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Article

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DETERMINATION OF CRITICAL SURFACE TENSION OF WETTING OF TEXTURED WATER-REPELLENT SURFACES

The object of study is aluminum textured with a femtosecond laser and modified with silanes to reduce surface energy. The presence of a special texture on the surface, such as protrusions or hairs, and the inherently low surface energy of the material allow maximizing the water repellency properties. The determination of the critical wetting surface tension by the Zisman method has a pronounced wetting transition point, but the coordinates of this point cannot be accurately predicted. In this work, the Zisman method is considered as a tool for comparing the effectiveness of modifiers for femtosecond laser-textured surfaces. In this work, periodic structures were created by laser ablation on the surface of aluminum, the surface was modified to achieve the Cassie state when wetted with water, and the critical surface tension of wetting was determined by the Zisman method. As a result, it is shown that the Zisman method in combination with the data on the water contact angle values is an effective tool for characterizing the quality of surface modification of textured samples. It is shown that for textured aluminum surfaces, the most effective modifier is silane, which maintains the Cassie wetting state, with a contact angle increased from 155 to 160°. Paraffin has been shown to be a less effective modifier with an implicit wetting plateau and a transition in the range of 30 to 40 mN/m. It is shown that the textures that have acquired water repellency in the course of spontaneous hydrophobization are very unstable to the action of liquids with reduced polarity, although they have high values of the water contact angle. In practice, the creation of water-repellent coatings on aluminum is a promising substrate due to their widespread use in the aviation, automotive, and energy industries due to their high mechanical strength, lightness, and stability of properties.

Keywords: *water contact angle, surface tension, water repellent coatings, superhydrophobicity, aluminum, femtosecond laser, silanes.*

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1. Introduction

The use of texture can increase the potential for the repulsion of liquids in surfaces with different polarities. This conclusion was drawn in a historical analysis of the nature of the «lotus leaf» effect, which has a water contact angle of more than 150°. Similar wetting anomalies are characteristic of a number of natural surfaces, including insect wings, leaf surfaces, etc. [1]. This effect is based on two factors: a special surface texture (the presence of protrusions, hairs) and the intrinsic low surface energy of the material of this surface [2]. The latter is determined by the chemical composition and, in the case of natural objects; waxes have the highest contact angle values [3]. Examples of more effective modern synthetic materials are organosilicon and fluorinated compounds, which have recently been widely used as water repellents [4].

A mathematical description of the effect was formulated in the studies of Wenzel, Cassie, and Baxter [2, 5], which was expressed in the well-known Cassie equation:

$$\cos\theta_{tex} = f_1\cos\theta_1 + f_2\cos\theta_2, \quad (1)$$

where $\cos\theta_{tex}$ is the contact angle of a two-phase heterogeneous surface; f_1 and $\cos\theta_1$ are the fraction of the surface occupied by phase 1 and its own contact angle θ_1; f_2 and $\cos\theta_2$ are respectively for phase 2.

For textured surfaces, it is assumed that phase 2 is air, the angle of wetting with water is assumed to be 360°, i. e. $\cos\theta_2$ is equal to one and the equation is transformed into the form:

$$\cos\theta_{tex} = f_1\cos\theta_1 + f_2. \quad (2)$$

An increase in the contact angle values will be observed with an increase in the f_2 and $\cos\theta_1$. Equation (2), however, does not describe the conditions for the stability of the Cassie state and considers the entire range of the eigenangles of the wetting phase of the solid surface. However, it is known that at certain values of this parameter, a transition to the Wenzel state is observed, the angles in which are determined by the roughness parameter. Also, one should not forget the influence of the capillary effect, which is described by the Washburn equation and consists of the distribution of the liquid phase in the surface capillary structure of the surface, which makes it impossible to measure the static contact angle because the condition of its stability is violated.

