Functionalization of surfaces by ultrafast laser micro/nano structuring

C Hairaye\textsuperscript{1,2}, F Mermet\textsuperscript{1}, T Engel\textsuperscript{1,2}, P C Montgomery\textsuperscript{2} and J Fontaine\textsuperscript{1,2}

\textsuperscript{1} IREPA LASER, Parc d’Innovation, 67400 Illkirch, France.
\textsuperscript{2} Laboratoire des Sciences de l’Ingénieur, de l’Informatique et de l’Imagerie (ICube), UDS-CNRS-INSA-ENGEES, UMR 7357, 300 bd Sébastien Brant, CS 10413, 67412 Illkirch, France.

E-mail: chairaye@unistra.fr

Abstract. In surface functionalization, micro- and nanotexturing with ultrashort pulse lasers is of increasing interest in industry. These two scales of structures can be obtained by a self-organization of the matter after laser irradiation, or by a micro-machining of the sample with successive ablations. Controlling key-parameters such as wavelength, laser fluence, spot overlap, number of repetitions and polarization, allows the generation of self-organized nanostructures called ripples or the creation of square-shaped micro-structures. In the first case, a surface textured with these nano-gratings presents a diffractive aspect or a permanent marking, but changes little the initial wetting behaviour of the surface. In the second case, the microstructures improve significantly the wettability of the surface, with an increase of almost 20° of the contact angle with a water droplet. So a large range of surface texturing can be performed with ultrashort pulsed laser technology, offering a wide range of applications, from biomedical to aeronautical.

1. Introduction

Functionalizing a surface with micro- or nanostructures is particularly challenging today as the structural size becomes smaller and the variety of materials requiring to be treated becomes wider. Texturing a surface with an ultrashort pulse laser is a fast and simple process that can be used to modify the properties of the irradiated area. Different micro- or nanostructures can be produced endowing certain specifications to the surface, which can be used to change its visual aspect \cite{1, 2} or its wetting behaviour, for instance to imitate the surface state of the lotus leaf \cite{3, 4}.

Ultrashort pulsed laser sources present a growing interest for industry because of the recent increase in their mean power, repetition rate and reliability. The resulting peak power that can be reached gives the possibility of processing almost all materials with high precision and a greatly reduced heat-affected zone \cite{5}.

The interaction between ultrashort laser pulses (100’s of femtoseconds) and a material surface is a complex process, in which many parameters come into play. Depending on the nature of the material and on the beam characteristics (wavelength, pulse duration, polarization, quality factor M\textsuperscript{2}), several process parameters such as the laser fluence, the spot overlap and the number of repetitions can be varied to control the interaction \cite{5, 6}. In fact, surface features rely greatly on the process parameters settings.

In this paper we present some initial results of a study aiming at the control of these key-parameters, in order to create different types of micro- and nanostructures. We first performed tests on
samples of stainless steel, textured by self-organized nanogratings, known as “ripples”. Then, by modifying the laser beam parameters, microstructures were created. In some cases, a colouring aspect change is obtained [2], and in others a modification of the wetting behaviour of the textured surface is observed [6, 7].

2. Experimental process

2.1. Material and laser system

Samples of AISI 316L stainless steel having a thickness of 0.5 mm were prepared with an ultrasonic bath of acetone followed by deionized water. No additional mechanical polishing was performed, leaving relatively significant striations and an initial roughness Ra of 69 nm.

The irradiating laser source used was the ultrafast pulsed fibre laser Tangerine (Amplitude Systèmes, France), with a central wavelength of 1030 nm, 300 femtoseconds of pulse durations and 100 µJ pulse energy at a repetition rate of 200 kHz. A Third Harmonic Generation (THG) module allows operation in the UV range, at 343 nm. Texturing tests were accomplished at IR and UV wavelengths. The spatial profile of the laser beam was nearly Gaussian (M² < 1.2).

The micro-machining MUSE-3D platform (Micro-Usinage Système Expérimental 3D, Optec, Belgium) includes an attenuator in the optical path to modulate the laser power and a beam expander to easily change the diameter of the laser beam, which is focused with a 100 mm focal length F-theta lens. Samples, placed on an X-Y translation stage, are scanned by the laser beam thanks to a galvanometric head. The laser beam polarization is linear, and it is possible to work with circular polarization by inserting a quarter-wave plate in the optical path.

2.2. Characterization devices

After laser irradiation, the samples’ topography was analysed with three different optical methods.

The InfiniteFocus 3D profilometer (Alicona Imaging GmbH, Austria) was used for measuring the size of the microstructures and the roughness. This instrument has a lateral resolution of 0.5 µm and a vertical resolution of up to 10 nm. It works on the focus variation method in white light, combining an optical system with a limited depth of field and vertical scanning.

