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Femtosecond laser manufacturing of highly hydrophobic hierarchical structures fabricated by combining surface microstructures and LIPSS

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Abstract

The manufacturing of metal surfaces with highly controllable wetting properties is becoming a very active and promising area in research and engineering. Based on nature examples like rose petals or lotus effect, an effective approach for this purpose is the combination of micro- and nano-structures into hierarchical structures. Traditionally these structures are manufactured by using different types of coatings or by processes which involve too many steps and techniques to become commercial solutions. However, this can be achieved by only using femtosecond laser ablation in air atmosphere. In this work we have developed hierarchical structures that consist of micro-patterned surfaces covered by nanostructures with this technique.

The first part of this work is a complete study to determine the microscale modifications produced on a stainless steel alloy (AISI304) surface at high pulse energy, different velocities, and focal distance in order to obtain microstructures with a selected depth of around 10 µm and line widths of 20 µm. The second part of the work is focused on finding the optimal irradiation parameters to obtain the nanostructure pattern. Nanostructures have been defined by means of Laser Induced Periodical Surface Structures (LIPSS) of around 250 nm high and a period of 600 nm, which constitutes the nanostructure pattern. Finally, dual scale gratings of 50 mm^2 were fabricated for a range of irradiation parameters (line period, fluence, velocity, ablated depth or focal distance) and their effect on the measured contact angle. Combining the micro-pattern with the LIPSS nano-pattern, highly hydrophobic surfaces have been developed with measured static contact angles higher than 150° starting from an initial contact angle of 75°.

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Femtosecond, laser, hydrophobic, hierarchical, LIPSS

1. Introduction

Wettability control of material surfaces and super-hydrophobic behavior have attracted a lot of interest in recent years because of its importance and applicability in fundamental research and practical applications. It has been widely reported that the leaves of many plants such as lotus leaves, rose petals or animals like Namib desert beetle show particular wetting characteristics like water-repelling or superhydrophobicity and easily rolling off the surface, super-wicking effect or wettability patterns with hydrophilic and hydrophobic areas which allows to effectively conserve the fog droplets [Bhushan et al, 2009]. These surface's wetting features are a direct consequence of their surface morphology because of the hierarchical structures that form their surfaces on the micro and nanometre scale, but also a matter of surface chemistry [Bhushan et al, 2009].

The wettability of a surface can be characterized by the CA (contact angle). A hydrophilic surface has a CA below 90°. A surface with a CA higher than 90° is known as a hydrophobic surface, and a surface with a contact angle above 150° and rolling angle below 5° is defined as a superhydrophobic surface. The states of water droplets on a solid surface are classified into two categories, namely the Wenzel state and the Cassie–Baxter state [Wenzel, 1936; Cassie et al, 1944]. The Wenzel state is characterized by a homogeneous interface where the liquid is completely wetting the solid surface. The Cassie-Baxter state is characterized by an inhomogeneous interface where air bubbles are trapped in the valleys between the nano- and micro-patterns, so that the liquid rests on a composite surface of solid and air. The corresponding contact angles for the Cassie–Baxter state are much higher than for the Wenzel state.

The design of anti-icing systems, self-cleaning surfaces [Vorobyev et al, 2014], or improved corrosion resistance surfaces [Mohamed et al, 2014], are examples of the potential industrial interest that the wettability control allows to explode. There are a few different techniques that can be used to modify the morphology and the chemistry of a surface, like photolithography, laser interference lithography or chemical vapor deposition among others [Bhushan et al, 2011; Rodriguez et al, 2009]. The problem is that normally these techniques involve several steps, additional materials, or delicate and time-consuming processes, which usually require high budgets and working inside a clean room.

