Wetting behavior of laser-structured metallic surfaces for potential use in offset lithography

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Abstract

The aim of this work is to generate two extreme wetting states on metallic surfaces by means of laser structuring/treatment and to examine the physical and chemical processes behind it. For this purpose, four different metallic samples were laser-structured and then stored in atmospheric air and examined at certain time intervals using contact angle measurement. Immediately after laser structuring, the samples have shown a superhydrophilic wetting behavior, which then changes to the opposite after 10 days at the latest and exhibit superhydrophobic wetting behavior. The samples were then subjected to a second laser treatment to produce extreme wetting behavior, similar to those of a conventional printing plate. Additionally, the topology of the samples as well as an XPS analysis was carried out. It could be shown that wetting properties for possible use in offset printing can be achieved by laser structuring and that a multiple modification of the wetting properties is possible.

Keywords: aluminum, superhydrophobic, superhydrophilic, XPS

1. Introduction and background

Offset lithography is a flat printing process and it is so called because the printing plate used contains printing and non-printing areas virtually on one level (Kipphan, 2000). The printing plate is traditionally built up in a physical-chemical layering process. High-purity aluminum (99.9%) is used as the base, which is then roughened electrochemically to create a very thin and highly porous aluminum oxide layer. This layer in turn is then coated with a light sensitive polymer, which can be selectively removed during the imaging process (Aull, 2001). Figure 1 shows the different layers of a conventional printing plate schematically (left) and a scanning electron microscope (SEM) image of a polymer drop and the aluminum oxide layer with corresponding wetting behavior (right). The approximately 1 µm thin polymer layer displays a hydrophobic wetting character and the about 0.3 µm thin aluminum oxide layer on the other hand behaves hydrophilic. These physical-chemical and surface-energetic conditions are used to apply the two process fluids, printing ink and dampening solution, to the printing plate in a targeted manner (Schmitt, 2007).

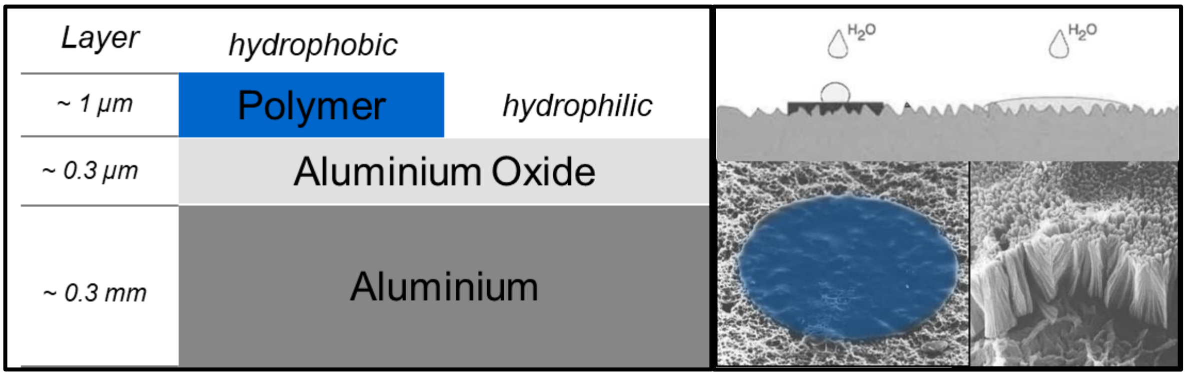

Figure 1: Schematic layout of a conventional printing plate (left) and REM recording of polymer dot and aluminum oxide with corresponding wetting behavior (right) (Kipphan, 2000), edited

