

Experimental evaluation of the hygienic performance of laser treated and sand blasted samples from AISI 316 stainless steel

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Abstract. There are strict and quite rigid hygienic requirements regarding the materials, which are meant to operate in contact with food products. Their surfaces shall not be prone to retaining contaminants. They must allow easy cleaning and sanitation. Currently there are plenty of available methods, which could be implemented to achieve this goal. Most popular and still widely used is the application of a Teflon coating. Because of its disadvantages, the global community of engineers is actively seeking for an alternative. In relation to this up-to-date problem, the article presents the results from an experimental evaluation of the hygienic performance of laser processed and sandblasted samples of AISI 316 steel. The evaluation was carried out using liquid contaminants such as tap water, cow milk, virgin olive oil and saline solution with grown *Bacillus Subtilis* bacteria in it. After processing the surface of the material with infrared laser and after subjecting it to chemical passivation with HNO₃, ultra-hydrophobic properties were accomplished. Treatment with ultraviolet laser resulted directly in ultra-hydrophobic surface without the necessity for chemical passivation. Sandblasting was found to be ineffective in spite of how it is advertised to companies. Obtained data also set directions towards attaining oleophobic surfaces.

1 Introduction

One of the key and most responsible tasks, which stand in front of the engineers working in the field of food processing industry, is to ensure the safety of the consumers by fulfilling a set of established and widely accepted design requirements aimed towards avoiding the contamination of the manufactured and treated goods. Hazardous contaminants, which may find their ways into the products, and subsequently into the users through consumption, could be various volatile, low-molecular chemical substances associated with toxic and/or cancerogenous effects, as well as traces of heavy metals, free radicals, radionuclides, allergens, water-based contaminants containing strains of living microbiological organisms and so on.

The surfaces of the primary and auxiliary technological equipment, which is used for processing of food products, shall be resistant to the frequent interactions with aggressive chemical compounds present in the composition of the mentioned products, and also in the agents used for cleaning and sanitation. The materials, which are intended to operate in direct contact with food, shall not undergo corrosion and/or erosion. They must not be prone to retaining contaminants on their free surfaces. The later shall be smooth and without open pores, allowing easy cleaning and effective sanitation.

There is an established and well-accepted set of requirements, which apply for the materials that are intended to be used in contact with food and pharmaceutical products. Many of these requirements are incorporated in great variety of regulations,

standards and even laws. Some of these are enforced within the boundaries of certain geographical regions, while others are global. Most of them come down to certain design rules and steps, which have to be followed in order to ensure that the surfaces of the materials tend to remain as clean as possible. They shall not retain contaminants and shall also allow easy and effective cleaning and sanitation. In majority of the cases, the contaminants, which end up on the surfaces of the materials, are in liquid form – they are either water-based or oil-based.

Considering the above stated, it is essential for the engineers, who are involved in designing the primary as well as the auxiliary technological equipment for the mentioned industries, to take the necessary measures in order to ensure that the materials, which are intended to operate in contact with food products, tend to repel liquid contaminants as much as possible. Presently there are many available methods, which could be used in order to enhance the hydrophobic properties of the exposed surfaces. The most common one, and still most popular, is the application of coatings based on PTFE (polytetrafluoroethylene). These coatings however are quite easy to damage. In addition, they tend to quickly wear out and deteriorate, which is generally seen as a serious drawback. This is why, the global community of engineers working in the food industry is actively seeking an alternative, thus the development of one such an alternative or optimizing the performance of an existing and currently implemented method is an up to date problem.

The wetting behavior of the materials is governed by the surface tension. It is a topic well-covered in the

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literature. When a droplet of some liquid is placed on the surface of a random material, the mechanical balance between the forces arising from the action of the surface tensions at the boundaries between the three medias (solid, liquid and air), causes the droplet to take a specific form (figure 1) characterized by the angle of wetting (or contact angle) θ . This is described by the Young's equation (equation 1) [1].

