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ASPECTS OF WETTING OF HYDROPHOBIZED SURFACES TEXTURED BY A FEMTOSECOND LASER

Extractive methods of obtaining textured surfaces to ensure superhydrophobic properties must have chemical treatment. This work is aimed at determining the influence of the chemical class of modifiers (silanes, perfluorosilanes, unsaturated long-chain carboxylic acids and low molecular weight polyethylene wax) and the level of micro- and nanotexture organization on the characteristics of surface wetting. The work involved texturing of anodized aluminum with a femtosecond laser to create structures. As a result, two types of textured surfaces were obtained: with a regular microtexture in the form of columns with a square section, and a disordered fractal nanotexture with a hierarchical structure. Chemical treatment of the obtained surfaces was carried out and their effectiveness was evaluated. The study of wetting properties of surfaces was carried out by the Zisman method both with individual solvents and with the use of mixtures of solvents. As a result of the work, it is shown that the choice of the modifier of aluminum surfaces textured by a femtosecond laser plays a decisive role in determining the wetting properties, namely the values of the water wetting angle and surface tension, at which the loss of stability of the Cassie state is observed. It is shown that the influence of the chemical composition of the modifier is more significant than the dimension of the texture on the surface. In particular, it is shown that in the case of using silanes and fluorosilanes, it is possible to achieve a water contact angle of 155-160° on nanotextures, while the loss of the Cassie state begins below 46-49 mN/m. When using hydrocarbon modifiers, it is possible to achieve the same high contact angles with water - 154° for oleic acid, but the stability of such surfaces is much lower - 55-65 mN/m. The difference in Cassie state stability between micro- and nanostructures was found to be within the measurement error.

Keywords: hydrophobicity, laser texturing, nanotexture, fluorosilane, surface modification.

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ОСОБЛИВОСТІ ЗМОЧУВАННЯ ГІДРОФОБІЗОВАНИХ ПОВЕРХОНЬ ТЕКСТУРОВАНИХ ФЕМТОСЕКУНДНИМ ЛАЗЕРОМ

Дана робота спрямована на визначення впливу хімічного класу модифікаторів та рівня організації мікро- та нанотекстури на особливості змочування поверхонь. У роботі було одержано два типи текстурованих поверхонь шляхом обробки анодованого алюмінію фемтосекундним лазером: з регулярною мікротекстурою у вигляді стовпчиків з квадратним перерізом, та неупорядкованою фрактальною нанотекстурою з ієрархічною структурою. Дослідження змочувальних властивостей отриманих модифікованих поверхонь було проведено методом Зісмана як окремими розчинниками, так і з використанням сумішей розчинників. У результаті роботи показано, що вибір модифікатора, а саме його хімічний склад, відіграє вирішальну роль у визначенні властивостей змочування, а саме значень кута змочування водою та поверхневого натягу, при якому спостерігається втрата стабільності стану Кассі. Зокрема, показано, що у випадку використання силанів та фторсиланів вдається досягти на нанотекстурах кута змочування водою в межах 155-160°, тоді як втрата стану Касі розпочинається нижче 46-49 мН/м. При використанні вуглеводневих модифікаторів можливе досягнення таких же високих кутів змочування водою - 154° у олеїнової кислоти, але стабільність таких поверхонь значно нижча – 55-65 мН/м. Виявлено, що відмінність у стабільності стану Кассі між мікро- та наноструктурами знаходиться в межах похибки вимірювання.

Ключові слова: гідрофобність, лазерне текстурування, нанотекстура, фторсилани, модифікація поверхні.

Formulation of the problem

Extractive methods of obtaining textured surfaces, for example, chemical etching, texturing with a femtosecond laser, etc. to ensure superhydrophobic properties of such surfaces should be duplicated by the following chemical treatment [1]. This can be done through a wide range of common modifiers. Despite the large number of works devoted to the preparation of extractable superhydrophobic surfaces, they do not contain a structured comparison of the effectiveness of modifiers. This work is aimed at determining the influence of the chemical class of modifiers (representatives of the class of silanes and perfluorosilanes, unsaturated long-chain carboxylic acids and low molecular weight polyethylene wax) and the level of texture organization (micro and nano) on the characteristics of surface wetting are analyzed.

Analysis of recent research

The lotus effect is based on the special topography of the wetted surfaces, which is combined with their low self-surface energy [2]. The latter is understood as a relative decrease in the van der Waals potential of the surface due to the minimization of polar interactions in the sense of the Owens-Wendt theory. Solid polymeric materials with their own surface energy in the range up to 20 mJ/m^2, as well as their corresponding thin layers of modifiers on more polar surfaces, are suitable for this task [3]. The latter is widely used to reduce the surface energy of relatively active materials - metals, oxides, carbonates, silicates, etc., including surfaces obtained by extractive texturing, for example, using laser ablation. Silanes and siloxanes [4] as well as carbon chain reactive modifiers [5] are used to hydrophobize such surfaces. At the same time, the issue of the influence of certain modifiers on the wetting characteristics of hydrophobized structures remains insufficiently studied.

