

A study on surface texture and wettability of femtosecond laser treated aluminum alloys

by

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Abstract

This research aims to study the effects of femtosecond laser treatment on surface texture and wettability properties. The first portion of this research studies 2024-T3 aluminum alloy concerning surface texture (e.g., roughness), wettability, and surface free energy. SEM images help aid the researchers in detecting minuscule changes in surface texture. Profilometry extracts topographical data from the surface. A contact angle goniometer measures contact angle, which follows the sessile drop method. Owens, Wendt, Rabel, and Kaelble's method calculates the surface free energy in conjunction with the contact angle. Femtosecond laser modification produces relatively uniform surface morphology at the macroscale. When looking at the microscale, surface morphology differs depending on the interplay between material melting and self-assembly, where the surface becomes rougher after laser treatment. Contact angle results show that all but the control sample and sample 7 exhibit hydrophobic behavior, i.e., contact angle $>90^\circ$, with Sample 1 having the most significant angle of 115° . The effects of laser parameters on surface energy is apparent. More work is needed to establish correlations among these three quantities: contact angle, surface energy, and laser parameters.

The second portion of this research studies aluminum alloy 6061 as the subject material with the primary goal of creating a superhydrophobic surface. A central composite design creates the laser surface texturing design of experiments. SEM images help aid the researchers in detecting minuscule changes in surface texture. A 3D optical profiler extracts topographical data from the surface. The sessile drop method incorporates a contact angle goniometer to measure the contact angle. The response surface method builds a second-order polynomial model for the contact angle and obtains optimized parameters to maximize the contact angle. This research shows that laser surface texturing can generate a wide range of surface profiles and roughness values with geometric features ranging from hundreds of μm to submicron. All three laser parameters (pulse energy, pulse duration, repetition rate) affect surface roughness and contact angle to some degree. To quantify the relationship between the contact angle, pulse energy, and pulse repetition rate, a response surface model for Al 6061 is identified and used to find the optimal conditions of $E=214 \mu\text{J}$, $t_p=10 \text{ ps}$, and $f_p=2427 \text{ Hz}$ with a predicted maximum contact angle of 161° . A confirmation experiment produces a contact angle of 168° , in good agreement with the predicted value.

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Chapter 1 - Introduction

1.1 Background

Femtosecond laser (fs) technology is used in many industries including surgical procedures [1, 2], pulsed laser deposition [3], and surface micro/nanomodification of materials [4]. During laser micromachining, ultrashort fs laser pulses result in a minimal heat affected zone, which allows for high precision and damage-free materials processing [5]. When considering surface micro and nano modification of materials, the femtosecond laser can be an effective tool due to reproducibility and less debris contamination. When irradiating a metal surface with femtosecond laser pulses or ripples, other self-organized structures can be formed in a simple one-step process. The structures formed using femtosecond laser is usually referred to as femtosecond laser-induced periodic surface structures (FLIPSS) [6]. FLIPSS have recently been discovered and researched when micromachining. As femtosecond laser irradiation produces micro/nano modification, these surface structures are becoming more known and relevant in superhydrophobicity. Due to the complexity of the laser machining process, the exact formation and mechanisms of laser-induced surface topographies remain in question. Researchers have studied laser ablation mechanisms based on physical models and molecular dynamics simulations [5]. While the results have helped describe or predict interactions of laser and materials, they do not account for various micromachining aspects and are still not understood on a deeper level.

Industrial use of femtosecond laser surface modification ranges from a variety of applications as well as material use. Metals such as aluminum and stainless steel are used in aerospace, annular pipes, and metallic molds. Thus, experimenting with these materials is common when treating the surface with femtosecond lasers. The goal to achieve surface wettability properties of hydrophobicity/superhydrophobicity is due to its potential applications in various fields such as self-cleaning, anti-icing, drag reduction, and more [7]. Aluminum has shown exciting results after being irradiated and appears to have less regular surface micro cones than other metals such as stainless steel [5]. The varying results of surface micro cones affect the surface properties and reactions towards various testing like wettability and surface free energy factors, giving reason to study further the results of femtosecond laser treated aluminum and stainless-steel surfaces.

1.2 Research Objectives

Based on the above discussion, various approaches target the desired surface outcomes and reproducibility in surface wettability when using a femtosecond laser. The general strategy reported in the literature includes surface microstructure alteration [8] and the combination of surface texturing and surface coating/chemical treatment [9,10] to achieve either hydrophilic or hydrophobic surfaces. Research suggests that laser texturing alone can control the wettability behavior of a material through surface morphology [11]. Research in recent years seems to indicate that a hierarchical structure consisting of micro and nano features created by ultrafast lasers can display superhydrophobic behavior [12,13], like the well-known structure of a lotus leaf in nature. The key to achieving hydrophobic or superhydrophobic surfaces from slightly hydrophobic or hydrophilic materials through surface texturing is to reach the Cassie-Baxter wetting state. As illustrated in Fig. 1.1a, a hydrophobic material with a smooth surface has an intrinsic contact angle of $\theta > 90^\circ$. A textured surface typically becomes more hydrophobic ($\theta_w > \theta$) if the liquid penetrates the microgrooves, known as the Wenzel state in Fig. 1.1b. The same textured surface may become superhydrophobic ($\theta_c > 150^\circ$) if the liquid stays on top of the asperities where air pockets are trapped inside, known as the Cassie-Baxter state in Fig. 1.1c. This situation is generally true for any rough surface in contact with a liquid, and the roughness geometry determines whether the equilibrium state will be Wenzel or Cassie-Baxter. In addition, an initially hydrophilic surface can also turn into a hydrophobic surface, if put in the Cassie-Baxter state. Although there has been extensive research to study the transition between these two wetting states [14,15] and the conditions for the existence of the Cassie-Baxter state [16,17], only rough guidelines exist for the type of surface texture that could enable a stable Cassie-Baxter state. Therefore, the pathways to use surface texture to reach the Cassie-Baxter state, i.e., a hydrophobic/superhydrophobic surface, still need to be studied. Hence, this research aims to use ultrafast laser surface texturing to modify two aluminum alloys to produce hydrophobic/superhydrophobic surfaces without needing surface coating. The first section studies the metal 2024-T3 aluminum alloy concerning surface texture (e.g., roughness), wettability (e.g., contact angle), and surface free energy. The second aims to use ultrafast laser surface texturing to modify Al6061 aluminum alloy to produce hydrophobic/superhydrophobic surfaces without the need for surface coating. An optimal operating condition for laser texturing will be established to produce hydrophobic/superhydrophobic surfaces for Al6061 material.

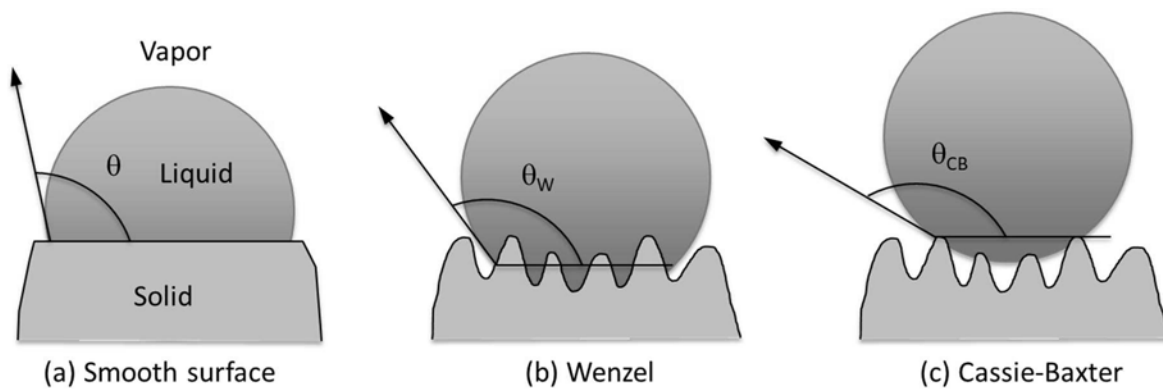


Figure 1.1 Illustrations of Liquid-Solid Wetting States for Hydrophobic Material with Different Roughness's

Chapter 2 – High Energy Femtosecond Laser Surface Modification of 2024 Aluminum Alloy

2.1 Introduction

For various classes of materials, laser ablation using femtosecond (fs) pulses enables processing with no or only minimal influence on the remaining material, especially when compared with lasers with longer pulse durations. For example, it is generally true that there is a reduction in the heat-affected zone when an fs laser is used instead of a nanosecond laser. Fs laser ablation allows texturing of material where engineers and scientists use the ablation to modify properties, such as tribological and wetting properties for a wide range of potential applications. This thesis aims to gain more knowledge on laser-treated surfaces because precise control of the surface properties remains challenging. The laser ablation process for metals with fs pulses consists of several steps beginning with the transfer of energy from photons to free electrons, diffusion and thermalization of these electrons, and a transfer of the energy to the lattice through scattering [18]. Because of the unique features of ultrashort pulse width and extremely high peak intensity, fs laser microfabrication has many definite advantages against the traditional laser processing techniques based on the longer pulse or continuous-wave lasers. Our group conducted laser peening of a 2024 aluminum alloy before to study its effect on residual surface stress, in which a laser beam directly irradiated the as-received aluminum sample surface in air without any absorption coating and transparent overlay for plasma confinement [19]. Fs laser can impart compressive residual stresses to a depth of more than 100 μm for this material, and the surface stress conditions alter significantly. However, the effects of laser peening on surface roughness and surface wetting properties in terms of contact angle and surface free energy were not the primary concern at that time.

Contact angle is the reaction of interfacial tension when a drop of liquid deposits on a solid. Once the liquid encounters the solid, it will spread on the surface based on the intermolecular interactions. Contact angle measurements appear in industries that utilize surfaces with unique functionalities such as anti-wetting, de-icing, and self-cleaning. Surfaces exhibiting hydrophilic or hydrophobic properties is favored in many applications, thus being one of the

most critical measurements to characterize surface behavior. For example, metal corrosion creates many problems economically and operationally for engineering systems like pipelines, automobiles, and naval vessels, which is caused by a surface exhibiting hydrophilic behavior [20]. Thus, moisture-repelling surfaces have many benefits, including applications in solar panels, sanitation, rust-free metals & corrosion resistance, which is caused by a surface exhibiting hydrophobic behavior [21]. Measuring the static contact angle of distilled water allows wettability factors to be known on fs laser irradiated areas. The samples' reaction to distilled water will be studied individually to indicate the wettability immediately.

Surface free energy (SFE) is the work done per unit area to produce a new surface. Surface tension is the force per unit length that causes the existence of a thin film (layer) across the surface because of cohesive forces across liquid molecules. SFE is the energy associated with the intermolecular forces at the interface between two media where the surface energy per unit area equals the surface tension. SFE is a quantitative measure of the distribution of intermolecular bonds at the air to a solid interface. Liquid systems can directly determine the SFE, equivalent to surface tension, by several experimental methods. Solid systems require indirect relationships between the contact angle and the surface tensions. Surface tension is the cohesive force of molecules at the surface of an element attracting one another to take up the least possible surface. It measures the force it takes to keep a liquid together and is the force acting over the surface of the liquid per unit length of the surface perpendicular to the force. Overall, SFE predicts solid to-liquid interactions and is essential so one can predict the behavior of any liquid on the surface by knowing the SFE. When the surface free energy of the solid is high, it is usually easily wetted by any liquid such as paints. SFE is known to be separate components of different adhesion forces.

This research aims to study the effects of operating conditions (e.g., pulse energy, beam spot size, pulse duration) on laser peening performance focusing on fs laser surface treatment and parameters. SEM is used to examine the surface microstructure. A 3D optical profiler is used to measure the area surface roughness. Specifics on wettability features hold a significant part of the contact angle goniometer method. The Owens, Wendt, Rabel, and Kaelble's (OWRK)'s model discussion concludes the explanation in the Results and Discussion section.

2.1.1 Materials Used

For this section of the thesis, the material in the study is aluminum alloy 2024-T3. This material is an excellent candidate for most processing techniques. It has high strength, and the heat-treatable alloy often offers fair corrosion resistance and a high strength-to-weight ratio [22]. This material is lightweight with a semi-smooth surface. Aluminum 2024-T3 is commonly machined to end-user specifications with typical applications in aircraft, marine, motorsports, gears, computer parts, and other commercial grade parts [23]. This alloy has copper as the primary alloying element [24].

2.1.2 Experimental Setup

Systematically in Figure 2.1 is the fs laser peening experimental setup. The high-energy fs laser can emit in a single shot mode or at a repetition rate from 10 Hz to 1 kHz. The maximum pulse energy is 100 mJ, and the pulse duration ranges from 25 fs to hundreds of fs. A shutter controls the laser exposure time of the sample, the fs laser beam focuses on the sample surface at normal incidence, and the workpiece material is aluminum alloy 2024-T3. Square samples of $38 \times 38 \times 2 \text{ mm}^3$ cut from a large plate are used in the experiments—the aluminum sample mounts on an XYZ translation stage. A laser scan pattern with 50% overlap is for the peening experiments.

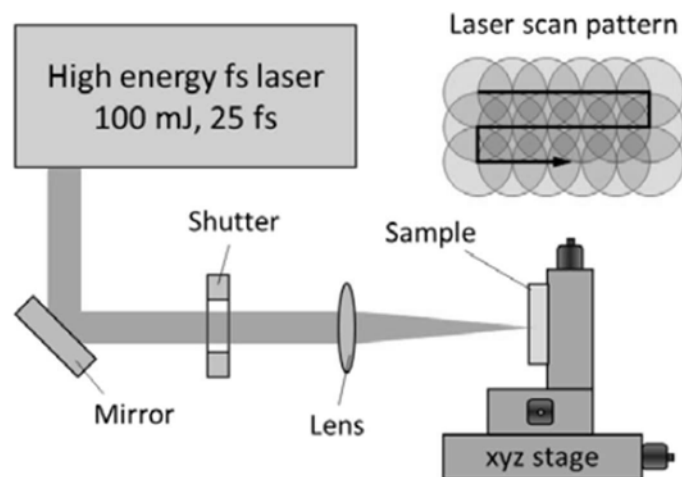


Figure 2.1 Experimental Setup and Scan Pattern for fs Laser Peening [19].

Table 1 lists the seven experiments conducted together with trial 0 for the untreated sample. The three values for pulse energy, beam spot size, and pulse duration are selected based on a single shot test matrix to find the conditions that produce good results, i.e., effective surface modification but no significant ablation. Experiments 4, 2, and 5 allow us to study the effect of pulse energy. Experiments 5, 6, and 7 demonstrate the effect of pulse duration. Experiments 1, 2, and 3 vary pulse energy and beam spot size so that laser fluence/intensity remains constant. These 8 aluminum alloy 2024-T3 samples are treated with an fs laser at various combinations of 100 to 800 fs pulse duration (t), pulse energies (E) of 25 to 75 mJ, beam diameters (D) of 400 to 560 μm , and laser intensity (I) of 3.8×10^{13} to 3.0×10^{14} (W/cm^2). Discussions are on the peening performance observations regarding surface texture, wettability, and SFE.

Table 2.1 Femtosecond Laser Peening Parameters

	Pulse Energy	Beam Diameter	Pulse Duration	Laser Intensity
Sample	E(mJ)	D(μm)	t(fs)	I(W/cm^2)
0	Control Sample - Untreated			
1	25	400	100	2×10^{14}
2	50	560	100	2×10^{14}
3	75	693	100	2×10^{14}
4	25	560	100	1×10^{14}
5	75	560	100	3×10^{14}
6	75	560	400	7.6×10^{13}
7	75	560	800	3.8×10^{13}

2.2 Experimental Methods

2.2.1 Ossila Goniometer

Contact angles give researchers an indication of how well or poorly a liquid will spread over a surface—the contact angle forms by the intersection of the liquid-solid interface and the liquid-vapor interface. The contact angle is geometric by applying a tangent line from the contact point along the liquid-vapor interface in the droplet profile [25]. Contact angles can be small or large depending on the physical properties of the solid surface. A small contact angle, $\theta < 90^\circ$, also called hydrophilic, correlates to a well-spread droplet. In contrast, a large contact angle, $\theta > 90^\circ$, also referred to hydrophobic, correlates to a droplet that does not spread well. To precisely measure the contact angle, a goniometer instrument is usually the instrument researchers use. The figures below represent the various tools used to obtain the contact angle.

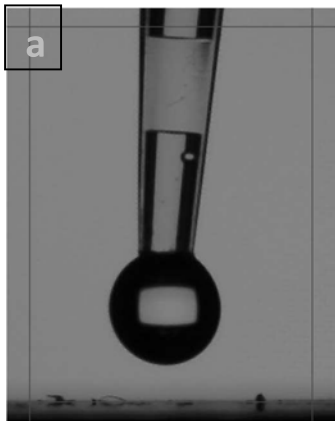


Figure 2.2 Ossila Contact Angle Goniometer

The first image (a) represents the video quality of dispensing the droplet. Image b represents the leveled platform where the sample is put and leveled before recording and analyzing the contact angle. Image (c) represents the camera used to record the video of the liquid droplet dispensed on the platform shown in the image (b).

The figure below provides a more in-depth visual of what the software displays. The software identifies three interfaces, solid-liquid (σ_{SL}), liquid-gas (σ_L), and solid-gas (σ_S). The result of this interface is the measurement of the contact angle (Θ_C).

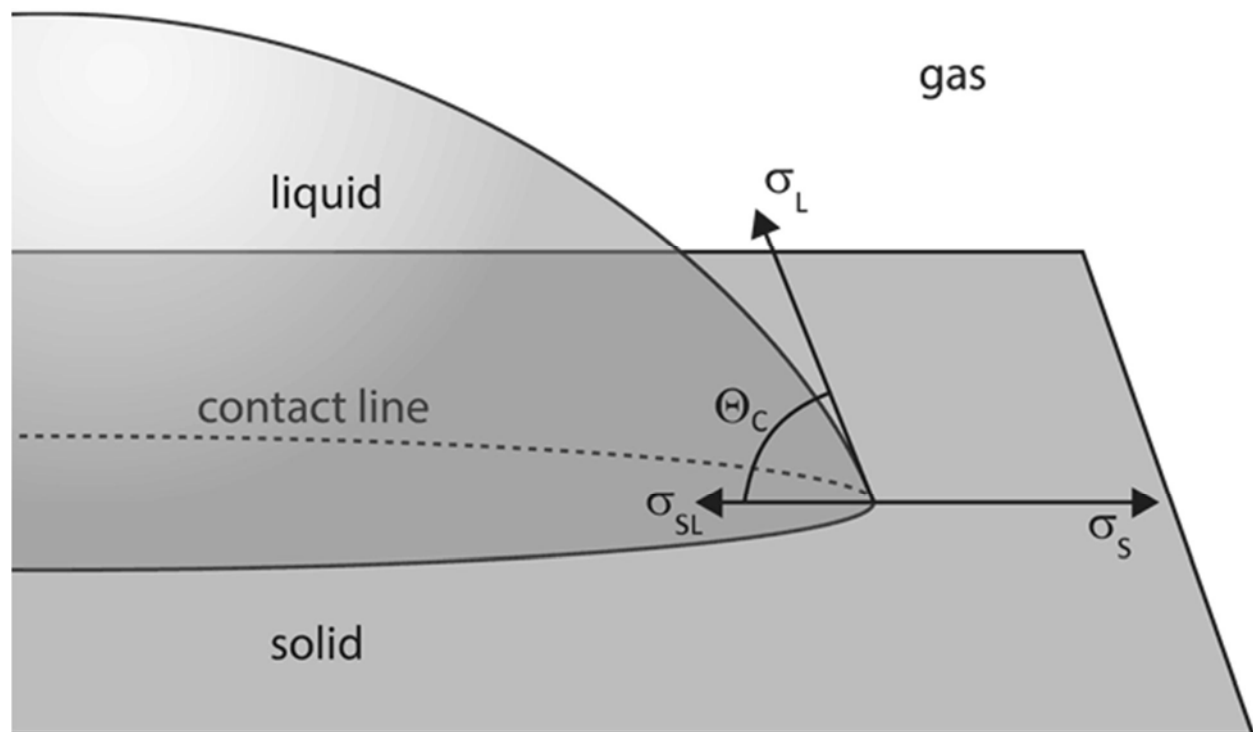


Figure 2.3 Contact Angle at a Solid-Liquid-Gas Contact Line [26]

2.2.2 OWRK Model

The measurements for the static contact angle of test liquids with known dispersive & polar components are to compute the surface energy of a solid. Those recognized dispersive & polar components are used in calculating the interfacial tension between the solid and a liquid

based on an appropriate model. This experiment uses the OWRK model, which considers the geometric mean of the dispersive and polar parts of the liquid's interfacial tension and the surface energy. Water, ethylene glycol, and thiodiglycol are used as reference liquids to test static contact angles. Each liquid has referable polar and dispersive components. Dispersive and polar interactions of liquids are to calculate the surface energy of a new surface by plotting each liquid and performing a regression analysis [27]. Determining the SFE of the solid allows for further investigation of how laser parameters affect the results.

