the non-treated aluminum alloy surface, Figure 3.7(a) demonstrates a contact angle measurement of 84.91° . This measured contact angle signifies the hydrophilic nature of the surface, implying its high propensity to be wetted by water.

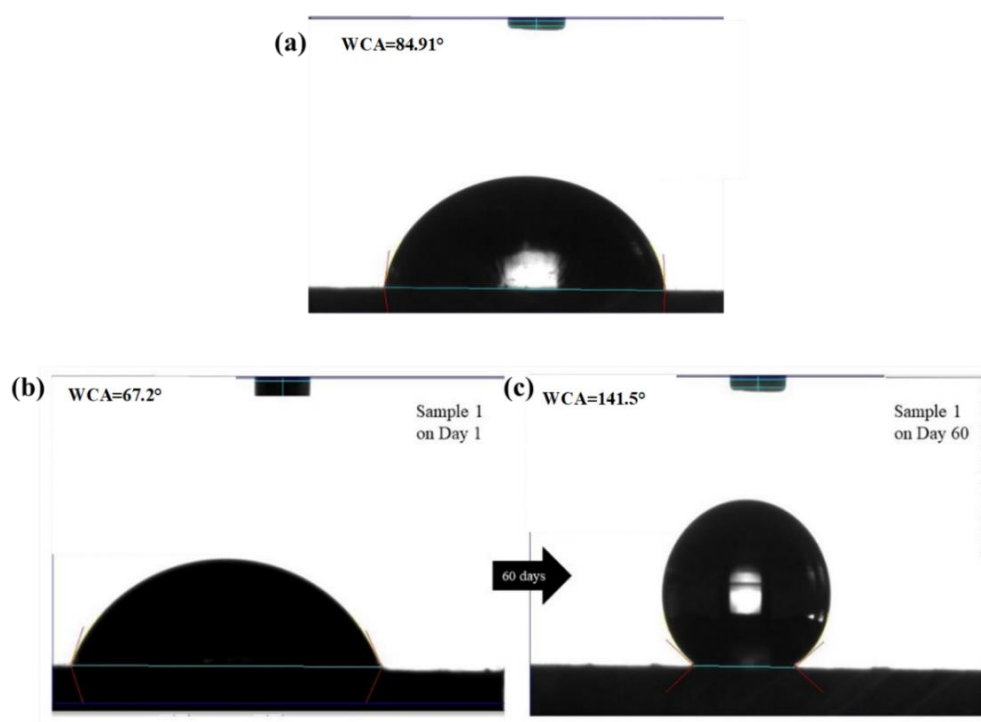


Figure 3.7 (a) Picture of a water droplet on the non-structured aluminium 7075 sample with contact angle of 84.9° ; (b) a water droplet on laser structured aluminium on day 1 showing hydrophilicity with a water contact angle 67.2° and (c) a water droplet on laser structured aluminium surface after 60 days showing hydrophobicity with a contact angle of 141.5° .

Prior to the aging process, the contact angles observed on laser-textured specimens (shown in Table 3.3) fell within the range of 11 - 65° . All of these values represent a substantially more hydrophilic surface than the non-structured sample, which displayed a contact angle of 84.91° . However, within a 60-day timeframe, the contact angles of the laser-textured samples progressively increased,

reaching the range of 100-142°, as illustrated in Figure 3.7 for the same sample (sample 1). This suggests that the initial instability of the laser-induced surface structures is overcome through an aging process, potentially involving chemical reactions such as oxidation and/or diffusion triggered by environmental exposure. The attainment of surface wettability stability has been previously reported by several researchers after a duration of 45 days [43, 44, 45]. Thus, in this study, the contact angle measurements were taken after 60 days. The results demonstrate that the wettability of the laser structured aluminium alloy is significantly affected by the laser process parameters such as laser power, hatch distance, and scan speed, as well as aging time. The regression equation derived for contact angle is as follows:

$$\begin{aligned} \text{Contact Angle} = & 7.92496 - 23768.8 h + 376.878 v + 7126.99 Ph - 6.6317 P^2 + \\ & 200042 h^2 + 96.6219 v^2 + 123.041 Phv - 42.5001 P^2 h - 24.8459 P^2 v - 53516.7 Ph^2 - \\ & 102.228 Pv^2 - 4515.88 h^2 v - 1269.25 hv^2 + 19.871 P^2 v^2 - 14494.1 Ph^2 v + \\ & 1078.7 Phv^2 + 776.929 h^2 v^2 + 3626.42 P^2 h^2 - 196.751 P^2 hv^2 - 6.1761 P^2 h^2 v^2 \end{aligned} \quad (4)$$

Where P is the laser power measured in W, h is hatching distance measured in mm, and v is the laser scan speed measured in mm/s.

Figure 3.8 shows the response surface graphs showing change in water contact angle with respect to change in laser power set at 3 W, 3.5 W, and 4 W. The graphs suggest that when the laser power is set at 3W the highest contact angle will be achieved at 0.8 mm hatch and 3 mm/s. However, when laser power is set at 3.5 W higher more hydrophobic surfaces can be achieved with hatch distance 0.1 mm and at higher speed of 5 mm/s.

When the laser power is set to 4 W, more hydrophobicity can be achieved when the hatch distance is set to be greater than 100 µm; and there is not much effect of the scan speed on the trend. This indicates that the surface structures are created efficiently when there is interaction between the laser and the material, and there is enough fluence to structure the surface of the materials.

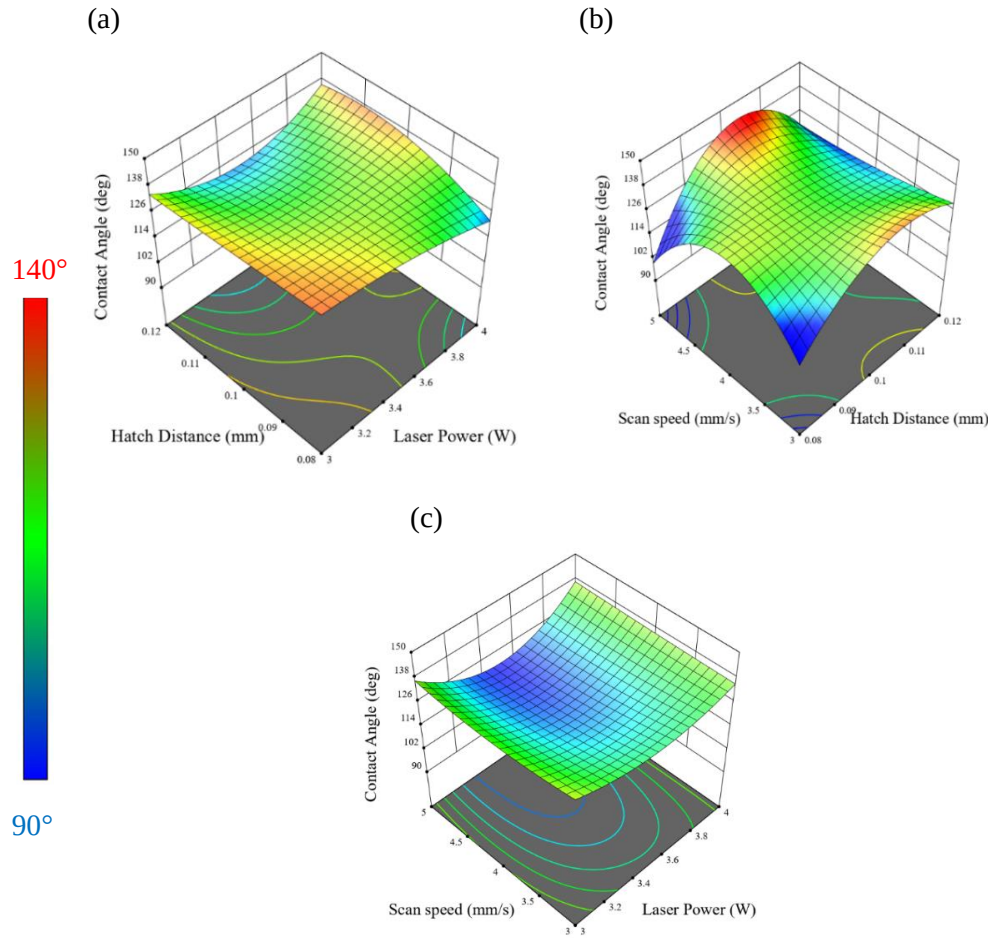


Figure 3.8 Response surface plots and contour plots of the contact angle shown from derived model at constant (a) scan speed ($v=4\text{ mm/s}$), (b) laser power ($P=3.5\text{ W}$), and (c) hatch distance ($h=0.1\text{ mm}$).

3.3.7. Numerical optimization

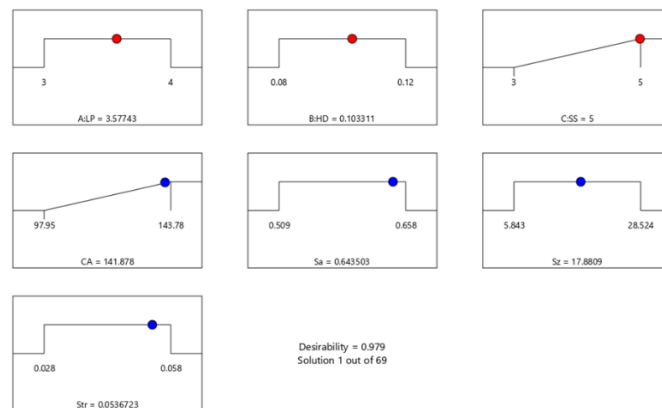
The numerical response optimization was also conducted in Design expert 13 software in order to find out the optimal laser surface texturing conditions at which the desirable surface properties such as increased hydrophobicity can be achieved. The same design matrix was used to determine the best laser process parameters to be set. In this investigation criteria were implemented to maximize the water contact angle, and the speed was also maximized so that surface texturing can be implemented on large surface area most efficiently within a practical period of time. The Table 3.5 below summarizes these criteria.

Table 3.5 Optimization criteria and their limits as used in this study

Parameter or Response	Limits		Criterion	Importance
	Lower	Upper		
Laser Power (W)	3	4	is in range	3
Hatch Distance (mm)	0.08	0.12	is in range	3
Scan speed (mm/s)	3	5	maximize	2
Arithmetic mean surface roughness S_a (μm)	0.509	0.658	is in range	3
Maximum height surface roughness S_z (μm)	5.843	28.524	is in range	3
Texture aspect ratio S_{tr} (μm)	0.028	0.058	is in range	3
Water contact angle (deg)	97.95	143.78	maximize	1

There were 69 optimal solutions generated using the simple regression analysis method. Desirability values were calculated (see supplementary information) to find out the most optimum process parameters to produce hydrophobic surfaces. The solutions with the highest desirability are presented in Figure 3.9

(a)



(b)

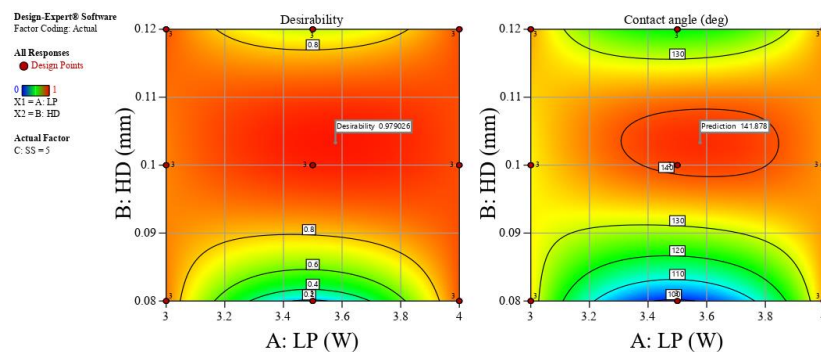


Figure 3.9 (a) Optimal laser process parameter conditions solution to produce a highly hydrophobic surface, with highest desirability of 98%; and (b) overlay contour plots solution for

each response shows the region of optimal laser surface texturing condition based on the criterion to enhance hydrophobicity

Validation of the developed model

In order to validate this model, confirmation experiments were carried out on the new samples with the predicted parameters and the contact angle measurements were again characterized for contact angle as shown in the Table 3.6. The contact angle measurements are provided in the supplementary information.

Table 3.6 Validation test results for confirming the optimization model's predictive power

Solution no	Laser power (W)	Hatch distance (mm)	Scan Speed (mm/s)		Contact Angle
1(97.9% desirability)	3.577	0.103	5.000	Predicted	141.87
				Actual	141.25
				Error (%)	0.43
23(97% desirability)	3.406	0.104	5.000	Predicted	141.064
				Actual	137.34
				Error (%)	2.71
69(87.1% desirability)	3.000	0.092	5.000	Predicted	132.685
				Actual	124.15
				Error (%)	6.43

The validation results demonstrated that the models developed are quite accurate as the percentages of error in prediction were low.

3.3.8. Surface topology analysis of the laser treated area

The qualitative analysis was conducted on the samples using scanning electron microscope (SEM) of the laser microstructure aluminium alloy samples. Micro scale structure was successfully obtained on the 7075 alloy substrates, which was shown to play a major role on the different properties of the surfaces.

Figure 3.10 (a) illustrates the micro-trenches formed on sample 1 through laser surface texturing using a laser power of 3 W, a scan speed of 3mm/s, a hatch distance of 80 μm and fluence of 2.914 J/cm^2 . The low power and slow scan speed resulted in the production of equally spaced, periodic trenches with a depth of 3.8 μm as measured by the profilometer data. Additionally, the laser

surface texturing process resulted in a debris-covered machined area, as well as nanostructures such as laser-induced periodic surface structures (LIPSS) on the layer, separated by uneven ridges and swells at the sub-micron level. These structures are primarily composed of oxides formed as a result of heating caused by laser irradiation. It is evident that the ridges and swells are periodically fabricated with substantial untreated areas in between the trenches.

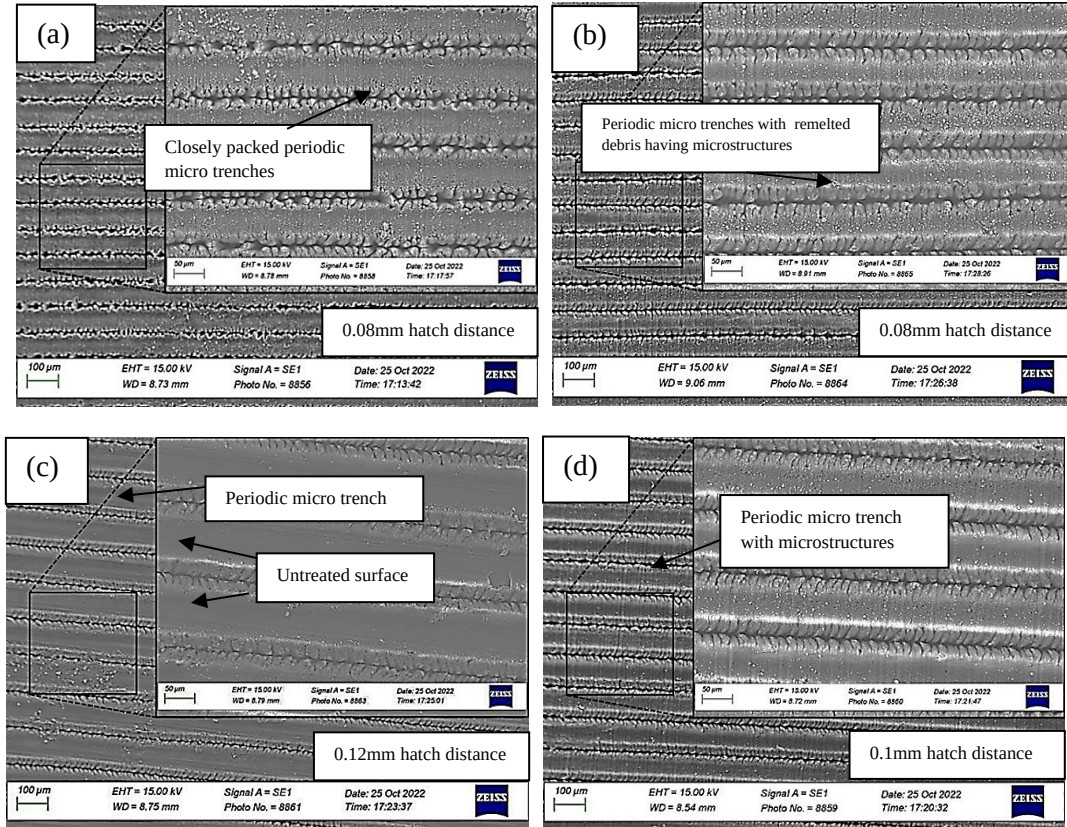


Figure 3.10 SEM images of the surface topology of the ultrafast laser structured 7075 for (a) sample 1, (b) sample 12, (c) sample 17, and (d) sample 23.

In Figure 3.10 (b) shows sample 12 where the laser process parameters were set at 3.5 W laser power, 5 mm/s scan speed, 80 μm hatch distance and fluence of 3.4 J/cm². It is observed that the trenches are closely packed and starting to merge, leaving very little untreated area between them, resulting in a highly rough surface. The average depth measured is quite high at 19 μm . By keeping the same fluence, a different structure with a higher hatch distance is seen in Figure 3.10 (c) (sample 17). The laser process parameters were set at 3.5 W laser power, 4 mm/s scan speed, and 0.12 mm and fluence of 3.4 J/cm². It is observed that the trenches are parallel to each other with untreated surface areas. The ridges and swells are periodic but less than those in Figure 9 (a). The effect of low scan speed is observed when comparing Figure 3.10(b) and Figure 3.10(c).

Figure 3.10 (d) shows sample 23 where it can be observed that the trenches are equally spaced with a hatch distance of 100 μm and were produced using laser processing parameters of 4 W and a

scanning speed of 4 mm/s and fluence of 3.88 J/cm². The non-processed area observed is smaller than that in Figure 3.10 (c). It is also observed that there are material deposits on the peaks, which form periodic surface structures that could be the result of oxidation caused during laser processing and aging. These periodic nano and micro surface structures act as porous surfaces that could trap air between the gaps, leading to highly hydrophobic surfaces. The maximum depth measured from the peak is 21 μm .

3.3.9. Surface chemistry analysis

The change in the wetting properties of the laser processed aluminium alloy samples can also be attributed to the changes in the surface chemistry of the samples. This can occur due to exposure of the samples to the atmospheric conditions, leading to oxidation of the aluminium alloy and formation of Al₂O₃ on the surface [37]. Additionally, a carbonaceous layer can also form on the textured surface, leading to the formation of non-polar regions and an increase in hydrophobicity. Aluminium alloy 7075 is a zinc-based alloy and when exposed to atmospheric aging, it leads to the formation of ZnO, which are also non-polar regions and may lead to an increase in hydrophobicity. To verify these theories [37, 39], X-ray photoelectron spectroscopy (XPS) measurements were performed on the surface of the laser-treated samples to determine their chemical composition. The XPS measurements were performed on the same four samples on the first day and after 60 days, when the samples turned to a hydrophobic state. This is performed to understand the change in chemical composition of the surface, and how it affects the wettability of the surface over the time.

Table 3.7 shows the results at day 1 and day 60 of the XPS analysis conducted in atomic percentage for the samples 1, 12, 17, and 23, as well as the recorded water contact angles for these samples, at day 1 and day 60.

Table 3.7 Atomic composition of laser surface structured samples determined by XPS on the day of and 60 days after laser treatment

Sample No.	WCA Day 1 (deg)	WCA Day 60 (deg)	Elements	Day 1 atomic %	Day 60 atomic %
1	67.19	141.5	Al	23.99	28.48
			C	34.14	9.04
			Zn	0.97	4.24
			O	40.90	58.24
12	18.14	97	Al	5.65	29.02
			C	82.41	11.82
			Zn	0.12	3.23
			O	11.81	55.93
17	11.35	123.5	Al	16.78	24.91

			C	41.92	15.86
			Zn	0.56	4.24
			O	40.75	54.99
23	21.31	141.72	Al	21.73	28.37
			C	41.90	11.76
			Zn	0.77	4.26
			O	35.60	55.64

In this study, it was observed that laser treatment led to a decrease in carbon content from 34% to 9% in sample 1, 82% to 11% in sample 12, from 41% to 15% in sample 10 and 42% to 12% in sample 23, compared to unchanged in the unprocessed metal with carbon content of 87%. Moreover, an increase in oxygen and polar components, results in the formation of oxides such as Al_2O_3 and ZnO .

A comparison of the O 1s peak for the unprocessed metal and a typical day 1 and day 60 processed sample (Sample 1) is shown in Figure 3.11. While some oxygen in the results may be due to surface adsorbates, the extension into lower binding energy in the O 1s peak is consistent with the presence of metal oxides, with the presence of metal oxide increasing strongly after processing and extending lower in aged samples. Deconvolved components were fit using Gaussian-Lorentzian functions, with additional components only included when they reduced the RMS of the fit. For the unprocessed sample, a single component at 532.0 eV gave the best fit, with any lower binding energy component below the limit of detection, indicating minimal metal oxides. A first component at ~532 eV with a second, lower binding energy component (529.6 - 530.8 eV) created a better fit for all processed samples. These results support strongly that the laser process induces metal oxides at the surface relative to the unprocessed sample. In the unprocessed metal, the Zn 2p peak was below the limit of detection, while 0.6 - 4.3 % Zn was found for the processed samples. Due to the close binding energies of Zn and ZnO 2p peaks (1021.7 and ~1022 eV), these were narrow peaks which could not be deconvolved into metallic and oxide components. For the Al 2p peak, the binding energy for metallic Al (72.6 eV) and Al oxides (74.6 - 75.6 eV) are more distinct. The Al peaks for all samples were centred at higher binding energies consistent with Al oxide. Fitting components, best fits were found for two components in all cases, with the smaller metallic low binding energy component (71.1 - 73.8 eV) having relative area for day 1 and day 60 of 4 and 30% for sample 1, 28 and 43% for sample 12, 38 and 42% for sample 17, and 38 and 36% for sample 23, compared to the higher binding energy component. For sample 23 the oxide level stays similar, while the result for the other samples shows a more metal rich signal for the aged samples, suggesting the Al oxide may diminish over time. As the oxygen signal does not decrease for the aged samples this could suggest an increase in ZnO for the aged samples, however this cannot be confirmed due to the close positions of the Zn and ZnO 2p peaks. ZnO thin films have established

hydrophobic properties, and increasing surface levels of ZnO could cause the increased hydrophobicity in the aged samples [274]–[276].

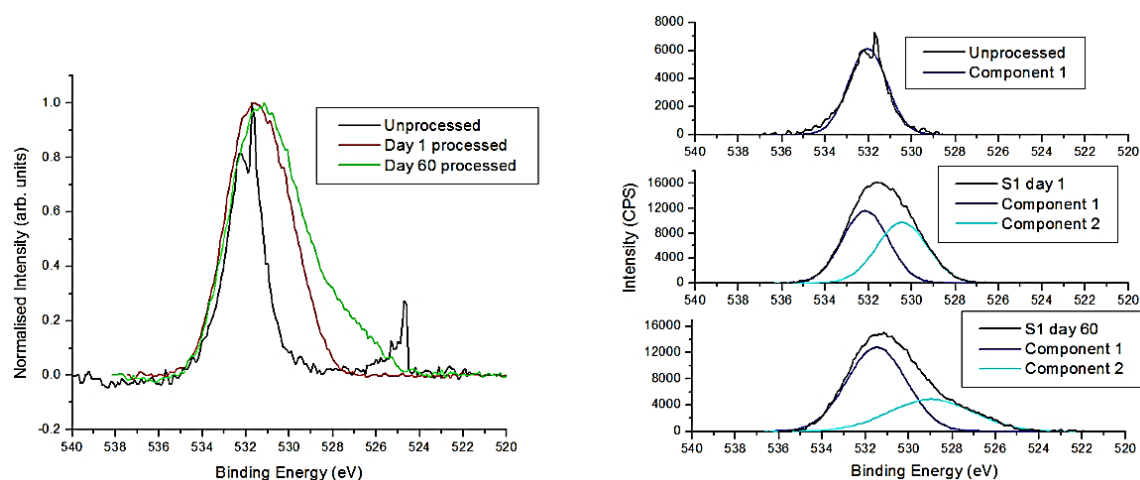


Figure 3.11 XPS spectra of the O 1s peak for unprocessed metal, and laser processed samples on the same day and the sixtieth day after laser processing for sample 1 (left), and with component fits for each plot (right).

The formation of zinc oxide and aluminium oxide is found to be largely dependent on laser process parameters, which significantly impacted the wettability of the surface. A lower percentage of zinc is found to correspond with a lower water contact angle. For instance, sample 12 (fabricated using laser process parameters 3.5 W laser power, 0.08 mm hatch distance, and 5 mm/s scan speed) exhibited the lowest contact angle of 97° and the lowest percentage of zinc at 3.23%. Conversely, the highest water contact angle was observed in sample 23 (fabricated using laser process parameters 4 W laser power, 0.1 mm hatch distance and 4 mm/s scan speed) and the highest percentage of zinc. Additionally, the percentage of Al₂O₃ on the surface was found to affect wettability, as observed by the difference in contact angles between sample 17 (with contact angle of 123.5° and manufactured using laser process parameters 3.5 W laser power, 0.12 mm hatch distance, and 4 mm/s scan speed) and sample 1 (with contact angle of 141.5° and manufactured using laser process parameters 3 W laser power, 0.08 mm hatch distance, and 3 mm/s scan speed) despite similar zinc percentages, which is in line with previous findings [247].

3.4. Discussion

The results of this study indicate that laser texturing using ultrafast femtosecond laser can be an effective method for modifying the surface properties of aluminium alloy 7075 materials despite various material challenges such as high reflectivity and high thermal conductivity [277]. The changes observed in surface morphology, surface roughness, wettability, and elemental

composition in this study suggest that femtosecond laser texturing treatment can be used to tailor the surface properties of materials for specific applications.

Moreover, the optimization of the process parameters of the laser plays a key role in finding out the best process parameter to get larger hydrophobicity, as greater hydrophobicity enhances the corrosion resistance and fouling resistance. The findings of this study also provide insights into the effects of femtosecond laser treatment on the surface properties of the material and fill the research gap in the research paper by Milles et al [247] on understanding the time-dependent evolution of wetting properties and finding out the relationship of the laser process parameters and wetting properties. Moreover, this chapter also provides an understanding of the surface chemical changes observed especially focusing on the enrichment of formation of zinc oxide on the surface which is one of the secondary reasons for hydrophobicity. Understanding surface chemical changes can help researchers optimize the laser texturing process to achieve desired surface properties.

The findings of this study have significant implications for various industries that require tailored surface properties for improved material performance in specific applications. For example, the marine industry can benefit from femtosecond laser texturing to enhance the corrosion resistance of aluminium alloys used in ship components. Similarly, the medical industry can benefit from tailored surface properties to improve the biocompatibility of implantable medical devices.

3.5. Contribution to thesis objectives

This research investigates the femtosecond laser texturing of aluminium alloy 7075 to enhance surface hydrophobicity, filling a critical knowledge gap on which process parameter setting is the best to produce a highly hydrophobic surface on aluminum alloy. By employing a design of experiments approach, the study examines the influence of laser parameters such as power, hatch distance, and scan speed on surface roughness and wettability. The findings highlight the optimal process parameter setting conditions for achieving maximum hydrophobicity, thus improving corrosion and fouling resistance. This work not only establishes a detailed correlation between laser process parameters and surface properties but also provides valuable insights for advancing applications in marine, medical, and other industries requiring tailored surface functionalities.

CHAPTER 4

Biofouling and Corrosion Protection by ultrafast laser texturing

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CHAPTER 4

4. BIOFOULING AND CORROSION PROTECTION BY ULTRAFAST LASER TEXTURING

4.1. Introduction

The buildup of undesirable material on solid surfaces is known as fouling. There are four main types of fouling such as chemical fouling (which includes scaling), biological fouling (biofouling), deposition (sedimentation or geofouling) fouling, and corrosion fouling [278]. Biofouling has been labelled as the most severe type of fouling among the various types of fouling in marine engineering. Surface biofouling is specifically observed in the marine environment where organisms attach themselves, grow, and secrete substances on various surfaces [279], [280]. This problem can be categorized into two types: microbial fouling and microbial fouling. Microbial fouling involves the formation of biofilms by microorganisms, while microbial fouling refers to the accumulation of larger organisms such as clams, barnacles, and mussels on submerged surfaces like ship hulls, propellers, and underwater structures [281], [282]. The mechanism of fouling in the context of marine biofouling can be understood through a successional model, which can be described as follows:

The initial stage involves the adsorption of organic materials and minerals onto a surface exposed to seawater, leading to the formation of a conditioning film (Stage 1). This conditioning film sets the base for the subsequent stages of biofouling. Following the formation of the conditioning film, primary colonizers, primarily comprising bacteria, begin to populate the surface, leading to the formation of a biofilm layer (Stage 2). This biofilm layer plays a crucial role in facilitating the adherence of subsequent microorganisms, setting the stage for further development. As the biofilm layer matures, it paves the way for the establishment of microfouling communities (Stage 3). These microfouling communities consist of a diverse community of microorganisms, including bacteria and microalgae such as diatoms and other species. Their presence further contributes to the complexity and stability of the biofouling ecosystem. Finally, as the biofouling community becomes more established and mature, macrofoulers, including macroalgae and marine invertebrates, settle onto the surface (Stage 4). These larger organisms become integral components of the biofouling community, adding to its biodiversity and ecological significance [283], [284]. This biofouling can cause several issues, including increased hydrodynamic drag, corrosion, reduction in heat transfer rate, and clogging intake and discharge flow systems [278], [285]. Therefore, in order to prevent biofouling, ideally it should be prevented at the (Stage 2) where

adherence of subsequent microorganisms on surface begins. Hence, to prevent or manage fouling, various strategies are employed such as mechanical cleaning, ultrasonic and electric treatments, and antifouling coatings are applied [74]. The cost of removing and mitigating this biofouling such as recoating and cleaning is estimated to be \$56M per year for the DDG-51 class of US navy ships [77].

Hydrophobicity and super-hydrophobicity of the surfaces are reported to have a direct correlation with the adhesivity of biomolecules. This is because of the interplay between the surface energies of the three phases involved, namely, the surface energy of the foulant, the surface energy of the substrate, and the surface tension of the suspending liquid [286]. These special types of surfaces have nano and micro textures that can be manufactured using different strategies such as chemical modification [287], coatings [288]–[290], physical strategies such as lithography [291], plasma treatment [292], [293], ultrasonic treatment [294]. However, most commercial marine coatings contain fluorine which increases marine toxicity potential and is harmful to the marine environment [295]. Hence there is a need to develop a non-toxic environment-friendly long-lasting solution for fabricating antifouling surfaces [296].

In recent years, laser nano-micro texturing has emerged as a promising approach for antifouling, offering a potential solution to mitigate biofouling while minimizing environmental impacts [297],[298]. The laser irradiance induces nano and micro surface structures on the surface of the material which reduces the surface energy of the substrate surface or enables specific interactions between the surface and the fouling material [299]. The nano and micro surface textures can be designed in a specific way such that it enables reducing the surface energy of a substrate weakens the adhesive interaction between the surface and any fouling material [300],[61]. To fabricate these nano and micro topologies effectively, ultrafast lasers can be used as they can produce topologies with higher dimensional accuracy and a lower level of defects, caused due to the heating produced from other longer pulse duration laser types [15], [22], [301].

Researchers have investigated and examined antifouling behavior on metallic surfaces with a view to improving the antifouling properties. Lutey *et al.* conducted an experimental study to tailor both wettability and surface morphology via ultrashort pulsed laser processing which improved the anti-bacterial capabilities of the 316 L stainless steel samples. The strategy involved inducing laser-induced periodic surface structures (LIPSS) and nano-pillars onto the surface [302]. Rajab *et al.* produced picosecond laser generated surface topographies on titanium alloy Ti6Al4V. These topographies exhibited anti-fouling properties as evidenced by the laser textured surfaces retaining less bacteria than the control surface [303]. In another recent study conducted by Yusuf *et al.*, the researchers investigated the impact of laser texturing on the material properties of TiO₂/ZnO ceramic coatings. They employed a picosecond laser system to create dimple-like textures on the

surface of the coatings. The presence of these dimples had a significant influence on the antibacterial properties of the TiO₂/ZnO coatings. The results indicated a reduction in optical densities (ODs), lower colony-forming units (CFUs), and a decrease in live cell bacteria. Moreover, the study also revealed that the increased surface area resulting from the dimples promoted bacterial attachment, thus facilitating the antibacterial effects of ZnO and TiO₂ as agents [304]. In a recent investigation by Nandru *et al.*, the impact of nanosecond laser texturing on surface biofilm formation was examined. The study involved the creation of square pit pattern and triangular pit pattern profiles with dimensions of 100 µm in width and 90 µm in depth, spaced at 250 µm intervals. The findings revealed that the square pit pattern exhibited a higher contact angle and demonstrated superior inhibition of biofilm formation compared to the triangular pit pattern. This reduction in bacterial attachment could be attributed to the interaction between surface hydrophobicity and the topographical features of the surface [305]. Uniform deposition of polystyrene particles on the laser textured surfaces is achieved and the deposited material is confined to smaller area [306]. In a recent research study conducted by McFadden *et al.*, the impact of treating commercially pure titanium (Ti) surfaces using a continuous wave (CW) fiber laser under argon (Ar) shielding on biofilm coverage of various bacterial species was investigated. The five bacterial species tested included both Gram-positive bacteria (*Staphylococcus aureus* and *Staphylococcus epidermidis*) and Gram-negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli*, and *Proteus mirabilis*). The study found that the biofilm coverage of all tested bacterial species exhibited a significant decrease after the treatment of the Ti surfaces with the CW fiber laser under Ar shielding. This reduction in biofilm coverage was attributed to two main factors: micro roughness of the surface and the formation of an oxide layer resulting from the recrystallization process occurring at the topmost layer of the material [307].

Aluminum alloy (7075) has become a notable material with its extensive applications in the marine industry due to their special properties, such as high strength, low density, satisfactory plasticity, and high corrosion resistance [308], [309]. It is significant to investigate algal corrosion behavior and mechanism with continued organic carbon starvation in the marine condition [298]. From this past research, various laser process parameters and effect of surface chemistry and antifouling efficacy have been extensively investigated. However, an area that remains largely unexplored has the potential of different pattern textures which can be fabricated using femtosecond laser in conferring antifouling capabilities. The literature review also shows that the effects of surface roughness on wetting behaviors have not yet been thoroughly studied.

In this study, we investigate the potential for using femtosecond laser processing in order to modify the surface properties to achieve a superhydrophobic surface which has marine antifouling abilities. Specifically, we concentrate on modifying the wetting characteristics of aluminium alloy 7075 material. We explore five unique texture geometries, namely parallel lines, cross hatching,

triangles, stars, and rhombus patterns and experimentally test these micro textures for antifouling abilities by rapid biofouling assessment using diatoms (*Nitzschia ovalis*). Our main goal was to determine the most effective texturing approach that produces algae-resistant surfaces suitable for application in the marine environment.

4.2. Materials and methods

4.2.1. Material

The material used in this project was commercially available aluminum alloy 7075 T6 (thermally treated, stress-relieved by stretching, and artificially aged), in form of flat plates with 30×30 mm and 2 mm thick which are supplied by Impact Ireland Metals Ltd. The chemical composition of the aluminium alloy 7075 is shown in Table 4.1.

Table 4.1 Chemical composition of aluminium alloy substrate 7075

Zn	Mg	Cu	Si	Mn	Fe	Ti	Al
5.8	2.8	1.5	0.1	0.17	0.22	0.03	Balance

The average roughness (S_a) of the bare plate was 400-500 nm before processing as measured by 3D optical profilometer. The surface of the samples was cleaned using isopropyl alcohol before laser processing.

