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ULTRAFAST LASER-INDUCED SURFACE STRUCTURING OF ANTI-FOULING STEEL SURFACES FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Metallic surfaces are increasingly used in medical applications due to their favorable material properties such as high strength and biocompatibility. In medical applications anti-fouling properties are an important requirement especially for implants and medical devices which come into contact with different types of fluid streams. These should be anti-fouling in order to prevent contamination and corrosion. Laser processing methods such as ultrafast laser processing is a one-step and scalable process for surface texturing. This process can be used to produce well-defined surface nano- and microscale superficial textures such as Laser-induced Periodic Surface Structures (LIPSS) which can enhance the anti-fouling capability of the surface.

In this study, micro and nano scaled LIPSS structures are manufactured on a biocompatible grade stainless steel 316L substrate using an ultrafast (<370 fs) and low power (<4 W) laser system. With an aim to optimize the anti-fouling properties, laser process parameters such as pulse energy, pulse repetition rate and beam scanning speed were varied to produce microstructures on the stainless-steel surface of varying dimensions. Surface roughness was analyzed using a laser surface profilometer and changes in the hydrophobicity were examined using water contact angle goniometry.

Keywords: Laser processing, ultrafast, antifouling, micro-scale texture, femtosecond laser processing, biomedical, stainless steel, surface structuring.

1. INTRODUCTION

Surface fouling is a much complex, undesirable and time dependent process and has different mechanisms in different types of surfaces which come in contact with the foulants such as macromolecules, microorganisms, and or suspended particles, which are either stationary or in motion in different applications [1].Within biomedical field surface fouling occurs especially biofouling on surgical equipment, protective gears, packaging, guide wires, sensors, prosthetic devices, and medical implants[2].

Metals are mostly used for implants, surgical equipment such as tools used for surgery and within prosthetic devices as they have excellent mechanical properties, inertness and hence are biocompatible [3]. Many metals such as titanium, gold cobalt, chromium, special alloys such as nickel titanium and medical grade stainless steel are becoming common in this application [4]. Stainless steels such as AISI 316L (complying to ASTM F138 and F139) and AISI 304 grades are especially used in biomedical applications because of their properties such as good ductility, work hardenability and fatigue properties and also its availability and low cost [5,6]. This is because the SS316L and SS304 contain low carbon percent and more than 12% of chromium which reduces the corrosion [7].

Surface treatment of stainless steel is important in the biomedical applications for improving the functional properties which include roughness, hydrophilicity, hydrophobicity and corrosion resistance [7]. There are various physical and chemical methods to produce functionalized surfaces which have anti fouling properties. Chemical methods such as paints and coatings have been used for long time for large surfaces in engineering and commercial applications [8]. However, these coatings and paint technique are not robust as they can be worn out by time due to erosion etc. Secondly physical treatments such as plasma treatments, bulk lithography techniques [9,10] are used for fabricating a three-dimensional microstructure that change the fundamental surface properties such as roughness, surface energy, porosity, capillarity and the surface structures that affects the wettability of the surface and makes them antifouling. Magin et al have reviewed various nontoxic environment friendly alternative physical, chemical and physio-chemical processes of generation of anti-biofouling surfaces [11]. However, these techniques are not robust as there are issues such as discoloration, thermal effects and mechanical wear [12]. Hence, ultrafast laser induced surface structuring is a novel technique to produce different types of artificial hierarchical topologies on the surface which affect the wettability and improves the fouling resistance [13].

In this process the periodic surface structures are produced by laser irradiation at fluences slightly higher than the ablation threshold. In this technique the ultrashort pulse laser beam of the ultrafast laser system is scanned periodically over the area to be processed and forms precise machined cuts at micro scale without generation of heat affected zones as discussed in the comparative study by Harzic et al on the nanosecond and femtosecond laser pulses [14]. In the review by Fadeeva et al the authors have discussed about liquid-repellent surfaces which are inspired from two biological models which are capable to be mimicked by using ultrafast laser processing [15]. Femtosecond laser technique has also demonstrated to be a promising method to produce structures at micro and nano scale on surfaces for its unique abilities and advantages such as low or almost no heat affected zone as the pulse duration is much less than the electron cooling time. This is considered to be extremely short time scale of interaction between the laser and material. Due to this high accuracy of the machined surface with less power consumption and robust surface structures are achieved [16].