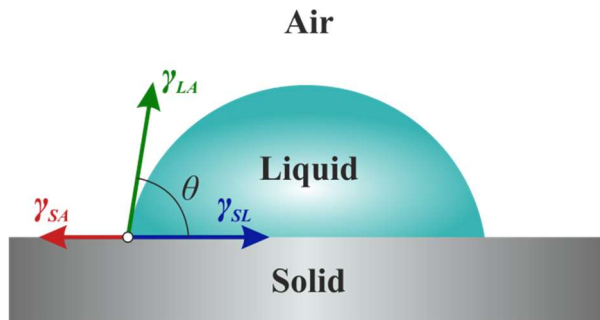


Fig. 1. Wettability of a flat smooth solid surface given by the wetting angle θ as described in Young's equation.

$$\cos \theta = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} \quad (1)$$

where: θ is the contact angle, γ_{sa} is the solid-air surface tension, γ_{sl} is the solid-liquid surface tension, and γ_{la} is the liquid-air surface tension [2 – 5].

If the angle of contact θ is lower than 90° , the surface is considered hydrophilic or also wettable. When θ exceeds 90° , the surface is considered hydrophobic or non-wettable. If the angle θ is greater than 150° , the case is widely accepted to be referred to as super hydrophobic (or ultra-hydrophobic) [3 – 5].

Young's equation however, describes an idealistic scenario as it treats the contact between the liquid and the material as a contact established on a perfectly smooth and flat surface, which is chemically homogenous. In reality, such a surface does not exist. The actual surfaces are rough to a certain degree. They frequently feature open pores while chemical homogeneousness is rather rare [6]. The effects of chemical heterogeneousness are taken into account in Cassie's equation (equation 2) as follows [7]:

$$\cos \theta_r = \sum_i f_i \cos \theta_i \quad (2)$$

where θ_r is a resultant wetting angle for a chemically heterogeneous surface, f_i is a relative portion of the i^{th} surface, which is characterized with a corresponding θ_i wetting angle [7].

From Cassie's equation (equation 2), two additional equations have been derived. They describe two wetting scenarios on a rough surface, which are referred in the literature as "wetting modes" [6]. The first wetting mode is when the liquid permeates the spaces (cavities) between the higher areas of the rough surface's micro-geometry (figure 2). It is described by Wenzel's equation (equation 3).

$$\cos \theta_w = r \cos \theta \quad (3)$$

where: θ is the contact angle for a flat and smooth surface, and r is a number greater than 1, which represents the ratio between the actual surface area of

contact and the surface area projected on the plane of the material [2, 6, 8, 9, 10].

The second wetting mode occurs when there is an air trapped within the cavities beneath the liquid (figure 3) – the cavities, which is formed between the higher areas of the rough surface's micro-geometry. This mode is described by the equation of Cassie and Baxter (equation 4):

$$\cos \theta_w = f_s (\cos \theta + 1) - 1 \quad (4)$$

where: θ is the contact angle on a flat and smooth surface, while f_s is a number smaller than 1 and greater than 0. It represents the relative portion of the solid surface area, which is in direct contact with the liquid [2, 3, 4, 5, 6].

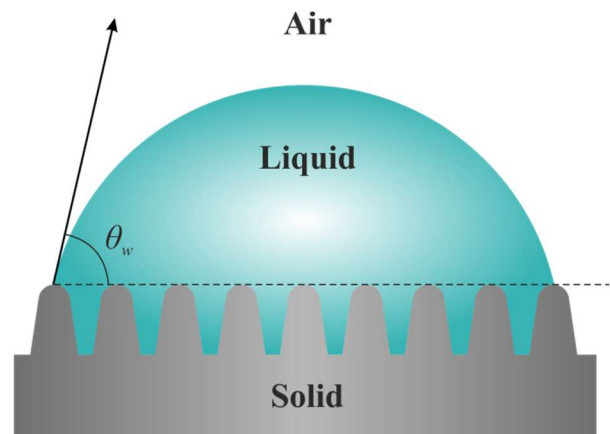


Fig. 2. First wetting mode, where the liquid fills the cavities formed between the higher areas of the surface's micro-geometry.

