HYDROPHILIC NANOSTRUCTURE FORMATION ON THE TITANIUM SURFACE BY DIRECT LASER IRRADIATION

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Abstract: In the present paper, the model of nanostructure formation on solid surface by microsecond laser pulses melting the material is described. It is shown that typical size of surface nanostructure formed depends on laser wavelength, pulse energy, pulse repetition rate, and pulse duration. Within present work a series of 6 experiments devoted to direct laser nanostructuring of titanium (Ti) and copper (Cu) surfaces is carried out. Besides, the effects of nanoroughness on the contact and sliding angles on hydrophilic surfaces were studied theoretically and experimentally.

Keywords: NANOROUGHNESS OF SURFACE, CONTACT ANGLE, NANOSTRUCTURED HYDROPHILIC SURFACE, LASER IRRADIATION

1. Introduction

At the present time nanostructures are paid additional attention for being an extremely promising object regarding its application in different fields of science, technology and medicine. Surface nanostructuring leads to improvement of nanotribological properties of materials, promotes rise of implants' biocompatibility, and corrosion resistance, and the tendency to denaturalization of surrounding proteins. In this work, following topography, surface energy, and the tendency to denaturalization of proteins forces lies in the foundation of surface tension's and capillarity's interpretation both in the old approach of Clairaut and Laplace and in the new approach of Bakker ([16]-[18]), which is based on introducing the pressure tensor in the interphase area. Description of microsurface forces should begin with definition of interphase energy on the surface of phase boundary of phases solid-liquid (and also phases liquid-liquid, liquid-gas, solid-solid) and proceed with definition of surface forces in the interphase area. It is known ([19]) that if both phases are fluid (liquid-liquid, liquid-gas), then their phase boundary can be stretched or shrunk not affecting the thermodynamic equilibrium; if one phase is solid and the other is liquid or gaseous, then surface of their phase boundary can experience only elastic deformations, however some degree of freedom appears if the liquid is able to slide on the sufficiently smooth solid material (for example, like when quicksilver slides down the glass; water slides on the paraffin surface; blood or body fluids slide down the burnished surface of a titanium implant, etc.); if both phases are solid, then behaviour of the phase boundary is similar to the case solid-liquid, however the implementation of a real phase contact is possible only with atomic smoothness or requires plastic deformation, or prior melting, or evaporation and condensation with subsequent crystallization. Only in the case when both phases are fluid, direct measurement of phase boundary tension is possible. In the case, when both phases are solid, direct measurement of phase boundary tension is achievable with some approximation if and only if in some temperature region yield point is lowered. In the case, when one phase is solid and the other is gaseous, direct measurement of phase boundary tension is impossible. The main mistakes made while measuring surface energy in the process of formation of a new surface are: (a)
omission of irreversible part of fracture work, which turns into heat or energy residual deformations; (b) omission of the fact that fresh (that is, just created) surfaces are in nonequilibrium state with higher energy – they appear to be covered by charge with density up to \(3.5 \times 10^{-3} \text{ C.m}^{-2}\), that consumes part of the fracture work. The special state of fresh surfaces is expressed not only by increased energy, but also by a higher chemical activity. Relaxation down to equilibrium state usually occurs for about ten minutes due to electron emission and surface conduction.