Also, several studies have been conducted to the examination of how processing parameters influence the roughness and wettability of metallic surfaces however there is no proper understanding of the key parameter which affects the antifouling ability of the surface. Long et al has demonstrated the generation of superhydrophobic surfaces with various adhesion properties using an ultrafast femtosecond laser, periodic microstructures with different heights and depths were obtained by altering the scanning speed of the laser beam. [12, 13]. The hydrophobic behavior of the surface is similar to the lotus effect or the shark skin effect. Studies suggests that artificial micro-nanoscale hierarchical structures with low wettability are capable to effectively reduce the microbes attached to the material's surface due to low adhesion effect. A similar work has been conducted by Sun et al using a picosecond laser for marine application [19]. From this study it is evident that two indicators of fouling resistance are contact angle measurement and the surface roughness. The higher the contact angle the lower the surface energy hence lower adhesion which makes it fouling resistant as it also has strong rejection effect on liquid foulants such as blood, urine and saliva, bacteria present in the fluid stream and other foulants especially in medical applications.

In this paper, an experimental study is conducted by using one-step femtosecond laser induced surface structuring of stainless steel 316L substrate plates and the study is conducted on the surface morphology, roughness, and wettability properties of the processed surfaces. The interaction behavior between water droplets on laser processed stainless steel (SS) was investigated and an attempt is made to bridge the gap between hydrophobic surface and antifouling properties.

2. MATERIALS AND METHODS

2.1 Material

The material used in this project is made up of commercially available Stainless steel AISI 316L in form of flat plates with 100×54 mm and 1 mm thick. The chemical composition of AISI 316L stainless steel is as mentioned in the **TABLE *1*** below.

316L Stainless steel Material	Composition by wt%
C	0.03
Mn	2.0
Si	0.75
P	0.045
S	0.03
Cr	18
Mo	3.0
Ni	14.0
N	0.1
Fe	Balance

TABLE 1. CHEMICAL COMPOSITION OF STAINLESS STEEL 316L [20]

Physical Properties	Units	
Density	kg/m^3	8000
Elastic Modulus	GPa	193
Thermal conductivity	W/m. K	16.3
Specific Heat	J/kg. K	500
Electric resistivity	nΩ.m	740

TABLE 2. PHYSICAL PROPERTIES OF STAINLESS STEEL 316L[20]

Stainless steel 316L material has excellent mechanical properties and also corrosion resistance and it can be used at high range of temperature. It is also highly machinable because of low content of carbon.

Application: This grade of stainless steel is used in various applications such as bioprocessing, food industry, chemical processing industry, marine applications, pulp and paper industry, medical surgical instruments, implants etc.

2.2 Laser Processing

In this study we used ultrafast femtosecond laser (NKT One Five Origami 10XP) that generates 400fs pulses with 1030nm central wavelength at a maximum pulse repetition rate of 1 MHz the beam diameter of laser at the focused position was 45 µm.

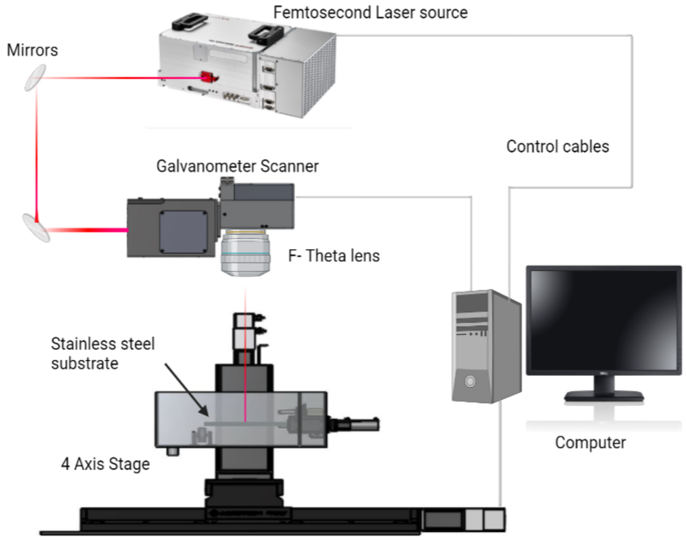


FIGURE 1:LASER PROCESSING SETUP

The laser beam was scanned in form of parallel line pattern using a galvanometric scanning system (Raylase FOCUSSHIFTER II) which formed array of parallel microgrooves on the stainless-steel material. The processing setup is as shown in the **FIGURE 1**.