4.2.2. Laser surface texturing

The ultrafast laser surface texturing was conducted on the aluminium alloy 7075 substrates using a laser system which was equipped with a high-energy industrial ultrafast laser source. This laser provides a stable low noise pulsed beam with an average wavelength of 1030 nm and a pulse duration <370 fs. The laser beam surface scanning with different for different pattern designs was conducted with a galvo scanner (Focusshifter-15, Raylase GmbH) and the beam was focused on the sample using an f-theta lens. Gaussian type of beam was present at the focal position which had a full width of the beam at $1/e^2$ measured to be 46.4 μm at a working distance of 220 mm from the lens of the galvo scanner. The laser texture pattern was applied across an irradiated area of 8 mm × 8 mm. The laser processing was conducted in the atmospheric environment at 20° C and a relative humidity of 60%. The sample was mounted on the 4-axis translation stage (PRO 225 Aerotech Inc) which was calibrated and kept stable with the focal point at the top surface of the sample. In this experiment, the laser process parameters were set as 3 W laser power, 100 kHz pulse repetition rate, and 4 mm/s scanning speed. The laser texturing setup schematic and actual picture is illustrated in Figure 4.1.

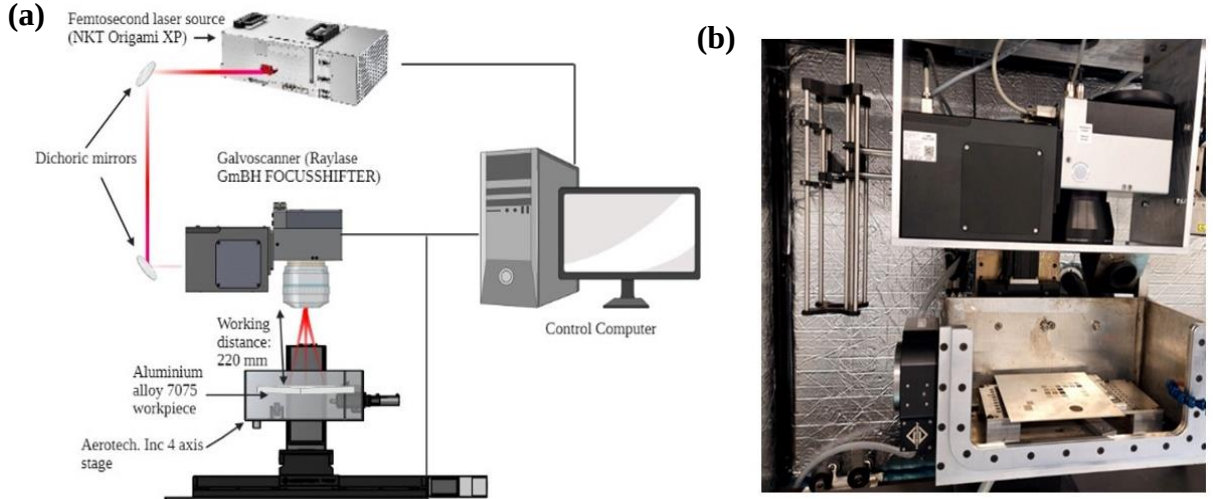


Figure 4.1 Laser surface texturing setup (a) schematic and (b) picture.

Based on the above parameters the fluence was calculated using the equation:

$$F = \frac{E_p}{A} \left(\frac{J}{cm^2} \right) \quad (1)$$

here E_p is the laser average pulse energy and A is the laser spot area. Using this equation, the fluence was calculated as $1.77 J/cm^2$. Five different laser scan strategies were used to produce five unique types of texture which are as shown in Figure 4.2. These textures were designed based on previous literature [310]. However, S4 is a texture which resembles the skin of a shark.

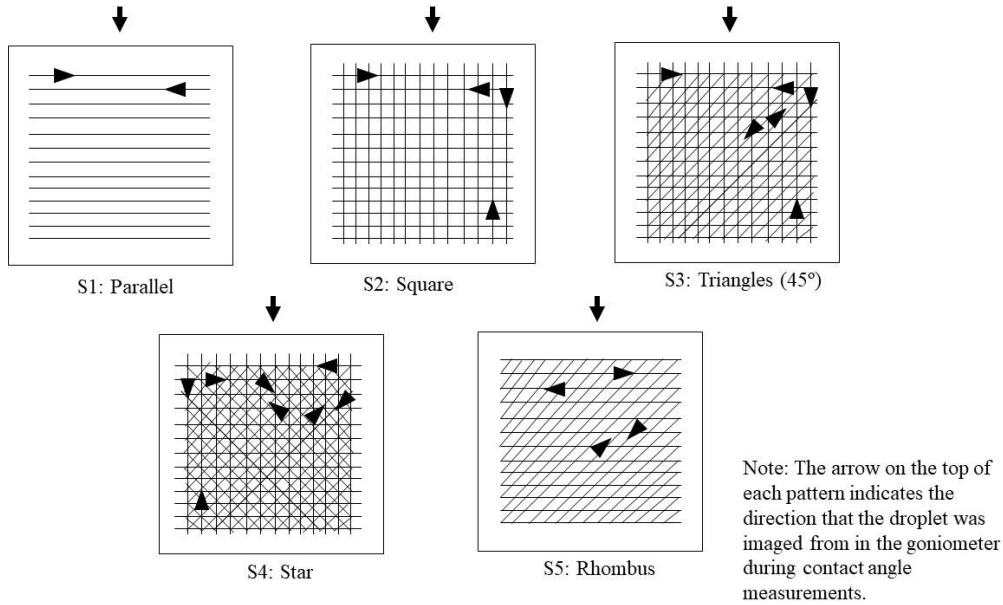


Figure 4.2 Schematic of the scan strategies used for the five different texture types produce (S1 to S5).

4.2.3.Surface characterization and biofouling experiment

Morphology

The laser-treated surfaces were evaluated using scanning electron microscopy which was performed using an Jeol JSM-IT 100 InTouchScope™ with LaB6 filament, accelerating voltage of 10 kV, and a beam current intensity of 20 pA. The evaluation was done in secondary electron diffraction mode. The images were taken at 100X and 1000X magnification for all the patterns. As the aluminum alloy samples are conductive no extra sample coating was required.

Surface Roughness

The different surface roughness morphology attributes such as S_a (arithmetical mean height), S_q (root mean square surface roughness), S_p (maximum peak height), S_v (maximum crest depth), S_z (maximum height surface roughness) were measured using a Bruker Contour GT 3D Optical Profilometer as per ISO standard 25178-2:2021 [271]. The measurements were made using a 10X lens and focusing on the sample using white light interferometry. The analysis of the surface roughness parameters was measured using inbuilt software Bruker's Vision 64 ® image analysis on the raw data.

Wettability

The wettability of the surface was determined using static water contact angle. The static water contact angle measurements were performed using a FTA200 Dynamic Contact Angle Analyser. The sessile drop profile was measured using the non-spherical liquid – vapor curve fit method which was performed with the FTA 200 software. The measurements were taken at ambient conditions (20° C and 60% relative humidity). For these measurements 10 µl of deionized water was used per applied droplet. The contact angles were taken three times (n=3) on each sample to ensure repeatability on the same day of the measurement.

Biofouling experiment

Biofouling assessment was performed using a 10 mL culture suspension of fouling organism, *Nitzschia ovalis*. Cell numbers were estimated by counting using an improved Neubauer bright line hemacytometer. The textures were firstly purged with nitrogen (N₂) gas to remove air pockets. Surfaces were immersed in the cell suspension for 3 h. Colonization of organisms on the candidate micro-textures was observed using scanning electron microscopy. All image analysis was performed using Fiji (ImageJ) image processing software. The images used in the analysis were scaled using the scale bar given in the images taken on the Keyence VHX2000E 3-D digital microscope. Images were cropped to approximately 2000 x 2000 µm. Image segmentation was performed using the Trainable Weka Segmentation plugin which uses machine learning algorithms to classify a red-green-blue or greyscale image into different classes. The user trained the software by drawing strokes defined as a training set of pixels (STP) over the region of interest (ROI) for

each class. An STP of two classes is necessary to start the segmentation. Two classes were used. Class 1 corresponds to the particles to be detected, in this case benthic diatom species, *Nitzschia ovalis*, appearing red. Class 2 corresponds to the background of the image, appearing green. These classes are comprised of sets of pixels that share similar visual characteristics such as colour, shape, or size. The segmentation process was carried out using the Fast Random Forest algorithm which employs machine learning using decision trees to classify data based on user-defined patterns for each class. This algorithm was chosen because of its computational efficiency, probabilistic output, ability to handle a wide variety of image input characteristics and interactive enhancement based on error handling. In addition, this algorithm avoids over-fitting the data by injecting randomness in the training trees and combining the output of multiple random trees into the final classifier; in our case 200 trees were performed using always in each analysis an out of bag error lower than 5% to arrive at the final classifier from which a probability map was obtained. The Random Forest algorithm proves to have robust performance when compared using eight evaluation metrics. The probability map was cropped and processed using an ImageJ plugin to cluster colour pixel driven by the user input developed by Biomedical Imaging Group (<http://bigwww.epfl.ch/>). This ImageJ plugin allows to segment a colour image by pixel clustering. Five red patterns were used for class 1 (corresponding to diatom cells) and five green patterns for class 2 (corresponding to the background). The percentage area covered by each colour was calculated using the K-means clustering algorithm. The analyses were carried out on an individual sample basis.

Electrochemical Corrosion test

Laser textured sample S4 with a star pattern, one produced on the same day and another aged for 90 days was used for the electrochemical corrosion test. The samples were cleaned with isopropyl alcohol and then put into the test rig after drying. The corrosion behaviour of the samples was investigated by open circuit potential (OCP) and cyclic polarization studies using the Gamry Interface 1000-E electrochemical setup. The exposed area was the laser-textured surface with a star pattern (S4). A standard three-electrode cell configuration was used with a saturated calomel electrode (SCE) as a reference, high-density graphite rod as a counter, and sample as the working electrode. 3.5 wt% NaCl was used as the electrolyte for corrosion studies at room temperature. Open circuit potential measurements were done prior to cyclic polarization studies for 3600s. Cyclic polarization was done in the voltage range of -0.3 V to $+1.0\text{ V}$ versus E_{OCP} (Vs SCE) with the forward and reverse scan rate of 0.166 mV/s as per ASTM standard G61-86 and with maximum apex current of 1 mA/cm^2 .

Surface chemistry analysis

The surface chemistry of the irradiated materials was analysed by X-Ray photoelectron spectroscopy (XPS). In this study, a Scienta Omicron XPS system equipped with a monochromatic Al $K\alpha$ X-ray source (operated at 280W and 14 kV) at a base pressure setup of $6 \times 10^{-7}\text{ Pa}$ with a

128 channel Argus CU detector was employed. The kinetic energy of the photoelectrons was determined using an analyser with a pass energy of 100 eV for the survey and 50 eV for high resolution spectra. The take-off angle between sample's surface normal and the electron optical axis of the spectrometer was 0°. The depth of layer analysed was 8 nm from the top of the surface. Spectra were referenced to the C-1s peak of adventitious carbon at a binding energy of 284.8 eV.

4.3. Results and discussion

4.3.1. Morphological analysis

The resulting patterns from the laser texturing are showing in Figure 4.3. In the parallel line pattern (S1), straight parallel cuts were made on the surface with a 0.1 mm hatch distance. In the cross hatched pattern (S2), straight parallel and perpendicular cuts were produced. Due to this scan strategy, the surface area increased significantly. The nano and microstructures were formed mostly on the crown region of the surface producing an enhanced surface area. The triangle pattern (S3) resulted in sharp peaks and valleys. SEM imaging depicted a well-defined triangular structure with clear boundaries indicating a surface topology with distinct features that would be found to influence the wetting behavior and surface interactions. Surface pattern (S4) exhibited a star-shaped pattern with multiple arms extending from a central point with a high degree of periodicity. The magnified SEM imaging illustrated a star pattern with fine details on the arms and a relatively small untextured area while sample S5 exhibited the rhombus shape pattern according to the planned scan strategy.

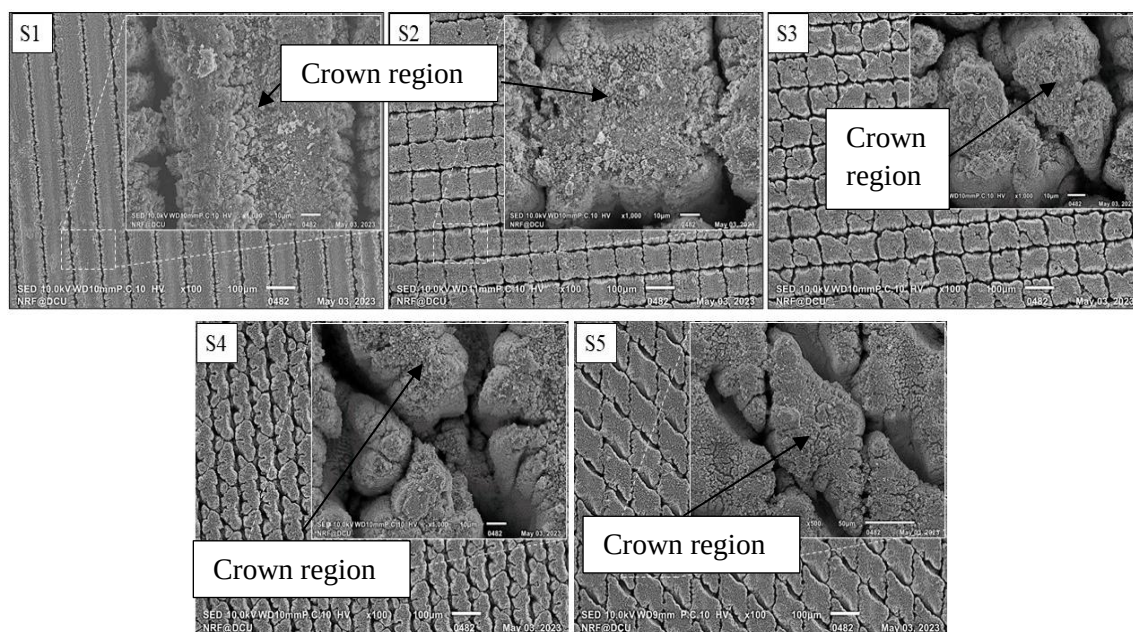


Figure 4.3 SEM images of the laser-processed aluminum alloy surface showing the different morphologies of different textures at 100X and 500X magnification (S1) shows parallel pattern,

S2 shows crosshatched pattern, S3 shows triangular pattern, S4 shows star hatch pattern, S4 shows rhombus hatched pattern.

4.3.2. Surface roughness

The surface roughness was measured by Bruker Contour GT 3D Optical Profilometer having white light interferometer with 10X magnification covering a surface area of $100 \times 100 \mu\text{m}^2$. All the surface roughness height parameters were measured accordance to ISO standard 25178-2:2021 [271]. Figure 4.5 shows how the five scan patterns altered the 3D topography and surface roughness properties of the Al samples. Samples were prepared with different scan strategies such as parallel hatch pattern (S1), cross hatch pattern (S2), triangle hatch pattern (S3), star hatch pattern (S4), and rhombus hatch pattern are shown in Figure 4.5 (b) – Figure 4.5 (f) respectively. When compared to pristine samples, different laser scan strategies had a substantial impact on increasing the surface area by increasing the surface roughness of the materials. Figure 4.5 (a) clearly shows that the pristine sample has the lowest surface roughness values as compared to other laser processed samples.

When compared to other scanning procedures, the star hatched pattern (Figure 4.5 (e)) has the highest Sa and Sq values, while the triangle hatch pattern (Figure 4.5 (e)) has the highest Sz values. However, it is observed that parallel hatch pattern (Figure 4.5 (b)) has minimum Sa, Sq, and Sz values. Figure 4.2 shows the comparison of surface roughness and depth values at different scan strategies.

Figure 4.5 shows the comparison of surface roughness values (Sa, Sq, Sp, Sv and Sz) at different scan strategies. From the graph it is observed that parallel hatch pattern has minimum surface roughness values.

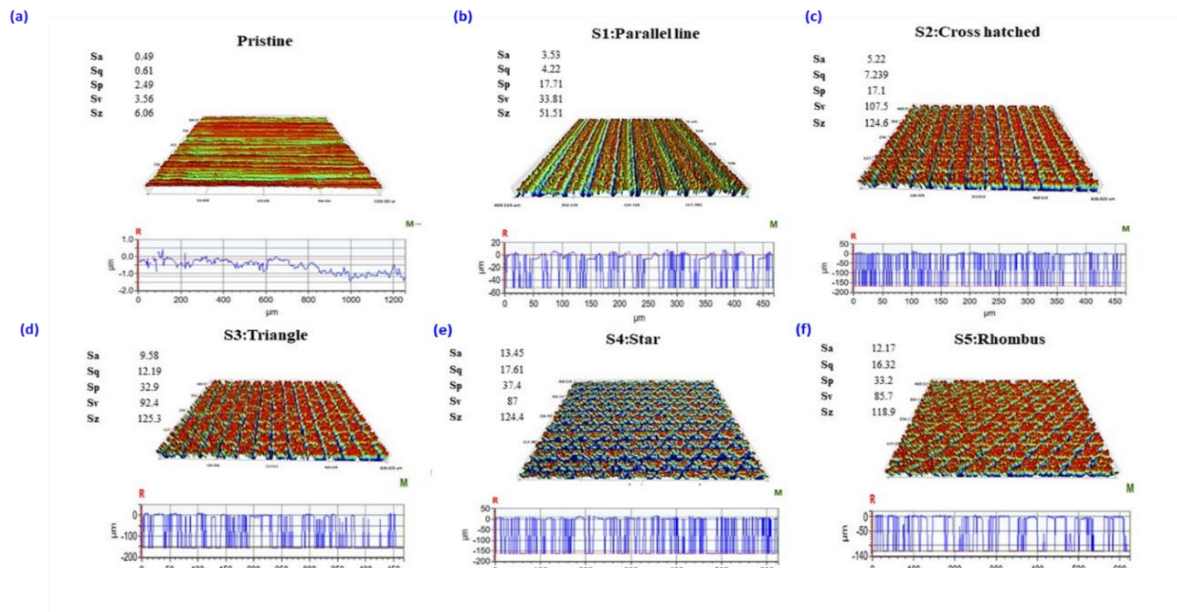


Figure 4.4 Surface profiles and scanning depth of (a) pristine and (b-f) samples fabricated using different scan strategies. μ

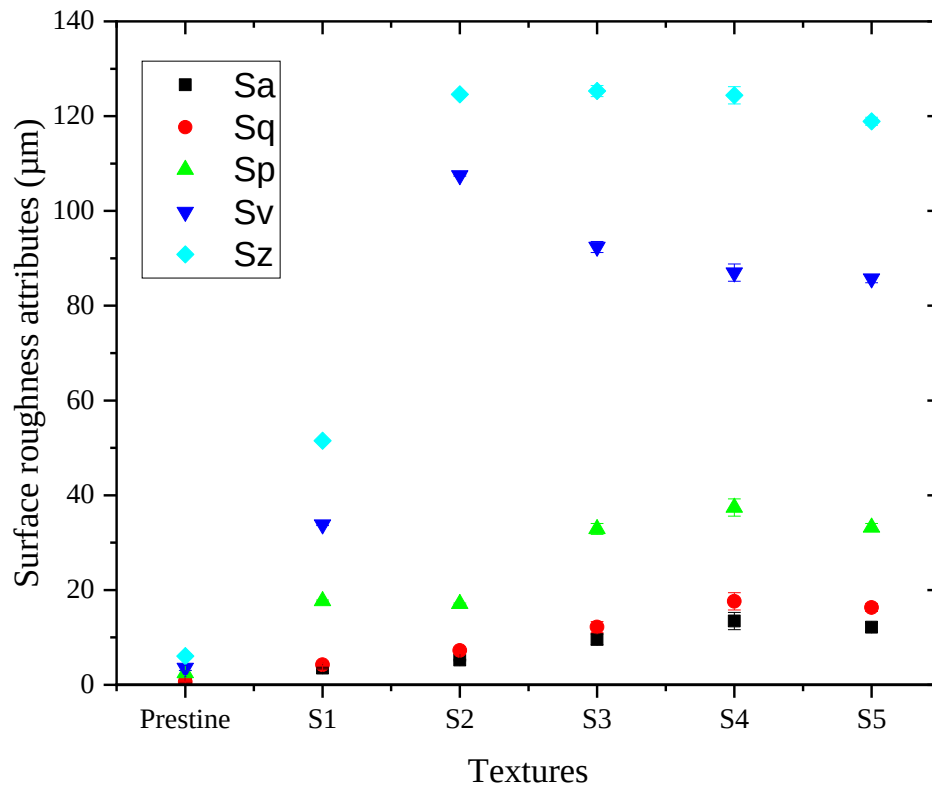


Figure 4.5 Distribution of different surface roughness attributes Sa, Sq, Sp, Sv and Sz for different textures fabricated by femtosecond laser texturing. The error bars shown are 95% CIs.

Different laser scanning strategies have been studied to understand their effects on surface morphology in laser surface texturing using ultrafast laser system. Significant variations in dimensional attributes are readily discernible among distinct laser-textured structural configurations with regard to lateral dimensions, topographical characteristics, and geometrical morphology, see Figure 3. This is because metal is partially melted and sputters from the matrix due to the high photonic impact energy action of the ultrashort pulsed laser. The sputtered metal is deposited on the non-laser irradiated area forming nano and micro-scale structures. These nano and micro textures formed adjacent to the micro grooves lead to a local increased in surface area and surface roughness [311], [312]. The S_a and S_p and parameters, determined during the roughness analysis, can be regarded as indicators of the quantity of potential contact points for *N. ovalis* algae cells, based upon their dimensional attributes (see Figure 4). The *N. ovalis* algae cells have dimensions of approximately $14\text{ }\mu\text{m} \times 6\mu\text{m}$ [313]. Sample S4 had the highest S_a and S_p values which were $37.4\text{ }\mu\text{m}$ and $13.45\mu\text{m}$ respectively. This is directly dependent on the pattern size. When the pattern size is smaller than the cell size, the surface has a better ability to prevent micro algae cell adhesion. These effects are also observed in case of bacterial adhesion by various researchers such as Lutey *et al.*[303], Rajab *et al.*[304] and Lu *et al.*[314]. However, if the S_a and S_p roughness are too low such as in case of S1, S2 and S3 then the cells can adhere and form a biofilm on these surfaces. While these values are solely rooted in geometric considerations and do not accommodate the presence of cellular or surface asymmetry, they give metrics for designing the topological features and establishing laser process parameters.

4.3.3. Wettability and its Transition

The surface wettability which is one of an important property to determine the adhesion of the surface of the laser-ablated samples was assessed by measuring their static water contact angles (WCAs) . Each recorded value was obtained as an average from three distinct locations on the samples. The increase in WCA values signifies a reduction in the wetting capability of the surfaces over time. The pristine aluminum alloy sample did not show any significant change in water contact angle. The pristine (without textures) sample had the water contact angle of $85 \pm 4^\circ$. The maximum

water contact angle achieved was on sample S5 which was 157.11° the transition is shown in Figure 4.6.

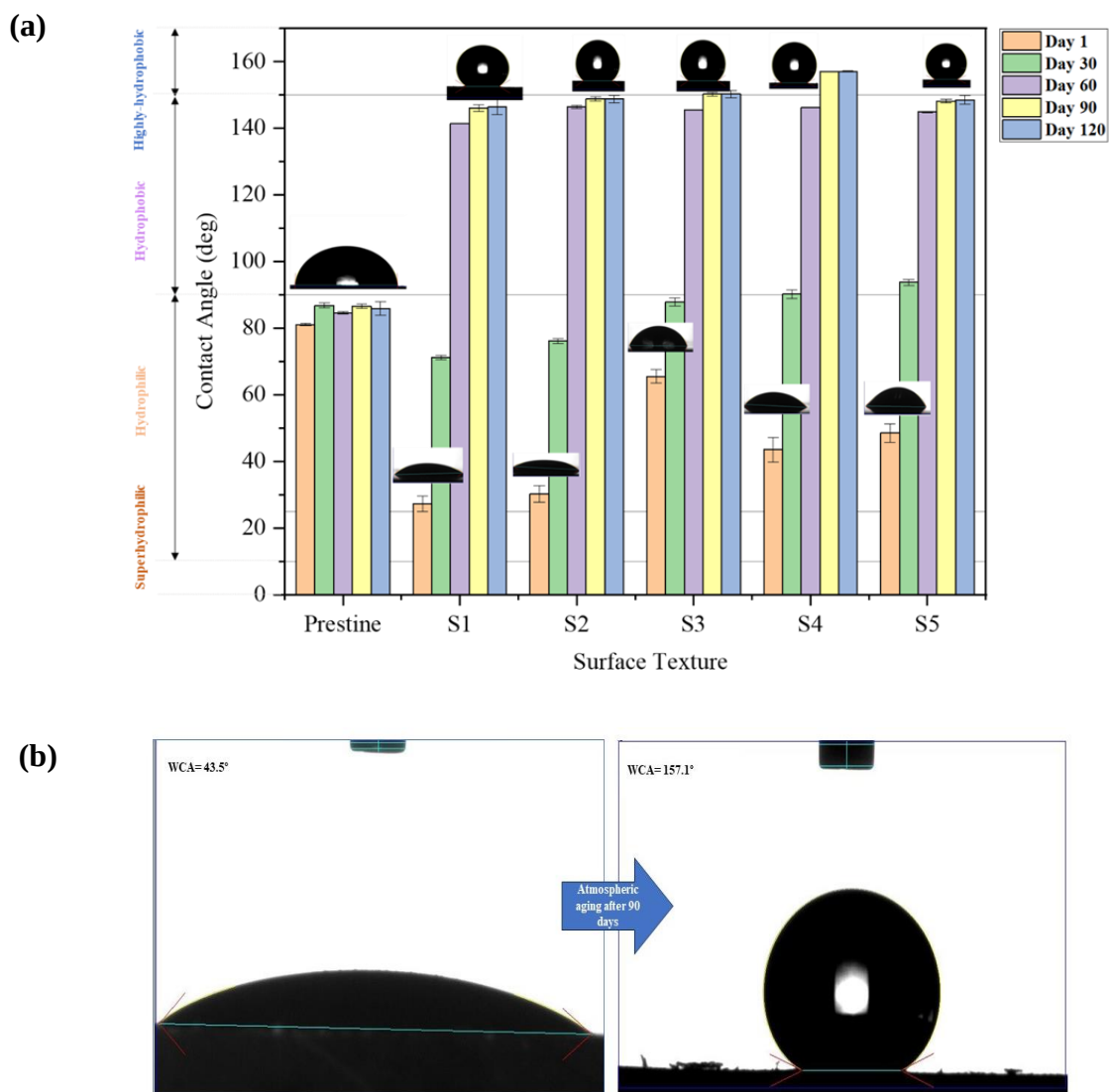


Figure 4.6 (a). Static water contact angle measurements ($10\ \mu\text{l}$ deionized water droplets) taken with time on the untreated reference and substrates and treated using femtosecond laser having five unique different patterns S1-S5. Error bars shown are the 95% CIs; (b) Wettability transition of laser textured sample S5 from highly hydrophilic (43.5°) to superhydrophobic (157.1°) in 90 days of environmental aging after laser processing.

After 30 days it can be observed that the water contact angle was increased in all the laser textured samples, especially in the S4 and S5 the samples were converted to hydrophobic ($\text{WCA} > 90^\circ$).

The observed change of time-dependence of WCAs for the surface textures created by laser texturing is particularly seen in case of aluminum alloy, when they were exposed to ambient air. A same effect is observed in previous literature by Yang *et al.*, which supports this theory of evolution of the surface water contact angle [315]. After 60 days from the day of texturing of ambient aging

all the textures were converted to highly hydrophobic (WCA > 90°). After 90 days from the day of laser texturing, the samples S3, S4 and S5 showed superhydrophobicity (WCA > 150°). However, after 120 days from the day of laser texturing there were no changes observed on any samples indicating that a steady state surface condition was reached. Achieving this steady state is different for different materials and different types of laser systems and texture designs. This state is also dependent on the ambient conditions [316]. The wetting behavior of the laser textured aluminum samples was evaluated by measuring the static water contact angle over a period of 120 days. In Figure 6a, the evolution of the static water contact angle with time is reported for the samples fabricated using the laser surface texturing method. It can be observed that on the day of texturing, the samples initially became hydrophilic. This is attributed to the level of surface oxide which is lowest initially which is also related to the energy applied on the aluminum surface during the laser texturing [314]. After 60 days it can be seen that the contact angle produced on the samples reached near to the water contact angle of the pristine sample of $85 \pm 4^\circ$. After 90 days the water contact angle reached the steady state (as there was no change observed even after 120 days) and two samples S3 and S4 became superhydrophobic (WCA > 150°). The highest water contact angle of 157° was achieved on S4 which had the star pattern. Similar findings have been reported by Cardoso *et al.*, specifically on the aluminum alloy material [246]. It can also be attributed that the ambient conditions also affects the wettability transition and the stabilization of contact angle after particular days as shown by previous literature by Hauschwitz *et al.* [317]. Antifouling and superhydrophobicity are closely related concepts as these surfaces have low surface energy and micro-nano dual structure which were found to be unsuitable for the attachment of fouling organisms, making them effective in preventing biofouling.

4.3.4. Effect on biofilm formation experiments

The prevention or delay of early settling and biofilm development is widely acknowledged as a means to avoid or postpone later fouling occurrences. The inhibition of biofilm growth holds significant potential to substantially mitigate the extensive damage inflicted by the subsequent increase of biological fouling populations. The study aimed to investigate the antifouling efficacy of various textures to assess their potential utility as antibiofouling techniques within the marine industry.

Biofouling assessment was performed using a 10 mL culture suspension of fouling organism, *Nitzschia ovalis* and the cell area coverage was assessed by image processing. Figure 4.7 shows the result of the biofouling assessment on all the surface textures. In Figure 4.7 the segmented colour image by pixel clustering is presented which shows diatoms in red color and the surface in green color. The percentage area covered by each color was calculated using the K-means clustering and the area coverage is presented in Figure 4.7 b.

It has been observed that laser-textured surfaces can prevent or decrease the formation of biofilms.

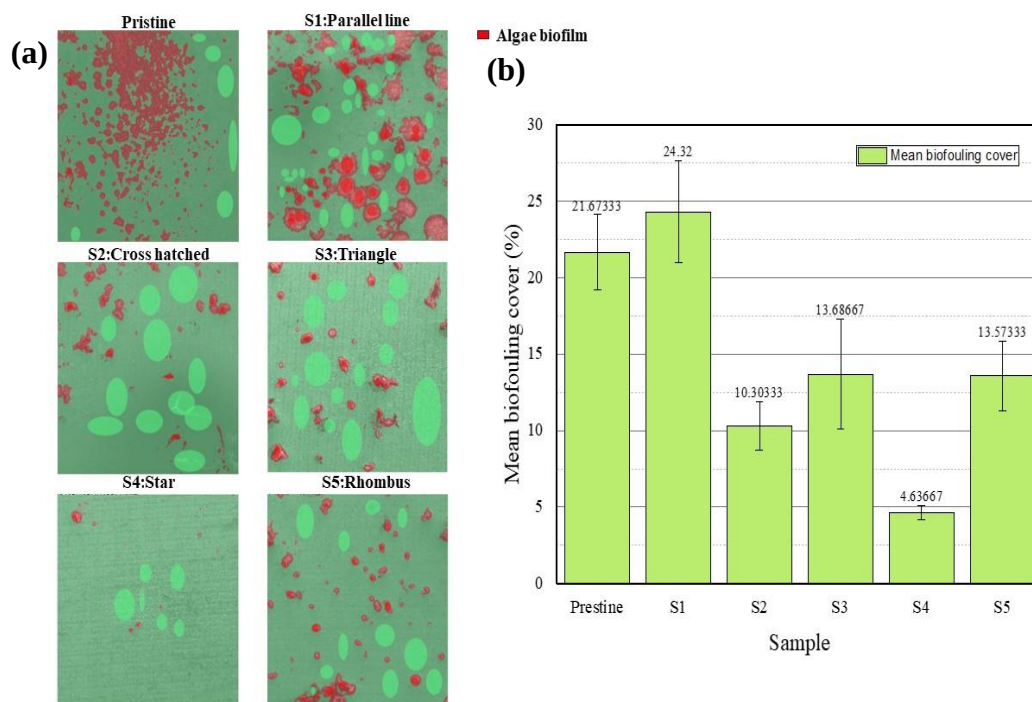


Figure 4.7 (a) Cropped Segmented images of *N. ovalis* biofilm on pristine sample and laser fabricated surface textures S1-S5; and (b) *N. ovalis* coverage on different samples immersed in cell suspension for 3 h. Error bars show the 95% CIs with (n=3).

The laser textured surfaces were exposed to the 10 mL culture suspension of fouling organism, *Nitzschia ovalis*. The behavior of test organisms on the candidate micro-textures was observed after three hour exposures of textures. In the context of surface attachment of diatoms, the behavior of diatoms was found to be significantly influenced. The biofouling assessment revealed noteworthy differences in the *N. ovalis* cell area coverage among the various samples. The mean biofouling cover is shown in the plot above in Figure 4.7 (b). Three trials were conducted on each type of texture in order to get repeatability of the results. The pristine aluminium alloy surface showed an average cell coverage of 21.6%. On a smooth, flat surface, diatoms exhibit a propensity to settle readily, establishing multiple attachment points, as illustrated in Figure 4.7 (a) Pristine. This result serves as a baseline for comparison with the laser-textured samples. Conversely, where surfaces have micro-textures, two distinct outcomes are possible for diatoms. Sample S1, characterized by

a particular laser texture, displayed an average cell area coverage of 24.32%. The higher percentage of cell coverage on S1 indicated that this particular laser texturing strategy or pattern is not as effective in inhibiting *N. ovalis* adhesion. The topography plays an important role here. If the size of the microtexture of the surface exceeds the scale of the diatom, it may settle within the recesses, forming multiple attachment points, and benefiting from protection against hydrostatic forces. This is due to the *N. ovalis* organisms having more surface area with the parallel line pattern in S1 to settle on, attach to and cover the surface, similar to colonization by *S. aureus* as reported in previous literature by Epperlein *et al.*, on LIPSS surfaces with straight parallel lines [318]. However, when the surface topography is smaller than the diatom, the diatom can settle on top of the surface features. The organisms have less surface area of their shell (frustule) composed of biogenic silica, in contact with the surface, therefore reducing the amount of attachment points that it can form, leading to weak attachment. Therefore, in case of sample S2 which has cross hatched pattern exhibited superior biofouling resistance, with an average cell coverage of only 10.30%. This finding suggests that the laser texture applied to S2 successfully hindered *N. ovalis* attachment, resulting in a significantly lower biofouling coverage compared to the pristine surface. One of the potential reasons for lesser attachment could be air entrapment which reduced the adhesion between the textures [319]. Sample S3, featuring a different laser texture with triangular pattern, showed an average cell area coverage of 13.68%. Although not as effective as S2, the laser texturing in S3 still provided moderate protection against *N. ovalis* adhesion.

Sample S4 with the star pattern showcased exceptional biofouling resistance, with an average cell coverage of merely 4.63%. This result indicates that the unique laser texture applied to S4 exhibited potent anti-biofouling properties. The potential reason for low biofilm formation on the star pattern (S4) is that there is a low surface energy and lower number of points for attachment of the diatoms where the *N. ovalis* can settle and form colonies, as evidenced by the higher S_p values for this surface. This finding is similar to the findings by Rajab *et al.* on colony of *Escherichia coli* on TiO_2 surface [320]. Also, this sample has lowest adhesion properties as it is superhydrophobic as observed in previous section of wettability. Sample S5, with rhombus pattern, displayed an average cell area coverage of 13.57%.

In recent study by Nanduru *et al.* on laser textured Ti6Al4V alloy surface which had square pattern with 200 μ m feature with and 134° contact angle, a reduction in biomass coverage from 50% to 20% was recorded [305]. However, our results show better biofilm inhibition on sample S4 which had 100 μ m hatch distance with 20 μ m feature width on which a reduction in the biomass coverage from 22% to 4% was recorded.

4.3.5. Electrochemical corrosion test

The corrosion test was conducted on the pristine sample and sample with star pattern (S4) texture which shows antifouling abilities. Both environmentally aged and sample produced on same day were considered for the corrosion test. The test was conducted using three electrode electrochemical setup with electrolyte as 3.5% NaCl solution. Potentio-dynamic polarization studies were performed and Tafel exploration was used to calculate corrosion parameters.

