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Development of Laser Induced Hierarchical
Surface Structures on Ti-6Al-4V using short and
ultra-short pulsed lasers for modified wettability
applications.

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Sincerely,

Daniel Huerta Murillo

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RESUMEN

En esta tesis, se investiga la viabilidad de la escritura directa por láser para la creación de superficies funcionales con una mejor humectabilidad en la aleación de titanio Ti-6Al-4V. La técnica de escritura directa por láser se empleó utilizando una estación de trabajo de láser pulsado de nanosegundos UV en el Centro de láser de la UPM. Las microestructuras creadas consisten en micro-pilares de forma cuadrada con diferentes longitudes (15 a 50 μm de ancho, 2-10 μm de altura), que se pueden variar con una resolución micrométrica. Los pilares fabricados con láser de nanosegundos exhiben una estructura con una forma cerrada en la parte superior como resultado del efecto térmico que se produce cuando se trabaja con láseres de nanosegundos, moviendo material fundido que se re-solidifica a la periferia de los micro-pilares. Estas estructuras han demostrado ser beneficiosas para el desarrollo de superficies hidrófobas en metales. La morfología de la superficie del área irradiada se caracterizó con microscopía electrónica de barrido y microscopía confocal.

Adicionalmente, se empleó la técnica de texturizado mediante interferencia directa de láser, utilizando un láser de pulsos de picosegundo para crear microestructuras periódicas con formas de línea y pilar, con la ayuda y colaboración del Instituto Fraunhofer en Dresde, Alemania. En un proceso de dos pasos, se realizó una segunda irradiación con láser en las mismas superficies para crear pilares periódicos con un período espacial de 2.6 μm . La estructura generada en la superficie es uniforme en toda el área procesada, mostrando un conjunto periódico de micro-pilares con una profundidad promedio de 0.9 μm tanto en la dirección vertical como horizontal y una profundidad promedio de 1.5 μm en el máximo de interferencia. La combinación de estas dos técnicas de procesamiento por láser permite la creación de estructuras jerárquicas bien definidas.

En colaboración con la Universidad de Birmingham, la formación de LIPSS se creó en la superficie de las muestras de Ti-6Al-4V, utilizando un láser IR de pulsos de femtosegundos con la técnica de escritura directa por láser. Los LIPSS de baja frecuencia espacial de femtosegundos se generaron en la parte superior de la estructura generadas con el láser de nanosegundos para crear una estructura de escala dual. El proceso de femtosegundo está libre de efectos térmicos, lo que significa que las estructuras fabricadas previamente no se vieron afectadas por este segundo proceso de láser. Los LIPSS generados muestran estructuras auto-organizadas de manera muy uniforme con un período espacial de aproximadamente 810 nm. La superficie final muestra una rugosidad de doble escala, lo que proporciona un método exitoso para generar estructuras jerárquicas.

Se realizaron mediciones estáticas de los ángulos de contacto para analizar el comportamiento de humectabilidad de las estructuras. Para todos los procesos con láser, las muestras fueron hidrofílicas inmediatamente después del procesamiento laser. Sin embargo, con el envejecimiento natural se observó un aumento en el ángulo de contacto estático. Empleando dos métodos de almacenamiento diferentes, se realizó una investigación de la importancia de las condiciones de almacenamiento en este proceso. Las muestras se mantuvieron en dos condiciones de almacenamiento diferentes: expuestas al aire ambiente y dentro de bolsas de polietileno. Se encontró que las bolsas de polietileno son beneficiosas para el envejecimiento de la superficie de las superficies de titanio fabricadas con láser, disminuyendo el tiempo de envejecimiento necesario para ser hidrofóbicas en comparación con el envejecimiento por exposición al aire ambiente. Las topografías jerárquicas mostraron una mayor repelencia al agua en comparación con las estructuras no jerárquicas. Especialmente, las estructuras jerárquicas alcanzaron un estado hidrofóbico con un ángulo

de contacto del agua de más de 160° después de 3 semanas de almacenamiento en bolsas de polietileno, en comparación con las superficies jerárquicas mantenidas en el aire que mostraron un ángulo de contacto de alrededor de 120° .

Espectroscopía foto-electrónica de rayos X se utilizó para analizar la composición química de las muestras almacenadas en diferentes condiciones. Los resultados indican oxidación en las zonas tratadas, mostrando un claro aumento en la concentración total de oxígeno en comparación con la muestra de referencia. Entre los compuestos de oxígeno, se observó una clara diferencia en el contenido relativo de moléculas de agua entre muestras con las mismas estructuras mantenidas en dos condiciones de almacenamiento diferentes. Para el caso de la muestra mantenida en el aire, se detectaron moléculas de agua, mientras que para el caso de la bolsa de polietileno, que muestra el ángulo de contacto más alto, no se encontraron rastros de moléculas de agua. Además, el análisis detallado de los espectros de C para las muestras procesadas mostró trazas de varios compuestos de carbonos polares y no polares, siendo la muestra que se mantuvo en una bolsa de polietileno quien muestra la concentración más baja de moléculas polares, la cual también mostró el ángulo de contacto más alto. Los resultados indican que la ausencia de moléculas polares afecta mucho la humectabilidad de la superficie.

Adicionalmente, se estudió la resistencia a la corrosión de las muestras procesadas. Se realizaron estudios de polarización lineal en las estructuras fabricadas para investigar el comportamiento de resistencia a la corrosión de los micro-pilares fabricados por escritura directa por láser y las estructuras jerárquicas en una solución de 0.5 M de NaCl. Los resultados muestran que incluso si la densidad de la corriente de corrosión y el potencial de corrosión no son mejorados en gran medida por las estructuras creadas con nanosegundos, las estructuras

jerárquicas si mejoraron claramente la resistencia a la corrosión por picadura del material (aproximadamente < 7 V) en al menos 1 V con respecto a la referencia valor, que fue de alrededor de 5,5 V.

El rendimiento hielo-fóbico de las superficies micro-estructuradas se investigó en condiciones atmosféricas de congelación en vuelo simulado para investigar la viabilidad de generar superficies hielo-fóbicas. Las superficies fabricadas con escritura láser directa no reducen la adhesión al hielo en condiciones de vuelo para las muestras testeadas, sin embargo, se deben investigar más combinaciones de los parámetros de las estructuras para evaluar qué topografía es más beneficiosa para reducir la adhesión del hielo en condiciones de vuelo.

ABSTRACT

In this thesis, the feasibility of direct laser writing for the creation of functional surfaces with enhanced wettability on titanium alloy Ti-6Al-4V is investigated. The direct laser writing technique was employed using a UV nanosecond pulsed laser work station in the Laser Centre of the UPM. The micro-structures consisted in squared shape micro-pillars with different length (15 - 50 μm length width, 2-10 μm height), which can be varied with a resolution of a few micrometers. The nanosecond laser fabricated pillars exhibits a closed-package structures on the top as a result of the thermal effect encountered when working with nanosecond lasers, recasting molten material in the periphery of the micro-pillars tops. These structures have been proven beneficial for the development of hydrophobic surfaces on metals. The surface morphology of the irradiated area was characterized with scanning electron microscopy and confocal microscopy.

Additionally, direct laser interference patterning using a picosecond-pulsed laser was employed to create line-like and pillar-like periodic micro-structures with the help and collaboration of the Fraunhofer Institute in Dresden, Germany. In a two-step process, a second laser irradiation was performed on the same surfaces using the direct laser interference patterning technique to create near sub-micron periodic pillars with a spatial period of 2.6 μm . The combination of these two laser processing techniques allows the creation of well-defined hierarchical structures. The surface structure generated by the DLIP technique is uniform all over the processed area, showing a periodic set of micro-pillars with an average depth of 0.9 μm at both the vertical and horizontal direction and an average depth of 1.5 μm at the interference maxima-maxima intersection.

Furthermore, in a collaboration with the University of Birmingham, the formation of LIPSS was created on the surface of the Ti-6Al-4V samples, using a IR femtosecond pulsed laser with the direct laser writing technique. The femtosecond low spatial frequency LIPSS were generated on top of the nanosecond patterned structure to create a dual-scale structure. The femtosecond process is free of thermal effects, meaning that the previously fabricated structures were not affected by this second laser process. The LIPSS generated show self-organized ripples in a very uniform manner with a spatial period of approximately 810 nm. The final surface exhibits a dual-scale roughness thus providing a successful method to generate hierarchical structures.

Static contact angle measurements were made to analyze the wettability behavior of the structures. For all the laser processes, the samples were hydrophilic immediately after the processing. Nevertheless, subsequent ageing was observed as the past of the time, showing an increase in the static contact angle. By employing two different storage methods, an investigation of the role of the storage conditions was undertaken. The samples were kept in two different storage conditions: exposed to ambient air and inside polyethylene bags. The polyethylene bags were found to be beneficial for the surface ageing of laser-fabricated titanium surfaces, increasing the ageing time when compared to ageing by exposure to ambient air. Hierarchical surface topographies exhibited higher water-repellency when compared to non-hierarchical structures. Especially, hierarchical structures reached a hydrophobic state with water contact angle over 160° after 3 weeks storage in polyethylene bags, in comparison with the hierarchical surfaces kept on air which showed a SCA around 120° .

X-ray photoelectron spectroscopy was used to analyze the chemical composition of the samples in different storages, showing that the samples were heavily oxidized, with the processed samples exhibiting a clear increase in the total oxygen concentration in comparison

with the reference sample. Among the oxygen compounds, a clear difference in the relative content of water molecules between samples with the same surface structure kept in two different storage conditions was observed. For the case of the sample kept in air, water molecules were detected, while for the case of the polyethylene bag, which shows the highest contact angle, no traces of water molecules were found. Furthermore, the detailed analysis of the C spectra for the processed samples showed traces of several polar and non-polar carbon compounds, with the sample kept in polyethylene bag showing the lowest concentration of polar molecules while also displaying the highest contact angle. The results indicate that the absence of polar molecules highly affect the wettability of the surface.

Additionally, the corrosion resistance of the processed samples was studied. Linear polarization studies were performed on the fabricated structures to investigate the corrosion resistance behavior of the direct laser writing micro-pillars and the fabricated hierarchical structures in a 0.5 M NaCl solution. Results shown that even if the corrosion current density and the corrosion potential were not greatly improved by hydrophobic DLW structures, the hierarchical structures clearly improved the pitting corrosion resistance of the material (approximately > 7 V) in at least 1 V with respect to the reference value, which was around 5.5 V.

Furthermore, the icephobic performance of micro-structured surfaces was investigated under atmospheric in-flight icing conditions to investigate the feasibility to generate ice-phobic surfaces. The laser processed surfaces manufactured with direct laser writing do not reduce ice adhesion under in-flight icing conditions for the samples tested, nevertheless, more patterns must be investigated in order to assess which topography is most beneficial for reducing ice adhesion in in-flight conditions.

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List of Symbols

The International System of Units (SI) is the appropriate metric system for measurements, nevertheless, in laser material processing, the use of derivate units is most suited for express some quantities, therefore, in some cases the use of the SI will not be applied.

Symbol	Description	Typical units
β	angle between incident beams	<i>rad</i>
Λ	spatial period	<i>m</i>
λ	wavelength	<i>m</i>
γ	interfacial surface tension	<i>N.m⁻¹</i>
θ	static contact angle	$^{\circ}$ (arc degree)
θ'	apparent contact angle	$^{\circ}$ (arc degree)
<i>r</i>	surface roughness factor	no unit
E_{pp}	energy per pulse	<i>J</i>
P_{avg}	average pulse power	<i>W</i>
f_{rep}	repetition rate of the laser	<i>s⁻¹</i>
τ	pulse duration	<i>s</i>
ϕ_0	pulse fluence	<i>J.cm⁻²</i>
ϕ	integrated fluence	<i>J.cm⁻²</i>
OF	overlapping factor	%
$2\omega_0$	spot diameter of the laser beam	<i>m</i>
v_{scan}	scan speed of the laser beam	<i>mm.s⁻¹</i>
ρ	density	<i>g.cm⁻³</i>
<i>F</i>	Faraday constant	96 485.3329 <i>s · A.mol⁻¹</i>
E_{pitt}	pitting potential	<i>mV</i>
E_{corr}	corrosion potential	<i>mV</i>
i_{corr}	corrosion current	<i>A</i>
τ_{int}	interfacial shear stress	<i>Pa</i>
ϵ	shear strain	<i>Pa</i>

List of Abbreviations

Abbreviation	Description
DLW	Direct Laser Writing
DLIP	Direct Laser Interference Patterning
IR	Infra-Red
UV	Ultra-Violet
LIPSS	Laser-induced periodic surface structures
HSFL	High spatial frequency LIPSS
LSFL	Low spatial frequency LIPSS
SEM	Scanning Electron Microscopy
SCA	Static Contact Angle
XPS	X-ray Photoelectron Spectroscopy
LWC	Liquid Water content
AFF	Freezing fraction approximation
MVD	Media Effective Volume Droplet Diameter
TAT	Total air temperature

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Chapter 1

Introduction

1.1 Motivation

Research over the last decades has proven that by creating or inducing different types of surface structures in the micro- and/or nano-scale on a wide range of different materials, functional properties can be modified or even enhanced. Materials with such structured surfaces have shown modified physical properties such as modified wettability or reflectivity, among others. These kind of surfaces that have different properties from the rest of the bulk material can improve the workability of different materials in several industrial applications. Specifically in the topic of wettability, plenty of attention has been put into understand the physical and chemical phenomena responsible for the modification of wetting properties in structured surfaces, as well as in the development of several methods for the fabrication of water repellant surfaces, known as hydrophobic surfaces, in a very wide range of solid materials.

The creation of artificial hydrophobic surfaces was inspired on the hydrophobic behavior observed on natural surfaces [1]. The lotus leaf is the most popular example of a natural hydrophobic surface. Lotus leaves exhibit a surface with high hydrophobic behavior in where the water droplets accumulate and then roll-off the surface, removing

dust and other contaminant particles as they do, thus creating a “self-cleaning” also known as the ‘Lotus effect’ [2]. It has been observed that the surface of these plants present a double scale or hierarchical roughness with both micron and sub-micron features together with a wax that contains non-polar methyl groups which are considered the cause for the hydrophobic behavior.

Current industrial markets demand highly rate products that can offer new features at a low-cost. Bio-inspired surface structures, containing features in the nanometer/micrometer scales, offer significant potential for the manufacture of functionalized surfaces. Several methods including chemical methods, plasma etching, molding or self-assembly of nano-particles, among others, have demonstrated positive results regarding the generation of hydrophobic coatings on micro- and nano-structures on metals and other materials surfaces for enhanced wettability in bio-inspired surfaces [3].

In this aim technologies to modify surfaces instead of creating composites or spreading coatings on surfaces, which involve several process, can offer new industrial opportunities. Among these fabrication methods, laser surface texturing for the creation of micro- and nano-structures on solid materials has showed to be a promising field of research for several years now. In laser machining, micro- and/or nano-structures can be induced on the surface of solid materials after being exposed to laser radiation, either under ambient air or with reactive ambient gases, using laser wavelengths from UV to IR and laser pulses with durations in the short and ultra-short range. When the laser is equipped on a work station controlled by computer with a fixed optical system, the surface of the sample can be modified with high accuracy, thus making laser micro- and nano-structuring a simple, fast and effective method for material processing.

1.2 Objectives

The general objective of this research project is to study and evaluate the performance of short and ultra-short pulse direct laser writing (DLW) for the generation of micro- and nano-structures for functional Ti alloy surfaces with modified wettability using emerging short/ultra-short pulsed laser technologies. Therefore, in the three year project, the particular objectives are focused on getting familiar with the state of the art of the different methods for surface structuring/patterning on Ti alloy, and based on that, develop a series of experiments that can allow to create novel structures for the creation of hydrophobic surfaces. Hence, the objectives of the project are focused on micro/nano-structuring by employing pulsed laser material processing methods, involving the following:

- Literature research concerning the use of surface topographies for controlling surface properties and the methods used for the creation of these micro/nano structures. ability, etc.) of DLW technology as well as other techniques for the development of hierarchical surface structures.
- Provide a systematic theoretical/experimental frame for the evaluation of short and ultra-short pulsed direct laser writing as a technique for the creation of functional surfaces for modified wettability applications.
- Evaluate the fabrication limits of DLW technology like feature size, structure quality, process ability, among others, involved in the creation of homogeneous patterns, to get first-hand knowledge of the manufacturing and characterization methods and the domains affecting laser-material interactions for the different structures achieved due to the different parameters used.

- Carrying out analytical and empirical analyses by characterizing different properties like topography, chemical composition and wetting behavior of the generated structures, by means of several characterization techniques, including confocal and scanning electron microscopy, x-ray photoelectron spectroscopy and water contact angle measurements.
- Analyse and design new approaches by modifying existing methods that can be upgraded to implement laser structuring/patterning processes in a better way for making specific surfaces for the required applications.
- Cooperate with other partners to compare and/or combine the evaluation of nanosecond, picosecond and femtosecond based procedures for the generation of technological surfaces using DLW and other laser technologies, to study the feasibility of combine different laser technology, i.e. hybrid technology, in order to create multi-scale structures patterns on the surface of Ti-6Al-4V.
- Based on this analysis, define the parameters that best adjust to the formation of hierarchical surface topographies for applications specifically, corrosion resistance and anti-icing capability, due to the modified wettability properties.

1.3 Thesis Structure description

Chapter 1. Introduction

The first chapter describes the motivation for this study, as well as the particular objectives that were seek to achieve in the three year project. Additionally, the structure of this thesis is also presented, briefly describing the content of each chapter.

Chapter 2. Manufacturing of functional surfaces with enhanced wettability: State of the Art

This chapter discusses the main concepts involved in the wettability of a surface, like surface roughness and surface chemistry, as well as the different models that describe this phenomena. Additionally, the state of the art in the different fabrication methods of artificial bio-inspired hydrophobic surfaces is presented together with some of the possible applications for this functional surfaces. Furthermore, two different laser techniques, direct laser writing and direct interference patterning, as well as the different types of structures that can be generated with laser are discussed.

Chapter 3. Material and methods

Chapter 3 is dedicated to the experimental methodology and the characterization techniques used in this study. A description of the micro-processing systems used is presented, as well as the techniques necessary for the correct irradiation of the samples. The different experiments developed for this work and the characterization techniques used to analyze the areas modified by the laser with the metallic film are also exposed.

Chapter 4. Analysis and discussion of results

In this chapter the results obtained in this study are presented. The surface topography of the generated structures is analyzed with microscopy techniques. Subsequently, the wettability of the patterned surfaces was also investigated using contact angle measurements. Afterwards, to study what causes this hydrophobic transition, chemical composition of the processed samples is presented and discussed. Furthermore, corrosion resistance studies were made to analyze the fea-

sibility of the patterned surfaces as a method to create anti-corrosive surfaces. Finally, results in the icing properties of the generated surfaces are presented.

Chapter 5. Conclusions

The last chapter of the thesis presents the conclusions reached from the results and discussion section of this thesis.

Chapter 2

Manufacturing of functional surfaces with enhanced wettability: State of the Art

In this chapter the basic concepts on wetting of surfaces and the manufacturing process are presented. The chapter start with a brief introduction of the principal concepts involved in the fundamental models of wetting: Young's Equation, Wenzel model and Cassie-Baxter model. Several techniques for the fabrication of hydrophobic surfaces are briefly discussed. Furthermore, laser material processing for the creation of functional surfaces with enhanced wettability, as well as the two laser processes used in this work, direct laser writing and direct laser interference patterning, are discussed. Finally some examples of the application of hydrophobic surfaces in several fields of technology are presented.

2.1 Basic concepts on the wetting of surfaces

Wetting and wettability are terms used to describe the interaction of surfaces with liquids and how the liquid spread over the surface. For the case of water, if a surface has a high affinity for water molecules the liquid will spread over the surface, behavior known as a hydrophilic

behavior. On the other hand, if the surface tend to repel the water molecules, the liquid will form spherical droplets resting on top of the surface, behavior known as hydrophobic. By trying to artificially replicate natural hydrophobicity, scientists have developed many methods to fabricate superhydrophobic surfaces. The literature exposes a great interest for theoretical research and practical applications [4, 5, 6, 7, 8, 9], developing several methods to create a proper micro/nano-roughness as well as surface chemistry able to generate the superhydrophobic properties required.

Figure 2.1: Schematic diagram of the three-phase interphase Source: Celia et al. [10]

When droplets are formed on the surface of a substrate, a triple interface between the solid, liquid and gas (usually air) will be formed as described in Fig. 2.1. In this triple interface, a common point to the three phase boundary known as a three-phase point can be identified, and by tracing a tangent line around the contour of the droplet shape in this point, an angle θ is formed between this line and the surface of the substrate known as the contact angle. The spreading behavior of water droplets in a homogeneous flat surface is affected by the surface free energy and is described by Young's equation [11, 12]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

where γ_{SV} is the surface free energy of the solid, γ_{LV} is the surface tension of the liquid-vapor phase, γ_{SLV} is the interfacial tension between solid and liquid phases, and θ is the contact angle. The contact angle is generally used as a way of characterization for the wettability of a surface in contact with a liquid to evaluate the wettability behavior of a surface. A contact angle between 0° and 65° or 90° by other authors, describes a hydrophilic behavior, if the contact angle has a value higher than that, $\theta > 90^\circ$, the surface is say to have a hydrophobic behavior. Furthermore, a third category known as super-hydrophobic has been observed in several natural and man-made surfaces, in this super-hydrophobic surfaces the contact angle is higher than 150° , additionally, some surfaces does not allow the formation of droplets, making the droplets roll over the surface; in this limit case the contact angle is consider to be 180° . Additionally to the contact angle, another parameter used for the characterization of the wettability of super-hydrophobic surfaces is the contact angles hysteresis, which is the difference between the advancing and receding contact angles when a droplet is placed on the surface. Contact angle for a liquid advancing across a surface is always larger or equal to that of one receding from the surface, and super-hydrophobic surfaces usually exhibit contact angle hysteresis of less than 10° or even 5° .

Young's equation describe the relation between the contact angle and the surfaces tensions of the three-phase boundary for the case of a smooth and homogeneous surface in contact with a droplet of water, which depends on the chemical composition of the solid and the liquid. Nevertheless, this limit case is very hard to re-create in real surfaces which does not have perfect smoothness and homogeneity, for this reasons the roughness of the surface must be taken into

account when studying the wettability behavior of the surface. It has been shown that real surfaces usually present a surface roughness with micro- and nano-features either in a periodic or random patterns and that the contact angle observed will not be the real contact angle but an apparent one measured from the average surface plane. Taking into account the surface roughness two models have been proposed and highly accepted by the scientific community: the Wenzel model and the Cassie-Baxter model. From those two model, the wetting of a rough surface can be classified into two different wetting regimes: homogeneous and heterogeneous. Fig. 2.2 shows a basic diagram of the different regimes consider in each model.

