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A REVIEW ON LASER TEXTURING TO ACHIEVE SUPER HYDROPHOBICITY

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Abstract— **The surface is said to be super hydrophobic if the contact angle is greater than 150°. This was achieved by surface modification. The most efficient method of modification of metal surfaces in order to achieve super hydrophobicity is surface texturing using laser radiation. The present paper provides insight on the flexible variation of laser radiation parameters to alter the geometric characteristic on metallic surface carried on Cu, Brass, 304, 316 steel, Titanium alloy (Ti6Al7Nb), Stainless steel (304S15), K9 glass, Aluminium (Al7075-T6), The titanium alloy (Ti-6Al-4V), with thickness of 0.3-0.6mm using fibre laser, by varying the fluence (55-93 J/cm^2), pulse energy, pulse overlap, scanning speed and by varying the laser power to maximum were reviewed. Review suggested that the best super hydrophobic surfaces were achieved by fibre laser texturing with a highest contact angle of 160° at a laser power of 20W and scanning speed of 50mm/sec with increased pulse overlap.**

Keywords— **Super hydrophobicity, laser radiation, anticorrosion, non-wettability, fluence, pulse overlap.**

I. INTRODUCTION

Nature exhibits excellent super hydrophobic surfaces with a high contact angle (CA) of greater than 150° in certain plant leaves such as lotus leaves, rice leaves, butterfly wings and cicada wings which are self-cleaning. This has attracted immense research interest to fabricate artificial super hydrophobic surfaces, which are used for numerous applications such as window glasses, solar cell panels and navigation of ships to prevent marine fouling [1].

It is widely known that a micro-/nano-scale hierarchical surface structure and a low surface energy are two key factors to achieve super hydrophobic surface. In recent research, nano-particle is regardless promising material to prepare super hydrophobic coatings, because the aggregates of nano-particle usually have multi-scale roughness including the nano-scale of primary nano-particles [2].

The low surface energy on plant leaves is due to waxy deposits on the surface. Therefore, altering the surface chemistry of substrates would be a way to make them super hydrophobic. There are three equations that give an idea about the wettability of surface under different conditions - The Young's equation, the Wenzel equation, and the Cassie-Baxter model [3]. Young's equation elucidates the wettability of a uniform surface by the equation:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} * cos\theta$$

Where, 'σ_{SV}' represents surface free energy of solid, 'σ_{SL}' denotes the surface energy between the solid and liquid and σ_{LV} expresses surface free energy between liquid- vapor interface.

Young's equation is based on the assumption of a perfectly smooth and homogenous surface. Surfaces in nature contain much roughness and defects. To deal with this, Wenzel established a roughness factor (r) in the equation, it is given as

$$\mathrm{Cos}\theta_w = \mathrm{r}.\frac{\sigma_{SV}-\sigma_{SL}}{\sigma_{LV}} = \mathrm{r}.\cos\theta$$

Where, θ_w = contact angle of a rough surface.

The Cassie- Baxter model which assumes that the liquid does not penetrate into the outgrowths on the surface rather is suspended on them. The Cassie-Baxter equation is given as

$$cos\theta_{cw} = f.r\ cos\theta + f - 1$$

Where 'f' is fraction of solid surface which is wetted, 'r' is the roughness factor, θ_{cw} is the contact angle.

Numerous approaches have been attempted to fabricate super hydrophobic materials, which include chemical mechanical etching, sol–gel process, layer-by-layer self-assembly, electro spinning, electrode position, CVD (chemical vapor deposition), laser deposition as well as laser texturing [4].

Today, there are many synthetic topography designs known to have super hydrophobic performance, that is, with water contact angle (WCA) near or above 150°. However, there is no systematic guideline for super hydrophobic topography designs. The selection of a topography design for a desired hydrophobic performance depends on many factors; besides the topography design, the choice of materials and the fabrication methods are two other key factors. The selection of material in most instances is governed by the application requirements [5]. In order to achieve the non wet ability of surfaces two tasks must be solved; first one is surface texturing in order to obtain the ordered different-scale relief with the selection of geometric parameters; second one is low surface energy on the material surface.

The most efficient method of the modification of metal surfaces in order to give them non-wet table properties is surface texturing using laser radiation. This method allows to precisely controlling geometric characteristics of the generated relief through the flexible variation of laser radiation parameters. It is worth mentioning that most studies recommend femto second laser complexes for the surface modification of various construction materials. However, an interest towards lasers with nanosecond pulses has significantly grown in the recent years. This is due to the fact that nanosecond laser systems considerably reduce time for the modification of surfaces in comparison with the femto second laser [6].

