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Study of surface hydrophilicity of metallic materials modified by ultraviolet laser radiation

Tatyana Sablina [a, *], *Marina Panchenko* [b], *Ilya Zyatikov* [c], *Aleksey Puchikin* [d], *Ivan Konovalov* [e], *Yurii Panchenko* [f]

Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences, 2/3 Akademichesky Avenue, Tomsk, 634055, Russian Federation

[a] https://orcid.org/0000-0002-5941-5732, sabltat@mail.ru; [b] https://orcid.org/0000-0003-0236-2227, panchenko.marina4@gmail.com; [c] https://orcid.org/0000-0003-3219-9299, zyatikov@lgl.hcei.tsc.ru; [d] https://orcid.org/0000-0001-6931-9800, puchikin@lgl.hcei.tsc.ru; [e] https://orcid.org/0000-0002-1166-1416, ivan@lgl.hcei.tsc.ru; [f] https://orcid.org/0000-0001-8017-7268, yu.n.panchenko@mail.ru

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ABSTRACT

Introduction. Surface modification using laser radiation is a promising direction in the field of creating new technologies for treatment metal materials, including those for medical purposes. The ability of lasers to change the surface characteristics of a material and, consequently, its interaction with the environment has attracted great interest among researchers. Despite numerous recommendations for the use of laser surface treatment, there is still lack of systematic and detailed studies on the influence of parameters on the structural-phase state and properties of the modified surface, especially concerning ultraviolet laser exposure. The **purpose** of this work is to study the hydrophilicity of the surface of TiNi alloy and stainless steel after UV laser treatment. **Materials and methods of the study:** experimental samples made of TiNi (TN-10) alloy and 12KH18N9T (AISI 321) stainless steel were locally (beam diameter 0.5 cm) exposed to a solid-state Nd:YAG laser at the wavelength of 266 nm, with a pulse duration of ~ 5 ns, and pulse repetition rate of 10 Hz. The material was exposed to a constant output radiation energy density of 0.1 J/cm^2, with a change in the exposure duration from 10 to 600 s. Before and after UV laser treatment, the wettability of the material surface and free surface energy were determined. The structure, elemental and phase composition, and surface topography of TiNi and steel were studied using scanning electron microscopy with the determination of the elemental composition by energy-dispersive spectroscopy, X-ray phase analysis, and profilometry. **Results and discussion.** Ultraviolet laser treatment of the surface of TiNi alloy and steel samples leads to an increase in their hydrophilicity. In the initial state, the contact angle of wetting is ≈75° for both materials, and after ultraviolet laser treatment it decreases to ≈11-13° for TiNi and to ≈22° for steel. The phase composition of steel does not change during laser treatment, and phases belonging to oxides are recorded on the surface of TiNi after 420 seconds of treatment. Ultraviolet laser treatment of TiNi alloy and steel leads to an increase in free surface energy, a change in the ratio of its components (a decrease in the dispersed component and a significant increase in the polar component), an increase in the oxygen content on the surface of both materials. With long laser exposure times (more than 300 seconds), microcracking occurs on the surface of the processed material, leading to an increase in roughness. The change in the surface topography (roughness) of TiNi alloy does not have a noticeable effect on the wettability of the surface of metal materials, and for steel samples, there is an insignificant tendency to reduce the contact wetting angle with increasing roughness. The degree of hydrophilicity of metal materials, characterized by the contact wetting angle, increases with an increase in the duration of laser exposure due to saturation of the surface with free oxygen and an increase in free surface energy (its polar component). Based on the studies, it can be concluded that ultraviolet laser treatment is an effective way to change the wettability of metal materials.

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Introduction

The main methods of changing the surface properties of metallic materials, used both in technology and medicine, are various types of surface treatment [1–5]. Surface modification using concentrated energy flows is one of the promising areas in the field of creating new technologies for treating metallic materials,

*** Corresponding author**
Sablina Tatyana. Yu., Ph.D. (Engineering), Engineer
Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences, 2/3 Akademichesky Avenue,
634055, Tomsk, Russian Federation
Tel.: +7 913 843-21-78, **e-mail:** sabltat@mail.ru

including materials for medical purposes (biomaterials) [1, 6–10]. The main purpose of surface treatment of metallic biomaterials is to obtain a modified layer with specific properties on the material surface. Such surface characteristics as wettability, surface energy, roughness, phase and chemical composition have a significant impact on the biocompatibility of materials in a physiological environment. In this case, both the corrosion properties and the ability to integrate biomaterials into living biological tissues largely depend on the wettability of these materials with biological fluids, aqueous solutions of salts and acids [4, 6, 7, 9, 11, 12]. In terms of interaction with biological fluids, cells and tissues, a hydrophilic surface is more preferable than a hydrophobic one. Unlike conventional materials, the surface of implants with increased hydrophilicity provides higher rates of osseointegration, i.e. interaction of biomaterial with bone tissue without the participation of connective tissue [13].

The ability of lasers to change the surface characteristics of material and, consequently, its interaction with the environment has attracted great interest among researchers in using this unique feature to improve the material behavior in biological environments [9, 11, 12, 14–17]. The advantage of using laser radiation for modifying the surface of various materials is that laser treatment is an environmentally friendly, non-contact and relatively fast method, and this method of treatment is characterized by high accuracy and the possibility of local influence. By adjusting the parameters of laser treatment, it is possible to selectively change the surface of the material without affecting its internal structure and volumetric properties. Nowadays, lasers are increasingly used as a tool for modifying the surface of various metallic materials and devices which are used as biomedical materials in cardiology, orthopedics and dentistry and other areas [11, 18–20].