Figure 2.2: Schematic diagram of the three different wetting states: a) Young, b) Wenzel c) Cassie-Baxter. Source: Tam et al. [13]

Opposite to the smooth flat homogeneous surface consider on Young's equation, the Wenzel model consider a surface with a roughness with nano- and micro-feature. The wetting of the surface happens in a homogeneous wetting regime where the liquid wet all the surface including the air spaces between the nano- and micro-features. The Wenzel equation consider a roughness factor to describe the wettability of a surface as follow [14, 15]:

$$\cos \theta' = r \cos \theta \quad (2.2)$$

where θ' is the apparent contact angle of the rough surface, θ is the contact angle for a flat surface as described by Young's equation, and r is the surface roughness factor, which is defined as the ratio of the true area to that of the apparent area of a surface, therefore, it follows that for a rough surface $r > 1$.

It has been established that according to Wenzel's equation, for a hydrophobic surface $\theta' > \theta > 90^\circ$ and for a hydrophilic surface $\theta' < \theta < 90^\circ$ hydrophilicity depending on the original wetting behavior of a surface, i.e., an originally hydrophobic surface ($\theta > 90^\circ$) will increase the contact angle as the surface roughness factor increases and an originally hydrophilic surface will become more hydrophilic by reducing the contact angle as the roughness factor increases. Nevertheless, it has been showed, that after a certain value of the roughness factor a hydrophilic surface will suffer a transition to the hydrophobic regime that is attributed to a transition from the Wenzel state to a Cassie-Baxter state as the surface roughness increases and the liquid stop wetting surface between the micro-roughness due to an air trapped in the empty spaces (see Fig. 2.3). Therefore, it is generally acknowledged that superhydrophobic surfaces can be generated by increasing the roughness of a hydrophobic substrate. Several studies have confirmed that it is possible to obtain superhydrophobic surfaces on hydrophilic samples by changing the roughness and morphology of the surface [16, 17, 18, 19].

In the Cassie-Baxter model, a heterogeneous wetting regime, where the wetting of the surface is a composite of wet areas and air gaps or "air traps" that repel the liquid from wetting the surface, is considered. In this wetting state, the contact angle does not wet all the surface of the material, instead the wetting is considered to happen in discrete sections of areas with a surface fraction f_1 surrounded by air pockets that avoid the wetting of areas of the material with a fraction surface f_2 ,

Figure 2.3: Schematic diagram of the air trapped between structures as proposed on the Cassie-Baxter model.

giving place to a composite surface of two species, where $f_1 + f_2 = 1$. The Cassie–Baxter equation is used to describe this wetting state as follow [20]:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.3)$$

where θ is the Cassie-Baxter contact angle, θ_1 is the contact angle of the wet surface fraction and θ_2 is the contact angle of the air pockets fraction. In the case of air, the contact angle with the droplet is 180° and thus the Cassie-Baxter equation can be re-writing as:

$$\cos \theta = f_1 (\cos \theta_1 + 1) - 1 \quad (2.4)$$

From the Cassie-Baxter equation it can be see that the apparent contact angle depends only on the fraction surface of the wetting zones

with a given contact angle. For this reason, for a good hydrophobic behavior, a minimum fraction surface or a high θ_1 are needed. Therefore, micro and nano-patterning can be beneficial for the creation of structured surfaces for the development of hierarchical topographies (Fig. 2.4) for surfaces with reduced surface fraction when in contact with water [21, 22, 23].

Figure 2.4: Schematic diagram of the air trapped between structures as proposed on the Cassie-Baxter model. Source: Eber and Bhushan [21]

2.2 Fabrication methods for Bio-inspired artificial hydrophobic surfaces

Several natural surfaces exhibit a hydrophobic or water repellent behavior, exhibiting very high contact angles in plants [24, 25] or on insect skin [26, 27, 28]. One of the most famous and referred natural surfaces that exhibit a high water repellency with contact angles over 150° is the lotus leaf [2, 29]. SEM micrographs of lotus leaves (Fig. 2.5) have shown that the surface of this plant present a topography that is a combination of a two different roughness: one is made of papillose epidermal cells in the micro-scale surface (1 to 10 μm) and the other is composed of three-dimensional epicuticular waxes in the nano-scale which grown in top of the micro-structures and are long chain hydrocarbons and exhibit an hydrophobic effect.

Figure 2.5: Superhydrophobic Lotus surface exhibiting the self-cleaning effect by removing dust from the surface by adhesion of on the particles of water.
Source: Kochet al. [30].

This kind of surfaces where two or more different types of structures with different length scales are present have been termed as hierarchical structures. Furthermore, it has also been observed that the super-hydrophobic effect of the lotus leaf is also partially caused due to the wax made by the epicuticular crystalloids that cover the cuticular. The wax secreted by the crystalloids exhibit a contact angle around 110° [31], so it does not shows a super-hydrophobic behavior by itself, however, the lotus leaves still displays a super-hydrophobic behavior. The reason for this behavior has been proposed as a result of the combination of the chemistry of the wax which reduces the surface free energy as well as the hierarchical topography of the structures which reduces the wetting area of the material due to the air pocket created. The water droplets on these surfaces readily sit on the apex of the nanostructures because air bubbles fill in the val-

leys of the structure under the droplet. Additionally, due to the high water repellency of the lotus leaves, water droplets tend to roll-off the surface, and while doing it, the water droplet collects contaminants on the surface, consequently creating a “self-cleaning” effect, also known as the “lotus effect” [2]. This self-cleaning property is one of many application that have been investigated in recent years by developing artificial hydrophobic and super-hydrophobic surfaces.

As it has been exposed by the wetting models described in the previous section, a rough surface is essential for enhancing hydrophobicity in a material and several natural hydrophobic surface indeed presents a hierarchical surface roughness. Nevertheless, as it can be seen in the composition of the lotus leaves, the wettability of a surface is also related to the free surface energy of the material. In awareness of this, several methods and techniques have been developed for the creation of artificial hydrophobic and super-hydrophobic surfaces with hierarchical structures and modified surface chemistry inspired in natural hydrophobic surfaces. From all the several methods developed for mimicking the structures of natural hydrophobic surfaces, two general categories can be termed, based on the type of approach used for the production of the hierarchical surface: top-down and bottom-up [32].

Top-down techniques for the generation of rough surfaces with enhanced wettability generally refers to fabrication methods in which the micro-structure on the surface is achieved by molding, carving or removing bulk material of the desired sample. This techniques usually involve lithography, templation, plasma treatment or laser micro-machining, among others. For the case of lithography and templation it is usually necessary the molding of a master piece and a replica substrate to recreate the original surface , while in a plasma treatment or laser micro-machining the process is more related to surface etching and material removal without the need of masks or templates.

Bottom-up methods, on the other hand, involve the building or designing of large and complex objects by integrating smaller building blocks or components. Bottom-up approaches that have been applied for the preparation of super-hydrophobic surfaces include chemical deposition methods such as chemical bath deposition, chemical vapor deposition, electrochemical deposition, colloidal assembly, layer-by-layer deposition via electrostatic assembly and sol-gel methods. This type of methods generally involve mostly self-assembly and self-organization. Self-assembly refers to a method in which components integrate and assemble naturally in the solution or gas phase until a stable structure with minimum surface energy is achieved. In this section some examples of the mentioned methods are presented.

Lithography and templation

Lithography, on a general level, is a method that allow the fabrication of hydrophobic surfaces by copying the features in a master piece and then transfer them into a replica which will have the opposite form. This technique allows to control the structure and the morphology of surface that will be produced, making possible to create surfaces patterned with pillars or pots with different shapes, like circular or squared, and different diameters, height, and spacing between them [33, 34, 35, 36]. Lithography has shown positive results for the fabrication of micro- and nano-structures for enhanced wettability. For example, Park et al. [37] used the lithography method for the creation of micro-structures fabricated by replica molding and self-replication with varying pillar separation in order to analyze the role of different geometry in the wettability behavior of the final structures. Contact angle results showed that the wetting state was either in the homogeneous Cassie regime or in the mixed regime of Cassie and Wenzel states depending on the values of s/d demonstrating the

relation between wetting transition and structural parameters of the micro-structured surface.

Additionally, a series of grating microstructure surfaces with different roughness parameters in polydimethylsiloxane (PDMS) membranes have been designed and fabricated using soft lithography by Li et al. [38] demonstrating that the contact angle and hydrophobic performance enhance with the decrease of the grating's width. These results exhibit the importance of the separation between the micro-features in the surface. The dependence of the contact angle values and the spacing between structures has been attributed to the air-pockets considered in the Cassie-Baxter model and the hydrophobic nature of PDMS.

Likewise, generally speaking, the templation process involves the use of a master piece with the desired features to be replicated, further replication of these features by molding of a replica, followed by lifting off the replica or dissolution of the templates to obtain the final surface as described by Fig. 2.6. Templation is useful for the preparation of polymeric super-hydrophobic coatings that imitate the natural surfaces that can be used as the master for the fabrication of these hydrophobic surfaces, for example like mimicking the structure of a lotus leaf or a gecko's feet [39].

Sun et al. [40] have used a lotus leaf as template, followed by a replication process of casting and lifting off PDMS, finally obtaining a negative replication of the lotus leaf structure (Fig. 2.6). The PDMS replicas were used then as a master for preparation of a positive replica of the lotus leaf. Super-hydrophobic, thus allowing to transform the hydrophobic PDMS material into super-hydrophobic material by topographic surface engineering without additional chemical modification.

Figure 2.6: Schematic illustration of the template process and SEM images and droplet photograph in the surface of (a) a natural lotus leaf and (b) its positive PDMS replica. Source: Sun et al. [40]

Plasma treatment

The plasma treatment of surfaces is made by means of etching of the material, known also as reactive ion etching. This method is a dry etch technique in which reactive atoms or ions are generated through a gas discharge by an electrical field, the surface is then patterned by removing material from the substrate by anisotropically etching thus inducing a roughness in the treated surfaces. In several cases, the surface pattern has been created by the plasma treatment after lithography or templating methods [41, 42], nevertheless, the plasma treatment can also be used before lithography or templating [43, 44], and sometimes the plasma treatment and lithography can even alternate with each other during the surface processing [45]. Plasma treatment of surfaces can cause a considerable change in the surface structure and several material processed with this technique have been used to generate a super-hydrophobic behavior. Superhydrophobicity is sometimes reached directly after the process, nevertheless in other

cases a post-treatment with a hydrophobizing agent is required.

Examples includes plasma treatment of low-density polyethylene to generate a resulting surface roughness within 500 hundreds nanometers achieving contact angles of 170° as is shown in the study of Fresnais et al. [46]. Additionally, patterned surfaces have been formed by combining the plasma etching method after or before lithography or templating methods, for example Zhang et al reported the fabrication of silicon cone arrays by using colloidal lithography where well-ordered mono-layer or double-layer particle arrays are used as mask to perform the plasma etching to form micro- or nano-scaled surfaces with contact angles up to 150° [47]. Also the formation of micro-structures on a silicon surface using deep reactive etching and further creation of nano-features on the previous micro-structures using XeF₂ etching was proven [48], as shown in Fig. 2.7.

Figure 2.7: Droplet on the hierarchical surface fabricated by plasma treatment. Source: Kwon et al. [48]

Chemical deposition

Chemical deposition is a process in which a chemical material is transported in the vapor phase to a heated substrate to form a thin film. This technique can be applied to create rough surfaces [49, 50, 51, 52]

or to deposit a thin layer of hydrophobic compound on a rough surface [53, 54]. Chemical deposition is then a process in which particles of some material self-assemble as it is deposited on a substrate. This technique is commonly used for the generation of thin films of crystalline inorganic material, like ZnS, CuS, InS, etc. Depending on the way of the deposition of the material, several sub-categories of this technique have been developed, such as chemical vapor deposition, chemical bath deposition or electrochemical deposition.

This technique has shown positive results in producing different surface morphologies such as nano-pins, nano-tubes, among others. For example, chemical bath deposition has been used by Hosono et al. [16] for the creation of nano-pin films using CoCl_2 and NH_2CO in water deposited in a borosilicate glass as substrate, giving place to brucite-type cobalt hydroxide films. After the deposition, the structure surface was treated with lauric acid to achieve a hydrophobic effect with a contact angle over 170° .

In the case of chemical vapor deposition, the process normally refers to exposing the selected substrate to a gaseous precursor to deposit the desired film or powder, and chemical reactions are involved during this process. Huang et al. [55] have reported the fabrication of a stable super-hydrophobic surface via aligned carbon nanotubes on a Fe-N-coated Si substrates coated with a zinc oxide (ZnO) thin film. The generated surfaces achieved a contact angle over 155° . Furthermore, the surface lost the hydrophobic effect after long exposure to UV illumination, becoming a hydrophilic surface, nevertheless, the hydrophobic behavior was restored after storage in darkness thus making a surface with tunable wettability. This is an example of a surface in which the wettability of a surface is determined by both its chemical composition and roughness.

Other chemical deposition methods such as the electrochemical deposition process can be used to deposit films of solid metal or its oxide onto electrically conductive substrates. Electrochemical deposition of zinc oxide, gold clusters, or silver aggregates have been used to prepare super-hydrophobic surfaces, nevertheless, in these examples the deposited structures were modified with self-assembled monolayers of other materials in order to lower the surface energy to enhance hydrophobicity.

Colloidal assemblies

Colloidal assemblies is a method that can be used to assist other fabrication techniques like chemical deposition, plasma etching or lithography process by assembling or aggregation of colloidal particles to make micro- or nano-structures for super-hydrophobic surfaces [56, 57, 58]. The colloidal assembly process is based on creating assemblies of monodispersed particles (i.e., particles of approximately the same size) through chemical bonding or van der Waals forces. The colloidal particles can vary from polymer beads to inorganic spheres. By controlling the sizes and scales of the assembling particles, multilayered roughness can be induced [59]. The multilayer is usually made by immersing the substrate into the solution of particles or spin-coating the solution onto the substrate. [60, 61]

Examples of rough surfaces made by this technique include the formation of multilayered crystal structures prepared by spin-coating of monodispersed silica particles of approximately 70 nm diameter [62]. The thickness of the colloidal crystals could be controlled by adjusting speed and time of spin-coating, giving place to a silicon nano-pillars array. Additionally, the hydrophobicity of the silicon nano-pillars was enhanced by coating the structures with fluorosilane through the silane

Figure 2.8: (a) SEM image of the self-assembly of polydisperse silica spheres. (b) Photograph of a 5 μL water droplet residing on this silica self-assembly modified with hydrophobic coating, corresponding to a sCA of about 129° .

Source: Zhang et al. [63]

coupling reaction, achieving contact angles over 150° .

Furthermore, binary colloidal assemblies for the creation of super-hydrophobic surfaces have been reported by Zhang et al. [63] by first doing colloidal assemblies of CaCO_3 -loaded hydrogel spheres on silicon substrates (Fig. 2.8). After that, a second colloidal assembly of silica nanoparticles or polystyrene beads was performed on top of the first assembly. Due to the hydrophilicity difference between silicon wafers and CaCO_3 -loaded hydrogel spheres, the region-selective localization of silica or polystyrene spheres leads to irregular binary structures with a hierarchical roughness. Additionally, subsequent modification with deposition of silver and self-assembled monolayers give place to super-hydrophobic surfaces with water contact angle of more than 150° .

Layer-by-layer deposition

Layer-by-layer (LBL) deposition is a fabrication technique for the creation of thin films. The fundamental principle of the LBL deposition rests on changing the charge of a substrate, and this allows the

construction of multilayered film by depositing alternating layers of oppositely charged materials (Fig. 2.9). LBL deposition technique is then based on the electrostatic charge interaction between different layers such as polyanion and polycation. This technique permits to control the thickness of the resulting layer with very high precision. Nevertheless, typical polyelectrolytes are very hydrophilic, therefore, a hydrophobization of the final surface is necessary. Additionally, to generate rough surfaces additional treatment is needed thus making this method less straight forward for the preparation of super-hydrophobic surfaces. To induce a roughness in the surface nanoparticles can be incorporated into the multilayer system in order to enhance the roughness effects in the multilayer films, but the films can also be roughened

Figure 2.9: Schematic of layer-by-layer composite coating. Each layer is deposited separately. Also shown are the chemical composition and charge of each layer. Source: Brown and Bushan [64]

by some other treatment technique.

Some examples of super-hydrophobic surfaces using the LBL technique include silicon surfaces using poly(allylamine hydrochloride) and poly(acrylic acid) as demonstrated by Zhai et al. [65]. In their study it was showed that by applying an appropriate combination of acidic treatments, pores on the order of 10 microns and a honeycomb-like structure can be formed on the PAH/PAA films. Super-hydrophobicity was achieved by coating the rough textured multilayer surface with a semi-fluorinated silane. It was proven that both the microstructure created by the combined acid treatments and the nanostructure induced by the deposition of silica nanoparticles, i.e. hierarchical structures, are necessary to create stable super-hydrophobic surfaces. Also, multilayered films of PAH and silica nanoparticles has been created by layer-by-layer deposition followed by a surface modification using a low surface energy material silane, to create a surface roughness with switchable wettability as demonstrated by Chunder et al. [66]. The surfaces can be created with a precise control over film thickness and roughness.

Sol-gel method

The sol-gel process is a method of producing solid materials from small molecules and is used for the manufacture of metal oxides. The process involves the conversion of monomers into a colloidal solution (sol) that acts as a precursor to an integrated network (or gel) of discrete particles or cross-linked polymers. A sol is usually prepared by hydrolysis of the corresponding oxide in the presence of a solvent. During the network formation process, a large amount of solvent are also impregnated in the network and a gel is formed. The sol can be applied either directly or combined with fillers such as silica nanoparticles. The resulting surface property depends on how the sol was prepared

and surface functional groups of the resulted gel. The sol–gel methods have been utilized to create superhydrophobic surfaces since the very early stage of mimicking lotus leaf’s surface structure [67, 68, 69, 70].

The sol–gel method has been employed to generate superhydrophobic surfaces and it involves a chemical solution deposition, during which the chemical solution or sol is utilized as a precursor on the selected substrate to form the gel-like network. Material of low surface energy and micro- or nanoparticles can be added into the network to induce the super-hydrophobic effect. For its compatibility with glass, this type of method is particularly favored in creating transparent and super-hydrophobic films on glass surfaces. Several examples of this method for the creation of super-hydrophobic surfaces can be found in the literature. For instance, Xiu et al. [71] used a eutectic liquid (choline chloride and urea) that served as a templating agent to prepare thin silica films on glass microscope slides with optical transparency and super-hydrophobicity. The method produced porous silica thin films with asperities after gelation in the presence of a base catalyst. After that, a fluoroalkyl silane treatment imparted the super-hydrophobicity to achieve a contact angle of approximately 170° . Furthermore, to enhance the transparency of the films, the sol solution was diluted with ethanol and then spin-coated on the substrates.

2.3 Laser patterning

Since the creation of the laser in 1960, almost 60 year ago, when the fabrication of the ruby laser was presented for the first time [72], the concept for a method that could be used to compress an amount of optical radiation into an extremely narrow pulsed emission was researched. In 1962, Mcclung and Hellwarth made the first modulated laser with an output peak power of 600 kW and a pulse width of the $0.12\mu s$ from a ruby laser [73]. A few years later the concept of compress the laser pulses to a shorter time with an increase in power was proposed, and the field of ultra-short pulses was created and developed during the years 1960s and 1970s. After the following development in laser technologies, which was the generation of ultra-short pulses with a duration of 30 fs in 1982 [74] followed by the invention of the chirped (frequency-modulated) pulse amplification method in 1985 for the generation of high peak power pulses [75], laser technology have become widely used, not only in industry, but in the daily life at customer scale in many devices and equipment, making it one of the most important tools in research, development and innovation. Nowadays, lasers have become an elemental machinery in all industries and are extensively used for all kind of applications worldwide, changing the way in which technology has evolved over the last decades. Among the several application for lasers in industry, laser material processing is one of utter importance and is a topic that has been widely investigated in recent years.

In laser micro-machining, the election of the laser system can be based on the desired final application of the modified surface. In the case of metal, if structures in the scale of tens of micrometers are required, the use of nanosecond pulsed laser has proven to be a valuable option for surface patterning due to the low-cost of ns lasers. Several surface patterned with nanosecond laser have proven to show positive

results in the creation of functional surfaces with enhanced properties in several types of material. However, if the application requires surface features in the sub-micron and nano-scale, the use of ps and fs is more feasible due to the highly defined structures than can be created due to the absence of thermal effects in the material surrounding the irradiated area. Likewise, ps and fs have proven to be beneficial in the fabrication of functional surfaces for a wide range of application on several materials. In this study, two different laser techniques were employed using ns, ps and fs sources for the creation of micro- and nano-structures in Ti-6Al-4V sheets for the creation of hydrophobic surfaces when hierarchical structures. The two techniques employed were direct laser writing and direct laser interference patterning. In the following section a brief description of the techniques as well as some examples of their use in several application will be presented.

2.3.1 Direct Laser writing

Direct laser writing (DLW) has demonstrated in recent years, to be a powerful mask-less, low-cost and single-step laser technology for the creation of precise patterns with micro and sub-micron features in several types of material. In the direct laser writing technique a laser beam, either continuous or pulsed, is focused onto a target sample and then translated over the area of interest that is going to be modified. The target material will interact with the incident laser light and several process can take place depending on the characteristics of the laser beam like average power, wavelength, polarization, and repetition rate or pulse duration in the case of pulsed lasers. Depending on the desired application, direct laser writing systems may have different setups, nevertheless, the basic concept and components are very similar. Typically, a direct laser writing system consist on a laser source, mounted and fixed in an automatized workstation, equipped with a

translational stage and/or a galvo scanner used for the displacement of the laser beam over the area to be processed (Fig 2.10).

Figure 2.10: Basic diagram of the direct laser writing method for material processing.

Direct laser writing process is generally based on the local ablation of the target sample when exposed to the high intensity laser beams. Due to the thermal differences involved in the interaction of the light and the material, which depends on the pulse duration of the laser used, several types of structures have been observed after the laser processing. When working with nanosecond laser pulses, thermal ablation is the main process in the creation of surface patterns, and high amounts of recast material can be produced if the laser power applied is too high.

Nevertheless, several researches have demonstrated that this recast material can be used in a beneficial manner when a structure with

highly defined periphery is not needed. For example, Jagdheesh et al. have demonstrated the feasibility to produce hydrophobic surfaces via nanosecond DLW [76] by drilling micro-holes on an aluminum sample (Fig 2.11.). They observed that the produced micro-holes are surrounded by recast material that was melted during the laser processing and then re-solidifies. Additionally, the depth and the width of the micro-holes increases in proportion with the number of laser pulses applied. The patterned surfaces exhibit a hydrophobic behavior that increases with the time. The increase in the contact angle was attributed to the change in the surface roughness, which can help to undergo a transition between Wenzel and Cassie-Baxter states of wetting, due to the creation of the micro-wall that surround the holes, nevertheless, also a chemical modification take place after the laser processing as it can be clearly observed in the ageing of the sample and the increased values in contact angle.