In the printing process, firstly, the entire surface of the printing plate is wetted with dampening solution. A fine dampening solution film forms on the non-printing areas and a droplet-like wetting takes place on the printing areas. The printing ink is then applied, which only adheres to the printing areas due to their surface energy properties. On the non-printing areas, the fountain solution film prevents the ink from wetting. In particular, splitting takes place in the dampening solution film, which is why there must always be a certain minimal amount of dampening solution on the printing plate. (MacPhee, 1998)
Nowadays, precisely these different physical-chemical conditions can be achieved on one level and directly next to each other using a simplified process: Laser surface structuring. This technology has developed considerably in recent years and decades, so that structures up to nanometer in size can be created on surfaces, in this case especially on metallic surfaces. There is a consensus within the research groups that shortly after laser structuring of pure aluminum, the processed surface assumes superhydrophilic (contact angle <10°) wetting behavior (Milles *et al.*, 2021), (Nishimoto *et al.*, 2009) and (Hauschwitz *et al.*, 2020), just to name a few. It has also been confirmed that after an aging period of several days only in air, the wetting behavior of the surface change to the opposite and became superhydrophobic (contact angle > 160°) (Dongre *et al.*, 2021). Since a topographical change in the surface is very unlikely, a change in the surface chemistry is propagated. One research group was able to determine an absorption of organic hydrocarbons from the air, which led to the formation of carboxylates and therefore to the change of wetting behavior. However, there is still debate in the field of surface chemistry. (Yalishev *et al.*, 2021)
The aim of this work is to use this modern surface structuring by laser to create a new and more ecological offset printing plate, which in the best case can be rewritable, in other words reusable. Our previous work (Knödl *et al.,* 2023) presented the laser-structuring of pure aluminum surfaces with chemical additives in an extensive post-treatment to achieve superhydrophobicity and their fluid-technical and surface-energetic investigation. In this follow-up work, the laser surface structuring is to be further optimized, surfaces with different wetting behavior on one level and next to each other are to be created and their wetting behavior is to be investigated. An XPS analysis (X-ray photoelectron spectroscopy) of the surface-structured aluminum sample is also carried out and an insight on the impact of additional laser treatment on topography and wetting behavior is shown.

2. Materials and methods

2.1 Procedure for laser-structuring of metallic samples

For fabrication of the laser-structured metallic samples a nanosecond fiber laser *F-9020* (KBA, Germany) was used, which has a wavelength of 1062 nm, a spot diameter of 53 µm, a range of frequency from 20 to 80 kHz, a max. laser power of 20 W, a focal length of 200 mm and a work area of 100 mm x 100 mm. Laser parameters were optimized from previous work and are shown in Table 1.

Table 1: Parameters for fabrication of laser-structured metallic samples

Parameter	Value
Hatching distance	50 µm
Laser scan speed	2000 mm/s
Laser power	15 W
Frequency	34.5 kHz
Resolution	40 lines/mm
Hatching strategy	Cross-pattern with two passes

A total of four samples were prepared: Pure aluminum (99,9 % Al) with a material thickness of 0.3 mm and AlMg3, anodized AlMg1 and stainless steel 1.4301 with a material thickness of 1 mm was used for sample fabrication. A surface of 90 mm x 90 mm was laser-structured for each material. This area was divided into 9 x 9 fields so that three contact angle measurements could be carried out per day (day 0, 1, 2, 3, 4, 6, 8, 11, 13, 15). The samples were stored in atmospheric air at a temperature of 21 °C ± 1 °C and a relative humidity of 40 % ± 5 %. Figure 2 shows the four laser-structured samples. The three left columns were used for water, the three middle columns for diiodo-methane and the right three columns for water as control element, because they were not laser-structured.