The works [1, 5, 9, 11, 14, 18–22] note that lasers are mainly used to modify the surface of metal implants in order to improve osseointegration, corrosion resistance and hydrophilicity. Metallic biomaterials based on titanium and its alloys, as well as stainless steel, are used in the manufacture of artificial heart valves, pacemakers, stents for blood vessels, bone and joint endoprostheses (shoulder, knee, hip, elbow), for auricles reconstruction, in facial surgery, and also as dental implants. These biomaterials prevail over other classes of biomaterials due to the synergistic combination of excellent mechanical properties, corrosion resistance and wear resistance, as well as long-term biocompatibility [12, 14, 19, 20, 23, 24].

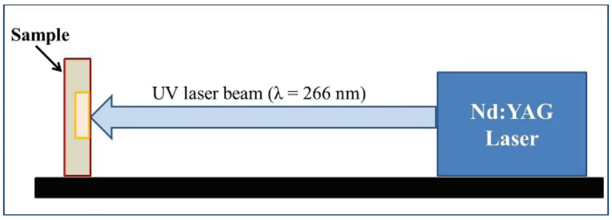
Recently, controlled laser treatment has been actively studied to change the topography, morphology, and physicochemical properties of the surface of biomaterials, including with the aim of reducing bacterial adhesion on the surface of implants and, thus, tuning its biological and other surface properties [11, 16, 17, 20, 22, 25]. *In vitro* and *in vivo* studies have been conducted to estimate the effect of laser treatment on adhesion, cell growth and proliferation, wettability, surface hardness, mechanical properties, surface morphology, antibacterial properties, and biofilm formation on the surface of implants [13, 15–17, 20, 23, 25, 26].

It should be noted that basically all studies on laser treatment on materials surface aimed at changing the morphology, topography and properties of the materials surface were carried out using radiation with a wavelength of $\lambda = 1{,}064$ nm or $\lambda = 532$ nm with high values of energy density or power [10, 15, 17, 25, 27]. Works on the study of the effect of ultraviolet (*UV*) laser radiation ($\lambda < 400$ nm) on the surface of materials are not many [20, 28, 29]. However, despite numerous recommendations on using laser surface treatment, there is still lack of systematic and detailed studies of the effect of laser radiation parameters on the structural-phase state and properties of the modified surface of metallic materials.

The ***purpose of this work*** is to study the hydrophilic behavior of the surface of *TiNi* alloy and stainless steel after *UV* laser treatment. The objective of this study is to conduct a comparative analysis of the contact angle, structure, topography, phase and chemical composition of the surface of *TiNi* and steel specimens before and after laser treatment with a change in the exposure duration.

Materials and methods of investigation

The experimental specimens in the form of plates with dimensions of 10×10×1.5 mm (length × width × thickness) made of an alloy based on titanium nickelide *TiNi* (*TN-10*), developed at the Research institute of medical materials and implants with shape memory (Tomsk) (identification mark — *TiNi*) and stainless steel *0.12 C-18 Cr-9 Ni-Ti* (*GOST 5632-72*) (*AISI 321*) (identification mark — steel) were taken for the study. The specimens were previously polished on *SiC* grinding paper of various grits *P600–2500* (*ISO6344*) and then polished to gloss with diamond pastes *ASM* or *ASN 3/2*, *2/1*, *1/0*. To remove surfactant contamination after polishing, the specimens were washed in an ultrasonic bath (*VGT-1620QTD*, China) successively in alcohol and acetone for 10 minutes. Ultraviolet laser treatment was carried out in air at normal atmospheric pressure and room temperature (22 ± 3 °C). Experimental specimens were exposed to radiation of the 4th harmonic of *Q*-smart 850 *Nd:YAG* laser (*Quantel*, France) at the wavelength of 266 nm. Pulse duration was ~ 5 ns, pulse repetition rate was 10 Hz. Experimental scheme of laser treatment is shown in Fig. 1, *a*. The material was treated stationary, without moving the specimen and laser beam, at a constant radiation energy density of 0.1 J/cm^2, and the duration of treatment was varied from 10 to 600 s. The area of exposure on the surface of the experimental specimens was limited by the diameter of the laser beam $d = 0.5$ cm (Fig. 1, *b*).



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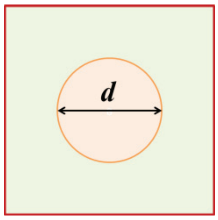


b

Fig. 1. Experimental scheme of *UV* laser treatment of specimen surface

Before and after UV laser treatment, the wettability of the materials surface was determined using the sessile drop method of test liquids (deionized water, glycerin) with known properties of surface energy at the contact angle. Contact angle was measured by photographing a drop on the surface of the material. To do this, a 3 μl drop of liquid from a micropipette was applied to the horizontal surface of the metallic material, after which the drop was photographed so that the optical axis coincided with the plane of the material surface and the drop. The height ***h*** and the length of the baseline **2*r*** of the drop were measured from the obtained photographs (Fig. 2), and the contact angle (**Θ**) was calculated using the semi-angle method using formulas (1, 2):

$$\Theta_1 = \tan^{-1} h / r, \quad (1)$$

$$\Theta = 2\Theta_1, \quad (2)$$

where h is the height; r is the half of baseline length.

At least 5 series of contact angle measurements were carried out for the original surface and for each treatment mode.