Theories available for SFE calculations commonly divide SFE into either two or three components. The OWRK method divides SFE into two; the total SFE is the sum of dispersive and polar components. Dispersive interactions are temporary fluctuations of the charge distribution in the atoms/molecules. Polar interactions comprise Coulomb interactions between permanent dipoles and between permanent and induced dipoles, e.g., hydrogen bonds [26].

This OWRK model considers the geometric mean of the liquid's surface tension's dispersive and polar parts and the solid's surface energy. More specifically, this is a mathematical theory based on two fundamental equations. These equations describe interactions between liquid and solid surfaces. The equations are as follows:

Good's Equation

$$\sigma_{SL} = \sigma_S + \sigma_L - 2\sqrt{(\sigma_S^D \sigma_L^D)} - 2\sqrt{(\sigma_S^P \sigma_L^P)} \quad (1)$$

Young's Equation

$$\sigma_S = \sigma_{SL} + \sigma_L \cos(\theta) \quad (2)$$

The notations for the above equations are: σ_L = overall surface tension of the wetting liquid, σ_L^D = dispersive component of the interfacial tension of the wetting liquid, σ_L^P = polar component of the interfacial tension of the wetting liquid, σ_S = overall interfacial energy of the solid, σ_S^D = dispersive component of the interfacial energy of the solid, σ_S^P = polar component of the interfacial energy of the solid, σ_{SL} = the interfacial tension between the solid and the liquid, and θ = the contact angle between the liquid and the solid.

Upon research, the developers of the OWRK method in combination with the Good's equation and the Young's equation work together to obtain an equation that has a linear form. The combination of the two results in:

$$\frac{\sigma_L (\cos\theta + 1)}{2(\sigma_L^D)^{\frac{1}{2}}} = (\sigma_S^P)^{\frac{1}{2}} \frac{(\sigma_L^P)^{\frac{1}{2}}}{(\sigma_L^D)^{\frac{1}{2}}} + (\sigma_S^D)^{\frac{1}{2}} \quad (3)$$

Due to the linear form of this combined equation, it is broken down into subsections:

$$y = \frac{\sigma_L (\cos\theta + 1)}{2(\sigma_L^D)^{\frac{1}{2}}} \quad (4a)$$

$$m = (\sigma_S^P)^{\frac{1}{2}} \quad (4b)$$

$$x = \frac{(\sigma_L^P)^{\frac{1}{2}}}{(\sigma_L^D)^{\frac{1}{2}}} \quad (4c)$$

$$b = (\sigma_S^D)^{\frac{1}{2}} \quad (4d)$$

From this, a regression line for determining the SFE is the result. To explain the regression line for determining the SFE, Y and X contain the known quantities, namely the measured contact angle and the dispersive and polar parts of the liquid's surface tension. The dispersive and polar parts for the solid are in the axis intercept b and in the slope m, respectively [28].

The accuracy of the result with a regression line based on just two points contains no information, thus contact angle measurements with at least three test liquids. The use of diiodomethane, ethylene glycol and thiodiglycol as test liquids yields satisfactory results [29].

The average contact angle for each liquid along with the total SFE, polar and dispersive parts are in the equation to calculate the coordinates. The total SFE (γ), polar (γ^p) and dispersive (γ^d) components for each liquid are gathered from [29] and [30].

Table 2.2 Polar and Dispersive Components of Each Liquid

Component	Liquid			
	Water	Diiodomethane	Ethylene Glycol	Thiodiglycol
σ_L	72.6	50.8	48.8	54
σ_D	21.8	49.5	32.8	38.5
σ_P	50.8	1.3	16	15.5

By using the table above as a guide for calculating the coordinates and the respective contact angles, the following equations can be used to determine the 2-dimensional data points.

$$Y = \frac{\sigma_L (\cos\theta + 1)}{2\sqrt{\sigma_L^D}}$$

$$X = \frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}}$$

2.3 Results and Discussion

2.3.1 Surface Texture

The figure below shows SEM images of laser-treated surfaces for all trials. Sample 5 with 75 mJ, 560 μm , and 100 fs has the most uniform surface morphology, consisting of micron-sized fused particles after laser irradiation—the uniformity by the optical image of Sample 5 shows confirmation of the surface spanning several millimeters. In comparison, Sample 3 has a beam spot size of 693 μm . The surface morphology is similar to that of Sample 5 but smaller particle size and less uniform distribution. When pulse energy decreases to 25 mJ, Sample 4 shows a sufficient particle size but wavy surface morphology. The effect of pulse duration is shown by comparing Sample 5 and Sample 7. With the pulse duration at 800 fs, the surface becomes nonuniform, and signs of melting appear with large, fused particles scattered over the surface. The most uniform surface is Sample 5 by using the highest laser intensity.

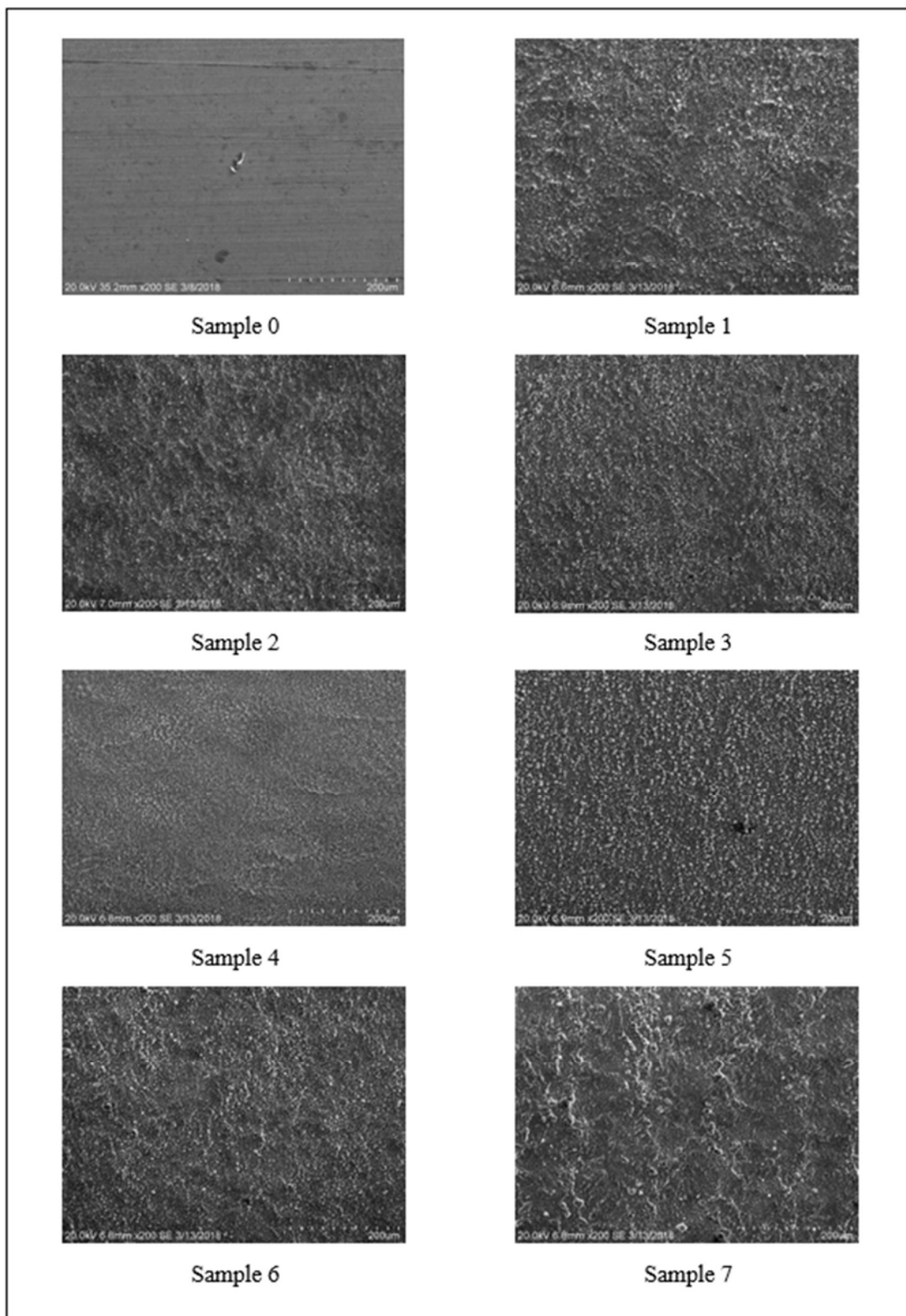


Figure 2.4 SEM Images

The figure below represents 3D profilometer topography images of each sample. Sample 0 is the untreated surface. From the results of the 3D profilometer, sample 0 exhibits the lowest values for the total surface area (μm^2), arithmetic mean height (μm), and skewness while exhibiting the highest value for kurtosis. Skewness measures the surface height distribution area's symmetry, with low values representing a cup-like surface structure. Kurtosis is a measurement of the surface peaks and curves with high values equating to more high peaks. Sample 5 has the highest value for the total area, followed by sample 6 and then sample 7; these results relate to the sample's pulse duration values, with sample 5 being the lowest at 100 fs, sample 6 at 400 fs, and sample 7 at 800 fs.

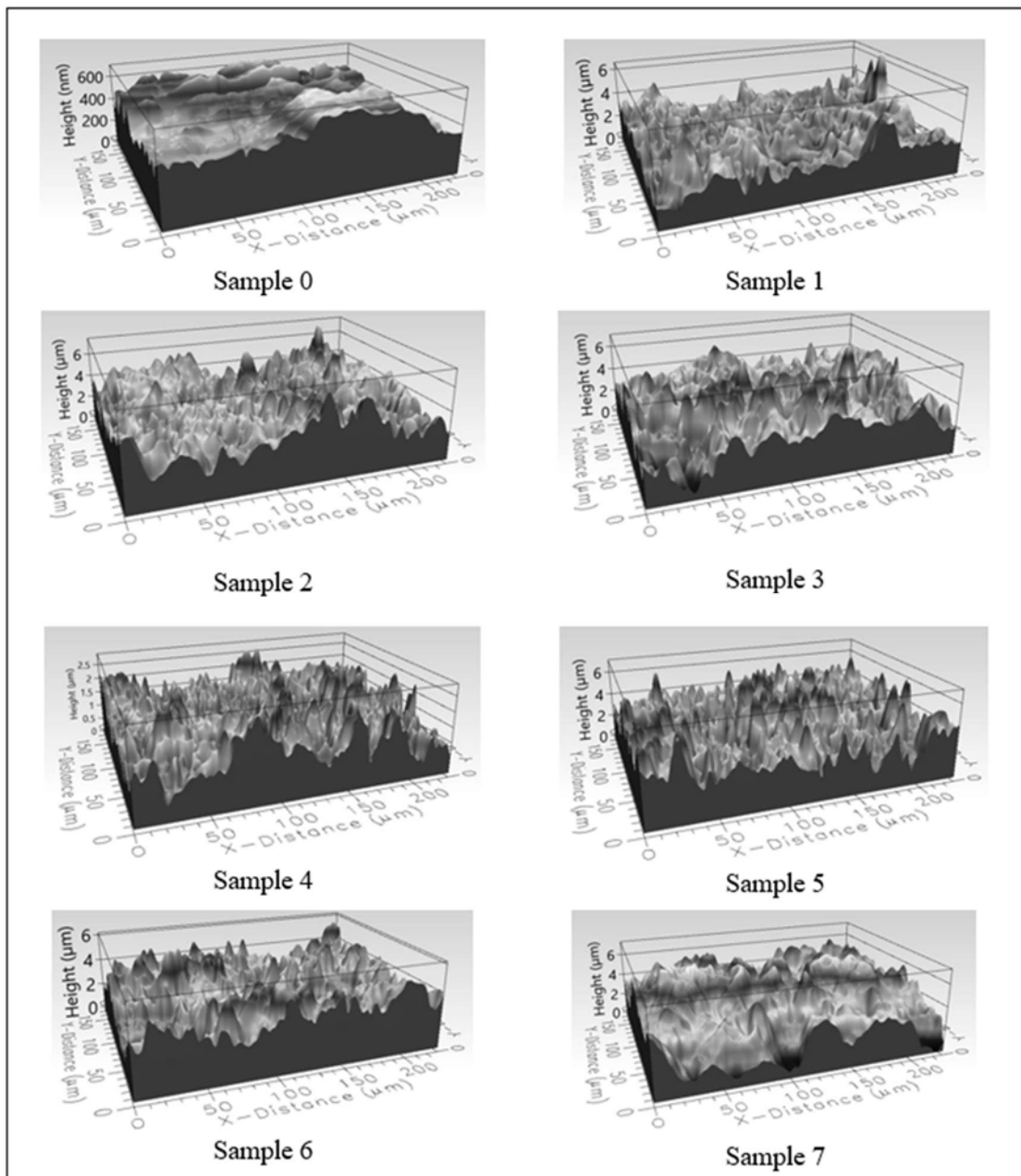


Figure 2.5 3D Profilometer Area Roughness Values

The graph below shows the trend between pulse energy and area surface roughness, gathered from 3D profilometer results. The numerical values are an average of three scans done in varying locations to represent the samples accurately. In summary, as the pulse energy increases, the area surface roughness value also increases.

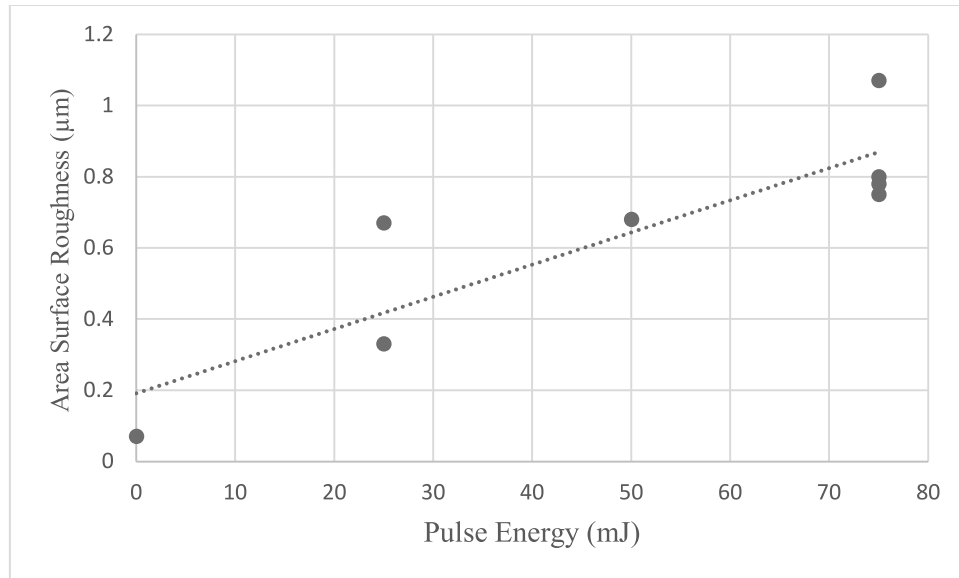


Figure 2.6 Area Surface Roughness vs. Pulse Energy

2.3.2 Wettability

For each liquid, three droplets were dispensed and recorded. Of these three measurements, the average is the reference. The figure below shows an image of a 2uL water droplet. The images presented are the median of the three measurements taken.

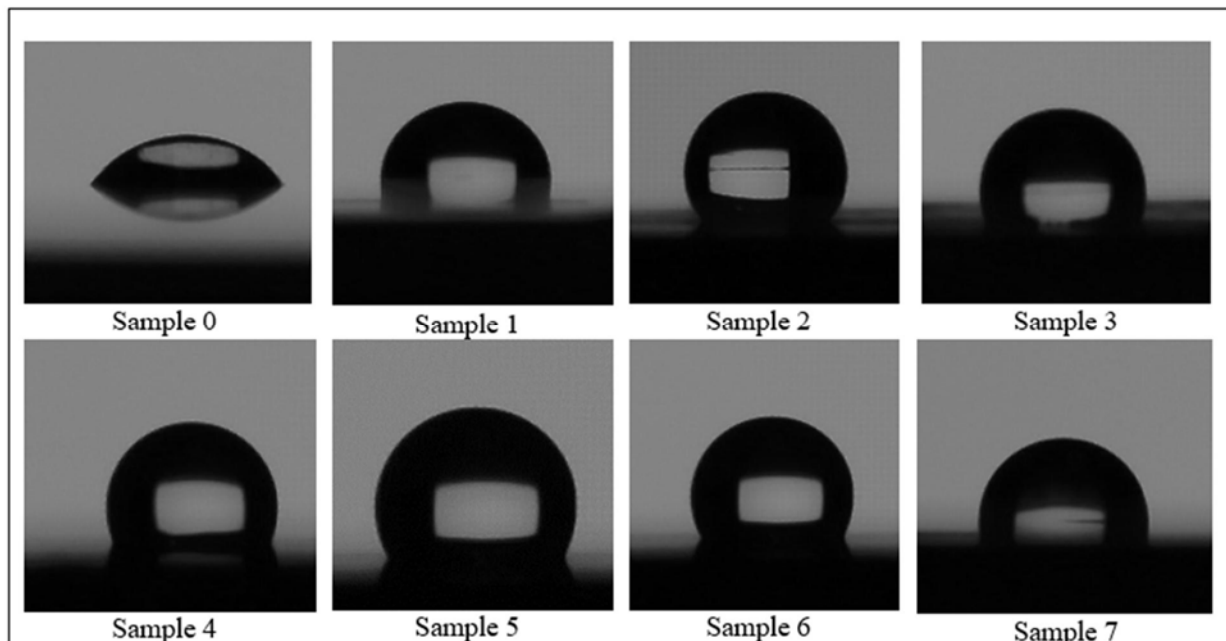


Figure 2.7 Droplet Images for Distilled Water

Figure 2.8 represents the contact angle on the aluminum samples corresponding to the four different liquids. All eight samples contain the same reaction towards thiodiglycol with a contact angle of 0°. The distilled water results are hydrophobic for all samples except for samples 0, untreated, and 7, which undergoes the highest pulse energy and most prolonged pulse duration.