Figure 2.11: SEM micrograph of micro-holes produced by nanosecond DLW for the creation of one-step process and the evolution of the contact angle in time for several patterns with different separation between holes. Source: Jagdheesh et al. [76]

Furthermore, Jagdheesh et al. also have investigated the role of the geometry of the patterns created with nanosecond DLW in the surface of aluminum alloy samples [77]. Two different geometries, micro-

channels and micro-pillars were fabricated to study the response of the contact angle. For the case of micro-channels, the SEM images shows again a strong presence of the high thermal effects that cannot be avoided when using nanosecond lasers. As the laser scans the surface, material is removed due to the ablation process, but also material in the surrounding zone is elevated to very high temperatures, leading to the melting of material, which take a liquid behavior. This molted material is additionally affected by the scanning speed and the pressure that is created during the process, which eject material as the laser make the ablation tracks. The re-solidified material give place to the formation of an additional structure beside the micro-channel as it can be observed on Fig. 2.12.a. The induced micro-wall that is formed in the periphery of the channels has a height of several micrometers, in the same scale than the depth of the micro-channels, therefore, giving place to a geometry with dual m-channels, one below the surface plain and one above the surface plain.

Figure 2.12: SEM image of the patterns fabricated via ns-DLW: (a) micro-channels, (b) micro-cell formation on top of the micro pillars. Source: Jagdheesh et al. 2016 [77]

Additionally, when doing a perpendicular scan of the laser over the first processed micro-channels, another geometry can be induced as it can be observed on Fig. 2.12.b. The generated pattern consist on

squared micro-structures, surrounded by micro-channels in both the x and y directions, with a periodic pattern of squared zones of unprocessed material surrounded by four micro-wall, creating a cell-like structure in the whole processed surface. They show in their study the dependence of the contact angle with respect with the size of the micro-structures, as structures with bigger unprocessed area showed a lower hydrophobic behavior, partially due to the highest space when considering the Cassie-Baxter state, but also the chemical modification that suffer the irradiated material, which leads to a higher contact angle. Nevertheless, smaller micro-structures showed a better hydrophobic behavior with contact angles up to 180° with excellent roll-off behavior [77]. These kind of structures that make use of the thermal effects which are unavoidable when working with nanosecond lasers are promising for the creation of hydrophobic surfaces on other materials as a low-cost and fast process.

In the case of direct laser writing employing ultra-short pulses, the technique has proved to be an advantageous approach for precise fabrication of 2D and 3D structures on several kinds of materials. Ultra-short laser pulses can fully ionize a wide range of solid materials with reduced or non-existent recast in the surrounding zones, giving place to structures with well-defined edges, contrary to nanosecond lasers. Therefore, ultra-short laser are a very capable tool for high-resolution micro-machining of structures in the micro- and sub-micron scales in different types of materials. DLW with fs and ps has been widely used as a patterning technique for applications on lithography from more than two decades [78]. In comparison to the conventional methods like lithography or electrochemical polymerization, direct laser writing (DLW) has several advantages for fabricate high precision structures in a relatively fast and reproducible manner without the need of a photomask. Additionally, the DLW technique can be adapted to be utilized for patterning samples in aqueous condition, which is the

most favorable situation for biological materials [79].

With the utilization of the ultra-short pulses, nonlinear optical processes such as two-photon absorption can take place, leading to the formation of three dimensional structures in the micro/nano scale without thermal damage. Among the structures that can be created with ultra-short pulsed lasers, laser-induced periodic surface structures (LIPSS) has been very reported in the last decades since the first report of this structures after laser irradiation on semiconductor using a ruby laser [80]. LIPSS have gained a lot of attention due to their potential applications for surface functionalization [81]. The generation of LIPSS is a phenomena in which periodic structures, typically in the form of ripples, are induced on the surface on a wide range of solid state materials by means of irradiation of trains of laser pulses with the appropriate energy and number of pulses, depending on the material and the characteristics of the laser source. This is a type of top-down method to produce nano- and micro-structures in a one-step process without the need of other components like mask or templates. Fig. 2.13 SEM micrograph in which the formation of nanostructures in a ZnO sample is observed after being irradiated using a 150 fs laser with a wavelength of 800 nm [82].

The periodic structures consist usually in long parallel ripples extended over the irradiated zones, with typical dimensions on the nano-scale, and with a periodicity that is always much lower (high spatial frequency LIPSS, HSFL) or close to (low spatial frequency LIPSS, LSFL) the laser wavelength used for the laser process [83]. The formation of LIPSS has been observed under different irradiation conditions on different materials (semiconductors, dielectrics and metals) with a direction of orientation either parallel (HSFL) [84] or perpendicular to the laser polarization direction (LSFL) [85]. Unlike LSFL, high frequency LIPSS have been observed generally using ultra-short

Figure 2.13: SEM micrograph of a ZnO sample after being irradiated with a pulsed femtosecond laser, with a duration per pulse of 150 fs in which the formation of LIPSS can be observed. Source: Dufft et al. [82].

pulses with duration in the regimen of picoseconds and femtoseconds. On the other hand, both LSFL and HSFL have been observed after a few tens of pulses deposited on the same site, while in other cases it has been observed after hundreds or thousands of pulses deposited. The formation of LIPSS have been investigated for several applications, including decorative purposes due to diffraction from the surface, anti-icing or self-cleaning applications [86, 87, 88]. For the case of nanosecond lasers, Satapathy et al. has demonstrated the creation of continuous and non- continuous laser-induced periodic structures on silicon substrate using a nanosecond laser [89]. Although several theories has been proposed trying to explain the formation process of LIPSS [90, 91, 92, 93, 94], the physical mechanism of LIPSS formation is not completely clear.

One of the theories on the formation of LIPSS, attributes the generation of these structures to a phenomenon of interference between the incident electromagnetic wave on the material and a wave reflected

and scattered on the surface of the material [95, 96, 97]; resulting in an interference pattern that creates a modulation of the intensity of the light that hits the surface of the material. This modulation of intensity generates a deposit of energy on the surface in a similar way to the interference pattern, so that energy only affects certain parts of the material, modifying certain areas and leaving others without any alteration, which results in the formation of the observed nanostructures. However, the formation mechanism is very complex to ensure that this interference phenomenon is solely responsible for the formation of these nanostructures, since the formation of LIPSS on surfaces depends not only of the irradiation conditions but also on the physical and chemical properties of the materials. For instance, other proposed theories for the formation of LIPSS are based on an effect of self-organization during the relaxation of the surface after entering a situation of non-equilibrium due to the energy of the incident pulses [98, 99]. In another case, Borowiec and Haugen propose the generation of the second harmonic as the phenomenon responsible for the formation of these nano-structures [100], while other theories present a classical electromagnetic approach, in fact, the dependence on periodicity and the orientation of the LIPSS with respect to the wavelength and the polarization of the light suggests that, in effect, the formation of these structures must be partially related to an electromagnetic phenomena.

Another of the possible explanations for the formation of LIPSS proposes to consider the interference between the incident wave and a surface plasmon-polariton, as the phenomenon responsible for the generation of LIPSS [101, 102]. A surface plasmon-polariton refers to an electromagnetic disturbance that propagates through an interface between a dielectric and an electrical conductor, resulting from the coupling of a photon with a surface plasmon (oscillation of a gas of free electrons in a metal). A surface plasmon-polariton is considered

to be responsible for the formation of LIPSS due to its characteristics, which include a wavelength smaller than that of the laser pulse, in addition to having a transverse magnetic (TM) mode, which can explain the formation of LIPSS perpendicular to the direction of the linear polarization of the pulse. One of the main difficulties that this theory presents is the fact that an SPP needs a metal-dielectric interface, while the LIPSS have not only been observed in metals, but also in semiconductors and dielectrics. It has been proposed that during irradiation with ultra-short pulses, the properties of a dielectric or semiconductor can be modified, behaving like a metal during the interaction of the pulse with matter [91], which would allow the generation of SPP during the LIPSS formation process using femtoseconds pulses. Although the SPP model for the formation of LIPSS coincides with certain cases reported, does not completely explain why the formation of LIPSS depends on the pulse fluence used, as well as the number of pulses that affect the same area [103, 104, 105]. The origin of the growth of LIPSS in surfaces keeps on being a subject of study, because the different types of LIPSS that can be found in the literature still do not find a general explanation that covers all the specific cases reported.

2.3.2 Direct laser interference patterning

It has been presented in the previous sections that a surface with a certain roughness or topography could enhance some surface properties of different materials, and furthermore, that a controlled periodic pattern is preferred over a random array of micro- and/or nano-features. Different technologies that are available for the creation of these structures have been briefly mentioned, nevertheless, the mission is not only to produce periodic patterns in the micro- and nano-scale, but to be able to produce them at low cost in industrial scale. Different mask-

less fabrication methods have been compared, focusing on the different fabrication speeds employed for each method in terms of unit area per unit time (cm^2/min) as well as in the length scales achieved for the surface roughness features that are produced. Typical fabrications speed ranged between 0.001 to 200 cm^2/min for features sizes between 0.1 and 100 μm [106], additionally it was observed that a lower fabrication speed has to be used for smaller structures. Direct laser interference patterning (DLIP) is a novel fabrication method that allows the production of periodic patterns in both nano- and micro-scale with high fabrication speeds [107, 108]. The DLIP technique has proven fabrication speeds up to approximately 0.1 m^2/min and structures lengths down to the nano-scale. Additionally, this laser technique allows the processing of different pattern geometries (line-like or cross-like patterns among others) on a wide variety of materials.

The DLIP technique, for the case of metals, is based on periodic

Figure 2.14: Schematic for the two-beams Direct Laser Interference Patterning (β corresponds to the angle between the laser beams and controls together with the laser wavelength the resulting spatial period).

Source: Bieda et al. [109].

ablation in interference maxima of an interference pattern created by two or more coherent laser beams that are overlap on the same area of a metal surface, thus creating a periodic intensity distribution on the irradiated area. To accomplish suitable coherency of the interfering beams necessary for the interference pattern to appear, a laser beam is split into several sub-beams, then this beams are joined together on the surface by using different optical configurations. Fig 2.14. shows the intensity distribution for a two-laser beam configuration.

Depending on their geometrical arrangement and the number of sub-beams a characteristic intensity distribution is obtained that can be described as follows [108, 109]:

$$I \propto \left| \sum_{j=1}^n E_j \right|^2 \quad (2.5)$$

Where E_j are the components of the light wave. For the case of two-beam interference, this equation has a solution given by:

$$I(x, y) = 2I_0 \cos(kx \sin \theta)^2 \quad (2.6)$$

where I_0 is the energy density of the incident laser beams, β is the angle between them, x and y are the lateral coordinates in the substrate's surface at $z=0$, and k is the wave number. According to this equation, both interference maxima and minima positions are perpendicular to the y direction. The grating period P of the interference pattern can be written as:

$$\Lambda = \frac{\lambda}{2 \sin \beta} \quad (2.7)$$

Where λ is the wavelength of the laser beam and β is the angle between the beams. Therefore, for a given wavelength, the spatial period of the interference pattern could be controlled down to half the wavelength ($\lambda/2$) for an ideal situation where two beams interfere with an angle of 180° .

By selecting suitably processing parameters, this technique has proven to be effective for the creation of different surface topographies on metals and polymers using nanosecond and picosecond lasers. For nanosecond pulses in metallic surface, the principal mechanism behind the material removal is extensive melting as well as ablation and the temperature of the surface is determined by thermal conductivity in an equilibrium process which obeys the Fourier's law of heat conduction [110, 111, 112]. On the other hand, when picosecond laser pulses are used, little thermal damage is observed due to the small duration of the pulses. Therefore, DLIP with ultra-short laser pulses (<100 ps) offers the opportunity to manufacture accurate and defined surface topographies with scales in the nano- and micro-scale [110].

For the case of metals, Aguilar-Morales et al. have demonstrated the feasibility to produce patterned surfaces with the DLIP technique using both nano- and picosecond pulses on stainless steel alloy. For the case of nanosecond, thermal effect are evident and cannot be avoided, giving place to structures with a lot of thermal damage, thus creating not so well-defined surface patterns as it can be observed on Fig. 2.15.a., on the other hand, for the case of picosecond laser, thermal effects can still be present but are less notorious, and a more defined pattern can be created as it can be observed on Fig. 2.15.b. Addi-

tionally, the picosecond DLIP structures reached contact angle values up to 145° , from a reference angle of approximately 68° [113, 114].

2.4 Roles of surface roughness and surface chemistry in wettability

As it can be seen from the previous sections, a hierarchical structure in the micro- and nano-scale can help to enhance the wettability of a surface, for example, Onda et al. used alkylketene dimer wax solidification to form fractal surfaces in a glass plate in an atmosphere of dry N_2 gas. This kind of wax coating presented a contact angle up to 170° for fractal patterns and 109° for a flat surface, underlining the importance of surface roughness [115]. Nevertheless, the requirement of a rough surface is not the only necessary condition to achieve a good hydrophobic behavior, since it has been proven that the surface chemistry of the base material as well as the chemical modifications after the processing also affects in great manner the wetting behavior of structured surfaces.

As it has been discussed, several fabrication techniques for hy-

Figure 2.15: Direct laser interference patterning structures on stainless steel for different pulse time regimes: a) nanosecond pulses and b) picosecond pulses. Source: Aguilar-Morales et al. [113, 114]

hydrophobic surfaces make use of chemical process for the generation of the micro- and nano-structures. Hydrophobic coatings and chemical deposition methods are good examples to underline the importance of surface chemistry modification to achieve enhanced hydrophobic properties. Several hydrophobic coatings reported are frequently based on silanes agents. Silane coupling agents are silicon chemicals whose molecules contain functional groups that form stable covalent bond with both organic and inorganic materials. Alkylsilanes and fluorinated alkylsilanes are very common hydrophobic silanes coating used to induce surface hydrophobicity. These hydrophobic coatings have been used for the creation of functional surfaces by combining hydrophobic coatings with micro- and nano-roughness fabricated with several production methods. For example, photolithography was employed by Öner and McCarthy to create patterns on silicon wafers, followed by a silanization of organosilane reagents by chemical vapor deposition [116]. The principal attribute of the silane coating in order to generate a hydrophobic surface is its non-polar nature. Hydrophilic surfaces usually are polar with a distribution of hydrogen bonding sites. An effective hydrophobic coating must remove or moderate hydrogen bonding acting as a shield for polar surfaces, avoiding the interaction with water by creating a non-polar interphase [117].

For the case of ZnO coating in nanotubes demonstrated by Huang et al. , the wettability behavior of the structured surface can be changed between hydrophobic and hydrophilic by UV illumination. UV irradiation only transform the chemical states of the surface generating electron-hole pairs in the ZnO film. Some of the holes can react with lattice oxygen, leading to the formation of surface oxygen vacancies; while some of the electrons react with lattice Zn^{2+} to form Zn^{s+} , surface trapped electron sites. Zn^{s+} tends to react with oxygen molecules adsorbed on the surface. Water molecules may direct into the oxygen vacancy sites, which leads to adsorption of the water molecules on the

surface.

Additionally to the artificial coatings used on patterning surfaces as a post-process in order to modify the chemical composition of the material for the creation of hydrophobic surfaces, natural transition between wetting state over the time due to the natural ageing process has also been reported by several researchers. It has been shown that after laser-based micro- and nano-patterning, some structured surfaces will be completely hydrophilic immediately after the process and will undergo a change in their chemical composition after some time in air conditions storage due to an ageing effect, which eventually can lead to a transition between hydrophilic and hydrophobic even reaching in some cases a super-hydrophobic behavior [88, 118, 119]. The transition time between hydrophilic and hydrophobic states of patterned surfaces has been studied for several materials as well as different storage conditions. This aging process depends largely on fabrication process, subsequent storage conditions and the initial composition of the material itself. The role of chemistry modification of the composition of the surface, specifically, polar and non-polar molecules have been proved to play a very important role in the wettability of a surface, therefore, a great amount of materials and fabrication processes has been studied to analyze the chemical composition of hydrophobic surfaces.

For example, Long et al. studied the wettability conversion behavior of picosecond laser structured copper surfaces in different atmospheres. The surfaces were initially hydrophobic after the laser process, nevertheless, after storage in ambient air, an increase in the contact angles was recorded. Results shown that organic compounds in the air are a crucial factor for the change of wetting behavior, since an atmosphere rich in CO_2 or O_2 seems to inhibit the wetting transition. Moreover, the relative amount of C–C/C–H bonds may be the

indication of surface polarity, indicating a more nonpolar surface which tends to be hydrophobic [120]. Also for the case of aluminum, Long et al. found that the storage of laser-processed samples in CO_2 , O_2 and N_2 inhibit also the transition between hydrophilic to hydrophobic, on the other hand, the transition was accelerated when the storage atmosphere was rich in organic compounds, like ambient air. Again, two critical values may be used to characterize surface polarity, the atomic ration of carbon concentration, and the relative concentration on non-polar compounds C-C(H) [121].

The transition in wetting properties is attributed to several mechanisms, including partial de-oxidation of the metals and adsorption of molecules in the environment. In general, adsorption of organic compound in the fabricated structures shows beneficial results in the transition to a more hydrophobic surface. This is a very slow process, and it has been shown that for the case of storage in ambient air, the wetting state transition can happen within some hours after the process, or it can take up to several days or weeks to achieve a good and stable hydrophobic state [119, 77, 122, 123].

Nevertheless, recent studies have presented some methods to accelerate the wetting state transition process. For example, Jagdheesh et al. have reported the hastening of this transition in wettability by using vacuum storage conditions. Laser processed samples of stainless steel and titanium alloy were stored in a vacuum environment. After 1 hour or less, the samples were super-hydrophobic with an excellent roll-off effect on water droplets. The transition in wettability was attributed to the absorption of carbon molecules found in the vacuum and produced by the vacuum pump [125]. Yan et al. also reported the change of the wetting behavior of Fe_2O_3 using vacuum ambient to accelerate the transition between wetting states [124]. The transition in the wetting properties observed were also attributed to the

Figure 2.16: Photo-responsive wettability transitions under the alternation of UV irradiation and dark storage for water droplets. Source: Yan et al. [124]

chemisorption of organic molecules produced by the vacuum pump. Additionally, the samples of Fe_2O_3 exhibited also a reversibly wettability that can be switched by the alternation of UV (254 nm) irradiation and dark storage as depicted in Fig. 2.16. After exposure to UV light for 3 to 4 h, the contact angle was found to be about 0° , afterwards, the hydrophilic surface was kept in dark storage for 7 days and its wettability recovered was recovered.

It is important then to have in mind the importance of the concept of surface energy together with the surface structure. By considering the array of atoms in the lattice of the material, when structures are formed, generally, atomic bonds are destroyed and material is removed or modified. By breaking the bonds between atoms new bonds can be formed. Atoms form bonds because it allows them to exist at a lower-energy state, so it takes energy in order to break these bonds and create a surface. This energy required to break the bonds is known as surface energy. By assuming the shape of a sphere, a water droplet can minimize its surface energy from a balance between minimizing energy through interfacial interactions and geometrical configuration

given by the Wenzel and Cassie-Baxter models.

2.5 Applications of modified wettability for functional surfaces

As it has been discussed in the previous sections, lotus leaves displays a self-cleaning property that allows the leaves to remove contaminant particles from the surface as the droplets roll-off the surface due to the super-hydrophobic effect. The super-hydrophobic effect is a result of a combination of a hierarchical structured surface and low free energy surface of the leaf. This super-hydrophobic property has been re-created in artificial surfaces fabricated with different techniques for different applications, some of them are presented in this section.

2.5.1 Modified wettability on textiles

A famous application of modified wettability has been seen in the textiles industry since the 1940's [126]. Nevertheless, recent research has deepen the understanding of the phenomena behind hydrophobicity, and new advanced manufactures techniques are bringing new functionalities to the textiles. A general approach to produce self-cleaning textiles is to apply hydrophobic coatings to modify the textile fibers and make them super-hydrophobic (or water repellent). The sol-gel process is an efficient method to provide multi-functional properties to the coated textiles. [127]

Several material are used for the production of the hydrophobic coating, such as: silicone coating by dipping conventional polyester and microfiber polyester textiles in a toluene solution of 4 wt% methyl-silicone and dried at 100 °C for 1 h [128]; addition of silica micro/nanoparticles (dual structures) to the interlaced fiber network of

hydrophilic cotton modified with hydrophobic polydimethylsiloxane (PDMS) to achieve a super-hydrophobic effect was demonstrated as show in Fig. 2.17. [129]; commercial fluoroalkyl water-born siloxane (FAS), silver nanoparticles and a reactive organic-inorganic binder in a sol-gel process for the preparation of multifunctional, water and oil repellent and antimicrobial finishes for cotton fabrics has been also demonstrated, this effect was attributed to the intrinsic antibacterial effect of silver nanoparticles and the low surface energy of the oleophobic finished cotton caused by FAS.

Figure 2.17: SEM images for particle-covered cotton textiles and the images of static water droplets placed on top. Source: Hoefnagels et al. [129].

Still, challenges exist for the self-cleaning fabrics. The water repellent textiles are expected to maintain their original external appearance after the surface treatments. They should exhibit appropriate softness and the hydrophobic coatings can present good durability for washing, sunlight, and high or low temperature exposure. Considering mass production in the textile industry, the procedure of cost-effective, eco-friendly will be appreciated.

2.5.2 Enhanced Corrosion Resistance

Among the several applications for hydrophobic surfaces and hydrophobic coatings, improved corrosion resistance of the materials is one of utter importance. The corrosion of a metal is a very common phenomena that consist in the deterioration of the surface of a material due to chemical reaction especially when the material is in contact with an aggressive media. The corrosion of a surface consist in the oxidation of the material and it can lead to a malfunction or a shorter life-time of the piece leading to the destruction of the material. Therefore, the study of anti-corrosive surfaces on several metals have been reported due to the importance of reducing the corrosion phenomena which can causes significant damage on the metals.

Figure 2.18: SEM images of pitting corrosion on superhydrophobic Al surfaces.

Source: DeLara et al. [130]

A well-established characterization technique for corrosion behavior are electroanalytical methods, in which a component or sample is analyzed by measuring the potential (volts) and the current density (amperes) in a electrochemical cell that contains the sample together

with other components in an aggressive aqueous medium. Among the different methods, voltammetry is a method in which information of the sample is obtained by measuring the current as the potential is varied. The corrosion behavior of a material is then characterized by a set parameters that describe the corrosion resistance of the samples tested. By using this method, DeLara et al. demonstrated the improvement of the corrosion resistance in super-hydrophobic aluminum sheets processed with direct laser writing [130]. The samples suffered pitting corrosion (Fig. 2.18) but showed an improvement in comparison with a unprocessed reference sample.