For large scale industrial production a faster and simple process is needed. In order to solve these problems, femtosecond laser micro-nano machining has emerged as an effective technique to create dual scaled surfaces with nano- and micro-structures in a single-step fabrication process [Vorobyev et al, 2014]. Hexafluoropropene and fluoroalkylsilane coatings are frequently used to greatly decrease the surface energies of the laser machined surfaces and to obtain the highest contact angles [Barberoglou et al, 2009]. However, these organic compound coatings have a poor chemical and thermal stability and are easily peeled off from the substrates. It has been demonstrated that only with the femtosecond laser texturing step, superhydrophobic surfaces can be obtained in different types of metals [Rukosuyev et al, 2014; Kietzig et al, 2011]. It has been also demonstrated that the hydrophobic behavior presented in the femtosecond-treated surfaces does not only depend on the surface roughness but also on chemical reactions and carbon compounds accumulation on the surface [Kietzig et al, 2009].

In this paper we present an easy single step laser texturing method to obtain highly hydrophobic structures starting from an initial hydrophilic metal surface. A study of the types of LIPSS (Laser Induced Periodical Surface Structures) generated on the AISI304 stainless steel surface depending on the irradiation parameters is also presented, as well as their effect on the static contact angle.

2. Materials and Methods

2.1. Materials

Austenitic stainless steel (AISI304) plates with a thickness of 3mm were used. The material has been treated as it was dispensed from the suppliers without any further pretreatment in order to ensure repeatability and to avoid any additional step in the fabrication process. The initial average surface roughness of the samples measured with mechanical profilometry was 650 nm. Before and after being treated by the laser the samples were cleaned in a 10 min ultrasonic acetone bath, followed by a 10 min ethanol bath.

2.2. Micro-nanomachining setup

Samples were machined in open air atmosphere with a Ti:Sapphire laser system consisting of a mode-locked oscillator and a regenerative amplifier which was used to generate 130 fs pulses at a central wavelength of 800 nm, with a 1KHz repetition rate. The pulse energy was adjusted with a two-step setup: a constant attenuator formed by a half-wave plate and a low dispersion polarizer. The 12 mm diameter laser beam was focused on the samples using a 10X microscope objective with a NA of 0,3. This objective together with a CCD camera was used for online monitoring the structuring process. A three dimensional translational stage moved the sample under the beam with different scan speeds allowing a variable overlap of pulses per spot. The laser fluence was controlled by varying the distance between the objective and the sample (increasing or decreasing the spot diameter). The layout of the experimental setup is shown in Figure 1.

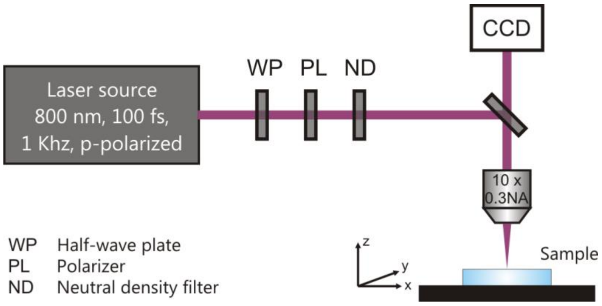

Fig. 1: Schematic layout of the femtosecond laser machining setup.

2.3. Irradiation parameters

In order to perform the micropatterns, the laser spot was focused on to the sample surface with a diameter of 20 µm. The scanning velocity was 1 mm/s and three overscans were performed in order to obtain an ablation depth of around 10 µm. The pulse energy was adjusted to 35µJ. Micro-patterns were performed in two different models, one dimensional trench patterns or two dimensional matrix patterns (Figure 2) that consist of ablated lines separated a certain distance (represented by the pitch value).

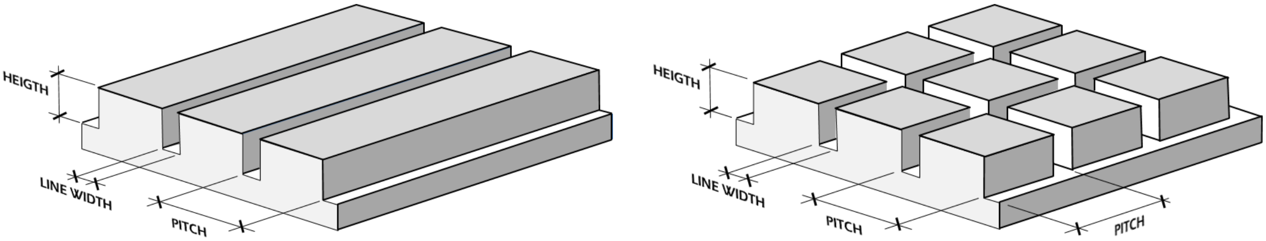

Fig. 2: Proposed trench (left) and matrix (right) micropattern models.

