doi: 10.56761/EFRE2024.R1-P-068101

UV laser treatment to enhance the surface wettability of TiNi alloy

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Abstract. The effect of UV laser treatment on the surface properties of TiNi alloy is investigated in this research work. The possibility of obtaining a surface with high wetting properties (water contact angle less than 10°) using treatment with nanosecond laser pulses at low energy density (0.1 J/cm^2) and a wavelength of 266 nm has been shown. The structure and phase composition of modified surfaces of the TiNi alloy were studied using X-ray phase analysis and scanning electron microscopy. Experimental data showed that the structure, roughness and phase composition of TiNi specimens remained virtually unchanged after UV laser treatment, but the oxygen content on the surface increased.

Keywords: ultraviolet laser radiation, wettability, surface treatment, microstructure, TiNi-based alloys, hydrophilicity.

1. Introduction

Currently, the demand for products made from biomedical materials (including stents, implants, dental braces, surgical instruments, etc.) is increasing, and at the same time the requirements for such products are also increasing. In addition to mechanical properties and custom design, a biomedical device must have a number of special characteristics, including unique morphology, topography, structure and surface chemistry. Therefore, it is necessary to search and develop surface modification methods that will achieve an optimal combination of all the necessary properties of biomedical materials.

TiNi-based alloys with properties such as shape memory effect, superelasticity and biocompatibility have found wide application in various fields of medicine, including orthopedics, maxillofacial surgery and dentistry [1]. There are a number of surface modification methods of these biomedical alloys, which make it possible to give them various physical, chemical and functional properties, these include: electron beam and ion plasma treatments, coating [2], the formation of multicomponent surface alloys, thermomechanical and sandblasting, electrochemical processing methods [3], as well as laser surface treatment technologies, including surface texturing and the creation of periodic hierarchical nano- and microstructures [4, 5].

Among various surface modification technologies, laser treatment of TiNi alloys has recently attracted great attention from researchers as a non-contact method that is applicable to implants of complex shape, and at the same time allows to change the surface energy, topography and structural-phase state of the surface, as well as promote biological response [6, 7]. The advantages of this method are the variability of parameters, high operation speed and the possibility of local impact. Despite the significant attention of researchers to this topic, at present there is no complete understanding of the mechanisms of changes in biocompatibility properties, in particular, wettability through laser surface treatment due to the multifactorial nature of this phenomenon and the high rate of change in the physicochemical properties and surface morphology under the influence of laser radiation. It should be noted that in the literature there exist limited publications that report the using laser radiation with a wavelength in the ultraviolet (UV) region [8]. On the other hand, most publications are devoted to the successes and advantages of longer wavelength (> 400 nm) laser radiation [4–7]. Therefore, the effect of UV laser treatment on the surface properties of metallic materials is not yet clear. The aim of this work is to reveal the effect of UV laser treatment duration on the wettability, microstructure, phase and chemical composition of the TiNi alloy surface.

2. Materials and methods

TiNi alloy (50.0–51.5%Ni, 0.5–1.5%Mo, 0.5%Fe, balance Ti, at.%) was used as base material in this study. Plates with a dimension of 10×10×2 mm^3 were mechanically polished to a mirror finish and cleaned ultrasonically with ethanol prior to the laser treatment.

The UV laser treatment experiments were performed in air atmosphere under normal incidence of the laser beam with a nanosecond Q-switched pulsed Nd:YAG laser. The laser delivered pulses at wavelength of 266 nm with pulse duration of 5 ns, pulse repetition rate 10 Hz and exposure time (t) from 10 s to 300 s. Target specimens were directly exposed to the laser beam of 5 mm diameter. Laser surface treatment was performed with a laser energy density of 0.1 J/cm^2, which is significantly lower than the energy density used in most previous reports [5–8].

Microstructure and morphology surfaces before and after laser treatment were analyzed using TESCAN VEGA 3 scanning electron microscope (SEM) equipped with an energy-dispersive analysis system and electron backscattered diffraction (EBSD) supply. The X-ray diffraction (XRD) analysis was done using DRON 8 diffractometer with Cu-K_α radiation. Surface roughness studies were carried out using a 3D non-contact profilometry system MicroMeasure 3D Station.