Formation of a new phase boundary is conjugate with consumption of work in order to move a part of molecules from the phases to the surface layer. In isothermal conditions the work of formation of phase surface's element \(dF\) is equal to increment of Helmholtz energy \(dU_\text{f}\) of the surface: \(dU_\text{f} = \sigma \cdot dF\), where \(\sigma\) is specific Helmholtz energy of the phase boundary, which decreases as the temperature increases and at critical temperature \(T_{c}\), achieves the approximate value of zero (in steam-and-liquid systems \(\sigma = 0\), and the difference between the phases disappears). The values of \(\sigma\) for the surface of a solid body on a border with a liquid are not identical to the corresponding coefficients of surface tension (\([20]\)). Accurate theoretical formulas for calculation of liquids' surface tension coefficient do not exist. The main methodological difficulty of calculation of surface tension is the problem of ensuring solid surface purity, when it is in contact with a liquid, as well as liquid's purity. There are some methods of experimental calculation among which the most popular are (\([21]\]): maximum gas bubble pressure method; capillary rise method; method of ring lifting; electromagnetic measurement methods; the drop weight method; hanging drop method; lying bubble or drop method. The simplest experimental method of determining the empirical dependence of phase boundary's specific Helmholtz energy on the temperature is the following relation obtained from the theory of corresponding states (\([22]\)): 
\[
\sigma = \sigma_0 \left(1 - \frac{T}{T_{c}}\right)^{1/3},
\]
where \(\sigma_0\) is determined by the experiments carried out with one constant value of temperature. This formula has shown itself well working for liquids with homonucleus molecules, however it can be approximatively used also for the majority of other liquids. For calculations of water's \(\sigma\) it is recommended to use the following interpolation formula: 
\[
\sigma = 0.235 \left(1 - \frac{T}{T_{c}}\right)^{1.265} \left(1 - 0.625 \frac{T_{c} - T}{T_{c}}\right).
\]

### 2.2. Wetting Process

In the introduction we mentioned (following the work (\([15]\))) the contact angle of wetting \(\theta\) between a solid surface and a tangent to the phase boundary gas-liquid. From the minimality condition of surface's Helmholtz energy (\([23]\), \([24]\)) one can obtain the following relation known as Young's law:
\[
\theta = \arccos \left(\frac{\sigma_\text{solid, gas} - \sigma_\text{solid, liquid}}{\sigma}\right).
\]
It is important to note that the contact angle is very sensitive to such difficult-to-control factors as roughness of a solid surface or presence of foreign impurity on the solid surface or in the liquid, particularly if this impurity is surface-active, which, concentrating on the thermodynamic phase boundary, cause surface tension lowering: for instance, R-OH alcohols; R-CO\(-\) aldehydes; R-COOH carboxylic acids; CH\(_3\)-, C\(_2\)H\(_5\)-, C\(_7\)H\(_{35}\)-, etc. hydrocarbon radicals; COH and COOH functional groups; oleic acid C\(_{17}\)H\(_{33}\)COOH; stearic acid sodium C\(_{17}\)H\(_{35}\)-, etc. hydrocarbon radicals; COH and COOH functional groups; R-OH alcohols, etc. Hydrophobic surfaces are speaking about implants) that the contact angle of wetting \(\theta\) depends also on hysteresis of wetting – on the direction of wetting a solid body surface by a liquid, that is, on the fact, whether the liquid is flowing on the surface or down it.