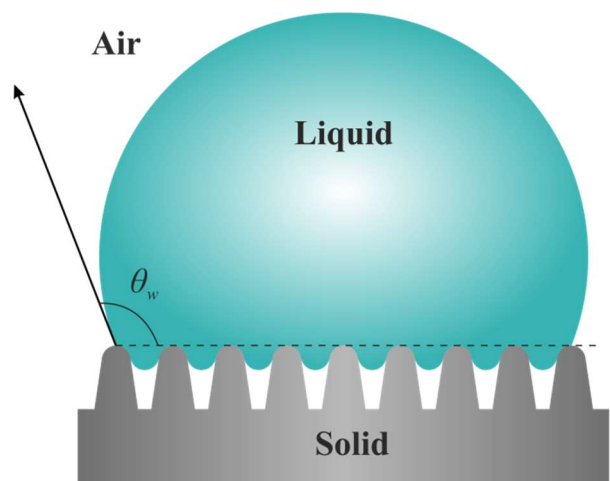


Fig. 3. Second wetting mode, when air is trapped beneath the liquid within the cavities formed between the higher areas of the surface's micro-geometry.

It could be seen from Wenzel's equation (equation 3) that increasing the roughness (expressed in the equation through the coefficient r) would cause a decrease for the wetting angle θ , thus attaining hydrophobic properties for naturally hydrophilic materials is inapplicable when the first wetting mode is involved. The realization of the second wetting mode however, could indeed result in a surface with hydrophobic characteristics, even if the base material itself is hydrophilic. This conclusion could be drawn

by analyzing the equation of Cassie and Baxter (equation 4). However, certain geometric conditions shall be met in order for this wetting model to occur. The micro-geometry of the surface shall be composed of higher areas (microscopic peaks) with sharp tips. The actual area of contact between the liquid and the material, expressed in Cassie-Baxter's equation through the coefficient f_s , must be as low as possible. The later could be accomplished by increasing the distance between the microscopic peaks and by making their tips sharper. There is a limit for this distance though, which is found to be proportionally tied to the liquid's capillary constant α (equation 5). The minimal height of these peaks is also restricted with the lowest value being dependant on this same constant [6].

$$\alpha = \sqrt{\frac{\gamma_{la}}{\Delta\rho g}} \quad (5)$$

where: γ_{la} is the liquid-air surface tension, $\Delta\rho$ is the difference between the density of the liquid and the density of the air and g is the Earth's gravitational acceleration. In order for the second wetting mode to take effect, the general size of the peaks must be significantly lower than the size of the droplet, thus the droplet shall be in contact with significant number of these sharp-tipped microscopic features of the rough surface [6].

Currently available methods for achieving hydrophobic properties for a surface of a material, which are alternative to the application of Teflon coating, rely on modifying its micro-geometry, so it becomes rough in such a way that its roughness profile meets the conditions for the realization of the second wetting mode. Presently there are several developed approaches, which could be implemented in order to do this:

- grafting and stimulated growth of nanoparticles [11 – 14],
- chemical etching [15, 16],
- laser texturing by surface ablation [10, 17, 18, 19, 20, 21].

Of all listed methods, the use of laser beam for texturing of surfaces, by the means of ablation (partial removal of material by melting and/or vaporization) is the method gaining better popularity. This is due to the fact that the expanding accessibility to laser technologies, along with the associated equipment becoming more diverse in terms of technical capabilities, is making the application of the method mentioned much easier and also far more cheaper.

The aim of the current article is to present the results from an experimental evaluation on the effectiveness of the laser ablation as a method for accomplishing hydrophobic and oleophobic properties of non-magnetic austenitic stainless steels. It should also be noted that this article is a continuation and expansion to our previous work, the results from which were published last year [22, 23]. Therefore, the results from the current article are closely related to the results published in the cited preceding articles.

In our previous work, the effectiveness of the laser ablation was experimentally evaluated using distilled water to carry out the experiments. For the purpose of

the current article, the evaluation was repeated, but with regular tap water, which is known to contain free ions and dissolved inorganic compounds, such as CO_3^{2-} , Cl^- , Na^+ , F^- , S^{2-} , SiO_3^{2-} , $\text{Si}(\text{OH})_4$, $[\text{SiO}(\text{OH})_2]_n$ and so on. The presence of these ions is established from publically available protocols from the local regulatory agency, which monitors the condition of the tap water and assesses its compliance with the domestic regulations. For the purpose of the current experiments, we haven't set any specific requirements for the water used, simply because we wanted to carry out the evaluation under conditions, which would be as close as possible to those common in manufacturing environment. In addition to the tap water, complex multiphase and multicomponent liquid systems, reminiscent to most of the contaminants common in the food processing industry were used to carry out the present evaluation and enrich the data from similar studies already available in the literature [10, 17, 18, 19, 20, 21]. These include: milk and saline solution, with specific strain of microorganisms grown in it (see section "Materials and methods" for details). In order to assess the feasibility of using laser ablation for achieving oleophobic properties, experiments were also conducted with olive oil, which is another common contaminant in the food industry.

