Pulsed laser modification of Al2O3 ceramics to controlling the surface wettability

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Abstract. In this paper nanosecond direct laser structuring was investigated for the surface modification of Al2O3 ceramic. A theoretical calculation of the roughness index was carried out according to the Cassie-Baxter model for three different patterns formed on the ceramic surface. The relationship between the assumed area of contact of a water drop with the surface of the material and the contact angle of wetting was investigated. This study shows that surface topography is not the only key factor responsible for surface wettability during nanosecond direct laser structuring.

1. Introduction

Laser processing, surface modification often refers to the modification of the surface topography by laser radiation, such as laser structuring, or laser texturing.

Changing surface properties using laser radiation is widely used in many fields of science and technology, including change in bacterial adhesion [1], manufacture of self-cleaning surfaces [2] and improve the tribological properties [3] of metals, polymers and ceramics. In recent years, researchers began to artificially design surfaces from different materials, controlling the surface wettability. Surface morphology plays a main role in the wettability of materials. The main factors that affect wettability are surface topography and its chemical composition [4]. Ceramics are very important for researchers, especially ceramics based on Al2O3, because they are biocompatible, have high thermal stability and high strength, and are also an affordable and cheap material.

The ablation mechanism is used to structure ceramics by laser radiation. When ablation, the material under the action of high energy in the laser pulse instantly evaporates, forming a hole around the evaporation zone [5].

So, in work [6] Kunz formed laser-induced periodic surface structures (LIPSS) using a femtosecond laser on the surface of a ceramic composite Al2O3. LIPSS were selectively fabricated on the metallic phase of the Al2O3-nZrO2-Nb composite using fs laser pulses. As a result, the contact angle (CA) of the composite surface with water was reduced from 68.4 ° for untreated samples to 40.9 ° for structured samples. Selectively structured composites with periodic geometry and controlled wettability are of particular interest for numerous biomedical and tribological applications.

In [7], Triantafyllidis processed the surface of a ceramic using a CO2 laser with a power of 1.3 kW. A laser was used to melt, followed by solidification of oxide ceramics. This process changed the surface roughness, due to which the contact angle of wetting changed. In this case, the smooth surfaces obtained
did not contribute to wetting, and those on which cracks originated made it possible to strongly wet the material. So, for example, it was found that with an increase in roughness, the contact angle of wettability decreases. At the same time, in this work, it was not possible to increase the wettability angle after laser treatment.

In [8], direct laser texturing with a picosecond laser was used to change the surface wettability. Textures were made in the form of micro-holes and micro-pillars. The results show that micro-reliefs or geometries created by laser treatment play a major role, rather than chemical changes induced at the surface, to increase the degree of hydrophobicity. Laser treated micropillars showed a superhydrophobic surface with CA measurement of 150° ± 3.

Nevertheless, the structuring of materials by nanosecond pulses is also important. So in work [9] the structuring of the surface of stainless steel 316L was carried out with a nanosecond pulsed laser. Moreover, a theoretical calculation was carried out in this work, which makes it possible to predict the contact angle after laser treatment.

In [10], the microstructuring of the ceramic surface with a nanosecond pulsed laser was carried out; as a result, it was shown that pulsed nanosecond laser radiation allows processing of alumina ceramics. In this case, the width and depth of the craters are influenced by both the pulse energy and the number of pulses at one point to the crater depth.

In this work, a study was carried out on the effect of surface topography on the wettability of Al₂O₃ ceramics using direct laser structuring by nanosecond pulsed laser radiation. There are three different strategies for the formation of surface topography that are considered, and the contact angles of wetting are measured by the standing drop method.

2. Materials and methods

Al₂O₃ ceramic specimens with 99.6% of purity are used in this study. Specimens has a dimension of 40x60x0.5 mm. The surface was cleaned from contamination by propanone before and after laser treatment.