In order to perform the LIPSS nanopattern the pulse energy was adjusted to10 µJ and the scanning velocity was increased to 3 mm/s. A defocussing distance of 200 µm was applied. The LIPSS nanopattern was performed covering all the micro-patterns as can be seen in Figure 3.

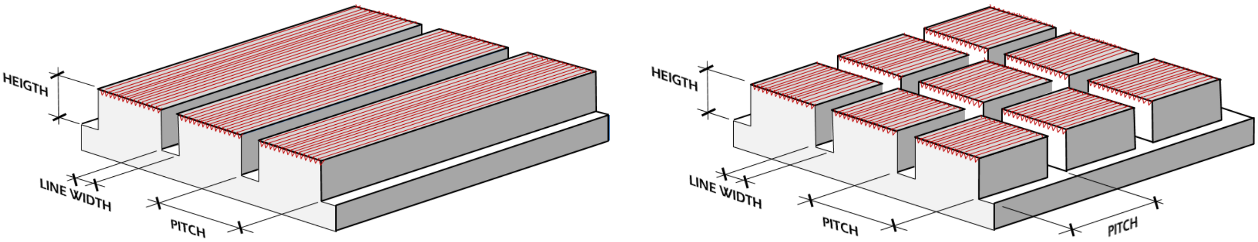

Fig. 3: Proposed trench (left) and matrix (right) micropattern models covered by a LIPSS nanopattern.

Samples were scanned in open air atmosphere for a range of pitch distances from 30 µm to 90 µm in 20 µm increments. In both micropattern models first the microstructure was fabricated followed by the nanopattern cover.

2.4. Characterization

The obtained surface morphologies were characterized by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and mechanical profilometry. A 3,5 µl droplet of distilled water was dispensed on each sample surface, and the whole process was recorded with a digital camera. In order to measure the apparent static contact angle, the recorded videos were analyzed and the contact angle measured using the sessile drop method.

3. Results and discussion

3.1. Morphological analysis

Hierarchical structures with a dual scale roughness were successfully fabricated for a range of pitch distances for both micropattern models (trench and matrix). FESEM images are shown in Figure 4. The ablated line width was 20 µm and the height 10.4 µm as measured by mechanical profilometry. In Figure 5 the LIPSS nanopattern can be appreciated covering all the micropatterned surface. The LIPSS generated for the structures were LSFL (Low Spatial Frequency LIPSS) according to the analysis of the LIPSS period performed by analyzing SEM images (an average value of 600 nm was obtained). Also an AFM analysis of the LIPSS nanopattern was performed in order to determine the height, obtaining a value of 250 nm (Figure 6).