Mogoda et al. investigated the corrosion behavior of Ti-6Al-4V alloy in concentrated sulphuric and hydrochloric acid solutions, finding that corrosion resistance decreases with time indicating the dissolution of the oxide film in the surface of the alloy and exhibiting the metallic alloy surface [131]. It was reported that the corrosion of titanium alloys in sulphuric acid solutions is because of the dissolution of the material as Ti^{3+} , which in the contact with the oxygen oxidizes into Ti^{4+} . As the concentration of Ti^{4+} grows the corrosion rate increases up to a critical concentration at which the film of TiO_2 is formed protecting the material as the surface passivates [132]. Passivation is extremely useful in mitigating corrosion damage, however even a high-quality alloy will corrode if a breakdown occurs in the passive film due to chemical or mechanical factors which could lead to pitting corrosion.

The corrosion resistance of a material is then very important, therefore several researchers have proposed different method for enhance corrosion resistance. Among those methods, the use of different kind of hydrophobic coatings or micro-structured hydrophobic surfaces have proven their efficacy to improve the corrosion resistance of several materials [133, 134, 135, 136]. Given their strong water repulsion proper-

ties, super-hydrophobic coatings are ideal for slowing the breakdown of the metal oxide layer of metal substrates, and thus preventing corrosion of the metal layer underneath.

Some examples of super-hydrophobic surfaces for enhanced corrosion resistance are presented below. For instance, copper cluster have been used for the production of super-hydrophobic surfaces by submerging polished copper surfaces into a n-tetradecanoic acid ethanol solution, the surface undergo a chemical reaction reaching the super-hydrophobic state, additionally it was shown that the super-hydrophobic surface can remain intact in seawater for over a month. Similarly, it has been stated that self-assembled monolayers, such as alkyl silanes and thiols, could be employed as corrosion protective coatings due their thin closely packed barrier films on the substrates. Additionally, is has been reported that electrochemical depositing of hydrophobic coatings on zinc electrodes which can be used to fabricate hydrophobic surfaces with an improved anti-corrosion behavior where 1 μm of the hydrophobic film can be used for the prevention of corrosion of mild steel.

2.5.3 Anti-icing

Ice accretion is the phenomena of the growth of an ice film in the external surfaces, an is a very important topic for the aeronautical industry, due to the formation of ice films in aircrafts rotorcrafts, which are exposed to super-cooled droplets of liquid water that impact in the surface and freeze after a very short period of time [137, 138]. There are different concepts for the characterization of surface icephobicity. One of them is the shear stress, i.e. the strength required to remove the ice from the test surface, which researchers use as a base to call “icephobic” surfaces those surfaces with shear strengths lower than

500 kPa [139] and as low as 15.6 kPa [140]. Another parameter for the characterization of icephobicity is the prevention of ice formation on surfaces. This depends on the ambient conditions and if whether a droplet of super-cooled water freezes at the interface with the surface and it can be characterized by time delay of heterogeneous ice nucleation [141, 142]. Furthermore, impact tests for bouncing-off of the droplets [143] has also been suggested implying that icephobic surfaces repel incoming small droplets at the temperatures below the freezing point [144]. With this concepts, a general view for the requirements needed for icephobicity can be observed. An icephobic surface then should prevent the accumulation of liquid water as well as the freezing of incoming water droplets, and in case ice is formed, the adhesion strength should be very low in order to remove the accreted ice in an easy way.

To face the challenges of surface icing, active methodologies have been deployed to remove accumulated ice through various mechanical and electrical methods, also surface treatment of substrates with de-icing fluids such as glycerol and ethylene glycol are also common. Nevertheless, the energy and time consumption plus the need for periodic treatment make “active” methods a non-ideal option and a “passive” approach through other coatings or surface engineering arise as an option.

Among these passive methods, super-hydrophobic surfaces have been observed to enhance the bouncing of incoming droplets that impact the surface, which could help to reduce the accretion of ice. Surfaces that help to reduce this adhesion of ice are known as ice-phobic surfaces and several researchers are investigated the feasibility of applying hydrophobic surfaces for the creation of ice-phobic surfaces. Surface modification is a promising strategy for producing icephobic surfaces with reduced ice accretion [145, 146, 147].

Figure 2.19: Difference of the freezing times for a droplet deposited on top of a un-coated hydrophilic surface (top row) and on a super-hydrophobic coated surface. Source: Wang et al. [148]

As it has been discussed, two regimes of wetting are accepted to happen on a patterned surface, i.e. the Wenzel and the Cassie-Baxter states. When a droplet is placed on a surface the effective contact area between the liquid and solid is reduced in the Cassie-Baxter state, and the air pockets prevent the wetting of deeper surface area. If the droplet were to be frozen, the reduced fraction of contact area give place to a reduction of the adhesion strength of the ice to the surface. Wang et al. has investigated the icing behavior of droplets on hydrophobic surfaces made by nano-fluorocarbon coating [148]. In their study, they find that the coated surface, which exhibited a higher contact angle than an un-coated substrate, need longer times exposure to low temperatures in order to fully freeze in comparison with the un-coated sample. Fig. 2.19 show an example of the different droplets frozen on the two substrates. These results show that the coated surface can be beneficial in delaying the starting icing time which leads to a longer time in the freezing process.

2.5.4 Anti-fouling

Fouling refers to the accumulation of unwanted material on solid surfaces and can lead to malfunction or damage of the component. Fouling is usually distinguished from other surface-growth phenomena in a sense that it happens only on the surface of a component or system performing a function, and that the fouling process impedes or interferes with this function. The fouling of materials can consist of either living organisms known as biofouling; or of non-living substance (inorganic and/or organic). In the case of biofouling, it make reference to the undesirable adherence of microorganisms, plants, algae, and animals to surfaces submerged in water, e.g. ships and underwater structures. For this reason, anti-biofouling on the hulls of ships and other marine-based architectures is a significant topic of practical interest. Traditional anti-biofouling coatings contain poisons that kill the adhered marine organisms. However, the poisons are now recognized to be dangerous to the marine environment and are increasingly posing risks to human health, making necessary to find a safer way of enhance the antifouling behavior of surfaces.

The fouling behavior of a smooth polysiloxane film was compared with a super-hydrophobic film roughened with embedded silica nanoparticles. Compared to normal substrates which exhibit fouling within a day, almost no microorganisms attach to the superhydrophobic surfaces in the first weeks of immersion [149]. Super-hydrophobic coatings revealed that the effect of nano-scale roughness is critical for the microorganism to not attach to the super-hydrophobic surfaces, as it was seen in the first weeks of the fouling tests. Nevertheless, after a long exposure to real marine environment, the anti-fouling property of the super-hydrophobic coatings will become gradually deteriorated. This is due to the absence of stability in the complicated real sea environment which still needs further development.

Additionally, nano-engineered super-hydrophobic surfaces fabricated by sol-gel process have been shown to demonstrate potential as a non-toxic antifouling alternative [150]. Integrating hydrophobic materials in the nano-scale, super-hydrophobic surfaces with high water contact angles ($>150^\circ$) and low hysteresis ($<10^\circ$) were fabricated. Three super-hydrophobic coatings differing in their chemical composition and architecture were tested against major fouling species. The study report the effect of air-infiltration on the zone of attachment of fouling organisms and it show promising results in the use of super-hydrophobic surfaces for antifouling applications. Nevertheless, a greater understanding of how nano- and micro- air-incursions interfere with settlement processes and the adhesive mechanisms of fouling organisms is still required.

As a final example, it has been reported a simple, one-step and environment-friendly process for the creation of a super-hydrophobic surface on magnesium alloy by a simple immersion process with a solution containing ferric chloride, deionized water, tetradecanoic acid and ethanol [151]. The coating exhibits micro-rough structure and a high contact angle ($>160^\circ$). The super-hydrophobic AZ31 magnesium alloy presents appropriate corrosion protection and antifouling properties with good ability to resist bacteria.

2.5.5 Anti-bacterial

Several super-hydrophobic surfaces have been proven to show beneficial results as anti-bacterial surfaces. Among them, it has been shown that antibacterial properties could be obtained not only by the application of an antibacterial active agent but also by applying oleophobic fluoroalkylalkoxysilane (FAS) finishes to the textiles [152]. It

seems that the presence of FAS, which is a coating with oil-repellent properties, prevents or at least hinders the adhesion of bacteria and their consequent growth and the formation of a biofilm on the finished fabrics. Other example of antibacterial on textiles has been demonstrated on cotton fibers fabricated with enhanced water and oil repelling behavior as well as anti-bacterial properties. The cotton fibers were also modified using a commercially available fluoroalkyl-functional water-borne siloxane with nano-size silver particles and a reactive organic-inorganic binder. The prepared fabrics have a long-lasting low surface energy, owing to the excellent adherence of the finishes to cotton fabrics and to the specific structure of the coatings

2.5.6 Drag reduction

Another application that has been showing potential results for super-hydrophobic surfaces is drag friction reduction in fluids due to the effect of air pocket in the Cassie-Baxter state, which helps to form an air layer between the solid and the fluid. The term drag defines a force that oppose to the movement of an object moving in a fluid. In fluid dynamics, when considering the movement of a fluid, two categories of flow are defined: laminar and turbulent flow. Laminar flow describes a flow composed of parallel continuous layers in which there are not changes of flow direction or swirls of fluids. Turbulent flow on the other hand, describes a fluid flow characterized by changes of pressure, flow direction and flow velocity. Reynolds number is a dimensionless quantity used to predict the behavior of how fast a fluid moves in relation with how viscous the fluid is, and it used to describe the behavior of drag phenomena.

Several amount of researchers have studied the feasibility of using super-hydrophobic surfaces for drag reduction applications. Moaven et al. [153] investigated the effects of super-hydrophobic nano-coating on

frictional drag force. In their study, a TiO_2 super-hydrophobic nano-coating was made by means of the sol-gel method on aluminum which recorded a contact angle of about 160° . The drag reduction values were 30% and 15% in laminar and turbulent flow. The results of the study shown promising results in application concerning fuel consumption reduction, reduction of CO_2 emission and speed increase in fluids. On another study, Du et al. performed a series of experiments to investigate the preservation of the air layer and its effect on drag reduction on hydrophobic surfaces with random micro-structures. The small thickness air layer was able to cover a large area on the surface proven to be beneficial to the formation of the slip effect and drag reduction effect. When air layer was removed, the vortical strength and drag would increase, which meant the drag reduction cannot be obtained without the air-water interface on structured super-hydrophobic surfaces [153]. Furthermore, Lyu et al. developed durable dual-scale structures for the creation of super-hydrophilic and super-hydrophobic surfaces on pure (99.5%) industrial aluminum sheets. Drag reduction was measured and compared on a super-hydrophobic, smooth and super-hydrophilic surfaces. Results showed that a considerable drag reduction was observed for the super-hydrophobic surface [154].

2.5.7 Optical applications

Additionally to the mechanical, chemical and biological applications, super-hydrophobic surfaces also have been used in several optical application for different functions. Optical transparency or anti-reflective properties are requirements for many optical devices and materials. The key for fabricating transparent or anti-reflective super-hydrophobic surface is to optimize the surface roughness, since surface roughness usually enhances light scattering and reduces transparency. Generally, for optical transparent surfaces, the roughness dimension should be lower than the wavelength of target light (380 nm up to 760 nm

for visible light), and is usually in the range of nanometer scale. For the vast majority of transparent and anti-reflective materials, the enhance or addition of properties like water repellency or self-cleaning effect can be very helpful and sometimes needed, for this reason making super-hydrophobic surfaces with good optical properties is a very interesting and promising topic of research and several positive results have been obtained.

Figure 2.20: Photograph of transparent surface with super-hydrophobic properties.
Source. Xiu et al. [71].

For instance, layer-by-layer method to fabricate transparent super-hydrophobic films was demonstrated by [155] using SiO_2 nanoparticles of various sizes to introduce into the multilayer thin film to adjust surface roughness. Due to the low refractive index of the resultant porous films, the obtained transparent superhydrophobic film is also antireflective. Also the fabrication of durable super-hydrophobic and antireflective surfaces was demonstrated by sol-gel processing using silica nanoparticles [156]. The processed surfaces showed excellent water repellency (contact angle $>160^\circ$) and a stable self-cleaning effect over 2000 hours of outdoor exposure. Additionally, the final super-

hydrophobic surface exhibits a fair antireflection effect with more than 3% increase in optical transmittance. Other example of optical applications for super-hydrophobic, was demonstrated by a new approach to create super-hydrophobic polymer coatings involving the formation of micro-porous layers through a simple polymerization in the presence of porogens. The method is applicable to a variety of substrates and is not limited to small areas or flat surfaces. The polymerized material can be ground into a super-hydrophobic powder, which, once applied to a surface, renders it super-hydrophobic. The morphology of the porous polymer structure can be controlled by composition of the polymerization mixture. Controlling the morphology allows to reduce the size of the porous structure from micro- to nano-scale, giving place to a transparent material with super-hydrophobic properties.

Chapter 3

Material and methods

In this chapter the laser surface processing techniques as well as the surface characterization techniques used in this study are presented in this chapter. The laser work stations and the methodology of the different laser processes used for the fabrication of micro- and nano-structured functional surfaces are described. In addition, the different techniques used for the surface characterization and analysis after the laser processing of the surface are listed together with a small description of the basic principles behind each characterization technique. The characterization techniques employed were chosen due to their capabilities for investigate the change in topography, chemistry and wettability of the surface.

In this study, two different laser surface processing were used: Direct laser writing (DLW) and direct laser interference patterning (DLIP). This techniques allow the creation of periodic micro-features for the case of DWL, and micro- and nano-features for the case of DLIP. Additionally, has it has been mentioned in the previous sections, the duration of the laser pulse affects in great manner the final shape of the induced structures and patterns. Three different pulse duration were used for the creation of micro- and nano-structures. Finally, the combination of both laser techniques (DLW and DLIP) was performed in order to generate hierarchical roughness for functional surfaces.

Several characterization techniques were used for the analysis of the laser-induced roughness on the Ti-6Al-4V samples to investigate the change in topography, chemistry and wettability of the surface. Scanning electron microscopy (SEM) and confocal microscopy (CM) was used for the analysis of the surface roughness before and after the laser processing of the surface. X-ray photo spectroscopy (XPS) was performed on the processed samples to investigate the change in chemical composition of the surface. Finally, static contact angle (SCA) was measured to observe the wettability behavior of the processed surfaces.

3.1 Titanium alloy, Ti-6Al-4V

Titanium was discovered in 1791 and it is the ninth most abundant element in the Earth, with an average concentration of 0.8% by weight, although its existence in concentrations that allow an economically viable extraction is not very common, except as rutile (TiO_2) and ilmenite ($\text{FeO} \cdot \text{TiO}_2$). Titanium is a transition element, such as iron, nickel or cobalt, whose electronic structure has an incomplete layer. This electronic structure allows titanium to form solid solutions with many elements, with an atomic size factor of up to 20%. From the beginning, it has been classified as light metal, although its density of 4.51 g cm^{-3} is almost twice the density of aluminum, due to its excellent mechanical strength/density ratio. Even though it was tried to obtain this metal in pure form for a long time, this was not achieved until 1910, by reducing the compound TiCl_4 with sodium, although the quantities obtained were very small. In 1937, Kroll developed a process for obtaining titanium consisting in the reduction of the titanium tetrachloride compound with magnesium in an argon atmosphere to avoid oxidation. This was the first process that allowed obtaining appreciable amounts of pure titanium, and is the method currently

used [157]. In the sixties its use was extended to other applications, such as the chemical industry, due to its excellent resistance to corrosion [158]. This resistance is caused by a passivation layer formed by titanium oxides, which spontaneously form on the titanium surface upon contact with the atmosphere. Other studied applications of titanium and its alloys are the structural applications in saline environments, for its resistance to corrosion [158, 159] and in the field of biomaterials [160], thanks to its excellent biocompatibility.

Ti-6Al-4V is the most common titanium alloy and its formulation varies slightly according to the standard or the chosen manufacturer. The alloy contains aluminum and vanadium, depending on the composition. Aluminum increases the temperature of the transformation between the alpha and beta phases while Vanadium decreases that temperature. Table 3.1 presents a comparison of the margins for the composition of Ti-6Al-4V by different regulations. The higher the content of oxygen, nitrogen, aluminum or vanadium, the greater the resistance, and vice versa, the lower its content, the greater the fracture toughness, the ductility, the corrosion resistance induced by tension and crack propagation speed.

Table 3.1: Composition of Ti-6Al-4V by different regulations.

	Composition [wt%]							
	Al	V	Fe	C	O	N	H	Ti
UNE-7301	5,5–6,5	3,5–4,5	0,25	0,08	0,13	0,05	0,012	Bal.
ISO 5832-3	5,5–6,75	3,5–4,5	0,30	0,08	0,20	0,05	0,015	
ASTM F136	5,5–6,5	3,5–4,5	0,25	0,08	0,13	0,05	0,012	

Titanium alloys are characterized by their excellent mechanical properties, high resistance to corrosion, low specific density, high melting point and other. Among these alloys, the alloy Ti-6Al-4V is special since it combines an excellent mechanical resistance with a great ca-

capacity of conformed, product of its biphasic microstructure constituted by the phases α and β , where the phase alpha offers little plasticity and tends to exhibit mechanical and anisotropic physical properties, while the phase beta exhibits good conformability due to its high ductility. The high strength, low weight ratio and outstanding corrosion resistance inherent to titanium and its alloys has led to a wide and diversified range of successful applications which demand high levels of reliable performance in surgery and medicine as well as in aerospace, automotive, chemical plant, power generation, oil and gas extraction, sports, and other major industries.

Titanium is a material used in many fields of industry, such as aerospace, naval, automotive and biomedical. Within the automotive field is used in the construction of parts for cars is highly competitive as springs, shock absorbers, connecting rods, among others, due to the lightness of titanium compared to other materials such as steel; this allows having a lower total weight of the car. In the same way in the biomedical industry, it is mainly used for the construction of joint prostheses (elbows, knees, hips) due to its compatibility with human tissue, as no rejection of the immune system towards the material is generated.

Although titanium is a material widely used and desired in many fields of industry, it has a great problem and is its low resistance to wear, which results in a shorter life compared to other materials. In addition, naturally produced oxide films have a low mechanical strength, reducing some of their uses; for example, in the use of bolts and nuts. This is why it is essential to look for ways and treatments to improve these properties; one of them, is the thermal oxidation, that allows to increase the thickness of the oxide films and thus increase the hardness, the wear resistance and the resistance to corrosion in the material.

The Ti-6Al-4V alloy was chosen in for this study because of it use in automotive and aerospace industries. The material was supplied by the partner Airbus Defence and Space GmbH, in the form of rectangular samples of 75x75x2.5 mm.

3.2 Fabrication methods

3.2.1 UV-nanosecond laser work station

In this study, the main technique for the surface patterning is direct laser writing using a solid-state nanosecond laser with a wavelength in the UV region of the electromagnetic spectrum for the creation of periodic square-shaped micro-pillars for surface patterning. Due to the nature of nanosecond laser pulses, very heavy thermal effect are observed when using UV-ns direct laser writing for micro-processing of metal surfaces. Because of this thermal effects, the nanosecond laser processing is mainly an ablation process, in which material is removed from the bulk due to the high local temperatures reached on the zone where the laser beam impacts the surface. The nanosecond DLW process starts with absorption of the irradiated laser train of pulses, this leads to an increase in temperature in the irradiated area followed by melting and vaporization of the material. Depending on the fluence, the vaporized cloud or plasma applies a pressure, ejecting the melted material upward and outwards for one pulse or sideways in the case of laser scanning, splashing melted material along the direction of the laser scanning. This melted material tends to re-solidify at the periphery of the crater or scanning channels.

For this study, the micro-patterns were fabricated inspired on the methodology reported by Jagdheesh et al. for the creation of squared-

shaped micro-pillars with UV-ns direct laser writing for the creation of functional surfaces with enhanced wettability and corrosion resistance [77, 130] in metals. For this work aerospace-grade titanium alloy (Ti-6Al-4V) sheets (2 mm thickness) were used as target samples.

The UV-ns laser used in this work was a solid-state Q-switched pulsed laser that generate pulses with a fixed duration of 30 ns at a repetition rate of 100 kHz and a wavelength in the ultra-violet (UV) range with 355 nm. The laser pulses present a Gaussian distribution of intensity. The laser work system has a beam delivery system that consists of an internal array of optical elements to focus the beam on the sample with an apparent spot size of 15 μm . Additionally, the work station (Fig 3.1.) is equipped with a translational table for the control of the position of the sample with a resolution of 0.1 μm . The system is controlled in an automatized manner by using a computer software developed by the fabricant.

Figure 3.1: Nanosecond laser micro-machining work station in CLUPM.

The laser process employed consist on the fabrication of micro-

channels on one scanning direction or the Cartesian axis as shown in Fig 3.2. and then a second laser scanning in the remaining direction, thus consisting on two complete scanning over the desired area to be processed. The scanning process was performed by moving the sample at a speed of 80 ± 0.025 mm/s while the laser beam remain fixed in position, thus is the sample the one doing the scanning movement. The scanning is doing as indicated in Fig. 3.2. The distance between adjacent scanning lines is typically referred as hatch distance (H.D.), and it can be varied as desired with a minimum value defined by the spot beam in such a manner that the thermal effect after each individual scanning lines do not affect the previously processed zones. In the case of the UV nanosecond laser employed in this work, the minimum hatch distance is $15\text{ }\mu\text{m}$. As it has been reported by Jagdeesh et al., hatch distances higher than $30\text{ }\mu\text{m}$ start to show a decrease in the hydrophobicity due to the high amount of area that is left unprocessed [77].

Figure 3.2: Laser scanning diagram for cross-like structures with nanosecond direct laser writing.

Additionally, the accumulated fluence due to the high pulse repe-

Table 3.2: Laser processing parameters for the fabrication of micro-cells on Ti-6Al-4V via DLW technique.

Avg. Laser Power (mW)	100 - 280
Repetition Rate (kHz)	20
Scan Speed (mm/s)	10
Hatch Distance (H.D.) (μm)	30 - 50
Beam spot size	15

tition rate of the laser affects the heat transfer in the surface of the metal alloy. By varying the repetition rate, the effect of the pulses numbers in a same spot can be observed when using the same pulse power for different repetition rates. By varying this two parameters (pulse power and repetition rate) it is possible to observe their influence in the accumulated fluence during the laser processing. High power pulses at low repetition rate will cause deep damage to the surface but will leave unprocessed areas as scanning the processed area due to the low number of pulses per spot, while low power pulses at high repetition rates can give more uniform ablation channels due to the high amount of pulses per spot, which give place to a higher and more stable accumulated fluence during the process. In this work the repetition rate was keep fixed at a value of 100 kHz. Table 3.2 show a complete list of the processing parameters used.

A laser pulse is composed of a large number of photons confined in a small region of space. The energy of the pulse then depends on the amount of photons it contains and has as unit the Joule [J]. The amount of energy that the pulse contains is the energy it manages to accumulate before the pulse is emitted according to the repetition rate frequency of a pulsed laser, so the energy per pulse is then related to the average power, P_{avg} and the repetition rate frequency, f_{rep} by the following expression:

$$E_{pp} = P_{avg.}/f_{rep} \quad (3.1)$$

The peak power of the laser pulse is defined as the amount of energy contained in the pulse between the duration of the pulse, τ , whose unit of measurement is the Watt [J/s]:

$$P = E_{pp}/\tau \quad (3.2)$$

Furthermore, an often used term in laser processing is the fluence. Fluence is defined as the irradiated energy per pulse per unit area of the material (J/cm²) :

$$\phi_0 = E_{pp}/A_p \quad (3.3)$$

where A_p is the area of the beam spot. The energy fluence thus determines the amount of laser energy that is delivered into the target using a single pulse.