These microgrooves were made with variable speed within range of 1 to 10 mm/s and hatch distance of 80µm, 100µm and 120µm on the processing area of 8 mm x 8 mm squares. The laser pulse energy was varied between 12-40 µJ and repetition rate was varied between 100-300 kHz were variable with each sample.

2.3 Design of Experiments

An experimental design was made using Response surface methodology with four factors or variables.

This was conducted to find out the explores the relationships between factors which were the laser parameters and response variables such as contact angle and the Sa, Sq, Sp and Sz roughness values. A total of 51 samples were created by this as shown below in **TABLE** .

Factors	**Symbol**	**Unit**	**Level 1**	**Level 2**
Laser pulse energy	E_p	µJ	12	40
Repetition rate	f	kHz	100	300
Hatch distance	h	mm	0.08	0.12
Scan speed	v	mm/s	1	10

TABLE 3. DESIGN OF EXPERIMENT PARAMETERS

Run	Repetion rate	Pulse Energy	Scan Speed	Hatch Distance
1	100	30	5.5	0.1
2	100	20	5.5	0.08
3	100	40	1	0.1
4	100	30	5.5	0.1
5	100	30	10	0.08
6	100	40	10	0.1
7	100	20	10	0.1
8	100	20	5.5	0.12
9	100	40	5.5	0.08
10	100	30	1	0.12
11	100	30	5.5	0.1
12	100	30	1	0.08
13	100	40	5.5	0.12
14	100	30	10	0.12
15	100	30	5.5	0.1
16	100	20	1	0.1
17	100	30	5.5	0.1
18	200	16	1	0.08
19	200	16	5.5	0.1
20	200	20	5.5	0.08
21	200	16	5.5	0.1
22	200	12	5.5	0.08
23	200	20	1	0.1
24	200	16	5.5	0.1
25	200	16	10	0.08
26	200	16	5.5	0.1
27	200	16	10	0.12
28	200	16	5.5	0.1
29	200	12	10	0.1
30	200	16	1	0.12
31	200	12	5.5	0.12
32	200	20	10	0.1
33	200	12	1	0.1
34	200	20	5.5	0.12
35	300	13	5.5	0.1
36	300	12	5.5	0.08
37	300	14	1	0.1
38	300	13	5.5	0.1
39	300	13	10	0.08
40	300	14	10	0.1
41	300	12	10	0.1
42	300	12	5.5	0.12
43	300	14	5.5	0.08
44	300	13	1	0.12
45	300	13	5.5	0.1
46	300	13	1	0.08
47	300	14	5.5	0.12
48	300	13	10	0.12
49	300	13	5.5	0.1
50	300	12	1	0.1
51	300	13	5.5	0.1

TABLE 4. DESIGN MODEL

This was conducted in order to obtain an optimal laser process parameters to make antifouling surface based on the responses such as surface roughness and contact angle.

2.4 Surface Analysis and Characterization

An optical profilometer (Bruker Contour GT 3D) was used to measure the roughness of the laser irradiated surface. The area surface texture parameters such as arithmetical mean height (Sa), root mean square (Sq), maximum peak height (Sp), maximum height (Sz) roughness values were measured using this technique.