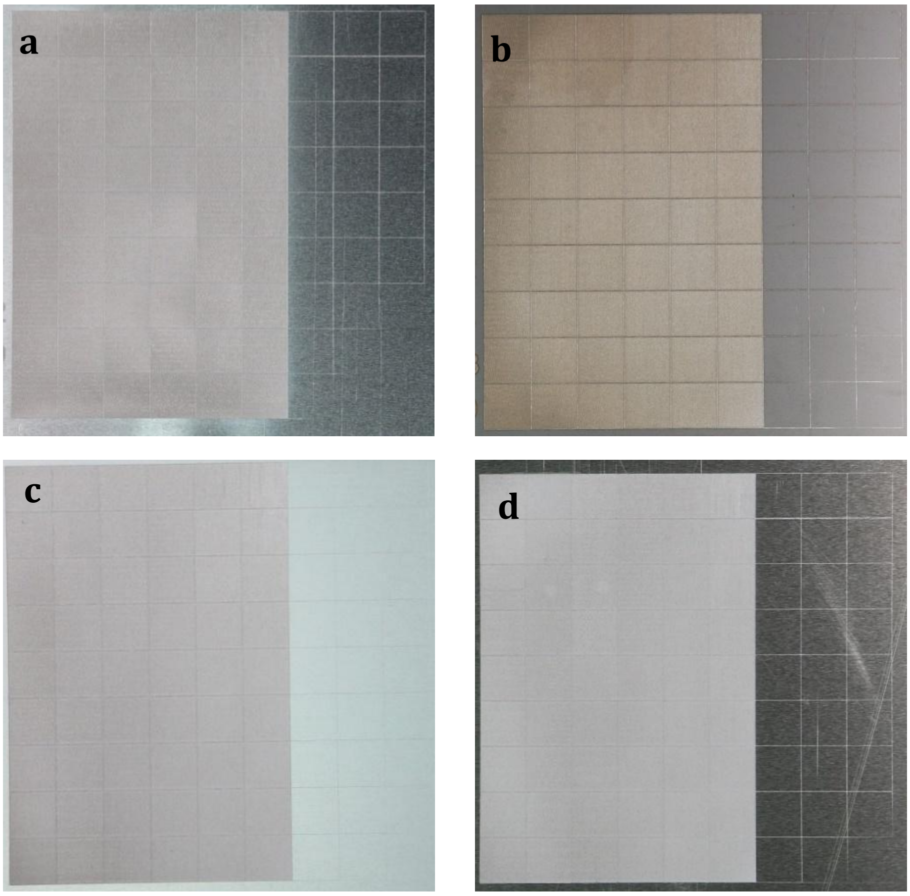

Figure 2: Images of metallic samples: a) pure aluminum, b) stainless steel 1.4301, c) anodized AlMg1, d) AlMg3

2.2 Contact angle measurements

DSA 100 (Krüss, Germany) was used for contact angle measurement of test fluids on the laser-structured metallic samples. Test fluids were water and diiodomethane which were dispensed from the automatic dosing unit of the machine. The surface tension (SFT) for these fluids with disperse and polar fractions are shown in Table 2. All drops had a volume of 2 µl and were applied by the sessile drop method. Interpolation algorithms to determine the contact angles were *tangent* (contact angle of 20° to 180°) for hydrophobic wetting and *circle* (contact angle of 0° to 20°) for hydrophilic wetting. All tests for contact angle measurement were performed at a temperature of 21 °C ± 1 °C and a relative humidity of 40 % ± 5 %.

Table 2: The SFT of the two test liquids including disperse and polar parts at 20°C (Ström, Fredriksson and Stenius, 1987)

SFT in mN/m	SFT (total)	SFT (disperse)	SFT (polar)
Water	72.80	21.80	51.00
Diiodo-methane	50.80	50.80	0.00

2.3 Microscopic confocal measurements and XPS analysis

The confocal profilometer *PLu Neox* (Sensofar, Spain) was used for topographical examination of the laser-structured samples. For the characterization of the laser-structured aluminum samples, the best results were obtained with the following settings: DI 20X lens (VSI), threshold 5 % and light 5.5 %.
The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a *Phi Versaprobe 5000* (Physical Electronics, USA). A 10 mm x 5 mm laser-structured sample (pure aluminum), which had been stored in air for 15 days, and a sample (also 10 mm x 5 mm) timely after laser structuring (12 h after) were analyzed.

2.4 Differentiation in superhydrophilic and superhydrophobic areas

For the sake of simplicity only one of the previously discussed laser-structured materials, in this case pure aluminum, was treated again with the same laser source after the material showed superhydrophobic wetting behavior after 15 days. The laser power and scanning speed parameters were varied. The aim was to find a laser power that is so low that the topology of the sample surface no longer changes, but that causes a reset of the surface chemistry and therefore causes superhydrophilicity again. For this purpose, the laser power was examined from 11 W to 5 W in 2 W steps and additionally the laser scanning speed was 2000, 4000, 6000 and 8000 mm/s, respectively.