The wettability of the specimens was assessed by measuring the static contact angle (CA) using the sessile drop technique in an atmospheric environment immediately after laser treatment. The droplets were released in a controlled manner onto the surface of the specimens from the tip of a micropipette. A 3 μL droplet of distilled deionized water was used for the CA measurement. After about one minute which is an appropriate time for a drop to be stabilized, images of the droplets on the surfaces were taken with a high-resolution CCD camera. All contact angles reported are the average of at least three wettability measurements on treated surfaces.

3. Experiment results and discussion

Fig.1 shows the results of measuring the contact angle of laser treated surfaces together with the initial surface (before treatment), shown as reference. Analysis of the presented experimental data showed that the surface hydrophilicity of the TiNi alloy increases regardless of the UV laser treatment duration. The untreated surface does not have strong hydrophobic or hydrophilic behavior. The contact angle is $\Theta = 75.0\pm3.8°$. With a short duration of laser treatment $t = 10$ s, a sharp decrease in the contact angle is observed. There is a gradual decrease in the water contact angle of the TiNi specimens with increasing t from 10 s to 120 s. The minimum contact angle value of $\Theta = 9.2\pm1.5°$ is achieved at an exposure time of $t = 120$ s. With a further increase in the treatment duration, a slight increase in the contact angle is observed. The values Θ are in the range of 10–20° at 120 s < $t \leq$ 500 s (Fig. 1).

Fig.2 shows the XRD spectra of the laser treated surface (at time t = 120 s и t = 300 s) and initial TiNi specimens. All X-ray diffraction patterns show reflections corresponding to the *B*2 TiNi phase, as well as low-intensity reflections of titanium carbide TiC (≈ 5%). There are no changes in the X-ray spectra of the specimens after laser treatment. Hence, according to XRD analysis, the phase composition of the specimens remains unchanged under UV laser irradiation.

The average amplitude surface roughness parameters before and after laser treatment were assessed. The polished untreated surfaces displayed a smooth surface roughness in the range of arithmetical mean roughness (*Ra*) is 73.5±7.0 nm. UV laser treatment does not have a significant effect on surface roughness parameters. The *Ra* values are in the range of 70–85 nm for UV laser-treated surfaces, which is close to the value of the *Ra* for the initial untreated state. Consequently, due to negligible changes in the relief and surface roughness, they cannot contribute to a significant increase in the wettability of the UV laser treated TiNi specimens.

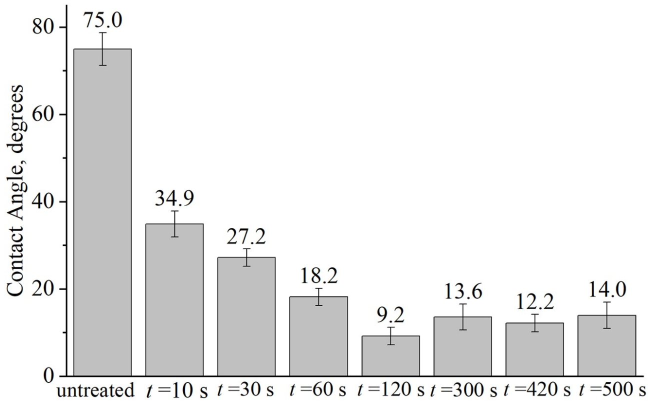

Fig. 1. Effect of UV laser treatment duration on the water contact angle of TiNi specimens

