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Transition from superhydrophilic to superhydrophobic state of laser textured stainless steel surface and its effect on corrosion resistance

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1 **Transition from superhydrophilic to superhydrophobic state of laser**
2 **textured stainless steel surface and its effect on corrosion resistance**

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16
17
18 **Abstract**

19 This work systematically investigates the evolution from superhydrophilic to
20 superhydrophobic surface state on corrosion behaviour of SS316L produced by Nd:YAG
21 nanosecond direct laser texturing (DLT). Results confirm perfect correlation among
22 wettability and corrosion, hence superhydrophobic surface with a contact angle of 169°
23 reflects in enhanced passivity, lower anodic dissolution and corrosion current reduction.
24 Characterization of the corrosion attack by 3D microscopy reveals high sensitivity of
25 superhydrophilic surfaces on corrosion propagation direction in regard to the laser beam
26 passage (90°/0°). However, this trend completely diminishes with superhydrophobic
27 development. Further, DLT also completely prohibits intergranular corrosion detected with
28 the non-processed sample.

29 **Keywords:**

30 A. Stainless steel

31 B. Polarization

32 B. SEM

33 C. Intergranular corrosion

34 C. Passivity

35 C. Pitting corrosion

36

37 **1. Introduction**

38 Recently, intensive research efforts have been devoted to synthesize lotus-like,
39 superhydrophobic, surfaces with water contact angle in excess of 150° and sliding angle
40 below 5° [1][2]. Such functionalized surfaces possess several unique beneficial properties, i.e.
41 extreme water repellency [3][4], self-healing [5], self-cleaning [6], reduced drag in laminar
42 and turbulent flows [7][8], enhanced heat transfer [9][10] and improved corrosion resistance
43 [11][12][13][14].

44 Artificial super-hydrophobic surfaces have been successfully fabricated via various
45 chemical methods, such as plasma etching, anodic oxidization, chemical vapor deposition,
46 sol-gel method, etc. [11]. Nonetheless, in recent years laser surface texturing has emerged as
47 a novel, versatile, clean and low waste nanotechnology for producing multi-modal surfaces
48 with micro/nano structure due to laser ablation and melting [2][5][7][15]. Emelyanenko et al.
49 [5] fabricated a superhydrophobic surface on 321H AISI stainless steel. Their results have
50 confirmed extreme water repellency with excellent functional durability under prolonged
51 abrasive wear and cavitation loads. Ta et al. [16] demonstrated that superhydrophobic
52 surfaces on SS304 with steady contact angle of 154° and contact angle hysteresis of 4° can be
53 fabricated via direct laser texturing (DLT) with cost-effective, compact nanosecond laser
54 system. Further, it has been shown [3][14] that nanosecond laser texturing of various Al
55 alloys can greatly improve resistance to localized corrosion attack in a sodium chloride

solution due to multimodal roughness with μ -cavities consisting of air entrapment hence preventing penetration of corrosive species at solution/metal interface.

However, despite considerable progress in this area, little attention has been paid to investigate transition from superhydrophilic to superhydrophobic effect on corrosion behaviour of laser textured stainless steel surface along with the influence of laser passage direction ($90^\circ/0^\circ$). Hence, the aim of this work is to study evaluation of hydrophobicity, i.e. water repellency and corrosion behaviour of direct laser textured (DLT) SS316L in an aggressive 0.6 M NaCl solution. Specific attention was focused on the collateral influence of bimodal surface topography to the initiation and propagation of corrosion.

2. Material and methods

2.1. Laser texturing

Surfaces of commercial AISI 316L stainless steel samples with diameter of 15 mm were textured by using a marking nanosecond Nd:YAG pulsed laser (LPKF, OK DP10) with a wavelength of 1064 nm, pulse duration of 40 ns (FWHM), pulse frequency of 25 kHz, and pulse energy of 0.22 mJ. A scanning head (Scanlab SCANgine 14) with an F-Theta focusing lens was used for delivery of a focused laser beam over the sample surface with beam spot diameter of 0.03 mm and a constant speed of 150 mm/s, first in the y (90°) and then in the x (0°) direction (e.g., see dashed lines in [Fig. 1a](#)). The distance between adjacent laser scanning lines – the so-called scan line separation equaled 50 μm in both directions. Before processing, all samples were ultrasonically cleaned in distilled water for 12 min and rinsed by ethanol.