In our previous experiments, we only used IR laser to conduct the texturing. Since we've gained access to a UV laser, the opportunity was used to evaluate its effectiveness as well. Our results from last year showed that the wetting angle θ_w for the treated surface is dependent on the performance of the passive layer [22]. The properties of the later could be enhanced by carrying out chemical passivation, which could in turn lead to a further increase of the resulting contact angle. This is why we enhanced the experimental work by combining the laser treatment with a subsequent chemical passivation, using hydrofluoric acid (HF) and nitric acid (HNO_3).

As mentioned in our previous two articles, the described experimental evaluation was in part initiated by representatives of some commercial entities, who sought advice from the academic community. Some of them testified that they had made investments towards obtaining an equipment designed to treat surfaces by the means of sandblasting – blasting the material with a stream of microscopic glass beads, which results in texturing. It has come to our knowledge that such equipment had been advertised to the companies as being effective in improving the hygienic performance of the treated materials. Since there seem to be no specific data (exact numerical values) available in the literature regarding the effectiveness of this treatment, we have decided to also conduct an experimental evaluation on it as well.

2 Materials and methods

For the purpose of the study, several samples of non-magnetic austenitic stainless steel AISI 316 were prepared. This particular steel was chosen because no much of experimentation with it is reported in the

literature [22, 23], and because it is one of the most widely used type of steel in the food processing industry. The test pieces were first subjected to electrochemical polishing until surface quality of a mirror was reached. By using a standard laboratory, microliter syringe, droplets from the liquids, used to carry out the experiment, were placed on the polished surface and the values for the contact angle θ were measured. The usage of the microliter syringe was necessary in order to ensure equal amount of liquid contained within the droplets.

Samples were then subjected to laser ablation using two types of lasers. The first laser was the same used in our previous experiments – an infrared pulsed laser, operating at the wavelength of 1064 nm. The maximal available value for the power of the laser, which is 20 W, was set. The frequency of the pulses was 100 kHz with 100 mm/sec scanning speed. The laser's focal distance was 205 mm. The second laser was fibre-based pulsed UV laser operating at the wavelength of 355 nm and 365 mm focal distance. The power was also set to the maximal available value, which was 6 W. The frequency of the pulses and the scanning speed are same as those for the IR laser. It shall be noted that at 355 nm wavelength, the energy of a single photon is equal to 3.49 eV, while at 1064 nm it is 1.16 eV, which is nearly 3 times of a difference. Another fact to consider is that for 1064 nm, the absorptivity coefficient for the steel is around 0.38 compared to 0.53 for 355 nm [24].

Immediately after laser ablation, some of the samples treated with the infrared laser were submerged in a hydrofluoric acid (HF) for 5 minutes. They were then rinsed with distilled water (dH₂O) and submerged in 30% solution of nitric acid (HNO₃) for 90 minutes. The purpose of the hydrofluoric acid was to clean the surface and remove any possible defective regions, so an optimal and uniform contact with the HNO₃ is guaranteed. The nitric acid itself was used as it is known universal passivation agent. Our decision not to carry out this chemical treatment for the samples processed with the UV laser is explained and justified in section "Results and discussions". After the chemical passivation with HNO₃, the samples were again rinsed with dH₂O and left to rest for 5 days. Droplets of the liquids used to carry out the experiments were then placed with the microliter syringe and the values for the resulting contact angle θ_w were measured. The method used to measure the contact angle is describes in our previous articles.

One particular sample, which was treated with the UV laser, was used for the purpose of SEM analysis. Immediately after being processed with the laser, it was subjected to a 30-minute long cleaning with acetone in ultrasonic bath, which operated at 40 kHz. The sample was then kept submerged in the acetone and was taken out of it right before being placed in the vacuum chamber of the SEM equipment.

The chosen scanning pattern (for the laser treatment) consisted of crossing perpendicular lines reminiscent to a network (see [22]). The parameter P, which governs the distance between the lines, was set to 0.04 mm. This value was chosen on the grounds on

the results from our previous experimental evaluation [22].