A solid-state Nd: YVO₄ laser with second harmonic generation and a galvanic scanning system was used for this experiment (Figure 1). Central emission wavelength 532 nm. The nominal output average power of 10 W, the maximum pulse repetition rate is 200 kHz. At a frequency of 50 kHz, the pulse duration is 20 ns with a pulse energy of 250 μJ. A f-theta lens with a focal length of F = 160 mm was used to focus laser radiation.

![Figure 1. experimental setup. 1 – case, 2 – laser system operating, 3 – solid-state Nd:YVO₄ laser, 4 – chiller.](image-url)

A water drop was applied to the treated surface for measurement the contact angle of wetting. Photos were taken with a digital microscope and the angle was measured by the tangential method. The shape of the drop is represented as part of the contour of the assumed circle. If determine the centre of the assumed circle then the contact angle is the angle between the tangent and this circle [11]. The droplet
volume was 8 μL of deionized water. Table with micro screw was used for height adjustment. The measurement scheme is shown in Figure 2

![Figure 2. Measurement scheme. 1 – digital camera, 2 – microscope, 3 – table with micro screw, 4 – specimen, 5 – water drop.](image)

3. Surface wettability models

To determine the dependence of the surface properties on the shape of microstructure were created 3 types of patterns using laser radiation: ‘columns’, ‘pits’, ‘peaks’. The schematic diagram of structures is shown in figure 3.

![Figure 3. Schematic diagram of surface topography. The laser treated area is indicated in black, untreated area is indicate in white.](image)

While creating a column-type structure, the laser beam passing sequentially along the surface in two perpendicular directions. During surface treatment to create a “pit” structure, periodic recesses were created by a coherent set of laser pulses. For a pit-type structure, there are 100 pulses for each recess. The “peak” structure was created by pulsed laser beam passing in parallel directions along the processing surface (the laser beam passed the whole processing surface, then repeated iteration was performed along the same trajectory of the same surface).
To determine the dependence of the hydrophobic properties of the surface on the parameters of the applied patterns, the period of the structure was changed, specifically, the distance between parallel lines of laser beam transmission or the distance between pulses for “pits” and “peaks”. The variable distance for each type of treatment is indicated in Figure 3 as $\Delta l$.

Two models describing hydrophobic surfaces were taken as a basis: Wenzel and Cassie-Baxter. Figure 4 shows surface wetting patterns. Both models are based on the idea of minimizing the surface energy at the phase separation.

In Young's [12] model, the contact angle of water droplet wetting depends on the surface energy at the boundary:

$$\cos \theta_Y = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}}$$

where $\gamma_{sv}$ - is the surface energy on the solid-gas boundary, $\gamma_{ls}$ - on the liquid-solid boundary, $\gamma_{lv}$ - on the liquid-gas boundary.

In the Wenzel model [12], a droplet of water will flow around all irregularities. The contact area of the droplet with the surface will change accordingly. In a steady state, the contact angle can be described by the Wenzel’s relationship:

$$\cos \theta_W = r \cos \theta_Y$$

where $\theta_Y$ - is the angle calculated from Young's ratio for the same substance, but with a perfectly flat surface. The factor $r$ is the surface roughness, which is defined as the ratio:

$$r = \frac{S_{re}}{S_0}$$

where $S_{re}$ - actual surface area, $S_0$ - projection of this surface on the horizontal plane.

In the Cassie-Baxter model [13], a droplet of water remains on the surface, while air traps in the roughness. The droplet ends up on an air cushion. The value of free energy, as in the case of the Wenzel state, does not coincide with the value for an ideal surface, therefore, the value of the contact angle will change. Based on the relations for free energies, the Cassie-Baxter relation was deduced:

$$\cos \theta_{CB} = f \cos \theta_Y - (1 - f)$$

where $\theta_Y$ - is the contact angle for an ideal surface, which can be calculated from Young's relation for the same substance, $f$ - is the part of the solid surface on which the particle is in a stable Cassie-Baxter state.[14]

In this paper, we considered the wettability model according to the Cassie-Baxter model. Unfortunately, we didn’t consider the Wenzel model because our calculation led to the value $\cos \theta_W > 1$. We suppose that Wenzel model it's necessary account additional factors of surface roughness.

