Hydrophobization of Metal Surfaces

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Abstract: This work describes possibility to create texturized surfaces by their modification using laser equipment with the aim to achieve steady heterogeneous wetting regime. Experimental results regarding the influence of laser radiation variables on wetting angle are given for steel (20Kh13) and aluminum (D16T) surfaces. This was aided by variation of main variables of laser impact, namely: radiation power (from 10 to 20 W), laser beam scanning speed (from 100 to 500 mm/s), pulse frequency (from 20 to 80 kHz). Analysis of the results has revealed that the maximum wetting angles for steel and aluminum surfaces are 147.64° and 150.27°, respectively, they have been obtained upon laser texturizing at the same variables of laser radiation. The influence of laser spot diameter on wetting angle has been determined upon impact on steel (20Kh13) surface. This has been aided by lenses the with focal lengths of 163 and 100 mm, their laser spot diameters are 59 and 25 µm, respectively. It has been revealed that, other conditions being equal, the wetting angles are higher at higher laser spot diameter (59 µm).

Keywords: hydrophobic surfaces, laser radiation, relief, roughness, wettability, wetting angle, wetting regime.

I. INTRODUCTION

Modification of metal surfaces aiming at achievement of hydrophobic state attracts more and more attention nowadays. Analysis of published works demonstrates that this interest is attributed to the fact that hydrophobic surfaces are characterized by certain unique properties required for numerous applications. For instance, hydrophobic surfaces promote decrease of hydraulic resistance upon transportation of fluid mediums [1–3], reduction of ice formation rates [4–6], intensification of heat exchange [7], and other positive effects, in particular, hydrophobic surfaces are characterized by higher corrosion resistance [2].

Hydrophobic surfaces with higher wetting angles (superhydrophobic surfaces) attract the highest practical interest. In the previous works [8], the authors mentioned that such surfaces could be obtained when the following requirements were satisfied simultaneously:

- decreasing surface energy at solid–gas interface below that at solid–liquid interface;
- texturizing of micro/nanoscale relief on surface.

In fact, texturizing of micro/nanoscale relief exerts influence not only on wetting angle but also determines thermodynamic state of surface. Two major states exist for hydrophobic surfaces (see Fig. 1): homogeneous wetting regime (Wenzel state), when the cavities of texture are filled with fluid [9], and heterogeneous wetting regime (Cassie–Baxter state), when the cavities are filled with gas, and contact of fluid and surface presents heterogeneous fluid–solid–gas interface [10–11]. Herewith, steady heterogeneous wetting regime is prevailing for numerous applications.

![Fig. 1. Homogeneous (a) and heterogeneous (b) wetting regimes on hydrophobic rough surface.](image)

The studies devoted to determination of texture parameters of relief formed on surface aiming at achievement of superhydrophic properties started in the 1950s [12, 13].

Among numerous existing methods of hydrophobization, it is possible to highlight three groups in terms of topology of texturized relief: texturizing of non-ordered relief, texturizing of relief with preset geometric parameters, and their combination aiming at improvement of nonwettability. The first group includes chemical and physical deposition, sublimation, electrochemical methods, and others; the second group includes lithographic and template methods.

Despite great amount of existing methods of hydrophobization of metal surfaces, another intensively developing method has been proposed based on texturizing of micro/nanoscale relief using laser equipment (laser ablation). Modified in such a way functional surfaces are applied in various fields including micromechanics [14], optics [15], optomechanics [16], and microfluidics [17, 18].

It should be mentioned that most of studies devoted to development of superhydrophobic surfaces based on application of laser
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equipment, were initially oriented at the use of femtosecond laser facilities [19], [20]. Subsequently, the relevant studies were reoriented to the use of lasers with nanosecond pulse durations [21]–[23]. It is related mainly with the fact that nanosecond laser systems decrease significantly surface modification time in comparison with femtosecond systems.

It has been mentioned in [14] that immediately after the impact of nanosecond laser radiation, the brass surface is characterized by superhydrophilic properties which during 30 days of holding in air under ambient conditions reached hydrophobic state with steady heterogeneous wetting regime (see Fig. 2). Analysis of surface morphology using scanning electron microscope (SEM) has demonstrated that micro/nanoscale relief structures induced by laser radiation enhance hydrophilic surface properties according to the Wenzel theory [9]. In addition, it has been demonstrated that atomic hydrogen content and wetting angle increase with time. This evidences that upon holding of modified sample in air under ambient conditions, there occurs sorption of carbonaceous compounds which decrease surface energy at solid–gas interface below that at solid–fluid interface.

Fig. 2. Images of droplets with the volumes of 5, 4, and 2 µl (from left to right) on modified brass surface at equal scale

This work discusses the influence of variables of nanosecond laser radiation on wetting angle on steel (20Kh13) and aluminum (D16T) surfaces.