In order to do more comprehensive study on the action of the UV laser, a single sample was treated by running a scanning pattern consisting of two straight perpendicular lines, which crossed each other at one point. After the treatment, the test piece was cleaned with acetone in the ultrasonic bath – 40 kHz for 30 minutes. Then it was brought to SEM (Scanning Electron Microscope) and EDS (Energy Dispersive Spectroscopy) analysis. The EDS analysis was done in order to check if the thermal effects from the laser would cause redistribution of the key alloying elements. Similar analysis was already done to assess the effects of the IR laser and the results are available in one of our previous articles on the topic [22].

To determine the wetting angles, the droplets where first photographed with a digital microscope (RS Pro). The measurements were then conducted using a software intended for image analysis – Optika Proview. More detailed description on the method used to measure the contact angle is available in [22].

The liquids used were as follows:

- tap water,
- cow milk with 3,6% fat content,
- virgin olive oil,
- saline solution (H₂O and 0,85% NaCl) in which *Bacillus Subtilis* bacteria were grown.

One separate sample was additionally treated with the IR laser and then subjected to chemical passivation by being kept in HF for 5 minutes, rinsed with dH₂O, submerged in 30% solution of HNO₃ for 90 minutes, rinsed with dH₂O once again and let to rest for 5 days. Then it was submerged in the suspension containing *Bacillus Subtilis* bacteria. The test piece was kept in this suspension for 24 h at 30° C. It was then subjected to a wet sterilization by being placed in an autoclave Biobase® at 121° C for 30 minutes. After cooling, the test piece was washed with sterile saline solution and the concentration of the bacteria in it was determined. The sample was once again submerged in the suspension for 24 h at 30° C and then placed in the autoclave (Biobase®) with the temperature set to 160° C where it stayed for 2.5 h. After cooling, the test piece was washed with sterile saline solution and the concentration of *Bacillus Subtilis* in it was determined by following protocol in accordance with ISO 18593:2018 "Microbiology of the foog chain - Horizontal methods for surface sampling". This procedure was only carried out with a sample treated with the IR laser – the reasons and the justification behind this decision are explained in the section "Results and discussion".

Another sample with the same dimensions, which was not subjected to laser ablation (left in its original polished state), was also submerged in the saline solution with *Bacillus Subtilis* in it. The test piece was kept in the suspension for 24 h at 30° C. It was then washed with sterile saline solution and the concentration of the bacteria determined.

In order to assess the hygienic performance of the sandblasting, as a method for surface texturing, few samples were subjected to it. The mean size of the

glass beads used was 300 μm . The treatment itself is normally carried out by directing high-velocity water stream with suspended microscopic glass particles. The equipment used for the purpose was a commercial one, supplied by Falch GMBH. After being blasted, few samples were subjected to chemical passivation with HNO_3 by following the procedure explained above. The wetting angles were then measured.

3 Results and discussion

The average values for the wetting angle θ on the smooth polished surface for the used liquids are given in table 1. Table 2 and table 3 contain the values for the wetting angle θ_w from the samples, which were treated with the IR laser, but were not subjected to chemical passivation and also for the samples, whose surfaces were textured with the IR laser and then underwent passivation with 30% solution of HNO_3 .

Table 1. Average values for the wetting angle θ on the smooth polished surface for the used liquids.

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle θ , °	83.89	58.92	82.10	32.71
Standard deviation, °	8.68	2.21	3.34	1.83
Number of measurements	20	20	20	20

Table 2. Average values for the wetting angle θ_w on the surface textured with IR laser – without chemical passivation.

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle θ_w , °	128.50	132.93	123.61	^{*)} UOB
Standard deviation, °	5.64	5.40	7.99	
Number of measurements	20	20	20	

^{*)}UOB – Ultra oleophilic behaviour

Table 3. Average values for the wetting angle θ_w on the surface textured with IR laser – with subsequent chemical passivation using 30% HNO_3 .