3. Results and discussion

3.1 Measurement of contact angles over time and confocal microscopy

As previously mentioned, a contact angle measurement was carried out over a timespan of several days to determine the change in wetting behavior. The four materials are summarized in Figure 3. Immediately after laser structuring, all samples showed absolute hydrophilicity, as both test fluids are apparently absorbed by the surface and no contact angle could be measured. After 11 days at the latest, all samples achieved superhydrophobic wetting behavior. This change in wetting behavior begins in the first few days after laser structuring. It can also be seen that stainless steel and AlMg1 do not cause any change in the contact angle with respect to the test fluid diiodo-methane, in contrast to pure aluminum and AlMg3. The water control moves around the 100° contact angle for all samples and does not change noticeably over time. Figure 3 d) additionally shows photos of drops on the surface of the laser-structured AlMg3 for the corresponding days. The reason for this change in wettability is discussed in one of the next sections. For this purpose, one sample was subjected to an XPS analysis. The initial superhydrophilicity can be explained by the formation of aluminum oxides. These oxides are very hydrophilic by nature, but the periodically rough surface also plays a role, which is discussed below.

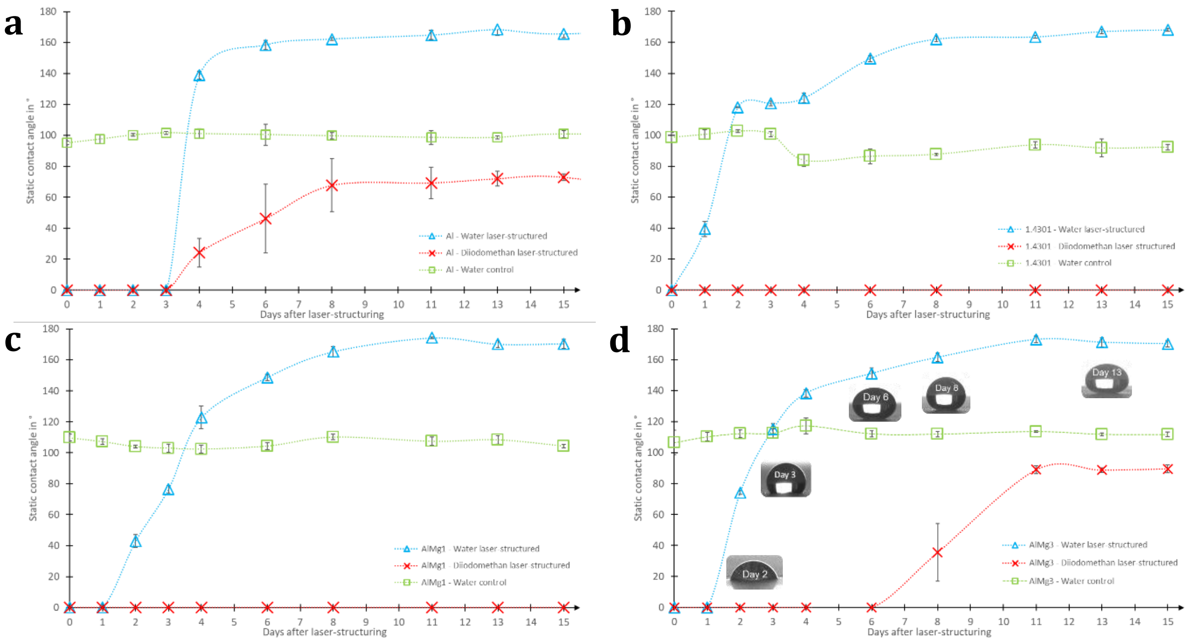

Figure 3: Contact angle measurements over time for a) pure aluminum, b) stainless steel 1.4301, c) AlMg1 and d) AlMg3

Examination with the confocal microscope revealed the results shown in Figure 4. The topography of the surface of the individual samples looks very similar. The distances between the individual laser pulses are approx. 50 µm horizontally and vertically and the spot size is also approx. 50 µm.

