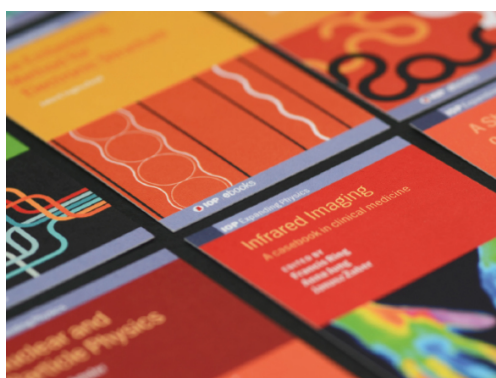


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# Colorization of copper surfaces by nanostructure modifications with ultrashort laser pulses

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**Abstract.** A colorization of copper surfaces after nanostructure modifications with ultrashort laser pulses was studied. Femtosecond laser has been used for experiments. A relative motion of the laser beam on the material was realized. Tracks on the material obtained in a multi-pulse mode with an energy density lower than the threshold ablation were studied using scanning electron microscopy and atomic force microscopy. By the surface treatment with a laser pulses duration smaller than 30 fs, almost-wavelength periodic structures were formed and finally the surface brightness was increased. It was demonstrated that small nanostructure modifications changed the surface colour significantly. Using backscattered and secondary electron modes of scanning electron microscopy images were obtained from four sample regions that showed different colours, such as dark purple-red, turquoise, yellow-orange and grey-green. It was found that one of the main reasons for the difference in colour of images is the oxidation degree.

## 1. Introduction

Ultrashort pulse lasers have been used to create surface micro- and nanostructures on metals and to obtain surfaces with peculiar optical properties or wettability [1-4]. For the first time, the colorization effect of a metal surface using ultrashort pulses was described in [5]. Such processes for the generation of surface-periodic structures by means of ultrashort pulses allows the colour marking of surfaces that have almost any hardness and composition, which is very significant for materials that are poorly oxidizable or have opaque oxides (for example, copper). Ref. [6] shows the possibility to achieve material modifications using ultra short pulses, via polarization dependent structures generation, resulting in specific colour patterns. These oriented nanostructures created on the metal surface, so-called ripples, show a periodicity usually less than a wavelength of the laser radiation and in a visible range of a spectrum. Ref. [7] confirms that the colorization phenomenon mainly due to a diffraction effect of the incident light on a laser-induced periodic surface structures. This may contribute to a flexible manipulating of the colorization effect by laser treatment of a pure copper. Compared to the colorizing process by a surface oxidation of a metal (temper colour), this process does not much change physical and chemical characteristics of the material surface.

In Ref. [8] a method was presented for controlling the nanoscale topology of a surface, as well as the chemical content of titanium surfaces by treatment using femtosecond laser, whose beam has an



asymmetric spatial distribution of flow in a processing zone. It can be supposed that phenomena found for titanium can also be observed with other materials, and it is also plausible that individual features will be present [9-11]. In Ref. [12] features of modifications in the nanostructure and colorization of copper have been studied during scanning with a beam of femtosecond laser, which had a nearly Gaussian distribution of energy density. It has been revealed that by scanning of a copper sample with an ultrashort pulse beam can be formed a combined microrelief containing a laser-induced periodic surface structures and a nanoroughness. Relatively minor nanostructure modifications obtained when forward and reverse scanning a copper surface with a ultrashort pulses beam in a multi-pulse mode can lead to a much colour change during surface colorization. In Ref. [13] the colorization in air of a copper surface by nanostructure modifications using femtosecond laser when changing only the direction of a scanning was studied. It was found that not only the nanostructure periodicity but also the oxidation degree is a reason for the visible difference in colour of images.