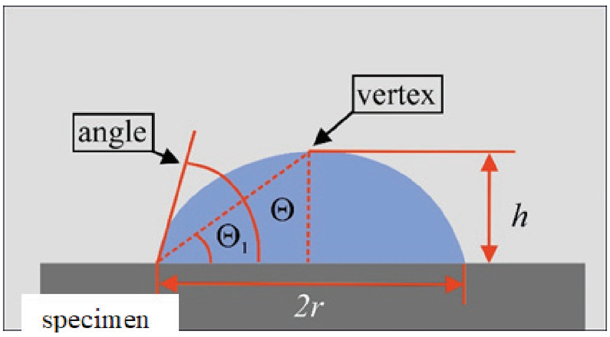


Fig. 2. Scheme of measuring the wetting contact angle

The free surface energy γ_s of the material before and after laser treatment was determined by the *Owns – Wendt – Rabel – Kjelble* (*OWRK*) method [30], using known reference data on surface tension, dispersed γ_d and polar γ_p components of the test liquids (water and glycerin) and the obtained data on the contact angle. The surface topography of *TiNi* alloy and steel before and after laser treatment was studied using the contact method with a profilometer for tribological tests (*Tt-Tribotechnic*, France) equipped with a high resolution diamond needle (7.55 nm along the ***Z*** axis) without a sliding element. The roughness ***Ra***, averaged over the entire length of the baseline equal to 3 mm, was measured in accordance with *GOST 2789-73*. At least 5 measurements were performed for each specimen. The structure and elemental composition of the materials surface before and after treatment were estimated using data obtained using a scanning electron microscope (*SEM*) (*VEGA 3 TESCAN*, Czech Republic) equipped with an energy dispersive analyzer (*EDS*). The phase composition of *TiNi* and steel specimens in the initial state and after laser treatment was determined from diffraction patterns obtained on a *DRON*-type X-ray diffractometer (*Burevestnik*, St. Petersburg, Russia) with filtered *CuK*α radiation in the range of scanning angles **2Θ** 30°–110°. Qualitative and quantitative analysis of X-ray diffraction (*XRD*) patterns was carried out using the *PDWin* and *CDA* software packages (*OJSC Burevestnik*, St. Petersburg, Russia).

Results and discussion

Measuring and determining the contact angle with deionized water is the simplest method for studying the wettability of material surfaces. Fig. 3 shows the graphs of the dependence of the contact angle of *TiNi* and steel surfaces and the duration of *UV* laser treatment. The insets (Fig. 3) show typical images of water droplets on the specimen surfaces before and after laser treatment. In the initial state, the contact wetting angles for *TiNi* and steel specimens are similar, measuring 75.0 ± 5.1° for *TiNi* and 75.4 ± 5.4° for steel. Ultraviolet laser treatment alters the hydrophilicity of both *TiNi* alloy and steel surfaces. The contact angle decreases as the *UV* laser treatment duration increases. Already after 10 s of treatment, a significant reduction in the contact angle is observed for both materials compared to its initial state. For *TiNi* specimens, the contact angle decreases more than twofold, while for steel specimens, it decreases by approximately 30 %. A sharp decrease in the contact angle is seen up to 120 s of treatment. With a further increase in the duration of treatment, the contact angle for *TiNi* specimens remains virtually unchanged at 11–13°, while for steel specimens, it continues to decrease gradually, reaching a minimum value of 22.6 ± 4.2° after 600 s of laser treatment. As observed in Fig. 3, increasing the duration of *UV* laser treatment reveals differences in the kinetics of contact angle changes for *TiNi* and steel specimens. The contact angle of *TiNi* decreases faster and more significantly compared to steel as the treatment duration increases. Moreover, the minimum values of the contact angle also differ. For the same duration of ultraviolet laser treatment, the contact angle of *TiNi* specimens is 1.5-2 times lower than that of steel ones.

Therefore, ultraviolet laser treatment of *TiNi* and steel specimens' surfaces effectively alters its hydrophilic behavior, making the *TiNi* alloy more hydrophilic than steel with the same laser treatment parameters. Since the wettability of materials is regulated by a thin surface layer (the first atomic layers of the surface), any change in the physicochemical properties of this layer can significantly affect it [31]. Currently, there is no consensus among researchers regarding the mechanisms of changing hydrophilicity through various surface modification methods. Numerous hypotheses exist about the causes of changes in the degree of hydrophilicity of materials, and these hypotheses are often contradictory. Surface wettability is greatly influenced by the phase and chemical composition of the surface, the surface microgeometry factor, its texture, roughness, structure, as well as the surface polarity, which is one of the important characteristics affecting the affinity for water [21, 22, 27, 32]. One hypothesis suggests that a decrease in the contact angle, indicating an increase in hydrophilicity, may result from cleaning the surface of materials from organic contaminants [4, 33–35]. On the one hand, it is known that contamination of the metal surface with organic compounds with a predominance of hydrocarbon groups in the molecule leads to surface hydrophobization, therefore, removal of these organic contaminants from the surface of materials can lead to a moderate increase in surface hydrophilicity [35]. At the same time, a number of studies report the absence of an effect