In laser material processing, laser ablation is defined as the removal of the material from a target sample due to absorption of laser energy. Ablation is noticeable only above a certain value of fluence (depending on the material and the pulse duration), thus the materials exhibit a characteristic limit or threshold at which the energy deposited by a single pulse can ablate the material, known as ablation threshold. The corresponding value of fluence for this limit is known as the threshold fluence (ϕ_{th}), meaning that a certain energy density value must be exceeded before the ablation process take place.

When several laser pulses are deposit in the same area of a material (as if often the case in material processing) the fluence can be consider as an accumulative parameter. This effect, known as incubation, has been investigated in metals for pulse durations varying between nanoseconds and femtoseconds. The integrated fluence, ϕ , refers to the cumulative total fluence after a train of laser pulses irradiated over the same area in a target sample. This total fluence, or integrated fluence, depends on the number of pulses that hit the target, N , as well as on the individual fluence in each pulse :

$$\phi = N\phi_0 \quad (3.4)$$

where the number of pulses depends on the repetition rate frequency and the exposure time of the sample to the laser radiation, t_{exp} :

$$N = f_{rep}t_{exp} \quad (3.5)$$

3.2.2 IR-femtosecond laser work station

Using the direct laser writing technique with a infra-red (IR) femtosecond pulsed laser, the generation of laser-induced periodic surface structures (LIPSS) was performed on the Ti-6Al-4V samples as a second process on samples processed earlier with UV-ns DLW, for the creation of hierarchical structures. This process was performed with the help and collaboration of the University of Birmingham (UoB) who give access to the laser work station with the IR-fs laser source. This method was performed for the creation of hierarchical structures for

enhanced wettability on functional surfaces inspired in the hydrophobic hierarchical structures found in nature. Specifically, the objective was to apply a second laser process to the square-shaped micro-pillars generated with UV-ns DLW in order to modify at nano-scale the remaining unprocessed area found on the top of the micro-pillars inside the micro-cells. IR-fs LIPSS generated with direct laser writing have proven positive results in the creation of hydrophobic surfaces, demonstrating the feasibility of this sub-micron structures for the creation of functional surfaces. Because of the ultra-short duration of the laser pulses, thermal effects are not present when working with fs pulses, for this reason, the previous UV-ns DLW structures are expected to remain still after the second laser processing, giving place to a surface with micro- and nano-features in the surface roughness.

Therefore, IR-fs LIPSS were formed on top of the UV-ns micro-pillars using a femtosecond pulsed laser source with an average power of 5W and linear polarization, which emit pulses with a duration of 310 fs and a central wavelength in the near-infrared domain of 1032nm, the repetition rate can be tuned to a chosen value by means of an external modulator (MOD) that is controlled by the software of the system. The system allows to select a repetition rate (f) from a maximum of 500 kHz and down to any value of f/N (N being an integer). The laser system uses a galvo-scanner with a 3D scan head and a 100-mm focal length telecentric lens to deflect the laser beam at normal incidence to the sample. The laser beam had a Gaussian profile and a spot diameter of approximately $35\ \mu\text{m}$ at focus. Laser processing was performed in atmospheric conditions and cleaned by compressed air. The process parameters used for the fabrication of the IR-fs LIPSS are shown in Table 3.3.

The laser processing for the creation of IR-fs LIPSS generated with direct laser writing is very similar to the UV-ns DLW process described

Table 3.3: Laser processing parameters for the fabrication of IR-fs LIPSS on Ti-6Al-4V via DLW.

Pulse Energy (μJ)	1.1
Repetition Rate (kHz)	100
Scan Speed (mm/s)	500
Hatch Distance (H.D.) (μm)	5
Beam spot size (μm)	15

before with some differences. The main difference between these laser processes falls on the pulse duration and the different thermal effects observed on those pulse duration regimes. IR-fs DLW does not present melted material on the periphery of the laser scanning in the surface, whoever, inside the projection of the laser beam in the surface, modification of the roughness due to ablation still occur. The volume of material that is ablated due to the laser process can be controlled depending on the accumulated and per pulse fluence. This can translate to a dependency of the ablation volume to the repetition rate and the pulse average power. Because of this, an optimization of those parameters is needed for the creation of LIPSS on the Ti-6Al-4V surface.

The optimization process consisted in finding a balance between the pulse power, the repetition rate and the scanning speed. This optimization process have been reported previously by Romano et al. for the creation of LIPSS on stainless steel [161, 162]. The desired area is processed by scanning lines in a one of the two Cartesian directions (x or y) in a bidirectional way along the selected axis as indicated in Fig. 3.3.

The scanning speed, v , can be varied from 100 mm/s to 1500 mm/s with repetition rates, f , tunable in a range from 50 kHz to 500 kHz. The spot diameter $2\omega_0$ is 30 μm . The distance between the lines

Figure 3.3: Beam delivery system of the fs laser system from the UoB, and scanning strategy of the laser patterning. Source: Romano, 2018 [161]

known as hatch distance can be varied with a resolution of $1 \mu\text{m}$, and the distance between two consecutive spot centres are given by:

$$d = \frac{v}{f} \quad (3.6)$$

The effective number of pulses per spot can also be calculated using $2\omega_0/d$, while the effective number of pulses per unit area, N , is:

$$N = \frac{\pi\omega_0}{dh} \quad (3.7)$$

The overlap between two consecutive pulses can be calculated in an approximated way using the geometrical equation:

$$OL = \frac{1}{\pi\omega_0} \left(2\omega_0 \cos^{-1} \left(\frac{d}{2\omega_0} \right) - d \sqrt{1 - \left(\frac{d}{2\omega_0} \right)^2} \right) \quad (3.8)$$

The average power P and the repetition rate f , can be varied, and the fluence can be calculated using:

$$\phi_0 = \frac{P}{2\omega_0^2 f} \quad (3.9)$$

The effective accumulated fluence per unit area, ϕ , can then be calculated approximately as follows:

$$\phi = N\phi_0 = \frac{P}{f dh} \quad (3.10)$$

3.2.3 IR-picosecond laser work station

In recent years, direct laser interference patterning (DLIP) has proven to be a successful technique for texturing materials down to the micro- and nano-scale with high quality at high processing speeds. The DLIP technique makes use of the interference patterns that are created when overlapping two or more coherent laser beams. The interference patterns create a periodic variation of the energy intensity distribution that is deposited in the surface of the target material. The DLIP technique can give place to different geometries due to the different interference patterns that are obtained when overlapping different number of coherent beams, thus allowing the creation of periodic surface patterns with controllable pitch and geometry.

This variation of energy intensity can be observed in the periodic modification of the surface roughness observed after the laser processing due to either photo-thermal or photo-chemical processes, depending on the material used, the laser wavelength and the pulse duration of the laser system. Additionally, the spatial period of the interference intensity distribution can be controlled by changing the angle between the beams. For the DLIP process, the laser work station system is equipped with a DLIP optical head, in which the main beam is split in two sub-beams by using a diffractive optical element (DOE), the sub-beams are then parallelized by a prism and finally overlapped in the focus point by using a lens with a focal distance of 40 mm. The whole system is controlled in a fully automatized way by means of a computer. The spatial period can be varied by varying the angle of incidence of the sub-beams.

Figure 3.4: DLIP system used for the processing of the target surfaces. Source: Aguilar-Morales, 2018 [113]

Furthermore, the line-like pattern that is obtained when using a two-beam configuration can be used to produce other geometries by doing sequential laser process in the same surface area. By irradiating the target sample in a two-step process, pillar-like structures can be induced in the surface of the material. This process consists in first, irradiated the sample to induce line-like structures, after the first process is complete, the samples are rotated a certain angle, usually 90° , and then irradiated a second time in the same surface area. The final result are pillar-like structures that are formed during the second process while the interference maxima ablates parts of the previous line-like structures created during the first irradiation. Nevertheless, during the laser processing, the second irradiation tends to destroy, either partially or completely, the first pattern induced in the surface, for this reason, the second irradiation must be done using a lower pulse power to guarantee a well-defined pattern at the end of the process.

The scanning of the area to be processed is performed by moving the sample in the vertical and horizontal directions, as shown in Fig. 3.5. When doing the laser scanning, an overlap of the pulses in the vertical direction is obtained, and for a homogeneous patterning the typical values range from 90 to 99% of pulse overlap. The pulse overlap can be calculated from the following equation as a function of the beam diameter, ϕ , and the distance between pulses, p :

$$OL = \left(1 - \frac{p}{\phi}\right) \cdot 100 \quad (3.11)$$

In this study, with the help and collaboration of the “Fraunhofer Institute for material and beam technology” (IWS), the processing of Ti-6Al-4V sheets using the DLIP technique was performed using a two-beam configuration, which give place to a line-like interference pattern, in order to investigate the feasibility of combining two laser

Figure 3.5: Diagram of laser scanning strategy followed for the DLIP technique.

Source: Aguilar-Morales, 2018 [113]

techniques (DLW and DLIP) to create periodic hierarchical surface structures for the creation of functional surfaces with enhanced properties like wettability or corrosion resistance.

The structuring of Ti-6Al-4V samples was performed using a two-beam DLIP system station produced by IWS (DLIP- μ FAB, Fraunhofer IWS), which produces DLIP pixels (irradiated area per pulse) with line-line interference patterns in a diameter of $160 \mu\text{m}$, also known as interference area (ϕ). The picosecond DLIP work station is equipped with an infrared (IR) Q-switched solid-state (Nd:YVO₄) picosecond laser (Innoslab) that emits pulses with a duration of 10 ps, a DLIP optical head that divides the main beam in two sub-beams, and a three-axis positioning stage auto-system with a resolution of 2.5 micrometers. To produce the pillar-like patterns, the samples were

first processed to create the line-like pattern and after that were rotated 90° in the x-y plane and irradiated for a second time with a lower pulse power, using the parameter in Table 3.4. The laser experiments have been carried out in ambient environment with no subsequent treatment.

Table 3.4: Laser processing parameters for the fabrication of IR-ps DLIP structures on Ti-6Al-4V.

Avg. Pulse power (mW)	160
Fluence first irradiation (J/cm^2)	0.8
Fluence second irradiation (J/cm^2)	0.55
Repetition Rate (kHz)	1
Interference area diameter (μm)	160
Spatial period (μm)	2.6

As it has been discussed, the spatial period of the structures generated by the DLIP process can go down to the micrometer scales. Nevertheless, the real minimal achievable spatial period that can be achieved on the surface of metals is controlled by the thermal properties of the material and the nature of the pulse duration (e.g. short or ultra-short pulses). For the case of nanosecond pulses, the principal process of the surface modification is based on local ablation and/or Marangoni convection. For instance, if the spatial period of the interference pattern is in the same order as the thermal diffusion length (l_t) (1 to 2 μm in metals processed with 10 ns pulses, for example) a low thermal contrast will be observed, i.e., low temperature difference between maxima and minima intensity, which prevent the local treatment of the material, giving place to molten material over the complete treated area. For a certain material the thermal diffusion length can be only shortened by reducing the duration of the laser pulse. Bieda et al. (2010) [110] observed that the structure heights for short spatial periods ($< 2\text{--}3 \mu\text{m}$) are generally limited to a few

nanometers on several metallic surfaces. Consequently, if picosecond pulses are used (i.e. 10 ps instead of 10 ns), the material can be precisely heated at the interference maxima positions, thus reducing the amount of melted material, allowing the fabrication of patterns in the sub-micrometer range.

3.3 Characterization techniques

Several characterization techniques were employed in order to evaluate different properties of the processed samples like surface topography, surface wettability and surface chemistry composition.

3.3.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is one of the most resourceful techniques available for the characterization of surfaces at micro- or nano-scale as well as for chemical composition characterization. This microscopy technique allow to the most recently developed devices to obtain high quality images with excellent resolution of objects down to a size of 5 nm or less, while conventional optical microscope have an optical limit and can only see down to micro-scale.

In basic terms, the SEM working process begins with the generation of an electron beam irradiated as a column. This beam of electron start traveling downward in a vertical direction to the place where the sample will be placed. It is important to have high vacuum conditions to avoid collisions between electrons and atmospheric molecules, for this reason the whole system is inside of an ultra-vacuum chamber. The electron beam then passes through a series of electromagnetic lens whose focal length is controlled by varying the applied voltage

Figure 3.6: Example of an SEM micrograph obtained by secondary electrons.

and current, used to focus the electron beam on the targeted surface which is scanned with the help of scanning coils. When the electron beam impact the surface of the sample, the energetic electrons of the beam trigger a series of process on the atoms of the material, like elastic and inelastic collisions as well as scattering of the electrons, and several forms of radiation are emitted depending on the penetration achieved by the electron in the material, giving different information which is measured as electromagnetic signals.

SEM works by detecting the signals of the secondary electrons and/or backscattered electrons that are ejected from the sample. Secondary electrons are emitted from the atoms on the surface of the sample when inelastic collision between the electrons of the beam and the atoms of the sample take place. Backscattered electrons, on the

other hand, are electrons reflected back after elastic interactions between the beam and the sample, and can take place in deeper regions of the material. Backscattered electrons are high sensitivity to differences in atomic number, the higher the atomic number, the brighter the material appears in the image, allowing to identify different elements in a sample. Secondary electrons, which are generated from the atoms near the surface, give detailed information about the surface topography with excellent resolution, making them more suitable to analyze the surface of the samples. The signal of secondary electrons is collected by a detector, typically a scintillator inside a Faraday cage, which is positively charged and attracts the secondary electron. The scintillator is then used to accelerate the electrons and convert them into light that is amplified by a photomultiplier to generate a high quality 2D-topography micrograph as shown in Fig.3.6.

3.3.2 Confocal microscopy

Confocal Microscopy (CM) is an imaging technique that utilizes a laser source to scan the sample rather than the classical illumination sources of conventional optical microscopes. In a confocal microscope, micrographs are obtained using a beam of laser light that is reflected downward by a dichromatic mirror, the beam then passes through an array of lenses to be highly focused into a small point at the focal plane of the sample that we want to observe, a computer-controlled scanning mirror can move or scan this beam in the x and y directions at the focal plane to capture the light that is reflected from the sample or the fluorescent light that is excited in the sample by the incident beam.

In optical microscopes, the collection of light from outside the focal plane which can give a blurry image; in confocal microscopy the collected light passes through a pinhole to be reduced, collecting only

light on the focal plane. This is the fundamental principle of a confocal microscope, which uses spatial filtering techniques to eliminate out-of-focus reflections or secondary fluorescence which may obscure the sample details in samples whose thickness is bigger than the immediate plane of focus of the beam. In principle, the focus plane of illumination is the same as the focal plane of detection, i.e. they are confocal and this creates a sharp image of the microstructural details of the sample. Confocal microscopy offers then increased resolution in the z direction giving much higher quality images compared to those obtained using conventional optical microscopy.

Fluorescent emission is created at each point of the scanned laser beam in the specimen focal plane with considerable fluorescence also being created above and below the focal plane. This divergent fluorescence, if it makes its way to the photon multiplier tube or detector, will cause blurring of the final image. To get rid of this light a detector pin-hole aperture is introduced between the detector and the specimen. Light outside of the specimen focal plane is largely excluded from hitting the photon multiplier tube. The geometry of the light in the focal plane is such that it passes through the pin-hole aperture and is detected by the photon multiplier tube. The signal detected is then reconstructed by computer software to form a 3D image of the topography of the surface (Fig. 3.7).

Confocal laser scanning microscopy is then a very valuable tool for obtaining high resolution images and 3D reconstructions of surfaces at micro- or nano-scales of very rough to smooth surfaces, allowing fine surface structures to become visible in a non-contact process. Another benefit of confocal microscopy is the time employed to obtain an image, given that within seconds the sample is scanned vertically in pre-defined steps during which every point on the surface passes through the focus level providing detailed information of the sample in high resolution in all three dimensions. Other main advantage over conven-

Figure 3.7: Confocal microscope from Leica showing the basic components and an example of a 3D image.

tional optical microscopy is that the images are taken point-by-point and reconstructed with a computer, rather than projected through an eyepiece. The measuring capabilities of confocal microscopes range from a few nanometers to several millimeters and therefore serving a wide variety of different applications where sub-micron lateral resolution and a vertical resolution in the nm range is needed. Typically an objective with a high numerical aperture (NA) is related to higher magnification, but reduces the field of view to a few microns only. To overcome this limitation of conventional systems, confocal systems feature ultra-fast topography stitching. By using the XY-stitching mode, individual 3D images are collect together in a larger image. The final surface data shows a continuous, highly precise image of a large surface area of the sample while keeping the perfectly in focus property of confocal microscopy.

3.3.3 X-ray Photoelectron Spectroscopy

The surface of a material is the place that interact with the external environment and other materials, consequently is of primordial impor-

tance to understand the physical and chemical interactions that occur in the surface at the first layers of the material. X-ray photoelectron spectroscopy (XPS) is a very used surface analysis technique that it can be applied to a broad range of materials to obtain valuable quantitative chemical information from the surface of the material being investigated.

XPS is typically accomplished by exciting the surface of the sample with monochromatic Al $K\alpha$ or Mg $K\alpha$ X-rays causing photoelectrons to be emitted from the sample; XPS works only in ultrahigh vacuum $< 10^{-9}$ Torr ($< 10^{-7}$ Pa) because of scattering of electrons in gases. When an atom of the sample absorbs an X-ray photon, an electron can be ejected. The kinetic energy of the electrons depend on the energy of the incident photon, $h\nu$, and the binding energy that hold the electron attached to the atom i.e. the energy required to eject the electron from the surface of the material. By using an electron energy analyzer to measure the kinetic energy of the emitted photoelectrons it is possible then to identify the elements present in the surface. The elemental identity and quantity of a detected element is determined from the binding energy and intensity of a photoelectron peak, respectively (Fig. 3.8).

The energy of an X-ray with particular wavelength is known, and the kinetic energies of the emitted electrons are measured, therefore the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \quad (3.12)$$

where $E_{binding}$ is the binding energy of the electron, E_{photon} is the

Figure 3.8: Example of an XPS spectrum showing the chemical composition of the analyzed sample.

energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the electron as measured by the instrument and ϕ is the work function that depends on both the spectrometer and the material, and is an adjustable correction factor that accounts for the few eV of kinetic energy given up by the photoelectron as it becomes absorbed by the instrument's detector and rarely needs to be adjusted in practice. The average depth of analysis for an XPS measurement is approximately 5 to 10 nm, therefore, in contrast to SEM which has a typical analysis depth of tens of microns, XPS is a surface analysis technique with a typical analysis depth on nanometers and is therefore better suited for the compositional analysis of ultra-thin layers and thin micro-scale surface features.

XPS measurements are given as spectrum which are a plot of the number of electrons detected or intensity versus the binding energy of the electrons detected as shown in Fig. 3.8. Each element detected on the measurement produces a characteristic peak of intensity at characteristic binding energy values that serve to identify each element on the surface of the material being analysed, the number of detected

electrons in each of the peaks is directly related to the amount of atoms of that element within the analysed volume. Additionally, these characteristic spectral peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The information XPS provides about surface layers and thin film structures is very important and useful for many industrial and research applications where surface chemical composition plays a critical role in the performance including: nanomaterials, corrosion, adhesion, electronic devices surface treatments, and thin film coatings used for numerous applications.

3.3.4 Static contact angle

Contact angle is used to characterization of the wettability of a surface when in contact with a liquid. When a droplet of water is placed on a surface, an interface between the liquid, the air and the solid is created in the zone of contact. This frequently considered case of a sessile drop on a solid surface in air is used to define the concept of contact angle. In the two-dimensional projection of a three-phase system, a three-phase point is a point which is common to the three phase boundary lines. When measuring the contact angle, this is the transition point between the liquid/solid, liquid/gaseous and solid/gaseous boundary lines.

Contact angles are used to classify in a basic note the wetting state of a surface (Fig.3.9). In the case of complete wetting the liquid will spread on the surface and the contact angle is 0° . Between 0° and 90° , the solid is said to be wettable or hydrophilic and the liquid still spread over the surface but start to reduce the contact area in the solid as the angle increase, and above 90° it is said to be not wettable or hydrophobic and the contact area reduce greatly. In the case

Figure 3.9: Contact angle values of different hydrophobicity states. Source: Krasowska, 2009 [163]

of ultra-hydrophobic materials the contact angle approaches the theoretical limit of 180° and the droplets cannot remain on the surface and will roll off. Depending on the material and ambient conditions, the contact angle can vary as a function of time, therefore, inhomogeneities and changes of wetting over time can be detected by means of the static contact angle. The contact angle plays an important role in many industrial processes where the behavior of the phase between liquid and solid substances needs to be checked or assessed, such as oil recovery, lubrication, liquid coating, printing, cleaning, hydrophobic or hydrophilic coating, spray quenching, among several other.

Static contact angle (SCA) make reference to the angle between the tangent of the contact point between liquid and solid in the interface and the baseline of the surface when the droplet is static over the sample. The angle between the solid surface and the tangent at the edge of the droplet is measured using the drop shape analysis, which is an image analysis method for determining the contact angle from the shadow image of a sessile drop. Typically, the droplet is metered with high precision using a needle and deposited onto a solid sample and wait until become stable on it (sessile drop) or instead of being dropped is located at the tip of a needle (pendant drop). Normally,

Milli-Q water droplets with a volume of several microliters ($5\text{--}15\ \mu\text{l}$) are dispensed in air conditions to do the measurements. When the droplet is still on the surface an image or video of the drop is recorded with the help of a camera and transferred to the drop shape analysis software. A contour recognition is carried out based on a grey-scale analysis of the image, then a geometrical model describing the drop shape is fitted to the contour. Static contact angle is typically defined by fitting Young-Laplace equation around the droplet but other fitting methods such as circle and polynomial can also be used. Fig. 3.10. shows an image of the comparison of static contact angle between a hydrophilic and hydrophobic surface.

Figure 3.10: Comparison of static contact angle between a hydrophilic and hydrophobic surface.

Another type of measurement that contrast with the SCA technique is the dynamic contact angle which is produced in the course of wetting (advancing angle) or de-wetting (receding angle) of the surface, the contact angle hysteresis is the difference between the advancing and receding contact angles. There are different ways to do the measurement of dynamic contact angle, one of them is to tilt the sample after the drop is placed on the surface (sessile drop) and measure the angle at which the drop start to roll in the surface known as rolling angle, typically ultra-hydrophobic surfaces have rolling angles of less than 10° .