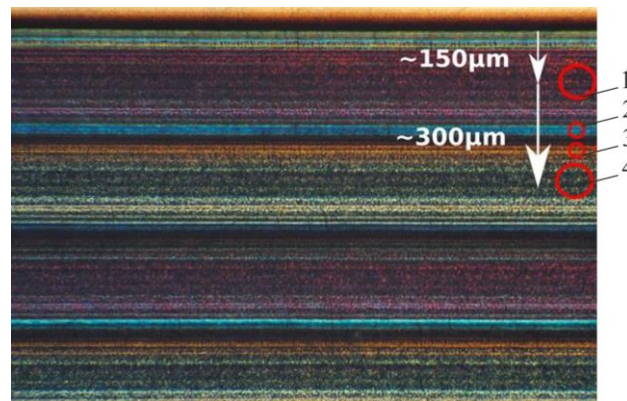
The purpose of this research is to investigate more details the oxidation result on the diffraction colorization of copper surfaces in the process of nanostructure modifications using laser with ultrashort pulses.

## 2. Results of experimental studies

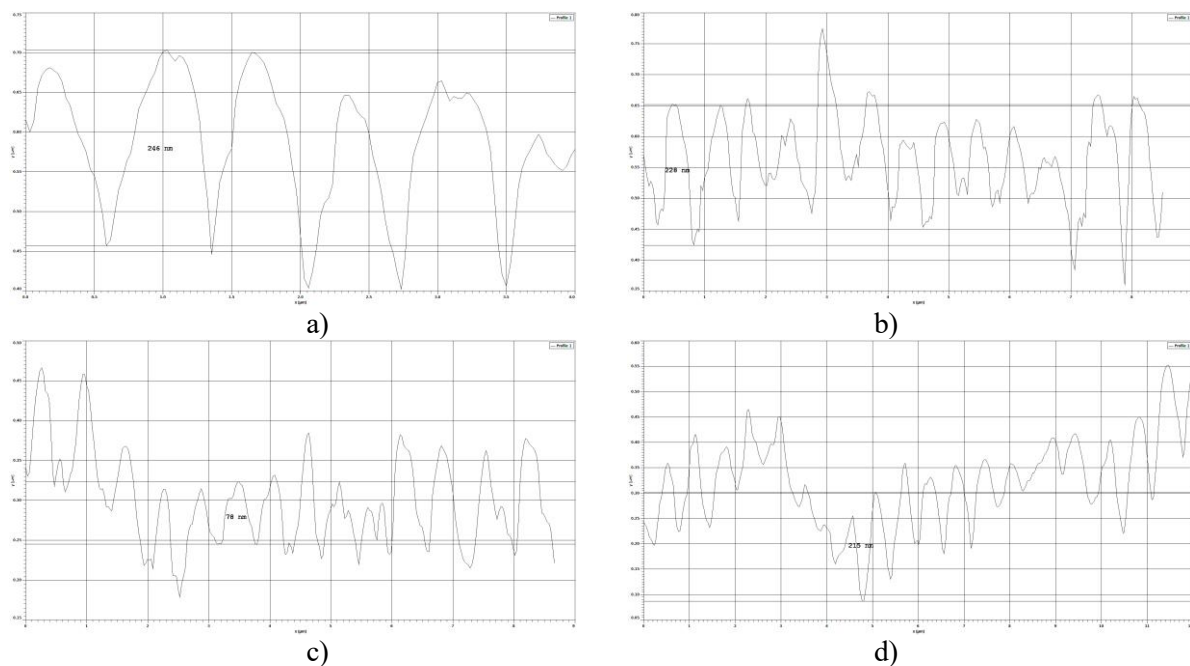
An ultrafast laser, whose pulse duration is defined smaller than 30 fs, was used for experiments. The femtosecond laser system parts are a titanium sapphire oscillator and an amplifier with maximal pulse energy 0.8 mJ and pulse frequency 1 kHz. Density distribution of energy was nearly Gaussian. The laser generates pulses with a pulse contrast bigger than  $10^9$ : 1. Central wavelength of emission had a value of 800 nm, and a bandwidth of approximately 100 nm. A metal mirror was used to focus the laser beam on the surface of plates from pure copper, and for sample treatment was used a 2D-positioning system. The spot size was chosen to achieve an average energy density of 1.05 J/cm<sup>2</sup>. Height and width of the laser spot were 0.26 mm and 0.27 mm respectively, with a total spot region of approximately 0.07 mm<sup>2</sup>. The laser beam has been focused and scanned over a surface of copper plates to obtain samples. The processed region had the size of 20×20 mm<sup>2</sup>. During laser processing, the plate first moved in the positive direction of the *x*-axis by 20 mm. The laser generation was interrupted at the end of this line and the copper plate was displaced in the positive direction of the *y*-axis by 0.28 mm. Then the generation was resumed and the plate was moved in the reverse direction along the *x*-axis. The whole process was completed until a region of 20×20 mm<sup>2</sup> had been treated by laser pulses.