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle θ_w , °	155.76	153.90	152.15	^{*)} UOB
Standard deviation, °	7.38	2.75	7.21	
Number of measurements	20	20	20	

^{*)}UOB – Ultra oleophilic behaviour

As one can see from the numbers in table 1 and table 2, there is a significant increase of the wetting angle for the tap water, the cow milk and the suspension, which contained *Bacillus Subtilis*. Hydrophobic properties are therefore achieved after the test pieces underwent texturing of their surfaces by the means of laser ablation. Regarding the tap water, the values are consistent with the results for the distilled water, which we obtained from our preceding research [22]. The cow milk is a good representative of many

liquid contaminants common in the food processing industry. Its basis is water with different salts and sugars dissolved in it. It also contains fatty acids, solid proteins and microorganisms.

After the samples were subjected to chemical passivation with 30% HNO_3 , a further increase of the wetting angle θ_w is observed (table 3), with the values exceeding the margin for what is considered to be ultra-hydrophobic behaviour.

The virgin olive oil sticks better to the steel, which is clearly seen from the low value for the contact angle θ measured on the smooth polished surface. Laser texturing actually results in ultra-oleophilic behaviour (table 2, table 3 and table 4) – the droplet spills immediately after being placed, which practically makes it impossible to do a measurement. This is because the first wetting mode occurs in this particular case. In order to attain oleophobic properties, the second wetting mode shall be the one taking place. The capillary constant α for the olive oil is a lower number (see equation 5) in comparison to the one for the water. This means that in order for the second wetting mode to take effect, the distances between the microscopic peaks shall be smaller and their tips sharper.

Table 4 shows the measured wetting angles on the surface, which was textured with the UV laser. As one can see the treatment results in ultra-hydrophobic properties without additional chemical passivation. Because of this, we have decided not to treat these samples with HF and HNO_3 . We simply thought that it would not be necessary, since values which exceeded 150° were directly achieved – for the tap water the contact angle θ_w went even beyond 160°.

Table 4. Average values for the wetting angle θ_w on the surface textured with UV laser.

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle θ_w , °	164.16	156.16	147.11	^{*)} UOB
Standard deviation, °	4.85	3.67	3.07	
Number of measurements	20	20	20	

^{*)}UOB – Ultra oleophilic behaviour

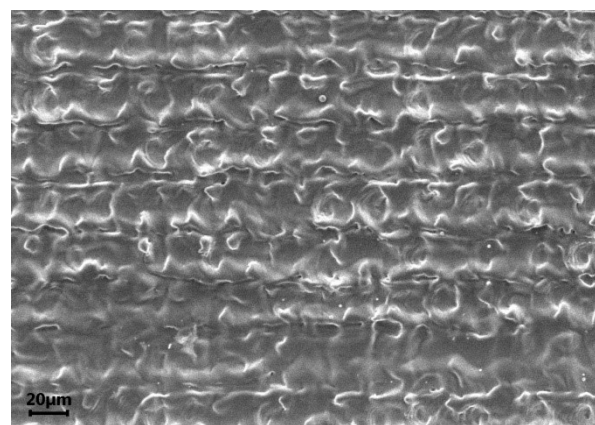


Fig. 4. SEM image of the surface textured with UV laser – 500X, 20 kV, 120 μA , SED.

The ultra-hydrophobic behaviour observed for the samples treated with the UV laser could be explained

with the micro-geometry of their surfaces (figure 4). As one can see from the SEM image obtained with the secondary electron detector (SED), the treatment results in convex areas (microscopic crests), which are scattered and rather chaotically distributed. They are also lower in height and have thinner tips. These specifics of the micro-geometrical characteristics contribute to a much smaller value for f_s in Cassie-Baxter's equation (equation 4), which in turn increases the angle of contact θ_w . The microscopic peaks on the surface textured with the IR laser are wider and more arranged (see [22]). This causes the liquids to establish contact on a surface with higher area relative to the entire surface area – higher value for f_s in Cassie-Baxter's equation (equation 4).

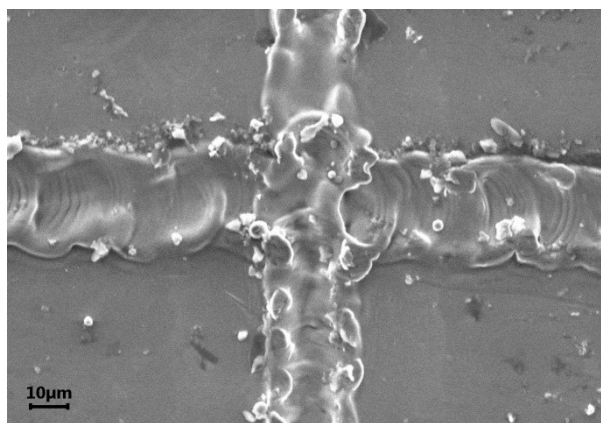


Fig. 5. SEM image of two single tracks left by the UV laser, 1000X, 20 kV, 120 µA, SED.