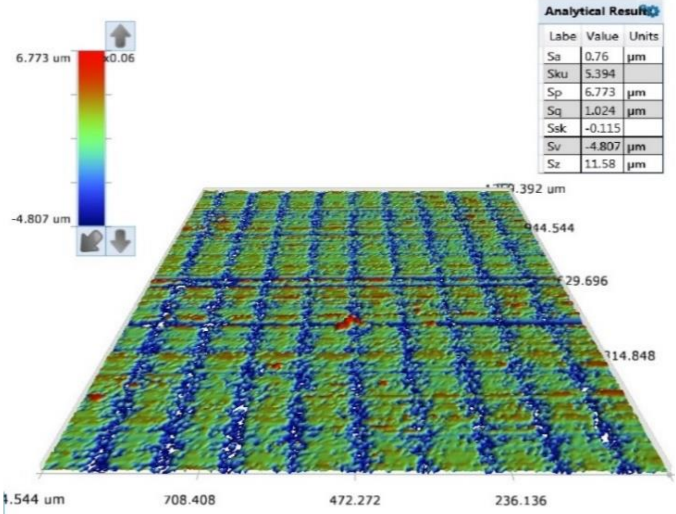
The wetting properties were measured by Contact angle analysis. FTA200 Dynamic Contact Angle Analyser was used for this. Contact angles describe the shape of a fluid drop in contact with a solid. contact angles are used to derive adhesion and wettability parameters of the surface.

3. RESULTS AND DISCUSSION

3.1 Surface Roughness

3D optical profilometer is an instrument which is rapid, nondestructive, and non-contact type of instrument which is capable of measuring the surface roughness and texture features on the surface. The **FIGURE 2** shows the optical profilometry measurement of 11th sample which showed highest contact angle.

The laser micromachined textures on the surface are in the micrometer range and were analyzed with different roughness attributes such as arithmetical mean height (Sa), and maximum height (Sz).



Analytical Results

Labe	Value	Units
Sa	0.76	µm
Sku	5.394	
Sp	6.773	µm
Sq	1.024	µm
Ssk	-0.115	
Sv	-4.807	µm
Sz	11.58	µm

FIGURE 2: OPTICAL PROFILOMETRY OF THE SURFACE TEXTURE OF STAINLESS STEEL 316L

To find the most affecting laser process parameter for the different attributes of the surface roughness mentioned above the response surface method was used. The below **FIGURE 3** shows the main effects plots which depict the most important parametes for roughness attributes such as Sa, and Sz Roughness. It is observed that the Sa values are mostly dependent on the hatch distance and scan speed however the Sz is mostly dependent on laser pulse energy and repetition rate.