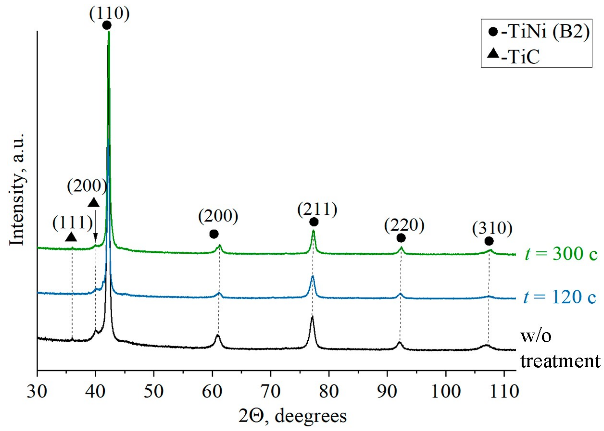

Fig. 2. XRD spectra of the TiNi specimens before and after UV laser treatment

The structural features and morphology of the untreated and laser-treated (t = 120 s, the largest change in wettability among the studied specimens) surfaces are shown in Fig. 3. The data obtained using SEM studies for the initial specimens confirm the XRD analysis data presented above about the presence of the TiC phase (dark areas in Fig. 3a) in the TiNi specimens. According to EDS analysis, the main phase (gray areas in Fig. 3) has a composition close to equiatomic and corresponds to the TiNi (*B*2) phase. The TiC precipitates are enriched in titanium and carbon (spectrum 3, in Fig. 3), the presence of nickel and other elements in the composition is caused by the features of the method. Due to the small precipitate size in the selected area for EDS measurement can identify elements of the TiNi matrix.

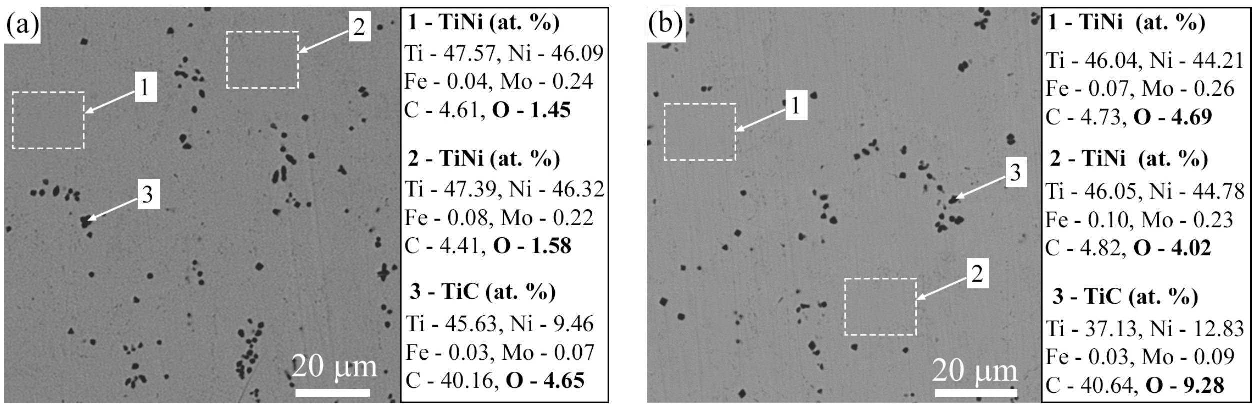

Fig. 3. Typical SEM images of surfaces combined with EDS analysis of phases:
(a) – initial (before laser treatment) TiNi specimens, (b) – UV laser treated (t = 120 s) TiNi specimens

According to SEM studies, no changes in the surface structure and morphology of the TiNi specimens are observed after UV laser treatment. However, exposure to UV laser radiation leads to a change in the chemical composition. An increase in oxygen content is observed in the laser-treated surfaces of TiNi specimens (Fig. 3). In view of the absence of any significant changes in the structural-phase state, morphology and roughness of the surface after UV laser treatment, the main contribution to the change in the wettability of the specimens can be considered to be an increase in the oxygen content in the surface due to the interaction of UV laser radiation with the TiNi alloy surface.

4. Conclusion

The effect of UV laser treatment on the wettability, microstructure, phase and chemical composition of the TiNi alloy surface was studied. Results indicate that on the TiNi alloy, wettability toward water improves significantly after the UV laser treatment at low energy density of 0.1 J/cm^2 and treatment duration of $t = 10–500$ s. The minimum contact angle is $\Theta = 9.2\pm1.5°$after treatment at $t = 120$ s. The UV laser treatment has little effect on the structure, morphology, roughness and phase composition of the TiNi specimens, but leads to an increase in the oxygen content on the surface. Therefore, UV laser treatment can serve as an effective method for controlling the wettability of a TiNi-based alloy while slightly affecting the structure and morphology of the treated material surface.

Acknowledgements

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (FWRM-2021-0014).

5. References

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