The principle of the laser surface treatment is basically the result of the interaction among the coherent light beam, the high energy density, the substrate nature and the surrounding atmosphere. The high laser energy density implies the occurrence of the light absorption that causes thermal effects, such as heating, melting or vaporization, or athermal effects, such as peening. The mechanisms of these interactions are influenced by several factors, such as wavelength, beam intensity, surface absorptivity and temperature [7].

Surface textured super hydrophobic metal surface can be used protect against to aerofoils and aircraft engines the accumulation of ice, during high altitude fly as well as to make more weather proof infrastructures [8, 9]. The area of applications of hydrophobicity is quite wide, including power transmission lines, pipes of air conditioners and refrigerators drag reduction, radar or telecommunication antennas, weather proof infrastructures etc. Furthermore, the super hydrophobicity should also enable other highly desirable functionalities, such as anticorrosion, anti-icing [10], anti-biofouling, anti-microbial, low flow resistance, and platelet anti-adhesion [11], which are intrinsically associated with the super hydrophobicity.

The selection of a topography design for a desired hydrophobic performance depends on many factors; besides the topography design, the choice of materials and the fabrication methods are two other key factors. The selection of material in most instances is governed by the application requirements. Steel, Aluminium, Copper and brass are widely used for electronic components and industrial devices due to their high electrical and thermal conductivity. However, they are easily affected by environmental conditions, such as high humidity leading to corrosion. Recently, it has been shown these problems can be prevented on these materials by creating a super hydrophobic surface.

The super hydrophobic behavior of Cu and Brass sheets was studied by **Duong et.al**. [12]. Authors used the Cu and Brass with a thickness of 0.45 and 0.6 mm. Fabrication of hierarchical structures on these metals was carried by using fibre laser (20 W EP-S). Constant pitch size between the adjacent microgrooves was maintained. The laser parameters used were nominal beam spot of about 21 μm, wavelength of 1064 nm and pulse width of~220 ns. A scanning speed of 75 mm/s and repetition rate of 25 kHz with three different fluences were applied separately to the work piece for copper (75, 84, 93 J/cm^2) and brass (55, 65, 75 J/cm^2). This work was focussed to achieve super hydrophobic surface of the metallic substrates by varying the fluence.

It is observed from this work that textured super hydrophobic surfaces on copper and brass can be achieved by using a compact and cost effective nanosecond fiber laser. Directly after fabrication, the samples exhibit hydrophilic behavior but gradually become super hydrophobic over time with the maximum contact angle being achieved after 11 days. The hydrophilic property is ascribed to the laser induced roughness. However, this role of surface morphology changes over time, which results in the surfaces becoming super hydrophobic. The steady state contact angle is about 152° with low contact angle hysteresis of 3–4°. The textured Cu surface exhibits the contact angle of 152° at a lower fluence of 75 J/cm^2 and Brass 152° at 55 J/cm^2.

Andrew Dunn et.al. [13] Performed the work on commercially available, grade 304, 316 stainless steel (SS304) and tests performed on Cr–Mo–Al ‘nit riding’ steel. A pulsed SPI 20WL laser (M^2~1.8) was used with wavelength of 1064 nm, pulse duration of 200 ns, maximum pulse energy of 0.8 mJ and nominal spot size of~50 µm (1/e^2 of maximum intensity), with a repetition rate of 25 kHz. The speed was varied. The authors studied the effect of pulse energy and pulse overlap on friction coefficient and roughness.

In the generation of individual craters, increasing the laser pulse energy increases crater diameter whereas increasing number of pulses increases the crater depth. It is come to know from this work that the crater diameter will be increased with increase in pulse energy; the higher crater diameter of 75μm at pulse energy of 0.8mJ with a single pulse was observed. With same pulse energy of 0.8mJ the crater diameter of nearly 84μm with five pulses was achieved. Similarly the crater depth increases with increase in pulse energy and number of pulses was observed. The higher depth was 65μm at pulse energy of 0.8 mJ with five numbers of pulses. The pulse overlap was also effect the crater depth and diameter, average crater depth increases with increase in pulse overlap. The average crater depth of 35μm was observed under pulse overlap of 95%. at pulse energy of 0.8 mJ. These correlations were affecting the roughness. The arithmetic average roughness of 1.78μm was observed at higher pulse energy of 0.8 mJ and 75% overlap. The friction coefficient was varying with increase in pulse overlap, the higher coefficient of 0.55 was observed on low pulse energy of 0.4 mJ and 0.85 on high pulse energy of 0.8 mJ when overlap was 75%.