### 2.3. The Phase Separation Surface's Equilibrium, and Axisymmetric Equilibrium Separation Surfaces of Phases

If the liquid rests relative to the coordinate system related to Earth, then in hydromechanics this rest is called absolute rest; if the liquid rests relative to the coordinate system which moves with uniform acceleration relative to Earth, then this rest is called relative rest. For both absolute rest and relative rest Euler's equations in the vector form hold: 
\[
\vec{F} - \frac{1}{\rho} \nabla p = 0,
\]
where \(\vec{F}\) is mass forces density vector, which, in the case of relative rest, includes inertial forces; \(\rho\) is liquid density; \(p\) is liquid pressure. Due to the fact that mass forces have potential in the majority of cases, one can write \(\vec{F} = -\nabla \Phi\), where \(\Phi\) is a force function. Consequently, Euler's equation turns into equation
\[
\nabla \Phi + \frac{1}{\rho} \nabla p = 0,
\]
whose general integral for the cases, when \(p = \rho(p)\), is the formula \(\Phi + \gamma = \text{const}\), called the equation of hydrostatics, where \(\gamma = \int \frac{dp}{\rho}\) denotes pressure function. It should be noted that, if the liquid is a heavy compressible liquid, then out of all mass forces only gravitational force affects it, so the general integral looks like \(\Phi = g \cdot z + \text{const}\), where \(z\) denotes the coordinate which is counted vertically up. For a heavy compressible liquid the general integral of Euler's equation has the form
\[
z + \frac{p}{g \cdot \rho} = \text{const},
\]
and this formula represents hydrostatic distribution of pressure. When a gas-liquid system is in the equilibrium state, then in each contacting phase, firstly, the equations of hydrostatics hold and, secondly, for every point on phase boundary defined by a position vector \(\vec{r}\) Laplace formula
\[
p_r - p_s = 2 \cdot \sigma \cdot H(\vec{r})
\]
is true, which means that on the boundary between two fluid phases the surface tension causes a pressure jump in the contacting phases, which is proportional to average curvature \(H\) of the phase boundary. From these two relations (equation of hydrostatics and Laplace formula) one can deduce the main differential equation of hydrostatic equilibrium
\[
2 \cdot \sigma \cdot H(\vec{r}) = (\rho_{\text{liquid}} - \rho_{\text{gas}}) \cdot \Phi(\vec{r}) + \text{const},
\]
whose general integral determines the shape of phase boundary. In the most practically important axial-symmetric problems on liquid there are: homogenous gravitational field with intensity \(g\), directed along vertical axis \(OZ\); centrifugal force field caused by uniform rotation of the gas-liquid system around the same axis \(OZ\) with angular velocity \(\omega\). In this case, the potential of mass forces has the form
\[
\Phi = g \cdot z - \frac{1}{2} \omega^2 \cdot d^2,
\]
where \(d = \sqrt{x^2 + y^2}\) is the distance to the rotation axis. When the system rests, potential of mass forces is determined by the formula \(\Phi = g \cdot z\), but the main equation of hydrostatic equilibrium has the form:
\[
2 \cdot \sigma \cdot H(z) = \delta \cdot g \cdot (\rho_{\text{liquid}} - \rho_{\text{gas}}) \cdot z + 2 \cdot \sigma \cdot H(0),
\]
where the term
\[
2 \cdot \sigma \cdot H(0)
\]
depends on the vertical axis \(OZ\) is pointed up (and the gravitational field is pointed down), and \(\delta = +1\) in the case, when the vertical axis \(OZ\) is pointed down. For a resting system
with a characteristic size \( L_{\text{ch}d} \). It is possible to use the main equation of hydrostatic equilibrium in order to obtain the scale of gravitational forces \( f_{\text{grav}} \leq g (P_{\text{liquid}} - P_{\text{gas}}) L_{\text{ch}d} \) and the scale of surface tension forces \( f_{s} \leq \frac{\sigma}{L_{\text{ch}d}} \). Then Bond number \( Bo \), which is the criterion of similarity in hydrodynamics and determines relation between external forces (usually, gravity) and surface tension forces has the following form:

\[
Bo = \frac{f_{\text{grav}}}{f_{s}} = g \frac{(P_{\text{liquid}} - P_{\text{gas}})}{\sigma} L_{\text{ch}d} \cdot \sigma.
\]

The condition \( Bo = 1 \) determines linear size of the region, where gravitational forces and surface tension forces are equal:

\[
L_{\text{ch}d} = \sqrt{\frac{\sigma}{g (P_{\text{liquid}} - P_{\text{gas}})}}. \tag{6}
\]

The quantity \( L_{\text{ch}d} \) is called capillary constant. For the majority of liquids with \( \rho \parallel \rho_{cl} \), \( \rho_{cl} \) is critical pressure), that is, in Earth conditions, the value of capillary constant varies within \( 1 \div 3 \) mm.