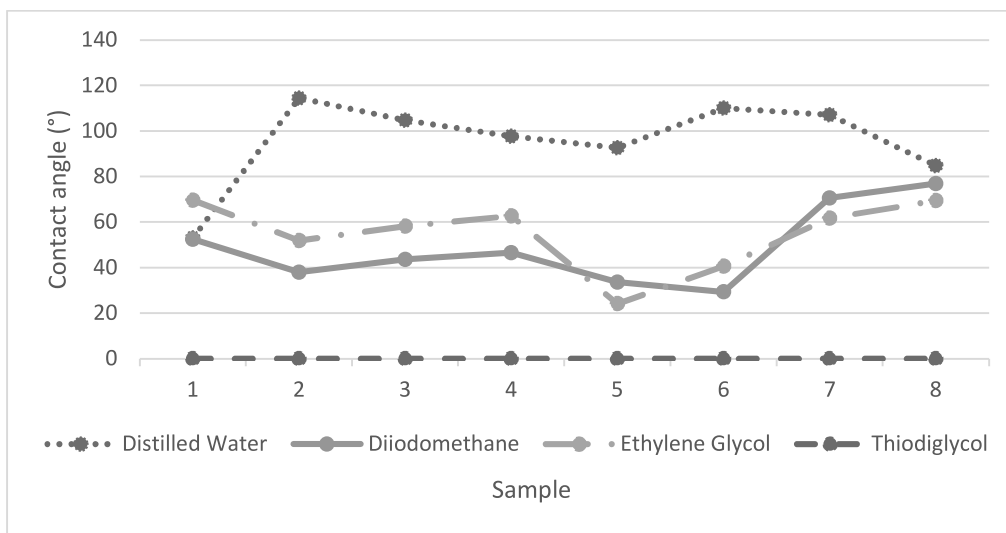


Figure 2.8 Contact Angles

An interesting trend can be seen for samples 6 and 7 when observing the contact angle for predominant polar liquid versus dispersive predominant liquid. The dominant polar liquid, distilled water, shows sample 6 contact angle higher than sample 7. The dispersive dominant liquids, diiodomethane and ethylene glycol, shows sample 7 with a higher contact angle than sample 6. Samples 6 and 7 undergo the highest levels of pulse energy.

2.3.3 Surface Free Energy

The following figure exhibits the results of the coordinate calculation for the liquids used in the study to form a regression line.

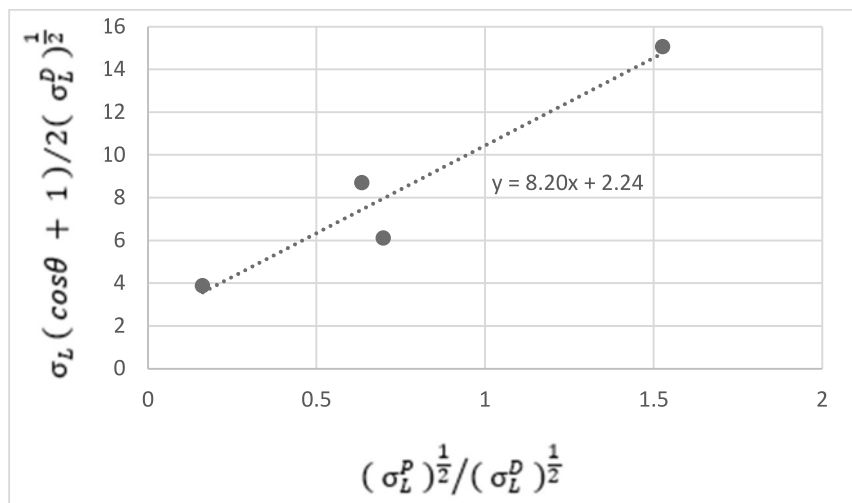


Figure 2.9 Regression Line to Determine Surface Energy

The regression between the points allows a linear equation to form based on the associated trend line. Rearranging equations 4b and 4d in the *OWRK* subsection of 2.2.2, the variables m and b are:

$$\sigma_S^P = \sqrt{m}$$

$$\sigma_S^D = \sqrt{b}$$

The two equations now have the suitable number of known variables to compute the polar and dispersive components of SFE. Figure 2.10 shows the calculated SFE values for each sample. It can be seen that the SFE of a laser treated sample can be smaller or larger than that of the untreated sample depending on the laser parameters.

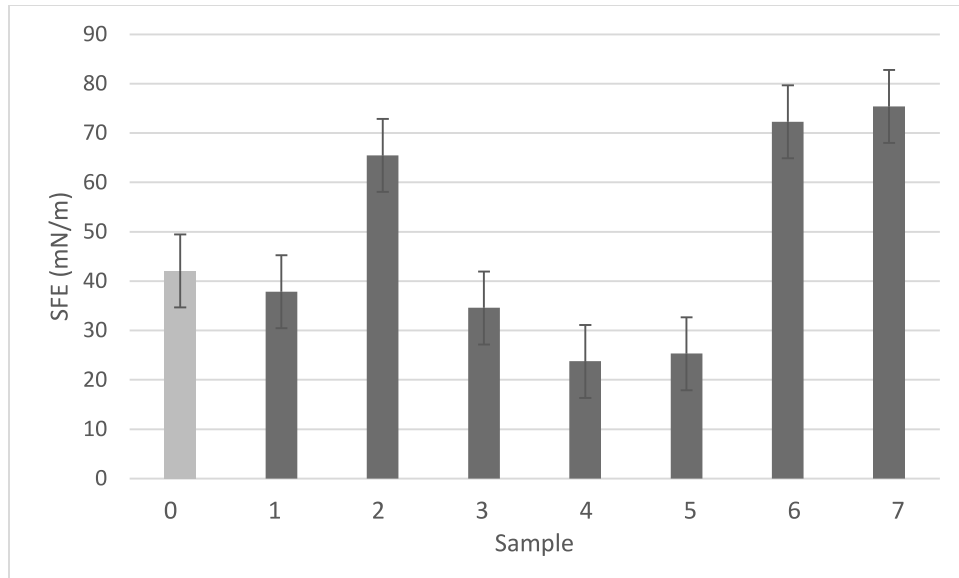


Figure 2.10 OWRK Model SFE Calculation Results

2.4. Conclusions

In this study, the surface texture and surface wetting properties of fs laser peened 2024-T3 aluminum alloy samples are investigated. The findings from this work are summarized below.

- Femtosecond laser modification produces relatively uniform surface morphology at the macroscale. At the microscale, surface morphology differs depending on the interplay between material melting and self-assembly. Melting is most apparent in this study's most prolonged pulse duration of 800 fs. Sample 4 has comparable surface roughness with the untreated sample. The surface becomes rougher after laser treatment.
- Contact angle results show that all but the control sample and Sample 7 exhibit hydrophobic behavior, i.e., contact angle $>90^\circ$, with Sample 1 having the most significant angle of 115° . Sample 7 was treated with the most prolonged pulse duration of 800 fs, while Sample 1 underwent the lowest values for all laser parameters.
- Surface-free energy for the laser-treated samples is determined using the OWRK model. The effects of laser parameters on surface energy are apparent. More work is needed to establish correlations among these three quantities: contact angle, surface energy, and laser parameters.

Chapter 3 – Wettability Study of Femtosecond Laser Textured 6061 Aluminum Alloy

3.1 Introduction

This research project is sponsored by industry and conducted by a team in the Department of Industrial and Manufacturing Systems Engineering at Kansas State University. This section of the thesis documents work and results from a portion of this project; most are efforts by the author of this thesis.

A current over-molding process at the sponsor's facility uses a carcinogen as the mold release agent, a health hazard. In addition, the mold release also builds up on specific areas of the mold, resulting in dimensional failures of the molded parts. Hence, the sponsor is interested in reducing or eliminating the use of the carcinogen mold release. This research aims to develop a laser surface texturing technique to create a superhydrophobic mold surface made of 6061 aluminum alloy, assuming that a superhydrophobic surface would also be phobic to the polymer currently being used at the sponsor's facility. Because surface oxidation after laser treatment often turns the surface to superhydrophilic, low temperature annealing is chosen as the next step after laser texturing to avert this adverse effect. A fundamental understanding of the laser texturing process and the wettability property relationship is key to optimizing the laser parameters. The approach uses a central composite design of experiments and response surface analysis to study the effects of laser treatment on the contact angle, a measure of the wettability property. The response surface analysis will offer directions to maximize contact angle by optimizing laser parameters.

3.2 Experimental Methods

3.2.1 Research Workflow

The overall research workflow is described as follows: The workflow starts with laser surface texturing through the central composite design of experiments. The textured samples undergo geometric observations using a 3D profiler and microstructurally using SEM microscopy. Next, the samples undergo low temperature annealing at 200 °C for 2 hours. The surface wetting property is examined through contact angle measurements using the Ossila

Goniometer described in *Chapter 2*. To understand the laser surface texturing process, the following interrelationships between (1) effects of laser parameters on surface texture (2) effects of laser parameters on surface roughness (3) effects of laser parameters on wettability, and (4) effects of surface roughness on wettability are investigated. Finally, the response surface method aids to optimize the laser parameters to maximize the contact angle.

3.2.2 CCD and Laser Processing Conditions

Central composite designs (CCD) are the most used response surface methodology. CCD is a factorial or fractional design with center points, augmented with a group of axial points (also known as star points) that let one efficiently estimate the first and second-order terms [35]. A CCD always contains twice as many axial points as there are factors in the design [34]. Axial points represent new extreme values (low and high) for each factor in the design. CCD is used in this research to determine the best conditions of laser parameters to produce superhydrophobic surfaces. The specific type of CCD used in this research is face-centered. For face-centered CCD, star points are at the center of each face of the factorial space. This variety contains five levels for each factor. The figure below visually represents the face centered CCD.

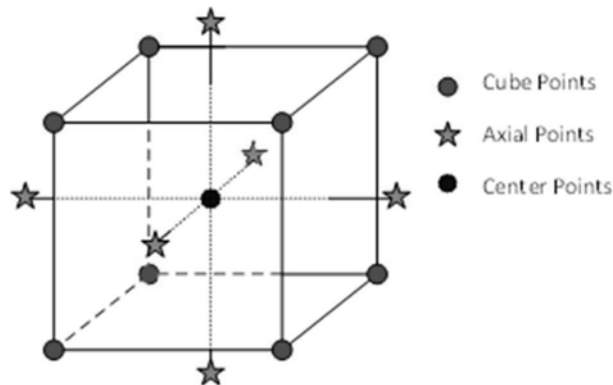


Figure 3.1 Face Centered CCD Design

The factors are pulse energy, pulse duration, and pulse repetition rate. Pulse energy, E (μJ), is the total optical energy content within a pulse. Pulse duration, t_p (ps), is the duration of the laser pulse emitted on the sample. Pulse repetition rate, f_p (Hz), is the frequency of pulses. These three factors are laser parameters that have a greater impact on the outcome of the surface than other laser parameters.

The five factor levels in the CCD design are determined by the capability of the laser and some preliminary laser surface texturing experiments. For each of the three factors of the CCD design, the five levels are determined by multiplying the center point values by -1.68, -0.68, 0, 0.68, 1 for the factor levels of lowest, low, center, high, and highest, respectively. Table 3 below lists the three factors and five levels for each factor.

Table 3.1 CCD Factor and Factor Levels

Factors	Factor Levels				
	Lowest	Low	Center	High	Highest
E (μJ)	50	120	225	330	400
tp (ps)	0.184	2	5	8	10
fp (Hz)	400	1130	2200	3270	4000

This design has three sets of points: axial, cube, and center. Axial points represent the factor levels from the center value to the lowest or highest values for each factor, resulting in 6 different points; these points are run orders 1, 3, 8, 9, 10, and 19 in Table 3.2. Cube points represent the low and high factor levels resulting in 8 different points; these points are 2, 4, 7, 13, 14, 15, 18, and 20 in Table 4. Center points represent the factor level center and are repeated 6 times throughout; these points are 5, 6, 11, 12, 16, and 17 in Table 3.2. Run order 0 represents the as-received sample that is free from any laser treatment.

Table 3.2 CCD Laser Conditions

RunOrder	E (μJ)	tp (ps)	fp (Hz)
1	50	5	2200
2	330	2	1130
3	225	5	4000
4	120	8	3270
5	225	5	2200
6	225	5	2200
7	120	2	3270
8	225	0.184	2200
9	225	5	400
10	400	5	2200
11	225	5	2200
12	225	5	2200
13	330	8	1130
14	330	8	3270
15	330	2	3270
16	225	5	2200
17	225	5	2200
18	120	2	1130
19	225	10	2200
20	120	8	2200

3.2.3 Experimental Procedure

The experimental setup for laser surface texturing is schematically shown in Figure 3.2. The ultrafast laser has pulse durations ranging from 184 fs to 10 ps. Pulse energy is adjusted by a half-wave plate and a cube polarizer. A focusing lens concentrates the pulse energy to a focal spot on the sample surface—the sample on a motorized xyz stage, controlled by the computer. As shown in the figure below, surface texturing is done through a continuous laser scan in the horizontal direction with constant stepping in the vertical direction. Figure 3.2a is the schematic of the laser surface texturing experimental setup, while 3.2b is the laser scan pattern.

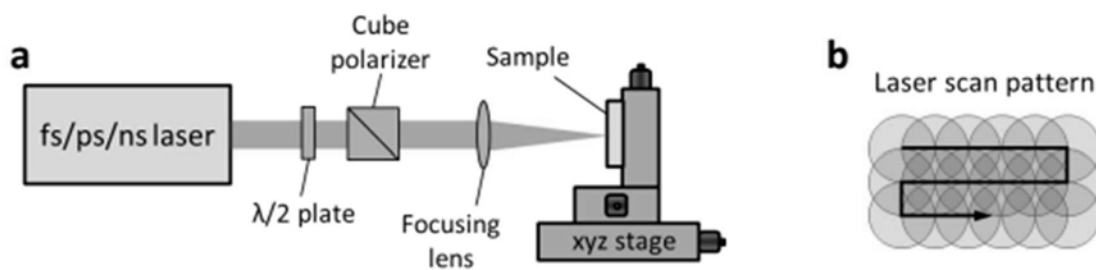


Figure 3.2 Femtosecond Laser Surface Texturing Experimental Setup

The sample material is aluminum alloy 6061, a precipitation-hardened aluminum alloy containing magnesium and silicon as its major alloying elements [31]. This material has good mechanical properties, exhibits good weldability, and is one of the most common aluminum alloys for general-purpose use. Aluminum alloy 6061 is one of the most versatile of the heat-treatable alloys and is popular for medium to high strength requirements, exhibiting good toughness characteristics [32]. Its applications range from transportation components to machinery and equipment applications while exhibiting excellent corrosion resistance to atmospheric conditions [32].

Laser surface texturing experiments conducted follow the CCD design as described in Section 3.2.2. To shorten the time required for metal's wettability transition from hydrophilicity to superhydrophobicity without requiring the use of any chemical coating process, an additional process of annealing [33 -34] is introduced. Annealing is performed in a conventional oven under ambient air at 200°C for 2 hours. The samples are treated usually within one day after laser surface texturing. No cleaning is done to the samples before annealing.

Scanning electron microscope (SEM) images of the samples are obtained by scanning the surface with a focused beam of electrons. The electrons interact with atoms of the samples, which produces various signals that contain information about the surface morphology. A 3D optical profiler is used to gather surface roughness values of the 20 samples. The instrument's software can measure up to 27 different surface roughness parameters. Five roughness parameters will be recorded:

1. The total surface area from 3D scanned images is known as Star in mm^2 units.
2. Arithmetic mean height expresses the absolute value of the difference in the height of each point compared to the arithmetical mean of the surface scanned, known as Sa in μm units.
3. Root mean square roughness, equivalent to the standard deviation of peak heights, is known as Sq in μm units.
4. Skewness, which measures the surface height distribution areas symmetry with low values representing a cup-like surface structure, known as Ssk.
5. Kurtosis, which is a measurement of the surface peaks and curves with high values equating to more high peaks, known as Sku.



Figure 3.3 3D Profiler Scan Location

Appendix C shows the five surface roughness parameters for Al 6061. On the samples, the measurements are from the center. Figure 3.3 shows the laser-processed area in gray with the untreated area in blue, where the symbol at the center of the laser-treated area represents the locations of the 3D scan. The images are taken with a 50x lens and zoom factor of 1, representing an area of $400 \times 340 \mu\text{m}^2$.

A standardized method was used during each measurement to gather surface wettability data. Prior to annealing, the wettability of the sample was measured daily once treated by the fs laser. As time passed, these measurements became weekly, with slight change detected. Before annealing, the wettability of the sample was measured in three separate locations with a

deionized water droplet of 2 μL . The purpose of measuring in three separate locations was to determine if the wettability remained consistent throughout the treated surface. The figure below shows a visual of where the three separate locations were throughout all samples of Al 6061.



Figure 3.4 Droplet Locations to Measure Wettability

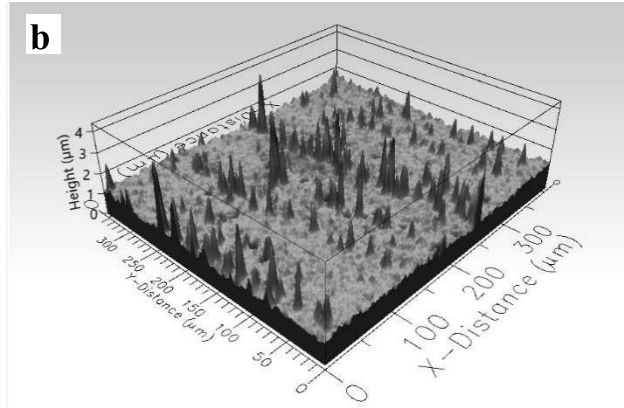
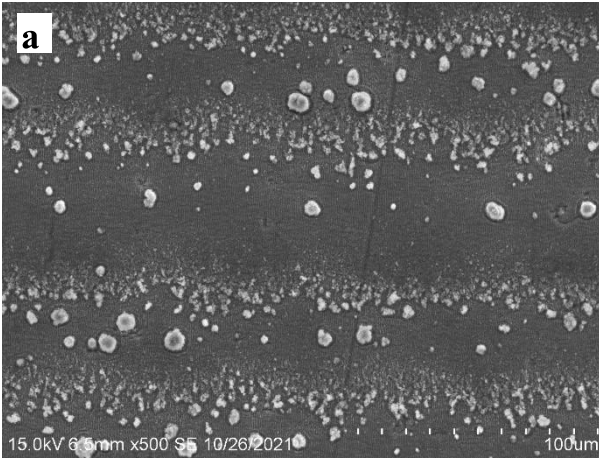
The instrument used was the Ossila Contact Angle Goniometer to measure the wettability of each surface and described in Chapter 2 under *Experimental Methods, Ossila Goniometer*. After annealing, the water droplet size increased to 10 μL based on the behavior of the 2 μL droplet. The location of these measurements corresponds to the blue dot, the center point, in Figure 3.4. Appendix D shows a complete graph of the contact angle, after annealing, over time for Al6061.