Stainless steel specimens were irradiated by **Saltuganov et.a** [14] in air with 1030 nm, 200 fs. Laser pulses with pulse energy upto 12 µJ were focused onto the 32 µm wide (the 1/e level) focal spot on the specimen surfaces using a 35 mm

focal-length lens, the laser pulse energy was kept at 2 µJ, the overlapping step Δ = 25 µm to produce a homogeneous 1×1 cm wide surface texture, laser pulses per spot was N˜1300.9-µm.
The super hydrophobicity was observed with a contact angle of 158° and a rolling angle of 20° by irradiating the stainless steel specimen at laser pulses of 0. 3 ps and laser fluence of 0.23 J/cm^2

Dot-matrix was fabricated on the K9 glass substrates using Photolithography by **Zhanget.al** [15]. Poly dimethyl siloxane (PDMS) was used to modify the micro-size structure. PDMS (elastomer hardener =10:1) was diluted by methylbenzene at the volume ratio of 1:8. A layer of PDMS thin film was coated on the surface of dot-matrix**.** A layer of candle-soot was burned on PDMS. Water flow was used to remove away the non-sticked soot particles. Then, the samples were baked at 85 ℃ for 2 hours. Duo-structure surfaces with both micro-size dot-matrix and nano-size soot particles were fabricated. In this work candle soot was used as nanostructures to fabricate wear-resistant super-hydrophobic surfaces on micro-size dot-matrix. Surface roughness change of dot-matrix before and after PDMS modification, and after candle soot coating was observed. The surfaces of dot-matrix were covered by branch-like soot particles and formed duo-structured roughness. Unlike hydrophilic glass, soot particles are also a type of low surface energy material as well as PDMS. They provided not only nanostructures but also low surface energy. The contact angle from 153° decreases to 150° with the size of the water droplets from 3 µL increases to 7µL. on the coated glass surface. The results exhibit that the WCA of pure dot-matrix surface was only 27° as the glass is a kind of hydrophilic material and the modification with low surface energy materials is indispensable to achieve hydrophobicity. After modification with PDMS, the dot-matrix surface convert hydrophilicity into hydrophobicity with contact angle is of 113°. Finally, super-hydrophobicity with WCA of 153±1° was achieved after the treatment of candle soot with sliding angle of 3°.

Nanosecond laser texturing to control the wettability was done by **Martin et.al [16]** on aluminium sheet of thickness 0.3mm using a 20W fiber laser. A pulsed fibre laser (20W average power, 1060nm wavelength, 9-200nS pulse length, 5 kHz to 250 kHz), focal spot size and a value of 23µm were used. Patches of approximately 10mm x 10mm were textured, using a parallel unidirectional hatch, with the hatch spacing being a variable.1064nm laser producing 60 ns pulses at repetition rates starting at 5kHz, were used. Authors were used nearly 208 samples and produced surfaces with contact angles ranging from 0° to 162°. This work suggested no clear trends could be identified in the relationships of the parameters to the resulting contact angle data. This author work demonstrated that hydro- and Super hydrophobic surfaces can be achieved at higher average powers and hence higher coverage rates. Hydrophobic surfaces with contact angles have been obtained, with the highest contact angles reaching 134° at average laser powers up to 220W.

The texturing on Titanium alloy Ti6Al7Nb was carried out by **Bogdan Antoszewski et.al** [17] with, laser type: diode-pumped disk laser pulse with harmonic generation 3, wavelength: 343 nm, average power: 5 W, pulse duration of 6.2 ps, pulse frequency of 400 kHz can be divided by a natural number from 1 to 10,000, the maximum pulse energy of 12.6 µJ, fluence 4.8 J/cm^2. Laser micromachining was carried out in argon by varying the power and speed of the scanning beam. This work focused on quality of texture obtained on the alloy. Textures produced with row wise by varying the parameters, row 1: power 50%, the laser beam scanning speed of 50 mm/s, row 2: power 50%, the laser beam scanning speed of 100 mm/s, row 3: power 100%, the laser beam scanning speed of 50 mm/s, row 4: power 100%, the laser beam scanning speed of 100 mm/s. After selecting the correct scanning speed of the laser beam and the power of laser, the impact of pulse frequency on the change of the depth of textures was analyzed. At a pulse frequency of 400 kHz, the texture with a depth of 40 microns was obtained. After double-scanning of the surface by a laser beam with a same pulse frequency of 400 kHz, the texture with a depth of 79 microns was obtained. With a pulse frequency of 400 kHz and then scanning the surface by alternate pulse, a texture depth of 63 microns was obtained. When choosing the pulse frequency of 133 kHz, the textures of 16 microns depth was obtained. When choosing the pulse frequency of 80 kHz, the textures of 10 microns depth was obtained. The best texture quality was obtained at the maximum power of the laserv100% and at the scan speed of laser beam of 50 mm/s with double scanning and a pulse frequency of 400 kHz.

