Laser-induced surface modification of metals and alloys in liquid argon medium

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Abstract. Micro and nanostructuring of metals and alloys surfaces (Ti, Mo, Ni, T30K4) was considered by subnanocosecond laser radiation in stationary and dynamic mode in the liquid argon, ethanol and air. Depending of structures size on the samples surface from the energy density and the number of pulses were built. Non-periodic (NSS) and periodic (PSS) surface structures with periods about λ-λ/2 were obtained. PSS formation took place as at the target surface so at the NSS surface.

1. Introduction

Micro and nano-structuring of metal surfaces is of significant interest, because it allows to extend optical, mechanical and magnetic properties of the initial materials. Structuring of the sample surface is possible to realize using different methods: chemical etching, lithography, mechanical impact, laser technology, and etc. Laser methods are distinguish by relatively simple and allow to avoid using of toxic and explosive substances in comparison with chemical methods [1].

The objective of this work was to obtain micro and nanostructures on the metals surfaces (Ti, Mo, Ni) and T30K4 alloy surface by laser ablation in liquid argon and their comparison with structures obtained in the ethanol and air media.

The focus of the work done on structures obtaining in liquid argon because argon is an inert gas and practically insoluble in molten metals that helps to minimize chemical interactions. Structures obtained by laser ablation in liquids characteristic by larger aspect ratio. Moreover, most of the laser ablation in a liquid medium experimental data is got at room temperature. Go to the cryogenic liquid medium can expand the applicability of the laser ablation method.

2. Experimental techniques

Structuring of the samples (Ti, Ni, Mo and T30K4) surface was produced by Nd: YAG laser (RL-PQ-30/300) radiation (λ = 1064 nm, τ = 250 ps, ν = 20 Hz, Q = 0.3 mJ, Q_S = 0.1÷ 1.57 J / cm^2). The traditional optical scheme for the laser ablation in liquids method was used [2].

In the case of use a liquid argon medium, this scheme was supplemented by a cryogenic chamber, which avoids its boiling point (Figure 1).

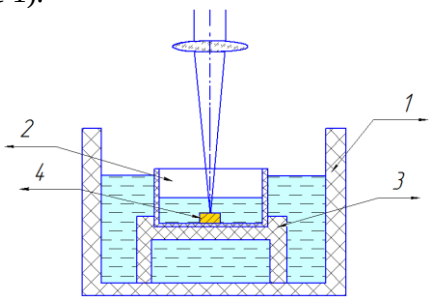

Figure 1. Sketch of the camera for target surfaces laser structuring in cryogenic liquids. 1 - thermally insulated cell filled by liquid nitrogen, 2 - polyethylene cell filled by cryogenic liquid (argon), 3 - plastic stand, 4 - sample.

Structuring of the surface was carried out in dynamic and stationary modes. In the case of a dynamic mode cell with the sample moved by Standa motorized tables relatively to the focal spot. Move options: speed of 500 μm/s, step offset by the other coordinate - 16 microns. In this mode, the irradiation of a titanium target in ethanol (95%) and liquid argon was realized.

In the case of a stationary mode cell with the sample remains fixed relatively to the focal spot. In this mode the dynamic of changes in the shape and size of the structures on the surface of Ti, Ni, Mo and T30K4 in liquid argon, ethanol and air media have been considered in the pulse number ranging from 50 to 20 000.

The overall view and element analysis of the obtained structures were received by using a scanning electron microscope Carl Zeiss Evo 50 with nitrogen-free energy dispersive X-Max detector 80 (EDX). The period of structures was determined by a fast fourier transform of surfaces SEM images. Spectrophotometric analysis of the samples was carried out using a spectrophotometer SF-56 with diffuse reflectance attachment.

3. Results and Discussion

As in the work [3] colour changes as a result of interaction of the subnanosecond IR laser pulses with a titanium surface in ethanol media in the dynamic mode with the difference energy density was observed. Key points: №1 - gray, the energy density is 0.112 J / cm^2; №3 - yellow, 0.125 J / cm^2; №5 - black, 0.145 J / cm^2; №8 - deep yellow, 0.203 J / cm^2; №14 - metallic gray, 1.570 J / cm^2 (Table 1).