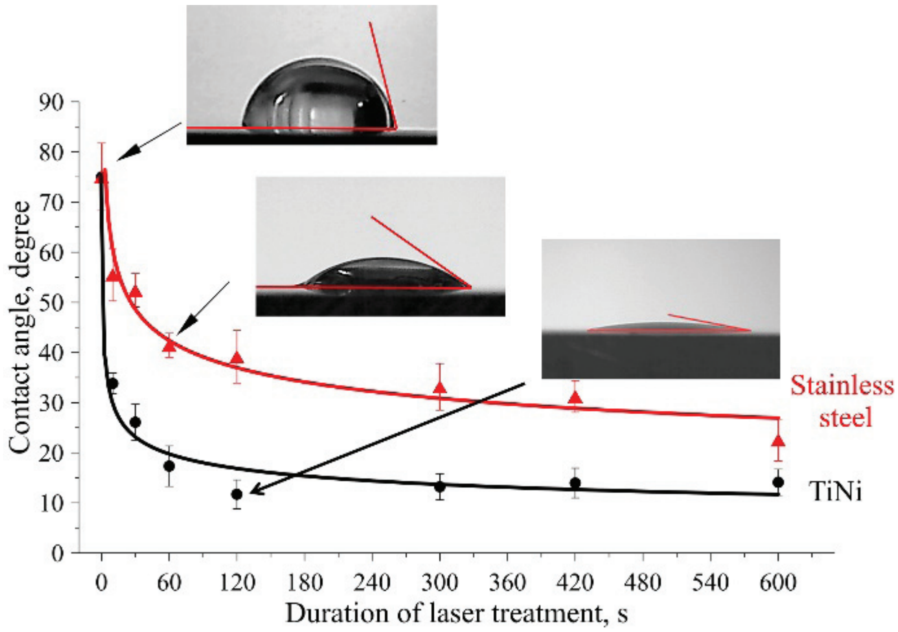


Fig. 3. The dependence of contact wetting angle on the duration of *UV* laser treatment

of cleaning the surface from organic contaminants on its hydrophilicity [36, 37]. On the other hand, metal oxides have increased hydrophilicity and can chemically alter the surface wettability due to its strong affinity for hydroxylation [27, 38]. An increase in hydrophilicity can also result from the process of photooxidation during surface treatment [35]. In particular, titanium dioxide becomes superhydrophilic when exposed to *UV* radiation due to its photocatalytic activity [39]. Several studies [26, 40] have reported on the laser oxidation of metal surfaces both during irradiation in water and in air, which is associated with possible processes of excitation, ionization, and dissociation of atmospheric oxygen. It is known that laser treatment, which causes surface oxidation and increases the oxygen content on the treated surfaces, can enhance its hydrophilicity [27]. However, a thin oxide film on the surface of metals does not prevent further interaction with oxygen [15, 41–43]. Therefore, in this study, a change in the hydrophilicity of metallic materials can also be attributed to the saturation of the surface with atmospheric oxygen and its subsequent oxidation.

The data on the change in the amount of oxygen on the surface of *TiNi* and steel after *UV* laser treatment, obtained using *EDS* during *SEM* study and *XRD* analysis, presented in Figs. 4–7, indicate the saturation of metallic surfaces with oxygen and the formation of an oxide film during ultraviolet laser treatment.

Figs. 4 and 5 show *SEM* images of *TiNi* and steel specimens with the results of *EDS* analysis in the initial state and after laser treatment.

According to the data obtained from scanning electron microscopy, the structure of the *TiNi* specimens consists of a *TiNi* matrix (light areas) and a small amount of *TiC* precipitates (dark areas) (Fig. 4, *a*). The elemental composition of the matrix primarily consists of *Ti* and *Ni* in a ratio that is close to equiatomic, and an insignificant amount of *Mo* and *Fe*. Additionally, the matrix contains carbon and a small amount of oxygen. The secondary phase precipitates contain *Ti*, *C* and *Ni* (Fig. 4, *b*). After 300 s of laser treatment, there is an observed increase in the oxygen content by approximately 10 times (Fig. 4, *c*), and a further increase in the treatment duration to 600 s results in an even more substantial increase in oxygen levels on the material's surface (Fig. 4, *d*). For the steel specimens subjected to *UV* laser treatment durations of 60–300 s, only minor changes in the oxygen concentration on the surface are observed, whereas after 600 s of treatment, the oxygen content increases to approximately 13 at. % (Fig. 5).

UV laser treatment results in an increase in the amount of oxygen on the surface. When comparing the oxygen levels on the surfaces of *TiNi* and steel specimens after *UV* laser treatment, it is evident that, under identical treatment conditions, the oxygen concentration on the *TiNi* specimens is significantly higher than that on the steel specimens. This difference may be attributed to the presence of a substantial amount of

