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DETERMINATION OF THE RESISTANCE OF WATER-REPELLENT PROPERTIES TO ULTRAVIOLET RADIATION ON SELF-HYDROPHOBIZED SURFACE TEXTURES OF AISI 304 STEEL

In this work, the object of the study were femtosecond laser textured steel samples. Using a femtosecond laser to texture the surface both in the direct-beam mode, which provides microtextures, and in the reflection mode, which leads to the formation of LIPSS-type nanostructures on the surface. Such hybrid complexes are optimal in terms of water repellency as they embody the principle of hierarchical textures. This approach is one of the promising ways to solve the problem of scaling the process of obtaining superhydrophobic metal surfaces. The aim of the work is to establish the stability of water-repellent properties of micro- nanotextures obtained on the surface of AISI 304 steel after spontaneous hydrophobization under the action of UV radiation. The study of the obtained textured surface by scanning electron microscopy to confirm the presence of nanotexture and by energy-dispersive X-ray spectroscopy to establish the elemental composition of the obtained microtexture were made in the work. The paper shows that the water repellency of AISI 304 steel surfaces textured at micro and nano levels by femtosecond laser after long exposure to the atmosphere increases to a superhydrophobic state with the value of contact angles up to 155°. It has been shown that such surfaces are sensitive to UV radiation. Depending on the type of structure, the loss of hydrophobicity under experimental conditions occurs in 15–45 minutes of exposure, and complete hydrophilization of the surface occurs after 100 minutes of irradiation. As a result, the obtained self-hydrophobic surfaces are not suitable for operation under the influence of sunlight. However, ultraviolet radiation can be used to pre-clean such surfaces from adsorbed organic contaminants.

Keywords: *water contact angle, surface tension, water repellent coatings, superhydrophobicity, femtosecond laser, AISI 304 steel.*

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1. Introduction

Texturing is an essential way to increase the ability of surfaces to repel liquids of different polarity by achieving the so-called Cassie wetting state [1]. It assumes that only part of the wetting liquid droplet area contacts the solid surface, the remaining part of it being in contact with air. The mathematical description of this state originating from the classical Jung, Wetzel and Cassi-Baxter equations is quite developed at the moment, although when passing from geometrically ideal to real structures, differences of predicted water repulsion indices from actually observed results become evident [2]. Nevertheless, the value of the contact angle remains an integral indicator for determining the quality of the obtained water repellent structure, which is used in a large number of modern publications on the subject.

It is known that in addition to surface topography, the overall water repellency of a surface is also determined by its own ability to wet, which in turn depends on its Van der Waals interaction potential [3]. For surfaces containing polar functional groups, this potential includes dispersion, polar (orientation, induction and polarization) and, for strongly polar surfaces, hydrogen [4]. For relatively non-polar surfaces, which include some polymers such as polyolefins, silicones, fluorinated polymers, as well as waxes and their treated polar surfaces, only the dispersion interaction is predominant, which sharply reduces wettability. Indeed, it is known that the wettability angles of paraffin are up to 100–105°, of teflon up to 150° and of polydimethylsiloxane up to 107° [5, 6]. The textured surfaces that correspond to them reach this index above 150 degrees, indicating their superhydrophobicity [7].

There is an impressive list of chemical reagents capable of binding to the surface through the formation of covalent and ionic bonds and owing to their difilic nature to give these surfaces significant water repellency. However, the phenomenon of self-hydrophobization of textures obtained on the surfaces of metals such as steel, aluminum, copper, and titanium has recently attracted attention. Studies [8–10] consider several hypotheses of the nature of this phenomenon, in particular that it is caused by adsorption of aliphatic combustion products of fuels present in the atmosphere of cities, special interaction with air carbon dioxide, etc. Nevertheless, even without considering the source, this property could be very practical, because in obtaining water-repellent surfaces, the step of chemical hydrophobation would be eliminated, and thus, increased manufacturability and reduced cost of finished products.