Table 1. The dependence of the samples surface color from energy density.

№	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Photography														
Energy density, J / cm^2	0.112	0.119	0.125	0.134	0.145	0.164	0.182	0.203	0.244	0.319	0.438	0.641	1.219	1.570

For samples №5 (black) and №8 (deep yellow) absorption spectra were obtained and presented on figure 2.

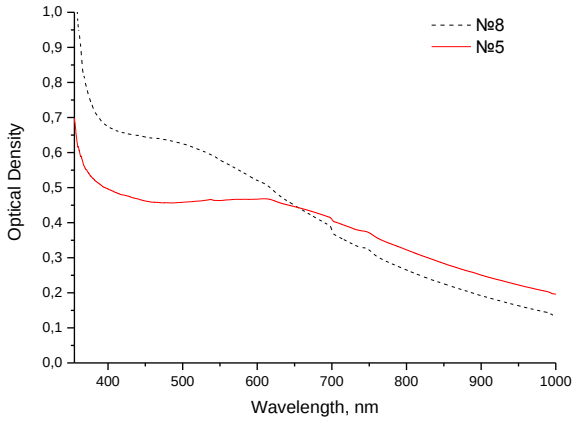

Figure 2. The absorption spectra of titanium surfaces irradiated in the ethanol environment (energy densities №8 - 0.203 J / cm^2, №5 - 0.145 J / cm^2).

In the transition from sample №5 to sample №8 shift of the maximum absorption band from 610 nm to 480 nm was observed. As shown in [4], such changes in the absorption spectra of the Ti surface may be associated with the different thickness of the oxide film on the sample surface.

Since the ethanol contains 5% of the water, in the laser ablation process the oxidative reactions are occurred, the speed of which will depend on the laser energy density. Elemental analysis showed that the maximum oxygen content was recorded on the sample surface №5 (black), its amount 23%. The surface sample №8 (deep yellow), in by turn, contains 15% of the oxygen. This can be explained by the fact that, depending on the oxygen concentration, the thickness of the oxide film is changed and, as a consequence, the interference absorption also changed [4].

Analysis of the surfaces by scanning electron microscopy irradiated in the ethanol environment showed cracking of the surface layer (figure 3a), which on the original sample was not observed. Nanoparticles / structures on the sample surface, which could affect on the sample color due to plasmon resonance phenomena, were not detected.

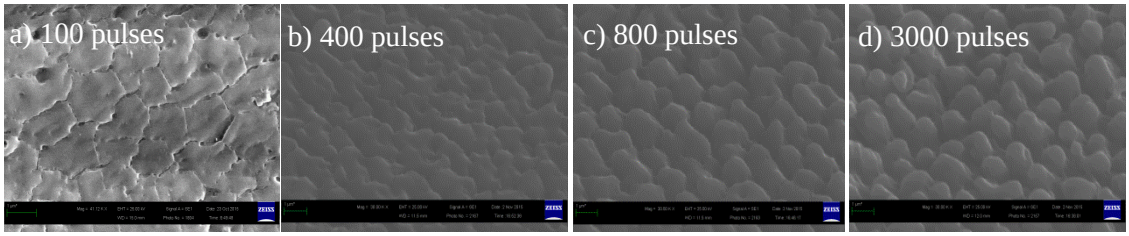

Figure 3. SEM images **a)** at a right angle, **b)** at an angle 45˚ of the titanium surface irradiated in ethanol medium. The energy density was 0.145 J/cm^2.

By increasing the number of laser pulses that act on a target, the cracking of the surface layer acts as a mask for developing structures (Figure 3 a-d), since the melting point of the oxide layer TiO = 1770 ˚C, TiO_2 = 1 870 ˚C, while the melting point of pure titanium - 1668 ˚ C.

In the case of laser ablation with the same parameters, but in the liquid argon so happens colouring of the sample surface and observed cracking of the surface layer acting as a mask for the structures growth. Energy density varied in the range of 0.2 to 1.2 J/cm^2 (Figure 4 a, b). The surface color after the impact of different energy density of radiation has a mostly yellowish tone, which may be due to a chemical reaction $Ti + TiO_2 \rightarrow 2TiO$, passing in argon at 1550 ºC and leads to the transformation of TiO_2 film in TiO.