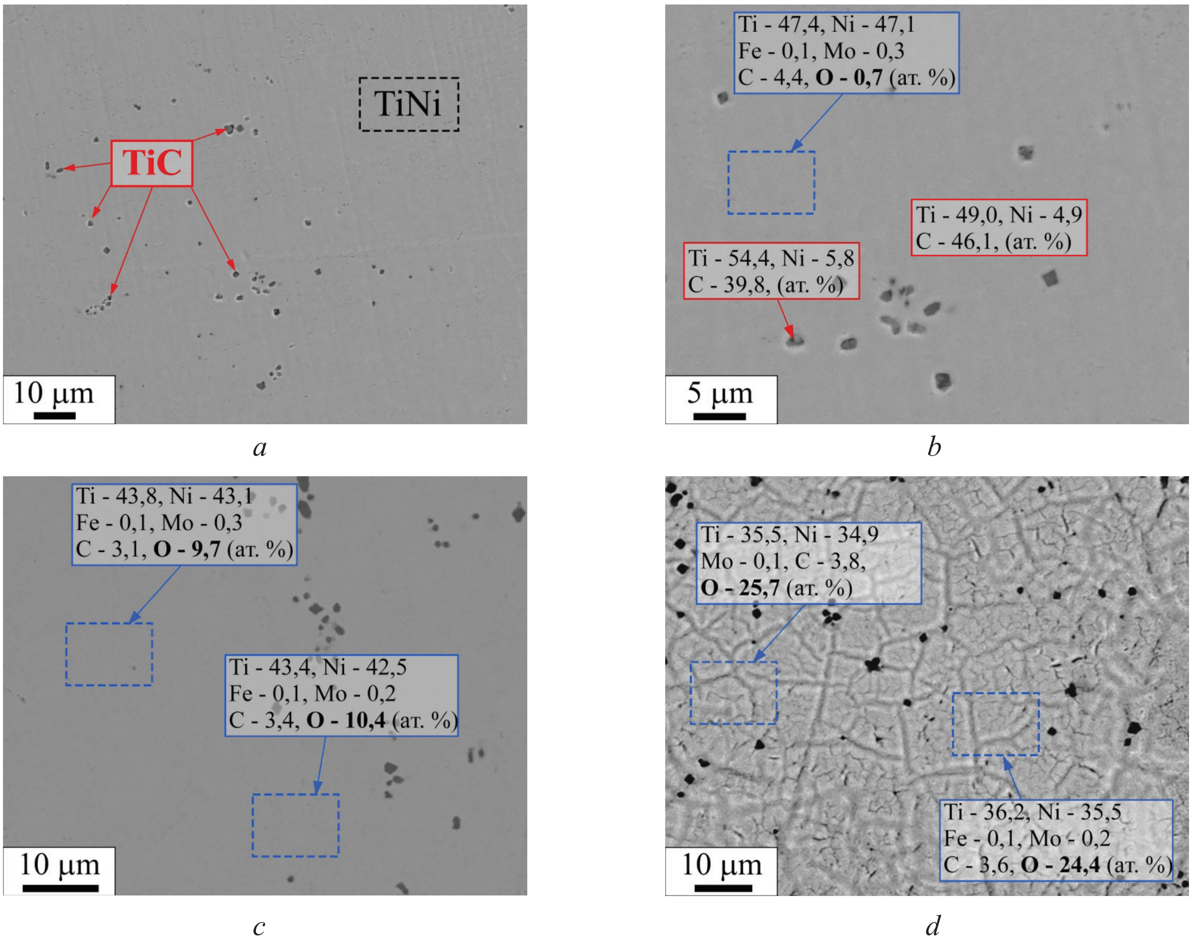


Fig. 4. SEM images of *Ni-Ti* alloy specimens with the results of *EDS* analysis before (*a, b*) and after *UV* laser treatment for 300 s (*c*), 600 s (*d*)

titanium in the *TiNi* alloy, which has a higher electronegativity and thus is considerably more chemically reactive in the presence of oxygen. Titanium is more prone to lose electrons and form oxides than iron, chromium, and nickel found in stainless steel. Additionally, titanium can lead to the formation of more stable oxides, such as TiO_2, compared to the typical oxides formed in stainless steel. The oxide film of TiO_2 also exhibits a more ordered and compact structure than the oxides formed on stainless steel surfaces, such as chromium oxides.

Figs. 4, *d* and 5, *d* illustrate that after 600 s of treatment, changes occur in the morphology of the *TiNi* and steel surfaces, leading to the formation of distinct surface textures on both materials. A crack network is observed on the *TiNi* surface, and the microcracking of a thin surface layer during long-term laser treatment is likely a consequence of the influence of the heat-affected zone caused by local heating during laser treatment, followed by rapid cooling after the end of treatment. This phenomenon is associated with the thermal gradient and stresses generated as a result of the rapid cooling of the treated material's surface. Microcracking can also be caused by the difference in the coefficients of linear thermal expansion of the base material and the metal oxide formed on the metal surface during laser treatment.

In contrast to the *TiNi* alloy, a granulated structure is developed on the surface of the steel specimens after 600 s of *UV* laser treatment. In [31], it was reported that similar granulated structures were observed on the surface of *AISI 316L* steel when subjected to laser irradiation at a wavelength of λ = 532 nm and a laser radiation power density of 1.1 J/cm². The formation of these structures was attributed to the rapid solidification of the molten zone after ablation. The formation of such a structure on the steel surface under *UV* laser exposure can also be caused by thermal processes, such as melting and evaporation of the material. Different surface morphology after *UV* laser treatment under identical conditions for *TiNi* and steel specimens is related to its different thermophysical and chemical properties. Microcracking on the