3.3 Results and Discussion

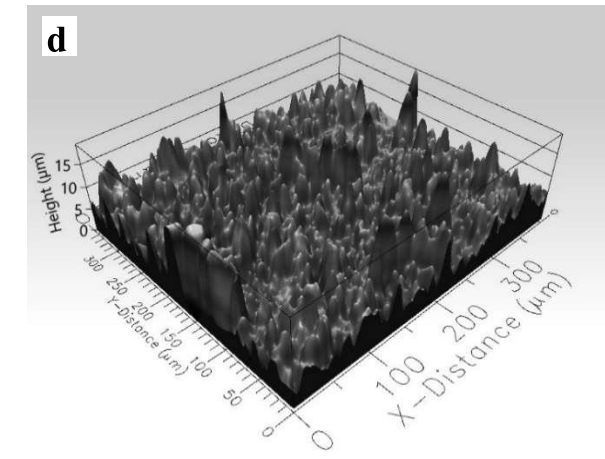
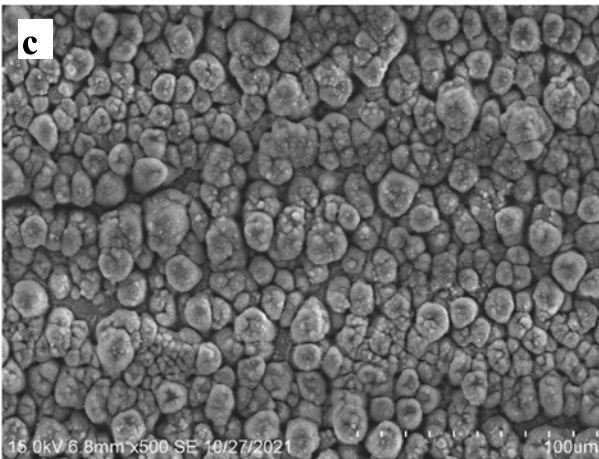
The purpose of this section is to learn about laser parameters, surface microstructure, surface roughness, and wettability to see if there are any correlations. First, conditions relating to one factor at a time are selected based on the CCD design. One of the laser parameters will change by exploring one factor at a time. In contrast, the other two laser parameters remain at a fixed reference value (e.g., pulse energy at 225 μJ , pulse duration at 5 ps, and pulse repetition rate at 2200 Hz). Discussion is following cause-effect relationships: effects of laser parameters on surface texture, effects of laser parameters on surface roughness, effects of laser parameters on the contact angle, and effects of surface roughness on contact angle. Second, utilizing all the 20 test runs from the CCD design, response surface analysis will be used to establish a regression model relating laser parameters to contact angle.

3.3.1 Effects of Laser Parameters on Surface Texture

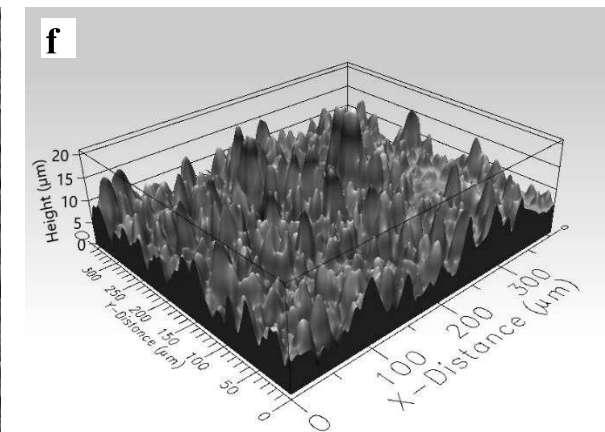
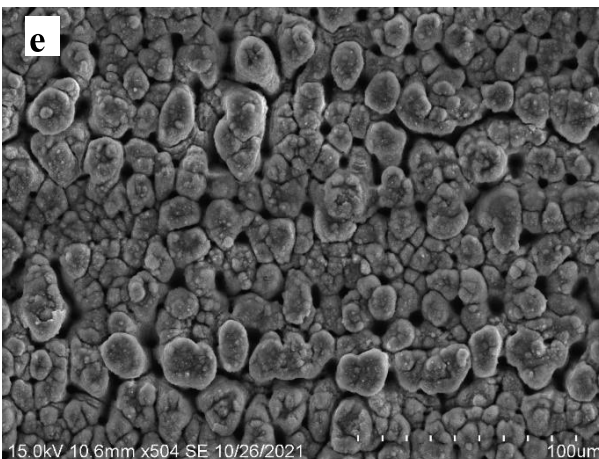
Surface textures presented in this section represent the wide range of surface morphology and profiles created in this study. Each experiment's SEM images and optical profiles are in Appendices A and B. These samples are grouped here to show the effects of the three laser parameters. Figure 3.5 shows three SEM images of laser textured Al6061 samples and the corresponding 3D profile images, with increasing pulse energy while keeping the other two parameters constant (e.g., pulse duration at 5 ps and pulse repetition rate at 2200 Hz). As the pulse energy increases, the number of asperities also increases, as seen in Figures 3.5b, 3.5d, and 3.5f. When the pulse energy is at 50 μJ there are few growths on the sample ranging from 1 μm to 3.5 μm in height. As pulse energy increases to 400 μJ , the surface not only has growth ranging from 5 μm to 20 μm but also has more material being displaced or ablated. The particle size appears to increase in proportion with pulse energy. At the highest pulse energy of 400 μJ , Al6061 appears to have columnar growth and splitting compared to the lowest pulse energy of 50 μJ , which appears to have little displaced material or ablation, as shown in Figures 3.5a and 3.5e. Multiscale features down to submicron levels are induced on the surface by laser irradiation.



(a) SEM Image and (b) 3D Profile of an Al6061 sample modified with pulse energy of 50 μJ



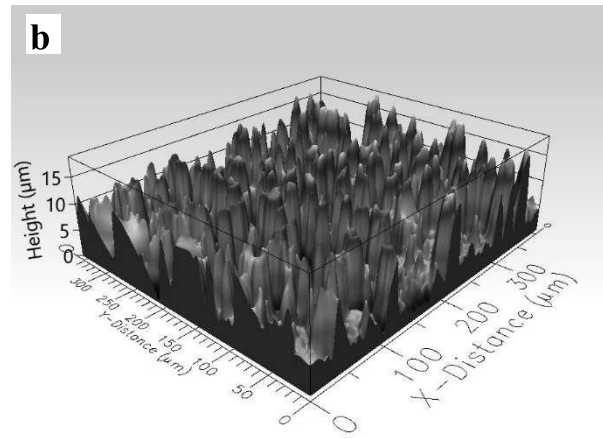
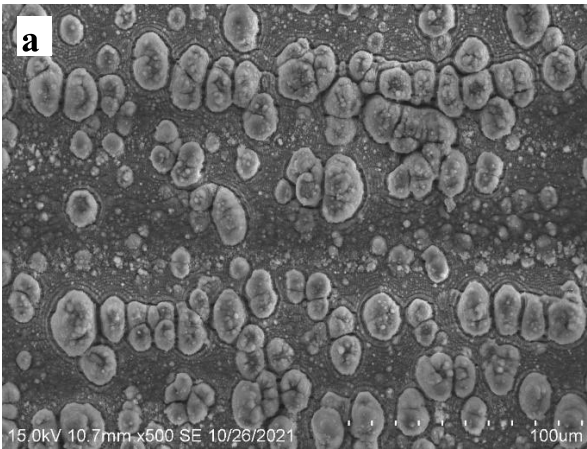
(c) SEM Image and (d) 3D Profile of an Al6061 sample modified with pulse energy of 225 μJ



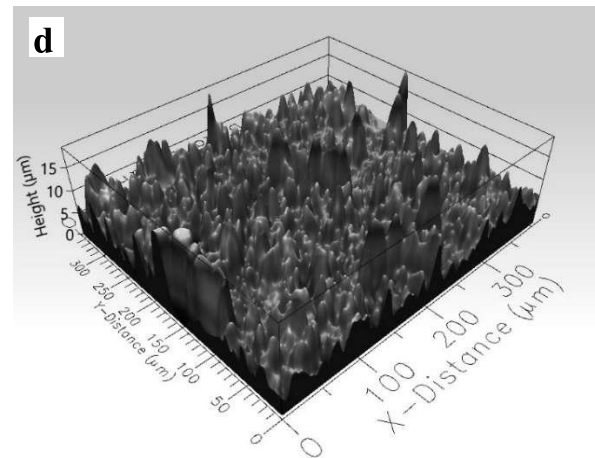
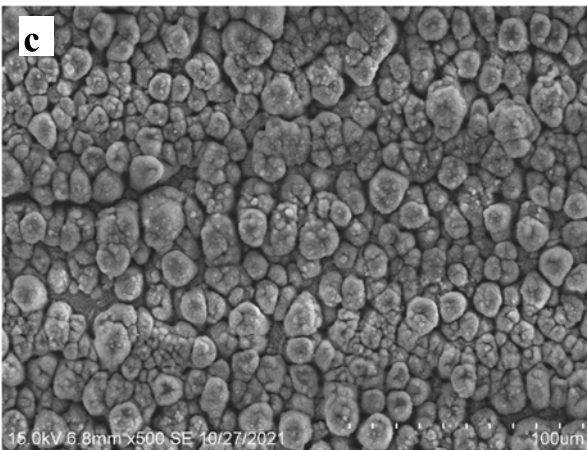
(e) SEM Image and (f) 3D Profile of an Al6061 sample modified with pulse energy of 400 μJ

Figure 3.5 Effects of Pulse Energy on Surface Texture, Al6061

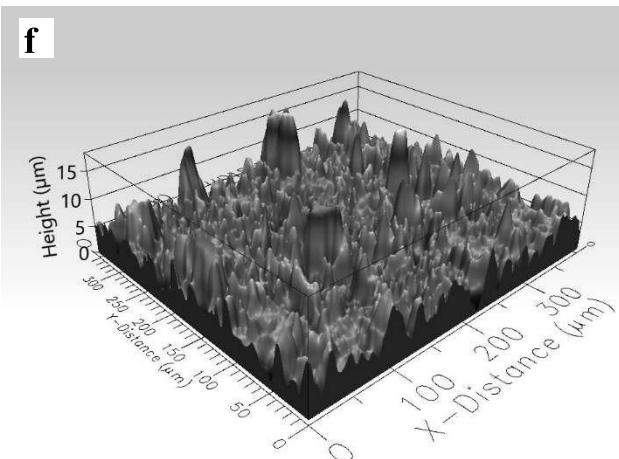
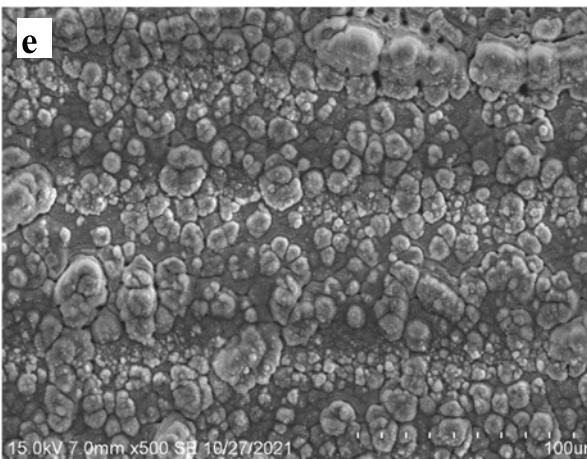
Figure 3.6 shows the SEM images and the 3D surface profiles for three laser textured surfaces of Al 6061. Of these images, pulse duration increases from 0.184 ps to 10 ps. Pulse duration shows an exciting trend, unlike that of the pulse energy. It appears that the pulse duration effect plateaus at 5 ps. To further explain, Figure 3.6a and Figure 3.6e are far more like each other; both appear to have material that is not deformed, ablated, or displaced. At the same time, Figure 3.6c appears to have more material deformed, ablated, and displaced. Figure 3.6b shows the most columnar growth, and Figures 3.6d and 3.6f have fewer growth or mounds of displaced material and less columnar growth. However, in Figures 3.6b, 3.6d, and 3.6f, growths and mounds of displaced material all seem to range in height from 0 μm to 15 μm .



(a) SEM Image and (b) 3D Profile of an Al6061 sample modified with pulse duration of 0.184 ps



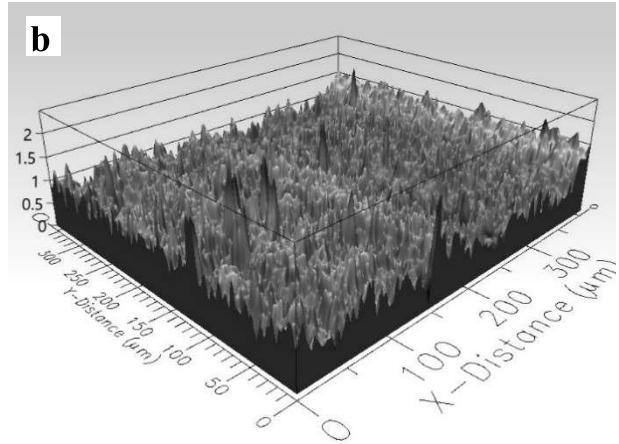
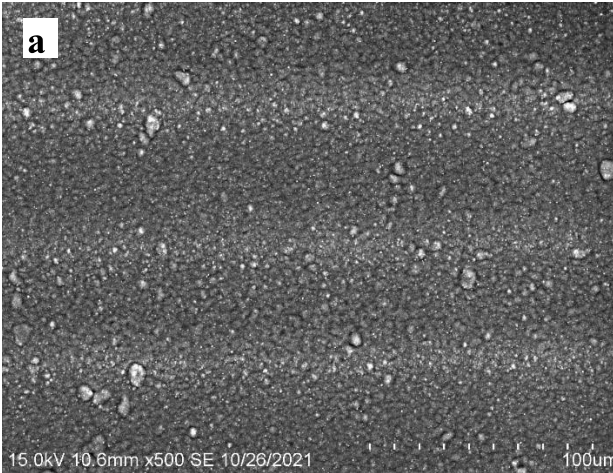
(c) SEM Image and (d) 3D Profile of an Al6061 sample modified with pulse duration of 5 ps



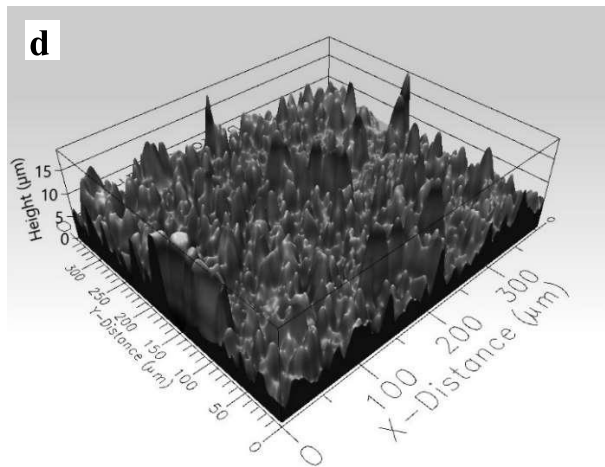
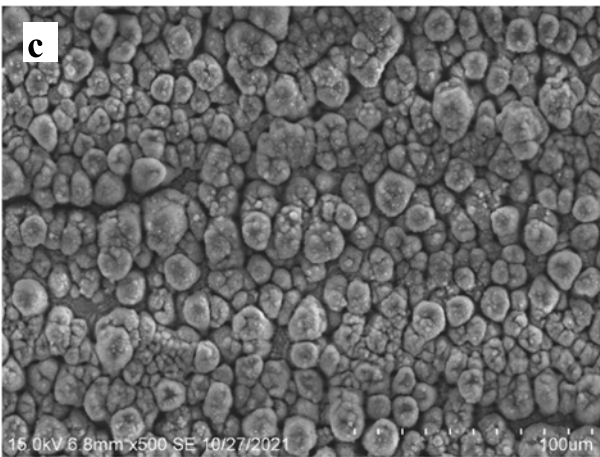
(e) SEM Image and (f) 3D Profile of an Al6061 sample modified with pulse duration of 10 ps

Figure 3.6 Effects of Pulse Duration on Surface Texture.

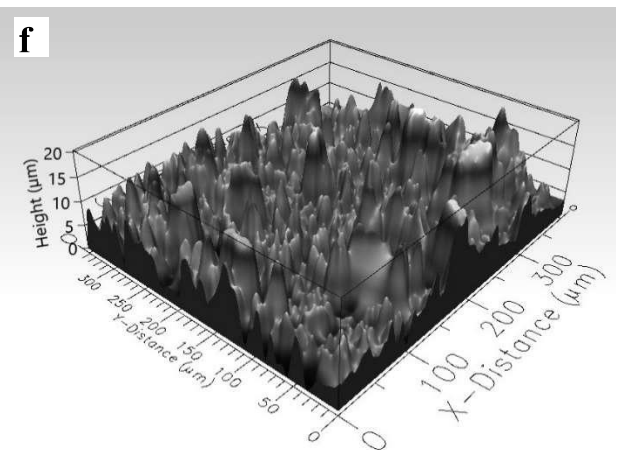
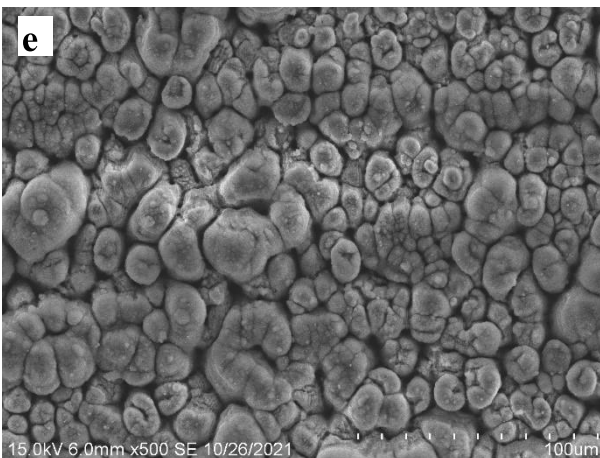
Figure 3.7 shows the SEM images and the 3D surface profiles for three laser textured surfaces of Al 6061. Figures 3.7a and 3.7b show results of pulse repetition rate being at 400 Hz, while Figures 3.7c and 3.7d show results of pulse repetition rate being at 2200 Hz, and Figures 3.7e and 3.7f show results of pulse repetition rate being at 4000 Hz, ten times the pulse repetition rate as Figures 3.7a and 3.7b. From observing the SEM images, Figures 3.7a, 3.7c, and 3.7e, it is apparent that the material changes by ablation, deformation, and displacement to an increasing extent as the pulse repetition rate increases. Figure 3.7a shows small areas of displaced material and has the most uniform surface compared to Figures 3.7c and 3.7e. There also seems to be more material showing columnar growth with an increasing repetition rate, as seen in Figures 3.7c and 3.7e. Surface pillars exhibit a more significant height difference reaching 20 μm at high repetition rates, as seen in Figures 3.7d and 3.7f, while Figure 3.7b shows growth reaching the height of only 1.5 μm .



(a) SEM Image and (b) 3D Profile of an Al6061 sample modified with pulse repetition rate of 400 Hz



(c) SEM Image and (d) 3D Profile of an Al6061 sample modified with pulse repetition rate of 2200 Hz



(e) SEM Image and (f) 3D Profile of an Al6061 sample modified with pulse repetition rate of 4000 Hz

Figure 3.7. Effects of Pulse Repetition Rate on Surface Texture.

3.3.2 Effects of Laser parameters on Surface Roughness

Figure 3.8 shows the effects of pulse energy on the average surface roughness. The other two laser parameters, pulse duration and pulse repetition rate, are fixed at 5 ps and 2200 Hz, respectively. As the pulse energy increases, the average surface roughness appears to increase as a logarithmic function. When the pulse energy increases from 50 μJ to 225 μJ , there appears to be a more significant change in the average surface roughness compared to when the pulse energy increases from 225 μJ to 400 μJ .

Figure 3.9 shows the effects of pulse duration on the average surface roughness. The other two laser parameters, pulse energy and pulse repetition rate, are fixed at 225 μJ and 2200 Hz, respectively. As the pulse duration increases, the average surface roughness appears to decrease as an exponential or linear function. As the pulse duration increases from 0.184 ps to 5 ps, the average surface roughness decreases faster than when the pulse duration increases from 5 ps to 10 ps. The results indicate a relationship between the pulse duration and the average surface roughness values. Compared to the pulse energy, the pulse duration appears to have more influence on the microstructure when looking at the average surface roughness value.

Figure 3.10 shows the effects of pulse repetition rate on average surface roughness. The other two laser parameters, pulse energy and pulse duration, are fixed at 225 μJ and 5ps, respectively. As the pulse repetition rate increases, the average surface roughness increases almost as a linear function. The results indicate a strong relationship between the pulse repetition rate and the average surface roughness value. Of the three laser parameters (pulse energy, pulse duration, and pulse repetition rate), pulse repetition rate seems to have the most substantial relationship to the average surface roughness value.