Thus, a region of laser treatment with femtosecond pulses of 400 mm<sup>2</sup> in size was obtained on the copper surface. Samples processing was started by moving in positive *x*-direction, and after displacement in the *y*-direction by a small amount, the movement direction was reversed. Such sequential processing, first in positive *x*-direction, followed reverse direction was performed. Moving speed was 3 mm/s, and the distance between two adjacent processing zones was at least 0.01 mm, i.e. without overlap. Experiments have shown that visible colours (with a more turquoise or more dark purple-red appearance) depend only on the moving direction. Figure 1 shows obtained using an optical microscope an image of the copper surface after laser treatment with different scanning directions. These experiments have shown result that relatively minor nanostructure modifications obtained when different scanning directions a copper surface with an ultrashort pulses beam that has a weakly asymmetric energy distribution can lead to a much differences in colour. Tracks on the material obtained in a multi-pulse mode with an energy density lower than the threshold ablation were studied using scanning electron microscopy and atomic force microscopy.

To determine the possible dependence of the visible colour on the surface topology, regions of different colours were studied using atomic force microscopy. The average length of the microrelief period on the sample surface turned out to be almost the same for all examined regions and was in the range 600–630 nm. Figure 2 presents height profiles of four regions of the sample that showed different colours, such as turquoise, yellow-orange, and dark purple-red. At first glance, there are no significant differences. Therefore, for these profiles, heights of local maximums were correlated with heights of corresponding local minimums. This made it possible to calculate the average height of the microrelief of each of these four regions.



