Laser Surface Structuring on Ti-6Al-4V using pulsed laser for modified wettability

Daniel Huerta Murillo
Contents

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- Introduction
- Structuring and patterning of surfaces with pulsed laser
- Wettability modification
- Chemical Composition of the surfaces
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Motivation

• Design and optimization of laser generated structures and patterns on metals inspired by natural biological surfaces.

• Evaluating the capability of surface structuring with pulsed laser for the creation of functionalized surfaces.

• Explore the combination of different laser processes, in order to create hierarchical surface topographies (multi-scale) with enhanced surface properties.

• Specifically, creation of hierarchical structures for hydrophobic surfaces with enhanced properties:
  – Self-cleaning effect
  – Water-bouncing effect
  – Enhance of corrosion resistance
Bio-Inspired Hydrophobic Surfaces

K. Liu, L. Jiang
Nano Today (2011) 6, 155–175

Lotus leaf (*Nelumbo nucifera*)

B. Bhushan, Y.C. Jung/Progress in Materials Science 56 (2011) 1–108
Wettability Models

Desired wetting effect for laser patterned surfaces

B. Bhushan, Y.C. Jung/Progress in Materials Science 56 (2011) 1–108
Structuring and patterning of surfaces with pulsed laser
UV-ns Direct Laser Writing

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>355</td>
</tr>
<tr>
<td>Max. Laser Power (W)</td>
<td>16</td>
</tr>
<tr>
<td>Repetition Rate (kHz)</td>
<td>100</td>
</tr>
<tr>
<td>Scan Speed (mm/s)</td>
<td>80</td>
</tr>
<tr>
<td>Min. Hatch Distance (H.D.) (µm)</td>
<td>15</td>
</tr>
<tr>
<td>Apparent beam spot size (µm)</td>
<td>15</td>
</tr>
</tbody>
</table>
Processing parameters for structuring - Polishing

Non-processed Surface  Polishing of surface at low power  Interface
Processing parameters for structuring - Focus
Processing parameters for structuring
Processing parameters for structuring – Power increase
Processing parameters for structuring – Hatch Distance
Processing parameters for structuring – Pulse effect
UV-ns Direct Laser Writing

UV-ns Direct Laser Writing

Scanning speed: 80 mm/s
Repetition Rate: 100 kHz
Hatch Distance: 20 µm
IR-fs Direct Laser Writing for LIPSS

LIPSS parameters - wavelength: 1032 nm, pulse duration: 310 fs, repetition rate: 100 kHz, fluence: 0.16 J/cm², spatial period: 810 nm
Dual-scale structures
Dual-scale structures

(a) ns-DLW without LIPSS  (b) ns-DLW with LIPSS.

DLW parameters - wavelength: 355 nm, pulse duration: 30 ns, repetition rate: 100 kHz, fluence: 5.65 J/cm², hatch distance: 20 μm

LIPSS parameters - wavelength: 1032 nm, pulse duration: 310 fs, repetition rate: 100 kHz, fluence: 0.16 J/cm², spatial period: 810 nm
Dual-scale Structures

(a) ns-DLW without LIPSS  (b) ns-DLW with LIPSS.

DLW parameters - wavelength: 355 nm, pulse duration: 30 ns, repetition rate: 100 kHz, fluence: 5.65 J/cm², hatch distance: 20 µm

LIPSS parameters - wavelength: 1032 nm, pulse duration: 310 fs, repetition rate: 100 kHz, fluence: 0.16 J/cm², spatial period: 810 nm
Wettability Results
Static contact angle values for non-hierarchical and hierarchical pillars in two different storage conditions.

Micro-pillars

Hierarchical Pillars
Chemical Composition Results
Chemical Composition

XPS full spectra for:

(a) Ti-6Al-4V Reference sample
(b) DLW patterned sample stored in air
(c) DLW patterned sample stored in polyethylene bag.
## Chemical Composition

<table>
<thead>
<tr>
<th>Sample/Element</th>
<th>Reference</th>
<th>Air storage</th>
<th>Bag Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (%)</td>
<td>0.93</td>
<td>9.64</td>
<td>12.36</td>
</tr>
<tr>
<td>Al (%)</td>
<td>0.31</td>
<td>2.89</td>
<td>3.39</td>
</tr>
<tr>
<td>C (%)</td>
<td>72.53</td>
<td>47.11</td>
<td>40.7</td>
</tr>
<tr>
<td>O (%)</td>
<td>16.57</td>
<td>36.81</td>
<td>40.35</td>
</tr>
<tr>
<td>Si (%)</td>
<td>0.78</td>
<td>1.38</td>
<td>1.73</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.48</td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td>Cl (%)</td>
<td>1.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K (%)</td>
<td>0.66</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na (%)</td>
<td>4.34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.25</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td>N (%)</td>
<td>2.04</td>
<td>1.55</td>
<td>0.87</td>
</tr>
<tr>
<td>V (%)</td>
<td>0</td>
<td>0.34</td>
<td>0.39</td>
</tr>
</tbody>
</table>
High resolution spectra from the O 1s, C 1s, Ti 2p and Al 2p regions
High resolution spectra from the Ti 1p & Al 2p
High resolution spectra from the O 1s