II. METHODS

A. Modification of Surfaces Using Laser Equipment

Experimental samples of steel (grade 20Kh13, flat plates with the sizes of 30x40 mm and the thickness of 3 mm) and aluminum (grade D16T, flat plates with the sizes of 30x40 mm and the thickness of 1 mm) were prepared with the aim of formation of multiscale relief on surfaces using pulse laser processing.

The surfaces were modified by means of FMARK NS–FB–20 laser facility (OOO TsLT, Russia). This facility is based on infrared ytterbium fiber laser with the wavelength of 1,064 nm capable to vary pulse duration from 4 to 200 ns, and rated power of laser radiation at output of focusing system of at least 20 W. Laser beam is focused on processed surface by means of MS–II–10 2-axis laser deflection unit (RAYLASE AG, Germany).

Laser beam travels by the surface along X axis in order to obtain relief structure in the form of linear pattern (see Fig. 3). The increment between the lines for all samples was constant equaling to 100 µm. Upon modification of experimental surfaces, the power of laser radiation varied from 50 to 100% of rated value (20 W), scanning speed of laser beam varied in the range from 100 to 500 mm/s, and pulse frequency of laser radiation was from 20 to 80 kHz.

The samples were marked as follows: NNN.FF.VVV, where NNN was the power of laser radiation set as percent of rated power N of source, FF was the pulse frequency f in kHz, VVV was the speed V of linear travel of laser beam along preset path on surface in mm/s.

Fig. 3. Schematic view of laser facility and travel path of laser beam

After modification of steel and aluminum surfaces, the experimental samples were held during 30 days in air under standard ambient conditions. Then, the images of texturized relief were obtained using SEM (see Fig. 4). It can be seen in Fig. 4 that under the impact of pulse laser radiation on metal surface upon beam travel along linear path, microscale grooves with lateral protrusions are generated, and at nanoscale level, the structure is characterized by non-ordered roughness.
Despite identical variables of lased radiation for the samples, the topology of induced relief on aluminum (see Fig. 4a) and steel (see Fig. 4b) samples is different.

B. Algorithm

Experimental surfaces were modified as follows:
- preliminary preparation (treatment by isopropyl alcohol, washing with distilled water, drying);
- installation of sample on X–Y table;
- focusing of laser beam on surface using scanner;
- texturizing of ordered multiscale relief at preset variables of laser radiation and travel path of laser beam.

Wetting angles were measured using OCA 20 instrument (DataPhysics, Germany). Aiming at more accurate values, the angles were measured six times in various points of modified surface of each sample: across (3 points) and along (3 points) the grooves (see Fig. 5), herewith, the measurements were averaged for analysis of the results.

III. RESULTS AND DISCUSSION

A. Influence of laser radiation variables on wetting properties

Fig. 6 illustrates measurements of wetting angle for modified aluminum (Fig. 6, a–c) and steel (Fig. 6, d–f) surfaces. Analysis of the results demonstrated that the maximum wetting angles for aluminum (150.27°) and steel (147.64°) were achieved at the same variables of laser radiation (laser power: 100% of rated; pulse frequency: 50 kHz; scanning speed: 500 mm/s).
It can be seen in Fig. 6 that for steel samples, variation of laser radiation exerts lower influence on wetting angles in comparison with aluminum samples. Thus, at laser radiation power of 10 W, the highest wetting angles for aluminum surfaces were achieved at the pulse frequencies of 20 kHz, and in the case of 15 W – at 50 kHz. Variation of laser beam travelling speed does not exert significant influence on angle of fluid contact with modified surface.

B. Influence of laser spot diameter on wetting angle

Aiming at determination of the influence of laser spot diameter upon impact on metal surface, two lenses with different focal length were tested. For the lens with focal length of 163 mm, the laser spot diameter was 59 µm, and for the lens with focal length of 100 mm, it equaled to 25 µm. The studies were carried out on experimental samples of steel 20Kh13 (flat plates with the sizes of 30×40 mm and the thickness of 3 mm).

Laser radiation variables were the same as in the studies of the influence on wettability. After modification by laser equipment, the samples were also held during 30 days in air under ambient conditions with subsequent measurement of wetting angles. The measurement results are illustrated in Fig. 7.
Fig. 7. Measurements of wetting angles of modified steel surfaces using lenses with the focal length of 163 mm and 100 mm

The measurements demonstrated that upon laser texturizing of steel (20Kh13) surfaces, the lens with focal length of 163 mm, with laser spot being 59 µm, provided higher wetting angles.

Maximum wetting angle, while using lenses with focal length of 100 mm, is 147.21 for the sample marked as 75N.20f.500v.

IV. CONCLUSION

Maximum wetting angles for experimental aluminum (150.27°) and steel (147.64°) surfaces were obtained at equal variables of laser radiation (laser power: 100% of rated; pulse frequency: 50 kHz; scanning speed: 500 mm/s);

Variation of laser radiation variables is less significant for steel in comparison with aluminum.

Using the lens with focal length of 163 mm, with laser spot being 59 µm, promotes higher wetting angles. Maximum wetting angle, while using lenses with focal length of 100 mm, is 147.21 for the sample marked as 75N.20f.500v.

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