The aim of this work is to determine what effect brings the use of different kinds of treatment agents of silane and functionalized hydrocarbon type on the wetting character and properties of femtosecond laser textured surfaces.

The tasks that were solved to achieve the stated aim were: texturing of anodized aluminum with femtosecond lased to obtain micro- and nanoscale structures; chemical treatment of obtained surfaces and determination of its effectiveness; study of wetting properties of surfaces using Zisman technique with the individual solvents and solvents mixtures.

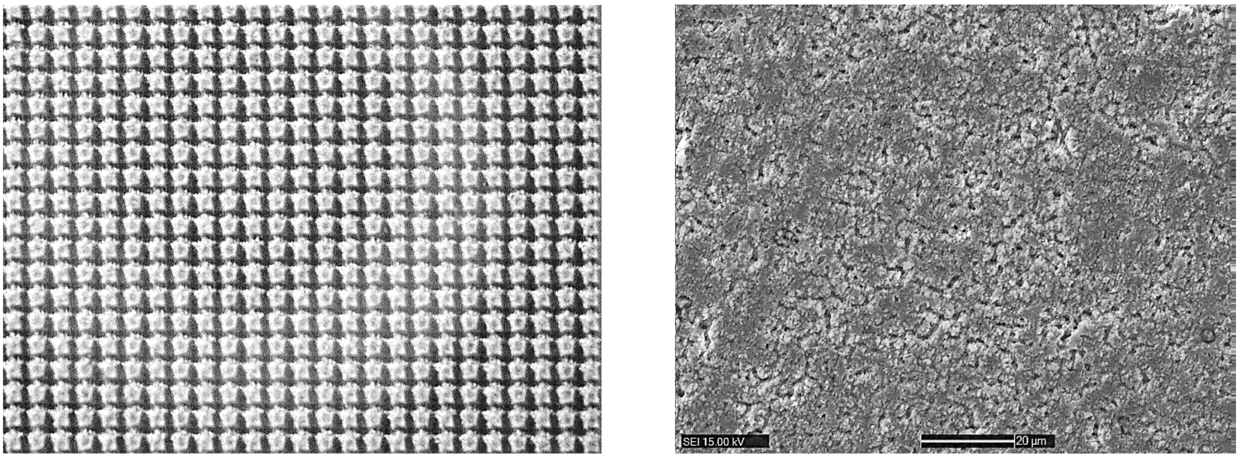
Presentation of the main material

In the work, substrates made of aluminum alloy brand 7500 were used, which were anodized before applying textures. The process took place in a solution of 2.4 M sulfuric acid with a lead auxiliary electrode. Anodic current parameters: density 2 A/dm^2, anodizing time 60 min, solution temperature not higher than 10 °C. Next, using a femtosecond laser (CARBIDE built into the FREEZER01 system from Evana Technologies, Lithuania), micro- and nanostructures were obtained. After texturing, the samples were cleaned by washing in an ultrasonic bath in isopropanol.

Silanes were used as modifiers: n-octyltriethoxysilane (Dynasylan OCTEO, Germany) (hereinafter OCTEO) and 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (Alfa Aesar, Germany) (hereinafter POTS) and hydrocarbon modifiers: oleic acid (hereinafter OlA) and microcrystalline polyethylene wax (hereinafter PEW). Treatment with silanes was carried out in two stages: impregnation of the surfaces in a 1% solution for 30 minutes, then evaporation of the solvent and exposure of the plates at a temperature of 135° for 30 minutes. Treatment with hydrocarbon modifiers included only the stage of impregnation in a 1% xylene solution and removal of the solvent at 80 °C in the oven.

The value of the water contact angle was measured by the sessile drop method. Water-ethanol mixtures at different concentrations were used to determine the critical surface tension [6]. To characterize the surface of the sample and determine the value of the contact angle, an optical microscope with a built-in Delta Optical HCDE-50 camera (China) and the corresponding ScopeTek View software (China) were used. For data reproducibility, five points were measured on each sample.

In the work, two types of textured surfaces were obtained (Fig. 1): 1) a regular microtexture in the form of columns with a square cross-section with a side of 30 μm and 15 μm between them, height 15 μm and 2) a disordered fractal nanotexture with the sizes of primary elements within tens of nanometers, and their agglomerates - tens of micrometers, which allows us to consider this structure as hierarchical.



a b

Fig. 1. The surface of samples textured by a femtosecond laser: a) microtexture; b) nanotexture

The quality control of the chemical modification was carried out according to the values of the contact angle of the obtained surfaces with distilled water until stable values were obtained (Table 1). The values of contact angles obtained for all textured samples in the case of using all modifiers are significantly higher than the angles on flat surfaces. The presence of this hysteresis indicates the achievement of the Cassie state, in which part of the solid surface of the contact is replaced by air.