Stainless steel (304S15) sheets (1 mm thick) were used in their experiments by **Jonathan et.al** [18]**.** The laser source was a nanosecond fiber SPI laser (20W EPS) with wavelength of 1064 nm. This laser was connected to a galvanometer scanner and F-Theta focusing lens for delivering a focused laser beam over the sample surface with nominal beamspotof21µm The beam profile has a Gaussian shape with M^2 = 1.1. Pulse duration of ~220 ns and repetition rate of 25 kHz were used for all fabrication processes. Microstructures on the samples were created by scanning the laser beam with a fixed speed of 150 mm/s, first in X and then in Y directions. The distance between adjacent laser scanning lines, the so-called scan line separation or pitch size, was kept constant for both paths. In this work effect of power and separation of scan line was analysed. Laser power strongly affects surface morphology of the textured surface so it should influence the surface wettability. For the fluences (33and 36J/cm^2), the roughness value was reasonable which allows for the development of super hydrophobicity. For these values of fluence the measured contact angle 152°was observed. To study the effect of scan line separation on the surface wettability, the laser fluence of 36 J/cm^2 was used for all samples. The contact angle was very low as 10°, for the smallest spacing of 10 µm and was moderate up to 130°, for the large spacing > 200 µm. For the spacing range 50-150 µm the contact angle observed were 150-152°.

Aluminium (Al7075-T6) was used to study the improvement of surface wettability through ultrasonic vibration by **H. Nouri et.al [**19]. Texturing of the surface was done by using conventional turning (CT) and ultrasonic vibration assisted turning-in three modes of linear vibration turning (LVT), elliptical vibration (EVT), and three-dimensional vibration turning (3D-VT) were implemented. The cutting depth was considered constantly (D =0.25mm). In this work the textured surface was achieved by non-conventional turning approach and the same can be compared with the surface produced by conventional turning. The wettability was reduced as the turning was shifted from CT to LVT to EVT to 3D-VT at all feed rates. The anisotropic angle was reduced from 40.1° to 35.2°.

Aluminium alloy AMG-6 surface texturing by [**Kseniya et.al]**[20] was carried and studied using wave- long laser texturing. They used Mini maker 2 M 20 laser system for texturing on the specimen. This work used the laser frequency of 99 Hz, Laser beam speed of 800mm/s and five different laser power (2,6,10,14,18 W). This work studied the properties of textured surface. The static contact angle of 120° at laser power of 18W which is the highest as compared to other textured surfaces produced at lower laser powers (2,6,10,14 W).

The titanium alloy, called Ti-6Al-4V, with 1 mm thickness sheet was used [**Milton Sérgio et.al.] [**21] in this study. The laser was a working on the green emission mode (532 nm). For the study, the pulse repetition rate (f) was fixed at 1 kHz and the pulse length (tp) was 100 ns. The working distance between the lens and the material surface was 200mm. Under the current optical configuration, the minimal spot radius (R) was 50 µm at the focal position. The beam speed was controlled by a computer and can be selected from 1 mm/s to 1 m/s. In this work different power (P) and speed (V) levels for a single run (N1) were used as parameters to produce the microstructures on the substrate. At high speed 100 mm/s, the discrete shots on the surface were visible and, at low speeds and high power, 25 or 50 mm/s and 20 W, the trail marks were noticed. The minimum value of roughness was 0.23 µm for N10, V100, P10 and the maximum value was 0.53 µm for N1, V100, and P20. The water repellent conditions were achieved at N1V50P05, N1V100P05, N2V25P05, N2V50P05, N5V25P05, N5V50P05, N5V100P10 and N10V25P10.

This review gives the average data for material and laser system parameters used are given in Table1.

Table 1 Materials and laser system parameter used

Material used	Cu & Brass, 304, 316 steel, Titanium alloy (Ti6Al7Nb), Stainless steel (304S15), K9 glass, Aluminium (Al7075-T6), The titanium alloy(Ti-6Al-4V),
Thickness	0.3 - 0.6mm
Texturing M/c	SPI fiber laser (20 W EP-S)
Pitch used	Constant/varied
beam spot size	20 -50µm
Wavelength	1030-1064 nm
Pulse duration	200-220 ns
Pulse Energy	0.8 mJ
Scanning speed	70 - 75 mm/s
Repetition rate	20 - 25 kHz
Fluence	75,84,93 J/cm^2 for Cu, 55,65,75 J/cm^2 for brass

Review suggests that, to achieve superhy drophobic surfaces the following areas of study are widely preferred by different researchers. (i)The effect of laser irradiation on surface structure (ii) Time effects on surface wet ability (iii) Super hydrophobic behaviour (iv) Impact of laser pulses (v) Impact of pulse energy (vi) Friction and hardness (vii) Ablation efficiency (viii) Study of variation of contact angle with different laser parameters.