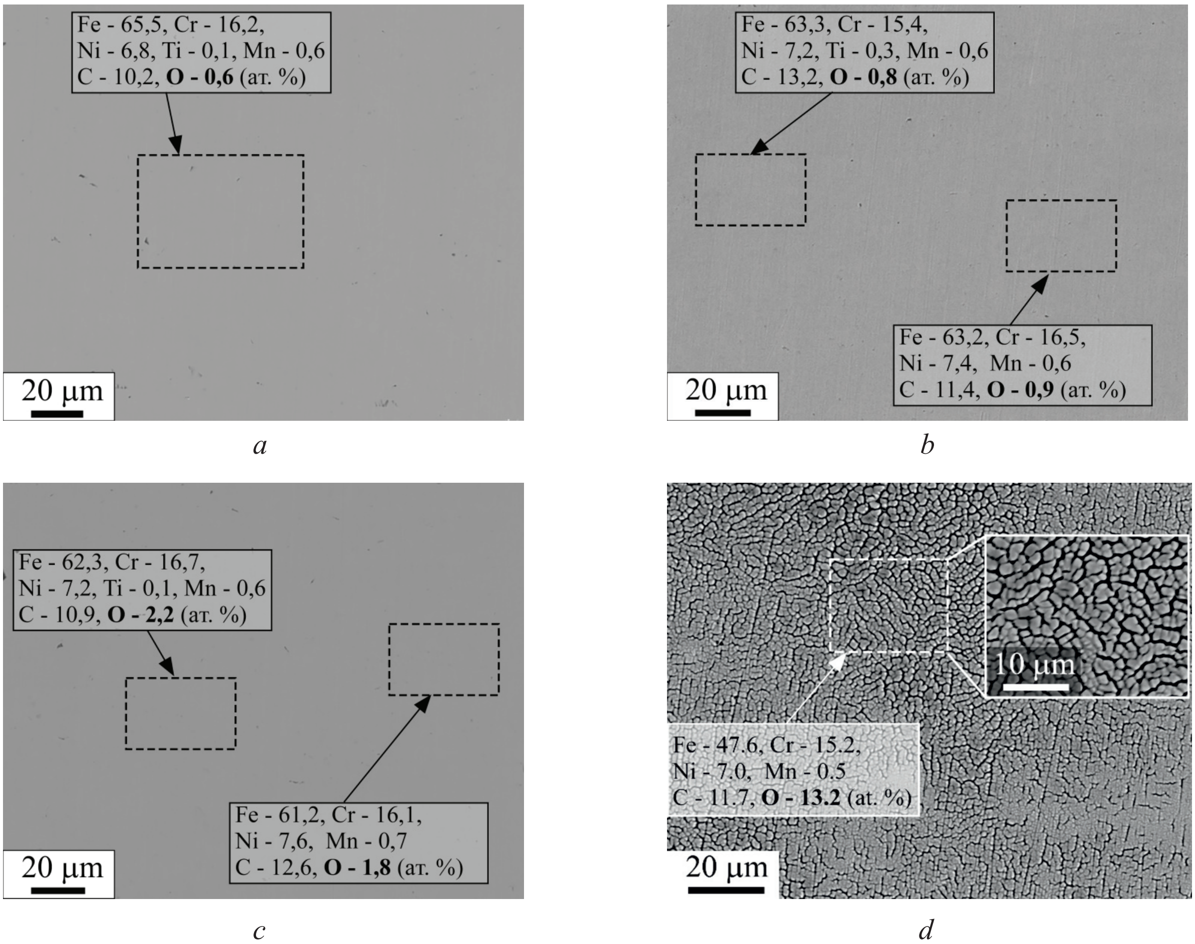


Fig. 5. SEM images of stainless steel specimens with the results of *EDS* analysis: initial surface (*a*), surface after *UV* laser treatment for 60 s (*b*), 420 s (*c*), 600 s (*d*)

surface of the *TiNi* alloy and the development of a granulated structure in steel contribute to an increase in the surface roughness ***Ra*** of the specimens, as indicated by the measurements of surface roughness of metallic materials before and after laser treatment. Initially, the ***Ra*** of the *TiNi* specimens is 40.9 ± 5.3 nm, while for the steel specimens, ***Ra*** is 27.7 ± 5.3 nm. Long-term *UV* laser treatment (600 s) results in a more than twofold increase in roughness: ***Ra*** increases to 82.3 ± 5.3 nm for *TiNi* and to 64.3 ± 6.2 nm for steel. Changes in surface topography (roughness) do not significantly affect the wettability of the *TiNi* alloy surface, while for steel specimens, a slight tendency to decrease the contact angle with increasing roughness is noted. These results are consistent with the results presented in [20, 27], which emphasize the complex relationship between roughness and surface chemistry in changing hydrophilicity and biocompatibility.

The formation of an oxide film on the surface of *TiNi* specimens after *UV* laser treatment is further substantiated by data obtained through *XRD*. Figs. 6 and 7 illustrate the *XRD* patterns of *TiNi* and steel specimens both before and after laser treatment. The *XRD* pattern of the initial *TiNi* specimens (Fig. 6, *a*) and the *XRD* patterns of the specimens after *UV* laser treatment for 10, 120, and 300 s (Fig. 6, *a*) contain only the peaks corresponding to the *B*2 phase of *TiNi* ($Ti_{49.5}$-$Ni_{50.5}$) and the phase *TiC*, which was formed during the material manufacturing process, with a volume fraction of 5–7 %. The *XRD* pattern obtained from *TiNi* specimens after 600 s of *UV* laser treatment (Fig. 6, *a*) indicates a change in phase composition. In addition to the primary *B*2 (*TiNi*) phase and *TiC* precipitates, peaks relating to the oxides TiO_2 and $Ti_4Ni_2O_x$ are also observed in the *XRD* pattern (Fig. 6, *b*).