Let us consider the expressions for calculating the dependence of the contact angle $\theta$ on $\Delta l$ for “columns” structure for the stable Cassie-Baxter states.

For the Cassie-Baxter state was gotten $f_p$ relationship, based on the geometric structure, expressed via variable $\Delta l$:
where \( d_b \) is the diameter of laser beam.

For the structure of the pit type for the Cassie-Baxter state, the following relation was derived:

\[
f_{pit} = \frac{4\Delta l^2 - \pi d_b^2}{4\Delta l^2}
\]

Additionally, the calculation was made for the structure of the “peak” type for the Cassie-Baxter state. It is worth noting, that at a distance \( \Delta l \) equal to the beam width \( d_b \) “peaks” structure actually transforms into a “pit” structure. A form for \( f_p \) was obtained from the following relations:

\[
f_p = \frac{\Delta l^2 - S_x}{\Delta l^2}
\]

Where

\[
S_x = \frac{\pi d_b^2}{4} - 8 \left( \frac{\pi d_b \alpha}{4 \times 360} - \frac{d_b \Delta l \sin \alpha}{4 \alpha} \right)
\]

And

\[
\alpha = \alpha \cos \frac{\Delta l}{d_b}
\]

The above expressions were obtained derived from the projection of the geometry being created, a schematic representation is shown in Figure 5

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**Figure 5.** Schematic image of the surface projection for the "peaks" type structure.

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To determine the Young contact angle, the angle was measured for a liquid drop on an untreated surface. Figure 6 shows a photo of an 8 \( \mu \)L droplet on an untreated surface.
4. Results and discussion
When laser pulses interact with the ceramic surface, radiation is absorbed, reflected, transmitted and scattered. As a result, a zone of material damage is formed as a blind hole, which corresponds to the profile of the laser beam. When processing ceramics, the difficulty is the lack of intrinsic absorption due to the high value of the band gap, so a single nanosecond pulse may not leave traces of damage. In order to start the treatment process, it is necessary to perform several passes in order to ensure heating of the material and the creation of defects on the surface, on which the absorption of laser radiation occurs. The treatment parameters are presented in Table 1.

| Laser parameters | Average power, W | Pulse repetition rate, kHz | Pulse energy, μJ | Beam diameter, μm |
|------------------|-----------------|---------------------------|-----------------|-----------------|
|                  | 10              | 50                        | 250             | 30              |

In the "columns" strategy, the treatment was performed so that the superimposed pulse lines remained between the columns of raw material, and then the surface profile was measured with a contour gauge. The surface contour for the "columns" strategy is shown in Figure 7 a). The surface profile is shown in Figure 8 a). It is assumed that different areas of the column will affect the change in the contact angle of wetting, since the contact area of the liquid droplet with the surface of the material will change. The size of the column was changed by adjusting the distance between the lines of laser beam motion. The result of the measurements is shown in Figure 9 a). We can see that the experimental curve does not coincide with the theoretical calculation. This may be due to the fact that the diameter of the beam has such a value that the drop spreads out and wets the entire surface and the Wenzel wetting model has more influence, as we can also see that after creating the texture, the surface wettability changes and therefore the surface energy also changes.