2.2. Surface morphology and wettability measurements

Surface morphology of untreated and laser textured samples prior to and after corrosion experiments were examined by a non-contact Alicona G4 3D optical Infinite-Focus

81 Measuring (IFM) device and JEOL JSM-6500F scanning electron microscope (SEM).
 82 Evolution from superhydrophilic to superhydrophobic state of laser textured samples was
 83 examined by static contact angle θ measurements using a goniometer of our own design.
 84 Here, a droplet with volume of 5 μL distilled water was delivered to the investigated surface.
 85

86
 87 **Fig. 1.** SEM micrographs of laser textured surfaces.

The transition from superhydrophilic to superhydrophobic state and its influence on corrosion behaviour was studied by using 4 samples (DLT#1-4), textured by same laser parameters, but exposed to ambient conditions ($T = 25^{\circ}\text{C}$, $RH = 35\%$) for different time periods after laser texturing, i.e. 30 min (DLT#1), 24 hours (DLT#2), 11 days (DLT#3) and 1 month (DLT#4), respectively. Before the transfer of samples to the electrolytic cell for corrosion experiments the contact angle measurements were performed and after that the samples were ultrasonically degreased in ethanol and rinsed in deionised water for 3 min each.

2.3. Electrochemical measurements

Electrochemical measurements were carried out with a PAR 263A potentiostat/galvanostat using a three-electrode component corrosion cell under static conditions. A saturated calomel electrode was used as a reference, graphite rod as a counter electrode along with the sample embedded in a Teflon PAR holder as the working electrode (1 cm^2). Test medium was a naturally aerated ($\text{pH} = 8.2 \pm 0.2$; $T = 23 \pm 1^{\circ}\text{C}$) 0.6 M NaCl solution prepared with deionised water.

Corrosion was tested using linear polarization resistance (LPR) and cyclic polarization (CP) electrochemical techniques. Before LPR and CP experiments open circuit potential measurements ($E_{\text{ocp}} = f[t]$) was performed for 60 min in order to stabilize the surface, whereas corrosion potential E_{corr} , was determined at the end of the stabilization process. LPR measurements were performed in the potential range $\pm 10\text{ mV}$ relative to E_{corr} using 0.1 mV/s potential scan rate. CP scans were performed with a scan rate of 1 mV/s , started at -250 mV vs. E_{corr} and increased in anodic direction up to 600 mV . Afterwards, the polarization direction was reversed and progressed in cathodic direction to the starting potential. All

electrochemical corrosion techniques were pre-tested to ensure the repeatability of the experiments.

3. Results and discussion

3.1 The effect of laser texturing on surface morphology

Surface morphology of DLT sample (Fig. 1) clearly indicates the structuring effect due to laser irradiation. As shown in Fig. 1a multidirectional structure due to different laser scanning directions ($90^\circ/0^\circ$) is well pronounced. The μ -nets have $50\ \mu\text{m}$ spacing corresponding to the scan line separation. The oriented structure along the second (last) laser texturing passage (Fig. 1b) indicates its primary solidification path (from left to right and vice versa) of the ablated/molten material. Further, SEM image at higher magnification (Fig. 1c) reveals multimodal oriented structures as a consequence of constant melting, ablation and deposition of the recast material during laser texturing.

Fig. 2. 3D surface topography of laser textured surface with schematic presentation of the line roughness measurements along the first laser scan (y_1 and y_2) and the second laser scan x (x_1 and x_2).

In order to evaluate the influence of DLT on the surface topography and roughness in both the vertical (y) and horizontal (x) directions of laser-beam scan an optical 3D microscope was

used. Fig. 2 shows the 3D topography of laser textured surface, where the distinctive influence of the second laser texturing path can be observed. Further, μ -channels are completely opened and parallel to the last laser scanning direction and closed to the opposite direction (first laser scan direction).