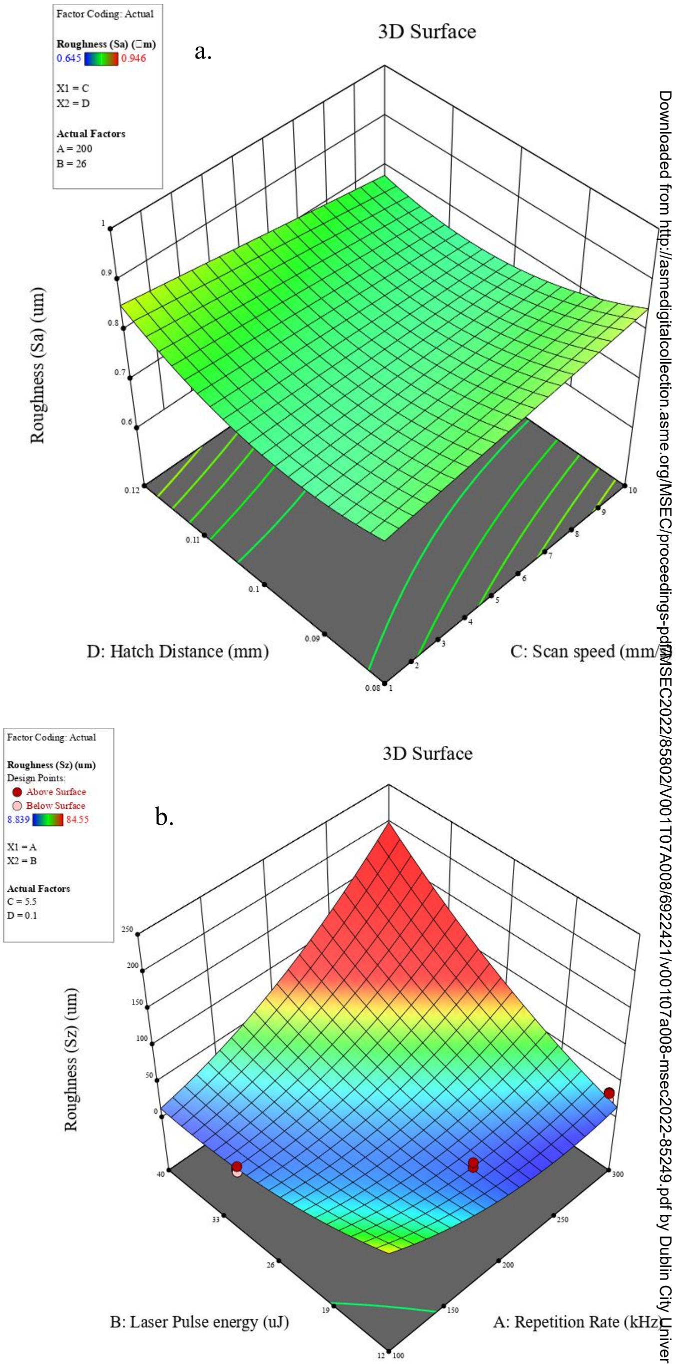


FIGURE 3: SURFFACE PLOTS OF LASER PARAMETERS SUCH AS HATCH DISTANCE, SCAN SPEED AND LASER PULSE ENERGY AND REPETITION RATE ON THE a. Sa ROUGHESS, b. Sz ROUGHNESS VALUES.

The above plots show that in terms of surface roughness the arithmetic mean roughness (Sa) almost is within range of 0.7 to 0.9µm however it is higher when the hatch distance is low and scan speed is high. The maximum height roughness values show very high deviation between 9 to 84 µm. The higher pulse energy and higher the repetition rate the more is the Sz values.

3.2 Contact Angle

Surface contact angle is normally influenced by surface morphology and chemical compositions. The contact angle of the water droplet was analyzed using a video-based optical contact angle-measuring device FTA200 Dynamic Contact Angle Analyser which can calculate many quantities of interest from the drop shape, including static, equilibrium, capillary, advancing & receding Contact Angle.

There are two models of measuring the surface energy used for contact angle measurement which are Wenzel's model and Cassie–Baxter model. The Wenzel's model is used for ideal material conditions hence Cassie–Baxter model is used for this system which determine the degree of wetting.

The contact angle was calculated at the point when the drop landed on the surface. The contact angle test was conducted on the fifty-one samples which were manufactured using different laser parameters. The volume of the water droplet was at an average of 13µl at a controlled flow rate of 1.2 µl/s. The flow rate was kept constant, and the droplet was captured as soon as it landed on the processed surface.

Initially the contact angle on the non-processed stainless-steel sample was observed to be 66.3 º as shown below in **FIGURE 4**.

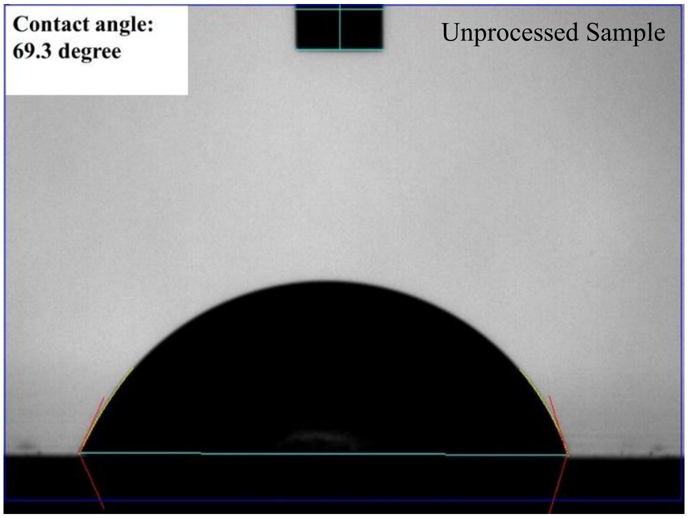


FIGURE 4: UNPROCESSED SAMPLE CONTACT ANGLE

The minimum contact angle was noted to be 21.8º showing hydrophilicity. The maximum contact angle observed was 130.6º showing hydrophobicity.