![Figure 6. Photo of a droplet on an untreated surface.](image)

![Figure 7. The surface profile of the patterns a) “Columns”, b) “Pits”, c) “Peaks”.](image)

When performing the "pits" pattern for material removal, processing was performed using the percussion method. The number of pulses per hole remained constant and only the distance between the "pits" changed during processing. It is assumed that an air cavity will form due to the recess, which will change the surface energy and allow less wetting of the ceramic surface. The surface contour for the "pit" strategy is shown in Figure 7 (b). The appearance is shown in Figure 8 (b).
The result of the measurements is shown in Figure 9 (b). We can see that, as in the case of "columns", the experimental dependence and the theoretical calculation do not coincide. We can assume that this is due to the fact that during percussion processing, a non-removable buildup of material is formed around the hole, which prevents the liquid drop from entering the air pocket.

![Figure 8. The surface profile of the patterns a) “Columns”, b) “Pits”, c) “Peaks”.](image)

When performing the "peak" pattern, the processing is similar to the "pits" type. The difference is that the processing is not percussive, but scanning. The speed is chosen so that the overlap between the pulses is small and there is a small peak between them. The distance between the peaks was chosen by varying the speed. It is assumed that at a certain size of the "peak" the drop is able to be held on them and due to the small size of the area, the wettability of the surface changes. The surface contour for the "columns" strategy is shown in Figure 7(c). The appearance is shown in Figure 8(c).

The measurement result is shown in Figure 9 (c). It can be seen that the dependence in this pattern is similar to "columns" and "pits". At the same time, when the velocity reaches a value greater than the beam diameter, the pattern begins to coincide with the "pit" type, but no excessive material buildup is formed. Moreover, the value of the contact angle also changes weakly as the distance changes. It is assumed that this phenomenon is due to the fact that, as in the case of columns, a depth of 3 μm is insufficient and complete wetting of the surface according to the Wenzel model occurs.

![Figure 9. Dependence of the contact wetting angle on the distance between the lines for the a) “Columns”, b) “Pits”, c) “Peaks”.](image)

Moreover, for all patterns dots with value < 30 μm do not form structure because gap value less beam diameter. It lead to deflect experimental curve at dots with value 30 μm.

Thus, to understand the full picture, it is also necessary to check how the depth and diameter of the beam affect the wettability of the surface in these types of patterns.

Figure 10 shows the appearance of droplets with the maximum contact angle of wetting for each pattern. It is worth noting that the most effective pattern was the column strategy. Using this strategy increased the wetting angle from 73° to 90°. The least effective was the "peaks" strategy, which increased the value of the wetting angle to 79°.
Thus, it can be concluded that nanosecond direct laser patterning allows to change the contact angle of wetting of the surface up to 90°. At the same time, it was found that the change in the surface topography is not the main factor in structuring.

Conclusions
The effect of three different patterns on the surface wettability of Al₂O₃ ceramics was investigated in this study. It has been determined that the surface wettability of ceramics after laser treatment is influenced not only by the structure and surface roughness, but also by other factors. Thus, it has been suggested that the beam diameter and processing depth plays a major role. This suggested is based on fact that changing the assumption contact area between liquid and solid did not lead of the expected hydrophobicity of the ceramic surface. Whatsoever, it was found that different strategies, methods, and patterns have effect on the change in surface wettability but it is necessary to take into account the chemical composition of the surface, the surface homogeneity and the energy parameters of the laser radiation.

Thus, nanosecond direct laser structuring allows to change the contact angle of wetting. All the studied patterns changed the contact angle after laser treatment. Structure “Columns” was increased the value of the contact angle of wetting from 73° to 90°, “Pits” to 87°, “Peaks” to 87°. Unfortunately, it was not possible to exceed the contact angle value of 90 ° in this study. Moreover, theoretical calculations show that by changing the surface topography it is possible to achieve not only a hydrophobic, but also a superhydrophobic surface of Al₂O₃ ceramic. We suggest that decreasing beam diameter and increasing structure depth for “Columns” and “Peak” pattern, and decreasing value ejected material for “Pit” pattern will let as achieve superhydrophobic surface of Al₂O₃ ceramic. Also, we suggest that its and new theoretical calculation will lead to the coincidence experimental and theoretical contact angle value.

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