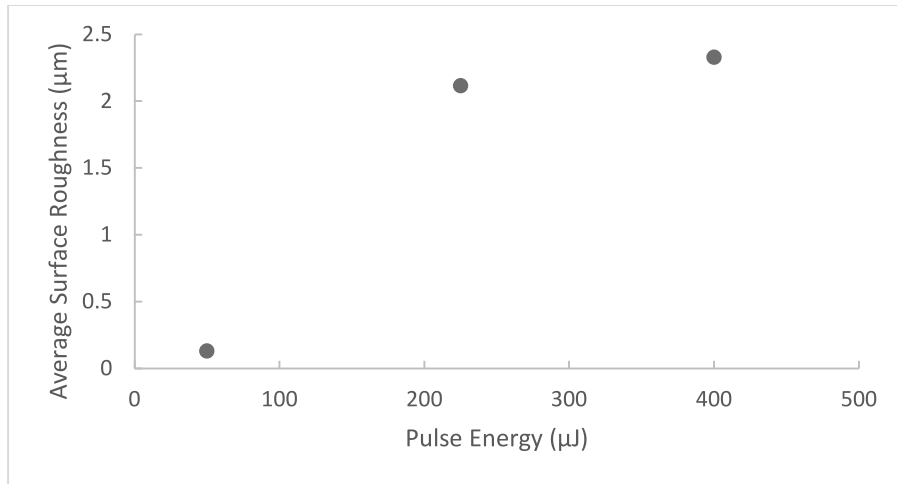


Figure 3.8 Effects of Pulse Energy on Average Surface Roughness



Figure 3.9 Effects of Pulse Duration on Average Surface Roughness

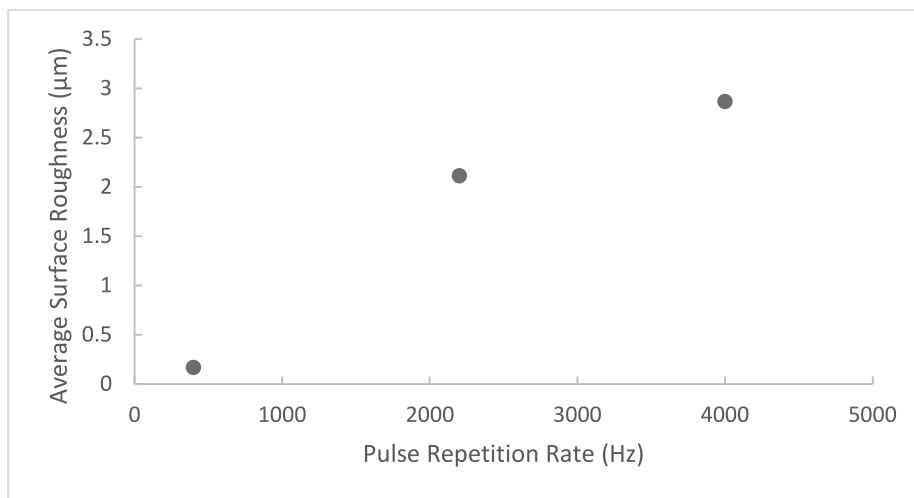


Figure 3.10 Effects of Pulse Repetition Rate on Average Surface Roughness

3.3.3 Effects of Laser Parameters on Contact Angle

Figure 3.11 shows the effects of pulse energy on contact angle. The other two laser parameters, pulse duration and pulse repetition rate, are fixed at 5 ps and 2200 Hz, respectively. As the pulse energy increases, the contact angle appears to increase first before leveling off at high pulse energy values. When the pulse energy increases from 50 μJ to 225 μJ , the increase in contact angle is over 40° , and the contact angle remains almost the same when the pulse energy increases from 225 μJ to 400 μJ .

Figure 3.12 shows the effects of pulse duration on contact angle. The other two laser parameters, pulse energy and pulse repetition rate, are fixed at 225 μJ and 2200 Hz, respectively. As the pulse duration increases, the contact angle increases nonlinearly for the range of pulse duration used, at a higher rate from 0.184 to 5 ps than from 5 to 10 ps.

Figure 3.13 shows the effects of pulse repetition rate on contact angle. The other two laser parameters, pulse energy and duration, are fixed at 225 μJ and 5ps, respectively. When the pulse repetition rate increases the contact angle increases nonlinearly, and the behavior is similar to the effect of pulse energy. It seems as if it is following a logarithmic trend; when the pulse repetition rate increases from 400 Hz to 2200 Hz, the difference between the two contact angles is more significant than when the pulse repetition rate increases from 2200 Hz to 4000 Hz, having a reduced difference.

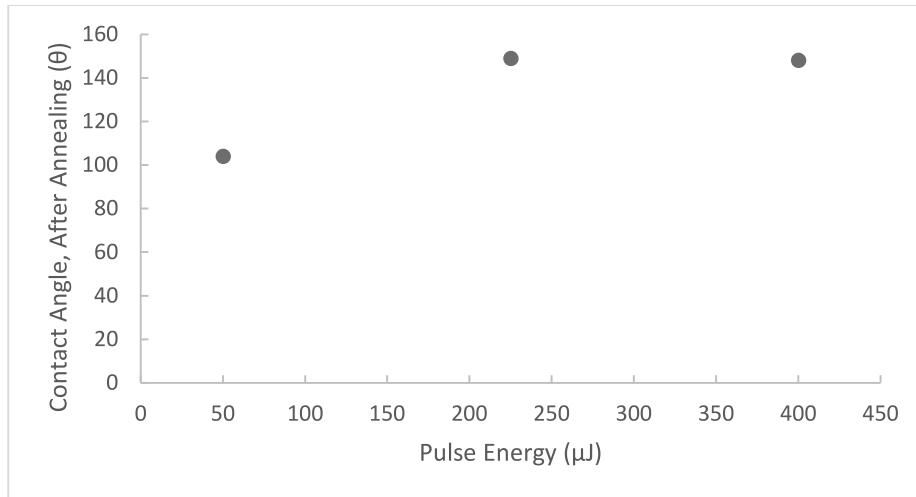


Figure 3.11 Effects of Pulse Energy on Contact Angle

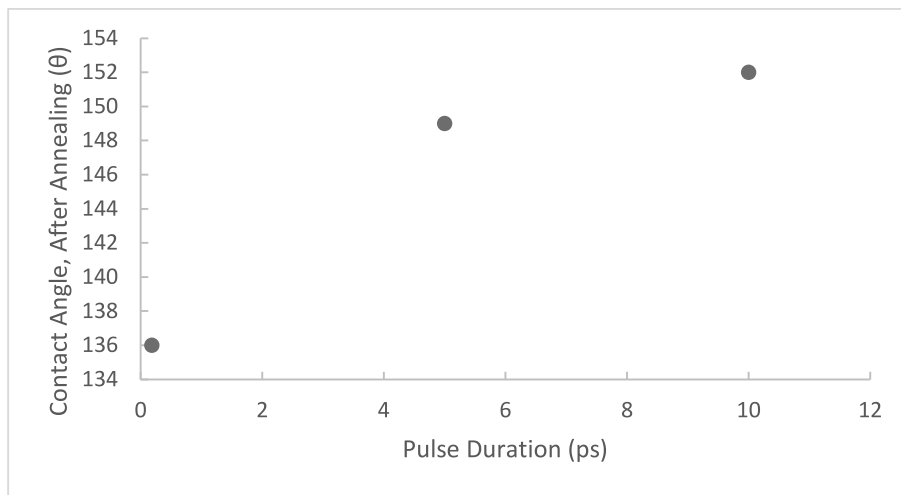


Figure 23.12 Effects of Pulse Duration on Contact Angle



Figure 3.13 Effects of Pulse Repetition Rate on Contact Angle

3.3.4 Effects of Surface Roughness on Contact Angle

Figure 3.14 shows the effect of the average surface roughness on contact angle, after annealing, treating the surface roughness as an independent variable. All samples show hydrophobic results regardless of the average surface roughness. The results suggest that when the average surface roughness is $0.5\text{ }\mu\text{m}$ or less, the average contact angle is hydrophobic, and when the average surface roughness is more significant than $1.5\text{ }\mu\text{m}$, the contact angle is more likely to exhibit superhydrophobic results. Aside from the observation mentioned, there does not seem to be a clear and direct trend when comparing the average surface roughness to the contact angles, but an optimal surface roughness seems to exist to maximize the contact angle.

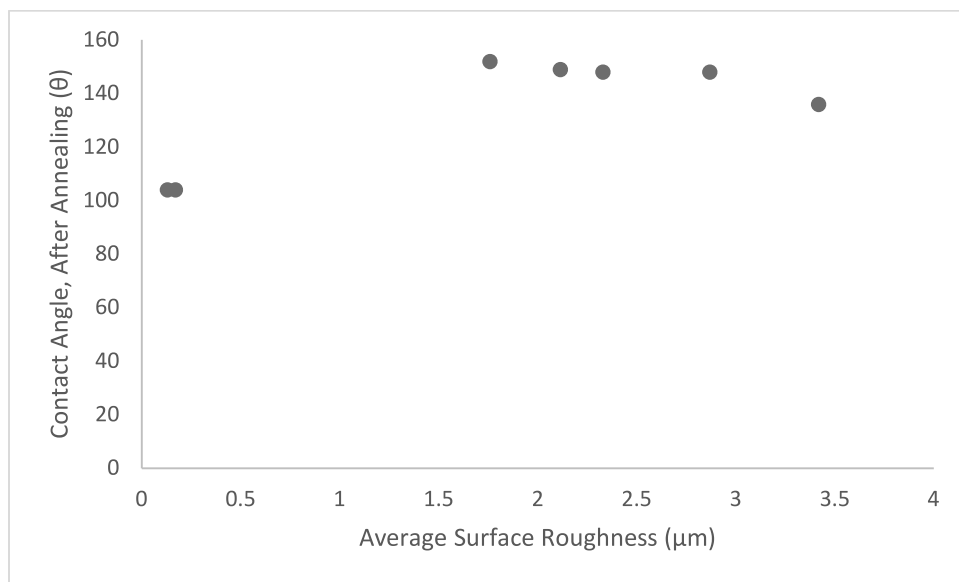


Figure 3.14 Effects of Average Surface Roughness, on Contact Angle

3.3.5 Response Surface Model

The results of contact angle for all the 20 test runs are shown in Table 3.3. Through the analysis in SAS software, a response surface model for the contact angle in favor of the factor levels (E, fp, tp) is obtained. The model can be described by the following equation:

$$CA = 54.73 + 0.22 * E + 0.03 * fp - 4.91 * e - 5 * E^2 - 4.8 * e - 5 * E * fp - 3.88 * e - 6 * fp^2 \quad (1)$$

Table 3.3 Experimental Design and Results

RunOrder	E (μJ)	tp (ps)	fp (Hz)	Contact angle (°)
1	50	5	2200	120
2	330	2	1130	157
3	225	5	4000	154
4	120	8	3270	150
5	225	5	2200	161
6	225	5	2200	148
7	120	2	3270	160
8	225	0.184	2200	158
9	225	5	400	132
10	400	5	2200	161
11	225	5	2200	160
12	225	5	2200	160
13	330	8	1130	150
14	330	8	3270	161
15	330	2	3270	156
16	225	5	2200	152
17	225	5	2200	159
18	120	2	1130	131
19	225	10	2200	158
20	120	8	2200	157

Analysis of variance (ANOVA) indicates that the model is highly statistically significant (p-value < 0.0001). The coefficient of determination (the ratio of the explained variation to the total variation) R^2 equals 0.80. The R^2 value suggests that the response surface model could provide good predictions. The lack-of-fit test shows that the lack-of-fit (p-value = 0.1884) was insignificant, indicating that the model fits well with the experimental data.

The response surface model explicitly relates contact angle to laser parameters. Contact angle can be predicted from the response surface model if the laser parameters are varied within the tested experimental ranges in this study.

3.3.6 Predicted Effects of Laser Parameters

The ANOVA showed that pulse energy E and pulse repetition rate f_p have significant effects on contact angle.

3.3.6.1 Effect of Pulse Energy E

The effect of pulse energy on contact angle as predicted by Eq. (1) is shown in Fig. 3.15a. The figure shows a quadratic relationship between pulse energy and contact angle. Contact angle increases as pulse energy increases from 50 to 315 μJ and then decreases as pulse energy increases from 315 to 400 μJ .

3.3.6.2 Effect of Pulse Repetition Rate f_p

The effect of pulse repetition rate on contact angle as predicted by Eq. (1) is shown in Fig. 3.15c. The figure shows a quadratic relationship between pulse repetition rate and contact angle. Contact angle increases as the repetition rate increases from 400 to 3088 Hz and then decreases as the repetition rate increases from 3088 to 4000 Hz.

3.3.6.3 Effect of Pulse Duration t_p

Pulse duration does not have any significant effect on contact angle.

3.3.7 Interaction Effects on Contact Angle

The two-factor interaction effects are shown in Fig. 3.16. The results indicate that contact angle is precisely predicted by the quadratic model and therefore can be used for further analysis.

The contour plot (projection of surface on a 2D plane) of contact angle (Fig. 3.16a) can be used to understand the interaction effect of factors on response variables by following the desired isoline (contour line with the same response value). For instance, in Fig. 3.16a, a contact angle of

160° can be obtained with E at 360 μ J and fp at 2000 Hz. Also, the same contact angle can be achieved from a lower level of E (e.g., 240 μ J) a higher level of fp (e.g., 2400 Hz).

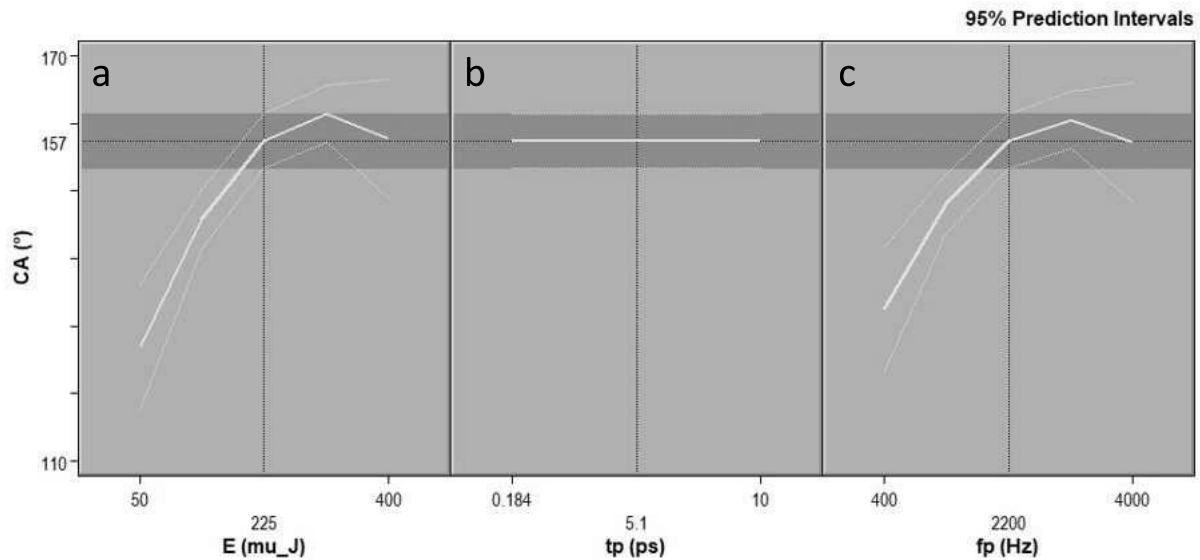


Figure 3.15 Prediction Profile Plot for Al 6061, Equation (1)

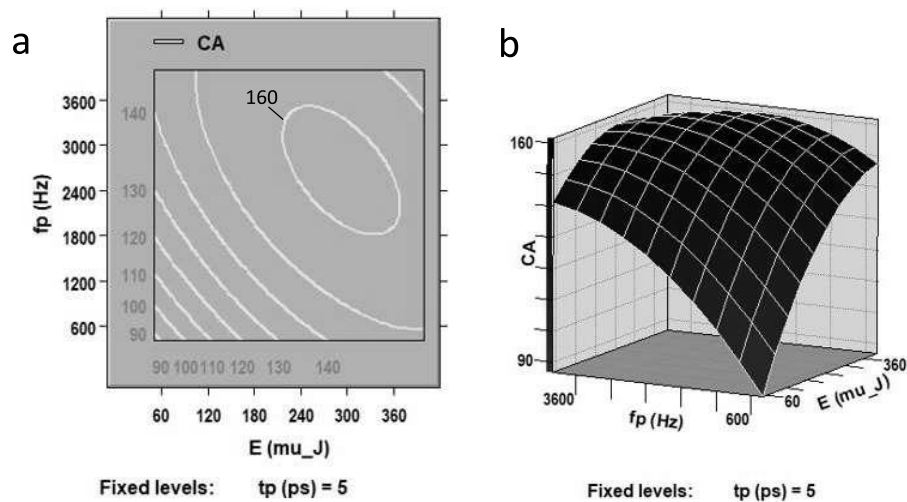


Figure 3.16 Contour Plot and Surface Plot for Al 6061, Equation (1)

3.3.8 Optimization of Laser Parameters

Minitab was used to analyze a multiple response optimization. The response goal was to maximize contact angle. The solution is shown in Table 3.4.

Table 3.4 Optimal Settings of Laser Parameters and Predicted Values

Optimal setting			Predicted values
E (μJ)	tp (ps)	fp (Hz)	Contact angle (°)
214	10	2427	161

To compare the results achieved from the model with experiments, additional confirmation experiments were conducted under the following laser parameter setting: pulse energy at 214 μJ, tp at 10 ps, and fp at 2427 Hz. As shown in Table 3.5, the contact angle obtained from the confirmation experiments is remarkably close to that estimated by the RSM models, implying that the RSM approach is appropriate for optimizing the laser parameters to maximum contact angle.

Table 3.5 Results of Confirmation Experiments

Value	Laser parameters			Responses
	E (μJ)	tp (ps)	fp (Hz)	Contact angle (°)
Experimental	214	10	2427	168
Predicted	214	10	2427	161
Error (%)	-	-	-	4.3

3.4. Conclusions

Surface roughness, microstructure, and contact angle are investigated for laser textured Al6061 samples. The response surface method predicts optimal laser parameters to maximize contact angle. The findings from this work are summarized below:

- Laser surface texturing can generate random roughness and regular patterns on Al6061 samples covering a wide range of roughness values with various multiscale geometric features from hundreds of μm to submicron sizes.
- Surface roughness increases nonlinearly with pulse energy and pulse repetition rate, and the effect is more significant for repetition rate. Surface roughness decreases slowly with pulse duration.
- All three laser parameters have a positive relationship with contact angle. Pulse duration has a weaker effect than pulse energy and repetition rate.
- Surface roughness has significant effect on contact angle. There seems to be an optimal roughness value for maximizing the contact angle.
- Annealing turns the laser textured surface from being hydrophilic to hydrophobic.
- A response surface model for Al6061 establishes the relationship from the contact angle to pulse energy and pulse repetition rate. A maximum contact angle of 161° is predicted with optimal conditions of $E=214 \mu\text{J}$, $t_p=10 \text{ ps}$, and $f_p=2427 \text{ Hz}$, which agrees well with that from the confirmation test.