Obviously, if one divides the equation of hydrostatic equilibrium

\[
2 \cdot \sigma \cdot H(z) = \delta \cdot g (P_{\text{liquid}} - P_{\text{gas}}) \cdot z + 2 \cdot \sigma \cdot H(0)
\]

by the quantity \( \sqrt{\sigma \cdot g (P_{\text{liquid}} - P_{\text{gas}})} \), then it turns into the following dimensionless form:

\[
2 \cdot H(\tilde{z}) = \delta \cdot \tilde{z} + C, \quad \tilde{z} = \frac{z}{L_{\text{ch}d}}, \quad C = 2 \cdot H(0) \cdot L_{\text{ch}d}.
\]

### 2.4. Melting Process

At sufficient energy density, duration and order of a laser pulse melting of solid body’s surface occurs – in our case, of ball-shaped titanium head of the human hip joint endoprosthesis. When the laser pulse irradiation stops, the process of cooling the processed surface starts and is carried out by the means of heat removal deep into the solid phase and subsequent solidification of the surface layer. It is supposed that the power of laser irradiation is such that phase transition solid-liquid occurs. Then, with appropriate approximation, temperature fields in the liquid \( T_{\text{liquid}}(x,t) \) and solid \( T_{\text{solid}}(x,t) \) phases can be described by following boundary value problem \([13],[26],[27]\):

\[
\frac{\partial T_{\text{liquid}}(x,t)}{\partial t} = a_{\text{liquid}} \frac{\partial^2 T_{\text{liquid}}(x,t)}{\partial x^2}, \quad 0 < x < y(t), \tag{7}
\]

\[
\frac{\partial T_{\text{solid}}(x,t)}{\partial t} = a_{\text{solid}} \frac{\partial^2 T_{\text{solid}}(x,t)}{\partial x^2}, \quad y(t) < x < \infty, \tag{8}
\]

\[
T_{\text{solid}}(x,t) \big|_{t=0} = T_{\text{solid}}(x,t), \quad y(t) \big|_{t=0} = T_{0}, \tag{9}
\]

\[
T_{\text{liquid}}(x,t) \big|_{t=0} = T_{\text{liquid}}(x,t), \quad y(t) \big|_{t=0} = T_{0}, \tag{10}
\]

\[
\lambda_{\text{liquid}} \frac{\partial T_{\text{liquid}}(x,t)}{\partial x} \big|_{y(t)} = H \rho y'(t) + \lambda_{\text{solid}} \frac{\partial T_{\text{solid}}(x,t)}{\partial x} \big|_{y(t)}. \tag{11}
\]

where \( y(t) \) is the moving boundary of the phase transition; \( Q(t) \) is the absorbed energy per surface unit for the time \( t < \tau \), where \( \tau \) denotes the duration of a laser pulse; \( a = \frac{\lambda}{c \cdot \rho} \) is thermal diffusivity, where \( \lambda \), \( c \) and \( \rho \) denote correspondingly thermal conductivity, specific heat and density of a metal \((a_{\text{solid}}, c_{\text{solid}}, \rho_{\text{solid}})\) or liquid \((a_{\text{liquid}}, c_{\text{liquid}}, \rho_{\text{liquid}})\); \( T_{0} \) and \( T_{1} \) denote correspondingly initial temperature of the solid body and the temperature of the phase transition; \( H \) is latent melting heat, which is absorbed on the moving phase boundary. Supposing that the temperature of the metal surface processed by laser pulse achieves phase transition point during the time \( t_{0} < \tau \) and the temperature of liquid phase varies slightly during further process \( t_{0} < t < \tau \), we can replace the boundary condition \((4)\) by the following more simple condition:

\[
T_{\text{liquid}}(x,t) \big|_{t=t_{0}} = T_{1} = T_{\text{liquid}}(x,\tau) \big|_{t=t_{0}} > T_{1}, \tag{7}
\]

where \( T_{1} \) is a temperature of molten metal on the surface that can be defined by heat balance equation. Combining \((1)\)-(3), \((5)\) and \((7)\) we can write that

\[
T_{1} = T_{0} + 2 \cdot c_{\text{liquid}} \cdot \rho \cdot \sqrt{a_{\text{solid}}} \cdot \left(1 - e^{-\frac{\rho_{\text{solid}}}{\sigma}}\right) \cdot \text{erfc} \left(\frac{\beta}{\sqrt{2} \cdot a_{\text{solid}}}\right) \times \left\{ -2 \cdot c_{\text{solid}} \cdot \rho_{\text{solid}} \cdot (T_{1} - T_{0}) \right\}, \tag{8}
\]

