The use of electrochemical deposition of metals at the surface microstructuring by laser ablation in liquids

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Abstract. Micron, submicron, surface-periodic and nanostructures were obtained by laser ablation in a liquid method on the titanium plate surface and the nickel foil surface. Electrochemical deposition of the nickel in the modified region of the titanium leads to the formation of conical structures 6 μm in height and filamentary nanostructures on the separated film. During deposition on the laser-modified nickel target, the separable film retains the period of the structures from which it is removed. The component titanium target coated with a nickel film was also irradiated. After separation of the nickel film, perforations with an average diameter of 1 μm and holes up to 50 μm in diameter were detected.

1. Introduction
Thin metal films are widely used in the creation of solar cells, thermocouples, photo resistors, reflective surfaces and many other devices [1]. The most commonly used methods for their production are: chemical or plasmochemical deposition from the gas phase and vacuum spraying. Modification of the thin film surface allows to expand the properties of the material and, as a result, the range of its use. Plasma or laser technologies are usually used to change the surface structure.

The method of laser ablation in a liquid allows, in the presence of a single laser source, to obtain a wide range of structures. So, for example, by varying the energy density of radiation and the number of pulses arriving at the target surface, it is possible to control the dimensionality and growth rate of the structures [2]. And depending on the target material and the choice of the liquid medium in which the irradiation takes place, it is possible to create chemically pure structures or, conversely, initiate the course of chemical reactions [3].

Using laser structuring in common with the technology of thin metal films growth on the massive metal samples surface with their subsequent separation will allow to optimize the process of the creating micron structured metal films. Therefore, the aim of this work was to obtain submicron and nanostructures on the nickel film surface using a combination of laser ablation and electrochemical deposition methods.

2. Experimental technique
The creation of micron and submicron structures on the surface of metal targets was carried out by laser ablation in liquids at cryogenic and room temperature [3]. The thickness of the liquid layer above the target surface was 5 mm. The Nd: YAG laser was used as a source of laser radiation: λ = 1064 nm, τ = 250 ps, ν = 20 Hz, Q = 0.3 mJ, Qₜ = 0.18-0.6 J / cm², 20000 pulses. The cell with the target remained fixed relatively to the focus spot. Laser treatment was provided on: a titanium plate 1 mm thick, a titanium plate coated with a layer of nickel 6-7 μm thick, and nickel foil 0.3 mm thick. The titanium plate and nickel foil were also coated with a layer of nickel after laser treatment.
The application of a nickel coating was carried out by an electrochemical method. Electrolyte composition was:

**Table 1. Electrolyte composition.**

| Name                      | Chemical formula          | Concentration, g/l |
|---------------------------|---------------------------|--------------------|
| Nickel sulfate 7 aq.      | NiSO₄·7H₂O                | 140-200            |
| Nickel 2-chloride 6 aq.   | NiCl₂·6H₂O                | 30-40              |
| Boric acid                | H₃BO₃                     | 25-40              |
| Sodium sulfate non aq.    | Na₂SO₄                    | 60-80              |

Electrolysis current: 1 (± 0.1) A / dm²; Electrolyte temperature: 45 (± 5) °C; The electrolysis time was 30 minutes.

The experiment of the surfaces structuring was divided on several parts:
- Laser ablation of a titanium plate in ethanol containing 5% water, and coating the synthesized structures with a layer of nickel 6 μm thick;
- Application of a nickel coating on the titanium plate surface and laser ablation of the resulting sample in ethanol containing 5% water;
- Laser ablation of nickel foil 0.3 mm thick in liquid argon, followed by coating of synthesized structures with a six-micron layer of nickel.

To separate the modified nickel coating with the sample to which it was applied, the outer surface of the nickel layer was covered with a glue composition and pressed to a flat metal substrate. After solidification of the glue composition, the metal substrate with the nickel film was separated from the bulk sample surface.

The analysis of the surfaces of the titanium plate, nickel foil and nickel coating at various stages of processing was carried out using a scanning electron microscope Carl Zeiss Evo 50 equipped with a nitrogen-free energy-dispersive detector X-Max 80 (EDX). To determine the period of synthesized structures, a fast Fourier transform (FFT) of SEM images was used.

3. Results and discussion

As a result of the of 20000 laser pulses impact on the surface of a titanium plate in an ethanol medium containing 5% water, conical structures with a characteristic diameter of 6 μm in the central region and 200 nm in the periphery were obtained (figure 1).

![Figure 1. SEM images of structures on the titanium plate surface, obtained by laser ablation in ethanol, containing 5% H₂O, method. 20000 pulses, 0.18 J / cm².](image)

The change in the size of the structures along the radius of the focusing spot is associated with the Gaussian distribution of the laser beam energy density. The formation of such structures under a multi-pulse exposure is due to uneven melting of the target surface, removal of the melt into the medium under the influence of a number of instabilities (Kelvin-Helmholtz or Rayleigh-Taylor) and further "dagger penetration" [4]. Uneven melting can be associated with various factors, including the presence of both the original oxide layer on the irradiated sample and the layer formed under laser heating conditions of the metal target in the oxidizing medium, which change the absorbing capacity...
of the target. Also, upon absorption of the laser radiation by the target, its thermal expansion leads to cracking of the surface oxide layer. This cracking during the irradiation plays the mask role, since the melting point of the oxide is higher than the melting point of pure metal [3]. Since the present work carried out a multi-pulse laser action with an energy density close to the ablation threshold, the removal of matter from the surface and the oxidation of the surface were rival processes. As a result, formation of an oxide layer was observed on the laser-induced structures surface (figure 1).