3.3.5 Corrosion characterization

The concept of corrosion makes reference to the degradation of the material when in contact with an aggressive media. Metals and their alloys tend to spontaneous decay and oxidation, and multiple factor can influence the corrosion process, between them the characteristics of the aggressive media and the properties of the metal. Generally corrosion can be classified in two general types: localized corrosion and uniform corrosion. In localized corrosion, the process of degradation of the material take place in very specific or localized zones and start to quickly propagate through the surface. Uniform corrosion on the other hand, is defined by a uniform degradation of the material without the presence of highly localized corrosion. Uniform corrosion is the simplest and more typical form of corrosion and it can be identified as process in which the most superficial layer of the material suffers damage due to the interaction with an aggressive medium like acids or saline solutions, this type of corrosion can oxide extensive areas of the material generating deterioration and wear of the surface, significantly reducing the lifetime of the work piece. Localized corrosion can have more impact on the lifetime of the material under aggressive environment since the damage that causes is in the form of material removal in great quantities in very small localized areas of the material in comparison with the exposed area. The pitting or holes that are created start to increase in depth and length with the time, and it may lead to complete piercing of the metal.

Electrochemical corrosion happens when two materials are in contact with an electrolyte. The process is attributed to an exchange of electrons between the solid and the liquid that give place to two types of reactions: reduction and oxidation. In the reduction process, the metal eject electrons to the solution $M \rightarrow M^+ + e^-$, which is facilitated by the presence of a suitable electron acceptor, creating positive

ions on the metal. In the oxidation process, the atoms in the metal absorb electrons from the electrolyte, these electrons can form bonds with O_2 or H_2O giving place to $4HO^-$ molecules in the electrolyte. In this manner, in the corrosion process the dissolution of the metal gives place to positive carrier M^+ , which transport the positive charges, thus creating a positive current known as the anodic current I_a that is responsible for the corrosion processes. Furthermore, another current is created when the electrons released are absorbed, known as cathodic current I_c . These two currents are the same but of opposite charge sign and are the corrosion current, therefore in equilibrium they eliminate each other and no current is detected, i.e. $I_a = |I_c|$ and $I=0=I_a + I_c$. Nevertheless, when an external potential is applied to the system, there is a change in these currents as the potential changes, giving place to a current that can be detected and measured.

In this work, electrochemical corrosion was characterized by using a voltammetry technique, in which a voltage is applied to a circuit known as a chemical cell that consists of a working electrode, a reference electrode, a counter electrode and an electrolyte. The measurements were made with the assistance of a potentiostat (Metrohm Autolab PGSTAT 302N) using a three-electrode cell (Fig. 3.11) containing a solution as electrolyte, in this case a 0.5 M NaCl solution, a stainless steel 316 counter electrode, a reference electrode and the test sample which is used as the working electrode. The reference electrode is used to obtain a reference constant potential that does not change during the measurements, for this study, the reference electrode was saturated potassium chloride 3 M.

The polarization analysis is then performed by varying the voltage from with a fixed increment (regularly around the 5 mV) and recording the current density. The data obtained by this technique can be displayed in a plot of current density vs. potential, known as a Tafel plot.

Figure 3.11: Three-cell used with the potentiostat for electrochemical corrosion characterization.

Fig 3.12 shows an example of a typical Tafel plot with the different zones of interest. In the initial stages of the test, for the first values of potential applied, a cathodic current is observed and at the voltage value E_{corr} , the anodic current disappears and a cathodic current start to be detected and the corrosion process start to take place. At the point E_{corr} , the current density exhibit the lowest value, known as current density of corrosion I_{corr} . The value E_{corr} or corrosion potential indicates the potential value at which a material under those specific environment conditions is corroded. After the corrosion potential, the surface start to form an oxide layer as the current increase, and after some time, a passivation of the current start to be observed, giving place to a passivation current. This passivation current is formed due to the oxide layer that is formed on the surface due to corrosion, this

thin oxide layer prevent further degradation of the material for a certain time range of potential values known as passivation zone.

Figure 3.12: Tafel plot with the different zones of interest.

As the voltage applied keeps increasing, the oxide layer will be broken and the material will start to deteriorate further, which will be observed on the Tafel plot as an intense raise of the current. The increase in the current after the passivation current is over is related to the pitting corrosion of the material, and after this pitting potential E_{pit} , the material will start to be destroyed very quickly as the localized corrosion start to spread over the surface on several random places of the exposed material. Typically, a surface with good anti-corrosion behavior present a higher value of corrosion potential at which the current changes from cathodic to anodic, and a lower value of current at that corrosion potential. Additionally, a higher pitting potential is a good quality for a better corrosion resistant material.

Other quantity that is used to characterize the corrosion resistance behavior of the material is the corrosion rate measured in mm/year and makes reference to the amount of material that is corroded in mm per year. The corrosion rate is measured using the formula:

$$CR = EW \frac{i_{cor}}{F\rho} \quad (3.13)$$

where F is the Faraday's constant (96,485 C/mol), ρ is the density of the material, and EW is the equivalent weight. The equivalent weight refers to the mass of a substance in gram that combines with or displace 1 gram of hydrogen, and it can be calculated for each element by taking its atomic weight and divided by its valence number. For the case of alloy, the equivalent weight can be calculated by taking the inverse of the sum of the EW of the individual elements that compose the alloys in more than 1%wt [164].

3.3.6 Anti-icing

Ice growth on external surfaces of aircrafts due to the attachment of super cold water droplets can be reduced by the implementation of ice-phobic surfaces. For this, hydrophobic surfaces can be a promising solution due to their water repellent nature. Short pulsed laser was employed for the creation of hydrophobic surface in a one-step process to manufacture. The effectiveness and durability of such surfaces in operational icing conditions was investigate via ice adhesion strength analysis and chemical stability of the textured surfaces with a UV nanosecond laser via Direct Laser Writing in collaboration with Airbus Central R&T. The anti-icing tests were performed by doing adhesion tests that were conducted in the lab-sized icing wind tunnel iCORE (icing and COntamination REsearch facility) of Airbus CRT

show in Fig 3.13. [165] The icing tunnel consist of a wooded closed-circuit wind tunnel with a ground area of about 10 m² in which air is accelerated by a radial fan, the air can be cooled down to a minimum total temperature T of -40 °C, nevertheless, due to the dimension of the tunnel a short response time before reaching a stable negative temperatures of around 15 minutes is needed.

Figure 3.13: Diagram of the icing wind tunnel iCORE. Source : Haunk et al. [165].

In the injection chamber, which follows the settling chamber, a

Figure 3.14: Glazed and rimed ice types. Source: Pervier, 2012 [166]

spray bar system composed of three individual nozzles generate a cloud of droplets with a median volume diameter (MVD) between $10\text{ }\mu\text{m}$ and $40\text{ }\mu\text{m}$ which are accelerated by the fan. The test samples which are in the shape of a cantilever, are fixed in a perpendicular manner with respect to the air flow to optimize the impact of droplets on the target on which atmospheric ice is accreted.

Depending on the conditions selected for the icing tunnel like temperature, air speed, and the liquid water content represent the density of super-cooled water droplets in the icing cloud different types of ice can be formed: glaze, rime, and a mix of both. Glaze ice makes reference to a type of ice that is hard, transparent and apparently smooth in the surface (Fig 3.14.a). Glaze ice is formed when a high liquid water content is present in the icing cloud and the temperature is not

Figure 3.15: Sequential images showing the oscillation process and the detachment of the ice film from the substrate at the frequency of resonation.

cool enough to freeze the droplets instantly, instead the drops impact the surface and a film of liquid water forms in the surface and start freezing slowly. On the other hand, rime ice exhibits a white color that eliminate the transparency, and the surface shows a roughness instead of a smooth surface (Fig 3.14.b). This type of ice appear when very low temperatures are achieved and a small liquid water contact is present in the icing cloud. In rime ice the drops freeze almost after contact, avoiding the formation of a liquid film, because of this air is trapped between the frozen drops, giving place to the white color observable.

The shear stress at the interface between the accreted ice layer and the cantilever was measured by a strain gauge sensor (placed on the back side of the cantilevers) as the ice is removed due to an applied mechanical vibration which causes the sample to start oscillating from the free side of the cantilever until the accreted ice breaks apart the adhesion in the interface with the sample [168] and the ice detach from the surface as depicted in Fig. 3.15.

Figure 3.16: Sequential images showing the oscillation process and the detachment of the ice film from the substrate at the frequency of resonance. Source: Thompson, 2018 [167]

Figure 3.17: Sequential images showing the oscillation process and the detachment of the ice film from the substrate at the frequency of resonance. Source: Pervier, 2012 [166]

The process start with the vibration of the sample with the accreted ice film, until a crack in the interface at the edge of the sample appears and start detaching the ice film. This crack is formed because the stress reaches a maximum at a certain frequency, known as resonance frequency. The data measured is displayed on a plot of the strain vs. time which has a sinusoidal form as show in Fig. 3.16. In the first stage of the vibration process, the sinusoidal wave shows a constant and relative small amplitude in the strain, and after the resonance frequency is reached and the crack in the ice film take place (Fig. 3.17), the strain measurement suffers then a sudden increase in the amplitude, indicating the first cracking of the ice. After that, the crack start to propagate to the interior of the sample, until complete or partial detachment of the formed ice from the surface take place. The measured shear is used to calculate the interfacial shear stress, with units Pa, using an equation derived from the Euler-Bernoulli beam theory [168, 167], where a lower shear strength indicates a better anti-icing behavior.

Chapter 4

Analysis and discussion of results

In this chapter the results for the fabrication of periodic surface microstructures on Ti-6Al-4V by means of direct laser writing with nanosecond laser pulses are presented. The characterization of the processed samples was performed with different techniques in order to analyze the surface topography, the surface chemistry, the wettability and the corrosion resistance of the produced structures.

4.1 Surface topography

4.1.1 Direct laser writing periodic surface structures

Direct laser writing technique was employed for the creation of periodic surface microstructures for the development of functional surfaces with enhanced wettability. The first step in the development of the structuring process was to analyze the influence of several processing parameters in the structures generated, in specific, the repetition rate and the laser power applied to the surface. Energy density is believed to be the maximum contributor to laser ablation. The intensity of the laser power deposited in the sample can be varied by modifying the spot size in the focal point, or increasing the pulse energy. A smaller focal point is not an option when the laser work station does not allow

modification in the optical system, therefore, only the control of the laser power remains available for changing the energy deposited in the sample.

As it has been discussed in the previous sections, the accumulated fluence is the parameter that reflects the amount of energy per area that is deposited in the sample (J/cm^2), and it is a parameter that is characterized by an accumulation processes when several laser pulses hit the same spot either totally or partially, giving place to an accumulated fluence that depends both on the repetition rate and the scanning velocity.

Cross-like micro-channels were patterned on the surface of Ti-6Al-4V samples via UV-ni using the direct laser writing technique. The cross-like channels generate an array of square-shaped micro-pillars. The process was performed using a $20\text{ }\mu\text{m}$ hatch distance, i.e. separation between two adjacent channels, a fixed repetition rate of 100 kHz and nine different values of avg. laser power, to observe the evolution of the micro-machining. Fig. 4.1 shows an SEM micrograph of the different modification made by changing the avg. power.

For a very low laser power of 15 mW, the micrograph in Fig. 4.1.a-b) shows that the surface has tracks slightly marked by the laser beam path, nevertheless, these tracks do not change the surface roughness in a considerable manner. As the power increases and due to the nature of the nanosecond pulses, the surface was rapidly heated on the zone irradiated with a power higher than 85 mW (Fig. 4.1 c), causing the material to melt and evaporate, and creating deeper micro-channels by means of an ablation process as the laser scans the sample. The molten material is ejected because of the vapor pressure and began to accumulate along the sides of the micro-channels, creating a micro-wall of recast material as it re-solidified along the laser path. For a

laser power range between 120-185 mW, the micro-structures obtained shown the more define micro-pillars created, where the material that was melted and removed as the laser scan the surface was deposit along the channels in a more homogeneous manner, giving place to deeper micro-channels. The cross-like scanning process thus created clear micro-pillars with a considerable amount of recast material on the top which act as micro-walls around the original surface that has not been irradiated with laser pulses. Additionally, small spheres of molten material that are created during the ablation process as material is ejected, can reach the center of the micro-pillars and re-solidified

Figure 4.1: Scanning electron micrographs of the top view of titanium alloy micro-structured surfaces showing periodic square-shaped micro-pillars for nine different avg. laser powers: a) 15 mW, b) 50 mw, c) 85 mW, d) 120 mW, e) 150 mW, f) 185 mW, g) 220 mw, h) 250 mW, i) 290 mW. (Scanning speed 80mm/s, 100 kHz repetition rate, H.D. 20 μ m.)

on the untreated surface. For the higher values of average laser power (220 – 290 mW), the amount of molten material start to increase and the recast around the micro-channels became more feverish and start filling previous channels, giving place to a more inhomogeneous definition of the micro-channels. Also more spherical particles of recast material are observed on the untreated area, thus reducing the quality of the patterning.

The height of the micro-walls, as well as the depth of the micro-channels depends on the laser power as observed in Fig. 4.1. For the laser powers which gives the more defined structures, the maximum height from the surface on the center of the pillars to the top of the wall and the maximum depth to the bottom of the channels was around 3 and 4 μm respectively. The micro-structures fabricated show strong evidence of thermal effects, becoming more visible as the laser power increases. Due to the increase of energy deposited on the surface, the temperature of the surface and the amount of melted material increases, giving rise to larger micro-walls when using higher power in comparison with the lower power values, for which the micro-pillars did not form properly as the material only got marked slightly, an effect similar to a laser polish. Additionally, for high powers, spherical-shaped particles can also be observed on the center of the micro-pillars because of metal vapor re-solidification as it can be observed on Fig. 4.1.(g-h). Due to the laser beam spot size and the thermal effects that accompany nanosecond laser ablation, a spatial resolution limit in the tens of micrometers is unavoidable when creating well organized surface micro-structures with the UV nanosecond laser system. If smaller features are required, the assist and combination of other fabrication techniques can be used. These DLW structures are of great interest due to their potential for enhancing the wettability behavior of the titanium alloy by means of a micro-structured surfaces. Jaghdeesh et al. has demonstrated the benefits of periodic μ -cell structures as a

way to create a super-hydrophobic surface on Aluminum alloys [77].

Another parameter that needs to be taken into account when micro-structuring hydrophobic surfaces and which has showed that it is influential for the development to achieve a good Cassie-Baxter state of wettability is the separation between each laser track known as hatch distance or pitch. This parameter define the distance between the length of the square-shaped micro-pillars and it can be changed with a resolution of tens of microns, with an inferior limit of 15 micrometers, being this the size of the laser beam, in order to avoid overlap of two

Figure 4.2: Scanning electron micrographs of the top view of titanium alloy micro-structured surfaces showing periodic square-shaped micro-pillars for nine different hatch distances: a) 15 μm , b) 17 μm , c) 20 μm , d) 25 μm , e) 30 μm , f) 35 μm , g) 40 μm , h) 45 μm , i) 50 μm . (Scanning speed: 80mm/s, repetition rate: 100 kHz, avg. power: 150 mW.)

consecutives scanning tracks. To analyze the effect of this parameter in the generation of periodic microstructures, several hatch distances values were used for the fabrication of squared-shaped micro-pillars with micro-cells (Fig. 4.2).

For all the hatch distances used, the DLW process allowed the creation of well-defined periodic surface patterns of micro-pillars. Fig. 4.3a) shows scanning electron microscope images of the processed surface areas. Typical thermal effects that occur during a nanosecond laser process are appreciated, where recast formation of the molten material has taken place. During the laser ablation, the molten material recast as the laser scan the sample, inducing the formation of micro-walls around the original surface forming a closed packet or μ -cell, also some residual granular particles are produced in the center of the micro-pillars due to the solidification of the molten material on the unprocessed area. In addition to the characterization by SEM, the laser irradiated areas were also analyzed by confocal microscopy. Fig.

Figure 4.3: a) SEM images of the titanium alloy sample after laser irradiation using nanosecond pulses. b) Confocal microscopy 3D image of the patterned μ -cell with a hatch distance of 50 μm (wavelength: 355 nm, pulse duration: 15 ns, repetition rate: 20 kHz, laser fluence: 5.65 J/cm², scan speed: 80 mm/s).

4.3b shows an example of a cross-sectional profile of the fabricated μ -cell on the SEM image.

Figure 4.4: Wall height values for four different avg. pulse powers (180 – 250 mW) as function of the hatch distances (30 – 50 μm).

The dimensions of these micro-structures depend strongly on the power used for the ablation of the micro-channels. Fig. 4.4 shows the relation between the hatch distances and the height of the walls of the μ -cell for four different avg. pulse power. As the power increases, the fluence over the surface area increase (due to the spot size remaining constant). Thus, the material is removed in a higher extent inducing the recast on the top while also re-filling the patterned micro-channel with the molten material as the laser scan the material during the laser processing. This can be observed by noticing that the horizontal and vertical micro-channels are not created in a symmetric way, as one of them is open in the direction of the laser writing while the other (the first one made) is blocked due to the recast of material as the perpendicular channels are made. This effect also affects the volume (width

and height) of the recast layer of molten material, i.e., the μ -cell.

For low avg. power values, the amount of ablated material is lower and well-defined structures are produced, therefore, the recast of the molten material is smaller, thus reflexing in lower altitude of the micro-walls. As the avg. laser power increases, more recast material starts to accumulate, giving place to higher walls, but less defined structures, due to the amount of uncontrolled recast. As the power increases, the amount of molten material is higher, thus growing the volume of recast material and the height of the micro-wall, reaching a maximum value of more than $5\text{ }\mu\text{m}$ for a Hatch Distance of $40\text{ }\mu\text{m}$. Additionally, it can be observed that micro-walls' height is influenced by the periodic distance between channels. When the distance is lower, there is an accumulation of recast material on adjacent walls, thus increasing height values. However, during the scanning process, perpendicular ablation to the direction of the previously formed walls decreases their height as the material is melted again. For higher hatch distances, there is less accumulation of recast material on adjacent walls, due to the large gap between the structures. The highest wall height values were measured for $40\text{ }\mu\text{m}$ of Hatch Distance, where the periodic gap promotes both accumulation of recast and fewer ablation of previously formed micro-walls.

4.1.2 IR-fs laser induce periodic surface structure

Using the direct laser writing technique with a infra-red (IR) femtosecond pulsed laser, the generation of laser-induced periodic surface structures (LIPSS) was performed on the Ti-6Al-4V samples as a second process on samples processed earlier with UV-nl DLW, for the creation of hierarchical structures. The objective was to apply a second laser process to the square-shaped micro-pillars generated with

UV-ns DLW in order to modify at nano-scale the remaining unprocessed area found on the top of the micro-pillars inside the micro-cells.

IR-fs LIPSS were formed on top of the UV-ns micro-pillars using a femtosecond pulsed laser source with an average power of 5W and linear polarization, which emit pulses with a duration of 310 fs and a central wavelength in the near-infrared domain of 1032nm. Laser processing was performed in atmospheric conditions and cleaned by compressed air. The optimization process consisted in finding a balance between the pulse power, the repetition rate and the scanning speed. This optimization process have been reported previously by Romano et al. for the creation of LIPSS on stainless steel [161].

Figure 4.5: SEM micro-graph of the IR-fs low spatial frequency LIPSS generated on Ti-6Al-4V surfaces (wavelength: 1032 nm, pulse duration: 310 fs, repetition rate: 100 kHz, pulse fluence: 0.16 J/cm², spatial period: 810 nm).

The structuring process employs a high pulse-to-pulse overlap in the direction of the laser scan path, for the case of Ti-6Al-4V, 28 effective

pulses per spot size were found to be necessary for LIPSS generation using a laser fluence per pulse of 0.16 J/cm^2 , a scanning speed of 500 mm/s and a pulse repetition rate of 100 kHz . The resulting morphology can be seen on Fig. 4.5, which shows self-organized ripples in a very uniform manner with a spatial period of approximately 810 nm .

Because of the ultra-short duration of the laser pulses, thermal effects are not present when working with fs pulses, for this reason, the previous UV-ns DLW structures are expected to remain still after the second laser processing, giving place to a surface with micro- and nano-features in the surface roughness.

4.1.3 Direct laser interference patterning periodic surface structures

To study the fabrication of DLIP micro-structures on Ti-6Al-4V, irradiations with a picosecond laser were performed. Once the laser parameters are fixed, line-like patterns with three different spatial periods ($1.1 \mu\text{m}$, $2.6 \mu\text{m}$ and $5.4 \mu\text{m}$) have been produced using the two-beam configuration. The structuring has been performed employing high pulse-to-pulse overlap in the direction of the interference lines. A detailed description of the process has been reported elsewhere [113, 114]. Fig. 4.6 shows an SEM micrograph of the line-like pattern for a period of $2.6 \mu\text{m}$.

Sequential experiments have been carried out considering an interference area of $160 \mu\text{m}$ while decreasing the pulse-to-pulse distance from $144 \mu\text{m}$ to $4.8 \mu\text{m}$, in the direction of the interference lines, while the laser fluence was kept constant with a value of 0.8 J/cm^2 . Fig. 4.7 depicts the relation between overlap used and the depth produced on the surface by DLIP for a line-like pattern and it can be appreciated

Figure 4.6: SEM micrograph of the line-like pattern for a period of 2.6 using the two-beam DLIP technique (wavelength:1064 nm, pulse duration: 10 ps, repetition rate : 1 kHz, fluence for the second irradiation:0.55 J/cm²).

the rapidly increase in depth for the spatial periods of 5.4 μm and 2.6 μm in the range of 80-97%. It can be seen that for the largest used spatial period the achieved depth was 2.5 μm , while for the spatial period of 1.1 μm the increase is barely noticed in comparison with the other two periods. The difference in depth may be related to the accumulation of heat for a large number of pulses. This effect is stronger for smaller periods due to the reduced distance between each interference maxima, leading to a pattern partially destroyed.

In a subsequent process in order to create the cross-like structure, the sample has been rotated 90° and irradiated again with the same value of overlap but with a change in the fluence. In this set of experiments, it was determined to reduce the fluence to 0.55 J/cm² in the second irradiation, because homogenous structures have been measured according with the process of high overlap followed. In Fig.

Figure 4.7: Relation between overlap used during the DLIP in the two-beam configuration and the average depth produced (wavelength: 1064 nm, pulse duration: 10 ps, repetition rate: 1 kHz, Fluence: 0.8 J/cm²).

4.8 are shown the measurements obtained using confocal microscopy of the cross-like structures produced with a spatial period of 2.6 μm . Both the structure depths in the horizontal and vertical directions as well as the intersection points are depicted. For all overlap values the depth of the cross-like was less than 1 μm with very close values for the horizontal and the vertical directions (superposition of the interference minima and maxima) except for the case of 95% pulse overlap. Also a trend can be noticed related with the increment of the depth in the intersections (superposition of interference maxima) in relation with the overlap used.