Chapter 4 – Summary

4.1 Conclusion

This thesis aims to study the effects of operating conditions (e.g., pulse energy, beam spot size, pulse duration, pulse repetition rate) on surface texture and wettability in femtosecond laser surface modification of aluminum alloys. The first section studies the metal 2024-T3 aluminum alloy concerning surface texture (e.g., roughness), wettability (e.g., contact angle), and surface free energy. The second section aims to use ultrafast laser surface texturing to modify Al6061 aluminum alloy to produce hydrophobic/superhydrophobic surfaces without the need for surface coating. The interrelationships between laser processing conditions, surface texture, and surface wettability are studied using a central composite design of experiments. An optimal set of laser parameters are established to produce superhydrophobic surfaces for Al6061 aluminum alloy. Some general takeaways from this project are listed below:

- Al 2024-T3 surface free energy for the laser-treated samples is determined using the OWRK model. The effects of laser parameters on surface energy are apparent. There is more work needed to establish correlations among these three quantities: contact angle, surface energy, and laser parameters.
- Al 2024-T3 Femtosecond laser modification produces relatively uniform surface morphology at the macroscale. At the microscale, surface morphology differs depending on the interplay between material melting and self-assembly. Melting is most apparent in this study's most extended pulse duration of 800 fs.
- Six out of the seven samples exhibit hydrophobic behavior after laser treatment, with Sample 1 showing the largest contact angle of 115° .
- Annealing Al 6061 at 200°C for 2 hours can produce a hydrophobic/superhydrophobic surface, showing a correlation to increased wettability factors.
- For Al 6061, definitive correlations exist between laser parameters, surface wettability, and surface texture.
- A response surface model between contact angle and laser parameters is established, which predicts the optimal laser parameters with a maximum contact angle of 161° . The validity of the model is confirmed with additional experiments.

4.2 Future Work

The current research has helped us gain insights into all aspects, from laser surface texturing to surface characterization to surface wettability study, as well as using CCD designs and RSM for process optimization. It has also moved us further toward our goal of creating a polymer phobic mold surface made of Al6061 through laser surface texturing. Some future work is listed below along this line of research.

- Use different pattern scans, for example, a grid pattern scan in laser surface texturing.
- Incorporate Taguchi design to optimize laser parameters while reducing the number of experiments and decreasing the number of resources used.
- Learn how to access the wettability of polymers on the metallic treated surface.
- Conduct pull-off testing to assess the bond strength between a polymer and textured surface.

References

- [1] Dr. Kreidl, K., “Femtosecond Laser-Assisted Cataract Surgery- Boulder Medical Center.” (Blog).
- [2] Hodgson, N., Laha, M., Lee, T., Steinkopff, A., and Heming S., 2019, “Industrial Femtosecond Lasers and Material Processing.” Industrial Laser Solutions, (Article).
- [3] Xu, S., Ding, R., Yao, C., Liu H., Wan, Y., Wang, J., Ye, Y., and Yuan, X., 2018, “Effects of pulse duration and environments on femtosecond laser ablation of stainless steel.” Applied Physics A Materials Science & Processing, pp. 124:310.
- [4] Peng, E., Tsubaki, A., Zuhlke, C., Wang, M., Bell, R., Lucis, M., Anderson, T., Alexander, D., et. al., 2017, “Micro/nanostructures formation by femtosecond laser surface processing on amorphous and polycrystalline Ni₆₀Nb₄₀.” National Library of Medicine, Vol 396, pp. 1170-1176.
- [5] Ahmmed, K., Ling, E., Servio, P., Kietzig, A., 2015, “Introducing a new optimization tool for femtosecond laser-induced surface texturing on titanium, stainless steel, aluminum and copper.” Optics and Laser in Engineering. Vol. 66, pp 258-268.
- [6] Wu, P., Cheng, C., Chang, C., Wu, T., and Wang, J., 2011, “Fabrication of large-area hydrophobic surfaces with femtosecond-laser-structured molds.” Journal of Micromechanics and Microengineering, Vol. 21, 115032
- [7] Fan, P., Tan, R., and Zhong, M., 2019, “Ultrafast laser enabling hierarchical structures for versatile superhydrophobicity with enhanced Cassie-Baxter stability and durability.” Langmuir, Vol. 35, pp. 16693-16711
- [8] Vorobyev, A.Y., and Guo, C., 2010, “Laser turns silicon super wicking.” Optics Express, Vol. 18(7), pp. 6455-6460.
- [9] Guerrero-Vaca, G., Rodríguez-Valverde, M.A., Castilla-Montilla, P., Alguacil-Salamanca, F., Rodríguez-Alabanda, O., Romero, P.E., Molero-Romero, E., and Ruiz-Cabello, F.J.M. Superhydrophobic cerium-based coatings on Al-Mg alloys and aluminized steel. Coatings, 2019, Vol. 9 (12), art. no. 774.
- [10] Kostal, E., Stroj, S., Kasemann, S., Matylitsky, V., Domke, M., 2018, “Fabrication of Biomimetic Fog-Collecting Superhydrophilic-Superhydrophobic Surface Micropatterns Using Femtosecond Lasers.” Langmuir, Vol. 34(9) pp.2933-2941.

- [11] Vorobyev, A.Y., and Guo, C., 2015 “Multifunctional surfaces produced by femtosecond laser pulses.” *Journal of Applied Physics*, Vol. 117(3): 033103.
- [12] Skoulas, E., Manousaki, A., Fotakis, C., and Stratakis, E., 2017, “Biomimetic surface structuring using cylindrical vector femtosecond laser beams.” *Scientific Reports*, Vol. 7, pp. 45114-45125.
- [13] Kunz, C., Müller, F.A., and Gräf, S., 2018, “Multifunctional hierarchical surface structures by femtosecond laser processing.” *Materials*, Vol. 11(5), pp. 789
- [14] Murakami, D., Jinnai, H., and Takahara, A., 2014, “Wetting transition from the Cassie-Baxter state to the Wenzel state on textured polymer surfaces.” *Langmuir*, Vol. 30, pp. 2061-2067.
- [15] Vrancken, R.J., Kusumaatmaja, H., Hermans, K., Prenen, A.M., Pierre-Louis, O., Bastiaansen, C.W.M., and Broer, D.J., 2010, “Fully reversible transition from Wenzel to Cassie-Baxter states on corrugated superhydrophobic surfaces.” *Langmuir*, Vol. 26(5), pp. 3335-3341.
- [16] Marmur, A., 2003, “Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be?” *Langmuir*, Vol. 19, pp. 8343-8348.
- [17] Lopes, D.M., Ramos, S.M.M., de Oliveira, L.R., and Mombach, J.C.M., 2013, “Cassie-Baxter to Wenzel state wetting transition: a 2D numerical simulation. *RSC Advances*.” Vol. 3, pp. 24530- 24534.
- [18] David D., 2007 "Femtosecond Laser Microprocessing of Aluminum Films and Quartz," Theses, Dissertations, and Student Research from Electrical & Computer Engineering. Vol. 2.
- [19] Lei, S., Yang, G., Wang, X., Chen, S., Prieb, A., and Ma, J., 2018 “High Energy Femtosecond Laser Peening of 2024 Aluminum Alloy,” *Elsevier Journal of Procedia CIRP*, Vol. 4, pp. 357-361.
- [20] ASM International, 2000 “The Effects and Economic Impact of Corrosion.” *Corrosion: Understanding the Basics*.
- [21] Mozumder M.S., Mourad A.-H.I., Perves, H., Surkatti R., 2019, “Recent developments in multifunctional coatings for solar panel applications: A review” *Solar Energy Materials and Solar Cells*, Vol 189, pp. 75-102.

- [22] Eramah, A., Rakin, M., Veljic, D.m Tadic, S., Radovic, N., Zrilic. M., and Perovic, M., 2014, “Influence of friction stir welding parameters on properties of 2024 T3 Aluminum Alloy Joints.” Thermal Science, Vol. 18, pp. S21-S28.
- [23] Coremark Metals, “2024-T3 Aluminum Sheet.” (Article).
- [24] Wayback Machine, “Alloy 2024.” (Article).
- [25] Yuehua, Y., and Randall L., 2013 “Contact Angle and Wetting Properties” , Springer Series in Surface Sciences, Vol. 51.
- [26] Dataphysics. “Dispersive & Polar Parts of the Surface Energy and Surface Tension.” Dispersive & Polar Parts of the Surface Energy - DataPhysics Instruments. (Article).
- [27] Krüss., 1999, “So you want to measure surface energy?” Academic Research, Polymers, Paper. (Article).
- [28] Dataphysics. “Determination of the surface energy of a solid.” DataPhysics Instruments, (Article).
- [29] Theodore E., & George E., William B., 1995 “Microbial attachment on orthodontic appliances: I. Wettability and early pellicle formation on bracket materials,” American Journal of Orthodontics & Dentofacial Orthopedics.
- [30] François, L., Antoine, C., Korantin, O., Maryline, M., & Patrick C., Nicolas B., 2018 “Thermoresponsive Water-Soluble Polymer Layers and Water-Stable Copolymer Layers Synthesized by Atmospheric Plasma Initiated Chemical Vapor Deposition,” ACS Applied Materials & Interfaces.
- [31] Sanders, R., 2001, “Technology Innovation in Aluminum Products.” The Minerals, Metals & Materials Society. (Article).
- [32] Wayback Machine, 2004, “Understanding Extruded Aluminum Alloys,” Alcoa Engineered Products. (Article).

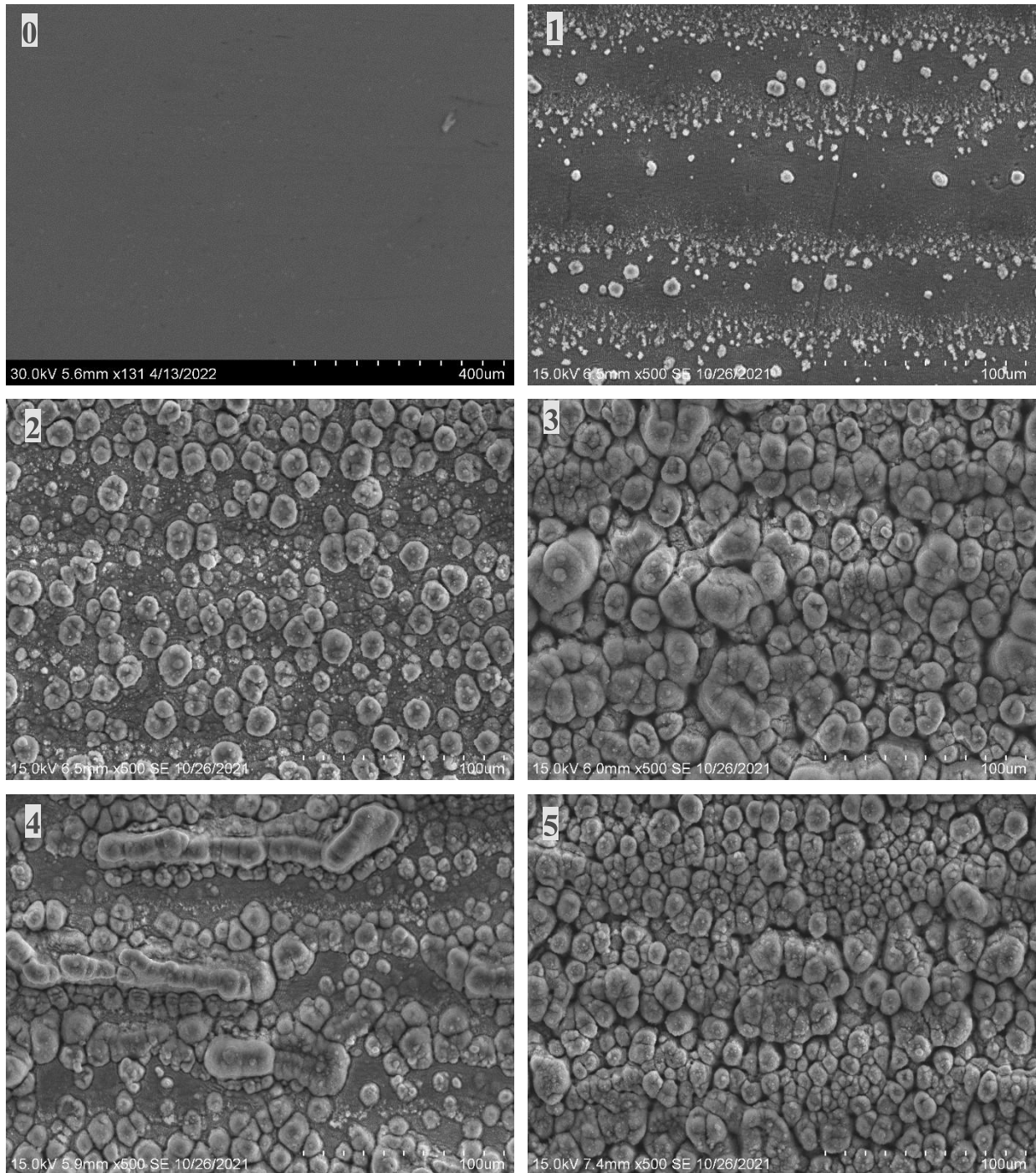
[33] Minitab, “What are response surface designs, central composite designs, and Box-Behnken designs?” (Article).

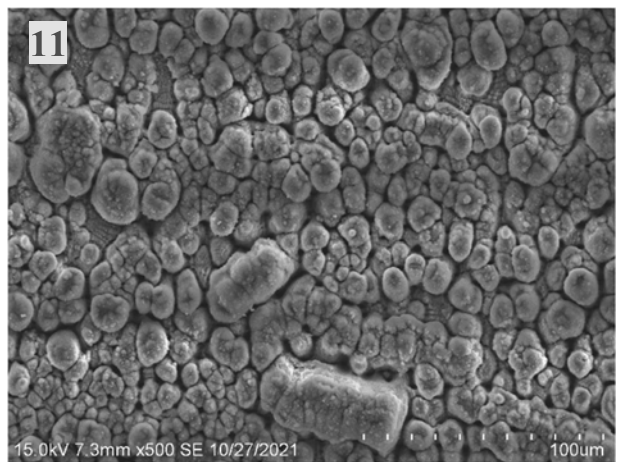
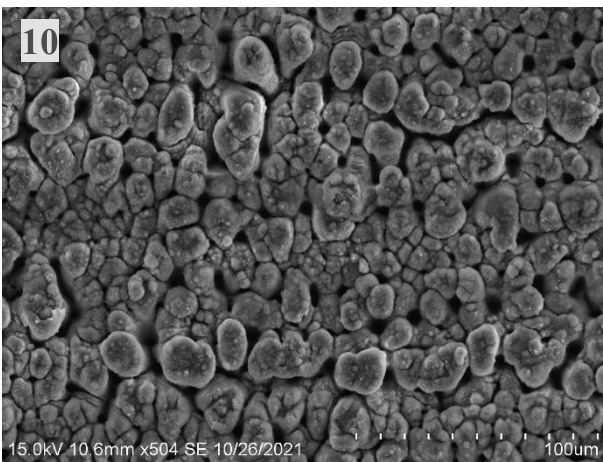
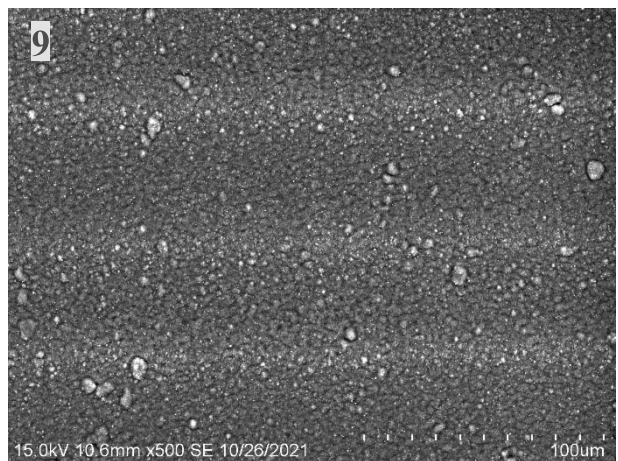
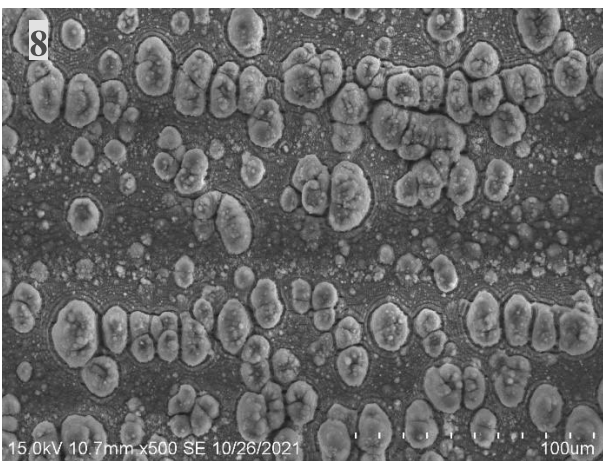
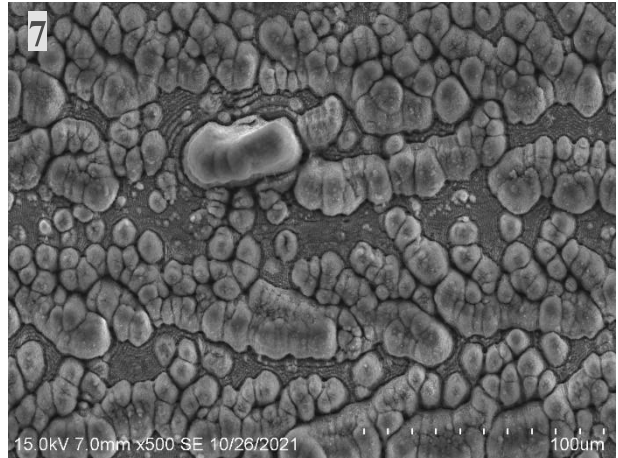
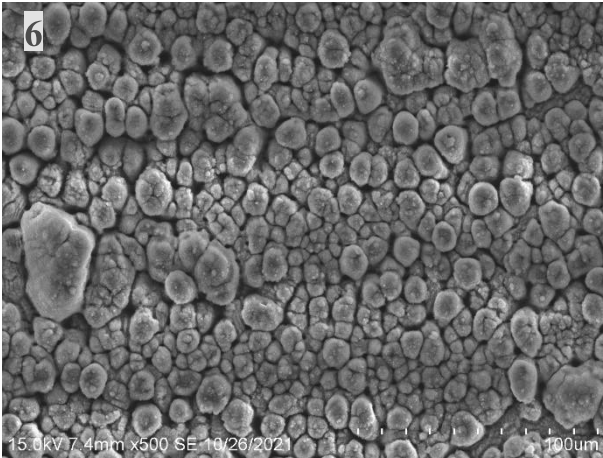
[34] [36] National Institute of Standards and Technology, “Central Composite Designs (CCD)” U.S. Department of Commerce. (Article).