The next stage consisted in electrochemical deposition of nickel on the structures described above. The growth of a nickel film on the titanium sample surface occurred in the “island” mode [5]. Analysis of the film after separation from the substrate showed that its total thickness was 7 μm (figure 2a).

Figure 2. SEM images of a nickel film separated from a laser-structured titanium plate: (a) side view. Scale bar is 3 microns; (b) general view at an angle of 45°. Scale bar is 10 microns; (c) the region of nickel deposition at the periphery of the focusing spot. Scale bar is 2 microns.

As a result of the electrochemical deposition of nickel in the central region of the modified titanium, the formation of nickel microstructures with a height of 6 μm, located on the basis of a thickness of 1 μm, was occurred (figure 2b). During precipitation of the nickel on the modified titanium periphery, a nickel film 7 μm thick was obtained, which repeated the relief of the original irradiated titanium surface and covered by filamentary nickel nanostructures (figure 2c). These structures are formed by the deposition of nickel in the cracks of the oxide layer on the surface of the irradiated titanium sample. Submicron nickel cells with nano inclusions were also found at the periphery (figure 3). Energy dispersive analysis of inclusions showed that they represent titanium dioxide.

Figure 3. (a) SEM-image of the nickel film surface, formed at the periphery of irradiated titanium target after separation from titanium; (b) energy dispersive analysis of the nickel film surface in region 1; (c) energy dispersive analysis of the nickel film surface in region 2.

It’s can be explained by the fact that during the separation of the nickel layer from the laser-induced structures, covered by an oxide, a part of the oxide layer remained on the film surface.

In order to exclude submission of target material, on which the nickel layer is deposited, into the structure of the synthesized nickel films, a 0.3 mm thick nickel foil was chosen as the mask. To minimize chemical reactions the process of creating laser-induced structures on the target surface was
carried out in a liquid argon medium. After exposing 20000 laser pulses on the nickel foil surface in a liquid argon medium, elongated micron structures modulated by surface periodic structures (SPS) were obtained (figure 4a).

![Figure 4. (a) SEM-image of characteristic structures on the nickel surface, obtained by laser ablation in liquid argon. 0.2 J / cm², 20000 pulses; (b) SEM-image of the nickel film surface, formed on an irradiated nickel target, after separation. The inserts show fast Fourier transforms of SEM images taken along a horizontal straight line.](image)

The formation of such structures may be due to the fact that the real surfaces of the materials are not absolutely smooth and the presence of even a slight relief and micro roughness can radically change the character of interaction and absorption of laser radiation by the matter. When an electromagnetic wave falls on a rough surface due to diffraction, surface electromagnetic waves (SEW) arise that propagate along the interface of two media and exist simultaneously in both of them. Interference of the SEW with the falling, reflected and refracted waves determines the nature of the electromagnetic field at the surface and its dissipation (absorption) [6]. The nickel film deposited on these structures and separated from them completely repeats the period of structures on the massive nickel (figure 4b). Two main periods can be distinguished: the period of surface structures, which amounted to 2.7 μm, and the period of modulating SPS, equal to 0.6 μm.

A separate part of the work is irradiation of a thin layer of nickel deposited on a massive metal substrate, in order to its effectively perforation without destroying the film. Irradiation of a titanium target coated with a nickel film leads to the formation of nickel structures, the general view of which is shown in figure 5a. When the average energy density in the laser beam reaches 0.26 J / cm², the penetration channels in the nickel layer reach the surface of the titanium and forming a hole with a few tens of microns in diameter in the center and micron perforations at the periphery (figure 5b).

![Figure 5. SEM-image of (a) nickel structures obtained by laser ablation of a titanium target, coated with a nickel layer, in an ethanol medium; (b) nickel film with perforations after separation from the titanium plate. 0.26 J / cm², 20000 pulses; (c) a hole obtained by laser ablation of a composite sample of titanium, coated with nickel, in ethanol medium. 0.6 J / cm², 20000 pulses. The insert show the elemental map.](image)
An increase the energy density up to 0.6 J/cm² leads to the formation of a channel in a nickel film and a titanium plate (figure 5c). In addition, on the surface of titanium, in contrast to nickel, structures that are a cracked oxide layer are observed. The distribution map by the elements, presented in the insert, shown that when the composite target is ablated in the liquid, titanium is not deposited on the nickel layer. This can be due to the high liquid and the target vapor pressure in the channel.

4. Conclusion
The combination of methods of the laser ablation of metals in liquids and electrochemical deposition of metals leads to the production of structured nickel films 6-7 microns in thickness. In the case of using a laser-modified titanium plate as a mask on a nickel film, micron cone-shaped nickel structures with an average height of 6 μm in the center and nanodimensional filamentary nickel structures at the periphery were obtained. Also at the periphery, submicron nickel cells with nanoinclusions of titanium dioxide were detected. Nano-layers of titanium dioxide are interest for research, because on them the first memristive element was implemented [7].

Using a structured nickel mask on a nickel film, the formation of micron surface structures modulated by submicron PPS was observed. Metallic masks obtained by the laser ablation method can be repeatedly used to create structures of a given shape and size on thin metal films, which expands the area of this technique use. By laser ablation of a component target consisting of a 1 mm thick titanium plate and a 6-7 μm thick nickel coating micron titanium and nickel structures in an ethyl alcohol medium were produced. At an average energy density of 0.26 J/cm² on a nickel film, a hole a few tens of microns in diameter at the center and micron perforations at the periphery were formed. By modulating the laser field, it is possible to achieve uniform perforation of the nickel film throughout the focusing spot.

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