The oxide phases identified on the surface of *TiNi* specimens after long-term laser treatment are most likely present on the surface of both the initial specimens and the specimens with a short duration of laser exposure, as evidenced by the data on the oxygen content on the surface obtained using *EDS*. Apparently,

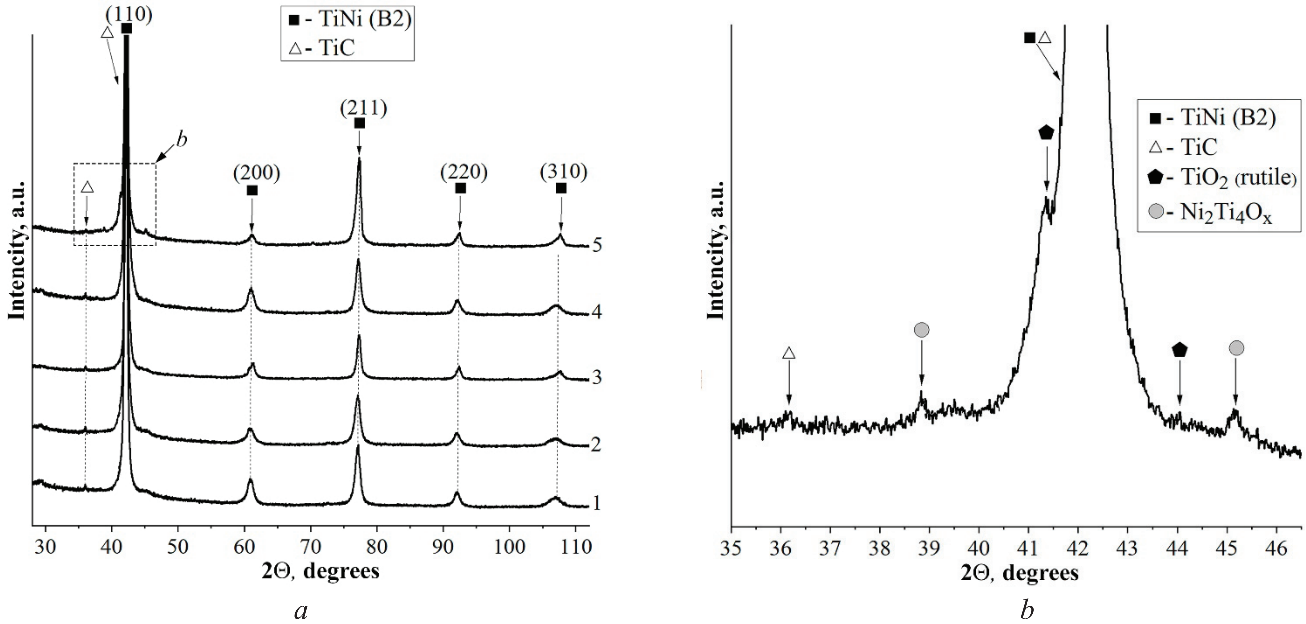


Fig. 6. XRD patterns of *Ni-Ti* alloy specimens in the initial state (*a*, **1**) and after *UV* laser treatment for 60 s (*a*, ***2***), 120 s (*a*, ***3***), 300 s (a, ***4***) and 600 s (*a,* **5**; *b*)

the small thickness of the oxide film (no more than 20 nm in accordance with [41–43]) and the insignificant amount of oxides, not exceeding 3 % of the sensitivity threshold of *XRD* method, do not allow to detect the oxides on the surface of *TiNi* by the *XRD* method. In the *XRD* patterns of steel (Fig. 7) before and after laser treatment, only phases identified as austenite and ferrite in a ratio of 75:25 were recorded. Even with *UV* laser treatment for 600 s, phases belonging to oxides could not be detected in steel specimens by the *XRD* method, which may also be due to limitations of the *XRD* method.

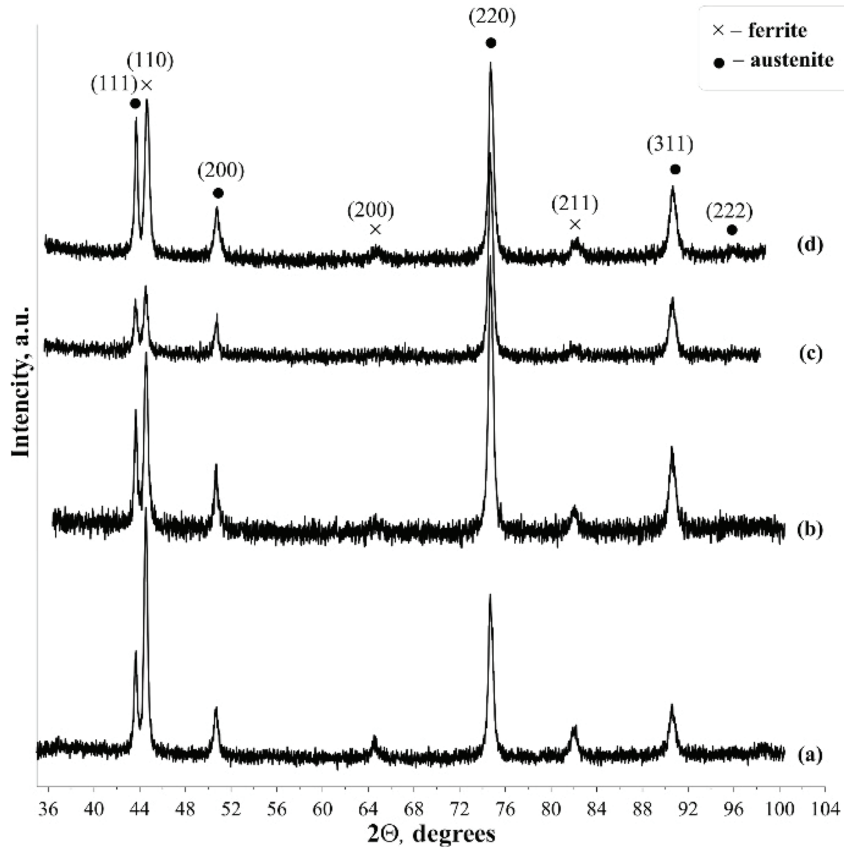
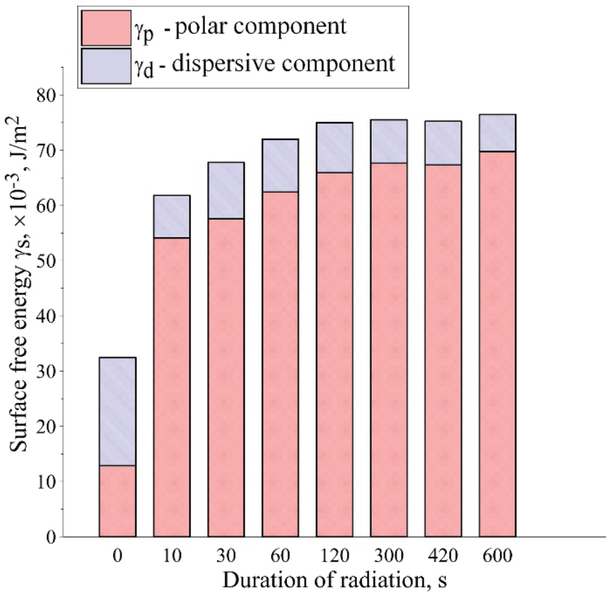


