PRODUCTION OF SUPERHYDROPHOBOUS SURFACES USING LASER TEXTURING

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ABSTRACT

This paper presents the results of the experimental research of the influence of laser radiation parameters on geometrical characteristics of the modified surface.

The authors assume that hydrophobicity of the laser-modified brass surface results from the sorption of carbon-containing organic compounds.

It has been shown that the formation of surface relief is implemented by the heterogeneous wetting regime.

Keywords: hydrophobicity, relief, laser radiation, surface texturing, hydraulic resistance.


1. INTRODUCTION

The analysis of Russian and foreign publications reveals a considerable interest of researchers towards the improvement of physical and chemical characteristics of surfaces of structural materials. In the last decade the control of surface wettability with various liquids, in particular, the formation of hydrophobic coating has drawn considerable attention since such coatings can substantially alter hydraulic and other characteristics.

According to the modern classification [1, 2], a surface is hydrophobic when the contact angle ranges from 90 to 180°. Surfaces with the contact angle over 120° are considered superhydrophobic, over 150° – ultahydrophobic.

The surface wettability control is of particular interest for researchers due to a wide range of applications. For instance, the hydrophobization of internal functional surfaces of pipelines in heat networks and heat exchangers can significantly reduce energy costs for the transportation of the coolant, increase the durability of the existing and new pipeline systems, as well as increase the turnaround period. National Research University "Moscow Power Engineering Institute" (NRU “MPEI”) has recently conducted comprehensive studies of the
impact of the hydrophobization of metal surfaces on hydraulic characteristics [3-5]. A special focus is laid on superhydrophobic surfaces with the contact angle over 120° but, as is shown in [6], large contact angles do not guarantee good water repellence. There is a number of surfaces from which liquid does not evacuate at large contact angles. From a practical point of view, a small rolling angle (less than 10°) is also of considerable interest in addition to the large contact angle of functional surfaces. This is the angle at which a surface should be tilted towards a horizontal plane so a drop could spontaneously evacuate from it.

The basics of superhydrophobic surfaces were laid in the middle of the 20th century [7, 8] but only in the beginning of the 21st century it became possible to formulate principles of the formation of the superhydrophobic state of material surfaces. In particular, it was determined that in order to achieve the non-wettability of surfaces the following tasks must be solved:

- Surface texturing in order to obtain the ordered different-scale relief with the selection of geometric parameters of its elements;
- Low surface energy on the material surface.

The most efficient method of the modification of metal surfaces in order to give them non-wettable properties is surface texturing using laser radiation. This method allows to precisely control geometric characteristics of the generated relief through the flexible variation of laser radiation parameters. It is worth mentioning that most studies recommend femtosecond laser complexes for the surface modification of various construction materials [9, 10]. However, an interest towards lasers with nanosecond pulses has significantly grown in the recent years [11-13]. This is due to the fact that nanosecond laser systems considerably reduce time for the modification of surfaces in comparison with the femtosecond laser.

In this work, the surface modification was carried out using laser complex FMark NS-FB-20 ("CLT" LLC, Russia) based on a fiber laser (Figure 1). The specified complex includes infrared ytterbium fiber laser FS-PS-NS with 1064 nm wavelength, with an ability to vary the pulse duration from 4 to 200 ns, average laser radiation power at the exit of the focusing system no less than 20 Watts. The focusing of the laser beam on the processed surface is carried out using two-axis departure system MS-II-10 (RAYLASE AG, Germany). The modification of the pipe surfaces was made using rotating device RZD-30M with the maximum speed of 6 RPM.

![Figure 1 FMark NS-FB-20 complex.](http://www.iaeme.com/IJMET/index.asp)

The measurement of contact and roll-off angles was conducted using OCA 20 (DataPhysics, Germany). Distilled water was used as liquid.
2. THE GEOMETRY OF TEXTURED RELIEF

In order to determine geometrical parameters of the relief obtained through the modification of the surface using laser radiation, we have produced and modified samples from brass L63-plates with the size of 30x30x1 mm and the following parameters:

- 6 samples at the constant power of 20 W and laser frequency 20 kHz, with the varied rate of the laser beam on the surface from 100 to 600 mm/s, with the increment of 100 mm/s;
- 6 samples at the constant scanning rate 100 mm/s and laser frequency 20 kHz, with the varied power from 10 to 20 W, with the increment 10% from the nominal power of the laser source (20 W).