Figure 4.8 (a) shows the open circuit potential of base and processed specimens. Potential spikes observed in the V-t curve for non-aged and pristine specimens suggests the occurrence of activation and re-passivation processes. Pristine samples reported the lowest OCP, at -723 mV, compared to non-aged and old specimens, which recorded OCP values of -772 mV and -809 mV, respectively. Cyclic polarization curves (Figure 4.8(b)) were used to obtain the E_{corr} (corrosion potential) and I_{corr} (corrosion current) of all the tested specimens. Table 4.2 shows the E_{ocp} , and I_{corr} of the specimens calculated using Tafel exploration. E_{corr} was found to be lowest for the pristine sample when compared to other specimens, following the trend of OC. In contrast, aged specimen exhibited enhanced corrosion resistance, as seen by a reduced corrosion current of $4.1 \mu\text{A cm}^{-2}$, as compared to both the non-aged and pristine samples, which measured $4.1 \mu\text{A cm}^{-2}$ and $5.22 \mu\text{A cm}^{-2}$, respectively.

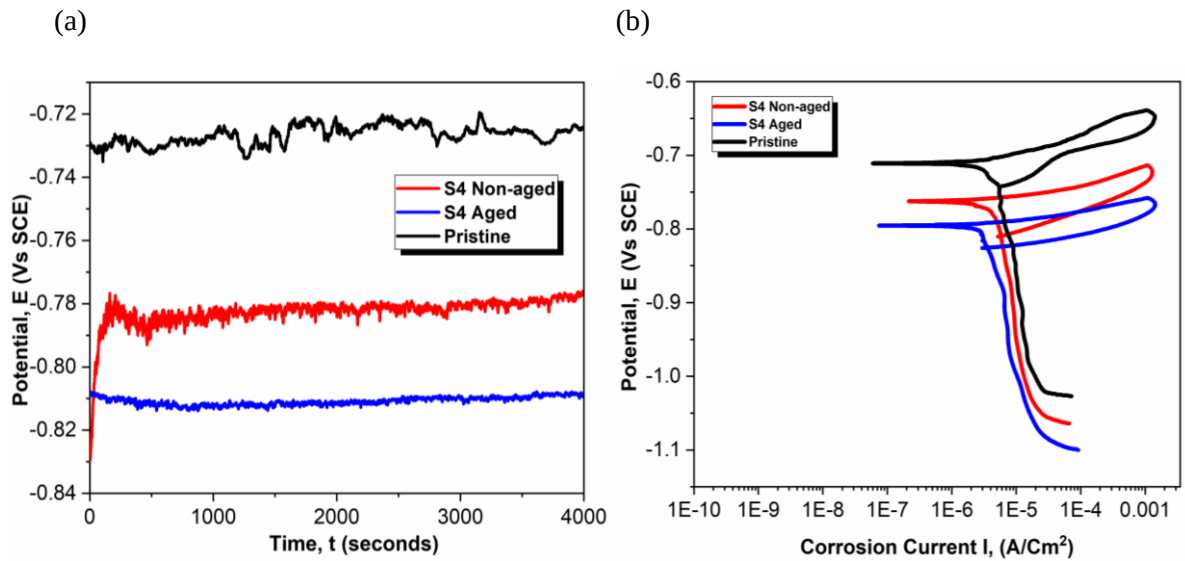


Figure 4.8 (a) Open circuit potential measurements (Potential, E vs time, t) obtained for 3600 s ;
(b) Cyclic polarization curves of the tested specimens in 3.5 Wt % NaCl electrolyte at room temperature using standard three electrode electrochemical set up.

Table 4.2 Open circuit potential (E_{ocp}), Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of pristine, laser textured, and laser textured and environmentally aged aluminum samples after 2 h of immersion in 3.5 wt% NaCl solution.

Sample	E_{OCP} mV (Vs SCE)	E_{corr} mV (Vs SCE)	(Vs)	I_{corr} $\mu\text{A cm}^{-2}$
Pristine	-723	-711		5.220
S4 Non-aged (1)	-772	-763		5.330
S4 Aged	-809	-795		4.1

An important evaluation factor for surfaces that will be employed in demanding marine conditions is their ability to resist corrosion. The electrochemical characterization of the base and processed specimens was therefore performed in salt water (3.5 wt % NaCl).

Potential spikes observed in the V-t curve (see Figure 4.8 (a)) for non-aged and pristine specimens suggests the occurrence of activation and re-passivation processes. These processes correspond to the initiation and healing of metastable pits. In contrast, the E-t curve of the aged specimen exhibits only a limited number of smaller spikes in magnitude. It signifies that a relatively stable passive layer was formed on the aged specimen compared to pristine and non-aged specimen. However, the lower E_{OCP} was recorded on the aged specimen might be due to the formation of ZnO as well as carbonaceous layer formed over time which leads to increased number of active sites created by laser processing, which could potentially hasten corrosion.

The aged specimen shows slightly lower corrosion current compared to the non-aged and pristine specimens. Thus, suggesting superior corrosion performance (25 % increase) compared to the other specimens. However, the passivity breakdown is apparent by the significant rise in the anodic current. In addition, all the tested specimens attained the maximum permissible current during anodic polarization. Therefore, the results suggest that the specimens exhibit weak resistance to pitting corrosion. The corrosion results suggest that the aged specimen exhibits superior corrosion resistance compared to both the pristine and non-aged specimens. Furthermore, the combination of laser processing and aging appears to enhance the corrosion performance of the aluminum alloy.

4.3.6. Surface chemistry analysis

The surface chemistry was analyzed by XPS. The penetration depth of XPS varies with the material and the binding energy of the peak being examined, however typically ~90% of the signal may be expected to come from within 5 nm of the surface. As such, the measurements are highly surface sensitive, and can be strongly influence by surface conditions such as roughness or surface contamination. Charging of samples under bombardment may lead to shifting of peaks. To account for the effect of surface charging samples were grounded, calibrated to the adventitious carbon peak, and checked against

expected results. As hydrophobicity is a surface phenomenon, the surface sensitivity of XPS may also provide greater insight than bulk composition characterization.

The surface compositions of the samples, calculated using the RSF-adjusted XPS peak areas, are presented in Table 4.3. The variation in composition is relatively small, and the carbon and oxygen signals may be, in part or total, contributions from surface adsorbates. Comparing the ratio of Zn to Al, samples 1, 2, 3, 4, and 5 have ratios of 0.29, 0.27, 0.32, 0.32, and 0.26, respectively.

Table 4.3 Atomic composition of the samples as determined by XPS

	C %	O %	Al %	Zn %
Sample 1	21	55	18	5
Sample 2	18	55	21	6
Sample 3	18	56	20	6
Sample 4	17	54	22	7
Sample 5	17	58	20	5

While some of the oxygen signal may derive from surface adsorbates rather than oxygen incorporated into the samples, extension into lower binding energies for the O 1s peak can indicate the presence of metal oxides. The unprocessed sample shows a peak centred at 532.0 eV. The peak was best fit with two components, at 531.9 and 533.6 eV, consistent with C=O and C-O from organic adsorbates, respectively. The laser processed samples all exhibit extension into lower binding energy compared to the unprocessed metal (see Figure 4.9). Deconvolved components were fit using Gaussian-Lorentzian functions, with additional components only included when they reduced the RMS of the fit. All processed samples were best fit with two components, a dominant higher binding energy component (531.2 – 532.0 eV) and a smaller lower binding energy component (527.5 – 529.2 eV). This strongly indicates the presence of some metal oxide(s) in all the processed samples. Sample 4 shows greater extension into lower binding energy, which may indicate greater oxidation in this sample.

The C 1s peak for the unprocessed metal was a strong, single component peak at 284.8 eV, indicating the dominance of adventitious carbon over any other adsorbates. The C 1s peak

for the laser processed samples show a similar broad shape and position. All processed samples fit best with three components (see Figure 4.10): a dominant middle component (284.9 - 285.2 eV), a smaller higher binding energy component (288.7 - 289.5 eV), and a smallest lower binding energy component (281.0 - 282.6 eV). The contribution of these components varies somewhat over the samples, with Sample 1 having 68, 17, and 15%, Sample 2 70, 17, 13%. Sample 3 78, 16, and 6%, Sample 4 68, 19, and 13%, and Sample 5 73, 16, and 11%, respectively. The large, clear change in the carbon peak between the unprocessed material and the laser processed samples suggests a mechanism for the increased hydrophobicity. However, just looking at the results from the laser processed samples, the small variations in specific carbon adsorbate types between the individual samples did not show a clear correlation with the hydrophobicity or anti-fouling performance. The middle components position corresponds with adventitious carbon (C-C) which is expected at ~284.8 eV binding energy, the higher binding energy component is likely COO^- carboxyl or ester groups (expected at ~288.5 eV), and the lower binding energy component is likely dehydrogenated carbon bonded to the aluminium (expected at ~282 eV) [321], [322]. C-O compounds (expected ~286 eV) or C=O (expected at ~287 eV) may be present but could not be distinguished or fit in these data. Previous works described the electron deficient alumina surface of aluminum alloys leading to superhydrophilicity after laser texturing, with adsorption of long chain organic compounds from the air leading to a transition to superhydrophobicity as the sample ages [260], [322], [323].

As the hydrophobicity of the laser processed samples was seen to increase over time, this is the likely mechanism in this work. The XPS characterization was carried out after 90 days of aging, with the broad carbon peak (compared to the unprocessed sample) indicating the increase in other adsorbed organic compounds after processing and aging and suggesting that these other compounds play a significant role in the enhanced hydrophobicity. These results support immersion treatments in chemical solutions after texturing as a key avenue in achieving the best hydrophobicity in the shortest timeframe [324].

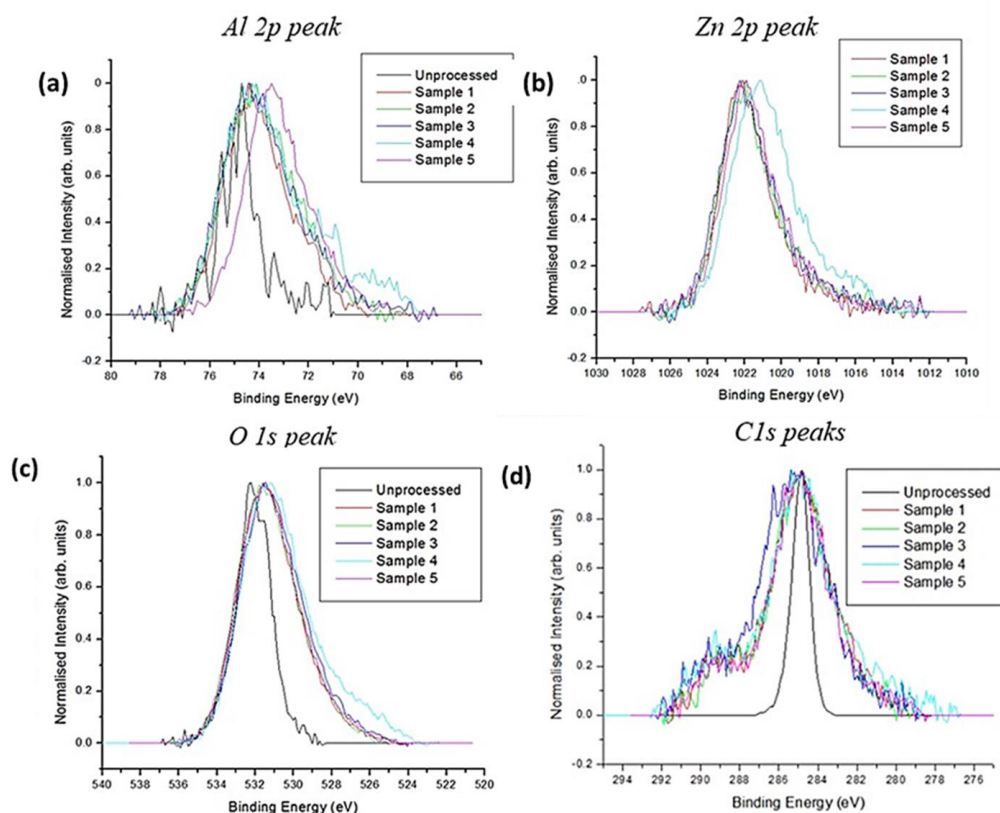


Figure 4.9 XPS spectra of Al 2p, Zn 2p, O 1s, and C 1s peaks for pristine and laser processed samples.

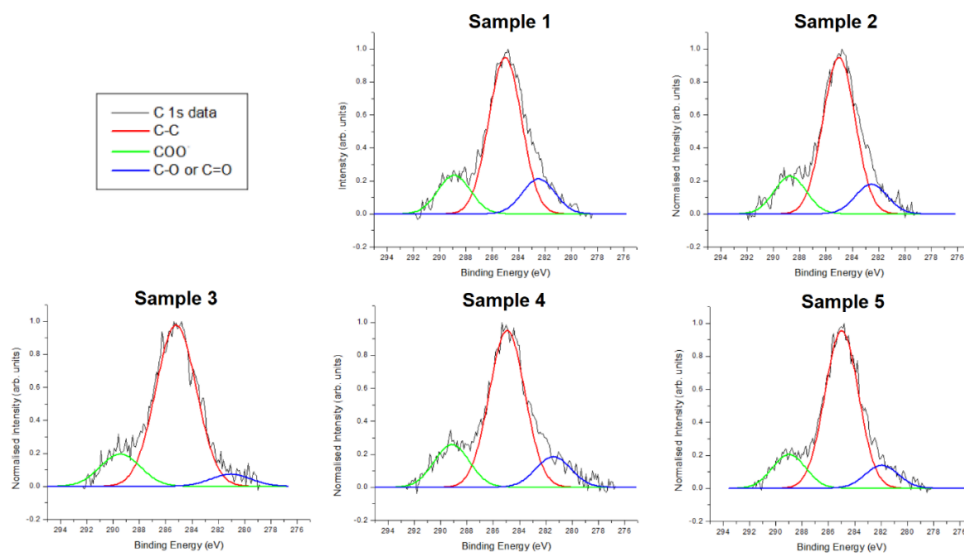


Figure 4.10 XPS spectra of the C 1s peak for the samples, with fitted components.

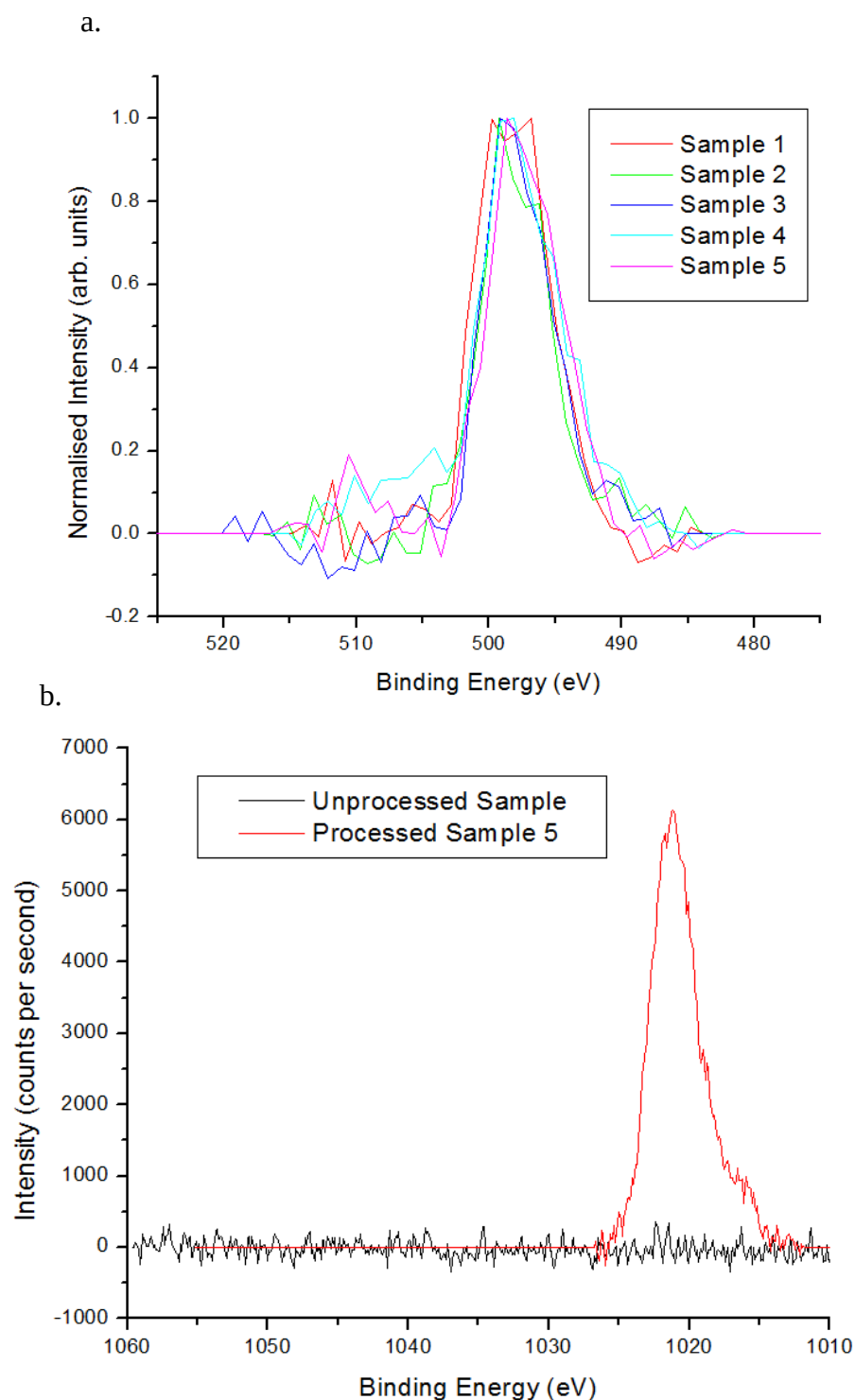


Figure 4.11 a. XPS spectra of the Zn LMM Auger peak for the laser processed samples, b. XPS spectra of the Zn LMM Auger peak for the laser processed sample 5.

For the Al 2p peak, the binding energy for metallic Al (72.6 eV) and Al oxides (74.6 - 75.6 eV) are reasonably distinct. The Al 2p peaks for all processed samples were centred at higher binding energies (73.5 – 75.0 eV, compared to a literature value for metallic Al of

~72.6 eV for the 2p 3/2) consistent with Al oxide (see Figure 4.9). The higher binding energy component contributed 76, 74, 78, 76, and 80 % to the full peak for samples 1, 2, 3, 4, and 5, respectively. These results suggest that the aluminium at the surface is significantly oxidised for all samples, with sample 4, which peaks at a visibly lower binding energy, exhibiting the highest oxidation. The unprocessed metal has a peak position of 74.7 eV, suggesting the material is initially oxidised and the laser processing may create a more Al rich metallic surface.

Zinc oxide may also be contributing to the indications of oxide, however due to the close binding energies of Zn and ZnO 2p peaks (1021.7 and ~1022 eV), making it difficult to distinguish. The Zn 2p peak position was 1022.1, 1021.9, 1022.8, 1021.1, and 1021.9 for samples 1, 2, 3, 4, and 5, respectively, see Figure 10. However, the Zn LMM Auger peak has a significantly different position of 494.7 eV for metallic zinc and 498.4 eV for ZnO. This peak was positioned at about 498.5 eV for all samples and is consistent with the presence of ZnO, see Figure 11. For the unprocessed metal, the Zn peaks were not detectable. This could be due to a higher concentration of zinc near the surface created by the laser processing. An increased concentration of ZnO at the surface may contribute to the wetting behaviour, as ZnO thin films have established hydrophobic properties [274], [325]. However, due to the low kinetic energy of the Zn 2p peak, it would also be strongly attenuated by a thicker surface layer in Figure 4.11. It is not possible to conclude that this mechanism is present, with the adsorbed carbon species described above being the most likely dominant contributor to hydrophobicity.

4.3.7. Input output correlation

To explore potential relationships between input process parameters and their corresponding responses, we employed Pearson correlation coefficients. By using these coefficients, we aimed to understand the relationship between the roughness attributes such as S_a , S_q , S_p , S_v and S_z , contact angle, biofilm coverage, and weight percentage of O, Al and Zn present on the texture.

It clearly shows in Figure 4.12 that the biofilm formation is indirectly proportional to the surface roughness while it also depends on amount of Zn percentage.

	<i>Sa</i>	<i>Sq</i>	<i>Sp</i>	<i>Sv</i>	<i>Sz</i>	<i>CA</i>	<i>Biofilm coverage</i>	<i>O %</i>	<i>Al %</i>	<i>Zn %</i>
<i>Sa</i>										
<i>Sq</i>	1.00									
<i>Sp</i>	0.97	0.96								
<i>Sv</i>	0.72	0.73	0.73							
<i>Sz</i>	0.82	0.83	0.84	0.98						
<i>CA</i>	0.73	0.72	0.83	0.81	0.86					
<i>Biofilm coverage</i>	-0.70	-0.72	-0.59	-0.72	-0.72	-0.42				
<i>O %</i>	0.67	0.67	0.78	0.79	0.83	0.98	-0.30			
<i>Al %</i>	-0.60	-0.60	-0.73	-0.73	-0.77	-0.97	0.20	-0.99		
<i>Zn %</i>	0.74	0.74	0.82	0.85	0.89	0.95	-0.61	0.89	-0.87	

Figure 4.12 Pearson correlation coefficients with the variables

4.4. Contribution to Thesis Objectives

This research contributes to the thesis by exploring the application of femtosecond laser texturing to enhance the antifouling properties of aluminium alloy 7075. Using the optimized process parameters effects of five distinct surface textures—parallel lines, cross hatching, triangles, stars, and rhombus patterns—on wetting characteristics and biofouling and corrosion resistance were examined. The study aims to identify optimal textures that reduce algal attachment. Utilizing rapid biofouling assessment with diatoms (*Nitzschia ovalis*), the research provides valuable insights into the correlation between surface morphology and antifouling efficacy. This work addresses a significant gap in existing literature, offering a non-toxic, environmentally friendly solution for marine applications.

CHAPTER 5

5. HARDNESS AND WEAR PERFORMANCE OF SURFACES USING COMBINING LASER TEXTURING AND SURFACE HEAT TREATMENT

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CHAPTER 5

5. HARDNESS AND WEAR PERFORMANCE OF SURFACES USING COMBINING LASER TEXTURING AND SURFACE HEAT TREATMENT

5.1. Introduction

Laser texturing has been explored for antifouling applications on aluminum surfaces in the marine industry [326],[230]. This technique demonstrates substantial promise in the development of antifouling surface textures with the capacity to mitigate or preclude biofouling while enhancing corrosion resistance—a vital necessity in marine settings [70],[327]. Laser texturing has been explored as a technique to enhance the tribological performance of aluminum alloy surfaces [328]. Studies have shown that laser surface texturing can improve oil retention and reduce the chances of scuffing on sliding surfaces, leading to enhanced operational performance and efficiency [329]. Laser parameters have been found to significantly affect the size and depth of texture on aluminum alloy surfaces, with dimples acting as solid lubricant reservoirs under solid lubrication [330]. Laser-induced self-organizing periodic surface structures and deterministic surface textures have been tested for their tribological behaviour, with the highest static coefficient of friction observed for a laser-textured cross pattern, indicating the potential of laser texturing for real-world applications [331]. Laser-assisted micromachining technologies have also been used to create micro textures on titanium alloy surfaces, with wavy laser surface texturing showing greater impact on wear resistance capabilities [332].

Nevertheless, the rigorous conditions prevalent in extreme marine environments give rise to heightened mechanical wear and tear at multiple locations. Consequently, these surface textures may experience accelerated degradation due to unavoidable environmental stresses. Therefore, it is a necessity to create robust textures that are highly durable. The durability of surface patterns at the contact interface plays a significant role in determining the lifespan of functional properties [333], [334].

Increasing the life of the aluminium surface can be achieved through various methods. One study found that the fatigue life of an Al-Mg-Si alloy was improved by polishing the surface, which reduced the size of microporosity and resulted in smaller cracks initiating [335]. Deep Surface Rolling (DSR) technology can also increase the fatigue life of metallic materials, including high-strength aluminium alloy, by introducing deep compressive residual stresses in the material surface. In another study, the approach is to use additional heat treatment and deformation, as well

as two-stage final annealing, in high-purity aluminium [336]. In another study, MXene nanosheets are used in combination with laser textures which improve the wear resistance and durability of the components [337], [338]. However, the stability of MXene coatings is not as good as other physical methods [339].

Laser beam hardening has been recognized in prior research as a promising technique for enhancing hardness and prolonging wear resistance [340]–[342]. Yang et al. discussed the effects of laser heat treatment on the surface of aluminium alloy, which resulted in improved local hardness and optimized corrosion resistance. Laser treatment reduced the number and continuity of pitting pits on the surface of the alloy and decreased intergranular corrosion and maximum corrosion depth [343]. Tolcha et al. investigated laser surface alloying of pure aluminium, which resulted in increased hardness and improved wear resistance of the alloyed zones [344]. By combining laser texturing and laser hardening, it is possible to achieve both improved surface hardness and modified surface topography and chemistry [345]. This combination can be used to create surfaces with increased roughness and enhanced adhesion, as well as to improve lubrication and wear behaviour [346]. The process of laser hardening and laser texturing combining involves using laser texturing to modify the surface topography and then applying laser hardening to produce hardened surfaces with the desired properties [347]. Surface roughness attributes influence tribological properties such as wear resistance. In practice, the most used parameters for surface roughness description are Sa, Sq, Ssk and Sku. Average surface roughness (Sa) offers a comprehensive characterization of height deviations but lacks sensitivity to subtle profile changes and waviness. Root means square deviation (Sq) is more responsive to deviations from the baseline than Sa. Skewness (Ssk) quantifies asymmetry, with zero indicating symmetrical height distribution, positive values indicating high peaks or filled valleys, and negative values indicating deep scratches or loss of peaks. Conversely, kurtosis (Sku) reflects the sharpness of the profile's probability density [348],[349]. Superior wear resistance properties have been reported using a combination of two processes femtosecond laser-induced periodic surface structures and surface hardening by fs shock peening in a recent study by Pan et al [350],[351].

From the literature mentioned above, it was found that the investigations of these two techniques, femtosecond laser texturing and laser hardening, are reported independent of each other. The majority of researchers have concentrated on either one aspect or the other in order to enhance performance. The synergic effect of both techniques has not been explored yet on aluminum alloy. We hypothesize that, the continuous wave laser hardening process can be used to enhance the mechanical surface properties for ultrafast laser textured samples and specifically that samples processed via this multimodal approach would exhibit a better wear resistance. Therefore, we explore the effect of multimodal laser texturing in this study. Three laser textures were fabricated using femtosecond laser processing. Laser hardening was conducted on these samples with varying

laser process parameters. The hardness and wear resistance were explored on each sample produced with the different parametric settings.

5.2. Materials and methods

5.2.1. Material

The material used in this project were commercially available unalloyed aluminum 1050 and aluminum alloy 7075 T6 (thermally treated, stress-relieved by stretching, and artificially aged), in form of flat plates with 100×30 mm and 2 mm thick which are supplied by Impact Ireland Metals Ltd. The average roughness (Sa) of the bare plate was 400-500 nm before processing as measured by 3D optical profilometer. The surface of the samples was cleaned using isopropyl alcohol before laser processing. The chemical composition of the aluminium alloy 7075 as shown in Table 5.1.

Table 5.1 Chemical composition of aluminium alloy substrates 7075.

Material	Zn	Mg	Cu	Si	Mn	Fe	Ti	Al
Aluminum alloy 7075	5.8	2.8	1.5	0.1	0.17	0.22	0.03	Balance

5.2.2. Laser surface texturing

The ultrafast laser surface texturing was conducted on the aluminium alloy 7075 substrates using a laser system which was equipped with a high-energy industrial ultrafast laser source (NKT Photonics Origami XP). This laser provides a stable low noise pulsed beam with an average wavelength of 1030 nm and a pulse duration <370 fs. The laser beam surface scanning with different for different pattern designs illustrated in Figure 5.2 was conducted with a galvo scanner (Focushifter-15, Raylase GmbH) and the beam was focused on the sample using an f-theta lens. Gaussian type of beam was present at the focal position which had a full width of the beam at 1/e² measured to be 46.4 µm at a working distance of 220 mm from the lens of the galvo scanner. The laser texture pattern was applied across an irradiated area of 8 mm × 8 mm.

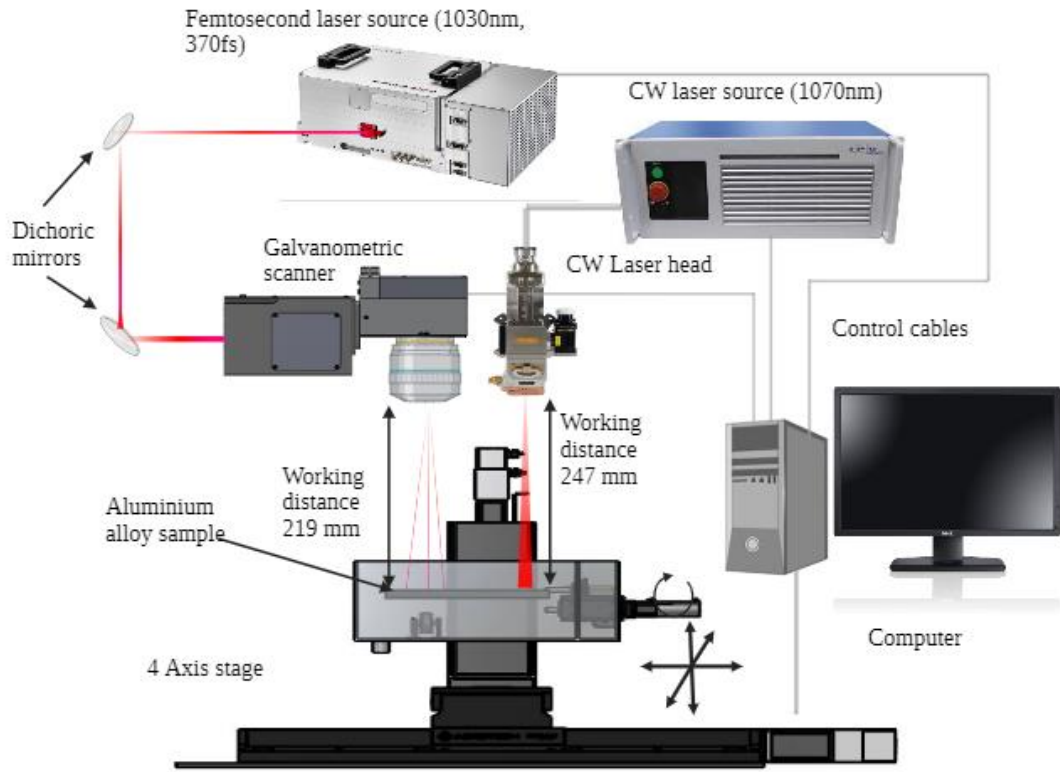


Figure 5.1 Multimodal laser surface texturing and hardening setup.

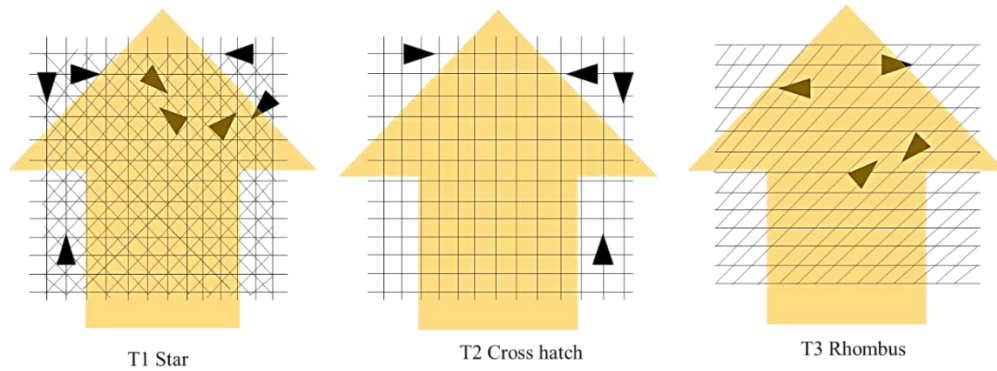


Figure 5.2 Schematic of the different scan patterns implemented for femtosecond laser texturing in black (laser spot size of $46.4 \mu\text{m}$) and the CW laser for hardening (laser spot size 6 mm by 6 mm) in yellow.

The laser processing was conducted in the atmospheric environment at 20°C and 60 relative humidity. In this experiment, the laser texturing process parameters were set as 3 W laser power, 100 kHz pulse repetition rate, and 4 mm/s scanning speed. The fluence of 1.77 J/cm^2 was kept constant in the experiments. The surface heat treatment of the laser textured samples was conducted, after laser texturing was performed, using a water-cooled continuous wave fibre laser source (IPG YLR 1000 WC). This laser provides a stable low noise beam with an average wavelength of 1070 nm. The rectangular beam of $6 \text{ mm} \times 6 \text{ mm}$ was used with beam mode quality

(M2 <1.1). The sample was mounted on the 4-axis translation stage (PRO 225 Aerotech Inc). The laser was focused on the top surface of the sample on which the laser textured samples were present. The stage was calibrated and was translated in the different set speeds as represented in the Figure 5.1 due to which the laser beam was scanned over the sample. The experimental setup involved varying the laser power and scanning speed to fabricate textured surfaces on aluminum substrates.

Table 5.2 The design of experiments laser process parameters and levels examined.

Parameter	Unit	Level 1	Level 2	Level 3
A Laser Power (P)	W	400	500	-
B Scan speed (h)	mm/s	1	2	3
C Texture		T1 (Star)	T2 (Square)	T3 (Rhombus)

Two laser powers, 400W and 500W, were utilized in conjunction with three scanning speeds of 1, 2, and 3 mm/s as discussed in Table 5.2. These parameters were selected based on preliminary pilot tests conducted on both plain and textured surfaces to ensure optimal process conditions. Initial pilot experiments revealed that below 400W of power, there was minimal lasting effect due to significant reflection of the incident laser beam by the aluminum surface. Consequently, the energy deposition was insufficient to induce noticeable surface modifications. Conversely, when the laser power exceeded 500W, distortion and crack formation were observed on the textured surfaces which compromised the integrity of the surface. Additionally, the range of scanning speeds encompassing 1 to 3 mm/s was selected to provide flexibility in controlling the traversal rate of the laser beam across the substrate surface. Table 5.3 shows full listing of the process parameters and associated levels investigated for each sample.

Table 5.3 Full listing of the laser hardening process parameters and associated levels investigated for each sample

Sample no	Laser Process parameter setting		
	Power (W)	Scan Speed (mm/s)	Texture
1	400	1	T1
2	400	1	T2
3	400	1	T3
4	400	2	T1
5	400	2	T2
6	400	2	T3

7	400	3	T1
8	400	3	T2
9	400	3	T3
10	500	1	T1
11	500	1	T2
12	500	1	T3
13	500	2	T1
14	500	2	T2
15	500	2	T3
16	500	3	T1
17	500	3	T2
18	500	3	T3

5.2.3. Surface Characterization and Wear Experiments

Morphology and surface chemistry

The laser-treated surfaces were evaluated using scanning electron microscopy which was performed using scanning electron microscopy (SEM) using an EVO LS15 instrument (Zeiss) equipped with a LaB6 filament, operating at an accelerating voltage of 10 kV and a beam current intensity of 25 pA. The evaluation was conducted in secondary electron diffraction mode. The images were taken at 100X and 1000X magnification for all the patterns. As the aluminum alloy samples are conductive no extra sample coating was required. The surface chemistry was analysed using the Oxford Instruments energy dispersive spectroscopy (EDS) system (Aztec).

Surface Roughness

The different surface roughness height attributes such as S_a (arithmetical mean height), S_q (root mean square surface roughness), S_{ku} (Kurtosis), S_{sk} (Skewness), were characterized using a Bruker Contour GT 3D Optical Profilometer as per ISO standard 25178-2:2021 [271]. The measurements were made using a 10X lens and focusing on the sample using white light interferometry. The analysis of the surface roughness parameters was performed using inbuilt software Bruker's Vision 64 ® image analysis on the raw data.