We shall mention of an unexpected effect, which we observed with the samples treated with the UV laser. After some experimentation, at one point the textured surface lost its hydrophobic properties. Quick examination with a simple magnifying glass revealed the reason straightway. Once we place the droplet and measure the wetting angles (at both sides of the droplet), the latter gets removed with a simple piece of clothing. What remains is a thin residual layer of liquid – where the contact with the surface would occur. Once the liquid contained in this layer evaporates, a residual solid deposit remains. In time, it slowly grows thicker and thicker, to a point where it fills up the cavities between the microscopic peaks. When this happens, the conditions for the second wetting mode to occur are no longer met. The wetting mode shifts from second to first and when this happens, the surface becomes hydrophilic. We tried to restore the ultra-hydrophobic properties by cleaning with NaOH and H₃PO₄, but to no avail. The residual solid deposit from the cow milk is mostly organic in nature (proteins, sugars, salts and so on), which is why we tried to remove it with NaOH. Tap water on the other hand, contains lot of dissolved ions and some inorganic compounds. Upon drying, it saturates and crystallization takes place, forming crystals such as those of CaCO₃, Na₂CO₃, NaCl, SiO₂.nH₂O, etc. We tried removing these using H₃PO₄. As it seems however, the usage of NaOH and H₃PO₄ affects the chemical properties of the passive layer, which causes a change in the observed wetting angle. This clearly showed that despite achieving ultra-

hydrophobic characteristics by treating the surface of the steel with UV laser alone (without subsequent chemical passivation), these ultra-hydrophobic characteristics appear to be unstable and extremely sensitive to minor changes of the micro-geometric parameters. In this particular case, these changes were caused by the residual solid deposits left after the vaporization of the used liquid contaminants. The hydrophobic properties attained after texturing with IR laser are much more stable and not so sensitive, simply because the microscopic peaks are much higher. The lower spaces between them are deeper and not so easily filled with solid deposits.

Figure 5 shows the SEM image of the two crossing single tracks left by the UV laser, obtained with the secondary electron detector (SED). One can see from the image that the laser causes surface melting and subsequent flow of this melt with direction away from the track, which leads to the formation of microscopic ridges from both sides. In comparison, the IR laser (see [22] where SEM images of the IR laser track are published) causes not only a partial melting, but also flash vaporization of small amounts of metal. The formed gaseous phase quickly expands, throwing bits of the surrounding liquid in all directions. The resulting higher areas are from building up of droplets of molten metal falling and solidifying on top of each other. The gaseous phase (in plasma state) also contributes by the means of condensation and subsequent deposition.

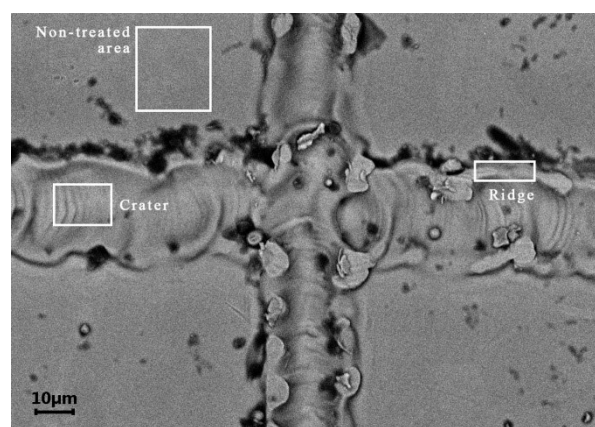


Fig. 6. SEM image of two single tracks left by the UV laser, 1000X, 20 kV, 120 µA, SED.

Table 5. Numerical results from the EDS analysis as shown on figure 6.