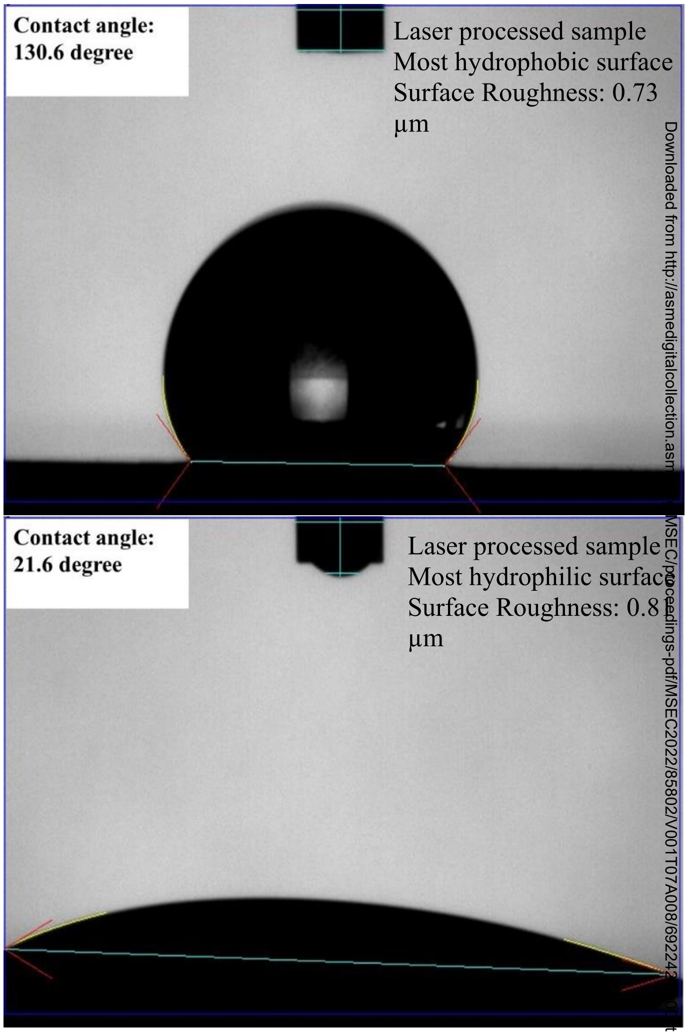


FIGURE 5: RESULTS OF CONTACT ANGLES ON UNPROCESSED SAMPLES AND LASER PROCESSED SAMPLES ON STAINLESS STEEL 316L.

The below **FIGURE *6***, shows the results of all the contact angles of the fifty-one samples.

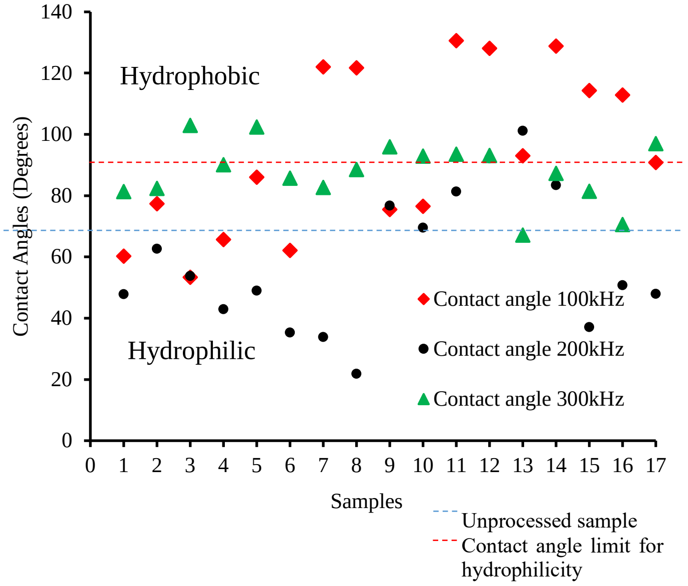


FIGURE 6: CONTACT ANGLE RESULTS OF ALL SAMPLES

From the data presented in **FIGURE *6*** both types of surfaces hydrophobic and hydrophilic are made on the stainless steel 316L substrates.