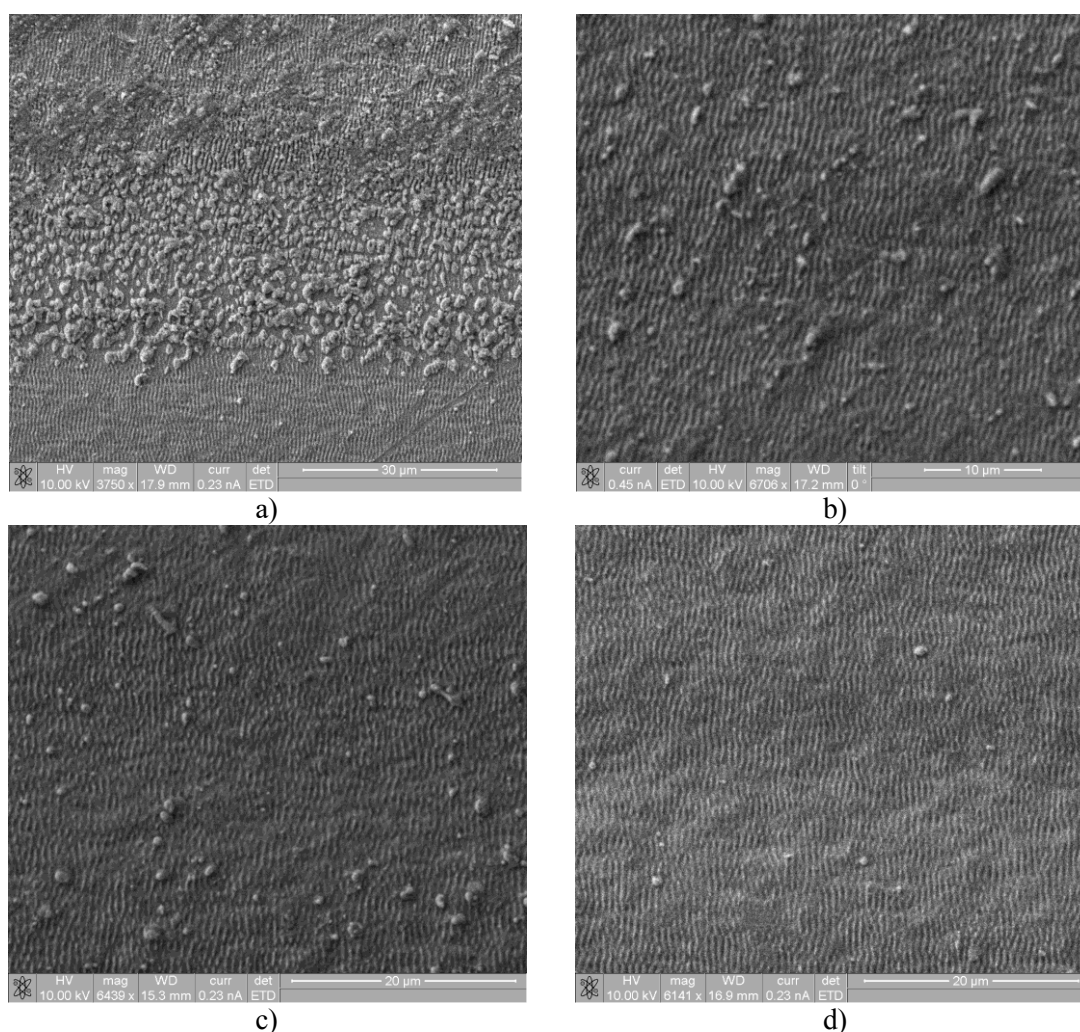
**Figure 1.** The copper surface after treatment with different scanning directions: 1 – dark purple-red; 2 – turquoise; 3 – yellow-orange; 4 – grey-green.



**Figure 2.** Height profiles of four sample regions showing different colours: turquoise (a), yellow-orange (b), grey-green (c) and dark purple-red (d).

It revealed that the average height of the microrelief was showed maximum values in a turquoise region and was 1.7 times greater than in the dark purple-red region. Grey-green and yellow-orange regions were characterized by an average height in the interval between those two values, and their average heights were closer to the value of the dark purple-red region. It has been demonstrated that small nanostructure modifications changed the surface colour significantly.

To study of laser treated tracks, an analytical scanning electron microscope FEI Quanta 200 was used. Figure 3 shows obtained using secondary electron mode of scanning electron microscopy images of four regions of the sample that showing different colours. Figure 4 shows images of the treatment zone of the sample, which obtained using optical and scanning electron microscopes. Images reveal that by scanning of a copper surface with an ultrashort pulse beam has been formed a combined microrelief containing a laser-induced periodic surface structures and a nanoroughness. It is determined that there are regions with a more numerous adhering particles and regions with a smaller quantities adhering particles. It turns out that visible turquoise regions have more numerous and large adhering particles than dark purple-red regions.