This is combined with the use of a high-performance and technologically advanced femtosecond laser for surface texturing both in the direct-beam mode, which ensures obtaining microtextures, and in the reflection mode, which leads to the formation of LIPSS-like structures on the surface [11]. It is such hybrid complexes that are optimal in terms of water repellency, since they embody the principle of hierarchical textures. In general, this approach is one of the promising ways to solve the problem of scaling the process of obtaining superhydrophobic metal surfaces. The surfaces of steel, in particular AISI 304 as a common alloy, are of high practical importance in this sense [12].

In addition to the water repellent properties themselves, their stability in environmental conditions, in particular to the action of atmospheric factors, is of particular practical importance. The main component of the list of such factors, along with droplets and vapor water, is the effect of ultraviolet radiation of the solar spectrum [13]. The contribution of light quanta of this range in the destruction of organic substances, including also polymers and coatings, is considered to be the most significant. However, the water repellency stability of hydrophobized textured surfaces remains insufficiently studied at the moment.

Considering the above, *the aim of this research* was formulated, which includes the establishment of the stability of water repellency of two-level micro-nanotextures obtained on the surface of AISI 304 steel after spontaneous hydrophobization under the action of ultraviolet radiation. This will make it possible to evaluate the possibility of using laser-textured steels without additional chemical treatment.

To achieve this aim, the tasks of obtaining micro-nano structures by exposure to femtosecond laser, fixing the process of self-hydrophobization and characterization of the initial water repellency of such surfaces, the study of the patterns of water repellency reduction under exposure to ultraviolet radiation were solved.

2. Materials and Methods

In this study, the micromesh was created on an AISI 304 low-carbon stainless steel substrate. The dimensions of the steel plates were 20x20x2 mm. Microtexture in the form of grooves was performed using a femtosecond Carbide laser (Light Conversion, Lithuania). Laser parameters for texturing are described in [14]. After laser ablation, the textured steel samples were washed with isopropyl alcohol and dried at 80 °C. The samples were then left outdoors for 3 months.

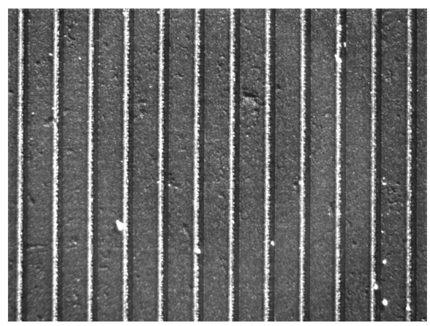
The UV resistance test was conducted according to ASTM D 4329 using a 400 W fluorescent lamp (340 UVA). The temperature of the samples during the test did not exceed 60 °C.

The sessile drop technique (using an optical microscope with a Delta Optical HCDE-50 digital camera and ScopeTek View software) was used to determine the water contact angle. For each surface, the contact angle was measured at five points.

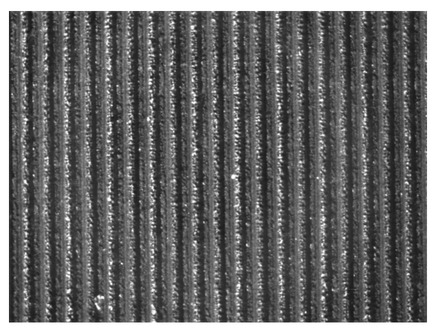
The surface of the textured samples was examined using an optical microscope and a MIRA3 scanning electron microscope (TESCAN, Czech Republic). The elemental composition of the surface was investigated by energy dispersive X-ray spectroscopy (EDS) INCA X-ACT (Oxford Instruments, UK).