An example of a treated surface with micro-pillars with a spatial period of 2.6 μm can be observed in Fig. 4.9a. This structure was

Figure 4.8: Depths measured in the cross-like structures on Ti-6Al-4V using different high values of overlap in the spatial period of $2.6 \mu\text{m}$ (wavelength: 1064 nm , pulse duration: 10 ps , repetition rate : 1 kHz , fluence for the second irradiation: 0.55 J/cm^2).

fabricated using an overlap of 93%. The surface structure generated by the DLIP technique is uniform all over the processed area, showing a periodic set of micro-pillars with an average depth of $0.9 \mu\text{m}$ at both the vertical and horizontal direction and an average depth of $1.5 \mu\text{m}$ at the interference maxima-maxima intersection.

Furthermore, during the processing of Ti-6Al-4V with the DLIP technique, the formation of LIPSS could be also observed at the interference maxima positions, giving place to micro-pillars with a rough top surface and thus producing in a one step process a dual-scale or hierarchical structures (nano and micro features) as shown in Fig. 4.9a). The micro-pillars exhibit a hierarchical structure that may be suitable

Figure 4.9: SEM micrographs of the Ti-6Al-4V sample showing (a) the micro-pillars generated using the DLIP technique (wavelength: 1064 nm, pulse duration: 10 ps, repetition rate: 1 kHz, fluence for the second irradiation: 0.55 J/cm², spatial period: 2.6 μ m.) and (b) laser induced periodic surface structures (LIPSS) produced over the DLIP pattern..

for wettability applications. According to Skolski et.al [81], the produced LIPSS (Fig. 4.9b) can be classified as Low Spatial Frequency LIPSS (LSFLs or type-s). Thus, the direction of the LSFLs is perpendicular to the direction of the laser polarization. The observed spatial period has a value of $790 \text{ nm} \pm 70 \text{ nm}$, which is slightly smaller than the used laser wavelength (1060 nm).

4.1.4 Hybrid-technology hierarchical periodic surface structures

DLW + IR-LIPPS

Hierarchical structures were generated by combining both UV-ns and IR-fs direct laser writing structures on the same surface. As can be observed on Fig. 4.10, the formation of IR-fs LIPSS did not destroy the previously patterned UV-ns micro-pillar, giving place to a well-defined dual-scale surface roughness. The IR-fs LIPSS can be observed both in the micro-walls and in the center of the micro-pillars in a very homogeneous way, showing also a smoother overall structure. These

dual-scale topographies are expected to show a better wettability behavior in comparison with the single UV-ns micro-pillars due to the roughness inspired on natural hydrophobic surfaces.

Figure 4.10: SEM micrographs of the dual-scale topographies on the surfaces of Ti-6Al-4V laser-patterned samples: (a) ns-DLW before LIPSS, (b) ns-DLW after LIPSS. (DLW structure: wavelength: 355 nm, pulse duration: 30 ns, repetition rate: 100 kHz, fluence: 5.65 J/cm², scan speed: 80 mm/s; LIPSS: wavelength: 1032 nm, pulse duration: 310 fs, repetition rate: 100 kHz, fluence: 0.16 J/cm², spatial period: 810 nm).

DLW + DLIP

Because of this difference of spatial resolution between the two previous techniques, the combination of both techniques has been investigated. For this purpose, firstly squared shaped micro-cells were generated by means of DLW with nanosecond pulses using the parameters reported before for a hatch distance of 50 μm . After that, a pillar-like pattern was produced using DLIP with a spatial period of 2.6 μm using the process parameters from the previous section. The result can be observed in Fig. 4.11.a) and 4.11.b) where the triple hierarchical structures (nano- and micro-features) generated by the combination of both techniques are visible. A cross-section profile of the obtained surface pattern is shown in Fig. 4.11 c).

Figure 4.11: a, b) SEM micrographs showing the dual-technique (DLW + DLIP) structures. c) Cross-section profile. (DLW: wavelength: 355 nm, pulse duration: 15 ns, repetition rate: 20 kHz, Fluence: 5.65 J/cm², Scan speed: 80 mm/s, DLIP: wavelength: 1064 nm, pulse duration: 10 ps, repetition rate: 1 kHz, fluence for the second irradiation: 0.55 J/cm², spatial period: 2.6 μm)..

The micrograph shows clearly that the second process with DLIP does not damage the previously fabricated μ -cell using DLW. In the center of the μ -cell, where the original topography of the sample along with some recast particles was observed before, a well-defined periodic structure has been fabricated. The results obtained for the fabrication of two different types of micro-structures generated with the two micro-machining techniques shows that, the DLIP technique can reach

a smaller spatial resolution between adjacent micro-structures in comparison with the resolution of the DLW technique which is limited by the spot size of the laser beam, thus giving place to a dual scale roughness surface. Additionally, the formation of LIPSS during the DLIP process gives the tools necessary for creating a triple scale roughness surfaces.

4.2 Wettability

4.2.1 DLW UV-ns periodic surface structures

A preliminary analysis have been made to see the effect of the μ -cell on the wetting properties of the Ti-6Al-4V by static contact angle (SCA) measurements, with a droplet size of $3\ \mu\text{l}$. The non-patterned sample was measured as a reference and recorded a SCA value of $67 \pm 2^\circ$ (Fig. 4.12.a). The DLW patterned samples were hydrophilic after the laser processing, reaching a SCA value of 91.3° , slightly improving the wetting properties of the material, as seen on Fig. 4.12.b, therefore the μ -cell structures by themselves did not increase in a well manner the wettability behavior of the Ti alloy samples. The lightly increase in the contact angle may be prompted due to the μ -cells patterned, as it has been probed on aluminum alloy samples [29] where it has been demonstrated that the C.A. depends on the hatch distance, showing a decrease in the C.A. as the separation increases. The μ -cell act as air traps that prevent the surface from wetting reducing the area of liquid-solid interface, thus a bigger separation allows the water to penetrate the μ -cell and wet the surface inside the structure thus increasing the wetting area, while on the other hand a smaller separation between structures give place to no well-define micro-cells.

Figure 4.12: Contac angle measurements: a) Reference, b) DLW μ -cell structures

4.2.2 DLIP IR-ps surface structures

The pillar-like structures made by means of DLIP were also highly hydrophilic immediately after the laser process, after 14 days in air storage, the DLIP structured sample recorded a SCA up to 70° (Fig. 4.13.c).

Figure 4.13: Contact angle measurements: a) Reference, b) DLIP structures

4.2.3 DLW + DLIP - Hybrid-technology hierarchical periodic surface structures -

Finally, the hierarchical structures made by the combination of the two laser micro-structuring techniques (DLW + DLIP) were also highly hydrophilic after the laser treatment, but became hydrophobic afterwards, recording a SCA value higher than 110° (Fig. 4.14.b) improving the C.A. value on comparison with the DLW and DLIP structures separately. This increase on the C.A. must be related with the presence of the hierarchical structures if the Cassie-Baxter model is considered. The combination of both structures (DLW + DLIP) may allow the surface to make a transition from the Wenzel state into a Cassie-Baxter state due to the presence of the hierarchical structures created, thus reducing the area of the liquid-solid interface.

Figure 4.14: Contact angle measurements: a) Reference b) Hierarchical Structures (DLIP + DLW + LIPSS)

4.2.4 Effect of storage condition on hierarchical structures with DLW + IR-LIPSS

Generally, the wettability behavior of a material depends on both the surface topography and the chemical composition. It is reported in the literature that after a laser structuring process, ageing will affect the wettability behavior of the surfaces due to a chemical change of the surface composition. Furthermore, recently the role of storage conditions after the laser patterning for fabrication of hydrophobic surfaces has been studied. This demonstrated that different storage conditions can affect the ageing process of micro-structured surfaces, either hastening or delaying the transition between hydrophilic and hydrophobic states. The fact that storage conditions may affect and change the chemical composition of the laser-patterned surfaces may be due to the chemical compounds to which the surface is exposed on the different storage conditions.

To analyze how the storage affects the ageing process and the wettability behavior of the Ti-6Al-4V patterned surfaces, two samples (processed with the same laser patterns) kept on two different storage conditions, ambient air and polyethylene (C_2H_4)_n bags, were used to observe and compare the evolution of the SCA for several weeks. The static contact angle measurements were made using a sessile drop

technique together with a video-based optical contact angle measuring system. Milli-Q water droplets with a volume of $10\ \mu\text{l}$ were dispensed in air conditions. The reference non-processed surface recorded a SCA of approximately 70° , without any significant change due to the storage conditions. The processed samples were highly hydrophilic immediately after the laser micro-machining.

Figure 4.15: Static contact angle values for UV-nl micro-pillars for three different laser fluences and two different storage conditions.

The evolution of the contact angles for samples kept in different storage conditions are shown in Fig. 4.15. This data clearly demonstrate that samples stored in the polyethylene bags exhibit an increase in the contact angle after the first week in comparison to samples stored in air. After one month of storage, the samples stored in the

bags shows an even clearer difference in comparison with the samples kept on air, reaching values over 150° . Since the surface topography was fabricated with the same parameters, the change in contact angles between the two storage conditions must be related to a change in the chemical composition of the surfaces, nevertheless, it cannot be denied that the micro-structures also play an important role in the transition between wettability states, since all the laser-patterned samples exhibit an improvement in the SCA values in both storage conditions when compared with the non-processed surfaces.

Figure 4.16: Static contact angle values for micro-pillars as well as hierarchical pillars in two different storage conditions.

Additionally, dual-scale samples were also kept in two different storage conditions. SCA measurements for hierarchical structures and

Figure 4.17: Photograph of droplets deposited on the hydrophobic surfaces fabricated on Ti-6Al-4V sheets with DLW.

single-scale structures on both air and polyethylene bags storage are shown in Fig. 4.16. It can be observed that dual-scale hierarchical structures exhibit an improvement in SCA against non-hierarchical micro-pillars for samples stored in both air and polyethylene bags, this demonstrate that a hierarchical roughness leads to an increase in surface hydrophobicity. However, once again, samples that were kept in polyethylene bags exhibit a faster ageing process, achieving a hydrophobic state with higher SCA for the hierarchical structures in a shorter time period when compared to the one stored in a polyethylene bag. Once again, demonstrating that both induced roughness and chemical change play an important role in the wettability transition.

Additionally, the contact angle hysteresis values of the hierarchical and non-hierarchical (DLW) surfaces were measured for both air and bag storage. The values are above 20° for the four samples, meaning that they do not reach a hydrophobic state with good rolling-off effect for the water droplets deposited in the surface, nevertheless, the results of the SCA clearly show an improvement in the hydrophobic-

ity when comparing the laser-patterned surfaces against un-processed surfaces. From these results, it is clear that a dual-scale or hierarchical surface structure is important to generate hydrophobic surfaces, as hierarchical structures show a higher SCA values in comparison to single-scale structures. Moreover, although the surface roughness can improve the wettability of the surface, the storage conditions and associated changes in the chemical composition of the surface must also play an important role as there is a difference in the SCA values for both the hierarchical and non- hierarchical structures kept in the two different storage conditions.

4.3 Surface Chemistry of DLW periodic surface structures under different storage conditions

To study the consequence of the two different storage conditions on the final surface chemical composition and the relationship with surface wettability, the surfaces of the DLW nanosecond laser patterned samples stored in air and polyethylene bags were analysed using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra of the bare material and the nanosecond laser treated surfaces in the two storage conditions are shown in Fig. 4.18. For the non-processed surface, the main elements found were carbon and oxygen, this is expected mainly because of contamination and oxidation of the surface due to the water molecules and other atmospheric contaminants. In addition to the C 1s and O 1s peaks, the reference sample shows a very small peak on the Ti 2p region. The bare surface contained also negligible amounts of Al, Ca, S, Si, Cl, K, N and a strong Auger peak at around 497.0 eV corresponding to Na KLL Auger emission, which disappears after the laser process.

Figure 4.18: XPS full spectra for (a) Ti-6Al-4V Reference sample, (b) DLW nanosecond laser patterned sample stored in air and (c) DLW nanosecond laser patterned sample stored in polyethylene bag.

Table 4.1: Relative surface element composition (% atomic concentration) of the unprocessed surface, an air stored DLW nanosecond laser patterned sample and a bag stored DLW nanosecond laser patterned sample.

Sample/Element	Reference	Air storage	Bag Storage
Ti (%)	0.93	9.64	12.36
Al (%)	0.31	2.89	3.39
C (%)	72.53	47.11	40.7
O (%)	16.57	36.81	40.35
Si (%)	0.78	1.38	1.73
S (%)	0.48	0.06	0
Cl (%)	1.1	0	0
K (%)	0.66	0	0
Na (%)	4.34	0	0
Ca (%)	0.25	0.22	0.21
N (%)	2.04	1.55	0.87
V (%)	0	0.34	0.39

The XPS spectra and the detailed atomic elemental composition of the main elements found, summarized in Table 4.1, shows an increase in the percentage of titanium concentration in comparison with the bare material for the case of the laser patterned samples on both storage conditions, this may be attributed to the removal of contaminants in the surface as a result of the laser process, nevertheless, the concentration of Al did not change considerably. Furthermore, the concentration of carbon on the reference sample was very high whereas for the processed samples a clear decrease in the C concentration can be observed. Additionally, the XPS analysis showed that despite the laser treatment leading to the removal of hydrocarbons from the surface, the relative amount of oxygen increased after laser patterning, suggesting the presence of significant amounts of metal oxides on the

surface. Additionally, due to contamination, the reference sample exhibit low concentration ($>6.6\%$) of S, Cl, K, and Na, that are not detected on neither of the laser patterned samples. Also a small percentage of Si was detected ($>2\%$); when found in high concentrations, the element Si must exhibit a peak on the XPS spectra around 103 eV, however, the concentration of Si found in all the samples does not account to exhibit a clear peak in Fig 4.18. The relative contribution of Ca is very similar for all samples, showing a very low concentration in comparison with the main elements found ($<0.25\%$). Furthermore, no concentration of V was found in the reference sample due to contamination, yet a small concentration was found after the laser process ($>0.4\%$). Lastly, N was found on the reference sample with a small contribution to the relative surface composition ($>2.1\%$) and diminishes after the laser process for both storage conditions ($>1.55\%$).

High resolution (approx. 0.4 eV) spectra from the Ti 2p, Al 2p, C 1s and O 1s regions are shown in Fig. 4.19 and Fig. 4.20. For the Al 2p region, all the samples shown a similar behavior; before and after the laser treatment the spectra show peaks at 74.6 eV and 75.0 eV corresponding to aluminum oxide (Al_2O_3) doublets, Al $2p_{3/2}$ and Al $2p_{1/2}$, respectively. No trace of metallic Al (expected at 72.6 eV) were observed, suggesting that all of the Al detected was at the surface and thus prone to oxidation. For the case of the Ti 2p region, the reference sample exhibits a very small peak doublet corresponding to titanium oxide (TiO_2), attenuated by the layer of atmospheric contaminants on the surface. This may be related to oxidation due to the water molecules in the ambient air, and no traces of metallic Ti were observed. After the laser processing, the surface of the sample exhibits a more intense Ti 2p signal due to the removal of contaminants from the surface. The peaks at 459.2 eV and 465.0 eV correspond to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ titanium oxide (TiO_2) doublet, indicating that the surface of the processed area is oxidized. Again, no evidence of metal-

Figure 4.19: High resolution (approx. 0.4 eV) spectra from the Ti 2p and Al 2p regions showing the different compounds.

Figure 4.20: High resolution (approx. 0.4 eV) spectra from the O 1s and C 1s regions showing the different compounds.

lic Ti was found, indicating a TiO_2 film of thickness greater than 6 nm.

Turning to the C 1s spectra in Fig. 4.20, the deconvolution of the data from the reference sample show four different carbon bonding environments: carbon-carbon (C-C) bonds and hydrocarbons species (C-H) at 286.1 eV, carbon-oxygen bonds (C-O) at 287.8 eV, carbonyl bonds (C=O) at 289.3 eV and carboxyl species (O=C-O) at 290.1 eV. After laser irradiation, the C-C/C-H peak is greatly reduced, due to the removal of surface contaminants during the laser ablation process. A chemical shift of 0.5 eV following the laser processing was observed and is attributed to the change in the surface potential as a result of the removal of a proportion of the hydrocarbon contaminants and the increase in the relative amount of metallic oxides at the surface. For the processed samples, the intensity of the C=O and O=C-O components was reduced to a near-negligible level. However, the C-O component only showed a reduction for the sample stored in the bag after laser processing, suggesting that the laser processing does indeed remove C-O but that the resulting surface is prone to subsequent C-O adsorption from the atmosphere. Carbon-oxygen bonds (C-O), carbonyl bounds (C=O) and O=C-O species are all polar molecules, which are related to a hydrophilic effect on wet surfaces due to the polarity of water molecules, whereas C-C and C-H bounds are non-polar and are related to the hydrophobicity of the material. This is in accordance with the results obtained for the two different storage conditions, as the sample with the highest static contact angle, i.e., more hydrophobic behavior, was the sample stored in the polyethylene bag. The XPS data show that, after 1 month of storage in a polyethylene bag, the contribution of the different polar carbon molecules found on the other two samples (reference and air stored) are almost negligible to the total chemistry composition of the surface, with the non-polar carbon molecules (C-C and C-H) the principal contributors.

Evidence for the formation of TiO₂ was corroborated by examining the O 1s spectra in Fig. 4.20, which clearly show an increase in the TiO₂ component at 530.7 eV in the processed samples. Four other components are present in the deconvolution, corresponding to aluminum oxide (Al₂O₃) and carbonyl groups (C=O) at 532.0 eV, O-C bonds and silica (SiO₂), atmospheric oxygen-containing compounds, and water molecules (H₂O). These spectra clearly show an increase in the relative amounts of TiO₂ compared to other compounds during the laser processing, but very little difference between the sample storage conditions. Because of the laser irradiation, some contaminants that were on the surface prior the laser process had been removed, consequently reducing the contribution of O-C/SiO₂ bonds, other oxygen-containing atmospheric contaminants, and H₂O molecules at 532.8 eV, 534.0 eV and 534.5 eV respectively. Furthermore, it also can be observed that for the polyethylene bag stored sample, the water molecules content has decreased to zero after the laser processing while exhibiting the highest SCA value, therefore, the removal of the H₂O molecules contribution to the O 1s peak can be attributed to the highly water-repellency observed on the sample stored in the polyethylene bag. Kietzig et al. has reported that a CO₂ environment is beneficial for a faster increase in the contact angle of laser patterned metallic samples due to absence of H₂O traces, furthermore, laser processed samples stored in water after the laser process never reach a hydrophobic state [88], which endorse our results found for polyethylene storage showing that an absence of water molecules is a key factor for the hydrophilic-to-hydrophobic transition. The XPS results suggest that the observed change in wettability can be attributed to a certain extent to the absences of carbon polar compounds, as well as H₂O molecules, as they were not detected on the sample with the highest SCA.

4.4 Corrosion resistance

Linear polarization studies were performed on the fabricated structures to investigate the corrosion resistance behavior of the DLW micro-pillars fabricated with 3 different laser power and the DLW+DLIP hierarchical structures. The measurements were made using a three-electrode cell using a 0.5 M NaCl solution as electrolyte, a stainless steel was used as the counter electrode, saturated sodium chloride 3 M was used as the reference electrode and the Ti-6Al-4V samples were used as the working electrode, the area surface exposed to the solution was 1 cm^2 and the polarization analysis was performed by varying the voltage from -0.3 to 8 V with an increment of 5 mV.

Fig. 4.21 and 4.22 shows the cyclic polarization curves or Tafel plots of the processed samples in order to compare the difference in the corrosion behavior between the reference sample, DLW micro-structures and DLW+DLIP micro-structures. These plots give valuable information for corrosion characterization and several parameter like the pitting potential (E_{pitt}), the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) can be obtained from them. The data from the Tafel plot is obtained by drawing tangent lines on the anodic and cathodic slopes on the polarization curves, these tangent lines intersect and by looking at the intersection point we can obtain the potential value (corrosion potential) at which the current density is the lowest (corrosion current density). The pitting potential refers to the potential value at which the material start to present topographic damage due to the high potential applied to the electrons of the surface. A material with enhanced corrosion resistance is often characterized by a lower corrosion current density and a higher corrosion potential as well as pitting potential. Table 4.2 shows the values for the corrosion current density, the corrosion potential and the pitting potential for the measured samples.

Figure 4.21: Polarization curves for the samples processed with DLW for three different hatch distances.

Figure 4.22: [Polarization curves for the samples processed with DLW + DLIP for three different hatch distances.

Table 4.2: Results for the corrosion current density (i_{corr}), corrosion potential (E_{corr}) and pitting potential (E_{pitt}) for all samples tested.

Sample	i_{corr} (nA/cm ²)	E_{corr} (mV)	E_{pitt} (V)
Reference	11.55	-137.07	5.73
DLW 15 μ m @ 1.1 J/cm ²	5.85	-19.94	5.61
DLW 15 μ m @ 1.6 J/cm ²	0.63	75.09	5.29
DLW 15 μ m @ 2.2 J/cm ²	2.56	131.32	5.45
DLW 17 μ m @ 1.1 J/cm ²	7.56	-99.07	5.49
DLW 17 μ m @ 1.6 J/cm ²	3.22	131.92	5.59
DLW 17 μ m @ 2.2 J/cm ²	7.41	52.91	5.52
DLW 20 μ m @ 1.1 J/cm ²	0.91	-34.18	5.62
DLW 20 μ m @ 1.6 J/cm ²	2.11	97.45	5.37
DLW 20 μ m @ 2.2 J/cm ²	9.54	35.77	5.52
DLW+DLIP 15 μ m @ 1.1 J/cm ²	54.24	-66.3	>7.5
DLW+DLIP 15 μ m @ 1.6 J/cm ²	36.55	39.4	7.23
DLW+DLIP 15 μ m @ 2.2 J/cm ²	14.54	-21.56	6.88
DLW+DLIP 17 μ m @ 1.1 J/cm ²	16.09	122.12	6.42
DLW+DLIP 17 μ m @ 1.6 J/cm ²	8.36	129.42	7.07
DLW+DLIP 17 μ m @ 2.2 J/cm ²	27.13	133.11	7.22
DLW+DLIP 20 μ m @ 1.1 J/cm ²	34.19	83.07	>7.5
DLW+DLIP 20 μ m @ 1.6 J/cm ²	24.65	280.58	7.05
DLW+DLIP 20 μ m @ 2.2 J/cm ²	22.15	416.82	7.07

From Table 4.2 and Fig. 4.21 it can be observed that the corrosion current density for the reference samples is 11.55 nA/cm², value that will be compared with the processed samples to test the corrosion resistance in terms of the reference sample, furthermore the corrosion potential and the pitting potential for the reference sample is -137.07 mV and 5.73 V, respectively. For the processed samples with the DLW technique it can be observed that the DLW micro-pillars with a hatch distance of 15 μ m exhibits the lowest current density overall with a value of 0.63 nA/cm², however, all the DLW samples have a lower corrosion current density when comparing with the reference. Addi-

tionally, the corrosion potential (E_{corr}) values of all the DLW structures are higher (more positive) than that of the reference samples, thus giving evidence of the improved corrosion resistance of the DLW processed samples. For the case of pitting potential, a small decrease was observed when comparing the DLW samples with the reference one but the changes are not significantly important. No significant difference or tendencies were found between the three different powers for all the hatch distances. For the case of the hierarchical structured surfaces, it can be observed that an increase in the current density (i_{corr}) take place for almost all the samples but one, when compared with the reference sample; nevertheless, the corrosion potential (E_{corr}) exhibit higher values for all samples respect to the reference. As it has been established, an enhance corrosion resistance of a material is often identified by a reduction on the corrosion current density and an increase in the corrosion potential, for the case of the hierarchical structures, the corrosion potential was improved, with values over 400 mV for the samples with a hatch distance of 20 μm with a fluence of 2.2 J/cm², indicating an improved corrosion resistance, but the current density was higher. Nevertheless, the pitting potential of the hierarchical structures was greatly increased, with a difference of more than 1.5 V in comparison with the reference samples as well as the DLW patterned samples, reaching an E_{pitt} of more than 7.5 V, thus demonstrating the importance of a hierarchical surface structure for an improved resistance to the damage of the material when exposed to high voltages.

