Micromachining using ultra short laser pulses (USLP) has evolved over the past years as a versatile tool for introducing functional features in surfaces at a micrometric and even at a sub wavelength scale. Being able to control the surface topography at this level provides a method to change the wetting behavior of a great number of materials. In most cases, when a surface has a natural tendency to be wetted (high surface energy), increasing its roughness will increase the spreading of water over it, and when it is naturally hydrophobic this roughness can dramatically enhance the water repellency. In this study, anti-ice properties of water repellent laser machined materials are investigated. Therefore, a stainless steel substrate (AISI 304L) has been textured with regular hatched patterns, using UV and green laser pulses of 6.7ps. In order to decrease the surface energy, a thin hydrophobic coating has been applied on top of these structures. Super-hydrophobic state has been reached for many of the samples, and small hysteresis values have been measured to confirm the so-called, self-cleaning, or “lotus effect” properties of the engineered surfaces.

Keywords: picosecond, anti-ice, ultra short laser pulse, super-hydrophobic, micro-machining

1. Introduction

The use of ultra short laser pulses (USLP) allows machining of features with a micrometric precision, as the laser beam can be accurately positioned and tightly focused into a spot size of several microns [1]. The guided laser beam selectively removes material from the predefined tracks, and the high energy that is concentrated in the spot instantly vaporizes the material according to a mechanism known as laser ablation, which produces very limited heat affected area [1]. In addition, ultra short pulse laser processing generates a self organizing effect on the processed area, known as Laser Induced Periodic Surface Structures (LIPSS), which have a periodicity of typically sub wavelength scale [2]. USLP machining also allows processing a broad range of materials, including metals, ceramics, glass and plastics [1].

Therefore, it is easy to create a dual scale roughness on a surface by means of USPL micro machining, with sizes in the order of magnitude of those of natural super-hydrophobic (SH) surfaces, like that of the Lotus leaf [3]. The SH state is reached when the water static apparent contact angle (APCA) exceeds 150° [4]. Due to the easy water roll off of on slightly tilted surfaces, freezing and accumulation of atmospherically deposited ice over SH surfaces is prevented under certain conditions [5].

The exceptional low wetting is achieved for materials with the proper composition and roughness. The easy roll of, which is required for the anti-ice properties of such surfaces, is related to the so called Cassie-Baxter state [6], where air pockets remain trapped in between the liquid-solid interface, see Fig 1(a). The Cassie-Baxter state is generally characterized by a low contact angle hysteresis (CAH) value, i.e. the difference between the advancing and receding water contact angle (CA_{adv} and CA_{rec}), and also by a low sliding angle [4]. Another situation, referred to as the Wenzel state [7], where the liquid continuously wets the surface while keeps a high static water contact angle, is also possible. The Wenzel state is related to high contact angle hysteresis or sliding angle values, and should be avoided for keeping the water repellant properties of the surface. Intermediate regimes, where water partially fills the gaps of the rough surface without reaching the deepest part of it, are also possible [8]. The key for producing water repellant surfaces with easy to roll properties is creating a roughness with high aspect ratios, which would prevent the transition from the Cassie-Baxter to the Wenzel state [8].

![Figure 1. Cassie-Baxter (a) and Wenzel (b) states.](image-url)
2. Experimental setup

A TRUMPF TruMicro 5050 was employed as the laser source, which delivers short pulses below 10ps at a maximum energy per pulse of 125 μJ at its central wavelength (1030nm). A Second and Third Harmonic Generator units (SHG & THG, respectively) were used for converting the laser source wavelength to visible and ultraviolet light at 515 and 343nm, with a maximal energy per pulse of about 63 and 31 μJ, respectively. An Intelly-scan 14 galvoscanner by Scanlabs was used for the beam guiding over the target, and an fθ telecentric lens with a focal length of 103 mm was employed for the final focusing of the laser beam.

The laser tracks were designed in a way that a rough surface consisting of paraboloid-shaped protuberances was generated, which yields the highest apparent CA values based in the simulations run by Marmur et al. for a number of different geometries [10]. The production of such shapes by USLP is feasible due to the Gaussian laser beam intensity profile, in combination with the accurate removal of material from the crossing straight lines of a regular hatched pattern, see Fig.2. The resultant topography is comparable to the protrusions of a Lotus leaf.

Changing the spacing between the laser tracks, referred here as hatch distance (hₜ), and the number of times that each pattern is subsequently machined, referred here as over scans (OS), allows changing the number of peaks per area and increasing its aspect ratio (AR); which is defined by the spacing between the peak and its height (d), see Fig.3.

\[ AR = \frac{d}{h_t} \]

The average power was selected in order to have the narrowest ablated tracks, with still a good material removal rate. The repetition rate and the beam speed were adjusted in order to have a high pulse overlap but preventing plasma shielding effects [11]. Table 1 shows the parameters that were applied.

After laser processing, the samples were coated via plasma enhanced chemical vapor deposition (PE-CVD) at the Fraunhofer Institut für Fertigungstechnik und Angewandte Materialforschung (Fraunhofer IFAM) in Bremen (Germany), in order to reduce the surface energy. Two diamond-like carbon (DLC) coatings were applied using a mixture of hexamethyldisiloxane (HMDSO) and oxygen as precursor gases. DLC coatings are known to have excellent tribological properties, which would improve the erosion resistance of SH surfaces. Furthermore, the generated coating can be turned into hydrophobic depending on the selected conditions in the plasma chamber [12].

Contact angle measurements were performed using distilled water in an OCA20 contact angle measurement system by Data Physics. Each measurement is the average of three runs that were performed in three arbitrary selected locations on each sample.