The roughness parameters obtained along valleys (x_1, y_1) and crests (x_2, y_2) of the specific direction in regards to the first (e.g., see y_1 and y_2 lines in Fig. 2) and second (e.g., see x_1 and x_2 lines in Fig. 2) scan lines path are listed in Table 1.

Table 1. Roughness parameters values in specific directions marked on Fig. 2.

Parameter	y_1	y_2	x_1	x_2
R_a [μm]	3.05	4.24	2.06	2.69
R_q [μm]	3.74	4.82	2.33	3.35
R_z [μm]	12.52	14.86	6.65	11.68
S_a [μm]	4.62 ± 0.15			

As can be seen from the results, roughness values parallel to the first laser beam passage reflects in much higher values compared to those obtained in parallel to the second scanning direction. For example, the roughness R_a achieved the minimum value of $2.06 \mu\text{m}$ along valleys of the μ -channels (x_1) produced during the second texturing path, whereas in the opposite direction (y_1) it equals $3.05 \mu\text{m}$ due to the metal ejection at the edges produced during the second DLT path. Similar trend was also obtained along crests, but with higher values of all roughness parameters in the first, i.e., y direction of laser passage path through the treated surface. Nonetheless, 5 separated measurements of 3D amplitude parameter on different DLT samples have confirmed good surface uniformity with an average S_a value of $4.62 \pm 0.15 \mu\text{m}$. For comparison, the non-processed sample achieved around 26 times lower S_a roughness with a value of $0.175 \pm 0.02 \mu\text{m}$.

3.2. Surface wettability development

The corrosion resistance of metals depends on several parameters, such as homogeneity and stability of the passive film, microstructural properties as well as surface roughness and wettability. Although higher surface roughness increases the wettability and sensitivity to localized corrosion attack, this is not necessarily true in the case of modified hydrophobic surfaces [11][14]. To examine the isolated influence of wettability on corrosion behaviour we used the inherent property of laser textured metal surface, where a transition from hydrophilic to hydrophobic state appears if such a surface is exposed to the air at room conditions [11][12][17]. During this process the surface roughness on microscale stays the same.

The contact angle of non-processed surface equals 97° , whereas immediately after laser texturing the surface is in super-hydrophilic state with a contact angle $\theta = 0^\circ$, i.e., the water forms a thin film covering the whole sample. When the textured surface is exposed to air at ambient conditions, the hydrophobicity is developed [11][12]. In our case, the contact angle increased to $\theta = 110^\circ$ in 11 days, while the superhydrophobic state with $\theta = 169^\circ$ and sliding angle below 1° was achieved in 1 month.

3.2. Linear polarization resistance (LPR) measurements

LPR measurements were performed after one hour's immersion at open circuit in the potential range ± 10 mV relative to E_{corr} using 0.1 mV/s scan rate. The corresponding values of polarization resistance R_p , determined from the slope of $E-i$ curves [$R_p = (dE/di)$] are given in Table 2.

The lowest R_p value in a 0.6 M NaCl solution was confirmed for the superhydrophilic samples DLT#1 & DLT#2, which achieved a value of $2.34 \text{ k}\Omega \text{ cm}^2$ and $13.37 \text{ k}\Omega \text{ cm}^2$, respectively. Both of these samples indicate lower corrosion resistance to uniform corrosion, compared to the non-processed/base 316L steel sample, which reached a value of $67.57 \text{ k}\Omega \text{ cm}^2$. However, with hydrophobic and superhydrophobic state R_p increases to $80 \text{ k}\Omega \text{ cm}^2$ and

94.24 kΩ cm², indicating enhanced resistance to the transfer of electrons to electro-active species in chloride environment [18].

Table 2. Characteristic results derived from electrochemical measurements of non-processed and DLT processed samples exposed to ambient conditions for different time periods: R_p from LPR, and E_{corr} , E_{pit} , E_{rp} and i_{corr} from CP curves.

