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## Erosion resistant anti-ice surfaces generated by ultra short laser pulses

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### Abstract

Wetting properties of a wide range of materials can be modified by accurate laser micromachining with ultra short laser pulses. Controlling the surface topography in a micro and sub-micrometer scale allows the generation of water-repellent surfaces, which remain dry and prevent ice accumulation under certain conditions. The use of ultra short pulse lasers provides a method to generate a pattern on the surface of hard materials with micrometric scale features that are required for reaching the super-hydrophobic state. Water repellent structures usually have a poor structural strength and as a result their properties are quickly deteriorated when used under working conditions; hence a durable surface is highly desired. The combination of laser processing with plasma techniques provides the means to create robust Lotus-like structures. This paper investigates the anti-ice properties of plasma deposited hard coatings, e.g. diamond-like carbon, in combination with laser machined patterns. These hard coatings with reduced surface energy and adjustable surface topography improve the erosion resistance of super-hydrophobic surfaces, and make them more suitable for use under harsh environmental conditions. © 2010 Published by Elsevier B.V.

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### 1. Introduction

Micro machining using Ultra Short Lasers Pulses (USLP) has gained interest during recent years as an accurate tool for machining a broad range of materials [1]. The size of the features that can be generated, provides the means for changing the wetting properties of materials. These properties are determined by both the surface chemical composition and topography. When a material has a high surface energy, increasing its roughness will increase the spreading of water over it, but when it has a low surface energy, it is possible to increase its natural water repellency. The later is referred to as the superhydrophobic state. A superhydrophobic surface is generally characterized by a high apparent water contact angle (CA), greater than 150°, and a low contact angle hysteresis (CAH), or sliding angle (SA) [2].

There are two models that describe the wetting of rough surfaces. According to the Wenzel model [3], the apparent CA that a water drop forms when is over a rough surface,  $\theta_r^w$  [deg], is given by

$$\cos \theta_r^w = r \cos \theta_f, \quad (1)$$

where  $r$  [-] in equation 1 is the ratio between the actual area and the geometric area, and  $\theta_f$  [deg] is the Young's contact angle of the smooth surface [4]. As  $r \geq 1$ , increasing the roughness of a high energy surface, with a  $\theta_f < 90^\circ$ , will enhance the wetting, yielding lower apparent CA's. Increasing the roughness of a surface showing a  $\theta_f > 90^\circ$  will have the opposite effect. Apparent CA values that approach 180° can be reached by increasing the roughness.

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According the Cassie-Baxter model [5], water drops sit only on top of the protrusions of the rough surfaces in a way that air is trapped in the solid-air composite surface. The apparent CA,  $\theta_r^c$  [deg], is given by

$$\cos \theta_r^c = f(\cos \theta_f + 1) - 1, \quad (2)$$

where  $f$  [-] is the fraction of the solid area that it is in contact with the liquid, and  $\theta_f$ [deg] is again Young's contact angle of the smooth surface. A superhydrophobic surface in the Cassie-Baxter state remains dry, as water drops that easily roll off and are hardly in contact with the surface. Wenzel and Cassie-Baxter states are depicted in figure 1(a) and figure 1(b), respectively.

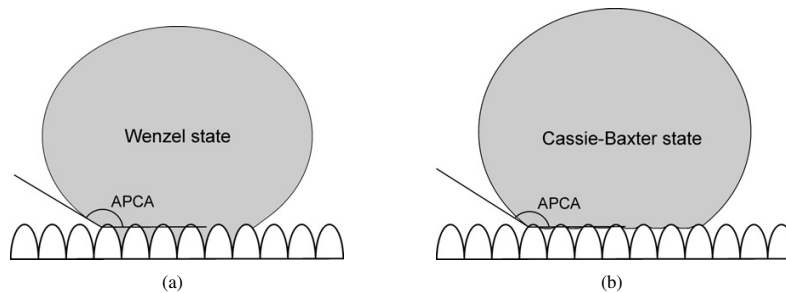


Fig. 1 : Water drop in the Wenzel (a) and Cassie-Baxter state (b).