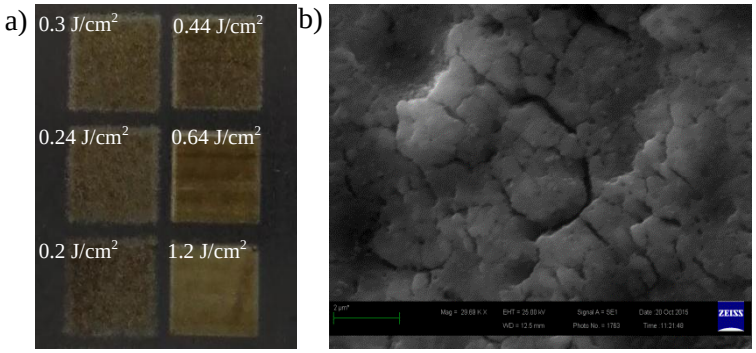

Figure 4. Titanium surface irradiated in liquid argon: **a)** photography of the target, **b)** SEM image of a sample irradiated at an energy density of 0.64 J/cm^2.

At stationary multi-pulse exposure due to the accumulative effect by displacing the melt by steam - gas cloud, the formation and growth of microcones with a base diameter from 1 to 6 microns in liquid argon was observed. Such structures receiving in room temperature liquids and air have been described in several papers [3, 5]. Displacing melt by the steam - gas cloud during laser ablation in liquids will be more active than during laser ablation in gases, that resulting to more developed structures (Figure 5).

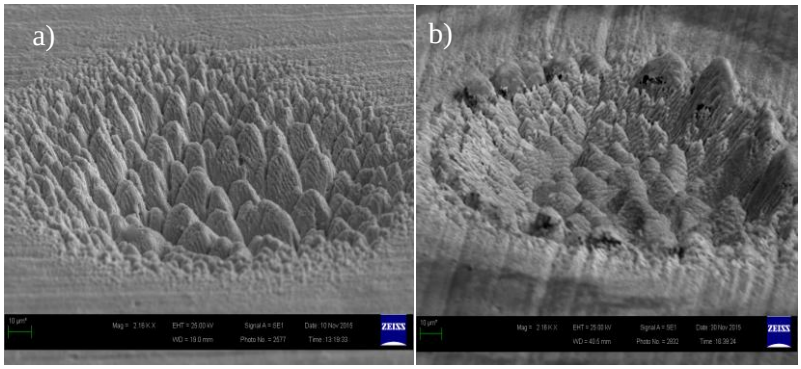

Figure 5. Comparison of the nickel surface modified in liquid argon **(a)** and air **(b)**; 20,000 pulses; 0.25 J/cm^2.

In the boundaries of the one laser spot resolved structures with different sizes (from 0.5 microns to 15 microns). It is also related to the inhomogeneity of the energy density distribution of the real laser beam on the target surface, and consequently, with various depth of the molten bath forming at laser spot center and at its periphery.

At an energy density of 0.3 J/cm^2 distinguish the different area sown by microcones (periphery), and the central "bowl" of the melt covered by drop-shaped microstructures (Figure 6). With the number of pulses growth, microcones, evolving towards the center on the periphery reborn in part-shaped structures, and a crater in the center is forming.

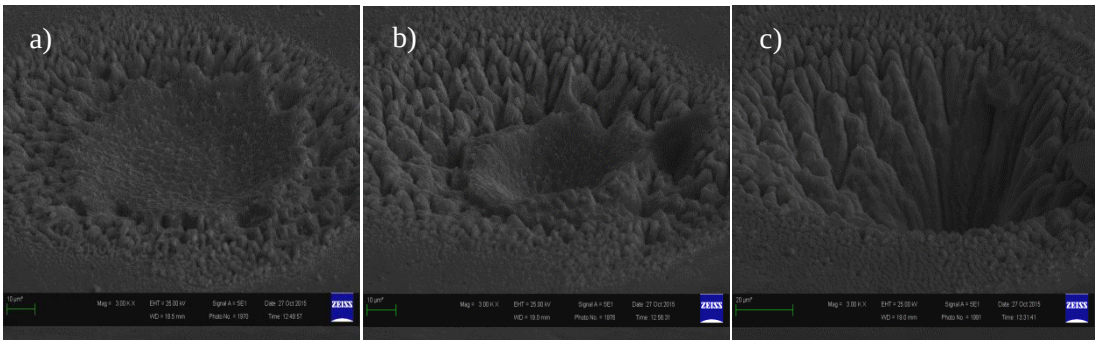

Figure 6. SEM image of the titanium surface, irradiated in liquid argon at an energy density of 0.3 J / cm^2: **a)** 100 pulses, **b)** pulses 300, **c)** 800 pulses.