The anti-ice performance of the patterns was tested in a climate chamber, referred to as the Eisomat, developed by the Fraunhofer IFAM. The climate chamber is able to run icing rain tests that simulate environmental icing conditions. The samples were placed in the sample holder, allowing cooling down for 45 minutes down to -5 °C at a relative humidity of 65% and a wind speed of 9 m/s at -5 °C. Then, water at 0 °C was sprayed for 10 seconds, and a photograph was taken of the sample’s surface. After 10 minutes a second photograph was taken. Subsequently, water was sprayed again for 10 seconds. Then, after 5 minutes a third photograph was taken. Finally, the wind speed was increased to 30 m/s for a few seconds, after which a fourth photograph was taken.

3. Results

SEM microscopic analysis of the samples was performed in order to study the surface after the coating process. Fig 4 shows the generated structures with increasing hₜ. Aspect ratios were estimated by measuring the spacing of the peaks from the SEM pictures and the depths by subsequently focusing an optical microscope at the tops and bottoms of the surface. The number of OS was adjusted in order to reach a sufficient AR, according to previous experiments, which yielded the highest apparent CA for this structure [13]. Measurements of APCA (for the non processed coated surfaces), CA₁₅, CA₁₂₀ and CAH are included in Table 2.
Sample number 4 was coated under slightly milder conditions, which resulted in a more hydrophobic coating, with a static contact angle of about 100° measured over the non laser-textured flat surface. Samples number 1, 2 and 3 were coated under equal conditions and a more energetic plasma coating, which led to an apparent CA of 92 degrees on the flat areas.

Fig 5 shows the pictures that were taken immediately after the icing rain test. The dark rectangles are laser machined areas and their anti-ice performance can be checked by comparing the size and density of frozen droplets with the surrounding areas, which are not machined but have the same chemical composition. It is shown that the sample with lowest CAH, Fig 5 (d), shows the best anti-ice properties; as the easy water roll of prevents ice accumulation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( h_d ), ( \mu m )</th>
<th>APCA flat</th>
<th>( \text{CA}_{\text{ad}}, ^\circ )</th>
<th>( \text{CA}_{\text{rec}}, ^\circ )</th>
<th>CAH, ( ^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>92</td>
<td>161.4</td>
<td>153.8</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>92</td>
<td>154.0</td>
<td>144.1</td>
<td>9.8</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>92</td>
<td>154.8</td>
<td>139.8</td>
<td>15.1</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>100</td>
<td>166.9</td>
<td>163.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Sample number 4 was coated under slightly milder conditions, which resulted in a more hydrophobic coating, with a static contact angle of about 100° measured over the non laser-textured flat surface. Samples number 1, 2 and 3 were coated under equal conditions and a more energetic plasma coating, which led to an apparent CA of 92 degrees on the flat areas.

Fig 5 shows the pictures that were taken immediately after the icing rain test. The dark rectangles are laser machined areas and their anti-ice performance can be checked by comparing the size and density of frozen droplets with the surrounding areas, which are not machined but have the same chemical composition. It is shown that the sample with lowest CAH, Fig 5 (d), shows the best anti-ice properties; as the easy water roll of prevents ice accumulation.
4. Discussion

CA measurements show that it is necessary to reach a minimum value of CAH in order to achieve a good anti-ice functionality. Low CAH is the result of the combination of high density packing of the protuberances and a surface with low surface energy. Increasing the spacing of the peaks increases the solid-liquid contact area, thus higher CAH. This leads to poor anti-ice properties and it is probably associated with the Wenzel state, were water wets the whole surface and therefore drops are cached and have difficulties to roll. It is remarkable that all the samples have a \( \text{CA}_{\text{ad}} \) above 150°, so can be considered SH. Samples number 3 and 4 show an equal \( \text{CA}_{\text{ad}} \), but the increased spacing between the peaks of sample number 4 would explain the increased CAH of sample 4 (9.8 vs. 15.1 degrees).

The sample with the lowest CAH value showed the best water and ice repellant properties. It is assumed that air was kept trapped in the “valleys” of the structure, so the liquid is seldom in contact with the surface, thus can easily roll before freezing. The anti-ice effect is then expected when water drops are unstable over a surface that is slightly tilted.

The contact angle measurements also suggest that the spacing between the peaks should be reduced below 18 \( \mu \)m in order to find the best water repellent properties. This is difficult due to the overlap between the laser machined tracks, as the (apparent) spot size was around 18-20 \( \mu \)m. Reducing \( h_d \) below the apparent spot size would lead to smaller aspect ratios, because of the increasing overlap between the laser tracks. Future work will include the use of lenses with smaller focal length and beam expanders, which will allow a reduction on the spot size, thus machining tracks with \( h_d \) below 18\( \mu \)m without reducing the AR.

5. Conclusion

USLP machining is a tool for creating a surface topology for SH surfaces. Low CAH is necessary for achieving a functional anti-ice surface. Although some samples showed high water contact angles, only the one with the lowest CAH showed the desired easy roll of and anti-ice effect. In order to create an efficient water repellent surface, a super hydrophobic structure with highly packed features and a large enough AR has to be created.

Acknowledgments

The NL-cluster, and as such, the research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 for the CleanSky Joint Technology Initiative (JTI) under grant agreement n° CSJU-GAM-SFWA-2008-001.

We thank Volkmar Stenzel, Dirk Salz, Björn Weber and Mathias Widrat from the Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung (IFAM) in Bremen (Germany), for the assistance with the icing experiments and the application of the plasma coatings.

References