\[
Q (t) = H \cdot \rho \cdot y(t) + \int_{0}^{\frac{y(t)}{r(t)}} c_{\text{solid}} \cdot \rho_{\text{solid}} \cdot (T_{\text{solid}} - T_{0}) \cdot dx, \tag{9}
\]

parameter \( \beta \) can be found from the following transcendental equation:

\[
2 \cdot \frac{c_{\text{liquid}} \cdot \rho}{\pi} \cdot (T_{1} - T_{0}) = \sqrt{2} \cdot H \cdot \rho \cdot \beta \cdot \left(\frac{\rho_{\text{solid}}}{\sigma} \right) + \frac{Q (t)}{\tau}. \tag{10}
\]

The formulas \((8)-(10)\) allow us to calculate melting depth of different solid materials irradiated by laser pulses of various duration and energy.

As it has already been mentioned above, under the influence of laser irradiation high temperature stress occurs in the metals. Deformation process in these conditions is followed by residual deformation, whose appearance is related to nonelastic effects and reorganization of crystal's defect structure. Stress' relaxation can have heterogeneous character due to formation of new structure zones called relaxation zones \([32]\) in the old excited structure. Depending on the state of the system, on the conditions of external influence, on the degree of process development it may occur that relaxation zones can be centers of a new phase, groups of dislocations and disclinations, microcracks, clusters of atoms and vacancies forming clusters, micropores, dislocation loops, etc. One can imagine the deforming as three simultaneously coexistent phases: relaxation field determined by the parameter \( q_{\text{rel}}(r,t) \), stress field \( \sigma_{ij}(r,t) \) corresponding to external load and relaxation zones with concentration \( n(r,t) \).
\( \varphi_{ij}(r, t), \quad \sigma_{ij}(r, t) \) and \( n(r, t) \) is defined by the following system of nonlinear differential equations:

\[
\begin{aligned}
\varphi_{ij}(r, t) &= -\kappa \cdot \varphi_{ij} + g_i \cdot n, \\
\dot{n} &= -\gamma \cdot n + \varphi_{ij} \cdot \sigma_{ij}, \\
\sigma_{ij}(r, t) &= \nu \left( \sigma_{ij} - \sigma_{ij}^{\infty} \right) - g_i \cdot \varphi_{ij} \cdot n,
\end{aligned}
\]

(11)

where parameters \( \kappa, \gamma, \nu, \quad g_i \) are material constants; quantity \( \sigma_{ij}^{\infty} \) is determined by the applied external loads and corresponds to the residual stress set as the result of relaxation.

In the system (11) the term \( -\kappa \cdot \varphi_{ij} \) is the decay of the relaxation process; the term \( -\gamma \cdot n \) is the relaxation field disintegration of the formed relaxation zones; the term \( \nu \cdot \left( \sigma_{ij} - \sigma_{ij}^{\infty} \right) \) describes the stress relaxation in linear approximation, when their interference is absent; the term \( g_i \cdot n \) is related to relaxation field generation due to formation of relaxation zones; the term \( \frac{\varphi_{ij} \cdot \sigma_{ij}}{g_i} \) takes into account the influence of the relaxation field \( \varphi_{ij}(r, t) \) and stress field \( \sigma_{ij}(r, t) \) on the generation of relaxation zones; the term \( g_i \cdot \varphi_{ij} \cdot n \) is caused by the influence of the relaxation field disintegration on the speed of stress relaxation. As the speed of alteration of the relaxation field is much lower than the speed of the processes atomic relaxation described by the constants \( \gamma \) and \( \nu \), in (7) one can use adiabatic elimination of variables. Taking into account possible spatial fluctuations whose role grows as temperature and external loads grow, we get the following kinetic equation for relaxation parameter:

\[
\varphi_{ij} = A \varphi_{ij} - B \varphi_{ij}^3 + D \Delta \varphi_{ij},
\]

(12)

where \( A = \frac{g_i}{g_i}, \quad B = \frac{g_i}{g_i}, \quad \kappa \gamma \nu \), \( D \) is diffusion coefficient of atoms in a warmed-up zone. If we take into account diffusion's dispersion, then equation (12) will turn into Ginzburg-Landau generalized equation \((13), \quad (14))\).