Due to the micrometric size of the structures that are required to reach the superhydrophobic state, wear of the surface when used under harsh environmental conditions could lead to a quick deterioration of the water repellent properties. A promising solution is the use of wear resistant diamond-like carbon (DLC) coatings, which are known for their excellent tribological properties [6]. When applied by plasma enhanced chemical vapor deposition (PECVD), DLCs composition can be tuned in order to reduce their surface energy. An increase of the roughness of a hydrophobic DLC will reduce its wetting, while keeping good wear resistance properties [7]. Two DLC coatings, with respectively low and high surface energy, were applied on a stainless steel substrate. The coated samples were directly processed with ultra short laser pulses (USLP).

Superhydrophobic surfaces can be used to prevent ice accumulation over structures, as liquid water would not have the time for freezing before rolling off [8], even when it is in a metastable supercooled state [9]. The potential applications of a durable ice repellent surface include power transmission lines protection, leading-edge protection for the aircraft industry, telecommunication antennas, etc. [10, 11, 12]

## 2. Experimental setup

A Trumpf TruMicro 5050 laser source, which operates at a central wavelength of 1030 nm, was employed for the generation of the laser pulses. A Second and a Third Harmonic Generation (SHG and THG) units were used for converting the central wavelength to 515 nm and 343nm, respectively. The employed average power was adjusted in order to machine the samples slightly above the ablation threshold of the material. The pulse repetition rate was fixed to 200 kHz, and the pulse duration was constant at 6.7ps for all experiments. The laser polarization was horizontally linear. Manipulation of the beam over the samples was performed by a two mirror galvo scanner system with a positioning accuracy of 1  $\mu$ m.

A 103mm  $f\theta$  telecentric-lens focused the laser beam to a spot with a diameter of about 30  $\mu$ m that resulted in an effective spot size of about 18  $\mu$ m, due to the Gaussian power density profile at focus and the ablation threshold. The effective beam diameter allows creating a topography on a surface with feature size of the same order of magnitude as those observed in natural water repellent surfaces, like that of the Lotus leaf [13].

The focused laser beam was scanned over the sample in a regular orthogonal hatched pattern, with a controlled distance between lines referred here to as 'hatch distance'. This pattern was applied a number of times, referred here to as 'over-scans', in order to increase the depth of the structures by subsequent removal of ablated material.

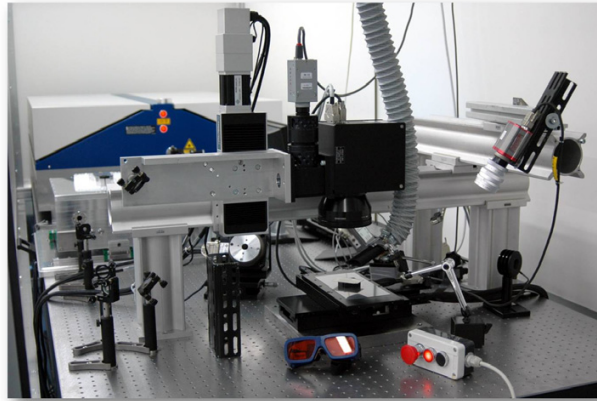


Fig. 2 : Experimental setup.

As the energy distribution of the laser beam is Gaussian, the applied average power was measured at the exit of the scanner system, and then averaged across the irradiated area. In all experiments the angle of incidence of laser radiation was perpendicular to the specimen surface. The samples were irradiated in air, at room temperature.

A 1mm thick stainless steel sheet (Werkstoff-Nr. 1.4544.9) was used as a substrate for two 12  $\mu\text{m}$  thick DLC coatings, which were kindly provided by the Fraunhofer Institut für Fertigungstechnik und Angewandte Materialforschung (Fraunhofer IFAM) in Bremen (Germany). Wetting properties of the laser machined DLC samples were measured in a Dataphysics OCA 20 contact angle measurement system, using 10  $\mu\text{l}$  distilled water drops.

### 3. Results

The topography of the laser-structured DLC coated samples was examined by a scanning electron microscope (SEM), and it is shown in figure 3. Figure 3(a) shows the topography of a DLC sample with high surface energy, which is indicated by an apparent CA below  $90^\circ$ , after laser processing. The surface is fully covered with 'peaks and valleys' resulted from the selective removal of material from the laser tracks, which have an horizontal spacing of 20  $\mu\text{m}$  (top to top), and a depth of about 12  $\mu\text{m}$ .