Out of 51 total samples 19 surfaces were hydrophobic, and rest were hydrophilic based on the theory that if the contact angle is greater than 90º it is hydrophobic. The unprocessed sample had contact angle 69º. These were mostly the samples processed with low frequency that is 100kHz and high frequency 300 kHz have higher contact angle than the unprocessed samples with reduced the surface energy or free energy of the surface. These surfaces show high fouling resistance as they have the low surface energy.

Response surface method was used to find the most influencing laser process parameter for the contact angle. The results show that two parameters which are repetition rate, and the hatch distance were the most influencing parameters. Below **FIGURE 7** shows the relationship between the contact angle numeric factors such as repetition rate and hatch distance. When the repetition rate was low at 100 kHz, and the hatch distance was 0.12 mm it resulted in highest contact angle that is 130º. And the lowest contact angle was recorded at 200 kHz repletion rate and 0.1 hatch distance.

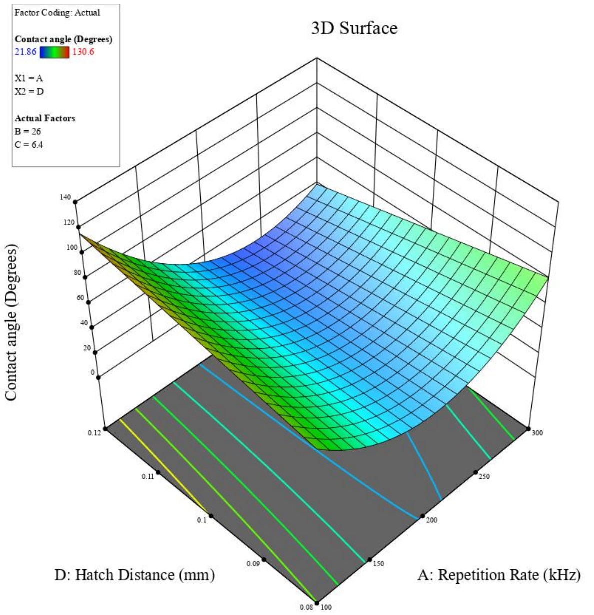


FIGURE 7: RESPONSE SURFACE PLOT OF THE LASER PARAMETERS SUCH AS REPETITION RATE AND HATCH DISTANCE ON CONTACT ANGLE MEASUREMENTS

From above **FIGURE *7***, it is evident that the contact angle is dependent mostly on two factors which are significant which are the repetition rate and hatch distance. It can be observed that the lower repetition rate with high hatch distance gives highest contact angle. Hence with these parameters the hydrophobic surfaces can be fabricated.

4. CONCLUSION

This paper provides an experimental study of ultrafast pulse laser surface structuring of medical grade stainless steel (AISI 316L) for which have unique antifouling abilities. Stainless steel surfaces were textured with femtosecond laser source and the beam was scanned using a galvo scanner in a parallel line pattern at different speeds, at different laser pulse energy and at different repetition rate with variable hatch distances.

A design of experiment was conducted for this which used response surface method to detect the most optimum sample which has highest and lowest contact angle which is a direct function of fouling resistance. The key findings were as follows.

- The maximum contact angle observed was 130º on the sample 11 which was manufactured with laser parameters 100kHz ,30µJ pulse energy, scan speed of 5.5 mm/s and hatch distance of 100µm. The average roughness of this sample was measured to be 0.76µm.
- From the contact angle testing 19 samples out of 51 were hydrophobic (CA≤90º)
- The laser process parameters to develop anti fouling surfaces were optimized by conducting response

surface analysis of the measured parameters such as surface roughness, contact angle and ice adhesion which are important in measuring degree of fouling.

- In the future optimization of these parameters can be conducted and for these various computational methods such as machine learning can be used to predict the results before setting up the parameters. Also, different type of structures can be investigated using different scan strategies.
- Biofouling can be detected using tests such as bacterial adhesion tests.

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