Sample/Condition	θ [°]	R_p [kΩ cm ²]	E_{corr} [mV _{SCE}]	E_{pit} [mV _{SCE}]	E_{rp} [mV _{SCE}]	β_a [mV/dec]	β_c [mV/dec]	i_{corr} [μA/cm ²]
Non-processed SS316L	97	67.57	-175	18	-195	330	169	0.72
DLT#1 (after 30 min)	0	2.34	-321	-66	-316	271	159	18.61
DLT#2 (after 1 day)	0	13.37	-212	-51	-214	330	102	2.53
DLT#3 (after 11 days)	110	80.04	-98	-4	-159	178	93	0.33
DLT#4 (after 1 month)	169	94.24	-162	219	-197	269	81	0.29

3.3. Cyclic polarization (CP) measurements

CP curves of non-processed SS316L and DLT samples are shown in Fig. 3a and b. All CP curves show typical active/passive behaviour in the forward (anodic) scan. Afterwards, a sharp increase in anodic current due to a stable pit growth or pit propagation at pitting potential E_{pit} is observed with a well-defined hysteresis in the reverse, i.e. cathodic scan. Further, no distinct primary passivation potential was detected, which is typical for stainless steel materials.

The various characteristic potentials such as E_{corr} , E_{pit} , and E_{rp} obtained from the CP curves in a 0.6 M NaCl solution are presented in Table 2, whereas their detailed description and definition is given in Ref. [19]. The current density i_{corr} in μA/cm² is calculated according to the Stern–Geary equation:

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2.303 \cdot R_p \cdot (\beta_a + \beta_c)} \quad (1)$$

where R_p [$\text{k}\Omega \text{ cm}^2$] is polarization resistance (determined from the LPR test) and β_a and β_c are the anodic and cathodic Tafel constants (in mV/dec) determined by the Tafel extrapolation method.

Fig. 3. Cyclic polarization (CP) curves in 0.6 M NaCl solution of non-processed SS316L sample compared to (a) DLT superhydrophilic samples and (b) DLT hydrophobic /superhydrophobic samples.

Experimental results presented in Fig. 3 and Table 2 confirms the tremendous effect of the surface state of direct laser textured 316L stainless steel on corrosion behaviour. From the CP scans it is clearly understood that DLT in the superhydrophilic state has inferior corrosion

resistance, compared with the base material. On the contrary, laser processed samples with developed hydrophobic/superhydrophobic state indicate superior corrosion resistance compared to the non-processed sample. A distinctive shift of the pitting potential can be noticed with the DLT#4 superhydrophobic sample ($\theta = 169^\circ$), which was exposed to the ambient condition for 1 month. Here, E_{pit} is located 201 mV more positive than with the non-processed 316L stainless steel sample, suggesting that pitting corrosion is unlikely to occur.

Further, the analysis of characteristic potentials obtained from the CP curves shows that among all the samples, the DLT#4 exhibits the highest passivity ($E_{\text{pit}} - E_{\text{corr}}$) with lowest anodic dissolution in the transpassive region. Moreover, the calculated values of i_{corr} confirm good accordance with the LPR measurements, indicating importance of transition from superhydrophilic to superhydrophobic state on the corrosion behaviour. Thus, i_{corr} values indicate the following order of the corrosion resistance: DLT #1 ($18.61 \mu\text{A}/\text{cm}^2$) < DLT#2 ($2.53 \mu\text{A}/\text{cm}^2$) < non-processed 316L < DLT#3 ($0.33 \mu\text{A}/\text{cm}^2$) < DLT#4 ($0.29 \mu\text{A}/\text{cm}^2$).

3.4. Influence of wettability development on corrosion propagation

3D surface morphology after CP corrosion tests with the insert of wettability evolution (the contact angle measurement) are shown in Fig. 4. The corrosion without any preferred direction is developed on non-processed surface (Fig. 4a). Contrarily, the 3D measurement of corroded hydrophilic surface (Fig. 4b) clearly reveals high dependence of the corrosion attack propagating inside μ -channels produced during the last laser beam passage, despite the fact that the lowest roughness was obtained along the valleys of these channels (see Fig. 2 and Table 1). This phenomenon can be explained by an opened μ -channel along the last laser scanning direction and barriers in the perpendicular direction (see Fig. 2). However, the development of superhydrophobicity reduces the preferred direction of corrosion propagation, as clearly visible from Figs. 4c-d.