The Leitz-Linnik microscope is an interference microscopy system developed at ICube, based on white light scanning interferometry and described in [8]. Its Linnik type objective (x50, NA = 0.85) gives a lateral resolution of 0.43 µm in visible light, an axial resolution of 1 to 15 nm depending on the algorithm used and nature of the surface to be measured, with a Basler avA1000-100gc camera (1024x1024 pel).

The Atomic Force Microscope XE-70 (Park Systems, Korea), placed within an acoustic enclosure, works in the non-contact mode. The 2 nm sized tip used as a point probe is a non-contact high frequency. The field size used was 25x25 µm for 256x256 pixels, with a lateral resolution of 0.1 µm.

The wettability of flat and textured samples was determined with the drop shape analyser DSA25 from Krüss. The sessile drop method was employed to measure the values of the contact angles, for 5 µL droplets of deionized water. Since no additional coating was applied on the textured samples, the wetting behaviour of the surface was therefore only due to its topography.

3. Results

Two approaches have been considered to texture the surface of the stainless steel samples: the first consists in a self-organization of the matter by irradiation with IR-light laser, and the second is achieved by micro-machining the metal with successive ablations in UV-light.

3.1. Self-organized micro- and nanostructures in Infra-Red

The phenomena of laser energy absorption and transfer during the laser-matter interaction, just below or at the ablation threshold of the material, are responsible for the self-organization of nano-structures that are known as “ripples” or “Laser Induced Periodic Surface Structures” (LIPPS) [6]. At a
wavelength of 1030 nm, the laser parameters studied to generate ripples are the fluence, the spots overlap, the number of repetitions and the beam polarization (linear or circular).

The results presented of the ripples are obtained for a one-step process with a focused diameter of about 47 µm, for a laser fluence of 0.81 J/cm². The overlap is maintained constant at 75% for both directions of scanning (longitudinal ≡ scanning rate / transversal ≡ hatch distance).

Linear and circular polarizations are used, leading to different types of nano-structures. When the laser beam is linearly polarized, fine ripples are created, as can be observed in the AFM results in figure 1. With the image field size being 13.8x13.8 µm, the lateral resolution is 50 nm. Their preferential orientation is perpendicular to the polarization direction. Analysis of these ripples shows a periodicity of about 1 µm, and a height of 0.5 µm. This analysis also underlines the presence of nanometric nodules superimposed on the ripples with a lateral size of 400-500 nm and with a height of up to a hundred of nanometers.

![AFM analysis of a textured surface by ripples in linear polarization: (a) 2D-view and (b) 3D-view.](image)

By adding a quarter-wave plate, the linear polarization of the laser beam becomes circular, resulting in the nano-structures self-organizing into a circular shape. The laser parameters are the same as in the previous case, with only the polarization changing. The circular nano-structures are about 1 µm wide and ~600 nm high, measurable by AFM.

To distinguish easily between both types of ripples, those created with linear polarization will be referred to as “linear ripples”, and those generated with circular polarization as “circular ripples”.

Roughness measurements were performed with the profilometer on the initial and textured surfaces. For the “linear” ripples, the roughness Rₐ is just a bit higher than that of the untextured surface (resp. 75 nm and 69 nm), and for the “circular” ripples Rₑ it is equal to 70 nm.

The results in figure 2 show views of the ripples obtained with the linear and circular polarization. The AFM observations show the difference in the topography for each test. In addition, comparisons are made with the results from Scanning Electron Microscopy (SEM), using a FEI Quanta-400 microscope. Comparable nodules observed on linear ripples by AFM in figure 1 are also present on the SEM analyses.

The results in figure 4 show these linear and circular ripples as measured with the optical profilometer and the Leitz-Linnik microscope (figure 4 (a), (b), (c) and (f), (g), (h)).

By varying the laser parameters, fine ripples evolve into coarse ripples [2], which are parallel to the direction of polarization. These kinds of structures are also obtained for a laser fluence of 0.81 J/cm² and a diameter of 47 µm, but with a greater transversal overlap equal to 99%. Measurements of these coarse ripples show a period of 4.3 µm for a mean height of 2.8 µm (see figure 4, pictures (d) and (i)).

3.2. Microstructures obtained by successive ablations in the Ultra-Violet

The use of the UV wavelength of 343 nm for femtosecond pulses has the advantage of higher laser fluences on smaller spot diameters.

This test consists in the micro-machining of parallel lines (vertical and horizontal), in order to create micro-protrusions in squares, as inspired from [7]. The focused laser beam of 31 µm diameter
successively ablates the surface, at a low fluence of 0.12 J/cm². It scans the sample with a longitudinal
overlap of 95%, and a transverse overlap of 15%. In order to obtain the desired depth of micro-
structures, this ablation is repeated 50 times.

Analysis with the InfiniteFocus profilometer and the interferometric microscope gives the
following measurements: the depth equal to about 12 µm, the width equal to 16 µm and the distance
between the micro-squares of 10 µm (see figure 4, pictures (e) and (j)).