A practical determination of the critical surface wetting tension can be made using the Zisman method [6]. As shown earlier, on textured surfaces, the Zisman graph differs from its canonical straight-line shape and has a clearly defined point of the wetting transition. The coordinates of this point can be predicted only very approximately, the existing equations, for example, the results in [7, 8], have low accuracy in such a prediction and are rather an outline of the probability, which significantly reduces their practical significance. There is a lack of actual information about the wetting of such surfaces, and the choice of modifiers for them is rather due to the usual set traditionally used in the industry. In this work, the Zisman method is considered as a working tool for comparing the effectiveness of certain modifiers of textured surfaces to increase their degree of repellency towards liquids.

As experimental samples, let's choose samples of aluminum alloy of the 7500 series, which is intended for use outdoors and is one of the most commonly used series of this metal. In the future, when creating water-repellent coatings, aluminum surfaces are the most promising substrates, which is due to their widespread use in the aviation, automotive, and energy industries due to their high mechanical strength, lightness, and stability of properties.

The aim of this research is to illustrate the use of the Zisman method on the example of modifiers of femtosecond laser-textured surfaces with a hybrid micro-nanostructure.

To achieve this aim, the following tasks are solved: creation of periodic structures by laser ablation on the surface of aluminum, selection and application of a modifier on these surfaces to achieve the Cassie state when wetted with water, determination of the critical surface tension of wetting by the Zisman method, construction and analysis of the corresponding graphs.

2. Materials and Methods

In this work, aluminum alloy grade 7500 was used as a substrate. On aluminum plates of size 15×15 mm and a thickness of 2 mm microtexture was created using the laser «Carbide» (Light Conversion, Lithuania). The technique and laser parameters that were used are described in [9]. After laser texturing, the aluminum samples were isopropyl alcohol and further dried at 80 °C for 15 min.

T-1 paraffin and octyltriethoxysilane (Evonik, Germany) were used to reduce the surface energy of the obtained textures. Octyltriethoxysilane was chosen as a more environmentally friendly alternative to fluorosilanes [10]. After texturing and washing, the sample was immersed in a 1 wt. % solution of octyltriethoxysilane in isopropyl alcohol for 60 min at room temperature. After soaking, the sample was incubated at 130 °C for 60 min according to the procedure [11].

Contact angle values were determined by the sessile drop technique. Water-alcohol mixtures mixed in different ratios according to the method described in [12, 13] served as test liquids to determine surface energy. An optical microscope with a digital camera was used to measure contact angles. For each test liquid, a contact angle was measured in at least five points. To determine the critical surface energy, the Zisman plot method was used [6].

3. Results and Discussion

The structure obtained on the surface of aluminum (Fig. 1) is characterized by a period of 60 μm, with the width of the trench being 45 μm and the width of the upper part of the protrusion being 15 μm. This structure is anisotropic in terms of the wetting direction.

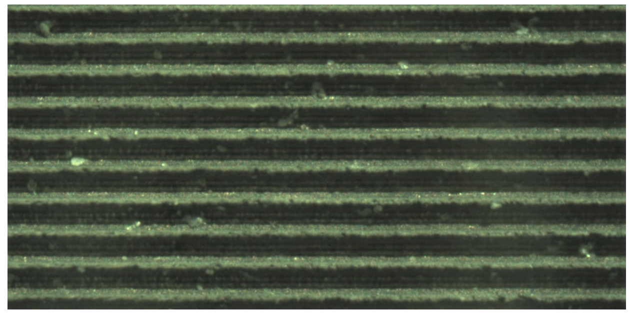

Fig. 1. Texture on the surface of aluminum (10× magnification)

The peculiarity of the obtained surfaces is the presence of texturing artifacts on the top of the protrusions (Fig. 1), the dimensions of which are close to micrometers. This adds an additional level of texture, which in itself can determine the characteristics of water repellency by reducing the contact area of the droplet with the surface, as shown in [14].

It should be noted that after the texture was obtained, the surfaces were left in air for two months, which led to their self-hydrophobization, a phenomenon described in [15] and probably associated with the adsorption of fresh aluminum oxide hydrocarbons from the air by the active surface. After determining the wetting characteristics of this surface, the hydrophobic layer was removed by annealing the plate at 400 °C for 1 hour and hydrophilization was controlled by the water contact angle values, which were less than 10°. The wafer was sequentially treated with hydrophobic agents, characterized, and annealed to regenerate hydrophilicity. This procedure was chosen because it ensured that the sample type was unchanged and made it possible to test different modifiers on the same substrate.