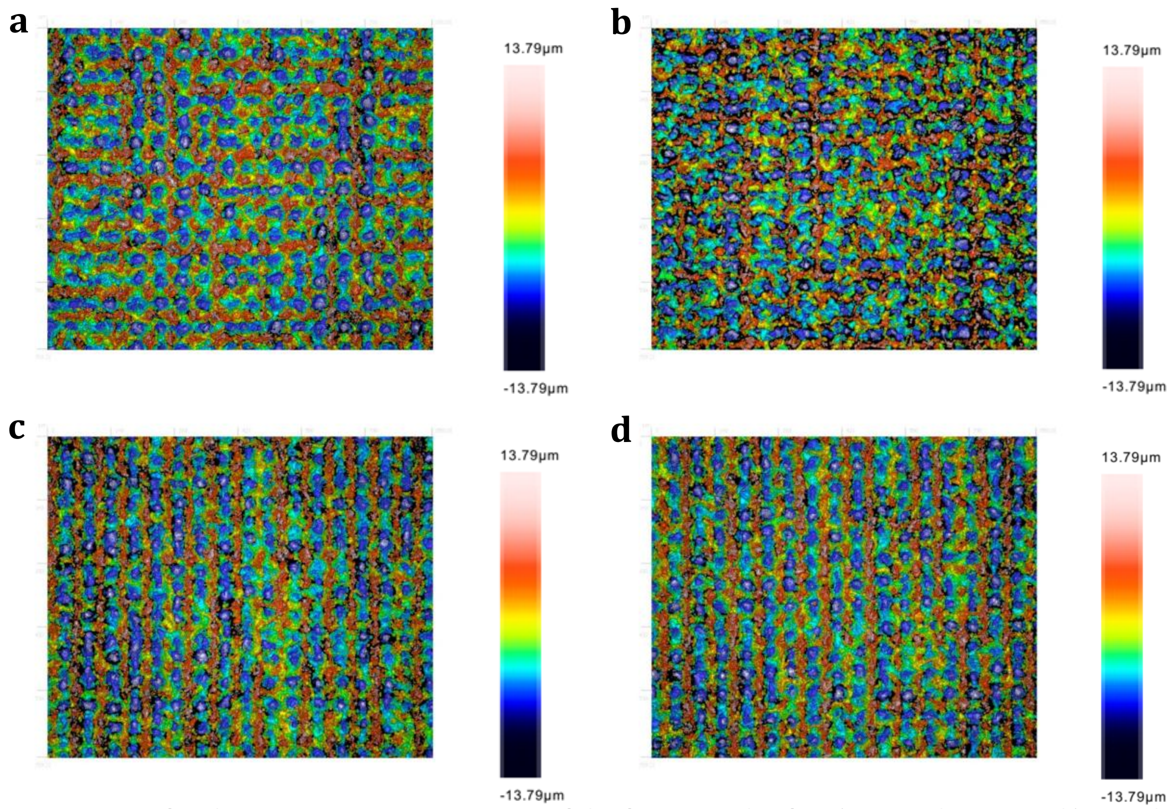

Figure 4: Confocal microscopy measurement of the four samples for a) pure aluminum, b) stainless steel 1.4301, c) AlMg1 and d) AlMg3

Table 3 lists selected roughness values with standard deviations of the individual. The number of surfaces (surface area: 850 µm x 709 µm) examined per sample was 3. It can be clearly seen that the roughness values of the individual samples are very close to each other. The following applies to aluminum and aluminum-magnesium alloys: the maximum height differences S_z are approx. 33 µm, the mean arithmetic height S_a is approx. 3.4 µm and the mean square height S_q is approx. 4.3 µm. It can therefore be said that good reproducibility of the topography could be achieved on aluminum and aluminum alloy materials with the same laser parameters. The stainless steel sample has slightly reduced roughness values, which indicates that it is more difficult for the laser to process this material.