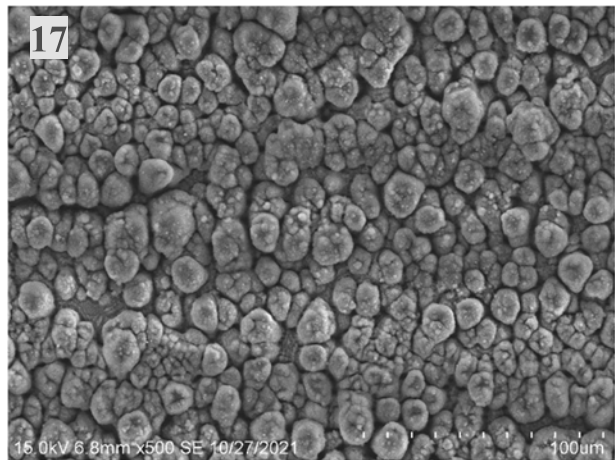
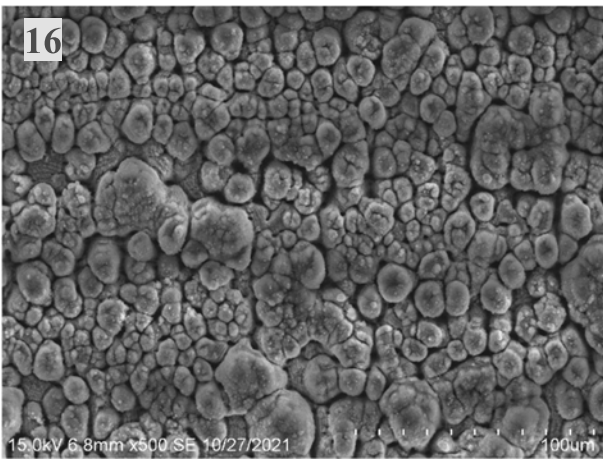
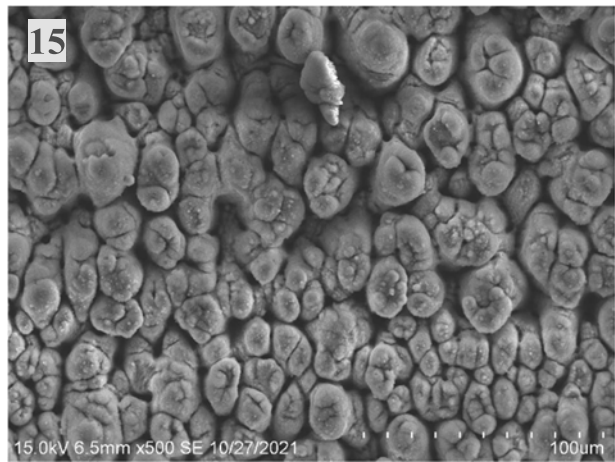
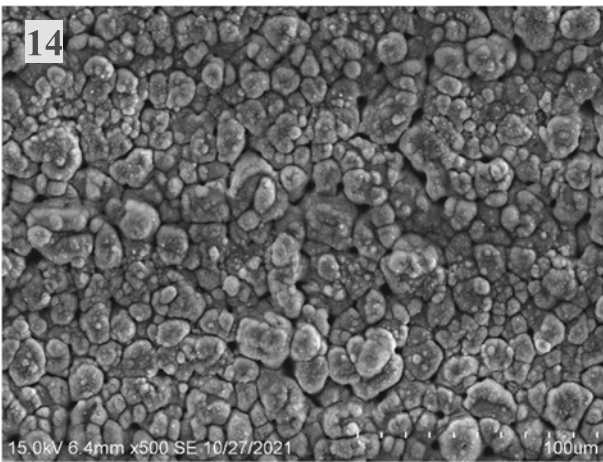
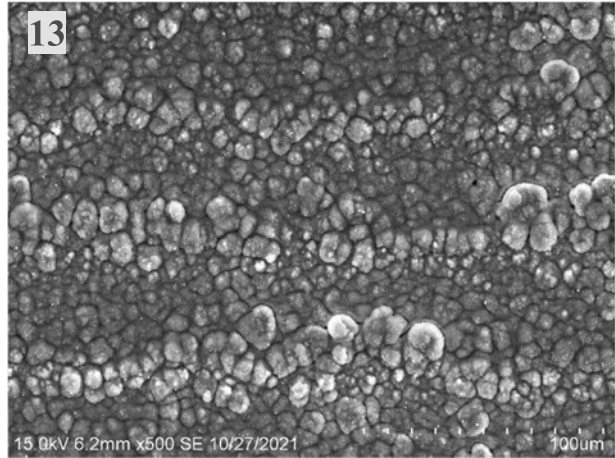
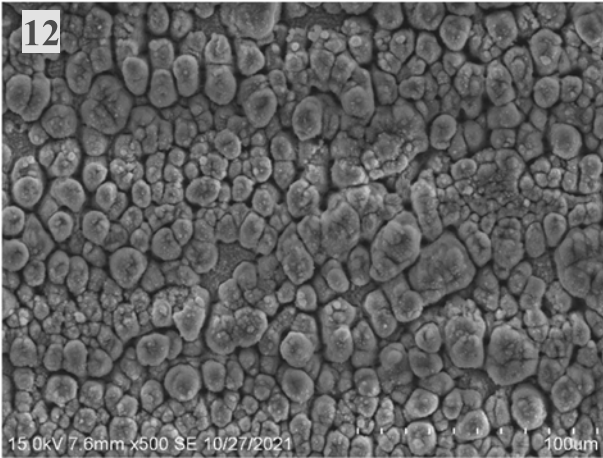
[35] Ngo, C.V. and Chun, D., 2017, “Fast wettability transition from hydrophilic to superhydrophobic laser-textured stainless-steel surfaces under low-temperature annealing.” *Applied Surface Science*, Vol. 409, pp. 232-240.

[36] Liu, W, Cai, M., Luo, X., Chen, C., Pan, R., Zhang, H., and Zhong, M., 2019, “Wettability transition modes of aluminum surfaces with various micro/nanostructures produced by a femtosecond laser.” *Journal of Laser Applications*, Vol. 31: 022503.

Appendix A – Microstructure Images







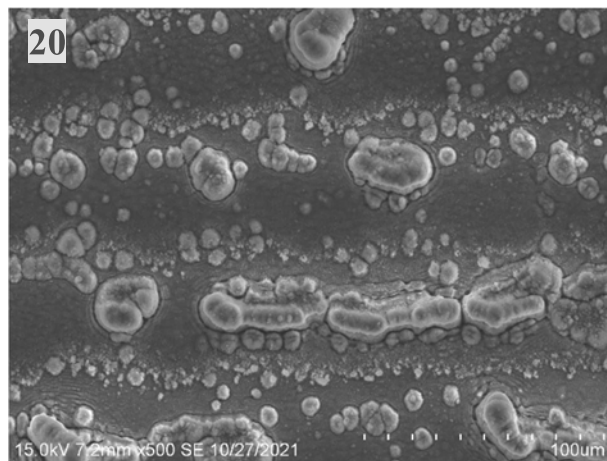
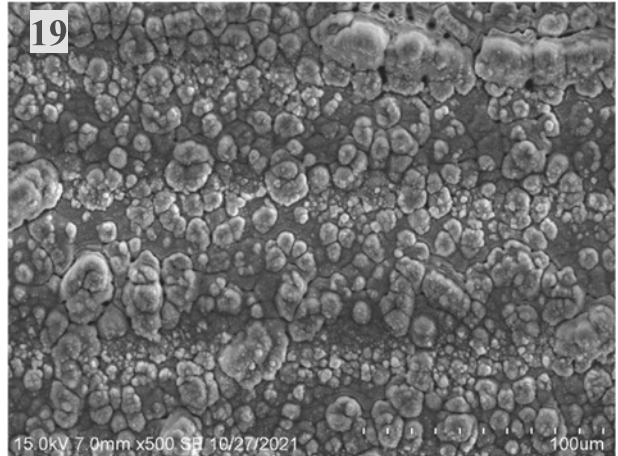
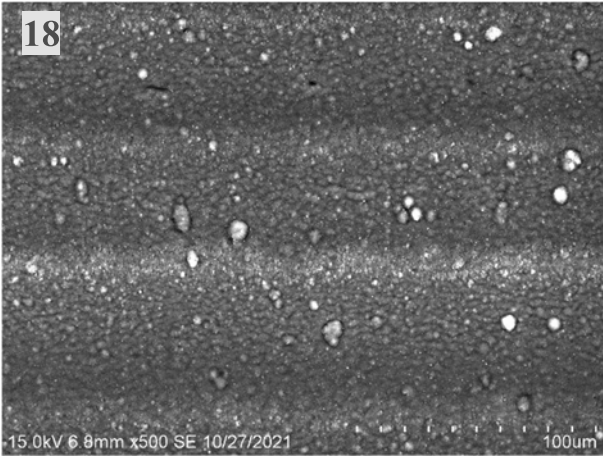
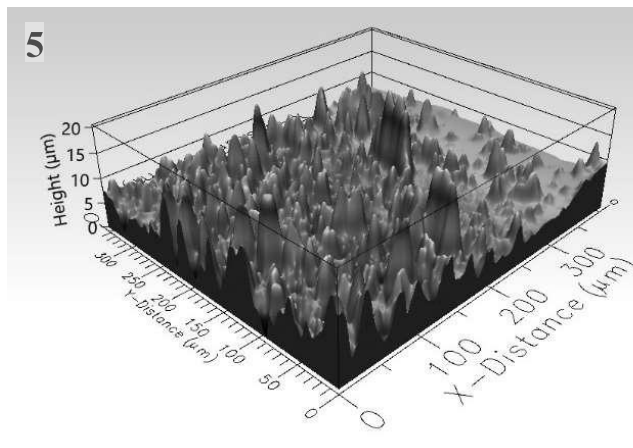
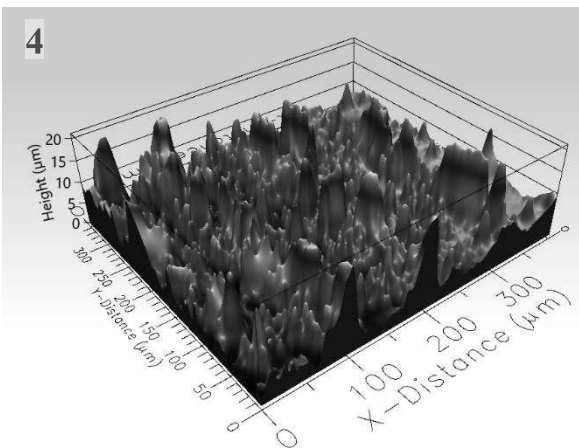
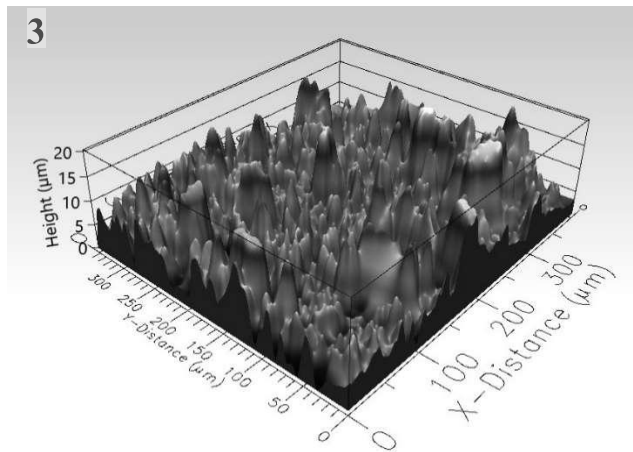
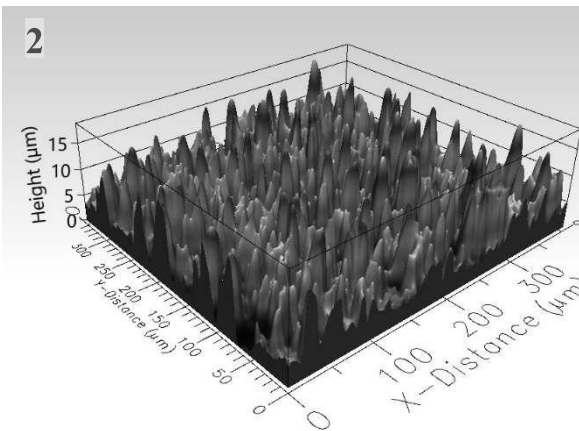
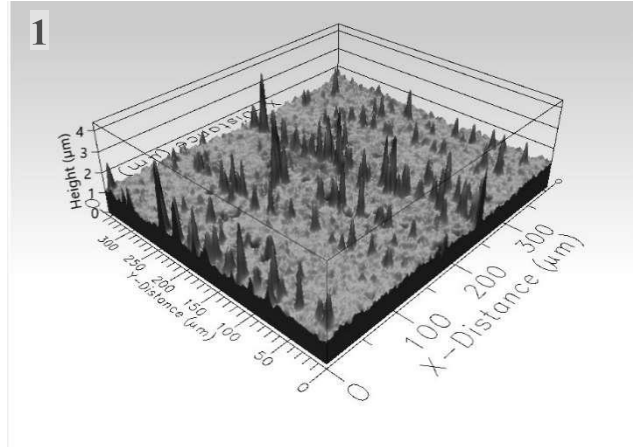
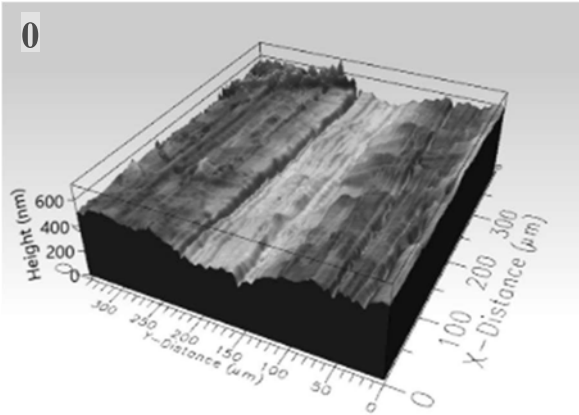
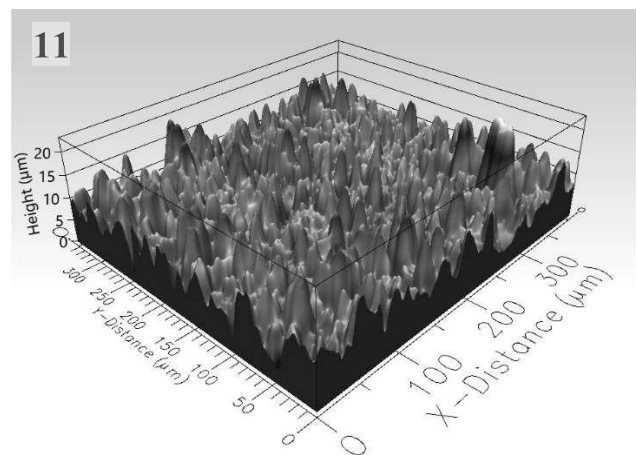
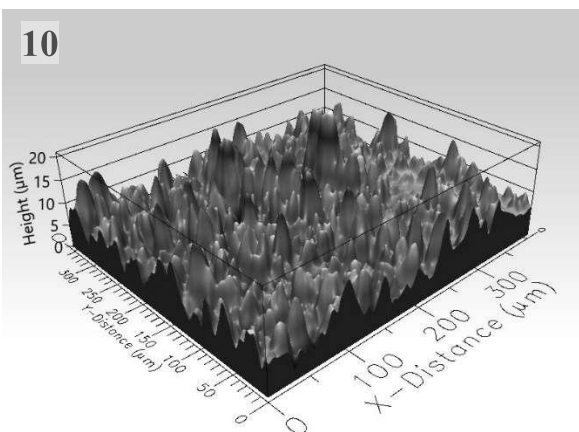
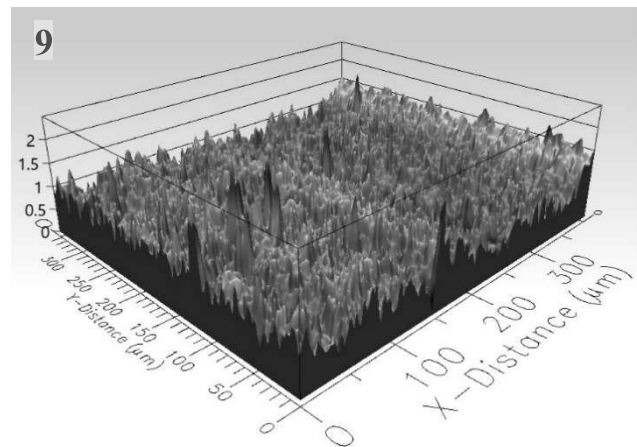
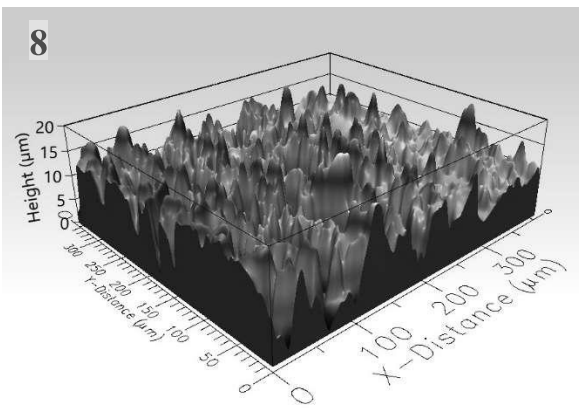
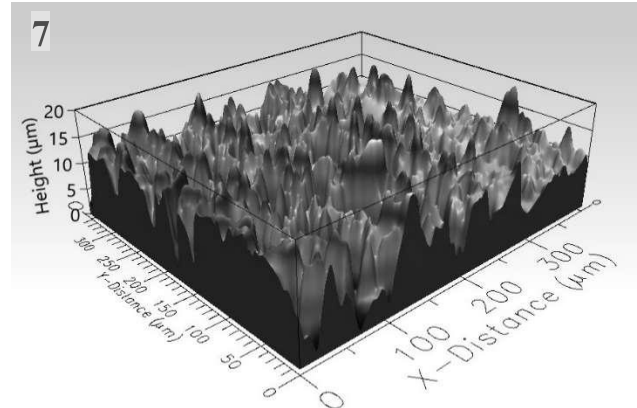
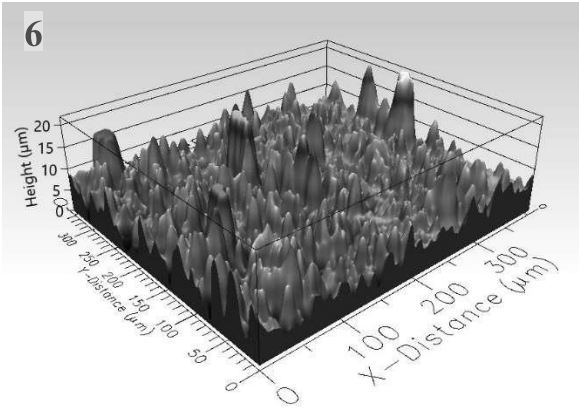
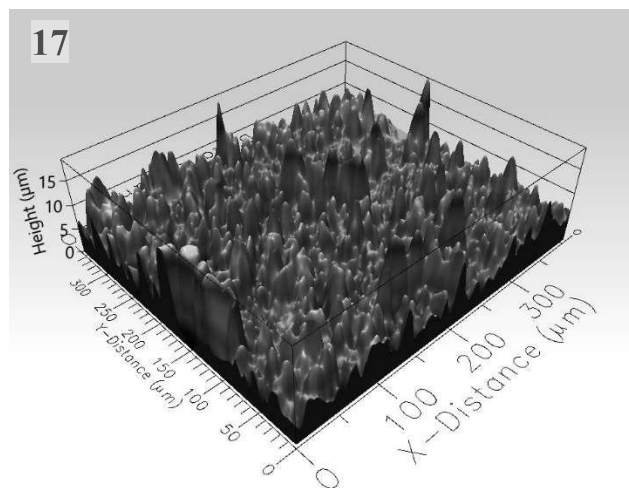
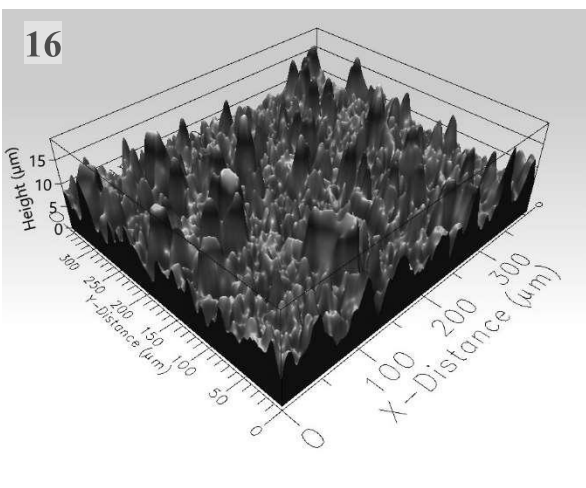
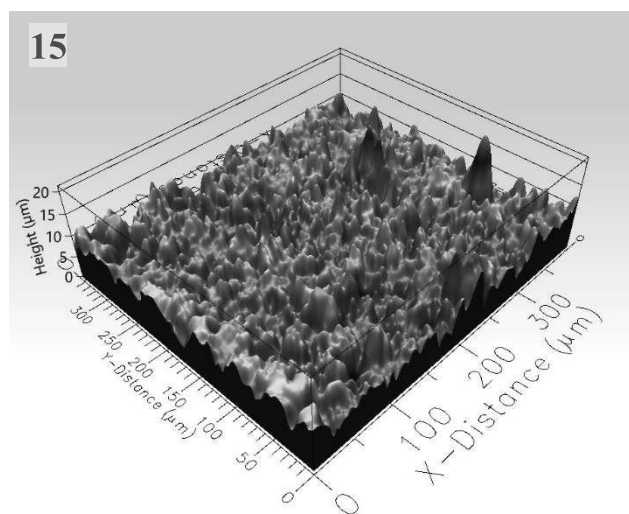
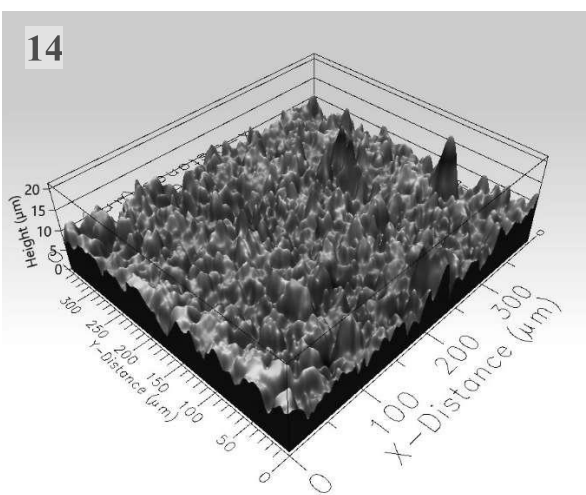
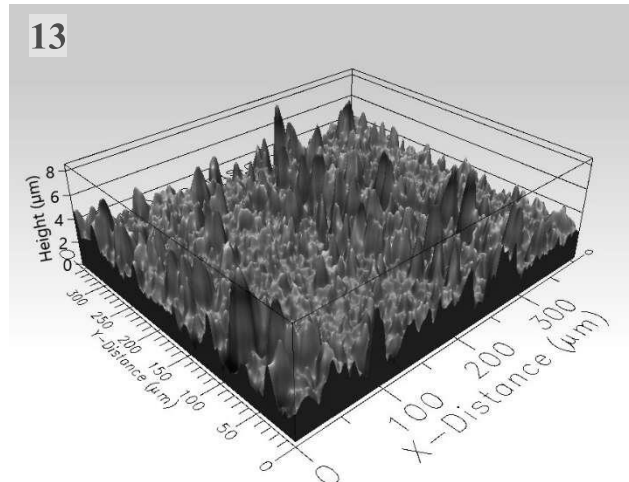
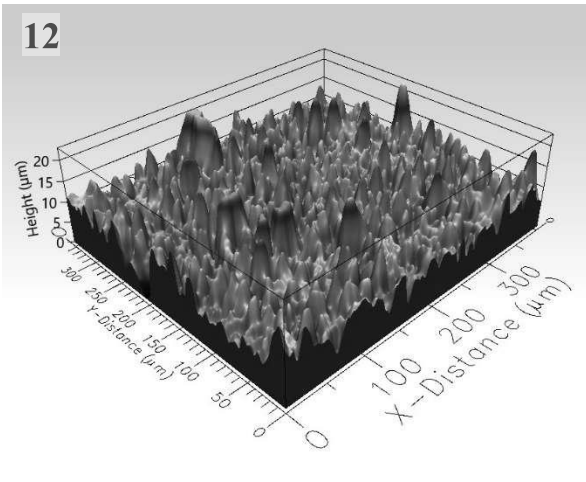