3. Results and Discussion

In the work, two types of textures on the steel surface were obtained (Fig. 1), which differ in the configuration of depressions and protrusions. The first of them, sample A (Fig. 1, *a*) has a period of 100 μm and a groove width of 30 μm, and the second, sample B (Fig. 1, *b*) – respectively 60 and 45 μm. It is obvious that the first structure has a much less specific surface fraction of depressions (which should account for the fraction of drop contact with the air) than the second structure (30 % and 75 %, respectively). On the surface of the protrusions, as well as on the surface of the troughs themselves (Fig. 2), there is an additional level corresponding to the LIPSS texture. Given that it has its own relief, the above surface percentages cannot be regarded as initial surface fractions for predicting contact, for example, by Cassi's equation. The resulting textures are oriented, and the protrusions and depressions have regular shapes.



a



b

Fig. 1. Surface patterns after femtosecond laser treatment: *a* – sample A (100 μm period, 30 μm groove width); *b* – sample B (60 μm period, 45 μm groove width)

The structure of the bottoms of the obtained cavities is also irregular and includes craters from high-speed laser pulses up to 10 μm in diameter, framed by smaller texture elements. The lateral walls of the grooves are also structured due to the angular impact of the beam.

The elemental composition of the sample was investigated by the EDS method during SEM. When comparing the composition in regions 1 and 2 (Fig. 2 and Table 1), which refer to the tops and troughs of the texture, respectively, it becomes obvious that the surface of the sample is uneven, primarily in terms of carbon content. Its content on the tops is increased, which may be related to the increased adsorption of hydrocarbons from the atmosphere by this layer as a result of the presence of nanotexture. Due to a decrease in the size of the elemental component, it is characterized by a more developed surface. Also, on the tops there is an increased oxygen content, which suggests a possible combination of oxidation processes (formation of various metal oxides composing the steel) and adsorption of oxygen-containing substances.

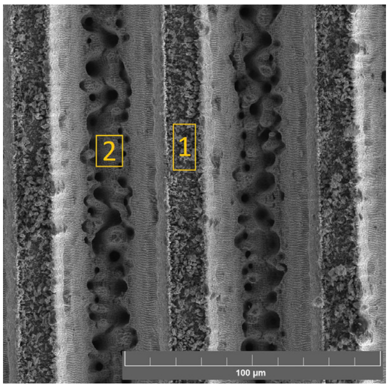


Fig. 2. SEM photo of the surface structure of the textured sample: 1 – area of the structure top; 2 – area of structure groove

Table 1

Surface composition according to EDS

EDS spectrum	All results are in wt. %						
	C	O	Si	Cr	Mn	Fe	Ni
Area 1	8.6	23.1	0.8	13.1	1.7	47.1	5.6
Area 2	3.9	3.5	0.3	18.7	1.8	65.6	6.2

After obtaining the textures by femtosecond laser action, the samples were left in a room for 2.5 months, after which their water contact angles were measured. As shown in Fig. 3, both of these samples exhibit high water repellency. Sample B, however, is superhydrophobic. This fact is an additional confirmation of the passage of self-hydrophobization, as the intrinsic wetting angle of the clean steel surface is below 90 degrees [15].

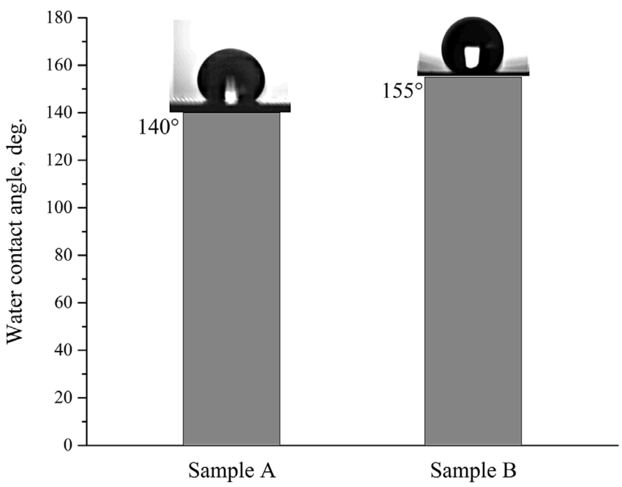


Fig. 3. Water repellency of textured sample surfaces after self-hydrophobization

The difference in the value of the contact angle is explained, first of all, by the textural features of the samples and, in particular, by the reduced contact area of the sample liquid drop in sample B compared to that of sample A, as it was mentioned above.