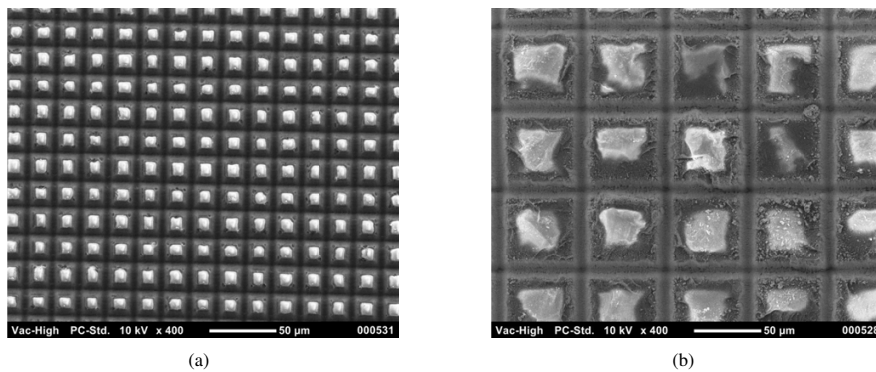


Fig. 3 : SEM images of textured (a), and partially textured (b) DLC coatings . Processing parameters (a): fluence 0.3  $\text{J}/\text{cm}^2$ , pulse frequency 200 kHz, beam velocity 600 mm/s, hatch distance 20  $\mu\text{m}$ , 20 over scans, laser wavelength 515 nm. Processing parameters (b): fluence 0.1  $\text{J}/\text{cm}^2$ , pulse frequency 200kHz, beam velocity 400 mm/s, hatch distance 60  $\mu\text{m}$ , 10 over scans, laser wavelength 343 nm.

Figure 3(b) shows the machined area of a DLC coating with low surface energy. This coating has been irregularly processed due to the high transmittance at the wavelength of the laser light of 343 nm. In this case, the laser pulses reach the metal substrate, and ablation takes place at the metal-DLC interface. The ablated material is ejected explosively and damages the coating. In order to avoid its complete removal, the distance between the scanned lines was increased. Table 1 includes the laser processing parameters that were employed.

Sample	Fluence (J/cm <sup>2</sup> )	Pulse frequency (kHz)	Beam velocity (mm/s)	Hatch distance (μm)	Overscans
DLC1	0.3	200	600	20	20
DLC2	0.1	200	400	60	10

Table 1: Laser processing parameters.

The static water CA of the base material and the DLC coated samples, both processed and unprocessed, was measured and is shown in table 2. In this table, DLC1 and DLC2 refers to the high and low surface energy coatings, respectively. It is shown that increasing the roughness amplifies the natural hydrophobic/philic properties of the material. When the static contact angle of a smooth sample is below 90°, DLC1, the machined pattern yields superhydrophilic properties. When the material has an initial contact angle greater than 90°, DLC2, the machined pattern increases the water repellency and it is possible to achieve superhydrophobic surfaces. The actual static contact angle of the superhydrophilic DLC1 sample could not be measured because the high spreading of the water drops formed a thin film, which completely covered the laser-processed area.

Stainless steel	DLC1	DLC2	Machined DLC1	Machined DLC2
78° ± 4°	75° ± 4°	98° ± 4°	≤ 35°	150° ± 4°




Table 2: Static CA measurements and images of 10 μL water drops over coated and uncoated samples. DLC1 and DLC2 refers to the high and low surface energy coatings, respectively.

#### 4. Conclusions

Hard superhydrophobic coatings have been investigated for their potential use as anti-ice surfaces. Diamond like carbon coatings with different surface energies were successfully applied on top of a stainless steel surface via PE-CVD. A laser process was developed in order to create a lotus-like structure in a DLC coating. This was achieved for a DLC sample with a relatively high surface energy, yielding a superhydrophilic behavior. A DLC coating with reduced surface energy was partially machined by USLP, and its water repellent properties were improved till reaching the superhydrophobic state.

#### 5. Future work

The difficulties of direct machining DLC coatings can be overcome by directly applying a thin PE-CVD DLC coating over a preprocessed laser-machined metal substrate. Ice tests will be performed in order to confirm the expected anti-ice properties of the hard superhydrophobic surfaces. Rain and sand erosion tests will determine the applicability range of the materials.

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