For \( \sigma_{ij} = \frac{g_i}{g_i} \), equation (12) has one stable solution \( \varphi_{ij}(r, t) = 0 \); if exceeding of the critical value \( \sigma_{ij} > \sigma_{ij}^{\infty} \) occurs, new coherent states of the system are realized with spatial periodicity, whose period can be calculated using the formula

\[
P = \frac{\frac{\sigma_{ij}^{\infty} - \sigma_{ij}}{2 \cdot \pi \cdot \sigma_{ij}^{\infty}}}{L \cdot W \cdot H}.
\]

Using the kinetic equation from the theory of surface nucleation \((2), \quad (28)-(30))\) as well as variational principle for the main laws of thermal conduction, one can obtain \((31)\) the following closed formula for characteristic size-radius of a crystalline phase nucleus in a supercooled liquid:

\[
r(t) = \frac{V_0}{\pi} \cdot e^{-\frac{U}{T} \cdot k \cdot T} \left( \frac{h}{U + h} + e^{\frac{U - h}{U + h}} \right),
\]

(11)

where \( V_0 \) is Debye oscillation frequency of atoms in a supercooled liquid; \( U \) is the activation energy for atom movement; \( k \cdot T \) is thermal energy; \( d \) is characteristic size for a single atom; \( h \) is the heat of phase transformation for one atom; \( \varepsilon \) is the average speed of melt cooling. Using the formula (11) one can precisely estimate characteristic size-radius of a crystalline phase nucleus, that is, the size of nanostructures appearing on the surface of the processing solid body, while it is melting under laser pulse irradiation.

3. Experimental Facility, Experiments and Results

Within present work we have carried out a series of 6 experiments devoted to direct laser nanostructuring of titanium (Ti) and copper (Cu) surface. All the processed samples had the same sizes: \( L \times W \times H = 5 \times 3 \times 0.1 \text{ mm} \). Samples’ surfaces had 14th surface finish class. Samples were placed in a laser facility chamber Nd:YAG crystal and were irradiated in a motionless laser beam. For a detailed analysis of the irradiated samples’ profiles we used a desktop scanning electron microscope Hitachi TM3030 with low vacuum regime, which allows to carry out the experiments without sample preparation and to investigate samples without prior metal deposition; controlled by a simple and understandable interface with the functions of automatic focus, contrast and brightness setting; equipped with two detectors – of secondary and reflected electrons, – owing to which it is possible to get comprehensive information about the surface of the investigated samples. Laser facility Nd:YAG crystal, which was used in order to carry out a series of experiments devoted to direct laser nanostructuring of surfaces of 4 titanium and 2 copper samples, has the following capabilities: laser wavelength: 532 nm; maximum pulse energy: 0.15 J; pulse repetition rate: 10 Hz; initial pulse duration: 5-9 ns; pulse duration: 5-400 µs. After repeated irradiation with one beam of microsecond Nd:YAG crystal-laser formation of nanosized structures on the copper and titanium surfaces was noticed. Laser irradiation intensity was maximal in the center of the irradiation spot and was going down closer to its periphery. After repeated pulse action on one surface patch a deep crater appeared in the spot’s center. However, on the periphery, where the laser irradiation intensity was lower, one could notice only some surface melting. Using SEM-analysis (that is, using scanning electron microscopy with X-ray spectrometry microanalysis) no submicrometer structures were detected in the central high-intensity part of the spot. However, formation of nanorelief was detected in the peripheral part of the irradiation zone. For all 6 samples we detected roughness of characteristic size along the surface on the surface in the peripheral low-intensity region of the spot as well as small-scale roughness in the form of saliences put over the surface. Round shape of the obtained nanoreliefs implies the surface being molten by the laser irradiation and subsequent crystallization with formation of the above mentioned submicrometer structures. Taking into account the possibility of slight material melting, we can consider a surface under thermal flow of pulsed laser irradiation which causes phase transition solid-liquid.