On figure 7 the dependence of the structures average diameter from the number of pulses for different energy densities was represented. The graph shows that with an increase the number of pulses at a constant energy density, microcones consolidation was observed. The energy density change leads to the possibility of a control structures growth rate. The surface structures were reported on the metals and alloys such as a Ti, Mo, Ni, T30K4. Presented dependences are in good agreement with the results obtained in [3].

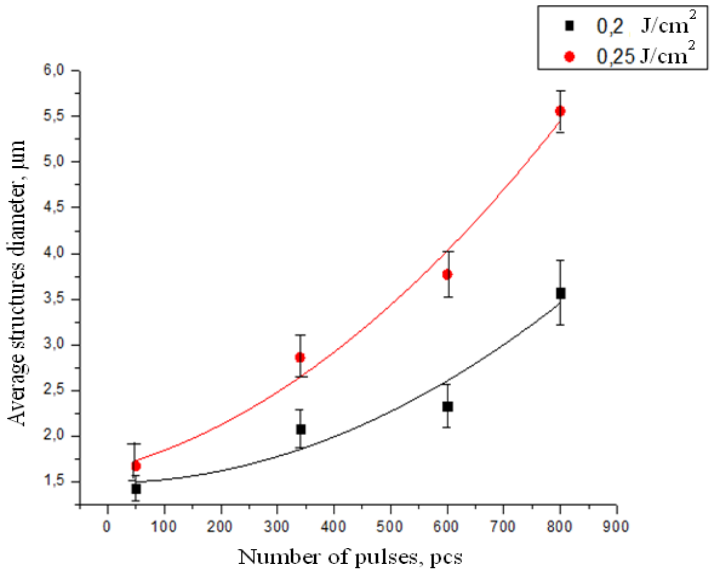

Figure 7. The dependence of the structures size from the number of pulses.

In the case of laser ablation of metals and alloys in the liquid argon and air, formation of surface periodic structures was observed (Figure 5). As shown in [6], this is due to the interference of the incident linearly polarized laser radiation with surface electromagnetic waves that arise at the interface between two media with dielectric constants of different sign at the scattering of light on the sample inhomogeneities. Orientation and period of structures depend on the target material, the environment surrounding the sample, as well as the wavelength, polarization, and intensity of the laser radiation.

At laser ablation in liquid argon in the center of the laser spot, where the energy density is maximum, on the microcones surface the nearwave PSS formation was observed (Figure 5,8a). On the periphery, in the formation conditions of the molten bath with substantially smaller depth, as well PSS formation was registered. The period of the such structures on metals as Ti, Mo, Ni is in the order of λ / 2. As an example, Figure 8b shows a typical image of such PSS obtained on the Mo surface at an energy density of 0.25 J / cm^2. The obtained PSS have two mutually orthogonal orientations that may be associated with the polarization rotation of radiation by an angle 90°, during the laser ablation process, by nonlinear optical shutter included in the laser construction.

