Direct Generation of Superhydrophobic Microstructures in Metals by UV Laser Sources in the Nanosecond Regime

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Generation of Modified Wettability Metallic Surfaces by Short Pulse Lasers

OUTLINE:

1. Introduction: The Search for Hydrophobic Surfaces
2. Basic Experimental Setup and Initial Results: Hydrophobicity Induced by Surface Patterning with Individual ns Laser Pulses
3. The Next Step: Extended Surfaces Patterning with ns Laser Generated Channels.
  - a) Effect of repetition rate / processing speed
  - b) Effect of hatch distance
4. Generation of Withstanding Superhydrophobic Surfaces with 2D-Micropillar Patterns
5. The Way for the Generation of Low Wettability and Bio-inspired Self-Cleaning Surfaces
6. Conclusions

INTRODUCTION.

§ The search for Hydrophobicity (1/3):

A. RANELLA et al.: Acta Biomaterialia, 6, 2711-2720 (2010)

INTRODUCTION (Cont.)

§ The search for Hydrophobicity (2/3):

$$S = \pi d^2 / 4L^2$$

M. McCARTHY et al.: Appl. Phys. Lett., 100, 263701 (2012)

INTRODUCTION (Cont.)

§ The search for Hydrophobicity (3/3):

A.M. KIETZIG et al.: *Langmuir*, 25, 4821–4827 (2009)

M. TANG et al.: *J. Laser Micro/Nanoeng.*, 6, 1-9 (2011)

EXPERIMENTAL SETUP (BASIC): THE IRRADIATION SYSTEM

Substrate	: Al
Thickness	: $> 50 \mu\text{m}$
Wavelength	: 355 nm
Laser Average Power	: 500 mW
Pulse duration	: 30 ns
Energy/pulse	: $\sim 2.50 \text{ mJ}$
Spot Diameter	: 10-20 μm
Fluence (Single pulse)	: 0.81-3.25 J/cm ²
Hatch distance	: 10-50 μm
Pulse Rep. Rate	: 25-250 kHz

**UV Radiation allows
smaller spot size !**

INITIAL RESULTS

Morphology / Microstructure

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Morphology / Microstructure

- For a given range of processing conditions, a microwall is formed above the metal surface. This contributes to coexistence of different length scales (**hierarchical microstructure**) and the creation of an **extra-structure allowing additional trapping of air**, thus improving the composite interface between the surface and the liquid which motivates **hydrophobicity**.
- This complex structured can be appropriately controlled in order to provide a range of surface wettability (**Contact Angle, CA**) properties.

INITIAL RESULTS

Wettability (Contact Angle, SCA)

- The SCA measurements were performed with 8-12 mL water droplets, showing a **high degree of repeatability**.
- A clear hydrophobic effect ($90^\circ \leq \text{SCA} \leq 150^\circ$) was introduced by the generated microstructure
- For the particular case envisaged, an **optimum value of SCA** was obtained around $P = 25 \text{ mm}$, reaching a maximum contact angle around 145° .
- The result was attributed to the variability of the degree of **hierarchical microstructure** generated under each parametric choice.

NEXT STEP: CHECK FOR REPRODUCIBILITY ON EXTENDED SURFACES

Generation of near-Superhydrophobic surfaces with 1D-microchannels

EXPERIMENTAL SETUP (I)

Study on the effect of Rep. Rate

Substrate	: Al, SS, Si
Thickness	: 100 μm
Wavelength	: 355 nm
Laser Average Power	: 500 mW
Pulse duration	: 30 ns
Energy/pulse	: 2.56 mJ
Spot Diameter	: 10 μm
Fluence (Single pulse)	: 3.25 J/cm ²
Hatch distance	: 20 μm
Pulse Rep. Rate	: 25-250 kHz

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RESULTS (I)

Morphology / Microstructure

RESULTS (I)

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RESULTS (I)

Morphology / Microstructure

RESULTS (I)

Analysis of Channel depth vs. Rep. Rate

EXPERIMENTAL SETUP (II)

Study on the effect of Hatch distance

Substrate	: Al
Thickness	: 100 μm
Wavelength	: 355 nm
Laser Average Power	: 500 mW
Pulse duration	: 30 ns
Energy/pulse	: 2.56 mJ
Spot Diameter	: 15 μm
Fluence (Single pulse)	: 2,83 J/cm ²
Pulse Rep. Rate	: 100 kHz
Hatch distance	: 10-25 μm

**UV Radiation allows
smaller spot size !**

RESULTS (II)

Analysis of Channel depth vs. hatch distance

$\varnothing=15 \mu\text{m}$

$F=2,83 \text{ J/cm}^2$

$f=100 \text{ kHz}$

$d=10\text{-}25 \mu\text{m}$

A: $d=10 \text{ mm}$

B: $d=15 \text{ mm}$

C: $d=20 \text{ mm}$

D: $d=25 \text{ mm}$

RESULTS (II)