Element/Location	Non-treated area	Crater	Ridge
Cr	16.95%	16.94%	15.44%
Ni	9.20%	7.71%	8.10%
Mo	2.27%	1.87%	2.08%
Si	0.47%	0.47%	0.56%

SEM image of the same crossing straight single tracks, but obtained with the back-scattered electron detector (BSED) is shown on figure 6. It reveals rather uniform distribution of the elements. EDS analysis was ran to check the exact concentrations of the key alloying components – on the non-treated area, inside the crater and on the ridge as shown on figure 6. The results are given in table 5. As one can see from the numbers, no significant redistribution occurs, indicating rather weak effects from the thermal action

of the laser beam. In comparison, the IR laser was found to cause much more noticeable changes in the concentrations of the key alloying elements, such as Cr, Ni and Mo (see [22]).

Table 6. Average values for the wetting angle θ_w on the sandblasted surface – without chemical passivation.

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle $\theta_w, ^\circ$	81.67	50.86	*NM	25.73
Standard deviation, $^\circ$	5.42	3.02		3.68
Number of measurements	20	20		20

*NM – not measured

Table 7. Average values for the wetting angle θ_w on the sandblasted surface – with chemical passivation using HNO₃.

Parameter/Liquid	Tap water	Cow milk	Suspension with <i>Bacillus Subtilis</i>	Olive oil
Wetting angle $\theta_w, ^\circ$	92.04	62.70	*NM	29.05
Standard deviation, $^\circ$	1.33	1.89		3.87
Number of measurements	20	20		20

*NM – not measured

Table 8. Concentration of *bacillus subtilis* before and after sterilization of a sample textured with IR laser and subjected to chemical passivation with 30% HNO₃.

Stage	Concentration of <i>Bacillus Subtilis</i> , cfu/mL
Before sterilization	1.2.10 ⁷
After wet sterilization	4.5.10 ²
After dry sterilization	4.0.10 ⁰

Table 6 and table 7 contain the numerical results for the measured wetting angles on the sandblasted samples – for the surface which did not undergo chemical passivation and for the surface, which underwent chemical passivation with 30% HNO₃. As one can see, contrary to the common believe established among the staff of commercial companies, sandblasting actually lowers the wetting angle, making the surfaces even more hydrophilic, which is consisted with the specifics associated with the first wetting mode. Chemical passivation on the other hand results in an increase of the angle.

Table 8 contains the numerical results from the determined concentration of the *Bacillus Subtilis* bacteria applied with the suspension of saline solution. As one can see from the numbers, the dry sterilization appears to be quite ineffective for the samples treated with the IR laser. This is due to the fact that this type of sterilization relies on the formation of condensation, as the droplets improve the conditions for more effective heat transfer. The textured surfaces however, repel these droplets, not letting the formation of condensation. This is why, wet sterilization at higher temperature and prolonged time for heat treatment is necessary to sanitize the hydrophobic surfaces. The concentration of the bacteria in the solution residual from the washing of the samples not treated with the laser was determined to be 1.8.10⁷ cfu/mL.

No samples textured with the UV laser as well as sandblasted test pieces, were subjected to treatment with the *Bacillus Subtilis* containing suspension. We have decided that it would not be necessary, since the UV laser was found to produce quite unstable hydrophobic properties, while the sandblasting actually increased the hydrophilic behaviour.

4 Conclusion

Experimental evaluation has been conducted on the effectiveness of using laser treatment for attaining hydrophobic properties on austenitic stainless steel. Despite the fact than similar experiments have been reported in the literature, the current experiment enriches the available data as it offers numerical results obtained with regular ion-containing tap water, as well as other liquids, which adequately represent contaminants, which are quite common in the food processing industry, such as cow milk, virgin olive oil and saline solution containing specific bacteria. In addition, the values for the wetting angle for virgin olive oil on a flat polished surface could be used for a further development of new methods or optimization of existing ones in pursuing of the aim to achieve oleophobic properties for stainless steel by implementing surface texturing with laser. A comparison has been made on the effectiveness of using infrared and ultraviolet laser beams for processing of the materials mentioned.

Experimental evaluation has also been conducted on samples textured by the means of sandblasting. Results for similar study are currently not found in the available literature. The obtained data are important, since this method is apparently advertised to companies operating in the field of food processing. It is being promoted as an effective way to improve the hygienic performance of the used materials (steel in particular) – a claim, which seemed to not be backed by specific and exact numerical data.

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