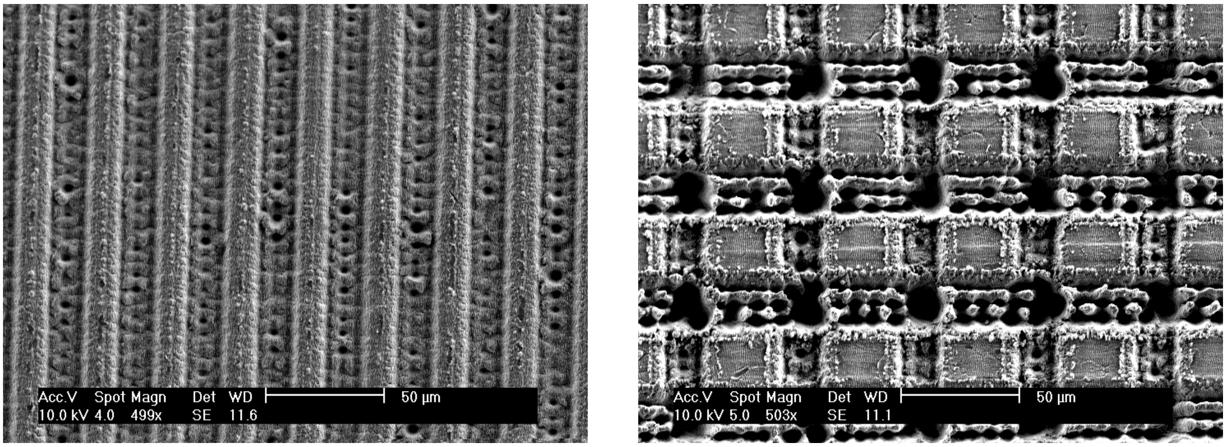

Fig. 4: Hierarchical structures fabricated with trench (left) and matrix (right) micropattern models covered by a LIPSS nanopattern and with a pitch distance of 30 µm and 50 µm.

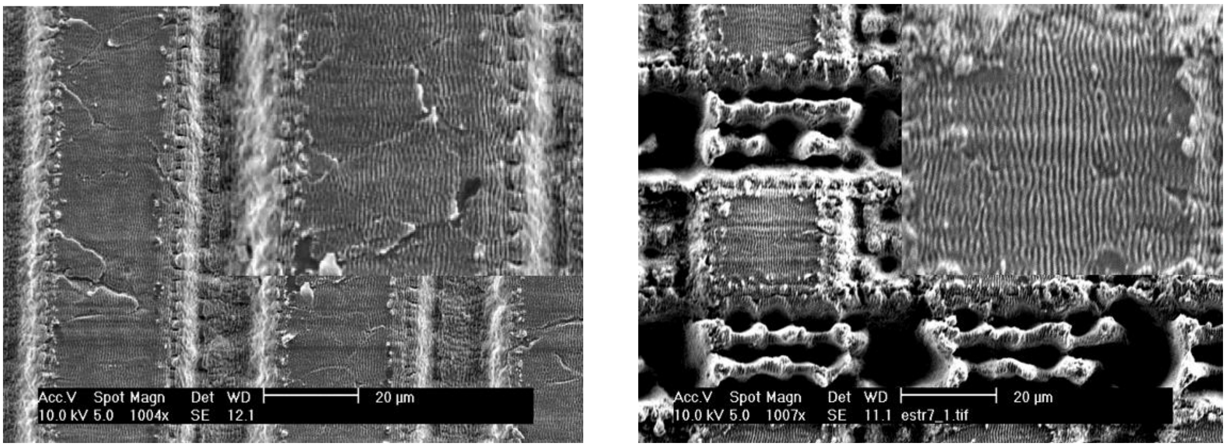

Fig. 5: Increased zoom images into the LIPSS nanopattern performed in the hierarchical structures fabricated with trench (left) and matrix (right) micropattern models with a pitch distance of 30 µm and 50 µm.