Microhardness

The micro indentation tests were conducted using the (Anton Paar, NHT3). In order to pursue a mechanical property evaluation at micrometre scale, instrumented micro indentation was performed on all the laser processed samples. The load control mode was used to perform the micro indentation-based analysis. Indentation was performed at maximum indentation load (P_{max}) of 1500 mN with loading-unloading time of 30 s each. Hold time of 10 seconds is used at P_{max} to

avoid the influence of creep on the hardness measurement. . Standard geometrically similar four-sided Vickers indenter with tip radius of ~ 200 nm was used for the experimentation. Prior to indentation, area function of the indenter was calibrated using standard fused silica sample. Five indentations were performed on each sample to obtain a statically significant data.

Wear Resistance

Friction and wear testing was performed under reciprocating sliding contact using ball-on-disc contact configuration and water drop lubrication. Tests were performed at room temperature ($22 \pm 2^\circ\text{C}$) and relative humidity of $50 \pm 5\%$. Before each test specimens were cleaned in ethanol and dried in air and a drop of distilled water (~ 0.02 ml) applied on the Al disc surface. Standard 100Cr6 bearing steel ball ($\phi 20$ mm, 58 HRC) was used as a stationary counter body, pressed against an oscillating Al flat sample. Oscillating frequency and amplitude were 15 Hz and 4 mm, respectively, resulting in the average sliding speed of 0.12 m/s. Normal load applied was 10 N, corresponding to the initial Hertz contact pressure of 400 MPa. Testing was performed for 600 seconds, which resulted in the total sliding distance of 72 m. During testing coefficient of friction was recorded continuously as a function of time. After the test average steady-state coefficient of friction was calculated and wear volume of the Al discs measured and analyzed using 3D focus-variation microscope Alicona InfiniteFocus G4.

5.3. Results and discussion

5.3.1. Surface micrograph and surface chemistry

Three different textures were created on aluminium samples using femtosecond laser system using 3 W laser power, 100 kHz pulse repetition rate, and 4 mm/s scanning speed with constant fluence of 1.77 J/cm^2 . The above textures were applied as these already have antifouling ability as per our previous study [352]. The above pictures show the microtextured surfaces before laser hardening and after laser hardening process. In Figure 5.3(a) and Fig 3(b) the observed morphologies displayed a star-shaped pattern (T1) characterized by numerous radial projections emanating from a central locus, exhibiting notable regularity in spacing. Microscopic examination at high magnification revealed intricate surface features along the projections, alongside a comparatively diminutive region lacking such textural complexity. Coarse textures with nanoscale features were observed on the micrometre scale surface textures due to the evaporation and recrystallization on the top of the surface. Subsequent to the laser surface hardening, the laser tracks resulting from the femtosecond laser processing have almost disappeared; however, the periodicity and geometric features have not changed. In Figure 5.3 (c) the cross-hatched pattern (T2), the generation of straight parallel and perpendicular incisions was observed. This scanning methodology led to a notable augmentation in surface area. Predominantly, nano and microscale structures were generated along the crown region of the surface, resulting in a heightened surface area. Figure 5.3

(d) shows the laser hardened cross hatch texture. The protrusion on the texture has reduced after the laser scan without disturbing the periodicity and geometric attributes. A boundary type feature was generated on the star and square textures after laser surface hardening of the femtosecond laser texturing, see Figure 5.3 (b) and (d). An oxide layer can be seen to have been produced on this of the texture. Figure 5.3 (e) exhibits a discernible rhombus-shaped pattern, characterized by the presence of interconnected geometric units forming a series of rhombus across the observed surface. These rhombuses had an angle of 45°. Figure 5.3 (f) shows the texture after the laser hardening. A coarse cauliflower-like surface texture boundary was formed adjacent to the texture which is similar to that reported previously in the literature after hardening is formed [353]. The surface chemistry characterization was conducted using energy-dispersive spectroscopy. The surface compositions of the laser textured and hardened samples, measured using the EDS, are presented in Table 5.4.

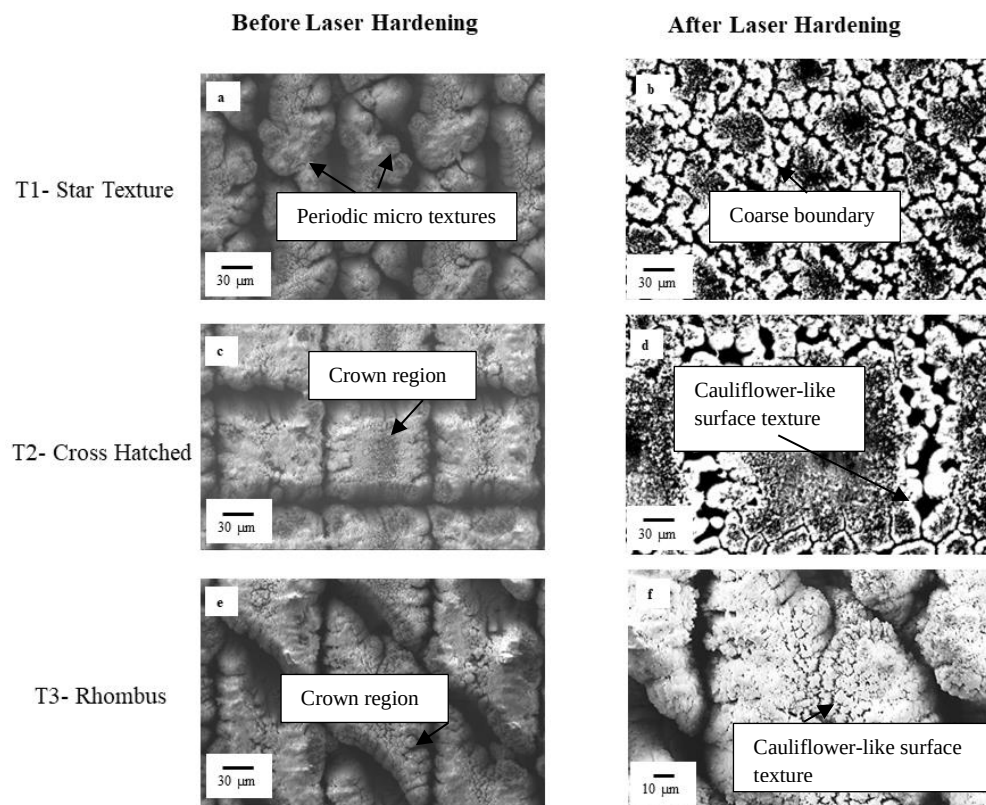


Figure 5.3 Different laser textures on the aluminum alloys before and after the laser hardening treatment.

Table 5.4 EDS results measured from the ultrafast laser textured and hardened aluminium surface.

	C %	O %	Al %	Fe %	Cu %	Mg%	Zn %
Sample 1 (T1)	4.48	42.93	52.2	0.39	0	0	0

Sample 2 (T2)	4.79	33.05	52.85	0.50	1.16	2.8	4.86
Sample 3 (T3)	4.25	35.49	50.94	0	0.95	2.82	0.24

5.3.2. Effect of multimodal laser texturing on surface roughness

Laser texturing and hardening produces textures which have different surface roughness values. The roughness depends on the scanning strategy, and the laser parameters of both texturing operation as well as laser parameters of laser hardening operation. Various roughness attributes stated in the previous research [348] by such as S_a (arithmetical mean height), S_q (root mean square surface roughness), S_{ku} (Kurtosis), S_{sk} (Skewness) are characterized. The Figure 5.4 show the surface roughness attributes for each laser textured and heat-treated sample.

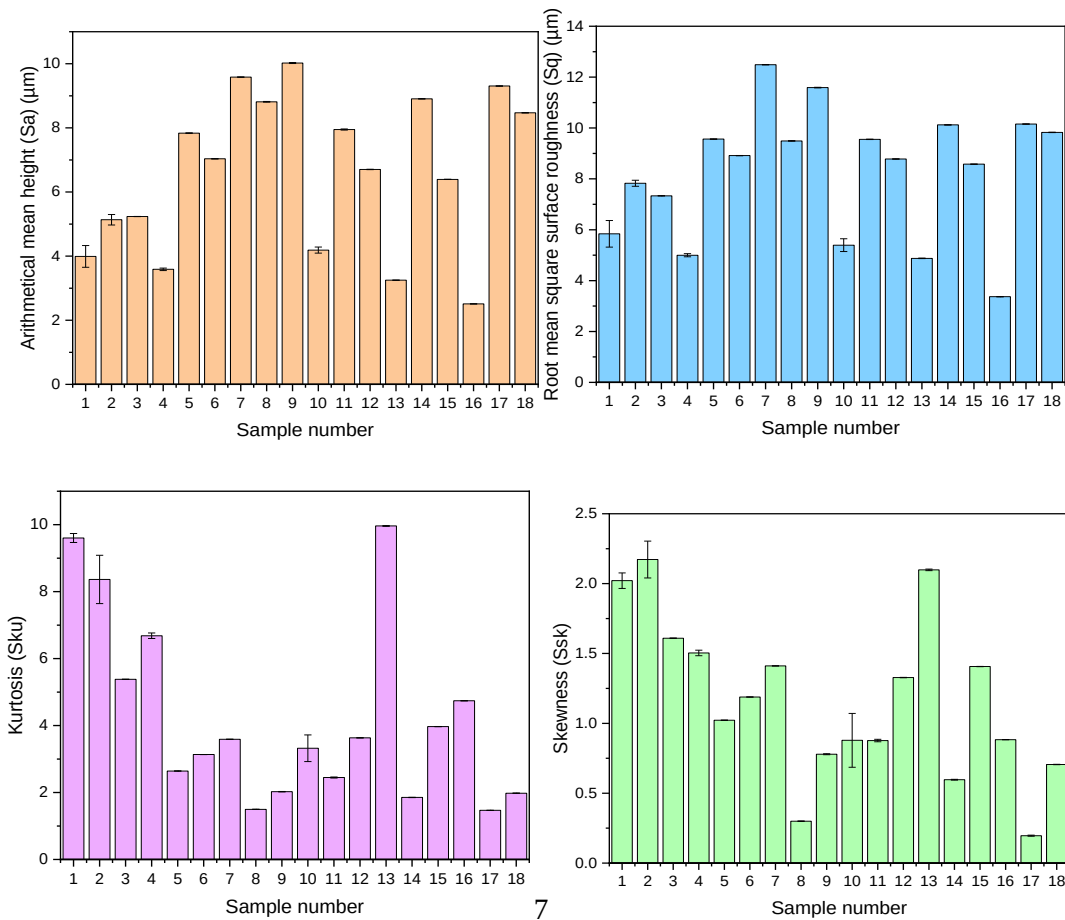


Figure 5.4 Distribution of surface roughness attributes S_a (arithmetical mean height), S_q (root mean square surface roughness), S_{ku} (Kurtosis), and S_{sk} (Skewness) of laser textured and heat-treated samples.

The pristine (non-textured) sample of Al 7075 had surface roughness values $S_a 0.43 \pm 0.0006 \mu\text{m}$, $S_q 0.52 \pm 0.001 \mu\text{m}$, $S_{ku} 2.59 \pm 0.03$, $S_{sk} 0.24 \pm 0.008$. Non-heat-treated femtosecond laser textured

sample of Al 7075 with star texture (T1) had surface roughness values S_a 7.99 ± 0.0006 μm , S_q 14.76 ± 0.02 , S_{ku} 14.22 ± 0.04 μm , S_{sk} 3.12 ± 0.014 . Sample with cross hatched texture (T2) had surface roughness values S_a 4.16 ± 0.02 μm , S_q 5.91 ± 0.03 μm , S_{ku} 29.16 ± 0.03 , S_{sk} 2.93 ± 0.018 . Sample with rhombus texture (T3) had surface roughness values S_a 6.39 ± 0.09 μm , S_q 11.52 ± 0.015 μm , S_{ku} 18.68 ± 0.015 , S_{sk} 3.72 ± 0.014 . Fig 5 displays the comprehensive results pertaining to the surface roughness attributes. Notably, sample 9 exhibits the highest values of S_a and S_q , while samples 7 and 16 demonstrate the lowest and highest values, respectively, within this context. Regarding skewness and kurtosis of surface roughness, sample 17 attains the lowest values, whereas sample 13 exhibits the highest values in this regard.

Three different laser scanning strategies namely star hatch pattern, cross-hatched pattern and rhombus pattern have been studied to understand their effects on surface morphology in laser surface texturing and hardening using an ultrafast laser system and heat treatment laser system. As the samples had constant parameters for texturing only the influence of the laser heat treatment was observed in this study. Clearly, it can be seen that the surface finish analysis of the textured and heat-treated reveals that alterations in laser parameters exert a substantial influence on the absorption of laser radiation, resulting in considerable variability in roughness values. Additionally, the phenomena of laser heat treatment and recrystallization of the textures are observed to occur. In some samples surface distortion at higher power and lower speeds. was also observed which resulted in high skewness and highly sharp textures with peaks and valleys. The influence of laser parameters such as laser power and scan speed and the influence of different textures (created by femtosecond laser texturing with constant parameters) is conducted using 3 level full factorial experimental design technique. Four mathematical models were developed for roughness attributes using response surface methods. The details of the ANOVA are provided in the supplementary information. Two numerical factors and one categoric factor were used in this study.

The regression equation derived for S_a , S_q , S_{ku} and S_{sk} is as follows

$$S_a = 6.6070 + 1.292055 B - 2.08809 C[1] + 1.3842 C[2] - 1.05094 AB - 1.0044 AC[1] + 0.9275 AC[2] \quad (1)$$

$$S_q = 8.2613 + 1.0155 B - 2.1009 C[1] + 1.190955 C[2] - 1.0790875 AB - 1.2041 AC[1] + 0.9019 AC[2] \quad (2)$$

$$S_{ku} = 4.2388 - 1.4545 B + 2.0779 C[1] - 1.1930 C[2] + 1.2518 AB \quad (3)$$

$$S_{sk} = 1.1654 - 0.3842 B + 0.3005 C[1] - 0.3047 C[2] - 0.2853 AB^2 \quad (4)$$

Where A is the laser power in (W), B is the scan speed in (mm/s), $C[1]$ is star texture (T1), $C[2]$ is cross hatched texture (T2), and $C[3]$ is rhombus texture (T3). The concordance between this model and the empirical data was assessed using both a normal plot of the residuals and a plot comparing predicted values to actual values (refer to supplementary information). The response surface 3D plots are plotted using the derived regression equations showing the effect of laser hardening parameters in Figure 5.5.

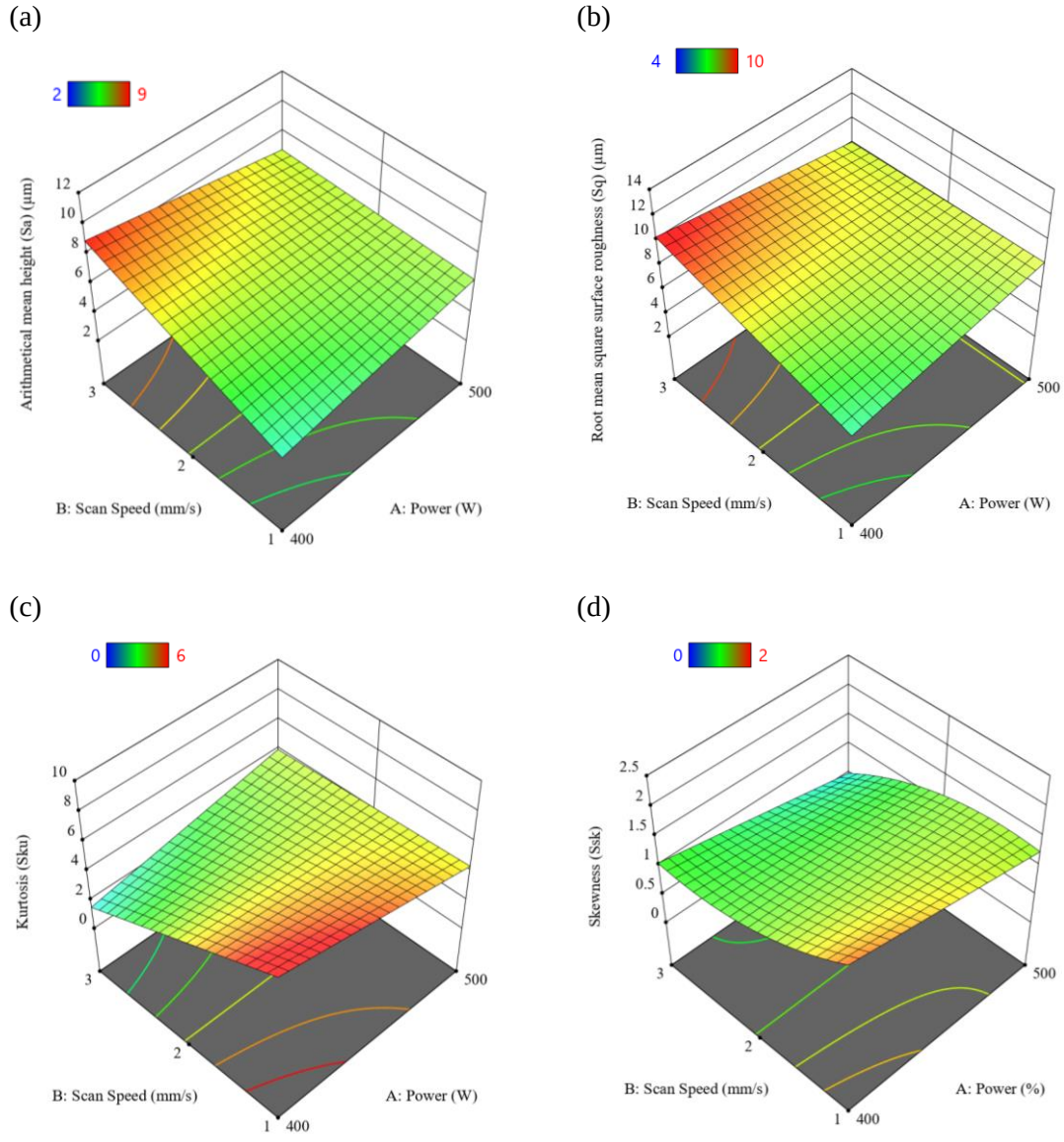


Figure 5.5 Effect of laser hardening parameters such as laser power (W) and scan speed (mm/s) on different surface roughness attributes such as (a) S_a (arithmetical mean height), (b) S_q (root mean square surface roughness), (c) S_{ku} (Kurtosis), and (d) S_{sk} (Skewness).

The surface roughness attributes such as S_a (arithmetical mean height), S_q (root mean square surface roughness), S_{ku} (Kurtosis), S_{sk} (Skewness) are significantly affected by the laser hardening process parameters. Laser scanning was identified as the most influential parameter on the average height

roughness (Sa) parameters, with a direct relationship. It can be seen that the increase in scan speed leads to an increase in average height roughness. The time of interaction of the laser beam and cooling rate during the hardening process influence the irregularities in the peak and valley of the surface texture. These findings align with previously documented results as reported in prior studies by Erinoshio et al on copper surface [354]. Evidently, a similar trend is seen in terms of root mean square surface roughness (Sq). However, the lower scan speed produces higher kurtosis surface roughness which shows the effect of degradation of the surface texture and surface deformation. The increase in laser power also results in deformation of the surface because of melting. The skewness is also higher at lower speed and lower power. However, the higher scan speed and laser power produces lower skewness. These findings are similar to study by Ürgün et al [355]. The agreement of this model with the experimental results was evaluated with normal plot of the residuals and a plot of the predicted vs actual values (see supplementary information). It can be seen from these graphs that deviations from the model are approximately normal and there are no significant outliers in either dataset.

5.3.3. Effect of multimodal laser texturing on micro hardness

To evaluate the mechanical response of laser processed and heat treated aluminium 7075 samples, indentation response of the material is evaluated using standard indentation load vs. indentation depth (P-h) curve. The indentation was done on the arbitrary locations on the sample. The hardness of all the samples is measured as per Oliver and Pharr method (OPM). are the characteristics terms associated with hardness measurement using OPM. By following OPM, first, H of both the systems are assessed using the following relation,

$$H = \frac{P_{\max}}{A_c} \quad (i)$$

In the above relation, A_c signifies the contact area of indentation. A_c is estimated using the relation $3\sqrt{3} h_c^2 \tan^2 \theta$, where h_c is the contact depth of indentation and θ is the angle of indentation. The hardness value of the pristine sample of Al 7075 without any texture was 1097 MPa.

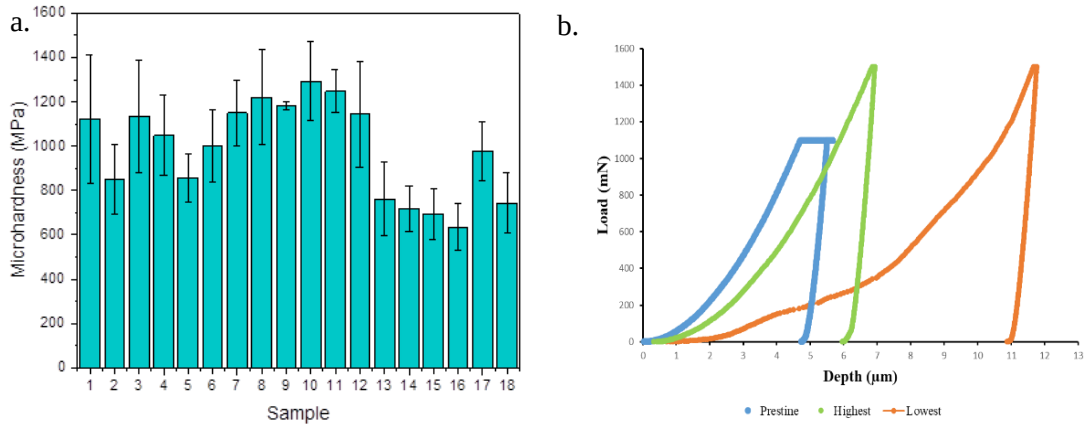


Figure 5.6 (a) Measured microhardness of each laser textured and hardened sample. Error bars shown are 95% CIs (n=5); and (b) load vs indentation depth plotting for the pristine (blue), hardest (green) and least hard (orange) specimens.

The results shown in Figure 5.6 indicate that eight samples underwent a process of hardening, whereas the remaining ten samples exhibited softening, which could be attributed to the effect of melting induced by elevated heat input and laser material interaction [356]. Notably, the sample denoted as sample 10, fabricated utilizing laser power of 500W with a scan speed of 2 mm/s and featuring a texture (T1) characterized by a star pattern, exhibited the highest hardness. This sample manifested no distortion and achieved a hardness value of 1291.90 ± 178.19 . The microhardness was increased by 17.8% compared to the pristine specimen. However, the sample identified as sample 16, produced with laser power of 400W and a scan speed of 1 mm/s with star pattern texture (T1), showed the lowest hardness due to heightened interaction resulting from the lower speed, consequently leading to softening.

A cubic model was developed to find out the relationship between laser hardening processing parameters and the resulting hardness. The details of the ANOVA are provided in the supplementary information. The regression equation developed is as follows.

$$\text{Micro hardness} = 847.0696 - 122.035 A - 73.9885 B + 13.8296 C[1] - 9.2975 C[2] - 147.6695 AB - 29.9283 AC[1] + 77.2385 AC[2] - 83.6814 BC[1] + 98.3738 BC[2] + 211.1657 B^2 + 70.2447 AB^2 \quad (5)$$

Where A is the laser power in (W), B is the scan speed in (mm/s), $C[1]$ is star texture (T1), $C[2]$ is cross hatched texture (T2), and $C[3]$ is rhombus texture (T3).

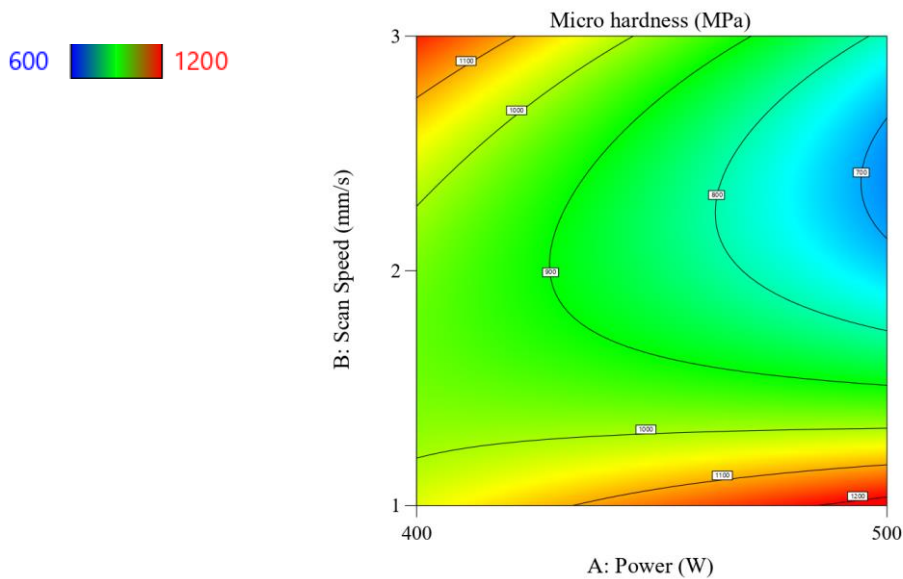


Figure 5.7 Contour plot showing the distribution of microhardness with respect to laser hardening process parameters Power and scan speed.

The contour plot in Figure 5.7, was plotted using the above regression equation and shows the distribution of microhardness with respect to laser scan speed (mm/s) and laser power (%) set. It can be seen that higher hardness can be achieved at low speed and high power; however, distortion can occur on surface in this condition. On other hand, at lower power and higher speed the higher hardness can be achieved. This finding is in consistency with previous findings by Barka et al [357]. The agreement of this model with the experimental results was evaluated with the aid of a normal plot of the residuals and a plot of the predicted vs actual values (see supplementary information). It can be seen from these predicated versus actual plots in the supplementary information that the developed model was able to predict the output response effectively and was statistically significant.

5.3.4. Effect of multimodal laser texturing on tribological properties

Analysis of the coefficient of friction

The reciprocating sliding wear test was conducted on all the non-heat treated and heat-treated samples. Non heat-treated Al 7075 (T1) shows initial friction of about 0.9. After running-in period of 150 – 200 seconds, coefficient of friction reaches steady-state value of about 1.8 although still showing slight upward trend as shown in Figure 5.8 (a). The corresponding wear scar is also shown which shows the worn texture having adhesive marks. When the textured surface was treated with laser heat treatment using CW laser both hardening and softening was achieved. The amount of hardening and softening of surface depends on the laser process parameters. On sample 16 as depicted in Figure 5.8 (b) with process parameters (laser power 400 W, scan speed of 1 mm/s and star texture (T1)) the steady state friction of about 1.5 was reached at the very beginning of the test

without pronounced running-in period. In this case coefficient of friction showed a very slight rise during the wear test. The corresponding image shows the wear scar with almost all texture removed along with adhesive and abrasive wear marks. The overall friction coefficient was reduced by 16% however the textures on specimen are destroyed at the wear tracks. This could be the effect of wear and surface smoothing. When laser surface textured surface is hardened using the process parameters of laser power 50%, scan speed of 2 mm/s and star texture (T1) is presented as this sample is the hardest sample as per previous section. In this sample, initial friction is 0.09. After running-in period of about 300 seconds, the steady state was reached with friction of about 0.3. The overall friction coefficient was reduced by 83% compared to the non-heat-treated sample. The results of the friction coefficient of this specimen are as shown in Fig 8 (c). Highly effective reduction is obtained in this specimen than all other specimens.

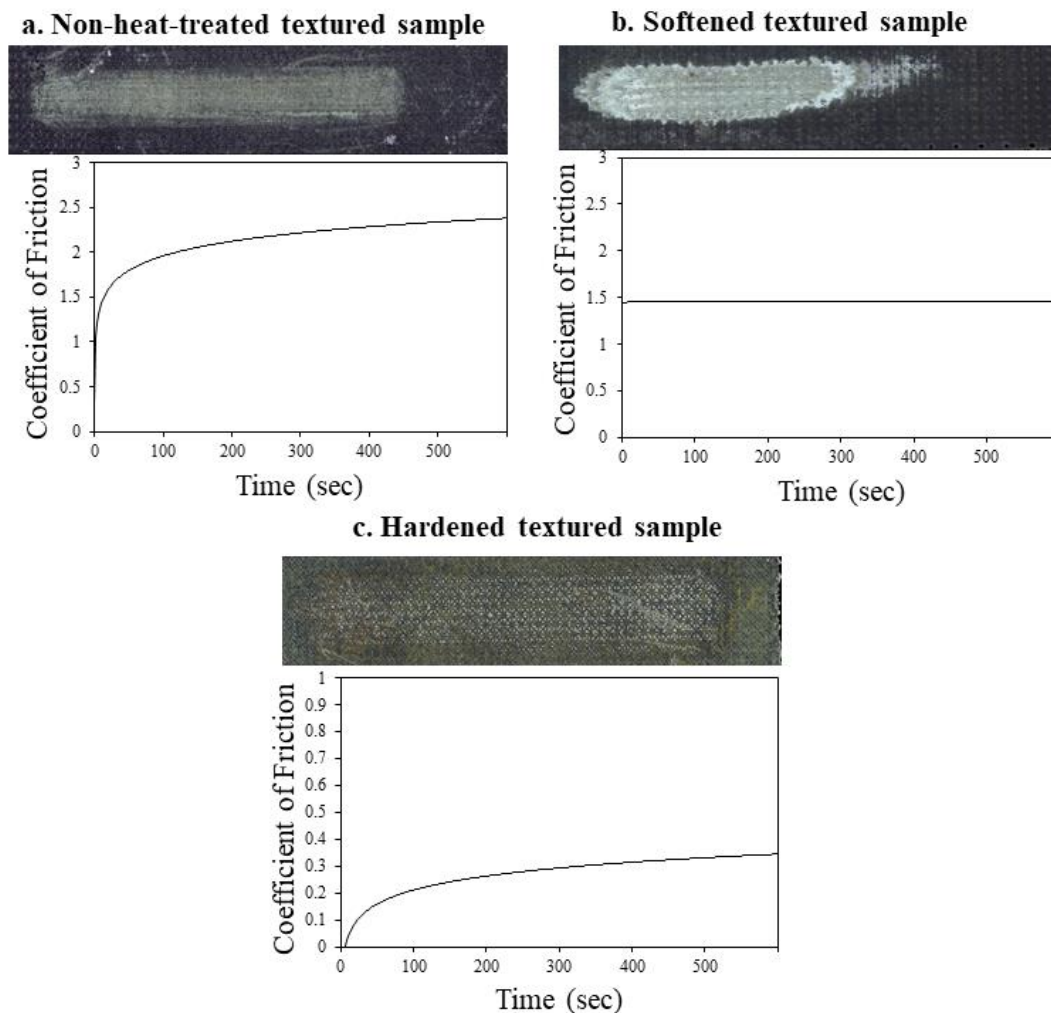


Figure 5.8 (a) Wear scars with and corresponding coefficient of friction (COF) trend plotted in log scale versus time curve for non-heat-treated textured surface, (b) wear scars and with corresponding coefficient of friction (COF) versus time curve for heat treated textured surface with laser power 400W, scan speed of 1 mm/s, texture T1, and (c) wear scars and with

corresponding coefficient of friction (COF) versus time curve for heat treated textured surface with laser power 500W, scan speed of 1 mm/s, texture T1.

Based on the observed outcomes of friction and wear track analysis as illustrated in Figure 5.8 across various sliding stages, it is deduced that the reduction in friction behaviour of Al 7075 alloys after ultrafast laser treatment can be attributed to the combined impacts of laser texturing and the formation of a laser-induced hardened layer. During the initial sliding stages, the presence of surface textures leads to a reduction in the effective contact area between the matrix and friction couples, thereby mitigating stiction [358]. The ploughing effects triggered by this debris caused during sliding could lead to more significant damage to the substrate. However, surface textures could mitigate this adverse influence through their ability to trap this debris [359]. From the results presented in Fig 9, it can also exert a critical effect on the friction performance improvement. To observe the effect of the laser process parameters all the results of the samples were analysed, and their average coefficient of frictions were calculated. These values were put into the experimental design to generate a model to find out the relationship between the average coefficient of friction with the hardening laser process parameters. The regression equation of the model is as follows.

$$\text{Coefficient of friction} = 0.56287 - 0.3647 A - 0.36065B + 0.4029AB \quad (6)$$

Where A is the laser power in (%), B is the scan speed in (mm/s).

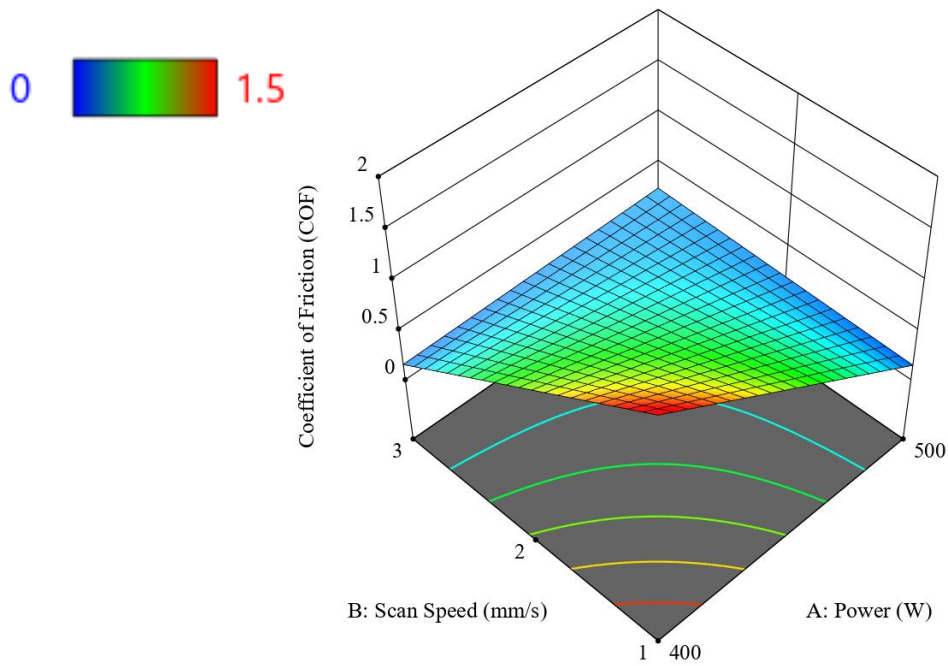


Figure 5.9 Response graphs showing the effect of the input processing parameters of laser hardening parameters such as laser power (W) and scan speed (mm/s) on average friction coefficient for all Al 7075 samples.

From the response 3D surface plot in Figure 5.9, it is clear that coefficient of friction of 7075 Al alloy is significantly affected by the laser hardening process parameters. As it can be observed that, the coefficient of friction is higher at low power and low scan speed (400 W power, 1mm/s scan speed). Whereas at higher power higher speed (500W power, 3mm/s scan speed) the coefficient of friction is reduced. In accordance with the findings delineated in the preceding section, optimal hardness is attained through the employment of specific laser processing parameters, namely 500 W laser power coupled with a scan speed of 2 mm/s. This configuration corresponds to a notably diminished average coefficient of friction, quantified at 0.22. Remarkably, this represents a substantial reduction of 76% in the coefficient of friction compared to the singularly textured sample. The higher the coefficient of friction the lower is the wear resistance expected [360].

Wear Volume

The wear volume of the Al 7075 plates was measured and analyzed using a 3D focus-variation microscope. The main wear mechanism for all specimens, untreated and laser textured and hardened, was sliding wear, combining adhesive and abrasive wear, and surface smoothening. The wear volume for untreated Al7075 alloy was $2.37 \times 10^6 \text{ mm}^3$. The volume measured on each sample is illustrated in Figure 5.10.