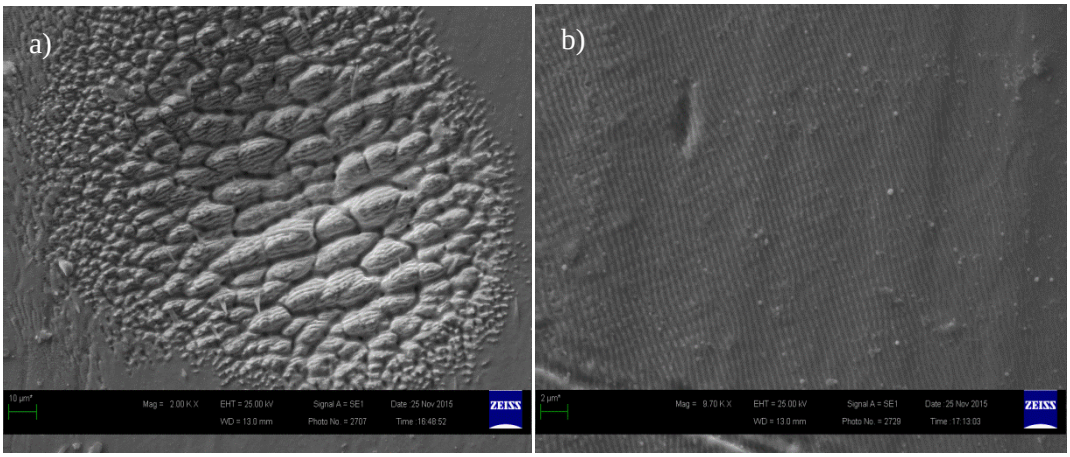

Figure 8(a, b) A typical SEM image of the structures obtained by laser ablation in liquid argon on the Mo surface. The energy density was 0.25 J / cm^2. **(a)** A general view, **(b)** an enlarged fragment of the sample surface at the periphery of the laser spot.

As a result of the T30K4 alloy laser ablation, apart the growth, the change in the ratio of the elemental composition of the surface structures was observed. This may be due to a difference of melting temperature of the alloy components (Figure 9).

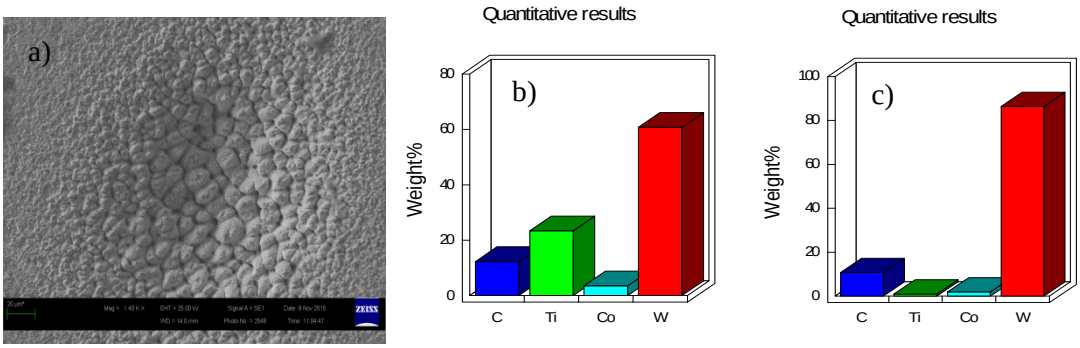

Figure 9. SEM image and elemental composition of the alloy T30K4 surface: **a)** SEM image of structures obtained during laser ablation in liquid argon, **b)** the elemental composition of the original alloy T30K4 surface, **c)** the elemental composition of the sample surface after laser ablation process in liquid argon.

4. Conclusion

Laser ablation method in liquid argon is enough promising because it makes impossible the chemical interaction both with remote from the surface material and with the target surface. This technique allows to obtain microcones with different sizes (from 0.5 microns to 15 microns) and surface periodic structures with periods of ~ λ, λ / 2. As well as in dynamic action it leads to changing in the spectral characteristics of a target.

Acknowledgments

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References

[1] Makarov G N 2013 *J. Physics-Uspekhi*. **183** 673
[2] Zijie Y, Douglas B Chrisey 2012 *J. of Photochemistry and Photobiology C: Photochemistry Reviews*. **13** 204
[3] Barmina E V, Stratacis E, Fotacis K, Shafeev G A 2010 *J. Quantum Electronics*. **40** 1012
[4] Stepanov A Y, Sotnikova L V, Vladimirov A A, Khaneft A V, Prosvirkina E V, Titov F V, Diaghilev D V 2014 *J. Polzunovsky messenger* **3** 53
[5] Makarov S V 2014 Nano and microstructuring of the surface of metals and semiconductors in the air by femtosecond laser pulses (Moscow: P.N. Lebedev Physical Institute of the Russian Academy of Sciences) p 149
[6] Libenson M V 1996 *J. International Soros Science Education Program*. **10** 92