The relief geometry was set in such a way that a step between lines of the laser beam passage was equal to 200 µm. An example of the created relief is presented in Figure 2 – the morphology and surface profile of the sample modified using laser radiation with the power of 20 W, scanning rate 100 mm/s and frequency 20 kHz.

Figure 2 (a) The morphology in 500 µm scale (left) and 50 µm (right); and (b) the profile of the modified sample surface using laser radiation with the power of 20 W, scanning rate 100 mm/s and frequency 20 kHz.
The variation of laser radiation parameters enables to form a relief with different geometric parameters on the solid surface. As it can be seen from the surface profile of the modified sample (Figure 2b) obtained using mechanical profiler Dektak 150 (Veeco Instruments Inc.), the relief is a channel with side protrusions. This type of the profile is due to the fact that the frequent contact between the laser beam moving with the given linear rate and the solid surface results in microexplosions that cause particles of molten metal to distribute along the contact border, forming a channel with side protrusions and a well-developed surface.

The results of the pioneering studies have allowed us to identify the influence of laser radiation parameters on geometric parameters for the created relief on the brass substrate (Figure 3). The surface of the sample in its original state was taken as a zero mark in relation to which the depth of channels and side protrusions of the relief were analyzed.

One can see from the dependence between the passage rate of the laser beam with the constant power and geometrical parameters of the resulting relief (Figure 3) that at the rates below 100 mm/s the depth of channels and the height of protrusions drastically increase. However, the time of the surface modification significantly increases at a low rate which could complicate its industrial application. On the contrary, the increasing of the scanning rate leads to a decrease in the absolute values of geometric parameters of the textured relief, making them useless for practical application.

A similar effect is observed when processing the brass surface at the constant scanning rate (100 mm/s) and the varied power of laser radiation (Figure 3b): geometrical parameters of the obtained relief do not give the desired effect at the laser power reduction below 10 W (50% from nominal power).
3. THE INFLUENCE OF LASER TEXTURING ON THE SURFACE WETTABILITY

In order to investigate the influence of the surface modification using laser radiation on wetting properties, the sample plate 30×30×1 mm in size was made from the brass L63.

The relief was created through the primary passage of the laser beam along the lines separated by 40 µm and the subsequent passage of the beam along the lines located perpendicular to the primary ones at the same distance between them with the following laser parameters:

- The laser radiation power of 20 W;
- The scanning rate of 100 mm/s;
- The laser frequency of 20 kHz.

The electron microscopic images of the modified surface immediately after processing and after 14 days of the air storage at standard atmospheric conditions were obtained Figure 4.
Figure 4 (a) The modified surface immediately after processing and (b) after 14 days of the air exposure at different scales (200 μm and 5 μm).

On the electron microscopic image of the modified surface one can see that immediately after the modification the surface morphology consists of "fluffy" particles of different shapes and sizes (Figure 4) and the modified surface has hydrophilic properties. After the air exposure at standard atmospheric conditions it is clear that the surface morphology changes and appears as "loose" particles (Figure 4b). The surface has the following wettability parameters: the contact angle is 135° and the roll-off angle is 8°.

The authors [14] suggest that the surface non-wettability manifests itself over time due to the oxidation of copper oxide CuO into Cu₂O. It is believed that the deoxidation of CuO, which occurs in case of surface defects is the heterogeneous nucleation and growth mechanism so the surface will consist of different areas with various degrees of wetting (CuO and Cu₂O). The molar ratio between Cu₂O and CuO increases over time and since Cu₂O is a hydrophobic material [15] the deoxidization process causes the change of surface wettability. The authors [16] deny this thesis and claim that all metals and their oxides refer to materials with high surface energy due to significant intermolecular and interatomic interactions and, thus, the surfaces of both oxides will possess hydrophilic properties.

Another version assumes that in terms of thermodynamics immediately after laser application the surface of the brass sample is non-equilibrium and has high surface energy, which results in the manifestation of hydrophilic properties [17]. In addition, the study [16] mentions that due to the highly active adsorption from air onto the surface the sorption of carbon-containing compounds occurs that contributes to the surface non-wettability.

Within the framework of this study, after 14 days of the air exposure the sample was thermally treated at 350°C and began to show hydrophilic properties.