Analysis of Static CA vs. hatch distance

PARTIAL CONCLUSIONS

- High degree of hydrophobicity (near-superhydrophobicity) on different materials (Silicon, pure aluminum and AISI 304 Stainless Steel) plates has been achieved **in a single processing step** by means of ns lasers working at **UV wavelengths** and with final applied energies in the range of 100-150 J/cm² and instant energy densities in the range of 10⁸-10⁹ W/cm². Better, stable superhydrophobic properties can be achieved by means of 1D-microchannel patterning.
- The desired hydrophobicity has been achieved by means of the generation of complex microstructures consisting of mixed micro-nano channels and interspacing walls resulting from laser ablation and melting/recast approaching **near-hierarchical** surface structure patterns.
- The obtained degree of hydrophobicity has been observed to critically depend in a first term on the pulse overlapping pitch applied to the surface. Optimum values of **contact angle (SCA) close to superhydrophobicity** have been achieved with particular choices of pulse overlapping pitches achievable by means of the high accuracy provided by the used lasers (working in the UV) .
- The key parameter of final micro-channel depth has been analyzed for different processing speeds/repetition rates, a clear **deleterious effect** having being observed for processing speeds **beyond a critical value** (around 100 kHz repetition rate / 25-40 mm/s linear process speed) for the three kinds of materials analyzed).
- Additionally, the obtained degree of hydrophobicity has been observed to depend critically on the hatch distance (distance between successive parallel 1D tracks), the existence of a **threshold value** drastically changing the **wettability character** of the treated surface having been found.

THE DEFINITIVE APPROACH: THE GENERATION OF mCELL PATTERNING

Generation of Withstanding Superhydrophobic Surfaces with 2D-Micropillar Patterns

EXPERIMENTAL SETUP (III)

Study on the effect of Hatch distance

Substrate	: Al
Thickness	: 100 μm
Wavelength	: 355 nm
Laser Average Power	: 500 mW
Pulse duration	: 30 ns
Energy/pulse	: 2.56 mJ
Spot Diameter	: 15 μm
Fluence (Single pulse)	: 2,83 J/cm ²
Pulse Rep. Rate	: 100 kHz
Hatch distance	: 10-25 μm

**UV Radiation allows
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RESULTS (III)

Comparison of CA for μ Channels and μ Pillars

$\varnothing=15 \mu m$

$F=2,83 \text{ J/cm}^2$

$f=100 \text{ kHz}$

$d=10-25 \mu m$

A: $d=10 \text{ mm}$

B: $d=15 \text{ mm}$

C: $d=20 \text{ mm}$

D: $d=25 \text{ mm}$

RESULTS (III)

mCells: The Key Feature for High Degree of Hydrophobicity

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mCells: The Key Feature for High Degree of Hydrophobicity

Table 1
Open circuit potential measurements and SCA.

	OCP (V)	Contact angle ($^\circ$)
Bare aluminum	-0.754	85 ± 3
P = 15 μm	-0.704	168
P = 20 μm	-0.695	180
P = 25 μm	-0.704	160

Table 2
Parameters extracted from cyclic polarization curves.

	E_{corr} (V)	I_{corr} ($nA\ cm^{-2}$)	Corrosion rate ($\mu m/year$)
Bare Aluminum	-0.753	215.3	1.867
15 HD	-0.781	14.4	0.166
20 HD	-0.810	11.3	0.124
25 HD	-0.747	82.4	0.918

L. Ruiz de Lara et al.: Materials Letters, 184 (2016), 100–103.

DISCUSSION: THE WAY FOR LOW WETTABILITY SURFACES

R. Jagdheesh et al.: J. Mater. Chem. A, 5 (2017), 7125–7136.

DISCUSSION: THE WAY FOR LOW WETTABILITY SURFACES

R. Jagdheesh et al.: J. Mater. Chem. A, 5 (2017), 7125–7136.

DISCUSSION: THE WAY FOR BIOINSPIRED LOW WETTABILITY SELF-CLEANING SURFACES

R. Jagdheesh et al.: RSC Adv., 6 (2016), 72933–72941

FINAL CONCLUSIONS

- The application of nanosecond laser pulses on flat surfaces of aluminium (Al) in a **one-step process** leading to the generation of **extended areas** of stable **superhydrophobic behaviour** has been reported.
- Both laser generated periodic structures consisting in **laser channels and laser pillars** have been successfully developed with the aid of a **30 ns** pulse, 100 kHz repetition rate and 300 mW average power laser emitting at $\lambda = 355 \text{ nm}$ working at selected focus diameter and scan speed for different hatch distance values. The resulting micropatterns were evaluated by scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) in order to make apparent the material/geometrical parameters of the generated structures and a direct measurement of static contact angle (SCA) was performed in order to evaluate the wettability of the generated surface.
- A conceptually relevant methodology has been defined for the **systematic generation of hierarchical-like micro/nano-structures** fulfilling the conditions for the generation of superhydrophobic surfaces through the generation of **m-cells** able to serve as air trapping structures responsible for a substantially inhibited wettability of the substrate.
- This development, in its road to industrial implementation, is now considered as the basis for the systematic **single-step generation of large scale extended surfaces with adjusted wettability** properties as required by the different kinds of self-cleaning applications. Undoubtedly, the demonstrated possibility of **use of ns lasers** with their present day industrial robustness and their amenability to processing workstations with high throughput properties will contribute to the industrial implementation of the described developments.

ACKNOWLEDGEMENTS

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*Thank you very much
for your attention!*

MICROMANUFACTURING EXPERIMENTAL SETUP AT CLUPM