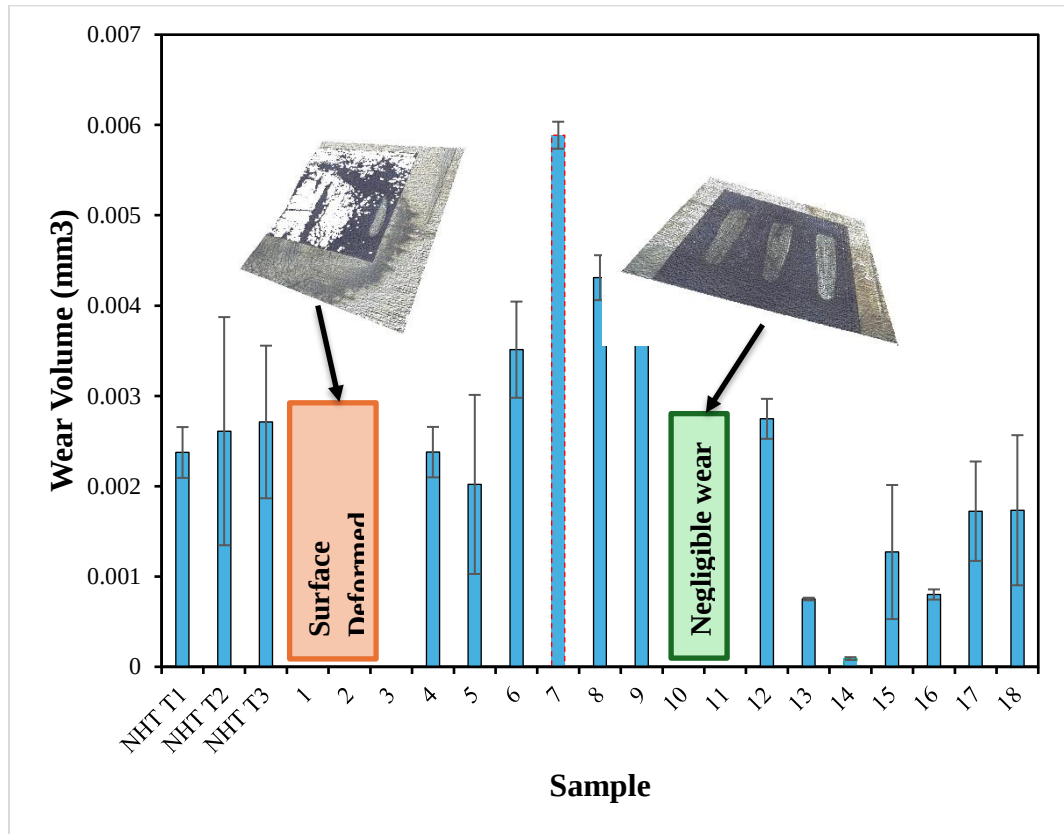


Figure 5.10 Measured wear volumes of each laser textured and hardened sample. Error bars shown are 95% CIs (n=3). In picture surface topographies for deformed surface and negligible wear conditions.

The Figure 5.10 shows the wear volumes. The non-heat-treated laser textured samples with textures T1,T2, and T3 had wear volumes of 0.0023 mm³ ,0.0026 mm³ and 0.0027 mm³. In some cases, it was impossible to get representative wear volumes, but this was mainly due to specimen deformation. The abrasive nature of the wear process altered the shape or structure of the specimens, making it harder to measure wear volumes accurately and reliably. In samples 1, 2, and 3 which were manufactured with laser power 400 W and scan speeds of 1, 2, and 3 mm/s. On samples 10 and 11 on the other hand there was negligible wear therefore the laser textures were unaffected by sliding wear. There was no wear removal in 600 cycles. Assuming the wear volume as a maximum of 0.007mm³ for deformed conditions and negligible wear condition as 0. These values were put into the experimental design to generate a model to find out the relationship between the wear volumes with the hardening laser process parameters. The regression equation of the model is as follows.

$$\text{Wear Volume} = 0.00167 - 0.0009 A + 0.00066 AB + 0.00187 B^2 - 0.0014 AB^2 \quad (7)$$

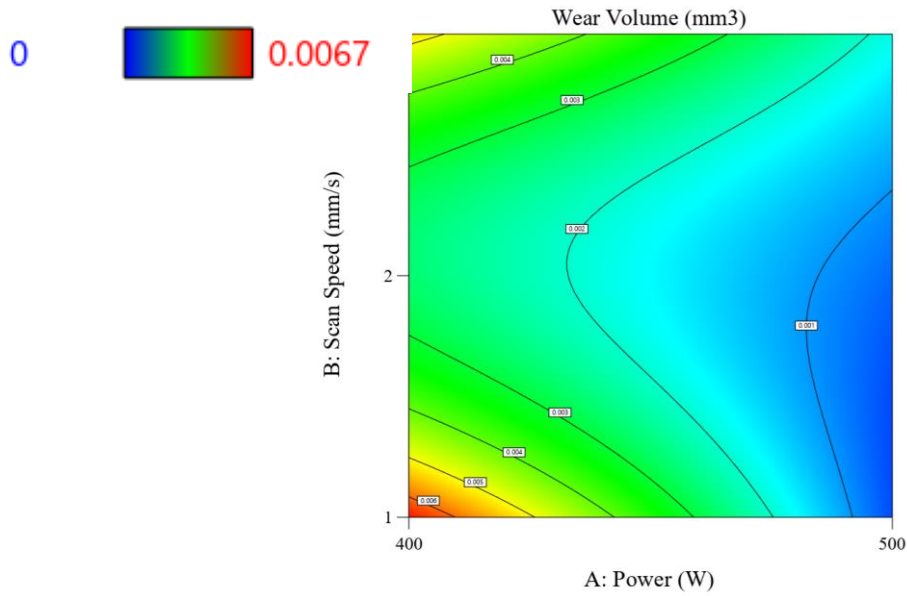


Figure 5.11 Response contour plots showing the effect of the input processing parameters of laser hardening parameters such as laser power (W) and scan speed (mm/s) on average friction coefficient for all Al 7075 samples.

From the response plot in Figure 5.11, it can be seen that the lowest wear volume is present in the blue region which is 500 W and lies between 1-2 mm/s scan speed. This blue region indicates the laser process parameters with the most wear-resistant characteristics.

The specific laser processing parameters used for surface texturing and hardening, such as laser power and scan speed, are optimized to achieve the desired surface characteristics that minimize wear. In this case, the parameters used for sample 10 are ideal leading to a notable reduction in wear volume compared to the untreated specimens. Hence, the anticipated enhancement in mechanical performance can be attained through a judicious selection of processing parameters.

5.3.5. Correlation between roughness, hardness, coefficient of friction, and wear volume

To explore potential relationships between input process parameters and their corresponding responses, we employed Pearson correlation coefficients. By using these coefficients, we aimed to understand the strength and direction of correlations among multiple variables such as surface roughnesses S_a , S_q , S_{ku} , S_{sk} , microhardness, coefficient of friction, and wear volumes. This information was visualized through a heat map displayed in Figure 5.12, which illustrates the correlations between the input process parameters and the response variables. Further analysis of these correlations, along with scatter plots, can be found in the supplementary document.

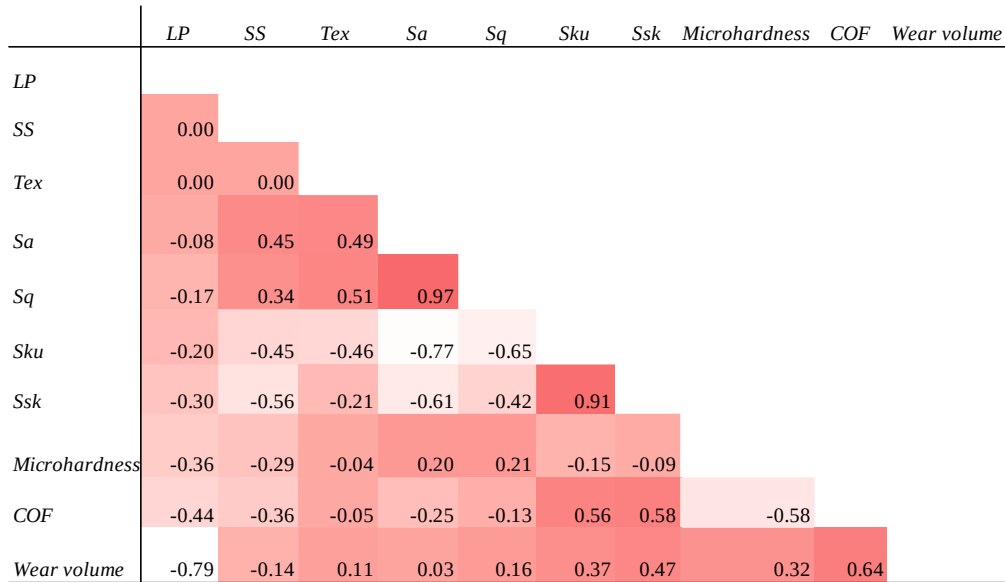


Figure 5.12 Heat map showing the correlation between input (Laser Power, scan speed, texture) and output (Sa, Sq, Sku, Ssk, Microhardness, COF and Wear volume).

This heat map (Figure 5.12) is an indicator of which laser parameters can be used especially to increase the hardness and reduce the coefficient of friction and wear volume. With this, the relationship between the laser process parameters and their hardness and wear resistance is established. The scatter plots of correlation coefficient for input and output are provided in the supplementary document.

5.3.6. Contact Angle Validation

Contact Angle validation experiments were conducted to test if the hydrophobicity is maintained after laser heat treatment. The Figure 5.13 shows the contact angle before and after laser heat treatment on sample 1 and sample 10. In sample 1 the water contact angle reduces by 18° from 148° to 130°. This could be due to effect of distortion of the sample. However, on sample 10 with optimum parametric setting the water contact angle only reduced only by 4° that is from 157° to 153°.

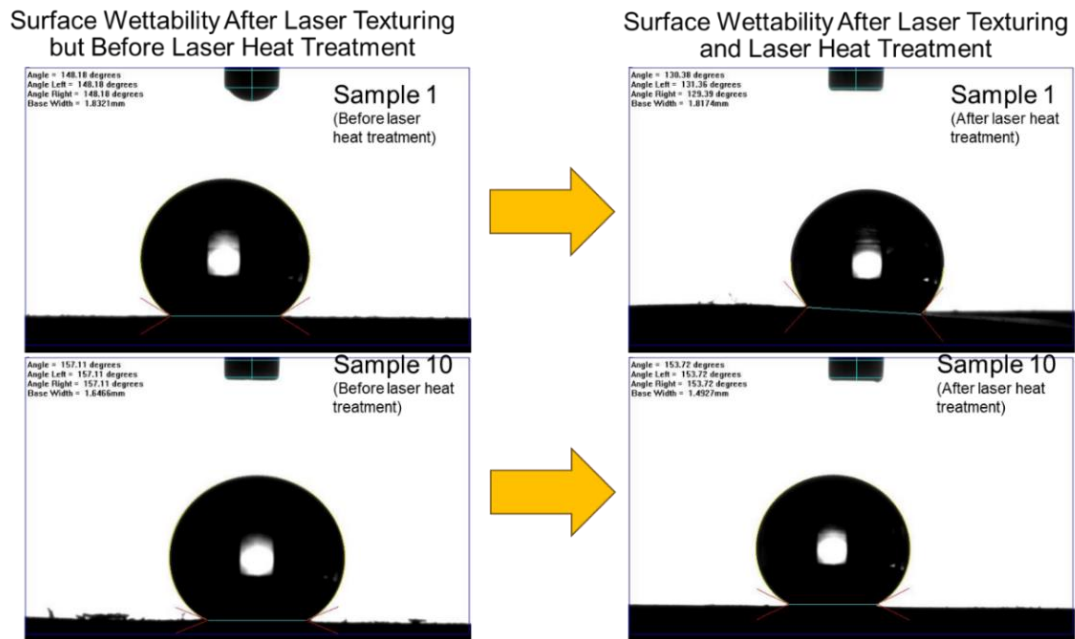


Figure 5.13 Contact angle validation of hydrophobicity

5.4. Contribution to the thesis

This research introduces a novel approach by integrating femtosecond laser texturing with continuous wave laser hardening to enhance the wear resistance and mechanical properties of aluminum alloy 7075 surfaces. By investigating three distinct femtosecond laser textures that were highly hydrophobic, antifouling and corrosion resistant, followed by laser hardening with varying process parameters, the study provides a comprehensive analysis of how this multimodal laser processing technique affects surface hardness and wear resistance. This synergistic method not only optimizes surface topography and chemistry but also significantly improves durability under extreme conditions. The findings offer a novel solution for creating robust, antifouling, and wear-resistant aluminium surfaces, addressing critical gaps in current marine engineering practices.

CHAPTER 6

6. CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

This thesis reported an investigation on the understanding of the interactions between femtosecond laser and the continuous wave laser beams on aluminium alloy surfaces by doing laser surface micro/nano texturing of this material, and their applications for improved hydrophobic, corrosion resistance, biofouling resistance, mechanical and tribological properties. Therefore, the interactions between the laser beam and the material's surface, along with the resulting morphological characteristics, chemical alterations, and functional changes, played a critical role in understanding the behaviour of surface-engineered materials across various application environments especially focusing on marine, aerospace and automotive industries.

The aim of this thesis stated in Chapter 1 was to develop a methodology for fabricating high-quality, repeatable nano and microstructures that enhance antifouling, corrosion-resistance, and wear-resistance characteristics on aluminum alloy. This thesis successfully demonstrated a proof of concept by achieving four key objectives. First, a laser-based approach was developed, incorporating optimized process parameters and pattern designs to fabricate micron-sized structures on aluminum alloy surfaces with precision, efficiency, and repeatability. Second, comprehensive characterization of the laser-processed substrate was conducted, focusing on both surface morphology and surface chemistry, which provided valuable insights into the mechanisms governing surface modification. Third, the study explored various functionalization methods for the laser-textured aluminum alloy surfaces to further enhance their performance and utility in real-world applications. Lastly, the applicability of the fabricated nano- and micro-structured surfaces was demonstrated through proof-of-concept assessments, including evaluations of antifouling properties, corrosion resistance, and wear performance, confirming the potential of these surface modifications in diverse engineering applications.

A comprehensive review is conducted in Chapter 2 on the current techniques of surface modification and characterization techniques to create hydrophobic, antifouling, corrosion and wear resistant surfaces. This study critically identifies several knowledge gaps in the current understanding of how different scan patterns and process parameters influence these properties explained in the field of laser-based surface modification of aluminum alloy 7075, especially ultrafast laser texturing with continuous wave (CW) laser hardening. Prior research had largely focused on these techniques in isolation, but their synergistic effects on surface properties, such as

hydrophobicity, biofouling resistance, corrosion protection, and wear performance, had not been thoroughly investigated.

Hydrophobicity plays a pivotal role in mitigating surface fouling, corrosion, and icing in critical marine and aerospace environments. This work investigates the potential of an advanced ultrafast laser texturing manufacturing process to enhance the hydrophobicity of aluminium alloy 7075 and fills the knowledge gap of Milles *et al* [247] through a full factorial design using the response surface method, the effects of changes in roughness attributes and wettability were studied and statistically significant mathematical models were developed to describe the relationships between laser process parameters and surface properties which fills up the research gaps found in Basset *et al* [261], Florian *et al* [263] and Yilbas *et al* [268].

Therefore Chapter 3 presents an experimental study on creating surface textures on an aluminum alloy (7075) using an advanced femtosecond laser texturing process, employing a design of experiments approach. The study measured surface height roughness (Sz), spatial roughness (Sa) profile parameters, surface profile aspect ratio (Str), and contact angle as output responses. Key factors such as laser power, hatch distance, and scan speed of the femtosecond laser system are investigated. The paper identifies the process parameters that lead to the most hydrophobic surface through response surface optimization. The impact of various femtosecond laser process parameters on surface roughness, chemical composition, and wettability is not well understood. The findings highlight the critical role of laser power, hatch distance, and scan speed in achieving optimal hydrophobicity.

The maximum water contact angle achieved was 142°, with an average height roughness (Sa) of $0.87 \pm 0.075 \mu\text{m}$, maximum height roughness (Sz) of $19.4 \pm 2.12 \mu\text{m}$, and texture aspect ratio of 0.042. This sample was manufactured with the process parameters of 3W laser power, 0.1 mm hatch distance, and a 4 mm/s scan speed.

The most influential process parameters for controlling surface roughness and wettability were identified and a combination of laser power, hatch distance, and scanning speed produced extremely hydrophobic surfaces with a maximum achieved water contact angle of 142° after 60 days. These results are in agreement with the previous results in which time dependence and the effect of ageing are shown [43, 44, 45].

Additionally, we conducted a qualitative analysis of the micron-level surface structures using scanning electron microscopy, finding highly defined surface structures with recast layers adjacent to the laser-textured area. The surface chemical analysis on this surface revealed the formation of a substitution of carbides with oxides and ZnO which leads to increased hydrophobicity due to changes in surface chemistry.

This work fills a critical gap by systematically investigating how laser process parameters influence surface properties such as roughness and wettability, aligning with the thesis focus on surface structuring and functionalization.

This represents a noteworthy advancement, as it not only establishes a correlation between process parameters and surface properties but also elucidates the significance of these parameters in determining the effectiveness of the manufactured surfaces in resisting water contact.

Despite extensive research into laser processing parameters, surface chemistry, and hydrophilicity, there remains a significant gap in understanding the influence of different laser-fabricated texture patterns on antifouling capabilities. Specifically, the potential of femtosecond laser-induced surface modifications to create tailored textures for antifouling applications has been underexplored.

The study in Chapter 4 addresses these gaps by investigating the application of femtosecond laser processing to modify the surface properties of aluminum alloy 7075, aiming to develop superhydrophobic surfaces with antifouling capabilities. In contrast to prior studies focused on individual process parameters or surface chemistry, this research takes a novel approach by exploring five distinct texture geometries. This chapter focused on the ultrafast laser texturing of aluminum 7075 which is used in structural and moving components in marine applications which are subjected to corrosion and biofouling. Five surface texture patterns of parallel, cross-hatched, triangle, star, and rhombus were produced on the aluminum alloy 7075 samples using the optimal laser process parametric setting in Chapter 3.

The findings of this study suggests that designed changes in surface morphology and surface roughness were produced and characterized on aluminum alloy specimens. Femtosecond laser texturing also led to a change in wettability, rendering the samples hydrophilic.

The variations in contact angle over time, up to 120 days, were recorded, with the triangle and star patterns gradually transforming to highly hydrophobic states, reaching contact angles of 150° and 157°, respectively. This is due to low adhesion on these surfaces similar to Cardoso *et al.*, [246].

Biofouling assessment using *N. ovalis* marine algae demonstrated a significant reduction in biofilm coverage, from 21% on pristine samples to 4.63% on the star texture (S4), marking a substantial 79% reduction in biofilm formation. This fills up the knowledge gap of attaining anti-biofouling surfaces and is in agreement with results by Nanduru *et al* [361]. the reduced biofilm formation on the star pattern (S4) can be attributed to its low surface energy and fewer attachment points for *N. ovalis* diatoms, as indicated by the higher Sp values for this surface. This observation aligns with the findings of Rajab *et al.*, [320] who reported similar behavior for *Escherichia coli* colonies on

TiO₂ surfaces. The experimental data has repeatedly shown that the laser textured surfaces are having an antifouling effect.

Corrosion studies revealed that the aged star pattern texture (S4) exhibited a reduced propensity for corrosion compared to non-aged and pristine counterparts, indicating a notable 25% improvement in corrosion performance relative to pristine samples.

The surface chemistry characterization using XPS analysis showed an increase in the formation of zinc oxide on the surface of the aluminum alloy 7075 samples, as illustrated in Figure 4.9, Figure 4.10, Figure 4.11, which significantly enhanced fouling and corrosion resistance.

However, while the exploration of texture geometries offers valuable insights, the study raises further questions regarding the long-term durability of these laser-fabricated textures in real-world marine environments. Ultrafast laser texturing allows for the precise fabrication of micro- and nanostructures on aluminium surface, which in turn affects critical properties like hydrophobicity, corrosion and antifouling performance. Laser hardening strengthens the mechanical characteristics of surfaces, greatly enhancing their resistance to wear and deformation studied by Babu *et al.* [362], Klocke *et al.* [341] and Buling *et al.* [342] .

As noted in the earlier literature, femtosecond laser texturing and laser hardening have typically been studied separately [326],[230]. Most researchers have focused on one technique or the other to improve performance, with little attention given to the combined effect of both. The synergistic potential of these two methods has not been thoroughly investigated or reported other than the research by Pan *et al.* [350] in which the superior wear resistance is achieved using femtosecond laser and hardening layer on cast aluminium.

The chapter 5 focuses on the effect of multimodal laser texturing and hardening and its effects on the tribological and mechanical properties of the aluminium alloy 7075 surface. After the femtosecond laser texturing operation, laser-based surface hardening was then performed on these textures using a continuous wave laser. The laser heat treatment was conducted using laser powers of 400 and 500 W with three different scan speeds of 1, 2, 3 mm/s.

The experimental findings show that the microhardness evaluation demonstrated a combination of hardening and softening effects on the laser-textured and hardened specimens. Specifically, the microhardness of the hardest sample exhibited a notable increase of 17.8% in comparison to the pristine sample. A regression model was developed using the response surface method which established a relationship between the hardness and process parameters such as laser power and scan speed. Laser power is the most influential factor affecting microhardness.

The predominant wear mechanism observed across all specimens, including both untreated and laser surface textured and hardened specimens, entailed sliding wear, characterized by a synergistic interplay of adhesive and abrasive wear mechanisms, alongside surface smoothing effects. The wear performance was evaluated by analyzing the wear volume and average coefficient of friction. . This configuration corresponds to a notably diminished average coefficient of friction, quantified at 0.22. Remarkably, this represents a substantial reduction of 76% in the coefficient of friction compared to the singularly textured sample. This work is consistent with the previous work by Yu *et al* [360].

Notably, the overall average friction coefficient on the laser-textured and heat-treated sample was reduced by 83% compared to the non-heat-treated sample. The wear volumes were characterized in which the most hardened sample had an 80% reduction in wear compared to the non-hardened textured samples.

The regression models were developed using the response surface method which established the relationship between the average coefficient of friction, wear volume, and the laser process parameters, thus allowing tuning of the wear characteristics and enhancing the tribological performance. The multimodal laser texturing-hardening processing strategy offers a simultaneous fabrication of surface textures using an ultrafast laser system and a hardened layer using CW laser on aluminum alloy 7075 surfaces. This approach increases wear performance through the synergistic effects from both the surface texturing and induced hardening. the laser texturing and hardening method generated a unique multi-scale surface texture, enhancing mechanical properties and wear resistance. These findings provide a valuable reference for future research and practical applications, bridging the gap in the existing literature and advancing the field of laser-material processing.

This research bridges a significant gap in understanding how multimodal laser processing can enhance the functional performance of aluminum alloy 7075. However, while the findings represent a step forward, they also reveal the limitations of current laser processing techniques. The optimization of surface texturing and hardening requires further investigation to address inconsistencies in hydrophobicity, biofouling, and mechanical properties. Additionally, more comprehensive studies are needed to assess the long-term durability and performance of these surfaces under real-world conditions, especially in industries like marine, aerospace, and automotive, where surfaces are exposed to complex and harsh environments. The study lays a foundation for future work but also underscores the need for continued refinement and innovation in laser-material processing.

6.2. Recommendations for further research

The current research has provided significant insights into the effects of laser texturing on aluminum alloy 7075 surfaces, particularly in terms of hydrophobicity, biofouling resistance, corrosion protection, and wear performance. However, the findings of this study also reveal several areas where further research is needed to build on the progress made and address remaining challenges. Future work in the field of laser texturing and surface treatment can focus on various avenues to extend the understanding of laser-induced surface modifications, enhance process control, and improve the long-term performance of textured surfaces. By exploring the following recommended areas, researchers can deepen the knowledge base and expand the application of laser texturing technologies across multiple industries.

Validation of Process Models and Experimental Equation

One of the key outcomes of this research is the development of a preliminary mathematical model that predicts the relationship between laser process parameters and the resulting surface properties, such as roughness and wettability. While this model serves as an important starting point for understanding the laser-texturing process, it requires validation to ensure its robustness and applicability to real-world applications. Future work should focus on validating the model using both analytical methods and experimental testing. Validation experiments can be conducted across a wider range of laser parameters and different material types to assess the model's accuracy and generalizability. In addition, analytical approaches, such as finite element modeling (FEM) could be employed to simulate the laser-material interaction and predict surface changes under different conditions. By comparing the model predictions with experimental results, researchers can refine the equation and improve its reliability. Such validation would enhance the model's precision, making it a valuable tool for optimizing laser-texturing processes in diverse applications.

Investigating the Longevity of Surface Effects

A critical aspect of laser-textured surfaces is the durability and long-term stability of the enhanced surface properties, particularly hydrophobicity and superhydrophobicity. In this study, the hydrophobic surfaces produced by femtosecond laser texturing demonstrated a significant increase in water contact angle over time, with some surfaces reaching superhydrophobic states. However, the persistence of these effects under real-world environmental conditions is not fully understood. Future research should focus on conducting long-term stability tests to evaluate how surface properties evolve over extended periods. Such studies could simulate harsh environmental conditions, including variations in humidity, temperature, and UV exposure, which are often encountered in marine, aerospace, and automotive applications. By understanding how these factors influence surface degradation, researchers can assess the lifespan of laser-textured surfaces and develop strategies to maintain their functional properties over time. This would be particularly

valuable for industries that require surfaces to retain their hydrophobicity and antifouling capabilities over extended operational periods.

Mechanical Properties of Oxide Layer and Durability Assessment

In addition to evaluating the long-term stability of surface effects, future studies should investigate the mechanical properties of the oxide layer that forms on laser-treated aluminum alloy surfaces. In this research, zinc oxide (ZnO) was identified as a key factor contributing to enhanced hydrophobicity and corrosion resistance. However, the mechanical characteristics of the ZnO layer, such as hardness, adhesion, and wear resistance, were not fully explored. Mechanical testing of the oxide layer would provide valuable insights into the durability of laser-textured surfaces, especially in applications requiring high resistance to mechanical stresses. By performing hardness and wear resistance tests, researchers can assess how well the oxide layer withstands repeated loading and abrasive forces. Additionally, adhesion tests could be conducted to evaluate the bond strength between the oxide layer and the substrate, which is crucial for ensuring the long-term integrity of the textured surface. Understanding the mechanical properties of the oxide layer would contribute to optimizing laser-texturing processes for applications that demand high durability, such as in the aerospace and marine sectors.

Mechanism of Superhydrophobic Transition

The transition from hydrophilic to superhydrophobic states observed in certain laser-textured surfaces is a phenomenon that warrants further investigation. While the current study identified surface texture geometries and process parameters that promoted superhydrophobicity, the underlying mechanism driving this transition remains unclear. Future research should explore the changes in surface chemistry, roughness, and possible environmental contamination that contribute to the development of superhydrophobicity. Advanced surface characterization techniques, such as Atomic Force Microscopy (AFM), X-ray Diffraction (XRD), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), could be employed to analyze surface morphology and chemical composition at the nanoscale. These techniques could help determine whether specific roughness attributes or chemical changes, such as the formation of new compounds on the surface, are responsible for the observed increase in water contact angle. Understanding the mechanism behind the superhydrophobic transition would enable researchers to better control the laser-texturing process and tailor surfaces for specific hydrophobic and antifouling applications.

Exploring Spatial Light Modulation for Enhanced Laser Texturing

A promising area for future research is the application of spatial light modulation (SLM) in laser texturing processes. SLM technology allows for precise control over the laser beam, enabling the rapid creation of complex and highly detailed surface patterns. While conventional laser texturing methods have been effective in producing micron- and nano-scale textures, they are often limited in terms of production speed and pattern complexity. By incorporating SLM into the laser texturing

process, researchers could significantly enhance productivity and create more intricate surface textures. This would be particularly valuable in industrial applications where high throughput and precision are required, such as in the fabrication of medical devices, electronics, or aerospace components. Future studies should focus on optimizing SLM parameters, such as beam shaping and intensity modulation, to maximize the quality and efficiency of textured surfaces. Additionally, investigating the feasibility of combining SLM with femtosecond laser systems could further improve the capabilities of laser-based surface engineering.

Designing Novel Surface Textures for Specific Applications

While this study focused on the effects of specific texture geometries, such as parallel, triangle, and star patterns, there remains significant potential for developing new surface textures tailored for particular applications. In the medical field, for instance, textured surfaces could be designed to enhance osseointegration in bone implants or improve the antibacterial properties of medical devices. Future research should explore the development of novel surface textures for specific industrial and biomedical applications. Experimental methods, coupled with computational modeling, could be used to design and evaluate the performance of these textures. By tailoring surface geometries to the unique requirements of different applications, researchers could unlock new functionalities and improve the performance of laser-textured materials in a wide range of industries.

Laser Texturing of Other Engineering Materials

While the current project focused on aluminum alloy 7075, future studies should expand the scope of laser texturing to include other engineering materials, such as titanium, stainless steel, and polymers. Each material exhibits unique physical and chemical properties, and the effects of laser texturing on these materials may vary. Investigating how laser process parameters influence surface properties like roughness, wettability, and mechanical performance across different materials would provide valuable insights into optimizing laser-texturing techniques for diverse applications. For instance, titanium is widely used in aerospace and biomedical applications, and understanding how laser texturing affects its corrosion resistance and biocompatibility could lead to the development of improved materials for these industries. Similarly, studying the effects of laser texturing on polymers could open up new possibilities in areas such as flexible electronics and packaging.

Incorporating In-Situ Feedback for Process Optimization

One of the challenges in laser texturing is ensuring consistent surface quality across large areas and complex geometries. Incorporating in-situ feedback loops during the laser-texturing process could address this issue by providing real-time monitoring and control of laser parameters. Sensors and control algorithms could be integrated into the laser system to detect defects, such as irregularities in surface texture or chemical composition, as they occur. By dynamically adjusting laser

parameters, such as power, scanning speed, and beam focus, in response to real-time feedback, researchers could ensure consistent and defect-free surface texturing. This approach would be particularly valuable for high-precision applications, such as in the manufacturing of microelectronic components or medical devices. Future research should focus on developing and implementing in-situ feedback mechanisms that enhance the reliability and repeatability of laser texturing processes.

Artificial Intelligence for Surface Pattern Design

Leveraging artificial intelligence (AI) for designing surface textures represents an exciting avenue for future research. AI algorithms, particularly machine learning, can analyze large datasets of successful texture patterns and predict optimal designs for new applications. This approach could significantly reduce the trial-and-error aspect of surface pattern design, accelerating the development of advanced textures with specific functionalities. For instance, AI could be used to generate surface patterns that optimize hydrophobicity, wear resistance, or biofouling prevention based on the desired application. Future studies should explore the use of machine learning to create databases of laser-textured surfaces and develop algorithms capable of predicting and designing novel patterns with enhanced performance. This integration of AI and laser-texturing technology could revolutionize the way surfaces are engineered, enabling the creation of highly functional materials for a wide range of industries.

While the current project has made substantial progress in understanding the effects of laser texturing on aluminum alloy surfaces, there are numerous opportunities for further research. By addressing the recommended areas outlined above, future studies can build on the findings of this thesis and contribute to the continued advancement of laser-texturing technologies. Expanding the scope of research to include different materials, validation of process models, and exploring new techniques and tools such as spatial light modulation, in-situ feedback, and artificial intelligence, will enhance the practical applications of laser-textured surfaces in industries like aerospace, marine, biomedical, and electronics. These efforts will ensure that laser-based surface modification becomes a widely adopted and optimized technique for improving material performance in real-world environments.

APPENDIX I

2.2.1. Beam profile measured by beam profiler.

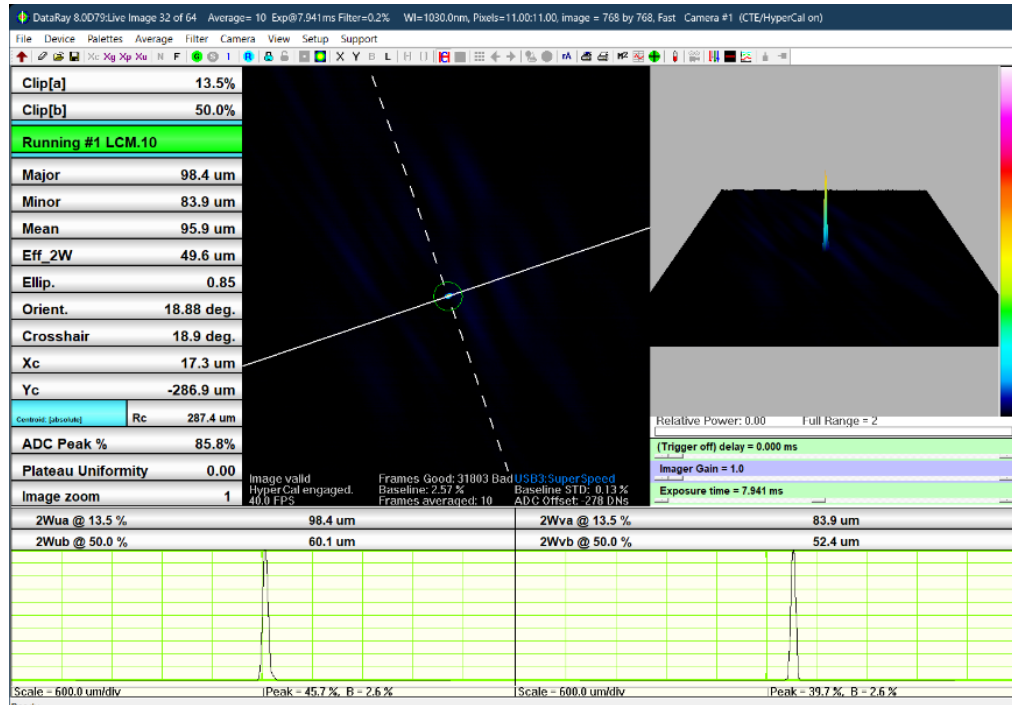


Figure 0.1 Beam profile at focus position.