Special attention is paid to the fact that in comparison with the survey [14] where after the processing of a non-wettable sample with methanol the modified surface became hydrophilic and eventually began to manifest hydrophobic properties again, this research demonstrates that after the thermal treatment of a hydrophobic sample it began to manifest hydrophilic properties, however, after the exposure of the sample to air under standard atmospheric conditions for 14 days the surface wettability remained at the same level, i.e. the sample remained hydrophilic.

In order to study surface wettability changes during the thermal processing of the modified sample we have determined atomic contents of elements (C), (O), Cu, Zn. The relative content of these elements was calculated for the original surface immediately after laser treatment, after 14 days of the air exposure, and immediately after the heat treatment.
The composition was determined using scanning auto emission electron microscope Tescan MIRA 3 LMU.

![Graph showing atomic content of C, O, Cu, Zn on the surface at different stages of study.](image)

**Figure 5** The atomic content of elements C, O, Cu, Zn on the surface at different stages of the study.

As it can be seen from Figure 5, after 14 days of the modified sample exposure to air under standard atmospheric conditions the atomic content of carbon has increased, and the content of Cu and Zn has proportionally decreased. This sample has become hydrophobic, as mentioned earlier. However, after the sample was thermally treated, the carbon content decreased and the sample became wettable.

It should be noted that the high content of carbon on the surface of the original sample does not provide a hydrophobic state. This is due to the fact that according to principles of obtaining non-wettability one should create a developed ordered relief on the surface and give it low surface energy.

Thus, the authors of this paper assume that a significant contribution to obtaining of hydrophobic properties for the laser-modified brass sample is made by the sorption onto the surface of organic compounds, because their removal from the surface (alcohol treatment, thermal treatment) leads to the loss of non-wettability.

4. HETEROGENEOUS WETTING

For the study of the hydrophobization of functional surfaces using laser, the L63 brass tube with the diameter of 16 mm was modified, while the relief geometry was created through the passage of the beam along the rotating tube surface so the step between the turns of the wound spiral was 100 μm. Here are parameters of laser radiation for the modification process:

- The laser radiation power of 20 W;
- The laser frequency of 20 kHz;
- The linear movement rate of the beam along the tube surface of 100 mm/s.

It is worth noting that the processing of inner tube surfaces is an interesting technique for the reduction of hydraulic resistance. In this survey, due to the technical impossibility to process the inner surface, we have processed the outer surface of the tube.
After the air exposure of the modified tube surface under standard atmospheric conditions for 14 days the analysis of the surface wetting parameters has been performed. In order to measure the contact angle of the surface drops of different volumes were used: 2, 4 and 5 μl. The different volume of drops was determined by the complexity of research due to the low roll-off angle and curvilinearity of the sample surface.

As a result, the measurement of contact angles revealed that the volume of drops affects the contact angle of the surface. The increase in the drop volume leads to the decrease in the contact angle (Figure 6).

![Figure 6](image)

**Figure 6** The dependence between the drop volume and the value of the contact angle on the hydrophobic surface.

As it was mentioned earlier, superhydrophobic surfaces with low roll-off angles that are only possible in case of the heterogeneous surface wetting regime are especially interesting from the practical point of view.

Different wetting regimes are known: homogeneous wetting (Wenzel regime) [9] when liquid is in contact with the entire surface of a solid body completely filling the cavities on the surface (Figure 8); and heterogeneous wetting (Cassie-Baxter regime) [10], in which air locates between the surface roughnesses and a drop contacts with separate ridges (Figure 8b).
Thus, it is important to note that the surface modification using laser radiation in order to give it hydrophobic properties, as seen in Figure 7, is accompanied by the pronounced formation of the heterogeneous wetting regime which opens wide prospects in terms of the surface wetting management.

5. CONCLUSION

The study demonstrates dependencies between the geometric size of the brass surface relief and the laser scanning rate and power.

It has been noted that the surface is hydrophilic immediately after the modification but it becomes hydrophobic over time. As a result, the relief images immediately after processing and after 14 days of the air exposure under standard atmospheric conditions were obtained. The chemical composition of the surface of the brass sample in the original state, immediately after the relief formation, after the 14 day exposure and after the thermal treatment was determined. It is expected that a visible change in the morphology of the modified surface occurs during the deoxidation of CuO into Cu$_2$O, and hydrophobic properties are acquired due to the sorption from air on the surface of carbon-containing organic compounds.

It has been shown that the formation of the surface relief is implemented by the heterogeneous wetting regime.

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REFERENCES


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