239

240 **Fig. 4.** 3D surface morphology after CP tests in a 0.6 M NaCl aqueous solution of (a) non-
 241 processed surface; and surfaces experienced the transition from (b) superhydrophilic (c)
 242 through hydrophobic to (d) superhydrophobic state.

243

244 With superhydrophobic state developed, this effect is completely eradicated, since in this
 245 case the μ -channel along the last laser scanning direction does not act anymore as a channel
 246 for microfluidic. Instead, the developed superhydrophobicity increases a trapping air and
 247 reduces the fractional area of liquid–solid interface, as suggested by the Cassie-Baxter's
 248 model [20]. Such hierarchical super-hydrophobic structure with entrapped air acts as an
 249 effective corrosion resistant coating thus making the penetration of water molecules and Cl^-
 250 ions to the surface more difficult [3][11][14].

Fig. 5 shows surface condition after the CP tests of non-processed and laser textured superhydrophilic sample (DLT#1), respectively. Although, both SEM images confirms pitting attack in the form of spherical/non-oriented pits with the base sample and completely oriented pits with DLT#1 sample, only the base/non-processed sample exhibited intergranular corrosion (IGC) attack. This is an additional important benefit of DLT process, since austenitic chromium-nickel (300 series) stainless steels are prone to IGC along the Cr-depleted grain boundary in the proximity of Cr_{23}C_6 chromium carbides [21]. Since these precipitates are nobler than the adjacent boundary the galvanic effect promotes the anodic dissolution of the more negative Cr-depleted grain boundaries. In contrast, as can be seen in Fig. 5b, laser texturing completely prevents IGC attack, even in superhydrophilic state. This phenomenon is most likely attributed to more homogeneous microstructure with smaller amount of galvanic cells inside the material as a consequence of melting and deposition of the recast material due to laser texturing.

Fig. 5. SEM images after CP measurements. (a) Base/non-processed 316L sample and (b) DLT#1 superhydrophilic sample.

4. Conclusions

Direct laser texturing (DLT) using a nanosecond Nd:YAG laser was confirmed as an effective method for fabrication of superhydrophobic surfaces on 316L stainless steel. It was

shown that the transition from superhydrophilic ($\theta = 0^\circ$) through hydrophobic ($\theta = 110^\circ$) to superhydrophobic ($\theta = 169^\circ$) state occurs due to exposure of the textured surface to ambient conditions, which enables examination of the isolated influence of wettability on corrosion behaviour.

LPR and CP results confirmed perfect correlation with the development of water repellency. The highest corrosion resistance with the highest polarization resistance ($R_p = 94.24 \text{ k}\Omega\text{cm}^2$), improved passivation ability, and lowest corrosion current density ($i_{\text{corr}} = 0.29 \text{ }\mu\text{A/cm}^2$) was measured on the superhydrophobic sample. The electrochemical measurements clearly demonstrate that both the hydrophobic and superhydrophobic surface experience lower corrosion activity as the non-processed surface with 26 times lower roughness. Improved corrosion resistance is directly associated with entrapped air inside hierarchical hydrophobic structure, which reduces the fractional area of liquid–solid interface which makes the penetration of corrosive species to the surface more difficult.

Further, the 3D topography of superhydrophilic surface after corrosion test revealed a strong preferential direction of corrosion propagation along μ -channels that are oriented along the last texturing passage (0°). However, this effect is significantly reduced by development of water repellency, resulting in non-oriented pitting attack. More importantly, presented results indicate that laser texturing completely inhibits the initiation of inter-granular corrosion as a consequence of more homogeneous microstructure with smaller amount of galvanic cells, i.e. Cr-depleted grain boundaries/ Cr_{23}C_6 carbides.

Acknowledgments

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351

Electronic Annex

Figure captions

Fig. 1. SEM micrographs of laser textured surfaces.

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Table captions

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