Another important corrosion parameter is the corrosion rate, which indicates the velocity at which the material is corroded when is in contact with an aggressive media and it measures the amount of material in millimeter that is corroded in one year (mm/year). The corrosion rates of materials determine the life-time of metal pieces, helping to determine when maintenance on an equipment is needed. Improving

the corrosion rate of a material then, is a topic of sheer importance that may be helpful for several industry applications, therefore, the corrosion rate of the processed samples was analyzed. The calculated corrosion rate (CR) was measured using the following equation:

$$CR = EW \frac{i_{corr}}{F\rho} \quad (4.1)$$

where F is the Faraday's constant (96,485 C/mol), ρ is the density of the material, and EW is the equivalent weight. The equivalent weight refers to the mass of a substance in gram that combines with or displace 1 gram of hydrogen, and it can be calculated for each element by taking its atomic weight and divided by its valence number. For the case of alloy, the equivalent weight can be calculated by taking the inverse of the sum of the EW of the individual elements that compose the alloys in more than 1%wt [164].

The corrosion rate (mm/year) for all the processed samples is showed in Fig. 4.23. A reference non-patterned virgin sample presented a corrosion rate value of 9.92E-05 mm/year. It can be see that the DLW micro-pillar achieve a better corrosion rate in comparison to the reference, nevertheless, when the DLIP structures are generated on top of the DLW an increase in the corrosion rate seem to take place, thus decreasing the corrosion resistance of the material. Additionally, not a clear difference can be observed for the tendencies of non-hierarchical structures when varying the hatch distance of the DLW micro-pillars, since the corrosion rate seems to show a very similar value for all three hatch distances, contrary for the case of the hierarchical structures (micro-cell patterned with DLIP structures), which shows the highest corrosion rate value measured and start decreasing for bigger hatch distances. Table 4.3 shows the obtained values for the corrosion rate for all samples. From the values of corrosion rate it can be ob-

served that DLW present a better corrosion rate compared with the reference as well as with the hierarchical combined structures.

Figure 4.23: Corrosion rate in mm/year for: a) the DLW and b) DLW+DLIP processed samples.

Pitting potential is another important parameter for the characterization of corrosion resistance, and is related to the voltage value needed for the destruction of the surface. Pitting potential values can

Table 4.3: Results for the corrosion rate of all the samples tested with the percentage in relation with the reference value.

Fluence / Hatch Distance		15 μm	17 μm	20 μm
1.1 J/cm ²	DLW	5.02E-05 50.62%	6.49E-05 65.44%	7.78E-06 7.84%
1.1 J/cm ²	DLW+DLIP	4.60E-04 463.80%	1.38E-04 139.14%	2.93E-04 295.42%
1.6 J/cm ²	DLW	5.46E-06 5.51%	2.77E-05 27.93%	1.81E-05 18.29%
1.6 J/cm ²	DLW+DLIP	3.10E-04 312.56%	7.18E-05 72.39%	2.11E-04 212.74%
2.2 J/cm ²	DLW	2.22E-05 22.38%	6.35E-05 64.03%	8.19E-05 82.58%
2.2 J/cm ²	DLW+DLIP	1.50E-04 151.24%	2.33E-04 234.93%	1.90E-04 191.57%

be easily identified in the cyclic polarization curves by looking at the point at which the current density suffer a sudden increase in value. The pitting potential for samples with different hatch distance at a fluence of 2.2 J/cm² is shown in Fig. 4.24 and it can be see then that the hierarchical structures fabricated with the combination of two laser material processing techniques are enhancing the pitting corrosion resistance of the material by at least 1 V in comparison with the original reference surface or the structures generated with DLW which exhibit no great difference with respect to the reference.

In the hierarchical structures the pitting of the surface may be delayed due to the reduction of surface area that make contact with the electrolyte. DLW micro-cell structures have been proposed to behave like closed air pockets that are beneficial for a higher hydrophobic behavior of the patterned surfaces by reducing the effective contact area between solid and liquid; and has been reported that when increasing the length of the micro-cell a reduction in the static contact angle was observed, possibly because of the increase of the central area of the DLW micro-cells, in which the liquid may get in contact [130, 77]. Due to the smaller dimensions of the DLIP micro-pillars fabricated inside the DLW micro-cells it may be possible to reduce even further the effective contact area for bigger micro-cells, this has effect has been reported before for the case of stainless steel when comparing the orig-

Figure 4.24: Pitting potential for the reference and processed samples.

inal granular surface against a nanocrystalline surface [169].

SEM micrographs of the corroded surfaces were taken in order to observe the damage that the structures may have suffered after the corrosion tests. Fig.4.25 shows the micrographs of the damage made on the micro-structures. It can be observed that when pitting of the material begin to take place on the original surface (Fig. 4.25.a), the damage that the surface undertake has the form of craters and seems to spread in a circular or elliptical manner. The center of the damage craters seems smooth except for a few micro-bumps formed at the center of the crater after the material removal, meanwhile, the periphery of the damage craters seems to be the last active part where the material was being removed due to the high potential applied (E_{pit} was 5.73 for the reference sample). The pitting of the surface seems to starts in small discrete random points or zones of the total tested area and begin to expand and spread from those points.

Figure 4.25: SEM micrographs after the corrosior tests of: a) the reference surface, b) DLW processed sampel and c) DLW+DLIP hierarchical samples.

Further analysis of the SEM images shows that for the DLW microstructured surfaces, the pitting corrosion exhibit a tendency to develop in a more pronounced elliptical way, as it can be observed that in this case (Fig. 4.25.b) the pitting of the surface almost take place along the direction of the micro-structures and start to expand in a more directional manner rather than expand directly in a circular or elliptical path as observed on the reference surface. Finally for the case of the DLIP+DLW hierarchical structures, the pitting potential was the highest found (more than 7.5 in some cases), and it can be observed in Fig. 4.25.c that the pitting of these type of structure leads to less material damage. The pitting process for these hierarchical structures also seems to start on random places and begin to spread from there in

a directional manner similar to the DLW structures, but the damage of the surface is less pronounced. This may be caused by the presence of the smaller DLIP micro-pillar on the center of the DLW micro-cells, which has been proven to be beneficial to prevent in some manner that water droplets make contact with the original material, thus reducing the surface area that is in contact with the electrolyte. The presence of pitting in the surface of the samples destroys the hydrophobic behavior obtained by the ageing process.

4.5 Anti-icing of DLW structures

To study the effect of direct laser writing on the capability for the creation of icephobic surfaces, two different samples processed with a one-step direct laser writing were analyzed using the wing tunnel in Airbus Central R&T described in the anti-icing characterization section. The samples were patterned using the UV-ni laser in UPM Laser Centre using the same parameters. For this study, square-shaped micro-pillars with micro-cells with a fixed hatch distance of 35 μm were fabricated using the parameter on the Table 4.4.

One of the samples were treated after the laser process with the hydrophobic agent Mecasurf® (perfluoropolyether by Surfactis, Angers, France), hence resulting in a two-steps process. SEM micrographs

Table 4.4: Laser parameters for the fabrication of micro-pillars with micro-cells using a UV-ni laser in UPM Laser Centre.

Pulse Power (mW)	130
Repetition Rate (kHz)	100
Scan Speed (mm/s)	80
Hatch Distance (μm)	35

were taken to analyze if a change in the topography take places after the icing test. Additionally, before the icing test, static water contact angles were also measured to compare the wettability behavior of the two samples, before and after the icing test. The wettability of the surfaces was characterized via static contact angle and dynamic contact angle using the sessile drop technique with a video-based optical goniometer (DSA 25, Krüss GmbH, Hamburg, Germany). Water droplets of 10 μl volume were deposited in atmospheric conditions in all measurements.

The ice adhesion tests were conducted in the icing wind tunnel iCORE of Airbus Central R&T [165]. The test samples were cantilevers with an area of 125x13 mm² which are fixed in one end to a holder connected to a vibrational system which is used to induce an oscillation via mechanical vibrations on the cantilevers until detachment of the ice take place [168]. The ice interfacial shear strength can be obtained from the shear stress measured at the interface between the accreted ice layer and the cantilever. Four different icing conditions that give place to four different ice types were used by modifying the icing condition as indicated in Table 4.5). The freezing fraction approximation was based on previous work carried out at Cranfield University [166]. The Liquid Water Content (LWC) represent the density of supercooled water droplets in the icing cloud, while the Median Effective Volume Droplet Diameter (MVD) is defined as the droplet diameter which divides the total liquid water content present in the drop distribution in half. Half the water volume is in larger drops and half the volume in smaller drops.

The ice layer thickness must be accurately determined, since it determines the position of the neutral axis of the composite beam calculated according to the Euler-Bernoulli model [170]. The interfacial shear stress, which primarily causes adhesive ice debonding, reaches its

Figure 4.26: Ice adhesion strengths of the tested samples.

maximum when the neutral axis coincides with the interface between the ice and the cantilever while no bending stresses are present. Therefore the ice thicknesses was chosen for the Ti-6Al-4V samples due to the mechanical properties of the substrate material, and was 3.55 mm.

Fig.4.26 shows the ice adhesion strength of the tested samples. In general a lower ice adhesion strength is desired. As it can be ob-

Table 4.5: Icing conditions used for the ice adhesion tests.

Ice Type	Total Air Temperature	Air speed	Liquid Water Content (LWC)	Mean Effective Volume Droplet Diameter (MVD)	Approximate Freezing Fraction
	°C	m/s	g/m ³	μm	-
Rime	-20	50	0.3	20	1.0
Mixed/Rime	-20	50	0.8	20	0.7
Mixed/Glaze	-5	50	0.3	20	0.55
Glaze	-5	80	1.0	20	0.2

served, the glaze ice case shows the highest adhesion between the four ice types due to the nature of this type of ice which is formed in a rather slow manner by liquid water on the surface, therefore, the impinging super-cooled water droplets do not freeze on impact, instead they run wet after the impact and travel through the surface, possibly filling the empty spaces between the DLW microstructures on the surface and then freeze in them, which results in an increased mechanical interlocking. Additionally, a small difference between the uncoated and coated samples can be observed for this glazed ice type.

For the other three types of ice, a noticeable difference between the ice interfacial shear strength can be observed in comparison with the glaze type. Nevertheless, no significant difference in ice adhesion strength can be observed between the two laser-treated samples in the three ice types, therefore according to the this results, the way of achieving the hydrophobic effect, either in a natural aging or artificially induced, do not play a role in reducing ice adhesion strength

Figure 4.27: Wetting of water droplets of different sizes on a laser-treated microstructured surface.

in atmospheric icing conditions. Some anti-icing surfaces has demonstrated ice interfacial shear strength as low as 15 kPa. In this study, the ice adhesion strength is in the range of the hundreds of kPa, and it may be related with the periodicity of the laser-produced microstructures. Typically, the droplets have a MVD of 20 μm , while the hatch distance on for this study was fixed on 35 μm . Therefore, a share of the impinging droplets are smaller than the manufactured features, thus they may insert themselves between two surface features and the Cassie-Baxter state ceases to occur as depicted in Fig. 4.27. It can be concluded that the surfaces designed and tested in this study are not appropriate to reduce the adhesion strength of ice mimicking atmospheric in-flight icing conditions typically encountered by aircraft, despite showing excellent super-hydrophobic properties.

SEM micrographs were obtained to analyze if the icing test change the topography of the tested samples. Fig. 4.28. shows that the microstructure do not change after 16 icing and de-icing cycles. Indicating the great resistance of the micro-structures under the harsh conditions of the icing test, therefore, demonstrating the drability of the micro-patters generated via DLW UV-ns.

Figure 4.28: SEM micrographs of the natural superhydrophobic laser treated samples: before (a) and after (b) the icing tests.

The wettability of the samples was also measured after the icing test to analyze if a change in wettability take place. Table 4.6. shows the values obtained from the contact angle measurements. The laser-treated samples hydrophobized with Mecasurf® were still superhydrophobic after the icing tests, due to the covalent bond between perfluoropolyether and the metal oxide. However, the superhydrophobicity on the one-step laser-treated samples was lost leading to a contact angle of 119° .

Table 4.6: Wetting properties of the samples manufactured before and after the ice adhesion tests.

Sample	Before Icing			After Icing		
	Contact Angle	Roll-Off Angle	C (atom (%))	Contact Angle	Roll-Off Angle	C (atom (%))
Ti6Al4V + Laser	$168^\circ \pm 1^\circ$	$10^\circ \pm 3^\circ$	$51,8 \pm 1.3$	$119^\circ \pm 1^\circ$	$>90^\circ$	$50,7 \pm 1.1$

Additionally, the chemical composition of the laser-treated samples after the ice adhesion tests was analyzed via XPS to understand the property of the surfaces after the consecutive icing and de-icing cycles. Table 4.6 shows the relative carbon content on the surfaces measured via XPS. Since no topographic Therefore the modification of the wetting properties is related to the surface chemical composition only, of which the C content is a representative parameter. Further, the large effect on wettability is most probably due to the removal of the adsorbed Carbon coating from the most exposed surface asperities only, which represent but a little fraction of the overall surface area. In summary, the supercooled droplets impacting at high speed interact with the surfaces similarly to a mechanical cleaning process, such as CO₂ cleaning, where particles and organic residues are removed from the most exposed or less protected surface asperities, causing a transition from the superhydrophobic to a hydrophobic state. No difference between the carbon content was observed, nevertheless, further analysis of the type of carbon compounds is needed since the non-polar C layer is only adsorbed on a superficial manner. Even if the minor C

loss in atom % does not seem to correspond to the decrease of SCA, it must be remembered that the relation between contact angles and surface energy is not linear and not even continuous.

Chapter 5

Conclusions

In this chapter the conclusions reached are presented based on the different experiments carried out and the results obtained by the different characterization techniques used.

5.1 Surface topography

Direct laser writing (DLW) with a UV nanosecond pulsed laser was employed for the generation of periodic structures on the surface of Ti-6Al-4V aerospace-grade sheets. The patterned structures consist of square-shaped micro-pillars (15 - 50 μm width, 2-10 μm height). The top of the micro-pillar is affected by the thermal effects of nanosecond laser material processing, recasting molten material in the periphery of the micro-pillars tops. The molten material re-solidifies and due to a cross-like process forms a micro-cell structure on the micro-pillars. These structures have been proven beneficial for the development of hydrophobic surfaces on metals. After several tests, which consisted on several sets of irradiations while changing the parameters of the laser, such as power attenuation, repetition frequency, separation between pulses (hatch distance or pitch) and the scan speed of the laser, we have found the combination of these parameters that leads to the creation of well-defined and periodic microstructures, that consist on a matrix of squared micro-pillars with a size of a few tens of micrometers.

Direct laser interference patterning (DLIP) using a picosecond-pulsed laser was employed to create line-like and pillar-like periodic micro-structures with the help and collaboration of the Fraunhofer Institute in Dresden, Germany. The surface structure generated by the DLIP technique is uniform all over the processed area, showing a periodic set of micro-pillars with an average depth of $0.9\ \mu\text{m}$ at both the vertical and horizontal direction and an average depth of $1.5\ \mu\text{m}$ at the interference maxima-maxima intersection. Additionally, the formation of LIPSS could be also observed at the interference maxima positions, giving place to micro-pillars with a rough top surface and thus producing in a one step process a dual-scale or hierarchical structures (nano and micro features).

Furthermore, due to the nature of the picosecond laser process which shows low thermal effects, direct laser interference patterning was used in order to create micro-structures (with a spatial period of $2.6\ \mu\text{m}$ and a height of $1.1\ \mu\text{m}$) in top of the bigger micro-pillars created with the DLW technique in order to create novel hierarchical surface structures. The resulting structures present a multi-scale structure and are a promising option to generate hydrophobic surfaces.

In a collaboration with the University of Birmingham, the formation of LIPSS was created on the surface of the Ti-6Al-4V samples, using a IR femtosecond pulsed laser. The femtosecond low spatial frequency LIPSS were generated on top of the nanosecond patterned structure to create a dual-scale structure. The femtosecond process is free of thermal effects, meaning that the previously fabricated structures were not affected by this second laser process. The LIPSS generated show self-organized ripples in a very uniform manner with a spatial period of approximately $810\ \text{nm}$. The final surface exhibits a dual-scale roughness thus providing a successful method to generate hierarchical structures.

5.2 Wettability

Static Contact Angle measurements were made in order to obtain a preliminary analysis on the wettability behavior of the structures created on during the collaboration with the Fraunhofer institute. The DLW and the DLIP structures shows a hydrophilic behavior immediately after the laser processing, and at that moment a process of ageing involving the adsorption of molecules in the ambient surrounding the processed sample, after two weeks of process, the samples show an improved wettability with contact angles up to 90° , nevertheless, still not an hydrophobic behavior is achieved. On the other hand, the novel hierarchical structures, created by combining both laser technologies, were hydrophobic and recorded a SCA value over 110° two weeks after the process in storage in natural ambient conditions, thus allowing the creation of hydrophobic surface that present a potential application on wettability technology.

Furthermore, to analyze the role of storage conditions on the ageing of the samples generated in the collaboration with the University of Birmingham, two storage conditions, air and polyethylene bags, were used for keeping the samples after the laser process to evaluate the ageing process of the samples. Static Contact Angle measurements were made to obtain an analysis on the wettability behavior of the structures created under the two storage conditions. The non-processed surface recorded a SCA of approximately 70° , without any significant change due to the storage conditions. After one month of storage, nanosecond processed samples kept in the polyethylene bag showed a clear shift away from hydrophilic behavior and achieving a hydrophobic effect, reaching values over 150° . For the dual-scale hierarchical structures (DLW structures combined with IR-fs LIPSS), SCA val-

ues showed an increase against the non-hierarchical structures, either kept on air or polyethylene bags, demonstrating that a hierarchical roughness is more prone to achieve a better hydrophobic state. Nevertheless, the hierarchical surfaces kept in polyethylene bags showed a higher SCA, over 160° , in comparison with the hierarchical surfaces kept on air which showed a SCA around 120° . The surface topography was the same for both samples, therefore, the change in SCA values between the two storage conditions must be also related to a change in the chemical composition of the surfaces.

5.3 Chemical composition

XPS results showed that the laser patterned samples were heavily oxidized, with the processed samples exhibiting a clear increase in the total oxygen concentration in comparison with the reference sample. It was found that the process samples were covered by the metallic oxides TiO_2 and Al_2O_3 , as well as other oxygen-containing compounds and hydrocarbons. Among the oxygen compounds, a clear difference in the relative content of water molecules between samples with the same surface structure kept in two different storage conditions was observed. For the case of the sample kept in air, water molecules were detected on the deconvolution of the O 1s peak, while for the case of the polyethylene bag, which shows the highest SCA, no traces of H_2O molecules were found.

Furthermore, the C 1s peak of the XPS spectra showed that a reduction on the carbon concentration took place after the laser processing. The detailed analysis of the C 1s spectra for the processed samples showed traces of several polar and non-polar carbon compounds, with the sample kept in polyethylene bag showing the lowest concentration of polar molecules while also displaying the highest SCA. The results

indicate that the absence of polar molecules highly affect the wettability of the surface.

These results indicate once more that a change on the surface roughness will improve the wettability of the surface, but it will also be necessary a change on the chemical composition of the surface which can be influenced by the storage conditions after the laser process. While the process responsible of the transition from hydrophilic to hydrophobic is complex and still not completely clear, this research illustrated that aging of laser-textured samples in simple polyethylene bags can lead to higher water contact angles values with a reduced time for the transition between hydrophilic and hydrophobic states.

5.4 Corrosion & anti-icing

Linear polarization studies were performed on the fabricated structures to investigate the corrosion resistance behavior of the DLW micro-pillars and the DLW+DLIP hierarchical structures in a 0.5 M NaCl solution. Linear polarization results shown that even if the corrosion current density and the corrosion potential were not greatly improved by hydrophobic DLW structures, the combination of DLW + DLIP structures clearly improved the pitting corrosion resistance of the material (approximately > 7 V) in at least 1 V with respect to the reference value, which was around 5.5 V. SEM characterization shown that pitting corrosion in laser patterned samples displayed a preference in the propagation of the material damaged along an axis of the periodic pattern created by laser material processing instead of a circular or elliptical propagation as was observed for the reference surface.

The icephobic performance of micro-structured surfaces was investigated under atmospheric in-flight icing conditions to investigate if

they could be potentially used on aircrafts. The laser processed surfaces manufactured in with DLW do not reduce ice adhesion under in-flight icing conditions. The microstructure actually enhances the mechanical interlocking between the ice and the surface, resulting in a higher interfacial adhesion strength in comparison with other ice-phobic surfaces. More experiments must be undertaken to investigate different patterns and laser technologies, in order to assess which topography is most beneficial for reducing ice adhesion in in-flight conditions.

5.5 Lines of future work

After the results and the conclusions obtained in this thesis, several lines of future research are still open. For instance, the micro-pillars with micro-cells on the top are proven to be beneficial for the creation of hydrophobic and super-hydrophobic surfaces on several material, nevertheless, little studies have been done in Ti-6Al-4V.

This thesis showed positive results in the creation of hydrophobic surfaces, nevertheless, the time for the transition between hydrophilic and hydrophobic could be a topic of research due to the natural ageing process which can take up to several weeks in ambient air. This time could be reduced by post-process storage, surface coating, or processing under chemical conditions distinct to ambient air. Additionally, the mechanical durability must be enhanced in order to fabricate durable hydrophobic surfaces.

In the case of hierarchical structures, since the methodology for the creation of the novel hierarchical structures with hybrid laser technology presented in this study is relatively new, several improvements could be made in order to create hierarchical structures with good wettability for several potential applications.

For the anti-icing application, more experiments must be undertaken to investigate different patterns and laser technologies, in order to assess which topography is most beneficial for reducing ice adhesion in in-flight conditions. One design rule for such surfaces seems to be that the microstructures must be smaller than the typical water droplet sizes, to avoid insertion and freezing of droplets into the structures themselves.

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