Besides, the InfiniteFocus underlines the different depths for these structures: the vertical lines are
deeper than the horizontal ones. There is also a small difference in the widths of the protrusions. These
deviations are assumed to be due to the slight ellipticity of the laser beam profile.

| “Linear” ripples | “Circular” ripples |
|------------------|-------------------|
| AFM XE-70        | Resolution: 100 nm / Size: 25x25 µm |
| FEI Quanta – 400 | Resolution: 100 nm / Size: 25x25 µm |

Figure 2. “Linear” and “circular” ripples on stainless steel observed with AFM and SEM.

4. Discussion

Nano-structures such as ripples can be used to change the visual aspect of a surface, by diffracting
white light on the created nano-gratings (see figure 3). As for the coarse ripples and the square-shaped
micro-structures, the textured surface is still darker and blackened: the marking is thus permanent.

Figure 3. Colouring effect of the different textured surfaces.

The wetting behaviour linked with the roughness of the surface and its topography was then
investigated. The results in figure 4 show the evolution of the contact angle of the droplet on the
textured and untextured surfaces with the dimensions of the micro- and nano-structures. The contact
angle values were obtained for a single series of measurements.
On the untextured sample \((R_a \approx 69 \text{ nm})\), the contact angle \(\theta_c\) is equal to 75°; the surface is hydrophilic. With fine “linear” ripples, the roughness is a little higher \((R_a \approx 75 \text{ nm})\) and the contact angle decreases to 55°; the hydrophilic nature is reinforced. Even if “circular” ripples are almost similar to the “linear” ones in terms of dimensions, the \(R_a\) of this textured surface is almost equal to the untextured one and the contact angle is thus nearly the same \((\theta_c \approx 79°)\). The roughness therefore enhances the wetting nature of the surface [9].

In the case of the coarse ripples, the droplet is totally absorbed by the micro-structures, making it impossible to measure any contact angle.

Concerning the ablated micro-structures created in UV, an increase of 17° for the contact angle is observed, being slightly higher than 90°. This result shows that it is possible to obtain a hydrophobic behaviour on a metallic surface by laser texturing, without any additional coating.

| Self-organized structures in IR | Ablated structures in UV |
|--------------------------------|--------------------------|
| Initial surface | Linear ripples | Circular ripples | Coarse ripples | Micro-squares |
| InfiniteFocus 3D profilometer | (a) | (b) | (c) | (d) | (e) |
| Leitz-Linnik microscope | (f) | (g) | (h) | (i) | (j) |
| Size & roughness | \(R_a = 69 \text{ nm}\) | Period = 1 \(\mu\text{m}\) \(\text{Height} = 0.5 \mu\text{m}\) \(R_a = 75 \text{ nm}\) | Width = 1 \(\mu\text{m}\) \(\text{Height} = 600 \mu\text{m}\) \(R_a = 70 \text{ nm}\) | Period = 4.3 \(\mu\text{m}\) \(\text{Height} = 2.8 \mu\text{m}\) | \(D^a = 12 \mu\text{m}\) \(A^b = 16 \mu\text{m}\) \(B^c = 10 \mu\text{m}\) |
| Photographs of 5 \(\mu\text{L}\) drops | (k) | (l) | (m) | (n) | (o) |
| Contact angle | \(\theta_c \approx 75°\) | \(\theta_c \approx 55°\) | \(\theta_c \approx 79°\) | Not measurable | \(\theta_c \approx 92°\) |

\(^a\) Depth of the square-shaped micro-structures.
\(^b\) Width of the square-shaped micro-structures.
\(^c\) Distance between the square-shaped micro-structures.

**Figure 4.** Summary of the different textured surfaces: measurements with the optical profilometer [(a) to (e)] and the Leitz-Linnik microscope [(f) to (j)], their size and roughness, photographs of 5 \(\mu\text{L}\) deionized water [(k) to (o)] and the contact angle measurements. (Scale: the black rectangle represents 10 \(\mu\text{m}\) for pictures (a) to (d), and for (f) to (j), and 20 \(\mu\text{m}\) for picture (e)).
5. Conclusions

In this paper we have demonstrated the potential of the micro- and nanotexturing of a stainless steel sample using irradiation with an ultrashort pulse laser. Two approaches have been considered.

The first consists in a self-organization of the nanostructured ripples in the IR-range (linear, circular and coarse ripples) allowing the creation of a colouring effect by diffraction or a permanent dark marking. In addition, the roughness of the ripples makes it possible to enhance the hydrophilic behaviour of the textured surface.

As for the second approach, surface texturing was performed by successive ablations of parallel lines at a UV-wavelength. Square-shaped micro-structures were created and their presence increased the contact angle of a water droplet to 17° by comparison with the untextured surface: a hydrophobic behaviour was observed, with no additional coating modifying the wetting behaviour.

We can thus see that there is real potential for surface micro- and nano-texturing with ultrashort pulsed laser technology, for the aeronautical, biomedical or luxury goods fields.

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