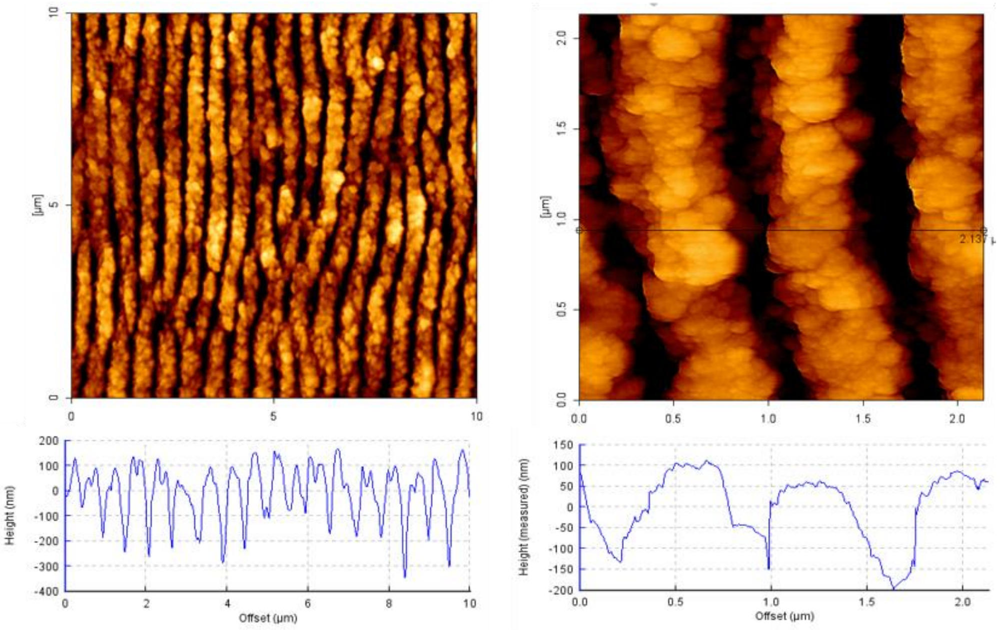

Fig. 6: AFM analysis performed on the LIPSS nanopattern fabricated which is covering the fabricated hierarchical structures.

3.2. Water contact angle characterization

The initial contact angle of the non-treated stainless steel surface was 75°. Right after the irradiation process the surface became very hydrophilic with contact angles smaller than 30°. The samples were stored in a clean room to open air atmosphere, and after 120 hours the treated surfaces became highly hydrophobic or even super-hydrophobic depending on the selected irradiation process. Once the change has happened the contact angle reaches a constant steady state value which is maintained in time. Contact angle measurements were repeated on a daily basis and the value of the contact angle was constant after at least 50 days after the femtosecond laser treatment. This change in the wettability behavior with the exposure to air has not any relation with the surface roughness introduced, because otherwise the hydrophobic behavior would have appeared just after the femtosecond laser treatment. Some authors have discussed this effect and attributed it to the chemical interaction with the ambient CO_2, resulting in an accumulation of carbon compounds on the femtosecond laser treated surface [Kietzig et al].

In Figure 7 the average steady state contact angle measurements are represented as a function of the pitch distance value and for both micropattern models with and without the LIPSS nanopattern covering the surface. It can be observed that when the LIPSS nanopattern is performed the measured contact angles are significantly higher. The highest contact angle measurements are found for the models with both micro- and nanopatterns fabricated with 30 µm pitch distance (Figure 8 and 9) reaching values of superhydrophobicity(above 150°). The different behavior of the non-treated surfaces and the treated ones can be observed in Figure 10. It is also important to remark that for pitch distances of 90 µm the measured contact angles never reached values higher than 120º, so the pitch distance of 70 µm could be considered as a limit value in order to reach a highly hydrophobic behavior.