The surface not treated with chemical modifiers has an unexpectedly high water contact angle of 159° (Fig. 2), which makes it superhydrophobic according to the definition given by [16] and puts it on the same level with effective chemical hydrophobic agents.

When the texture is treated with paraffin, the Cassie state is achieved, which can be seen by comparing the contact angle of the texture with the intrinsic value of the contact angle of this material (102°). However, it is the least effective of the water repellents, which can be explained by the lack of chemical interaction between this inert material and the oxide surface, resulting in the need for a relatively large amount of material for wetting, which likely changes the texture of submicron layers on the lattice surface.

The intrinsic surface energy values of the modifiers were measured after application to flat surfaces of aluminum samples without texturing. According to the classical Zisman method (Fig. 3), the surface energy was assumed to be equal to the critical surface tension of the test liquid at which the contact angle is 0°, which was achieved by extrapolation (Fig. 3). Therefore, it was found that the lowest free energy is characteristic of the surface of octyltriethoxysilane and is 18 mN/m, paraffin has a surface energy of 19 mN/m, and the hydrophobic self-adsorbed layer is within 23 mN/m.

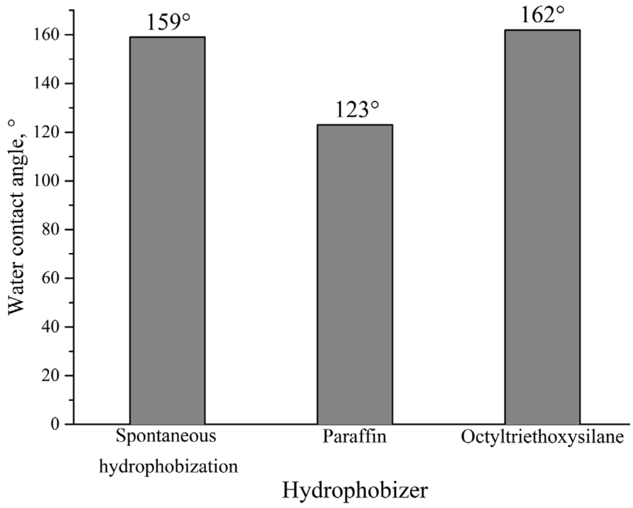

Fig. 2. Comparison of hydrophobization efficiency

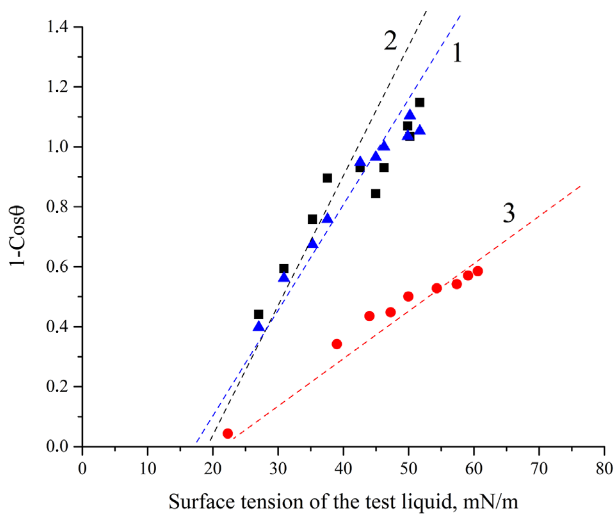

Fig. 3. Zisman plots for flat aluminum surfaces treated with:
1 – octyltriethoxysilane; 2 – paraffin; 3 – spontaneously hydrophobized

The Zisman plots for textured surfaces (Fig. 4) have hysteresis compared to flat surfaces, caused by the fact that the surface of the test substance droplet is partially in contact with the air contained in the texture grooves. The least stable in relation to liquids with lower surface tension compared to water is a texture with a hydrophobic layer formed spontaneously. The transition of wetting states for it begins already at 62 mN/m, the curve touches the abscissa axis at 46.5 mN/m. This is an overestimated value of the critical surface energy, which can be explained by the capillary effect (Fig. 3).