The surfaces obtained were placed in an environment of ultraviolet radiation, which led to a gradual loss of water repellent properties, as can be seen in Fig. 4. Already after the first 15 minutes of UV exposure, sample B loses its superhydrophobicity, although it loses its hydrophobicity only after 45 minutes of exposure. Sample A loses it much earlier and is already hydrophilic by this time. Differences in wetting of the samples disappear at the hundredth minute of the test.

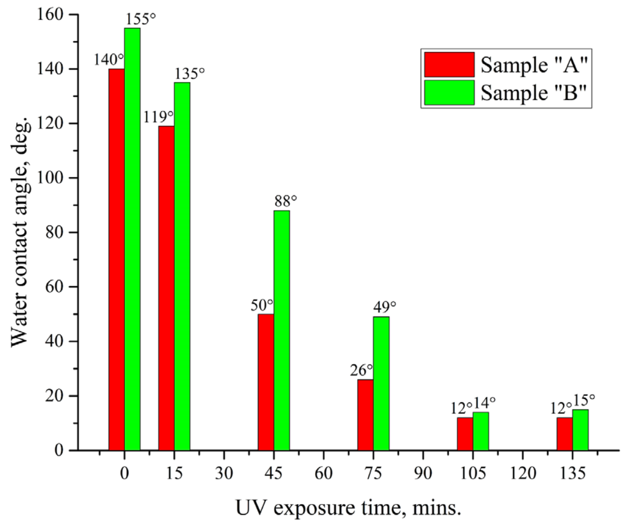


Fig. 4. Wetting surfaces with water depending on the duration of exposure to ultraviolet radiation

From the results of the experiment it follows that the layer of organic matter formed on the surface in the course of self-hydrophobization is unstable to the action of ultraviolet radiation, and therefore such surfaces require more effective protection from sunlight or the use of other ways of surface treatment. The latter can be implemented by a number of methods, such as chemical application from the gas phase, impregnation with hydrophobizer solutions, etc.

On the other hand, ultraviolet light can be seen as an effective way to clean such surfaces of substances adsorbed from the air before further treatment. This makes it possible to separate in time the stages of texture and chemical hydrophobization, as well as to activate the reactivity of the surface. When choosing an effective mode of such cleaning, it is necessary to take into account the structural features of the surface.

The practical significance of the study is that it reveals the problem of instability of the superhydrophobic layer on the laser-textured surface, which makes it impossible to use in the aerospace and automotive industries, but the proposed method of stability assessment may become the main one for solving this problem in the future.

This study has limitations in the lack of information on the stability of superhydrophobic properties in other environmental factors such as humidity, temperature and exposure to contaminants. The study focused on textured AISI 304 steel surfaces. A similar effect of self-hydrophobization can be observed for other metals, such as textured aluminum, but the resistance to UV light and nature of this phenomenon may differ. Therefore, the results obtained may not be applicable to other alloys and metals. In addition, the effect of different laser parameters on the hydrophobic properties of textured surfaces is not investigated.

The conditions of martial law in Ukraine did not affect the research and the obtained results.

4. Conclusions

It is shown that the water repellency of AISI 304 steel surfaces textured at the micro- and nano-level by femtosecond laser increases to a superhydrophobic state after prolonged exposure in a normal room atmosphere. However, such surfaces are sensitive to UV radiation. Depending on the type of structure, the loss of hydrophobicity under experimental conditions occurs in 15–45 min of exposure, and complete hydrophilization – after 100 min of irradiation.

This leads to the conclusion that the surfaces obtained by self-hydrophobization are not suitable for operation under the influence of sunlight. However, ultraviolet radiation can be used to pre-clean such surfaces from adsorbed organic pollutants.

Conflict of interest

The author declares that he has no conflicts of interest with respect to this study, including financial, personal, authorship or other conflicts that could affect the study and its results presented in this article.

Financing

The study was conducted without financial support.

Data availability

The manuscript has no associated data.

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