Table 3: Surface roughness data (S_a, S_q, S_z) and corresponding standard deviation of laser-structured samples

Sample	S_a in µm	S_q in µm	S_z in µm
a) Pure aluminum	3.03 ± 0.39	4.11 ± 0.48	31.81 ± 2.56
b) Stainless steel 1.4301	1.75 ± 0.05	2.17 ± 0.06	17.90 ± 0.54
c) AlMg1	3.34 ± 0.02	4.16 ± 0.04	33.71 ± 1.09
d) AlMg3	3.60 ± 0.08	4.48 ± 0.07	34.12 ± 1.79

3.2 Results of 2nd laser treatment with dosed intensity

A second laser treatment should take place over the now superhydrophobic firstly laser-structured surface so that two opposing wetting behaviors can prevail on one surface. Figure 5 shows the pure aluminum sample with the additional laser treatment.

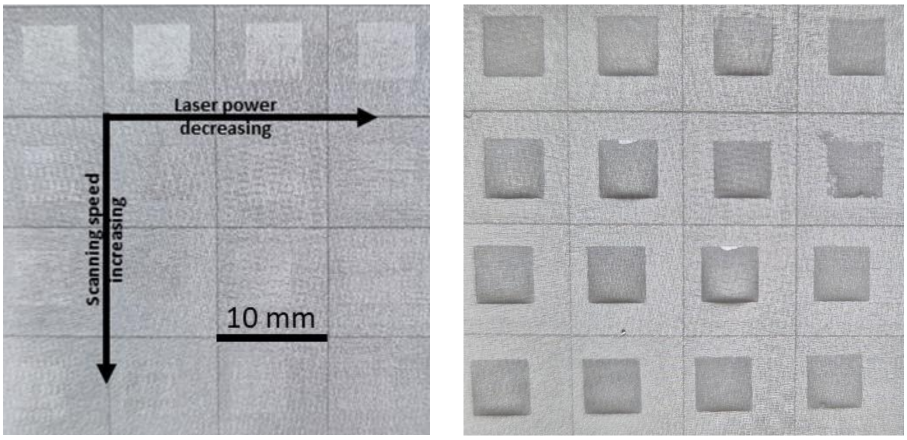

Figure 5: Image of 2nd laser treatment of pure aluminum with varying scanning speed and laser power (left) and water wetted surface (right)

As the laser power decreases and the laser scanning speed increases, the subsequently treated surface is almost indistinguishable to the naked eye. Also, it can be clearly seen that the water-wetted surface only accepts water in the areas that have undergone the second laser treatment. For a detailed examination of the surface structure, the samples were again examined with the confocal microscope. The Results can be seen in Figure 6. A visual comparison of the surface topologies (surface area: 850 µm x 709 µm) shows no major differences. However, the comparison with Fig. 4 (a) shows that a certain irregularity can be seen on the sample surfaces which have undergone second laser treatment.