Fig. 7. XRD patterns of stainless steel specimens before (*a*) and after *UV* laser treatment for 60 s (*b*), 420 s (*c*) and 600 s (*d*)

It is assumed that revealed surface changes of the studied materials as a result of laser treatment affect the free surface energy. Fig. 8 shows the dependences of the free surface energy for *TiNi* (Fig. 8, *a*) and steel (Fig. 8, *b*) specimens on the duration of *UV* laser treatment. For both materials, with increasing duration of *UV* laser treatment, a significant increase in free surface energy is observed. After laser exposure, a change in the ratio of dispersed γ_d and polar γ_p components of surface energy occurs. If in the initial state for both materials the ratio γ_p/γ_d was approximately 50/50, then after irradiation a decrease (more than 2 times) in the dispersed component and a significant increase in the polar component are observed. With an increase in the duration of laser treatment, the value of dispersed component γ_d changes insignificantly and does not exceed 10 mJ/m^2, while the value of polar component γ_p increases by 2–5 times.



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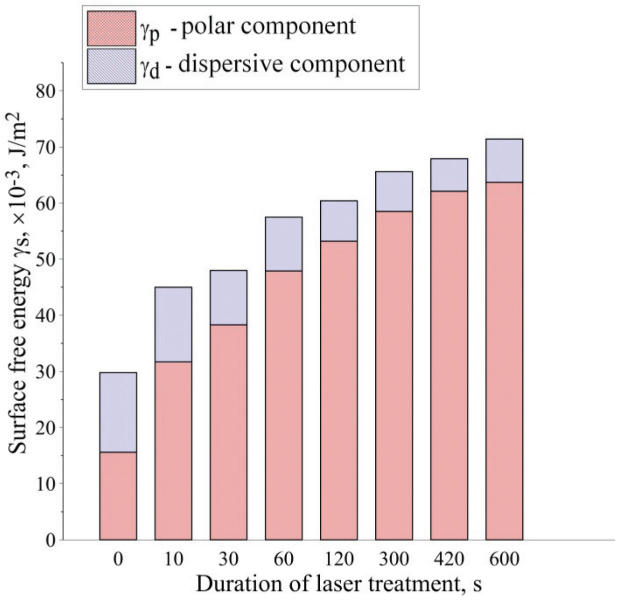

b

Fig. 8. Free surface energy γ_s and its components (polar γ_p and dispersed γ_d) of *Ni-Ti* alloy (*a*) and stainless steel (*b*) depending on the duration of *UV* laser treatment

Such a significant increase in the polar component indicates the surface activation as a result of laser treatment and indicates the presence of polar functional groups on the surface (*-OH*, oxides, carboxyls), which are capable of forming hydrogen bonds with liquid molecules and contribute to increased hydrophilicity.

Thus, an increase in free surface energy and a significant increase in its polar component during *UV* laser treatment of both *TiNi* and steel specimens are associated with the saturation of metallic materials surface with atmospheric oxygen, its additional oxidation and the formation of an oriented layer on the surface, in which the polar groups of molecules responsible for the generation of the polar component are facing the air.

Conclusion

1. The study demonstrates that ultraviolet laser treatment of the surfaces of *TiNi* and steel specimens enhance hydrophilicity. In the initial state, the contact wetting angle is ≈75° for both materials, but after *UV* laser treatment, it decreases to 11–13° for *TiNi* and ≈22° for steel.

2. An increase in the duration of *UV* laser treatment results in a tenfold or greater increase in the amount of oxygen on the surfaces of the metal materials compared to its initial state. The long-term laser treatment (600 s) causes changes in the surface morphology of the treated materials and an increase in roughness.

3. Ultraviolet laser treatment of the surfaces of metal materials leads to an increase in free surface energy from 32.4 mJ/m² to 76.5 mJ/m² for *TiNi* specimens and from 29.8 mJ/m² to 71.4 mJ/m² for stainless steel specimens, primarily due to a significant increase in the polar component.

The main factors contributing to the increased hydrophilicity of *TiNi* and *0.12 C-18 Cr-9 Ni-Ti (AISI 321)* steel specimens after *UV* laser treatment are the increased oxygen content, the formation of oxide phases, and a significant increase in the polar component of free surface energy.

Based on this research, it can be concluded that ultraviolet laser treatment is an effective way to change the wettability of the surface of metal materials.

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Conflicts of Interest

The authors declare no conflict of interest.