Figure A. 1 SEM Images, Aluminum 6061

Appendix B – 3D Profile Images







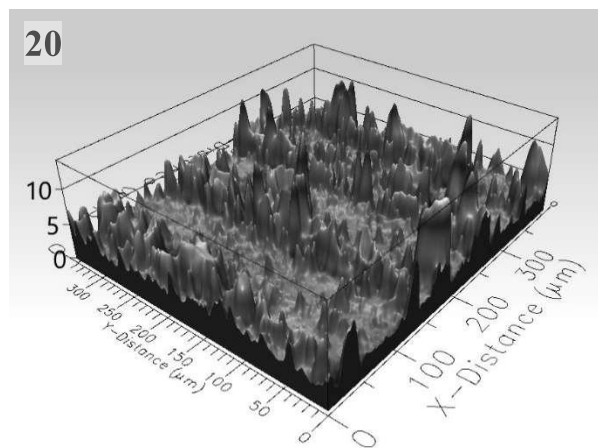
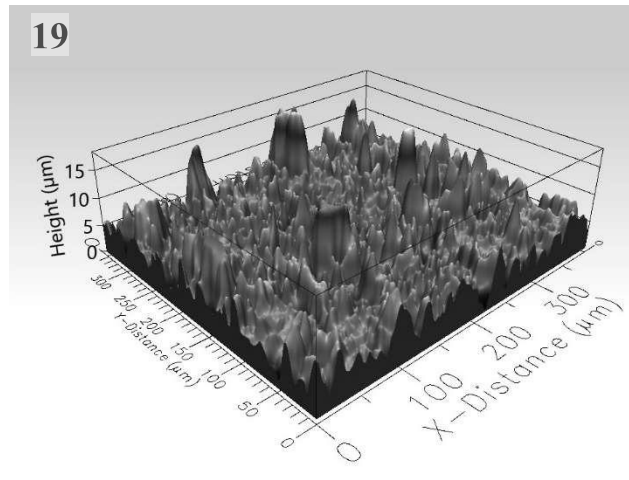
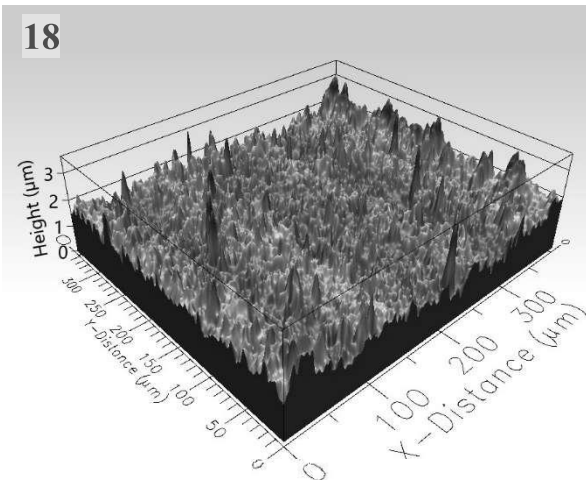


Figure B. 1. 3D Profile Images, Aluminum 6061

Appendix C – Surface Roughness Parameters

Table C. 1. Surface Roughness Parameters for Aluminum 6061

RunOrder	Sdar (mm ²)	Sa (μm)	Sq (μm)	Ssk	Sku
0	0.13	0.04	0.05	-0.48	3.05
1	0.13	0.13	0.22	3.78	32.7
2	0.18	2.58	3.16	1.04	3.42
3	0.16	2.87	3.68	1.12	4.00
4	0.17	2.76	3.68	1.46	5.03
5	0.15	1.77	2.48	1.62	7.29
6	0.16	2.25	3.04	1.45	5.98
7	0.16	2.97	3.62	0.06	2.4
8	0.19	3.42	4.06	0.90	2.67
9	0.13	0.17	0.23	0.46	3.98
10	0.16	2.33	2.99	1.01	4.30
11	0.16	2.25	2.90	0.68	4.03
12	0.16	2.19	2.83	0.71	3.96
13	0.14	0.69	0.93	1.04	5.10
14	0.15	1.68	2.17	0.27	4.16
15	0.16	2.95	3.67	0.43	2.84
16	0.16	2.24	2.91	0.82	3.84
17	0.16	1.99	2.61	1.05	4.49
18	0.13	0.28	0.36	0.51	3.64
19	0.16	1.76	2.37	1.29	6.02
20	0.15	1.27	1.73	1.90	7.24

Appendix D – Contact Angle

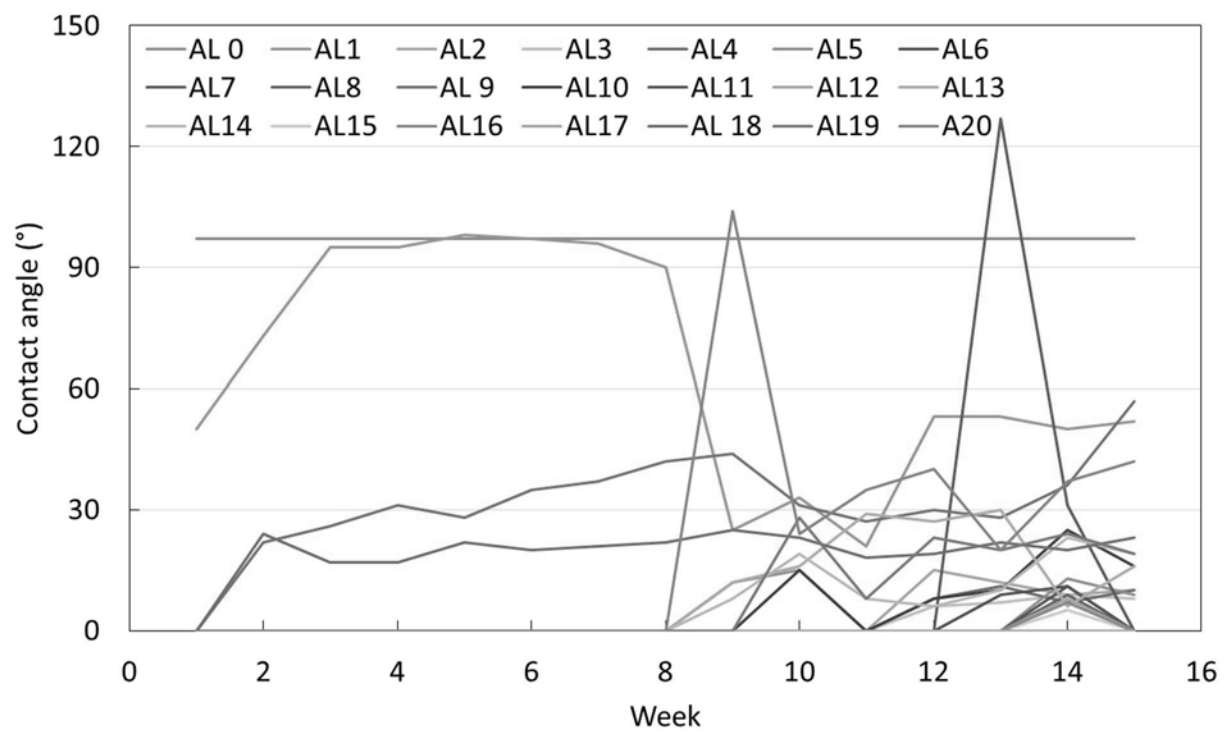


Figure D. 1. Aluminum 6061, Contact Angle Overtime, Before Annealing

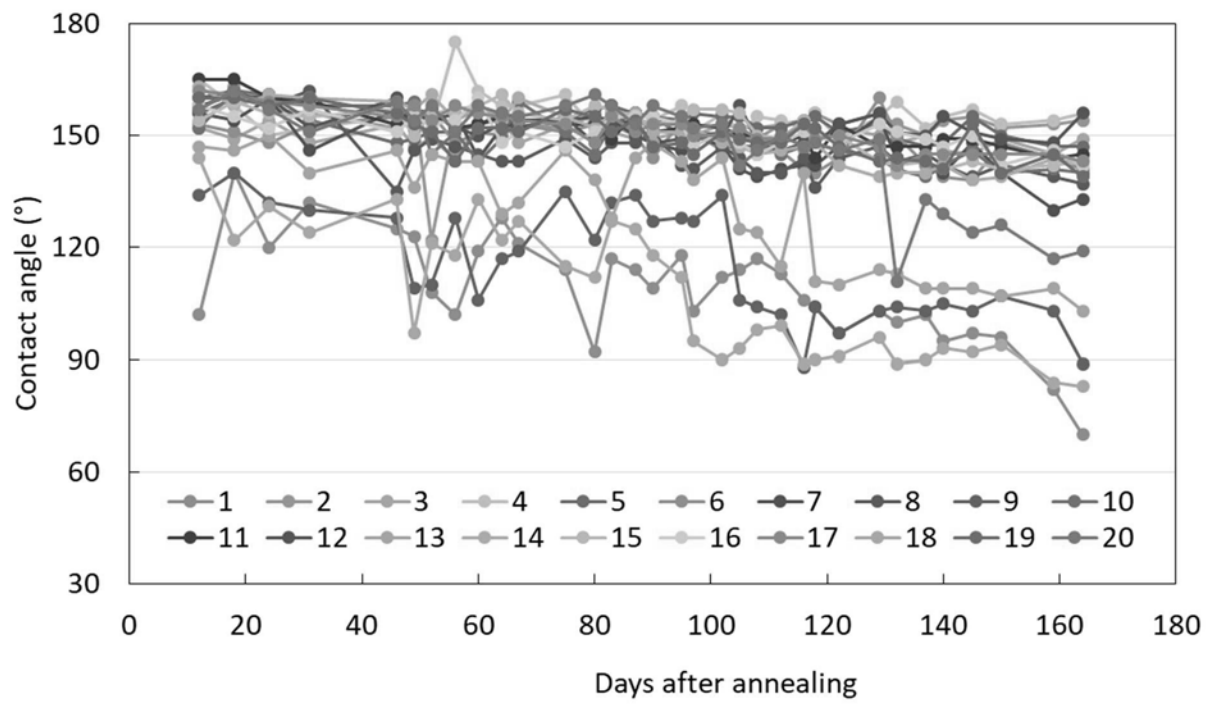


Figure D. 2. Aluminum 6061, Contact Angle Overtime, After Annealing

Table D. 1. Aluminum 6061, Contact Angle Before Annealing

WEEK	AL1	AL2	AL3	AL4	AL5	AL6	AL7	AL8	AL9	AL10
1	50	0	0	0	0	0	0	0	0	0
2	73	0	0	0	0	0	0	0	22	0
3	95	0	0	0	0	0	0	0	26	0
4	95	0	0	0	0	0	0	0	31	0
5	98	0	0	0	0	0	0	0	28	0
6	97	0	0	0	0	0	0	0	35	0
7	96	0	0	0	0	0	0	0	37	0
8	90	0	0	0	0	0	0	0	42	0
9	25	0	0	0	12	0	0	0	44	0
10	33	0	0	0	15	0	0	0	31	15
11	21	0	0	0	0	0	0	0	27	0
12	53	15	6	8	0	0	0	0	30	8
13	53	12	7	11	0	0	27	0	28	10
14	50	9	9	7	13	11	31	9	36	25
15	52	10	8	10	9	0	0	0	57	16
WEEK	AL11	AL12	AL13	AL14	AL15	AL16	AL17	AL18	AL19	AL20
1	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	24	0	0
3	0	0	0	0	0	0	0	17	0	0
4	0	0	0	0	0	0	0	17	0	0
5	0	0	0	0	0	0	0	22	0	0
6	0	0	0	0	0	0	0	20	0	0
7	0	0	0	0	0	0	0	21	0	0
8	0	0	0	0	0	0	0	22	0	0
9	0	0	12	8	0	0	0	25	0	104
10	0	0	16	19	0	0	0	23	28	24
11	0	0	29	8	0	0	0	18	8	35
12	0	0	27	6	0	0	0	19	23	40
13	0	0	30	10	0	0	0	22	20	20
14	11	8	6	23	5	7	0	20	24	37
15	0	0	16	19	0	0	0	23	19	42

Table D. 2. Aluminum 6061 Samples 1-10, Contact Angle After Annealing

DAY	AL1	AL2	AL3	AL4	AL5	AL6	AL7	AL8	AL9	AL10
12	102	157	152	165	156	153	156	160	134	152
18	140	163	149	158	160	151	154	162	140	162
24	120	157	154	150	161	148	160	158	132	161
31	132	156	148	152	154	153	146	162	130	158
46	125	152	153	155	148	155	157	135	128	158
49	123	159	147	151	149	155	154	146	109	159
52	108	122	149	152	151	156	154	149	110	145
56	102	154	144	175	151	148	156	147	128	151
60	119	157	153	162	153	151	144	145	106	143
64	128	155	154	158	156	150	152	143	117	149
67	121	153	148	158	154	153	154	143	119	159
75	114	152	153	161	154	151	154	149	135	151
80	92	149	155	152	157	153	155	144	122	145
83	117	158	151	155	158	153	154	148	132	153
87	114	154	149	152	156	150	150	148	134	156
90	109	152	149	154	155	144	148	151	127	155
95	118	155	151	158	154	154	146	142	128	150
97	103	150	150	151	156	151	150	141	127	149
102	112	151	153	156	155	146	147	147	135	149
105	114	149	152	151	155	148	141	144	106	147
108	117	149	152	155	152	150	139	140	104	147
112	113	153	153	154	152	146	141	140	102	145
116	106	154	146	152	154	141	142	144	88	147
118	104	156	148	156	155	140	142	136	104	148
122	97	153	152	149	151	144	147	144	97	146
129	103	156	150	155	153	160	155	147	103	144
132	100	153	148	159	149	150	144	143	104	141
137	102	150	150	152	147	142	143	145	103	139
140	95	154	146	155	148	139	140	142	105	142
145	97	155	145	157	155	138	148	139	103	146
150	96	152	149	153	150	138	140	142	104	140
159	82	153	145	154	147	144	130	139	103	141
164	70	154	149	156	147	141	133	137	89	140

Table D. 3. Aluminum 6061 Samples 11-20, Contact Angle After Annealing

DAY	AL11	AL12	AL13	AL14	AL15	AL16	AL17	AL18	AL19	AL20
12	165	158	147	163	154	158	162	144	160	157
18	165	161	146	158	159	155	161	122	160	162
24	160	160	150	161	156	152	159	131	158	157
31	159	152	140	160	155	157	158	124	160	151
46	153	160	146	159	157	151	155	133	156	159
49	157	152	136	157	150	155	158	97	153	154
52	156	157	145	161	156	153	154	121	151	158
56	152	152	143	154	157	154	158	118	143	151
60	153	150	143	158	158	160	156	133	152	158
64	157	153	129	154	161	148	155	122	152	156
67	154	152	132	160	156	151	154	127	151	155
75	153	155	146	155	154	147	153	115	157	158
80	153	148	138	152	158	151	148	112	155	161
83	149	153	128	156	157	155	155	127	151	158
87	156	154	144	156	155	155	151	125	154	153
90	151	148	148	151	153	155	153	118	147	158
95	152	149	143	151	154	153	153	112	148	155
97	153	151	138	152	157	147	150	95	145	152
102	152	150	144	148	157	151	150	90	151	153
105	150	158	125	147	156	148	152	93	149	142
108	150	148	124	145	150	145	149	98	148	146
112	148	146	115	146	149	148	149	99	148	150
116	150	148	140	147	154	151	153	89	153	147
118	144	148	111	148	149	150	149	90	152	148
122	153	153	110	142	150	148	150	91	147	146
129	147	156	114	139	143	153	147	96	143	149
132	147	151	113	140	142	151	142	89	144	111
137	147	150	109	140	143	149	145	90	143	133
140	149	155	109	142	141	147	145	93	141	129
145	149	151	109	138	143	150	145	92	153	124
150	147	149	107	139	141	142	145	94	140	126
159	144	148	109	144	142	146	145	84	145	117
164	145	156	103	142	143	142	143	83	139	119