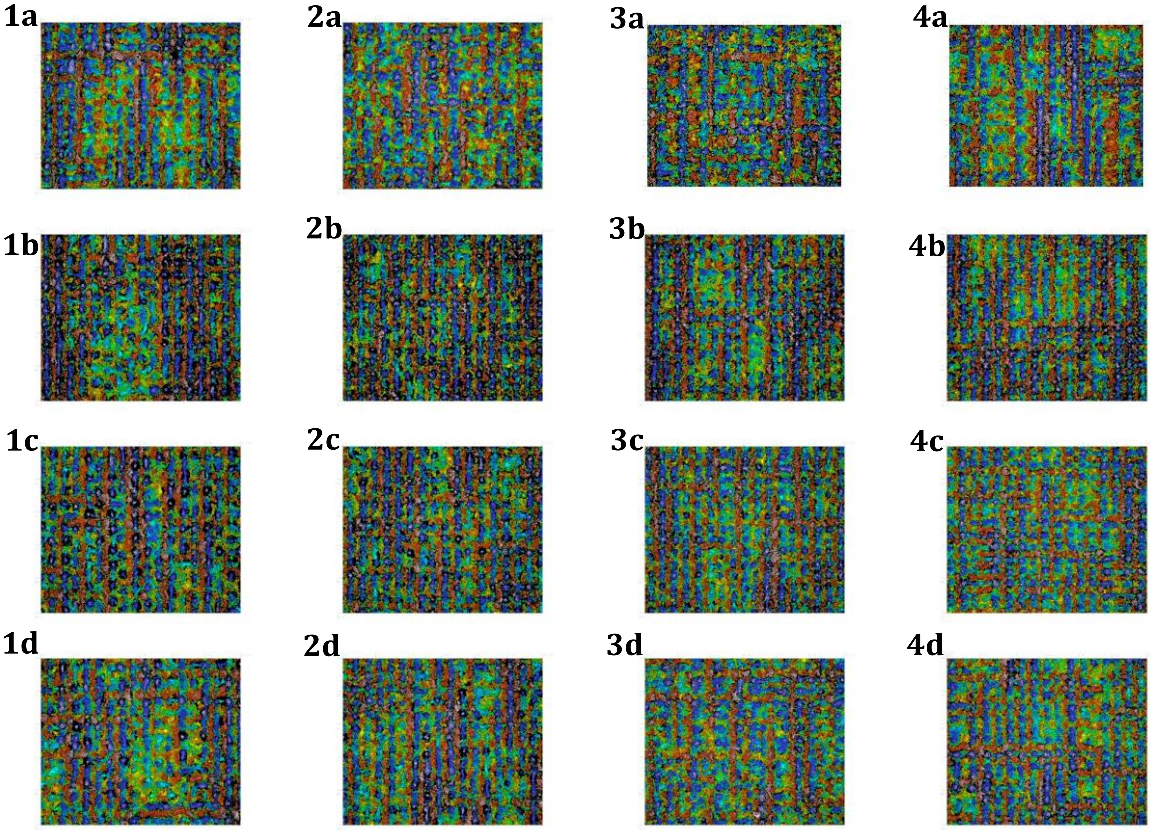

Figure 6: Overview of the surface topology after 2nd laser treatment; parameter variation corresponding to fig. 5 and table 4

Unfortunately, contrary to our expectations, no clear trend in the parameters for surface roughness can be identified within the variations from Table 4, but a comparison with the values from Table 3 a) (pure aluminum) shows that the roughness values are around two to four times higher. Unfortunately, this indicates a change in the surface topology by second laser treatment. Further tests should be carried out to show to what extent these topology changes will influence re-writability of the metallic surfaces to reuse them.

Table 4: Surface roughness data of the variations of the 2nd laser treatment

Variation	S_a in µm	S_q in µm	S_z in µm
1a) 2000 mm/s – 11 W	6.64	8.49	61.22
2a) 2000 mm/s – 9 W	5.28	6.75	58.08
3a) 2000 mm/s – 7 W	7.29	9.10	58.07
4a) 2000 mm/s – 5 W	8.14	10.54	91.17
1b) 4000 mm/s – 11 W	10.40	12.70	83.21
2b) 4000 mm/s – 9 W	12.18	14.53	85.09
3b) 4000 mm/s – 7 W	12.84	15.89	105.08
4b) 4000 mm/s – 5 W	13.24	16.05	108.04
1c) 6000 mm/s – 11 W	10.55	12.98	90.69
2c) 6000 mm/s – 9 W	12.93	15.43	89.53
3c) 6000 mm/s – 7 W	9.06	11.65	83.13
4c) 6000 mm/s – 5 W	7.86	9.91	77.59
1d) 8000 mm/s – 11 W	9.35	11.70	104.97
2d) 8000 mm/s – 9 W	10.25	12.80	88.10
3d) 8000 mm/s – 7 W	7.55	9.68	95.96
4d) 8000 mm/s – 5 W	8.64	10.77	77.99

3.3 Results of XPS-analysis of pure aluminum

For the XPS-analysis a freshly laser-structured sample and a sample stored for 30 days were investigated. Figure 7 shows the spectrum of the binding energy of the two samples. When comparing the graphs, the intensities for oxygen (O KLL and O 1s) and aluminum (Al 2s and Al 2p) are higher for the freshly laser-structured sample, but lower for carbon (C 1s). This indicates a higher number of oxides in the freshly laser-structured sample. Storage at atmospheric air apparently degraded these oxides and enriched carbons, which would explain the change in wettability. Other research groups had comparable findings with XPS-analysis (Hauschwitz *et al.*, 2020), (Cardoso *et al.*, 2017).