<table>
<thead>
<tr>
<th>Compounds Found</th>
<th>Group name</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Carbon-Carbon &amp; Hydrocarbons bonds</td>
<td>530.7</td>
</tr>
<tr>
<td>Al₂O₃/O=C</td>
<td>aluminum oxide &amp; Carbonyl bonds</td>
<td>532.0</td>
</tr>
<tr>
<td>O-C/SiO₂</td>
<td>O-C bonds &amp; Silica</td>
<td>532.8</td>
</tr>
<tr>
<td>Atmos. O</td>
<td>atmospheric oxygen-containing compounds</td>
<td>534.0</td>
</tr>
<tr>
<td>H2O</td>
<td>Water molecules</td>
<td>534.5</td>
</tr>
</tbody>
</table>

- Increase in the TiO₂ component at 530.7 eV in the processed samples.
- Highly oxidized after laser processing
- Polyethylene bag stored sample: the water molecules content has decreased to zero after 1 month storage, exhibiting the highest SCA value.
After laser processing, C-C/C-H decrease in a significant manner.

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.

C-C and C-H bounds are non-polar and are related to the hydrophobicity of the material.

<table>
<thead>
<tr>
<th>Compounds found</th>
<th>Group name</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C/C-H</td>
<td>Carbon-Carbon &amp; Hydrocarbons bonds</td>
<td>286.1</td>
</tr>
<tr>
<td>C-O</td>
<td>Carbon-Oxygen bonds</td>
<td>287.8</td>
</tr>
<tr>
<td>C=O</td>
<td>Carbonyl bonds</td>
<td>289.3</td>
</tr>
<tr>
<td>O=C-O</td>
<td>Carboxyl bonds</td>
<td>290.1</td>
</tr>
</tbody>
</table>
Wettability modification of laser-fabricated hierarchical surface structures in Ti-6Al-4V titanium alloy

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\begin{abstract}
In the present work, a study of laser-based surface structuring of aerospace-grade titanium alloy (Ti-6Al-4V) with subsequent ageing by employing two different storage methods is undertaken. The titanium alloy samples were patterned using UV-Nd and IR-Nd pulsed lasers in a two-step process to fabricate bio-inspired hierarchical structures. The resulting surface structure consisted in regular periodic square-shaped micropillars covered by 810 nm-periodic LPSS. After the laser processing 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. The micro-structured surfaces were characterised by using confocal microscopy, scanning electron microscopy, static contact angle measurements and X-ray photoelectron spectroscopy.
\end{abstract}
Corrosion Resistance
(Preliminary Results)
Corrosion Measurements

In a typical polarization curve, better corrosion resistance surfaces present a lower corrosion rate, which correspond to:

- Higher corrosion potential $E_{corr}$
- Lower corrosion current density $I_{corr}$
Corrosion Measurements
SEM images after corrosion test
SEM images after corrosion test
Hierarchical Structures for corrosion tests
Hierarchical Structures for corrosion tests
**Conclusions**

- UV nanosecond pulsed direct laser writing (DLW) has been employed on a high strength titanium alloy (Ti-6Al-4V) in order to create periodic square micro-pillars.

- IR femtosecond pulsed direct laser writing (DLW) was used to generate low spatial frequency LIPSS on top of the nanosecond patterned structure to create a dual-scale structure.

- Two storage conditions, air and polyethylene bags, were used for keeping the samples after the laser process to evaluate the aging process of the samples.

- 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°.

- Hierarchical structures became hydrophobic and recorded a SCA value over 150°.

- For the dual-scale hierarchical structures, SCA values 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 XPS data show that, after 1 month of storage in a polyethylene bag, the contribution of the different polar carbon molecules 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.

- The XPS results suggest that the observed change in wettability can be attributed to a certain extend to the absences of carbon polar compounds, as well as H2O molecules, as they were not detected on the sample with the highest SCA.
Thank You For Your Attention!!!

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Young equation

$$\cos \theta_0 = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Wenzel equation

$$\cos \theta = R_f \cos \theta_0$$

$$R_f = \frac{A_{SL}}{A_F}$$

surface roughness factor, $R_f > 1$

$A_{SL}$ surface area

$A_F$ flat projected area