Table 1

Wettability of textured surfaces

Texture level	Modifier	Contact angle, deg.
-	PEW	106
micro		123
nano		142
-	OlA	42
micro		132
nano		154
-	OCTEO	93
micro		142
nano		160
-	POTS	98
micro		152
nano		160

An obvious fact is the more pronounced water-repellent ability of surfaces with nanotextures compared to microtextures. An unexpected fact is the relatively small difference in the efficiency of silane (OCTEO) and its fluorinated equivalent (POTS) on the nanotexture, which, however, becomes obvious on the microtexture, where the angle difference is 10°. The nanotextured surface wetted with oleic acid also exhibits significant water-repellent properties, inferior to silanes by only 6° and remaining superhydrophobic. Polyethylene wax does not fulfill this condition, although Cassie state is still preserved. A possible explanation for the decrease in indicators in this case may be the fact that this last material is able to change the geometry of the surface of the texture (due to crystallization or the formation of an adsorption layer with a significant thickness) in the direction of lower efficiency. An interesting fact is the reduced values of wetting angles on the flat surface of anodized aluminum coated with oleic acid, which can be explained by the loss of orientation of molecules that are essentially surface-active and contain both polar and non-polar parts.

To establish wetting properties, the Zisman method was used, previously described by us in [7]. In contrast to flat surfaces, in the case of textured surfaces, the character of the curve changes noticeably (Fig. 2). The curve for a textured surface contains a characteristic "shoulder" of hysteresis, which corresponds to the Cassie state, the stability of which begins to be lost at certain values of the surface tension of the test liquid. The position of the shoulder in the work was determined by the tangent method and for PE wax it is 58 mN/m. The critical surface tension of wax is 26 mN/m, which is close to this value in polyethylene [8].

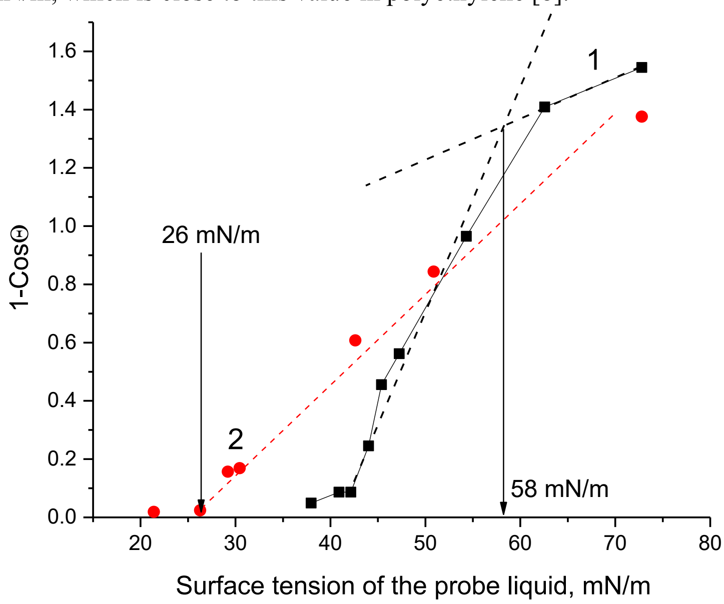


Fig. 2. Zisman plot for: 1) micro-textured Al surface coated with PEW; 2) flat aluminum surface coated with PEW

The presence of hysteresis between the curve of the textured surface and the straight flat one draws attention. The classic Cassie-Baxter equation can be used to describe its upper part, and the Wenzel equation to describe the lower part [9].

The results of determining the point of loss of stability of the Cassie state (Table 2) indicate that the chemical composition of the modifier plays a decisive role in the formation of the stability of the Cassie state on such surfaces. The use of OCTEO and POTS silanes has a relatively close efficiency with a threshold of maintaining stability at the level of 45-50 mN/m regardless of the characteristic size of the structure. The transition to hydrocarbon modifiers reduces stability by increasing these values to 55-65 mN/m.

Table 2

Energy of textured surfaces according to the Zisman method

Texture level	Modifier	Surface energy on the "shoulder", mH/m	Critical surface energy, mH/m
Micro	PEW	58	42
Nano		56	44
Micro	OIA	65	41
Nano		63	47
Micro	OCTEO	48	38
Nano		49	39
Micro	POTS	46	32
Nano		49	38

An interesting fact is the small difference between the efficiency of micro- and nanostructures in the sense of the stability of the Cassie state, which is within the measurement error.

Conclusions

It was shown that the choice of modifier of femtosecond laser-textured anodized aluminum surfaces plays a crucial role in determining the wetting properties, namely the values of the water wetting angle and surface tension at which loss of Cassie state stability is observed. The influence of the chemical composition of the modifier is more significant than even the dimension of the texture.

In particular, it is shown that in the case of using silanes and fluorosilanes, it is possible to achieve a water wetting angle of 155-160° on nanotextures, and the loss of the Cassie state begins below 46-49 mN/m. When using hydrocarbon modifiers, it is possible to achieve the same high wetting angles with water - 154° for oleic acid, but the stability of such surfaces is much lower - 55-65 mN/m.

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