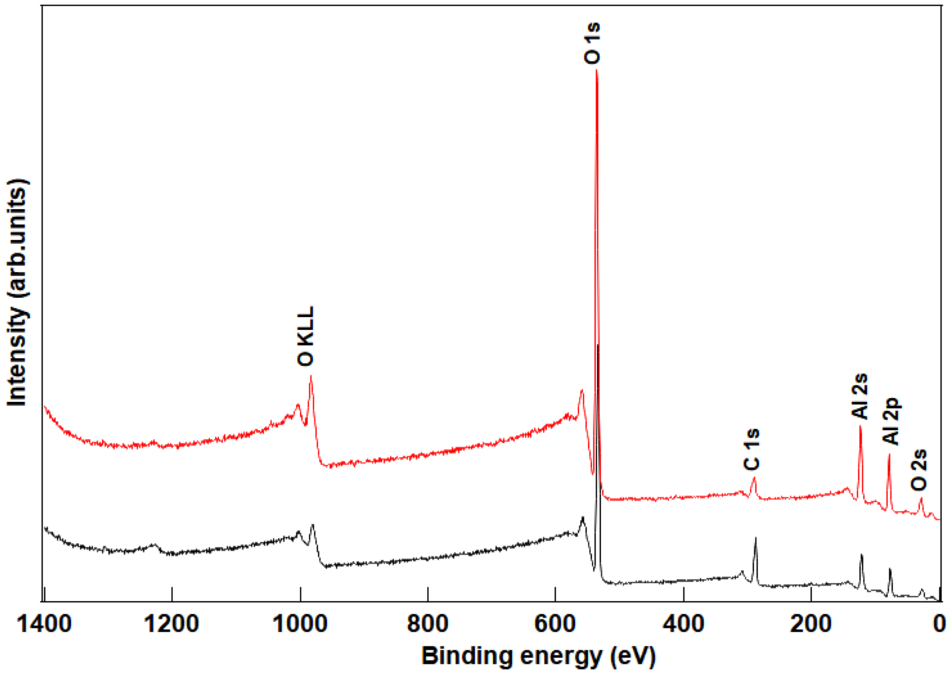

Figure 7: Intensity vs. binding energy of freshly laser-structured Al-sample (red) and 30 days stored laser-structured Al-sample (black)

4. Conclusion

This study demonstrates that laser structuring of metallic surfaces can effectively induce extreme wetting behaviors, transitioning from superhydrophilicity to superhydrophobicity over time. The results confirm that immediately after laser treatment, all tested materials exhibit superhydrophilic behavior, which reverses to superhydrophobicity within approximately 10–15 days due to surface chemistry modifications, likely involving organic hydrocarbon adsorption. Furthermore, XPS analysis supports the hypothesis that oxidation and carbon enrichment play a crucial role in this transition.

A second laser treatment was explored to selectively revert superhydrophobic areas back to a hydrophilic state, with the goal of creating rewritable offset printing plates. While successful in altering wetting properties, the process also introduced topographical changes, suggesting the need for further optimization to ensure surface stability and reusability.

Overall, this research highlights the potential of laser structuring for ecological and sustainable printing applications by eliminating the need for chemical coatings and enabling reusability. Future work will focus on refining laser parameters to minimize unintended topographical changes and enhance long-term stability of the wetting properties paving the way for more practical and commercially viable applications in offset lithography. In addition, wetting tests will be carried out with the process fluids printing ink and dampening solution of the offset lithography process and the resolution capacity of superhydrophilic and superhydrophobic areas on the surface will be investigated.

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