Table 0.1 Pearson correlation data

Samples	LP	HD	SS	CA	Sa	Sz	Str
1	3	0.08	3	141.51	0.93	21.6	0.439
2	3	0.08	4	140.46	0.91	18.4	0.452
3	3	0.08	5	137.77	0.89	14.3	0.43
4	3	0.1	3	138.45	0.78	18.6	0.049
5	3	0.1	4	136.7	0.77	13.3	0.037
6	3	0.1	5	137.34	0.74	7.4	0.03
7	3	0.12	3	142.19	1.81	21.4	0.352
8	3	0.12	4	135.13	1.38	14	0.032
9	3	0.12	5	136.28	0.9	9.3	0.042
10	3.5	0.08	3	109.06	2.82	21.5	0.45
11	3.5	0.08	4	138.73	1.9	19.9	0.448
12	3.5	0.08	5	97.95	1.28	17.3	0.448
13	3.5	0.1	3	137	1.57	21.8	0.152
14	3.5	0.1	4	135.59	1.43	13.1	0.437
15	3.5	0.1	5	135.7	1.04	9.6	0.511
16	3.5	0.12	3	133.59	1.94	25.6	0.066
17	3.5	0.12	4	123.54	1.36	22.3	0.509
18	3.5	0.12	5	114.01	0.97	13.6	0.535
19	4	0.08	3	133.33	2.49	26.9	0.085
20	4	0.08	4	122.07	2.34	21.3	0.134
21	4	0.08	5	135.93	2.03	17.5	0.504
22	4	0.1	3	141.72	2.74	29.2	0.454
23	4	0.1	4	138.75	1.26	21.1	0.289
24	4	0.1	5	137.31	0.95	18.8	0.51
25	4	0.12	3	137.01	3	23.5	0.049
26	4	0.12	4	138.55	2.98	22.1	0.439
27	4	0.12	5	138.39	2.33	21	0.522
28	3	0.08	3	141.1	0.89	18.3	0.439
29	3	0.08	4	139.21	0.88	16.4	0.424
30	3	0.08	5	132.17	0.77	13.8	0.046
31	3	0.1	3	136.73	0.7	21.5	0.035
32	3	0.1	4	137.07	0.71	17.5	0.066
33	3	0.1	5	134.79	0.68	7.6	0.03
34	3	0.12	3	135.07	1.73	22	0.048
35	3	0.12	4	137.12	1.37	16.3	0.031
36	3	0.12	5	136.69	0.84	11.2	0.053
37	3.5	0.08	3	103.49	1.91	21.7	0.452
38	3.5	0.08	4	132.44	2.63	19	0.45
39	3.5	0.08	5	99.15	1.28	17.5	0.455
40	3.5	0.1	3	136.56	1.43	19.7	0.088
41	3.5	0.1	4	129.6	1.14	13	0.433
42	3.5	0.1	5	143.08	1.09	9.1	0.494
43	3.5	0.12	3	124.58	1.01	21.8	0.059
44	3.5	0.12	4	123.16	1.98	18.4	0.423

45	3.5	0.12	5	122.7	1.86	16.3	0.512
46	4	0.08	3	127.93	2.44	24.5	0.092
47	4	0.08	4	122.2	2.33	15.6	0.107
48	4	0.08	5	136.48	1.18	21.3	0.501
49	4	0.1	3	137.07	2.13	28.8	0.449
50	4	0.1	4	133.58	1.24	17.7	0.438
51	4	0.1	5	136.74	0.9	12.2	0.527
52	4	0.12	3	134.33	1.95	22.8	0.067
53	4	0.12	4	130.99	2.39	22.4	0.084
54	4	0.12	5	138.4	2.47	21.1	0.52
55	3	0.08	3	141.73	0.8	18.4	0.446
56	3	0.08	4	138.27	0.87	16.6	0.428
57	3	0.08	5	127.23	0.89	13.6	0.248
58	3	0.1	3	130.99	0.67	10.2	0.027
59	3	0.1	4	138.8	0.69	20.3	0.037
60	3	0.1	5	130.57	0.69	9.7	0.034
61	3	0.12	3	131.09	4.06	15.9	0.045
62	3	0.12	4	133.19	2.41	11.1	0.029
63	3	0.12	5	137.89	1.38	24.5	0.053
64	3.5	0.08	3	112.2	0.8	19.4	0.439
65	3.5	0.08	4	129.45	2.91	22	0.449
66	3.5	0.08	5	103.25	2.16	17.1	0.437
67	3.5	0.1	3	135.01	1.42	9.3	0.084
68	3.5	0.1	4	126.41	1.12	13.8	0.437
69	3.5	0.1	5	143.78	1.16	19.8	0.501
70	3.5	0.12	3	133.96	1.87	13.6	0.059
71	3.5	0.12	4	122.71	1.18	28.5	0.422
72	3.5	0.12	5	121.22	0.97	17.7	0.545
73	4	0.08	3	126.97	2.53	18.5	0.49
74	4	0.08	4	119.62	2.2	23.3	0.114
75	4	0.08	5	136.11	2.1	18	0.51
76	4	0.1	3	136.56	2.1	17.7	0.466
77	4	0.1	4	134.89	1.26	22.4	0.437
78	4	0.1	5	133.61	0.89	18.6	0.527
79	4	0.12	3	133.42	2.45	22.5	0.051
80	4	0.12	4	134.44	2.22	22.4	0.116
81	4	0.12	5	137.69	1.69	21	0.51

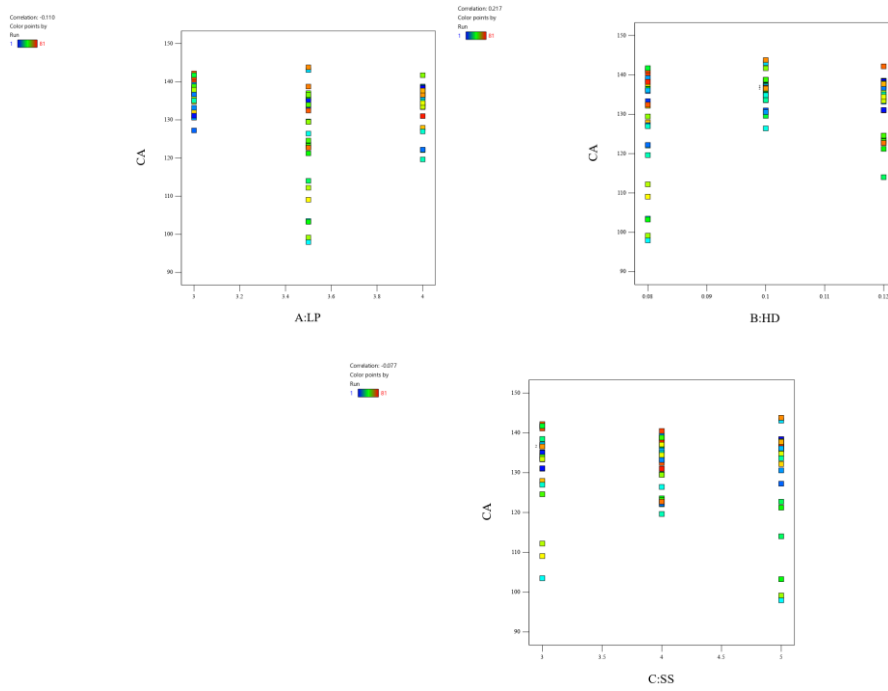


Figure 0.2 Scatter plots showing the correlation of contact angle with laser process parameters such as laser power, hatch distance and scan speed.

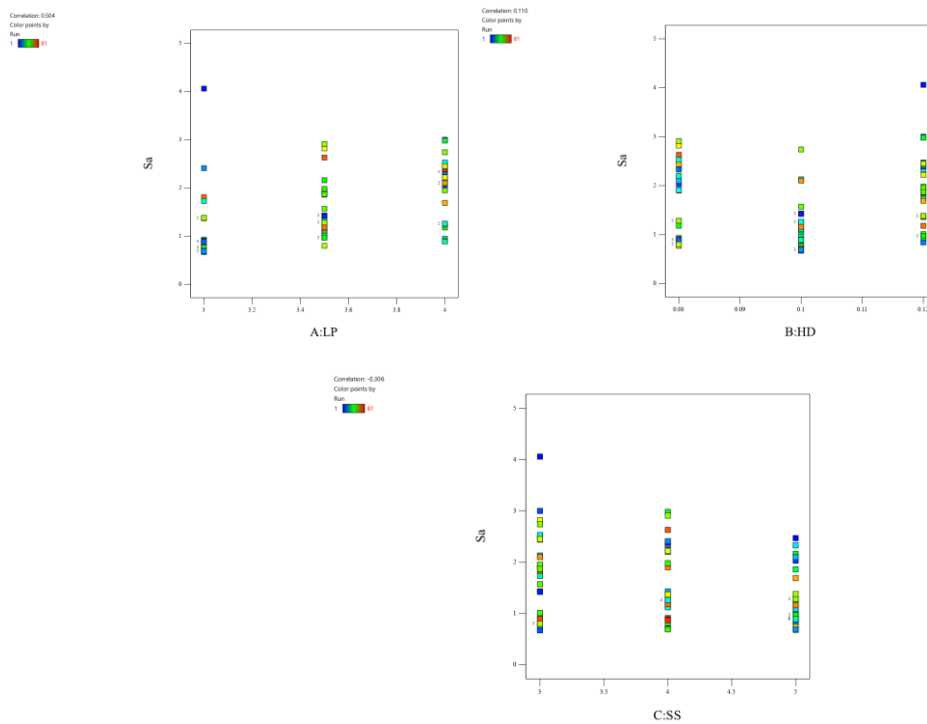


Figure 0.3 Scatter plots showing the correlation of average surface roughness (Sa) with laser process parameters such as laser power, hatch distance and scan speed.

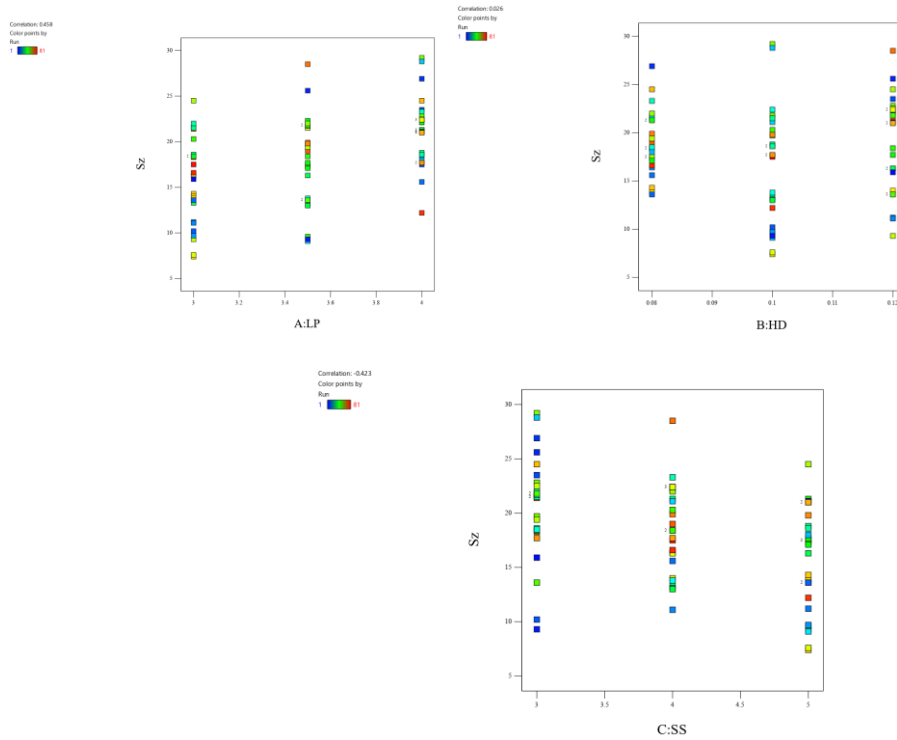


Figure 0.4 Scatter plots showing the correlation of maximum depth surface roughness (S_z) with laser process parameters such as laser power, hatch distance and scan speed.

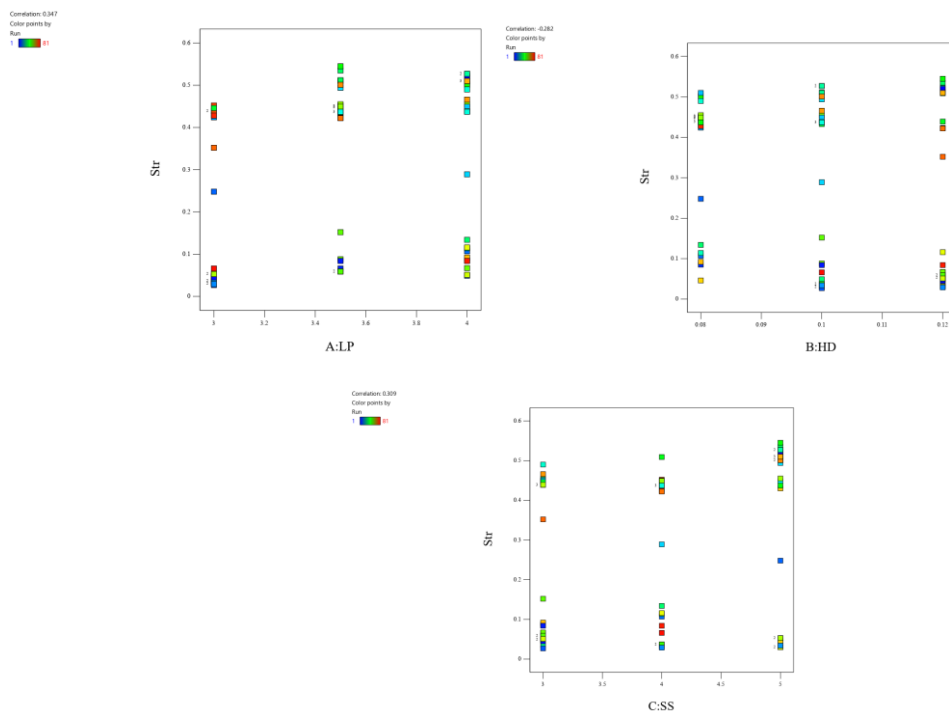


Figure 0.5 Scatter plots showing the correlation of texture aspect ratio (Str) with laser process parameters such as laser power, hatch distance and scan speed.

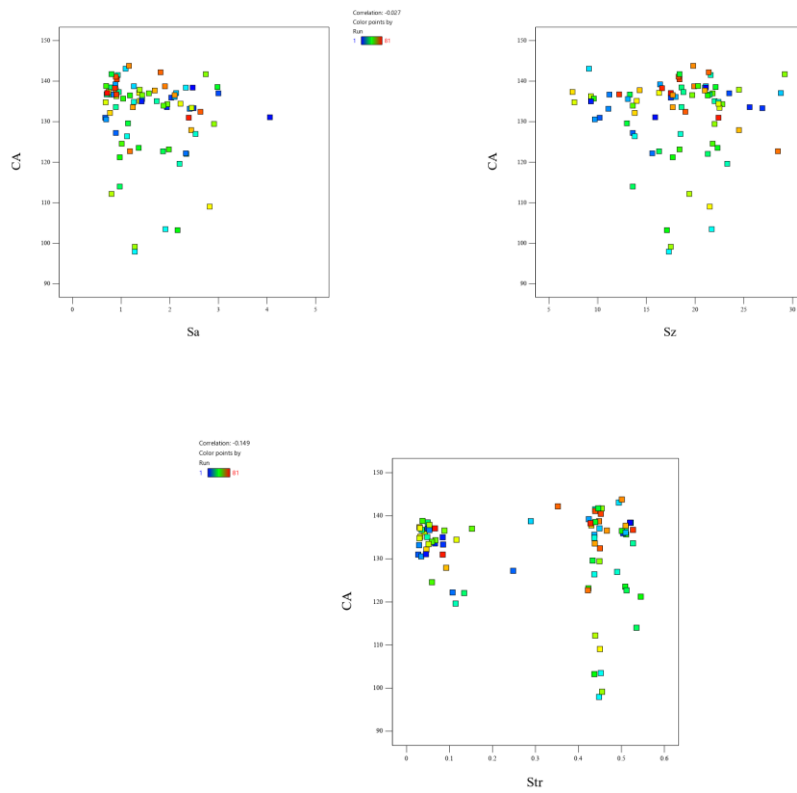


Figure 0.6 Scatter plots showing the correlation of water contact angle with other surface roughness attributes such as average surface roughness (Sa), maximum depth surface roughness (Sz) and texture aspect ratio (Str).

2.2.2. Analysis of variance

ANOVA for S_a (Reduced Quartic model)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.55	12	0.2125	23.27	< 0.0001	significant
A-LP	1.12	1	1.12	122.67	< 0.0001	
B-HD	0.0433	1	0.0433	4.75	0.0328	
C-SS	0.2261	1	0.2261	24.75	< 0.0001	
AB	0.1119	1	0.1119	12.25	0.0008	
AC	0.1066	1	0.1066	11.67	0.0011	
BC	0.0266	1	0.0266	2.91	0.0923	
A ²	0.1015	1	0.1015	11.12	0.0014	
B ²	0.0477	1	0.0477	5.23	0.0253	
ABC	0.0634	1	0.0634	6.94	0.0104	
A ² B	0.1784	1	0.1784	19.53	< 0.0001	
A ² B ²	0.0655	1	0.0655	7.18	0.0093	
AB ² C	0.1062	1	0.1062	11.62	0.0011	
Residual	0.6210	68	0.0091			
Lack of Fit	0.1136	14	0.0081	0.8639	0.6000	not significant
Pure Error	0.5074	54	0.0094			
Cor Total	3.17	80				

Note: The Model F-value of 23.27 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 0.86 implies the Lack of Fit is not significant relative to the pure error. There is a 60.00% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

ANOVA for S_z (Reduced Quartic model)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	985.29	9	109.48	7.95	< 0.0001	significant
A-LP	202.68	1	202.68	14.72	0.0003	
B-HD	0.3200	1	0.3200	0.0232	0.8792	
C-SS	351.65	1	351.65	25.55	< 0.0001	
AB	8.60	1	8.60	0.6251	0.4318	

A ²	54.40	1	54.40	3.95	0.0507	
B ²	166.43	1	166.43	12.09	0.0009	
A ² B	0.0181	1	0.0181	0.0013	0.9711	
AB ²	9.60	1	9.60	0.6975	0.4064	
A ² B ²	53.78	1	53.78	3.91	0.0520	
Residual	977.27	71	13.76			
Lack of Fit	186.77	17	10.99	0.7505	0.7379	not significant
Pure Error	790.50	54	14.64			
Cor Total	1962.56	80				

Note: The Model F-value of 7.95 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 0.75 implies the Lack of Fit is not significant relative to the pure error. There is a 73.79% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

ANOVA for Str (Reduced Sixth model)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.86	16	0.1789	27.99	< 0.0001	significant
A-LP	0.2683	1	0.2683	41.98	< 0.0001	
B-HD	0.2596	1	0.2596	40.61	< 0.0001	
C-SS	0.2329	1	0.2329	36.43	< 0.0001	
AB	0.1865	1	0.1865	29.17	< 0.0001	
BC	0.1654	1	0.1654	25.88	< 0.0001	
A ²	0.3459	1	0.3459	54.11	< 0.0001	
C ²	0.0554	1	0.0554	8.66	0.0045	
A ² C	0.1327	1	0.1327	20.76	< 0.0001	
AB ²	0.4090	1	0.4090	63.98	< 0.0001	
AC ²	0.0697	1	0.0697	10.91	0.0016	
B ² C	0.0254	1	0.0254	3.98	0.0503	
A ² BC	0.0543	1	0.0543	8.50	0.0049	
A ² C ²	0.1020	1	0.1020	15.96	0.0002	
AB ² C	0.4082	1	0.4082	63.85	< 0.0001	
ABC ²	0.0556	1	0.0556	8.69	0.0045	
A ² B ² C	0.0388	1	0.0388	6.07	0.0165	
Residual	0.4091	64	0.0064			

Lack of Fit	0.0624	10	0.0062	0.9720	0.4781	not significant
Pure Error	0.3467	54	0.0064			
Cor Total	3.27	80				

Note: The Model F-value of 27.99 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 0.97 implies the Lack of Fit is not significant relative to the pure error. There is a 47.81% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

ANOVA for Contact angle (Reduced sixth model)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7210.14	20	360.51	33.99	< 0.0001	significant
B-HD	162.34	1	162.34	15.31	0.0002	
C-SS	32.62	1	32.62	3.08	0.0846	
AB	230.48	1	230.48	21.73	< 0.0001	
A ²	142.69	1	142.69	13.45	0.0005	
B ²	70.04	1	70.04	6.60	0.0127	
C ²	146.27	1	146.27	13.79	0.0004	
ABC	67.50	1	67.50	6.36	0.0143	
A ² B	225.05	1	225.05	21.22	< 0.0001	
A ² C	42.55	1	42.55	4.01	0.0497	
AB ²	267.77	1	267.77	25.25	< 0.0001	
AC ²	92.03	1	92.03	8.68	0.0046	
B ² C	208.22	1	208.22	19.63	< 0.0001	
BC ²	975.31	1	975.31	91.96	< 0.0001	
A ² C ²	131.72	1	131.72	12.42	0.0008	
AB ² C	124.53	1	124.53	11.74	0.0011	
ABC ²	89.76	1	89.76	8.46	0.0051	
B ² C ²	1009.42	1	1009.42	95.17	< 0.0001	
A ² B ² C	186.73	1	186.73	17.61	< 0.0001	
A ² BC ²	777.29	1	777.29	73.29	< 0.0001	
A ² B ² C ²	1489.16	1	1489.16	140.41	< 0.0001	
Residual	636.37	60	10.61			

Lack of Fit	61.99	6	10.33	0.9714	0.4534	not significant
Pure Error	574.37	54	10.64			
Cor Total	7846.51	80				

Note: The Model F-value of 33.99 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 0.97 implies the Lack of Fit is not significant relative to the pure error. There is a 45.34% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Model Significance factors

Table 0.2 ANOVA significance parameters for RSM analysis

Response	p-value	
	Model	Lack of fit
Arithmetic mean height (Sa)	< 0.0001	0.85
Maximum height (Sz)	< 0.0001	0.08
Texture aspect ratio (Str)	< 0.0001	0.89
Contact Angle (CA)	< 0.0001	0.45

xNote: If the p value = <0.05 is significant; the p value > 0.05 is non significant

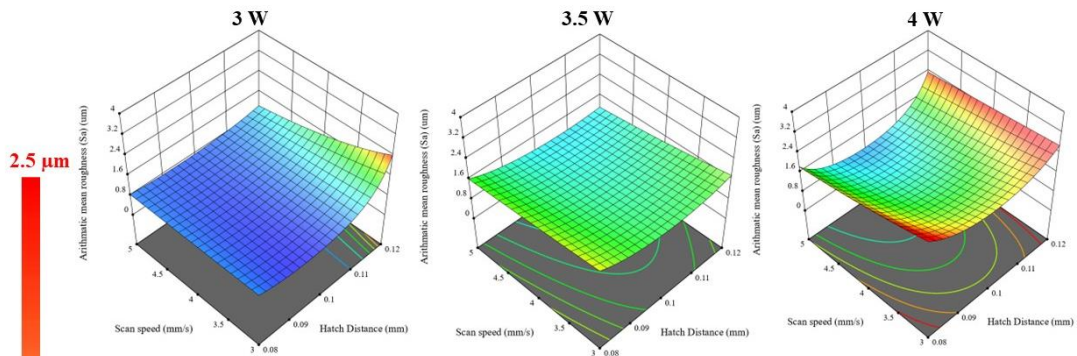
Table 0.3 ANOVA significance adjusted and predicted R² parameters for RSM analysis

Response	Adjusted R ²	Predicted R ²
Arithmetic mean height (Sa)	0.7695	0.7168
Maximum height (Sz)	0.6602	0.5611
Texture aspect ratio (Str)	0.8436	0.7889
Contact Angle (CA)	0.8919	0.8513

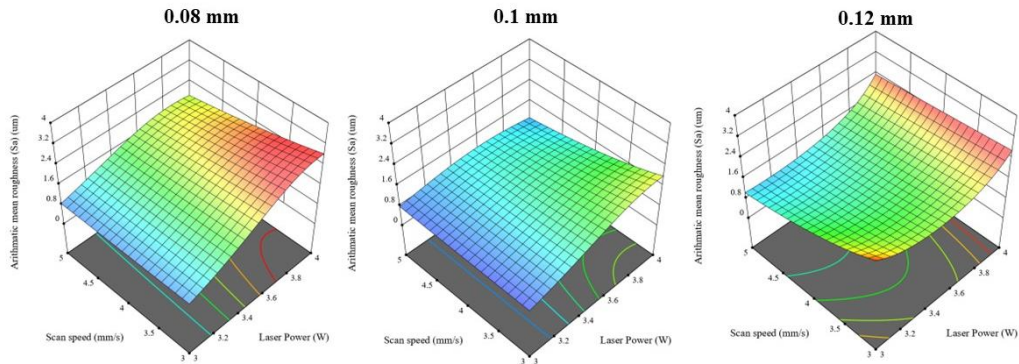
2.2.3. Results of height roughness (S_a), (S_z) with varying laser process parameter

Effect on arithmetic mean roughness (S_a)

Effect of laser power on the arithmetic mean roughness (S_a)



Effect of hatch distance on the arithmetic mean roughness (S_a)



Effect of scan speed on the arithmetic mean roughness (S_a)

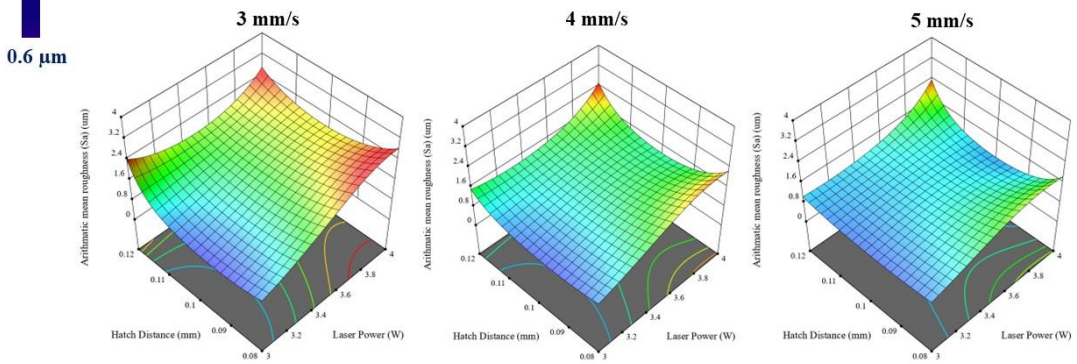


Figure 0.7 The response surface method (RSM) graphs showing the effect of the input processing parameter such as laser power, hatch distance and scan speed on the output measured arithmetic surface roughness (S_a) values

Effect on maximum height roughness (S_z)

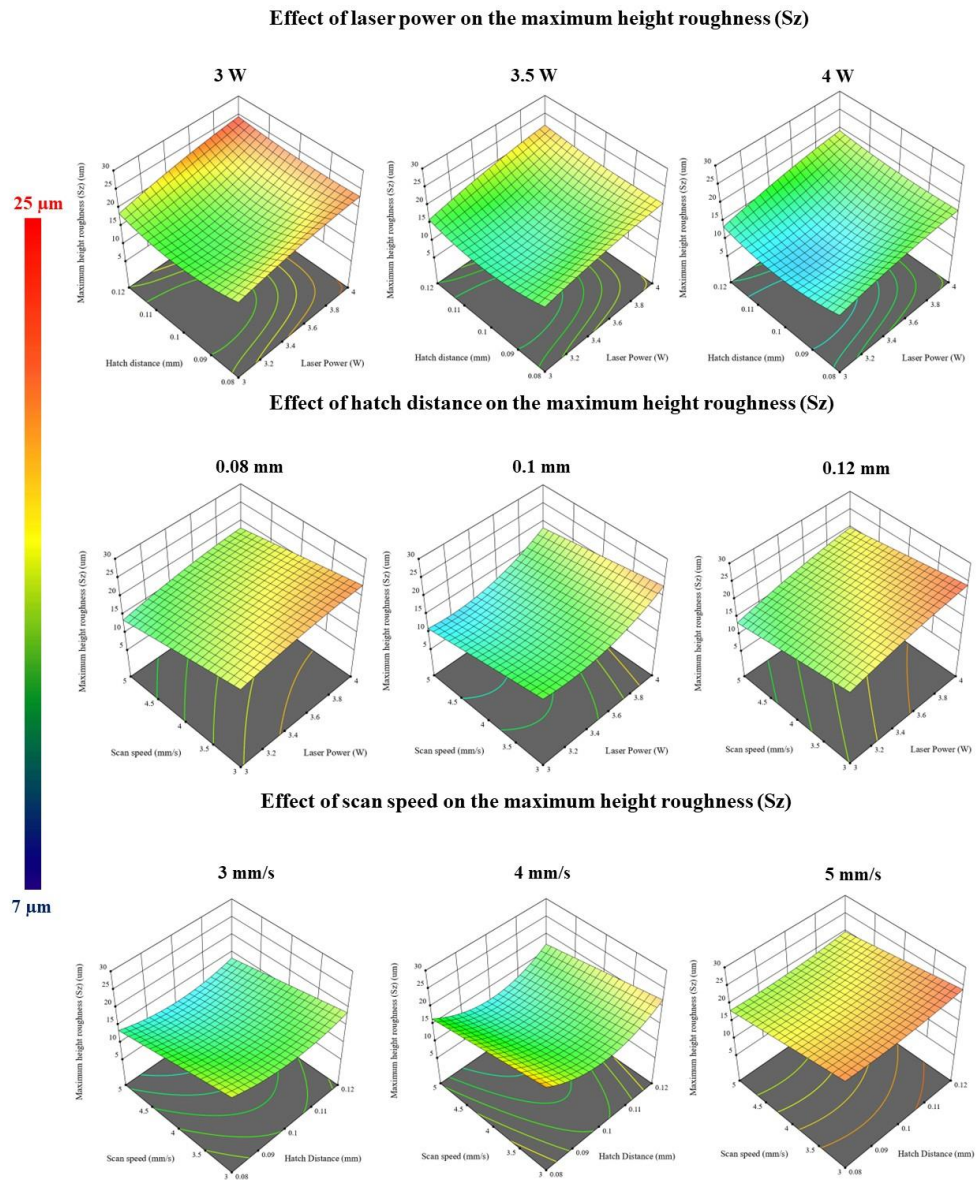


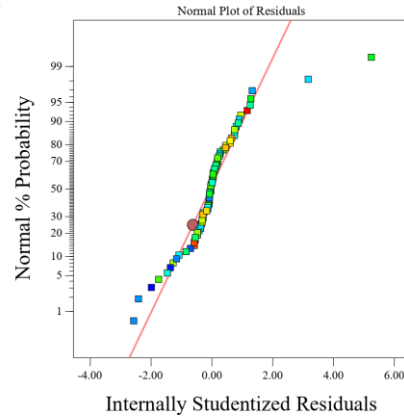
Figure 0.8 The response surface method (RSM) graphs showing the effect of the input processing parameter such as laser power, hatch distance and scan speed on the output measured maximum height surface roughness (S_z) values.

2.2.4. Model significance parameters of Sa and Sz data.

Design-Expert® Software

Sa

Color points by value of
Sa:
0.509 0.658

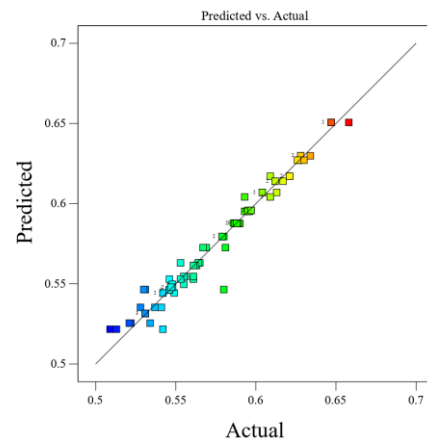


Design-Expert® Software

Sa

(adjusted for constant)

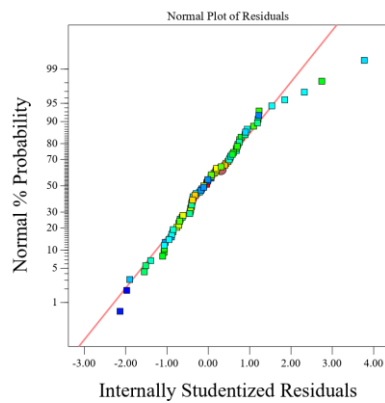
Color points by value of
Sa:
0.509 0.658



Design-Expert® Software

Sz

Color points by value of
Sa:
0.509 0.658



Design-Expert® Software

Sz

Color points by value of
Sa:
0.509 0.658

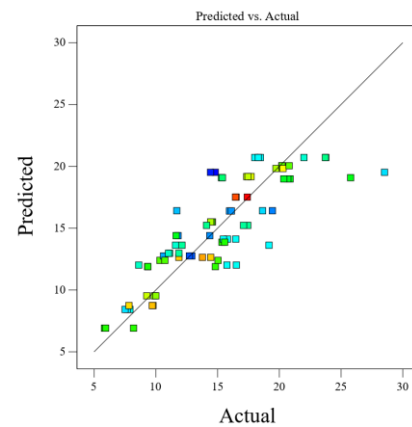


Figure 0.9 Normal probability with internally studentized residuals for (Sa) and (Sz) models and predicted vs actual curve for arithmetic mean roughness (Sa) and (Sz) model derived.

2.2.5. Results of spatial roughness (Str) with varying laser process parameter

Effects on texture aspect ratio (Str)

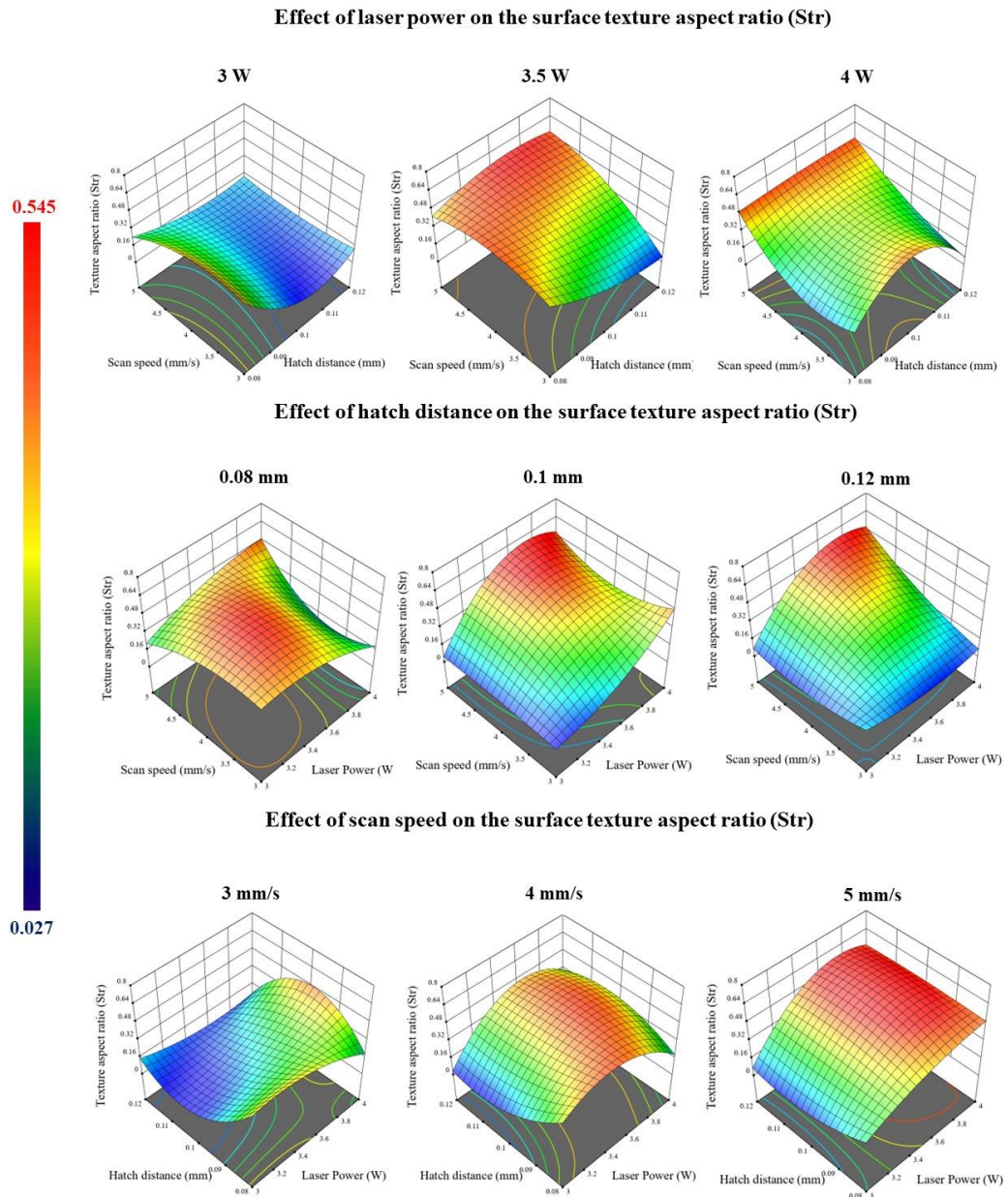


Figure 0.10 The response surface method (RSM) graphs showing the effect of the input processing parameter such as laser power, hatch distance and scan speed on the output measured texture aspect ratio (Str) values.

2.2.6. Model Significance parameters for Str

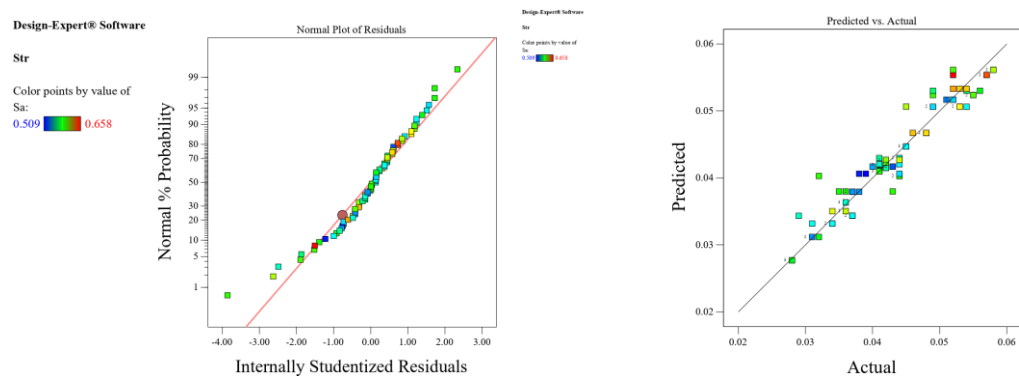


Figure 0.11 Normal probability with internally studentized residuals for (Str) model and predicted vs actual curve for arithmetic mean roughness (Str) model derived.