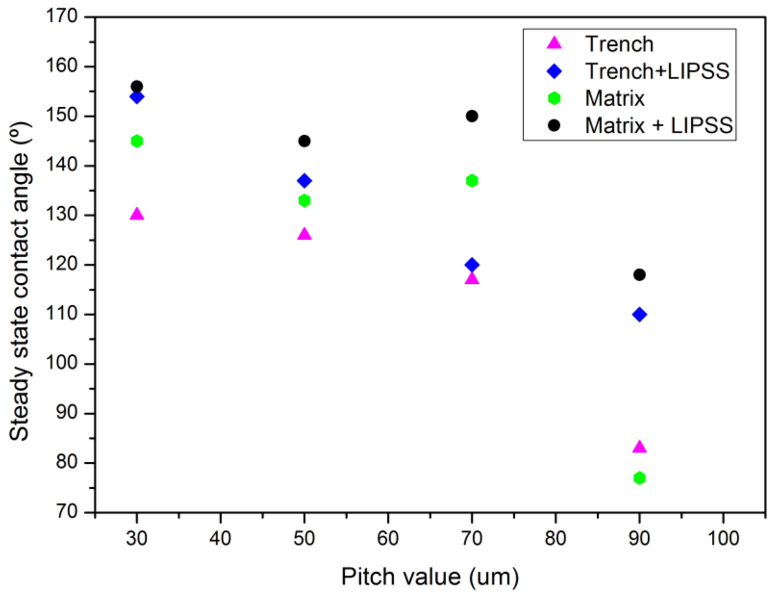

Fig. 7: Steady state apparent contact angle measurements for the different fabricated structures.

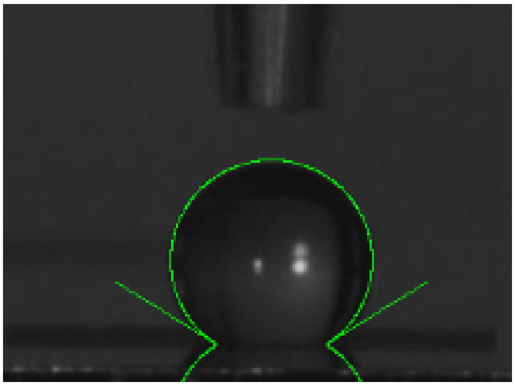

Fig. 8: Droplet deposited on a trench + LIPSS hierarchical structure fabricated with 30 µm pitch distance, with a contact angle of 153º.

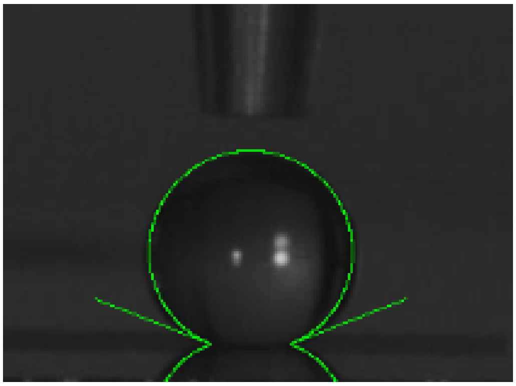

Fig. 9: Droplet deposited on a matrix+ LIPSS hierarchical structure fabricated with 30 µm pitch distance, with a contact angle of 158º.

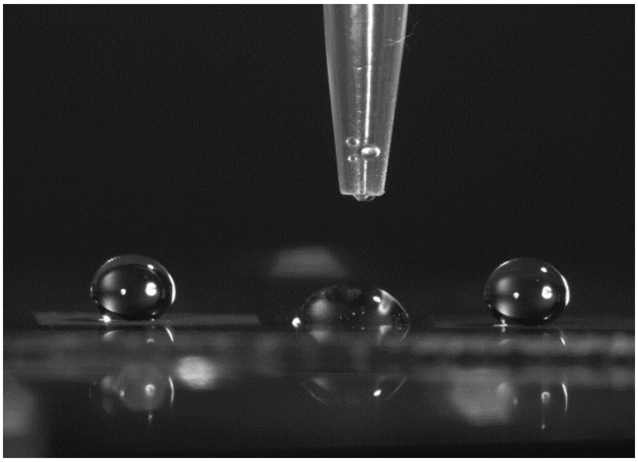

Fig. 10: Comparison between the droplet deposited on a non-treated surface (middle) and two treated ones with different fabricated hierarchical structures.

4. Conclusions

Hierarchical structures have been fabricated by a single one-step fabrication process for a range of parameters in a highly controllable way. It has been shown that adjusting the pitch distance value highly hydrophobic structures can be obtained from an initially hydrophilic surface. For pitch distances higher than 70 µm the measured apparent contact angles are significantly lower, therefore a limit has been established in order to obtain highly hydrophobic behavior with the structures that we have fabricated. It has also been demonstrated that only when the LIPSS nanopattern is performed covering the surface the contact angle values reach superhydrophobic levels.

5. References

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