II. THE EFFECT OF LASER IRRADIATION ON SURFACE STRUCTURE [DUONG ET.AL]

Prior to fabricating the microgroove structures, the effect of individual pulses on the surface was studied. The craters are formed due to the rapid heating of the copper, resulting in melting and evaporation (ablation), at the location of the laser radiation. Most of the material from the center the crater was re-deposited in the area surrounding the crater. The total amount of removed material depends on laser fluence. The crater diameter increased from approximately 27 to 30 µm under fluence of 55 and 75 J/cm^{2}respectively. It is noted that, due to high pulse overlap, the depth of channels is larger than that of the craters created by a single pulse.

III. TIME EFFECTS ON SURFACE WETTABILITY

[Duong et.al]

The laser treated surfaces becomes hydrophilic immediately after fabrication. However, the surface wettability decreases over time, as indicated by the increase in contact angle. The first measurement after processing was made after the samples were left under ambientconditionsfor20-25 days. It can be seen that the contact angle exhibits a sharp increase during the first ten days, which then slows to a gradual growth before finally reaching a steady state, the steady state was reached after about 11 days for copper and brass samples irradiated with75 and 55 J/cm^{2}respectively. However, it took much longer, approximately 30 days, for copper irradiated with93J/cm^2.The samples with larger d (100μm to 75μm) appear to become hydrophobic faster than those with smaller d (50 to 25 μm). It has been clear that, the laser textured copper and brass surfaces become hydrophilic directly after fabrication , the wet ability changes to hydrophobic over time.

IV. SUPERHYDROPHOBIC BEHAVIOR

[Duong et.al]

A high contact angle (>150°) is only one important characteristic of a super hydrophobic surface. Another vital factor is small contact angle hysteresis or rolling-off angle (not exceeding 10°) this value can be measured by comparing advancing and receding angles of a droplet on a tilted surface. It was also found that rolling-off angle for all the samples could be as small as 2°. The potential to create such laser textured super hydrophobic surfaces on copper or brass could enable the fabrication of devices which are highly water resistant, potentially improving corrosion resistance.

V. IMPACT OF LASER PULSES AND PULSE ENERGY

[Andrew Dunn et.al.]

The effect of increasing number of pulses was studied. The number of pulses per crater was varied between one and five for each array of craters generated at various pulse energies. Crater depth was found to increase linearly with number of pulses for pulse energies greater than the ablation threshold (0.2 mJ to 10Jcm^{-2}). Results showed that the diameter of the crater is independent of the number of pulses used. From the results where the number of pulses was varied, the crater depth was found to be almost unchanged by changing the pulse energy when above the ablation threshold, while the diameter increased linearly with pulse energy. The crater diameter, however, is very much dependent on the area of the central part of the beam for which the fluence exceeds the ablation threshold, explaining the dependence on pulse energy.

VI. STUDY OF CONTACT ANGLE AT DIFFERENT LASER PARAMETER

In the study single variable correlation analysis fails to provide any significant correlations between contact angle and any single process variables. A number of derived variables are also tested, these include pulse peak power, pulse intensity pulse fluence, inline incubation, hatch incubation (given by spot diameter / hatch spacing), area incubation, total fluence, specific energy (average power divided by the focal spot diameter and traverse speed multiplied together), and area coverage rate. The highest contact angles reached was 134° at average laser power up to 220W.

VII. CONCLUSION

The textured super hydrophobic surfaces on copper and brass can be achieved by using a compact and cost effective nanosecond fiber laser. The super hydrophobic over time with the maximum contact angle achieved was 152° with a low hysteresis of 3-4°. Increasing the laser pulse energy increases crater diameter whereas increasing number of pulses increases the crater depth. Increasing the pulse overlap an increase in surface roughness. Super hydrophobic surfaces with contact angles up to 160° have been produced using a fibre laser at average powers up to 20W, and hydrophobic surfaces with contact angles up to 134° with a DPSS laser running at average powers up to 220W. The best texture quality was obtained at the maximum power of the laser and at the scan speed of laser beam of 50 mm/s.

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