2.2.7. Results of contact angle with varying laser process parameter

Effect on contact angle

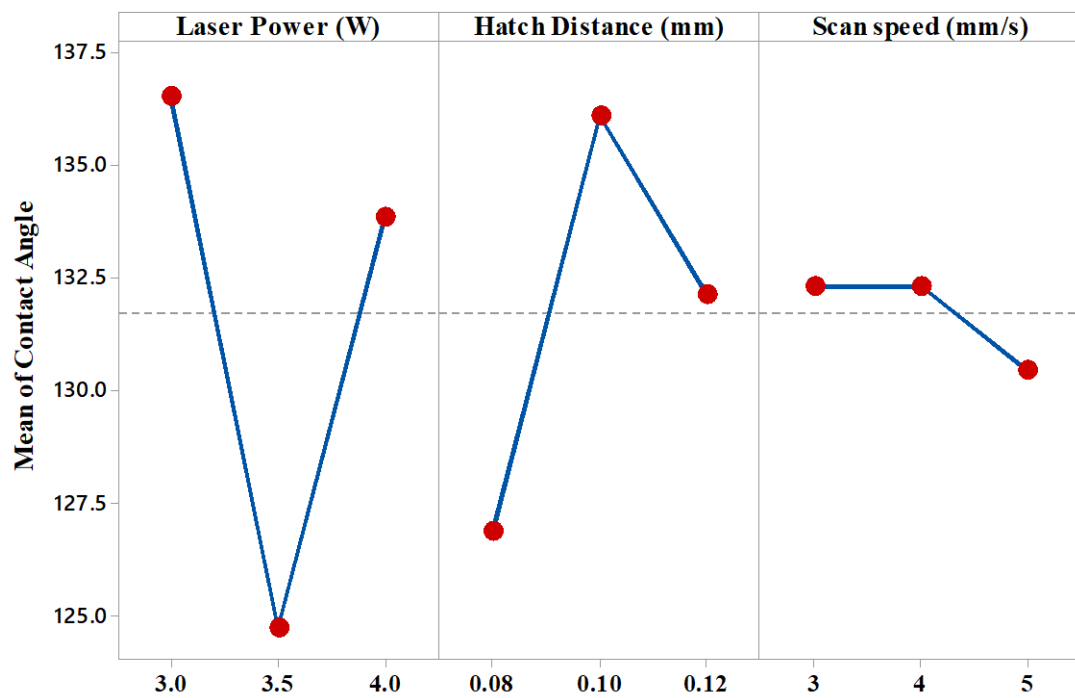


Figure 0.12 Mean Effect plot of water contact angle showing the effect of the input processing parameter such as LP- laser power, HD- hatch distance and SS- scan speed.

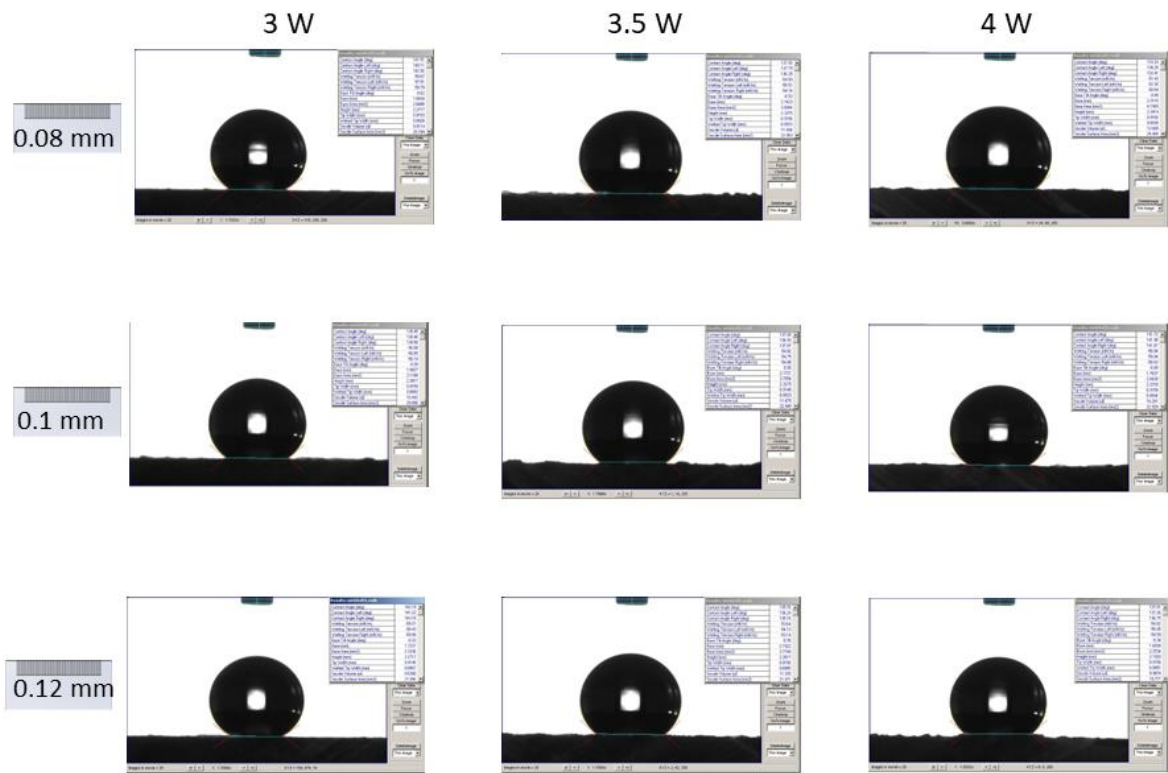


Figure 0.13 Contact angle measurements with different powers and hatch speeds with 3 mm/s scan speed.

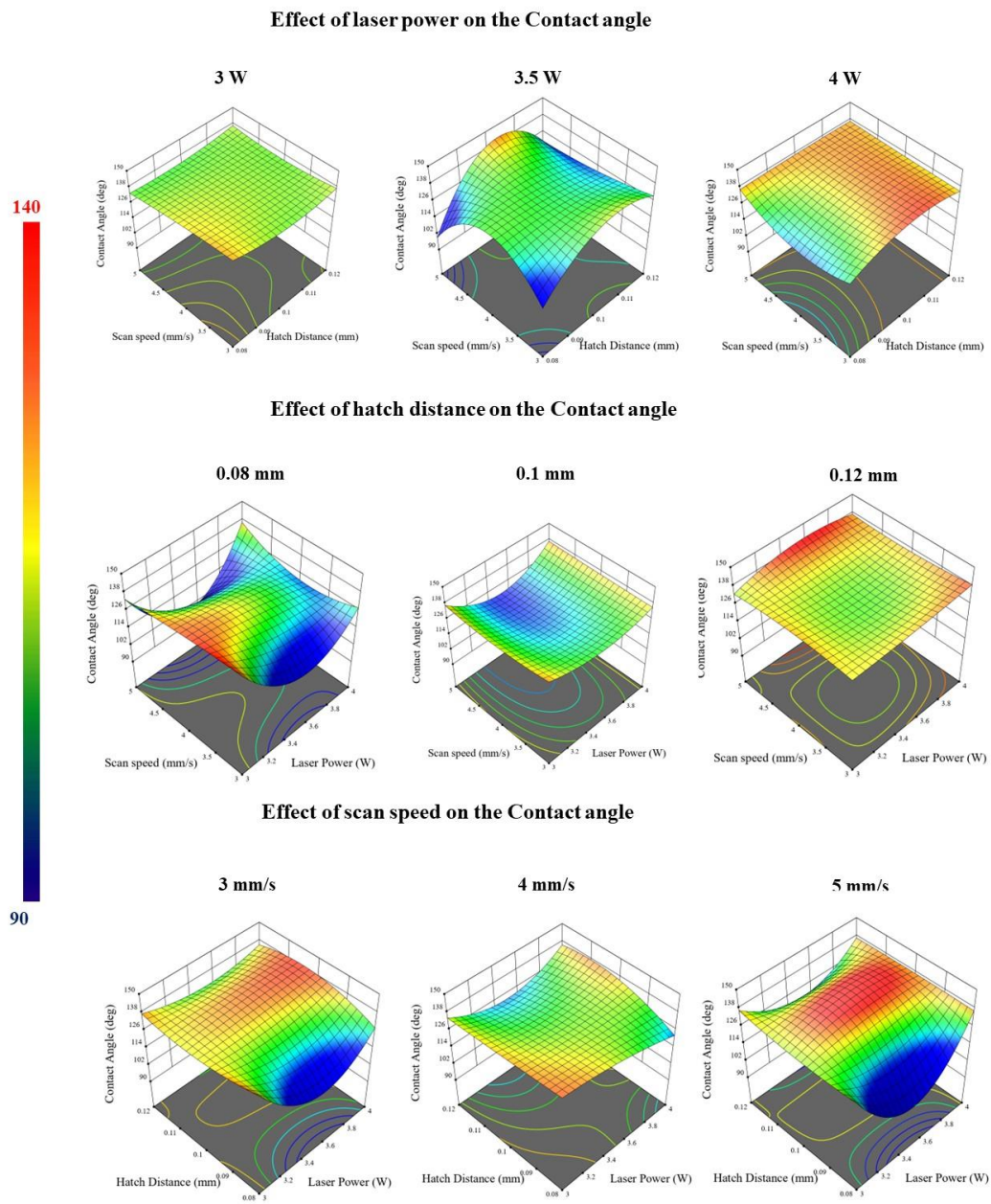


Figure 0.14 The response surface method (RSM) graphs showing the effect of the input processing parameter such as laser power, hatch distance and scan speed on the output measured water contact angle values.

2.2.8. Model significance parameters of contact angle

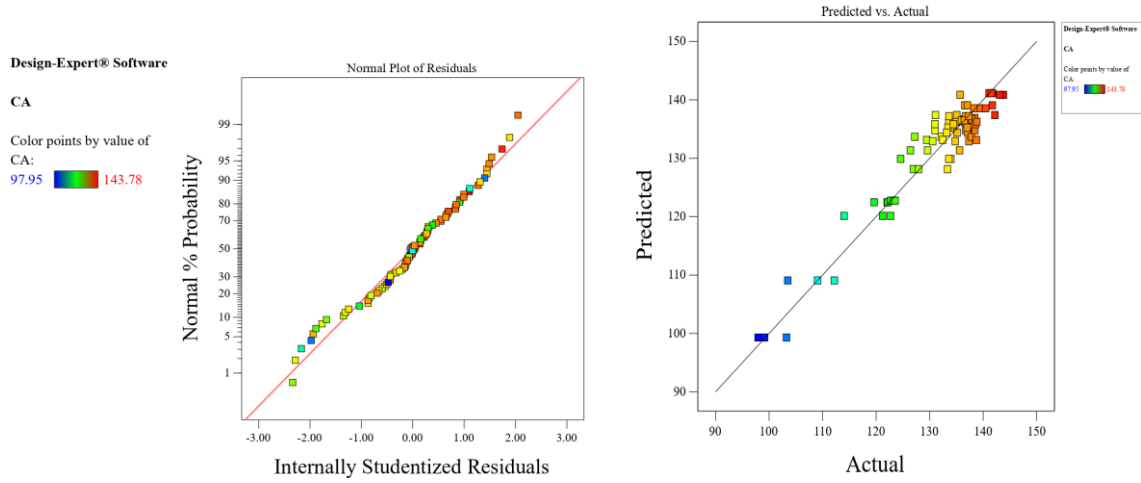


Figure 0.15 Normal plot and predicted vs actual results for contact angle measurements.

2.2.9. Results of numerical optimization

Table 0.4 Solutions as obtained by Design-Expert based on the criterion. (Note: The three highlighted solutions were validated)

Number	LP	HD	SS	CA	Sa	Sz	Str	Desirability	
1	3.577	0.103	5.000	141.878	0.644	17.881	0.054	0.979	Selected
2	3.580	0.103	5.000	141.875	0.644	17.893	0.054	0.979	
3	3.592	0.103	5.000	141.872	0.643	17.917	0.054	0.979	
4	3.590	0.103	5.000	141.865	0.644	17.919	0.054	0.979	
5	3.572	0.104	5.000	141.863	0.643	17.855	0.053	0.979	
6	3.599	0.103	5.000	141.863	0.642	17.927	0.053	0.979	
7	3.542	0.103	5.000	141.845	0.645	17.752	0.054	0.979	
8	3.593	0.103	5.000	141.844	0.644	17.928	0.054	0.979	
9	3.570	0.103	5.000	141.843	0.645	17.870	0.054	0.979	
10	3.610	0.104	5.000	141.833	0.641	17.935	0.053	0.979	
11	3.566	0.104	5.000	141.822	0.642	17.823	0.053	0.978	
12	3.583	0.103	4.999	141.847	0.643	17.887	0.054	0.978	
13	3.527	0.103	5.000	141.813	0.645	17.677	0.054	0.978	
14	3.611	0.103	5.000	141.813	0.643	17.955	0.054	0.978	
15	3.570	0.105	5.000	141.757	0.641	17.822	0.053	0.978	
16	3.605	0.102	5.000	141.698	0.645	17.952	0.054	0.977	
17	3.492	0.103	5.000	141.689	0.645	17.454	0.054	0.977	
18	3.470	0.103	5.000	141.552	0.646	17.290	0.054	0.975	
19	3.457	0.105	5.000	141.346	0.642	17.142	0.053	0.973	
20	3.704	0.105	5.000	141.292	0.632	17.812	0.051	0.972	
21	3.593	0.103	4.983	141.527	0.642	17.821	0.053	0.971	
22	3.749	0.103	5.000	141.111	0.631	17.600	0.051	0.970	
23	3.406	0.104	5.000	141.064	0.642	16.644	0.053	0.970	
24	3.686	0.100	5.000	140.638	0.642	17.804	0.054	0.965	
25	3.818	0.102	5.000	140.345	0.622	17.018	0.049	0.962	
26	3.744	0.107	5.000	140.134	0.622	17.615	0.048	0.959	

27	3.832	0.104	5.000	140.129	0.618	16.979	0.047	0.959	
28	3.835	0.105	5.000	140.016	0.616	16.993	0.047	0.958	
29	3.833	0.101	5.000	139.932	0.622	16.743	0.049	0.957	
30	3.890	0.103	5.000	139.329	0.610	16.218	0.045	0.950	
31	3.890	0.105	5.000	139.219	0.608	16.409	0.044	0.949	
32	3.877	0.100	5.000	139.191	0.615	16.097	0.047	0.949	
33	3.914	0.101	5.000	138.843	0.607	15.680	0.045	0.945	
34	3.923	0.102	5.000	138.748	0.604	15.665	0.044	0.944	
35	3.955	0.105	5.000	138.117	0.597	15.559	0.041	0.936	
36	3.961	0.101	5.000	137.971	0.597	14.802	0.043	0.934	
37	3.990	0.102	5.000	137.443	0.590	14.484	0.041	0.928	
38	3.987	0.108	5.000	137.398	0.592	15.624	0.039	0.928	
39	4.000	0.103	5.000	137.224	0.587	14.499	0.039	0.926	
40	4.000	0.104	5.000	137.224	0.588	14.581	0.039	0.926	
41	4.000	0.111	5.000	137.153	0.594	16.317	0.037	0.925	
42	4.000	0.113	5.000	137.120	0.597	16.763	0.036	0.924	
43	4.000	0.115	5.000	137.047	0.602	17.598	0.036	0.924	
44	4.000	0.117	5.000	136.986	0.606	18.212	0.035	0.923	
45	4.000	0.119	5.000	136.920	0.611	18.822	0.035	0.922	
46	4.000	0.088	5.000	136.908	0.604	12.653	0.047	0.922	
47	4.000	0.086	5.000	136.806	0.610	12.580	0.049	0.921	
48	3.998	0.120	5.000	136.740	0.614	19.144	0.035	0.920	
49	4.000	0.084	5.000	136.700	0.617	12.562	0.051	0.920	
50	3.000	0.120	5.000	136.641	0.617	19.829	0.051	0.919	
51	3.001	0.119	5.000	136.290	0.616	18.622	0.050	0.915	
52	3.110	0.104	5.000	136.252	0.614	11.191	0.045	0.914	
53	3.000	0.120	4.967	136.482	0.619	19.147	0.051	0.909	
54	3.090	0.110	5.000	135.395	0.611	12.459	0.045	0.904	
55	3.065	0.109	5.000	135.107	0.609	11.757	0.044	0.900	
56	3.094	0.112	5.000	135.001	0.610	13.327	0.046	0.899	
57	3.026	0.114	5.000	134.769	0.608	13.877	0.045	0.896	
58	3.041	0.110	5.000	134.748	0.607	11.907	0.044	0.896	
59	3.032	0.113	5.000	134.717	0.608	13.773	0.045	0.896	
60	3.000	0.112	5.000	134.663	0.606	12.490	0.044	0.895	
61	3.000	0.080	5.000	133.670	0.553	13.624	0.042	0.883	
62	3.000	0.080	4.985	133.757	0.553	13.697	0.042	0.881	
63	3.000	0.080	4.967	133.866	0.552	13.786	0.042	0.878	
64	3.022	0.096	5.000	133.057	0.588	7.444	0.039	0.875	
65	3.000	0.087	5.000	132.888	0.566	8.991	0.039	0.873	
66	3.000	0.088	5.000	132.808	0.568	8.428	0.038	0.872	
67	3.000	0.089	5.000	132.797	0.569	8.343	0.038	0.872	
68	3.000	0.090	5.000	132.744	0.571	7.922	0.038	0.871	
69	3.000	0.092	5.000	132.685	0.574	7.326	0.038	0.871	

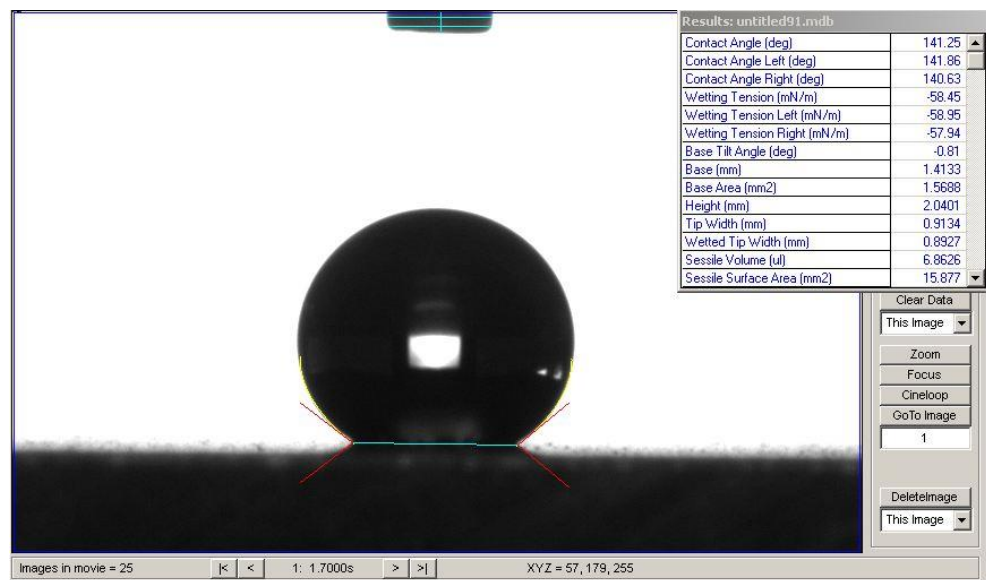


Figure 0.16 Validation of the predicted solution 1 (with CA 141.87° at 97.9% desirability) showing the measured contact angle of 141.25 °.

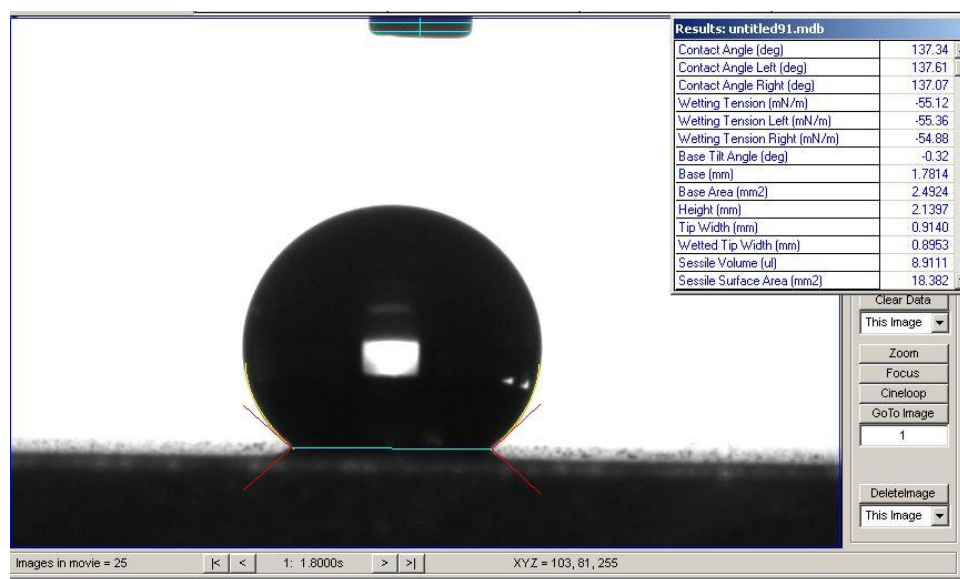


Figure 0.17 Validation of the predicted solution 1 (with CA 141.064 ° at 97% desirability) showing the measured contact angle of 137.34 °.

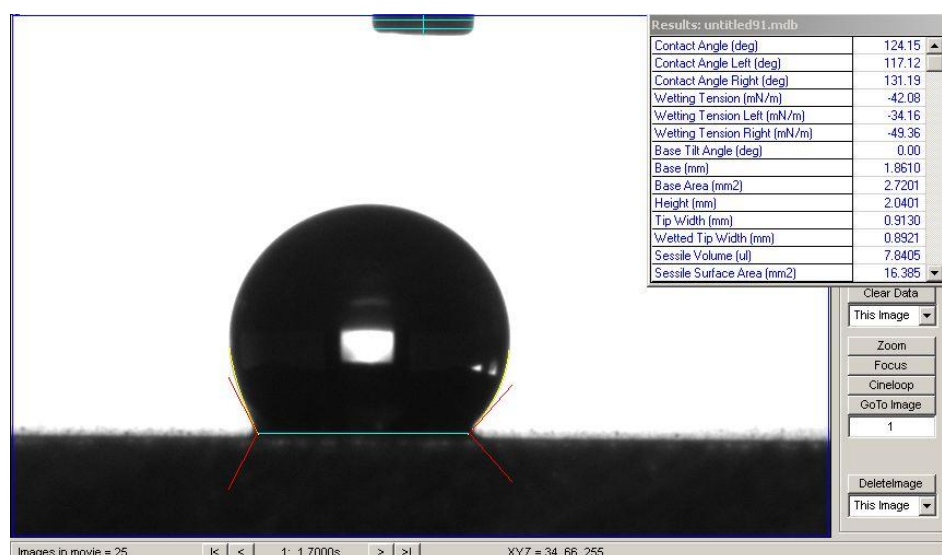


Figure 0.18 Validation of the predicted solution 1 (with CA 132.685° at 87.1% desirability) showing the measured contact angle of 124.15 °.

2.2.10. Results of XPS analysis data

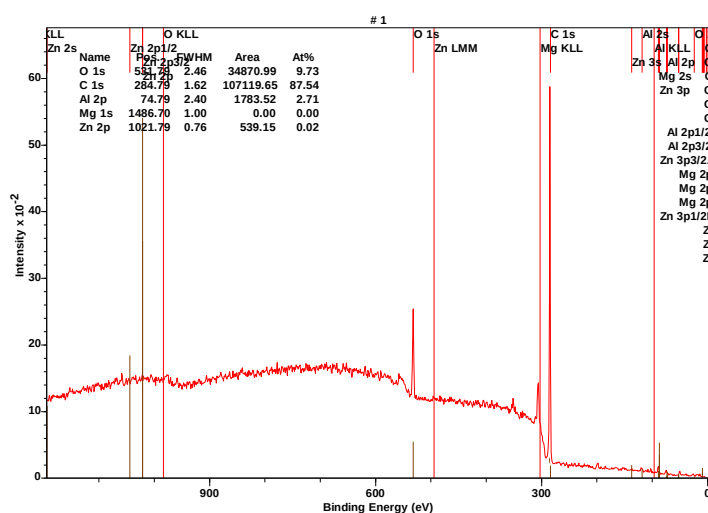
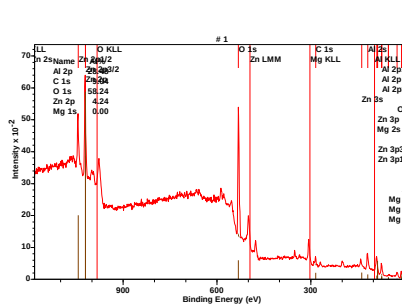
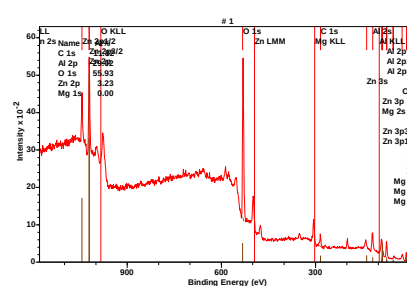


Figure 0.19 XPS of the aluminium alloy 7075 sample without laser texturing.

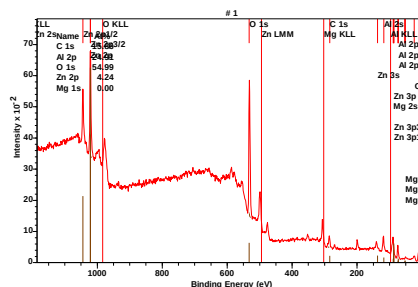
Day 60



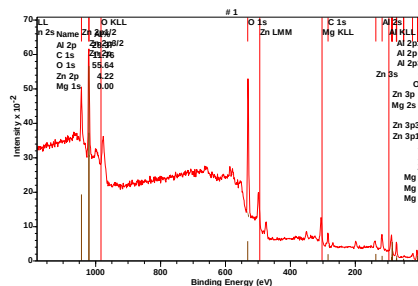
Day 60



Day 60



Day 60



sample 1, b. sample 12, c. sample 17 and d. sample 23.

APPENDIX II

5.1.1. Results of all the test

Table 0.1 Factors (laser power, scan speed, texture) and responses (Sa, Sq, Sku, Ssk, microhardness, COF, wear volume)

Sam ples	Factors			Responses						
	LP (W)	SS (mm/s)	Tex	Sa (μm)	Sq (μm)	Sku	Ssk	Microhard ness (MPa)	COF	Wear volume (mm ³)
1	400	1	1	3.992	5.839 67	9.603	2.021	1123.24	1.455 65	0.007
2	400	1	2	5.1346 7	7.827 67	8.365 67	2.172 33	850.804	3.682 03	0.007
3	400	1	3	5.2366 7	7.333 67	5.381 67	1.609 33	1134.99	0.643 275	0.007
4	400	2	1	3.5893 3	4.997 33	6.682 67	1.503 67	1047.5	0.732 36	0.00237 741
5	400	2	2	7.837	9.563 67	2.642 33	1.022 33	858.564	0.296 61	0.00201 974
6	400	2	3	7.0356 7	8.915 33	3.135	1.188 67	1001.25	0.339 652	0.00351 182
7	400	3	1	9.5833 3	12.48 8	3.589 33	1.411	1149.69	0.308 494	0.00588 647
8	400	3	2	8.814	9.491	1.497 67	0.3	1220.18	0.502 509	0.00430 924
9	400	3	3	10.024	11.58 97	2.025	0.779 333	1181.25	0.388 333	0.00430 865
10	500	1	1	4.1883 3	5.394 33	3.322	0.878 667	1291.91	0.026 404	0
11	500	1	2	7.9493 3	9.554	2.448 67	0.877	1247.85	0.036 753	0
12	500	1	3	6.7043 3	8.783 33	3.633 33	1.328	1144.55	0.350 952	0.00274 62
13	500	2	1	3.2506 7	4.875 33	9.962 67	2.098 33	762.939	0.269 645	0.00075 0922
14	500	2	2	8.906	10.12 23	1.852 67	0.596 667	717.883	0.060 203	9.16E- 05
15	500	2	3	6.3936 7	8.579	3.969	1.406 67	694.282	0.369 034	0.00127 125
16	500	3	1	2.5103 3	3.368	4.741	0.883 333	634.78	0.129 809	0.00080 0922
17	500	3	2	9.307	10.15 53	1.467 33	0.196	976.015	0.315 626	0.00172 34
18	500	3	3	8.4713 3	9.827	1.979 67	0.705 333	743.566	0.223 451	0.00173 399

5.1.2. Analysis of variance

ANOVA for Reduced 2FI model

Response 1: Sa

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	85.17	6	14.19	11.37	0.0004	significant
B-Scan Speed	20.03	1	20.03	16.05	0.0021	
C-Texture	40.63	2	20.32	16.28	0.0005	
AB	13.25	1	13.25	10.62	0.0076	
AC	11.25	2	5.63	4.51	0.0372	
Residual	13.73	11	1.25			
Cor Total	98.90	17				

Factor coding is **Coded**.

Sum of squares is **Type II Classical**

The **Model F-value** of 11.37 implies the model is significant. There is only a 0.04% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced 2FI model

Response 2: Sq

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	83.47	7	11.92	5.46	0.0084	significant
A-Power	3.03	1	3.03	1.39	0.2661	
B-Scan Speed	12.38	1	12.38	5.66	0.0386	
C-Texture	39.96	2	19.98	9.14	0.0055	
AB	13.97	1	13.97	6.40	0.0299	
AC	14.13	2	7.06	3.23	0.0826	
Residual	21.85	10	2.18			
Cor Total	105.32	17				

Factor coding is **Coded**.

Sum of squares is **Type II Classical**

The **Model F-value** of 5.46 implies the model is significant. There is only a 0.84% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case B, C, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced 2FI model

Response 3: Sku

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	83.34	4	20.84	6.40	0.0045	significant

B-Scan Speed	25.39	1	25.39	7.80	0.0152	
C-Texture	39.15	2	19.57	6.01	0.0142	
AB	18.81	1	18.81	5.78	0.0319	
Residual	42.33	13	3.26			
Cor Total	125.67	17				

Factor coding is **Coded**.

Sum of squares is **Type II Classical**

The **Model F-value** of 6.40 implies the model is significant. There is only a 0.45% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case B, C, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced Cubic model

Response 4: Ssk

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.85	4	0.9622	6.71	0.0037	significant
B-Scan Speed	1.77	1	1.77	12.37	0.0038	
C-Texture	1.10	2	0.5496	3.84	0.0491	
AB ²	0.9774	1	0.9774	6.82	0.0215	
Residual	1.86	13	0.1433			
Cor Total	5.71	17				

Factor coding is **Coded**.

Sum of squares is **Type II Classical**

The **Model F-value** of 6.71 implies the model is significant. There is only a 0.37% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case B, C, AB² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced Cubic model

Response 5: Micro hardness

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7.495E+05	9	83272.80	25.56	< 0.0001	significant
A-Power	1.018E+05	1	1.018E+05	31.25	0.0005	
B-Scan Speed	65691.73	1	65691.73	20.16	0.0020	
AB	2.617E+05	1	2.617E+05	80.32	< 0.0001	
AC	54598.46	2	27299.23	8.38	0.0109	
BC	67583.43	2	33791.72	10.37	0.0060	
B ²	1.784E+05	1	1.784E+05	54.75	< 0.0001	
AB ²	19737.30	1	19737.30	6.06	0.0392	
Residual	26062.43	8	3257.80			
Cor Total	7.755E+05	17				

Factor coding is **Coded**.
Sum of squares is **Type II Classical**

The **Model F-value** of 25.56 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, AB, AC, BC, B², AB² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced Cubic model

Response 6: Coefficient of Friction (COF)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.1868	12	0.0156	42.11	0.0003	significant
A-Power	0.0797	1	0.0797	215.52	< 0.0001	
B-Scan Speed	0.0019	1	0.0019	5.20	0.0714	
C-Texture	0.0019	2	0.0009	2.52	0.1748	
AB	0.0354	1	0.0354	95.88	0.0002	
AC	0.0234	2	0.0117	31.59	0.0015	
ABC	0.0181	2	0.0090	24.48	0.0026	
AB ²	0.0085	1	0.0085	22.88	0.0050	
B ² C	0.0180	2	0.0090	24.29	0.0027	
Residual	0.0018	5	0.0004			
Cor Total	0.1886	17				

Factor coding is **Coded**.