The curve corresponding to the sample treated with octyltriethoxysilane shows the highest hysteresis values, and the wetting transition begins at a surface tension of 37 mN/m. The curve corresponding to the paraffin-coated sample does not appear to contain a pronounced plateau corresponding to the Cassie state, and the Zisman plot shows that this modifier is not very suitable for obtaining effective water repellency. However, for this sample, the transition of wetting states also occurs at relatively low values of surface tension, in the range of 30 to 40 mN/m. This can be explained by the high intrinsic polarity of the modifier. A small hysteresis and an unexpressed transition, however, indicate that when such structures are wetted with water, a mixture of Cassie and Wenzel states is observed with the possible predominance of the latter.

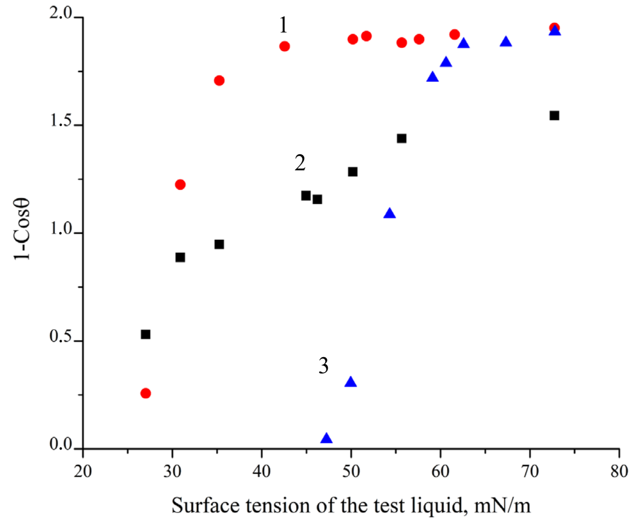

Fig. 4. Zisman plots for the surface of the textured sample treated with:
1 – octyltriethoxysilane; 2 – paraffin; 3 – spontaneously hydrophobized

The texture critical surface energy determination technique described in this work can be used to compare the effectiveness of surface modifiers and in justifying the choice of the type of modifying agent. The results of determining the stability of Cassi wetting obtained in this work indicate that alkoxysilanes have the highest efficiency for aluminum oxide surfaces and, therefore, can be recommended for obtaining a stable superhydrophobic wetting state for such surfaces.

The results obtained are applicable to those textures in which the Cassi state is realized. In the case of mixed Cassi-Wenzel state (which can be confirmed by low values of wetting angles, usually in the range of 110–135°) or Wenzel state, comparison of the obtained angles loses objectivity. Achieving a pure Cassie state is also conditioned by texture features, e. g., on purely microscale surfaces or on surfaces with non-optimal geometry, the presence of a partial Wenzel condition significantly impairs the accuracy of the method.

The results of the study could have been greatly expanded by considering the most effective modifiers such as fluorinated alkoxysilanes, as well as functionalized hydrocarbons such as those containing amine or carboxyl groups, which in turn would have given the technology greater biocompatibility.

The increase in the number of the considered modifiers was limited by the conditions of martial law in Ukraine, in particular by logistical difficulties with delivery of foreign reagents, limited access to some research techniques that could enrich the depth perception, etc.

4. Conclusions

The paper shows that the Zisman method in conjunction with data on the water contact angle values is an effective tool for characterizing the quality of surface modification of textured samples. In particular, it is shown that for aluminum surfaces treated with a femtosecond laser to obtain a hydride micro-nanotexture, the most effective modifier is silane, which maintains the Cassie wetting state at a surface tension of the liquid above 37 mN/m, with the contact angle varying from 155 to 160 degrees. It was shown that paraffin is a less effective modifier with an implicit wetting plateau and a transition in the range of 30 to 40 mN/m. Its contact angle with water is only 123 degrees. It is shown that the textures that have acquired water repellency in the course of self-supported hydrophobization are very unstable to the action of liquids with reduced polarity: the wetting transition occurs at 62 mN/m, but have high water contact angles – up to 159 degrees.

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.

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The study was conducted without financial support.

Data availability

The manuscript has no associated data.

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