3.1. Experiment 1

In this experiment copper foil was taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd:YAG crystal were chosen: laser wavelength (LW): 532 nm; pulse energy (PE): 0.14 J; pulse repetition rate (P RR): 10 Hz; pulse duration (PD): 130 µs. Results of a single pulse action on this sample are shown on the Fig.1. The obtained nanostructured surface has a good hydrophilic property: water was used as the liquid.

Fig. 1 Nanostructured copper surface (one-time processing) with a good hydrophilic property. PE=0.14 J; PD=130 µs.
### 3.2. Experiment 2

In this experiment copper foil was again taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd³⁺:YAG crystal were chosen: laser wavelength: 532 nm; pulse energy: 0.14 J; pulse repetition rate: 10 Hz; pulse duration: 130 µs. Results of a twofold pulse action on this sample are shown on the Fig. 2. The obtained nanostructured surface has a much worse hydrophilic property: water was used as the liquid.

![Nanostructured copper surface (twofold processing) with a bad hydrophilic property. PE=0.14 J; PD=130 µs.](image)

### 3.3. Experiment 3

In this experiment titanium foil was taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd³⁺:YAG crystal were chosen: laser wavelength: 532 nm; pulse energy: 0.15 J; pulse repetition rate: 10 Hz; pulse duration: 100 µs. Results of a single pulse action on this sample are shown on the Fig. 3. The obtained nanostructured surface has a very good hydrophilic property: both water and physiological solution 0.9% NaCl were used as the liquid.

![Nanostructured titanium surface (one-time processing) with a very good hydrophilic property. PE=0.15 J; PD=100 µs.](image)

### 3.4. Experiment 4

In this experiment titanium foil was again taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd³⁺:YAG crystal were chosen: laser wavelength: 532 nm; pulse energy: 0.15 J; pulse repetition rate: 10 Hz; pulse duration: 130 µs. Results of a single pulse action on this sample are shown on the Fig. 4. The obtained nanostructured surface has a good hydrophilic property: both water and physiological solution 0.9% NaCl were used as the liquid.

![Nanostructured titanium surface (one-time processing) with a good hydrophilic property. PE=0.15 J; PD=130 µs.](image)

### 3.4. Experiment 5

In this experiment titanium foil was again taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd³⁺:YAG crystal were chosen: laser wavelength: 532 nm; pulse energy: 0.15 J; pulse repetition rate: 10 Hz; pulse duration: 85 µs. The processing was implemented by the stripes with use of a lens for focusing of laser beam. Results of a single pulse action on this sample are shown on the Fig. 5. The obtained nanostructured surface has the following hydrophilic property: the liquid (water and physiological solution 0.9% NaCl) flows only in one direction.

![Nanostructured titanium surface (one-time processing with a lens for focusing of a laser beam): the liquid flows only in one direction. PE=0.15 J; PD=85 µs.](image)

### 3.4. Experiment 6

In this experiment titanium foil was again taken as a sample, and for its laser processing the following characteristics of microsecond laser facility Nd³⁺:YAG crystal were chosen: laser wavelength: 532 nm; pulse energy: 0.15 J; pulse repetition rate: 10 Hz; pulse duration: 300 µs. Results of a single pulse action on this sample are shown on the Fig. 6. The obtained nanostructured surface has a very good hydrophilic property: both water and physiological solution 0.9% NaCl were used as the liquid.

![Nanostructured titanium surface (one-time processing) with a very good hydrophilic property. PE=0.15 J; PD=300 µs.](image)

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### 5. References