Sum of squares is **Type II Classical**

The **Model F-value** of 42.11 implies the model is significant. There is only a 0.03% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, AB, AC, ABC, AB², B²C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

ANOVA for Reduced Cubic model

Response 7: Wear Volume

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0001	4	0.0000	26.78	< 0.0001	significant
A-Power	5.597E-06	1	5.597E-06	6.47	0.0245	
AB	5.344E-06	1	5.344E-06	6.18	0.0273	
B ²	0.0000	1	0.0000	16.21	0.0014	
AB ²	7.943E-06	1	7.943E-06	9.18	0.0097	
Residual	0.0000	13	8.648E-07			
Cor Total	0.0001	17				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 26.78 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

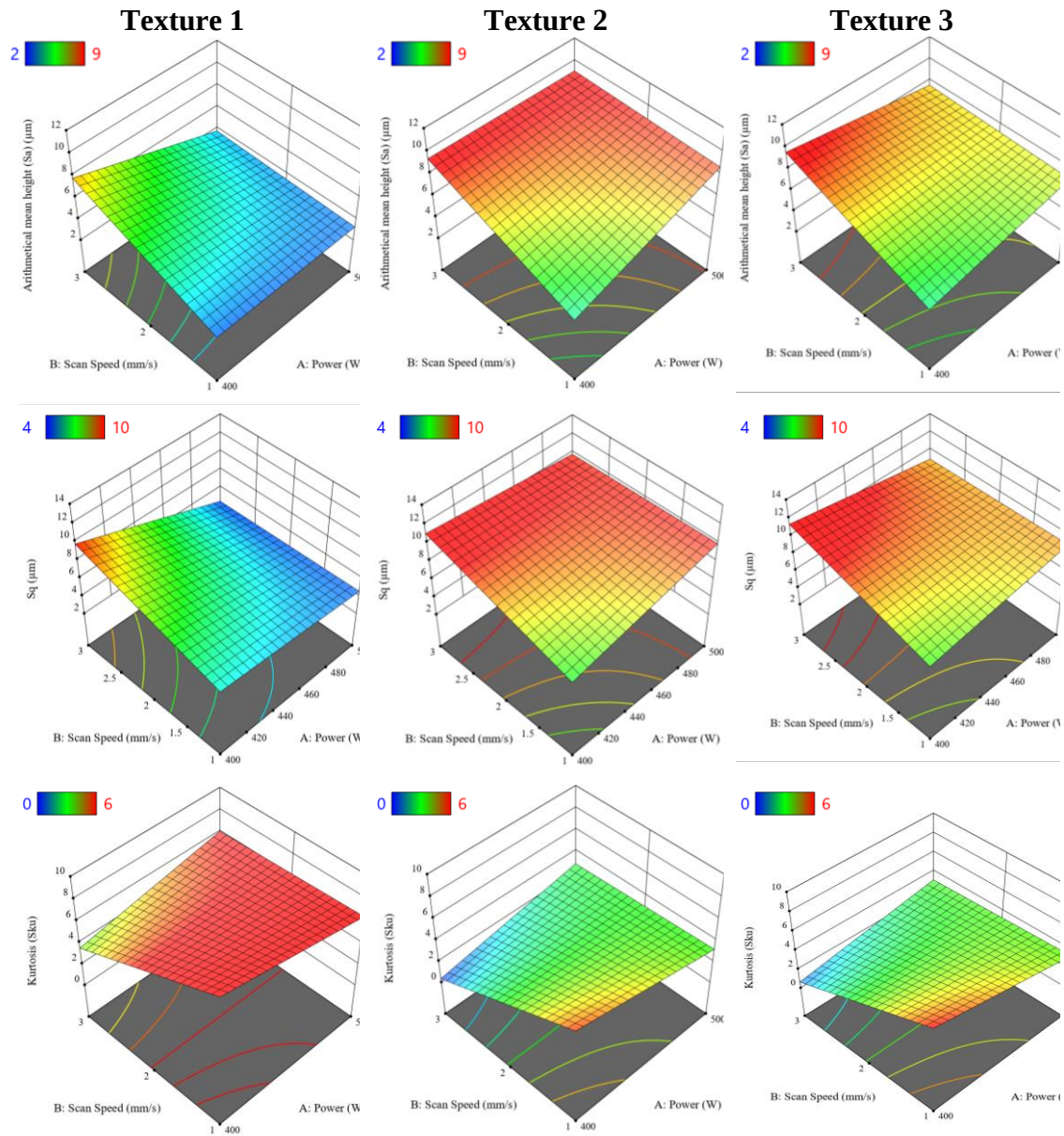
P-values less than 0.0500 indicate model terms are significant. In this case A, AB, B², AB² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

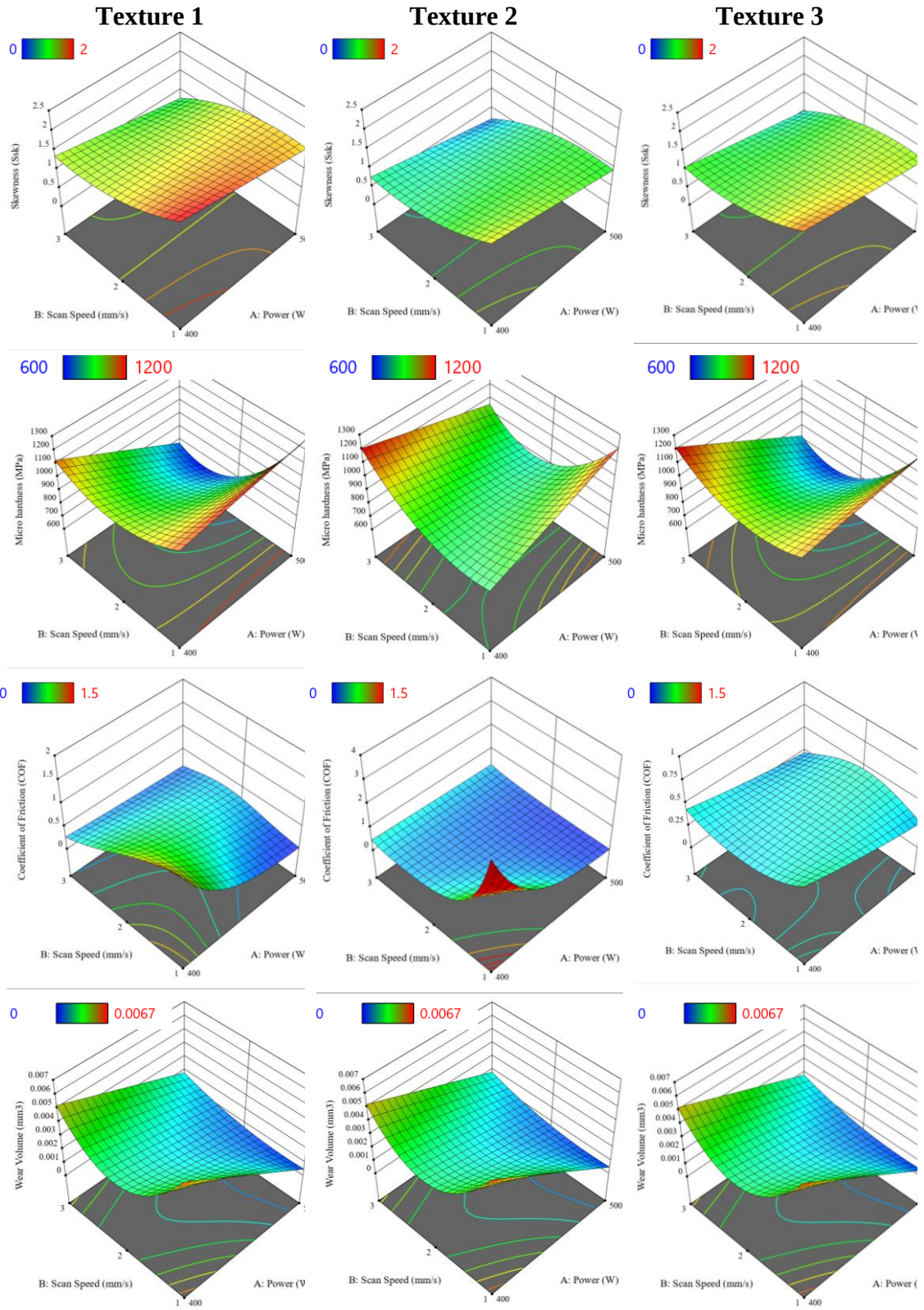
5.1.3. Model significance factors

Table 0.2 ANOVA significance R² and predicted R² parameters for RSM analysis

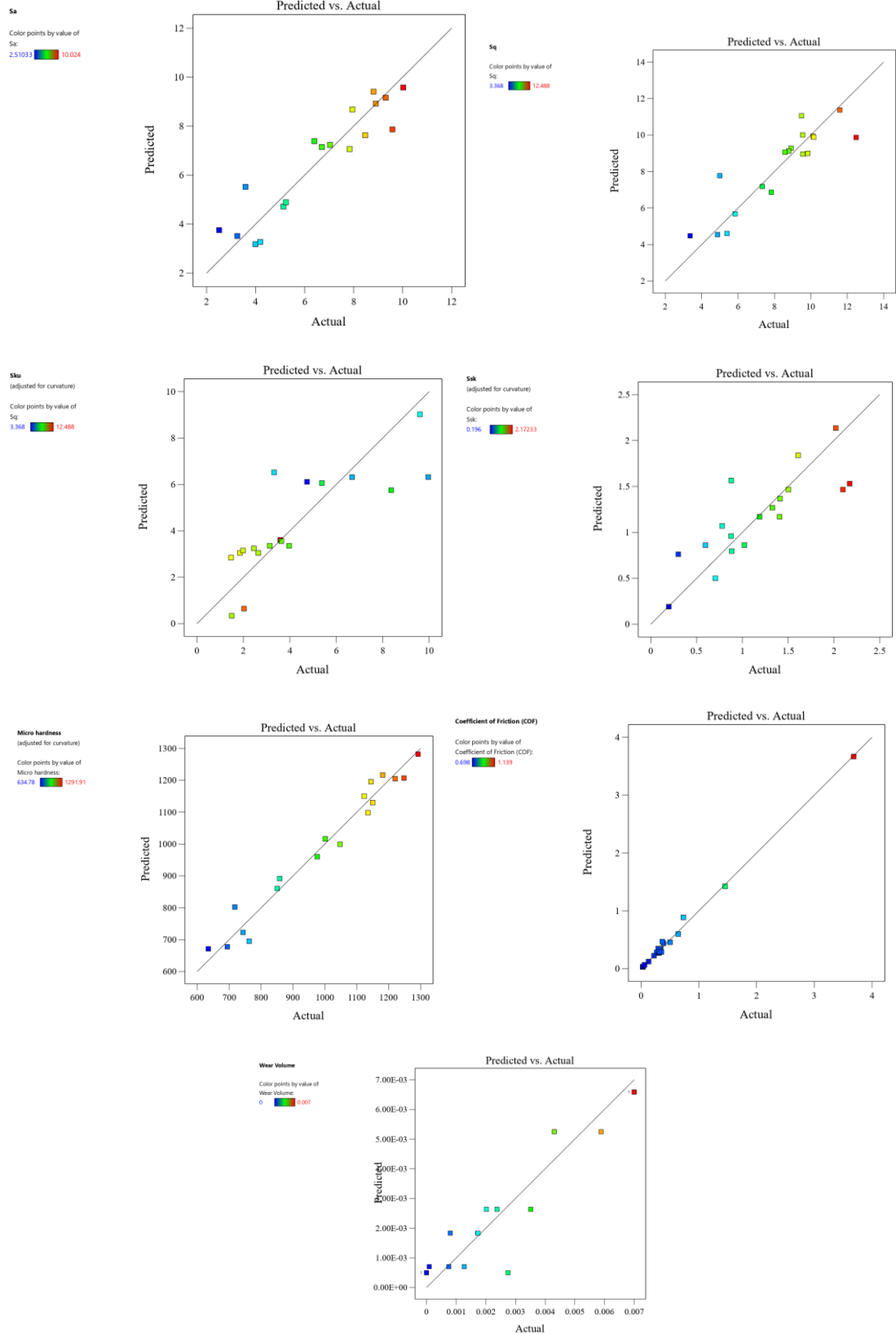
Response	R ²	Adjusted R ²
Arithmetic mean height (Sa)	0.8612	0.7854
Root mean square (Sq)	0.7925	0.6473
Kurtosis (Sku)	0.6632	0.5596
Skewness (Ssk)	0.6738	0.5735
Microhardness	0.9664	0.9286
Coefficient of Friction	0.9902	0.9667
Wear volume	0.8912	0.8585

5.1.4. Texture wise distribution of arithmetic mean height, root mean square height, kurtosis, skewness, microhardness, coefficient of friction, wear volume

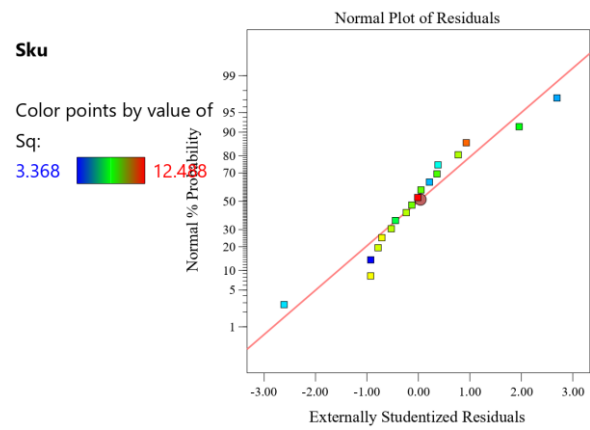
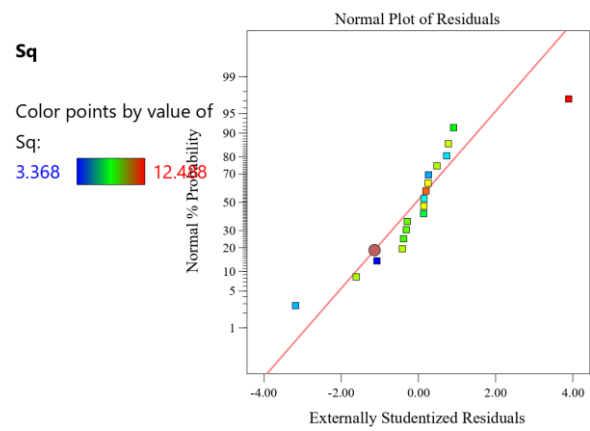
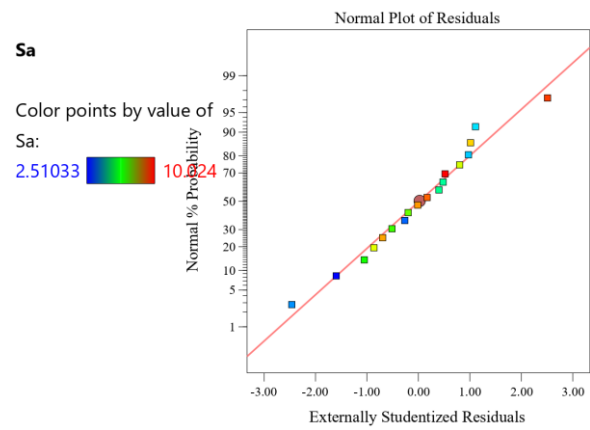


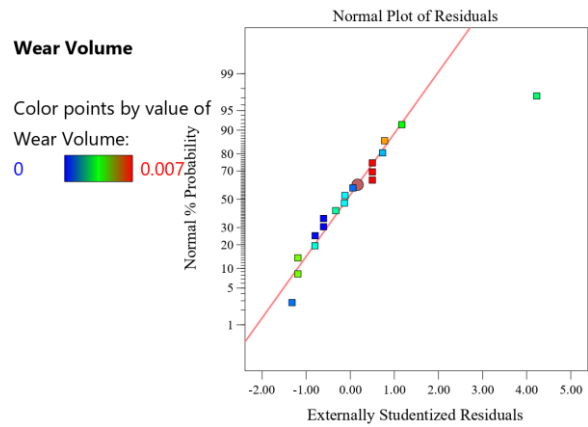
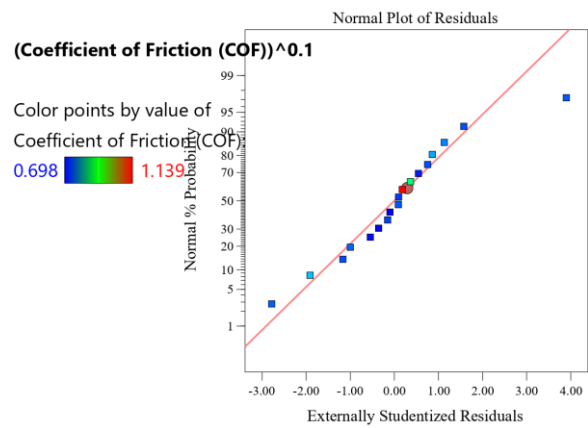
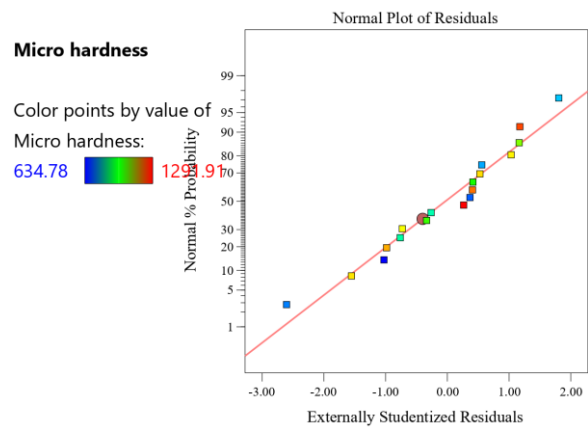
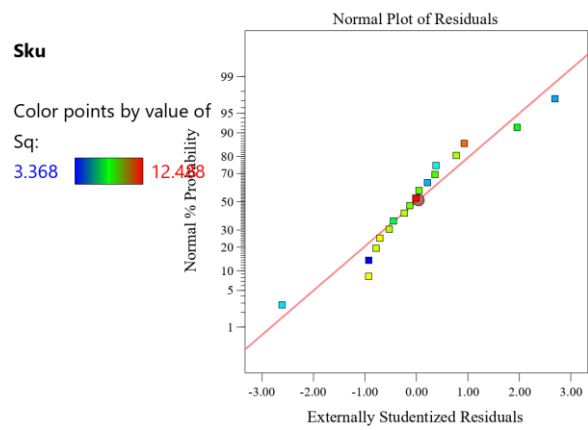


5.1.5. Model significance Predicted vs Actual graphs



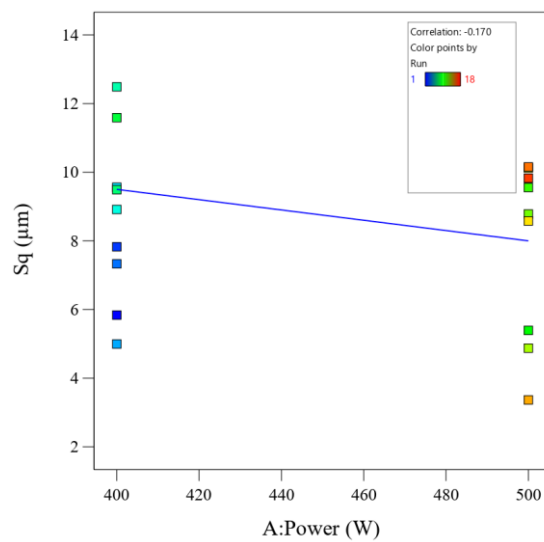
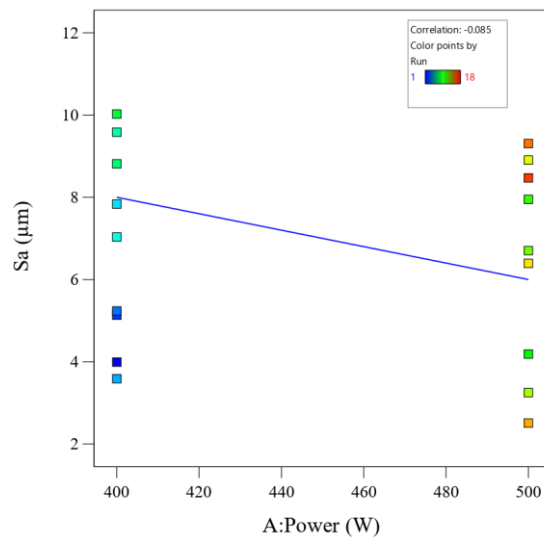
5.1.6. Normal plots of residuals to test the significance of results.

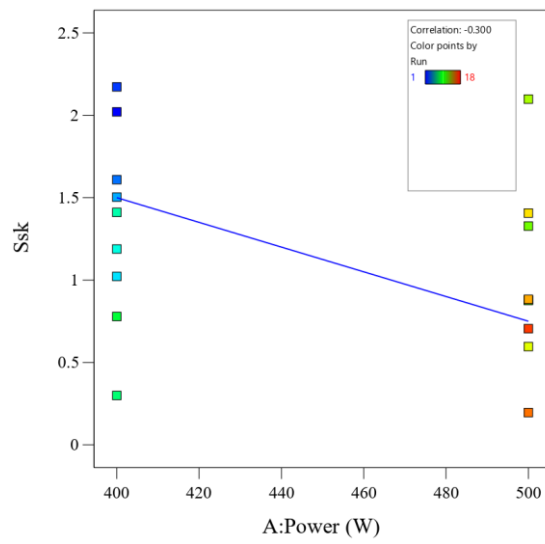
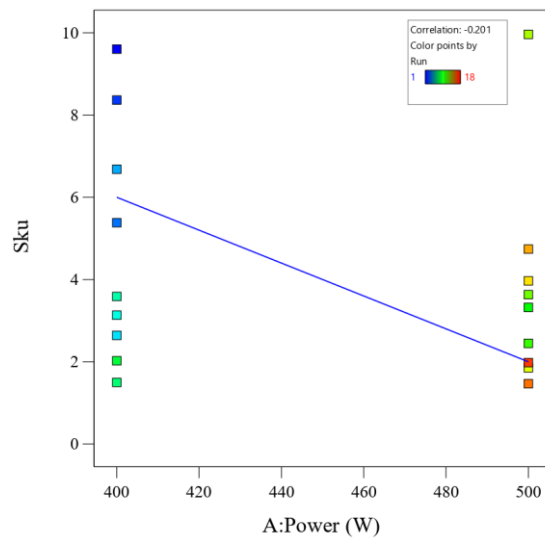


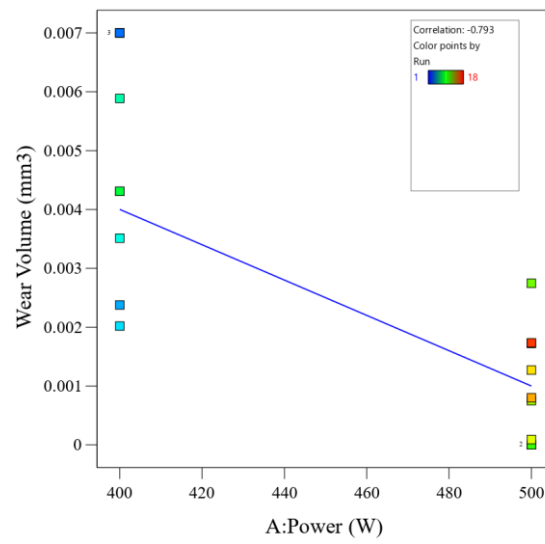
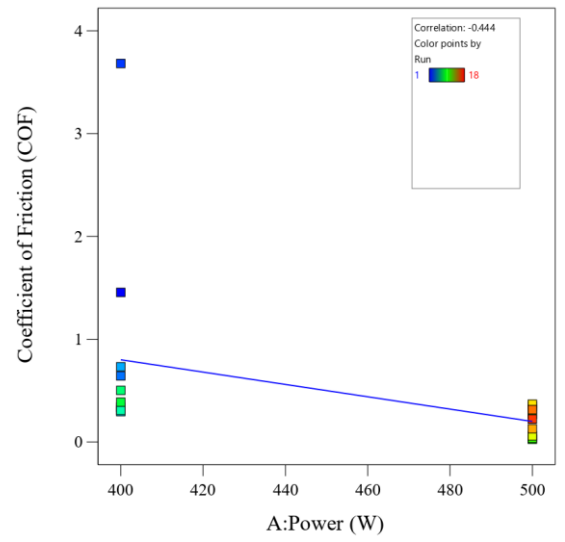
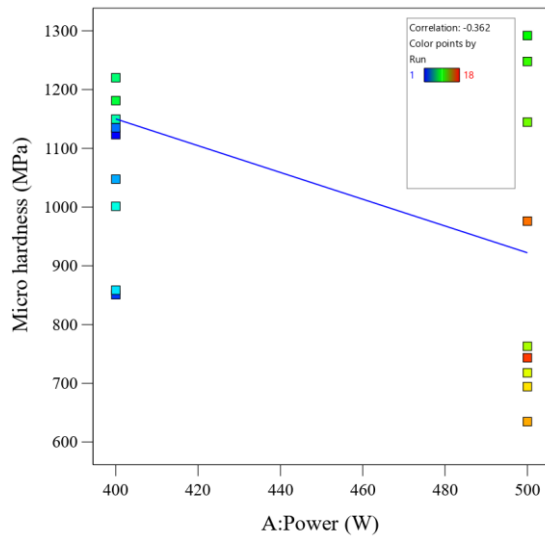


5.1.7. Pearson correlation coefficient.

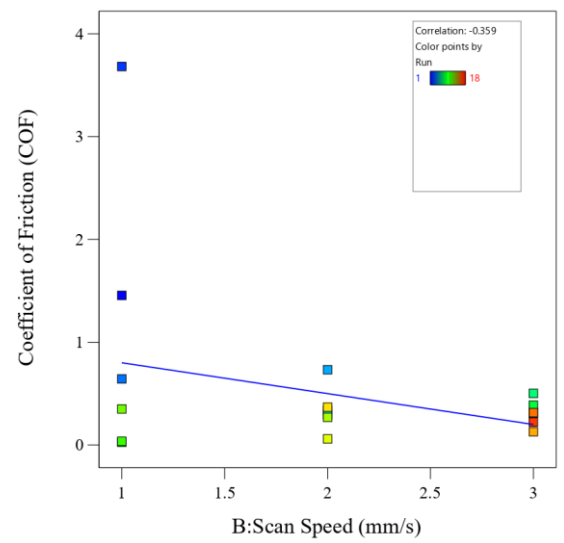
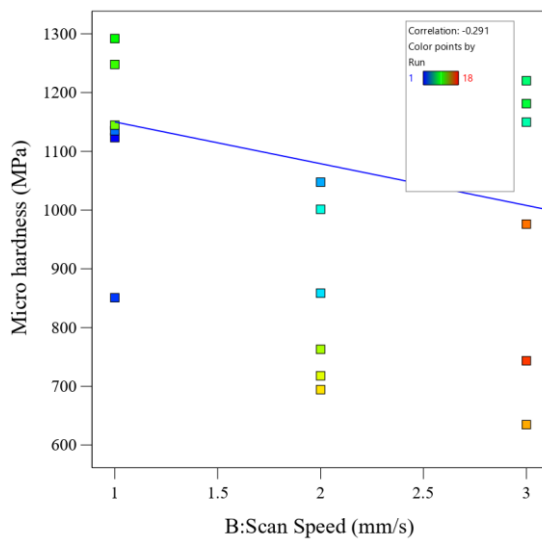
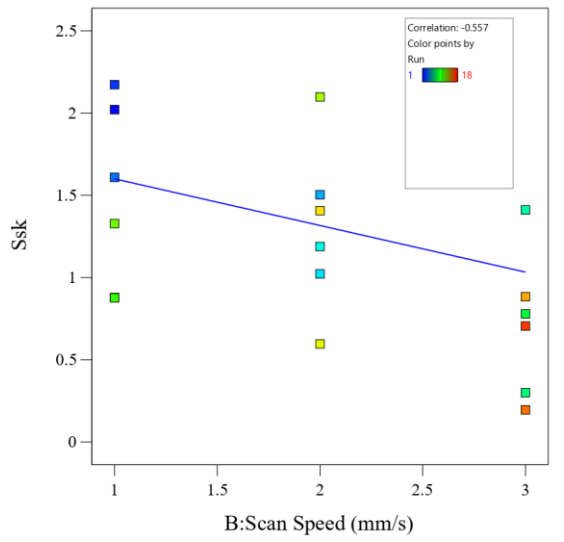
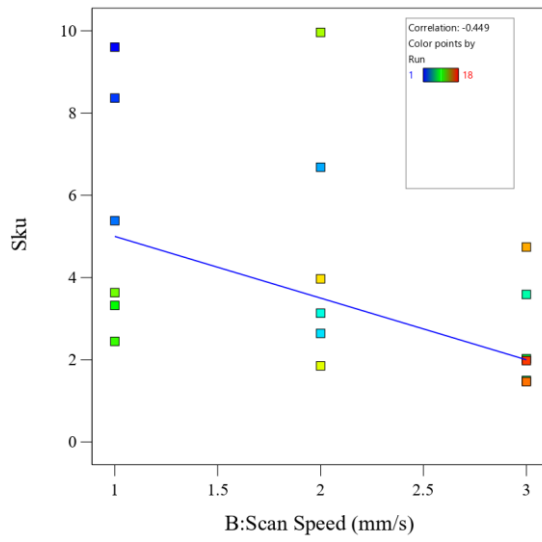
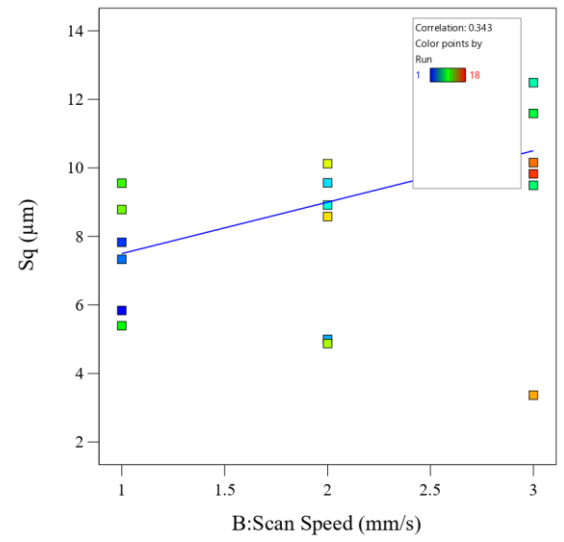
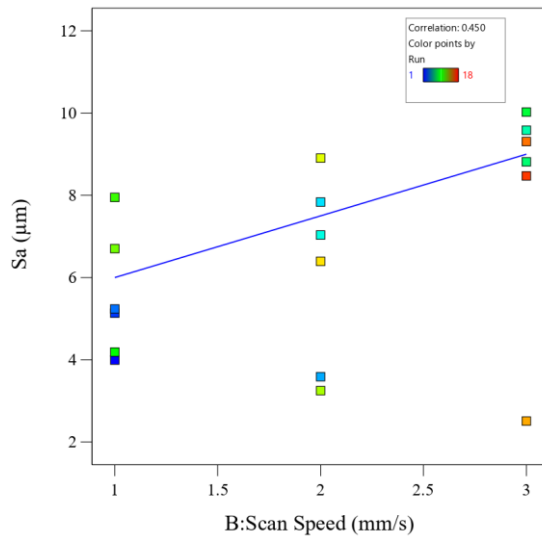
Input- Output correlation graphs- Input: Power

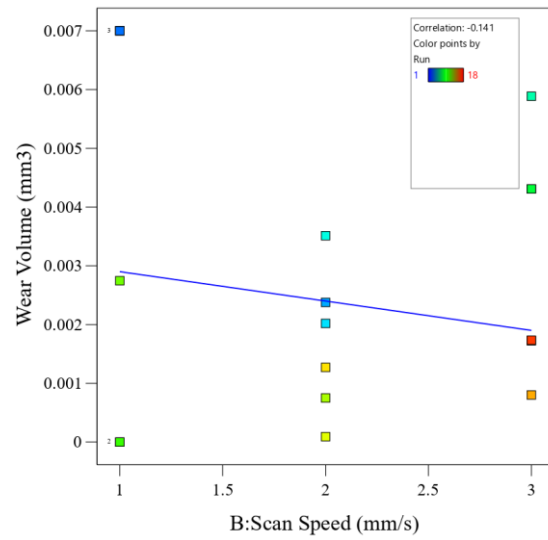




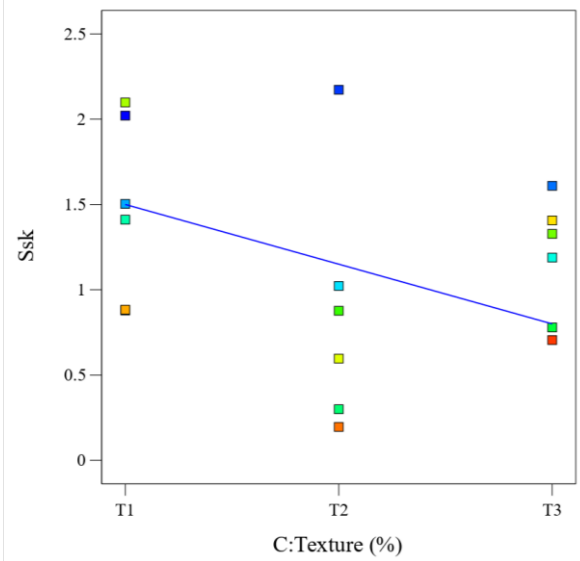
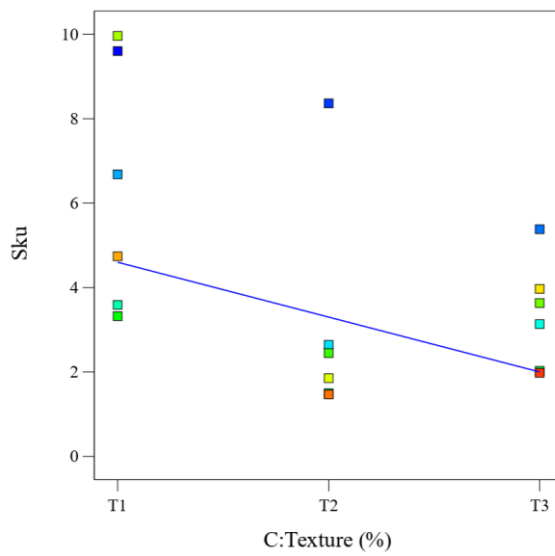
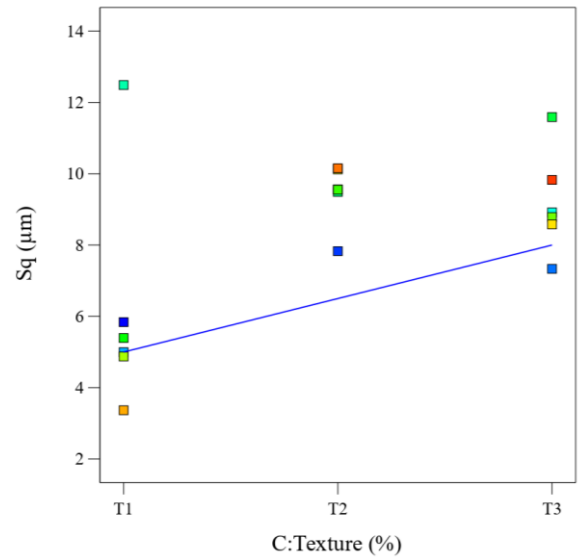
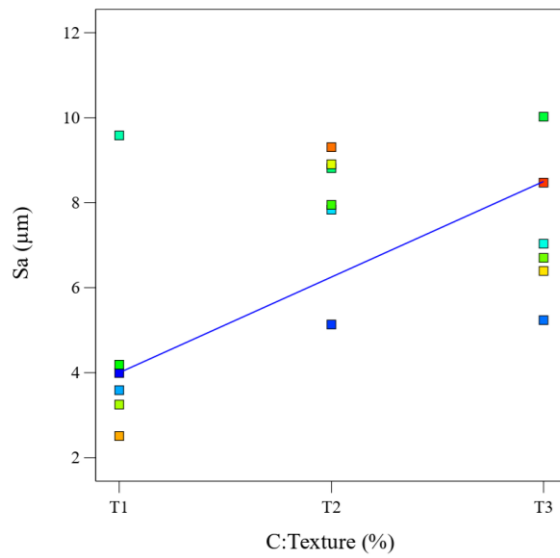


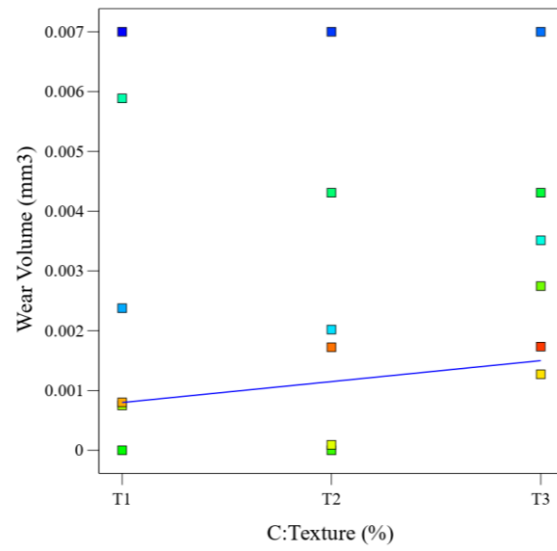
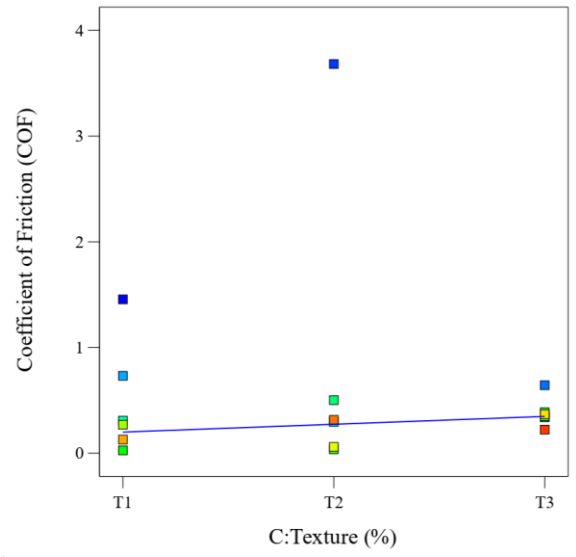
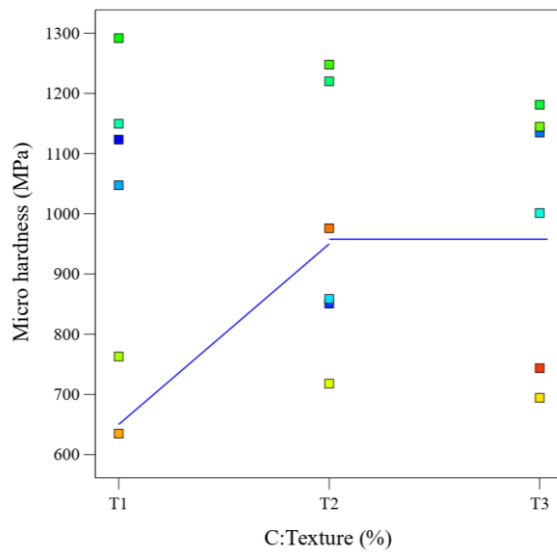
Input- Output correlation graphs- Input: Scan Speed





Input- Output correlation graphs- Input: Texture





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