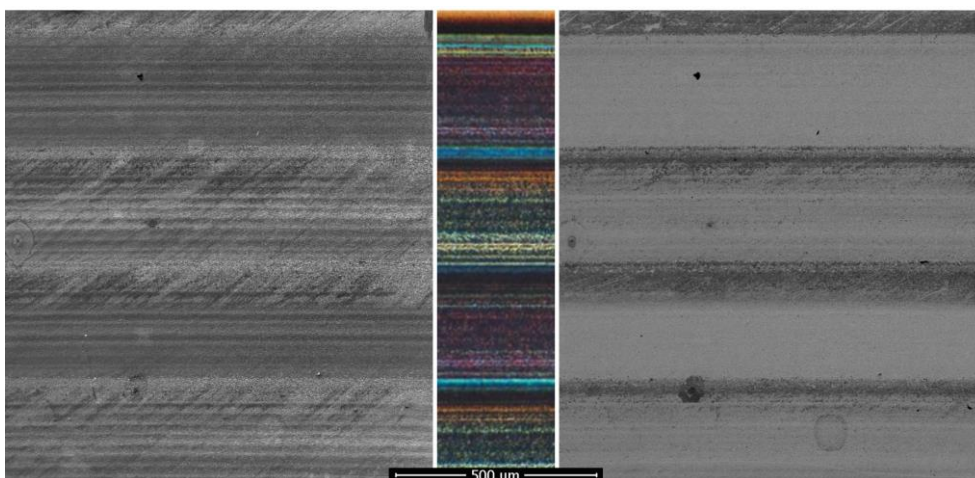
**Figure 3.** Obtained using secondary electron mode of scanning electron microscopy images of four regions of the sample that showing different colours: turquoise (a), yellow-orange (b), grey-green (c) and dark purple-red (d).

Since the electron backscattering intensity depends mostly on the size of the atom nuclei of the material in the specimen, i.e. on the atomic number, then according to these images, elements can be distinguished. In the backscattered electron image, regions consisting elements with a high atomic number will have a looks brighter compared to lighter elements. The atomic number of copper (29) is greater than that of oxygen (8), and hence in the backscattered electron image, the area consisting of unoxidized copper will look much brighter. Figure 4 (right) shows backscattered electron images of the four regions. A quantitative analysis of these images is rather difficult to make, but a qualitative description shows that the obtained image of the sample region of dark purple-red colour compared to other regions looks much brighter, whereas the turquoise region of sample is much darker than other regions. In backscattered electron images correspond the brighter regions to greater copper content and lower oxygen content. Performed using energy dispersive X-ray analysis technique study of the chemical composition of the surface layer of the sample has shown that the content of oxygen in turquoise regions (up to 12 wt %) is much higher than in dark purple-red regions (up to 2 wt %). Figure 5 shows zones with different oxygen content on the surface. It was determined that adhering particles that had a shape close to a spherical consist of copper oxide.

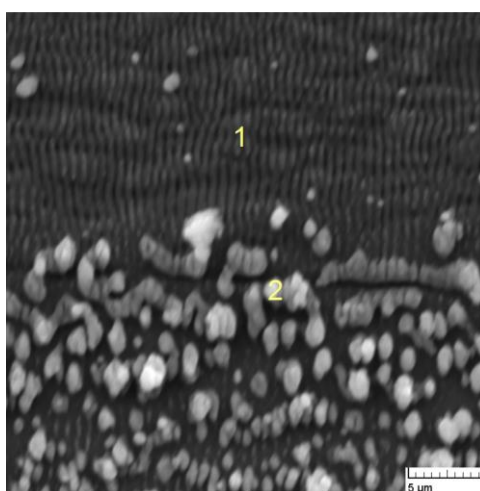
Of course, metallic materials have a limited electron penetration depth, and, therefore, EDX spectra are more sensitive for the surface layer of the sample of such materials. However, it is not the surface that is analyzed, but the entire volume of excitation, i.e. the interaction volume of electrons with



matter (which has a drop-shaped form), which in this case does not allow to widely interpret such analysis results. Nonetheless, a surface chemical analysis allowed to determine that the content of oxygen in turquoise regions is much higher than in dark purple-red region. It was found that one of the main reasons for the difference in colour of images is the oxidation degree.



**Figure 4.** Obtained using an optical microscope image (in a middle), as well as secondary (left) and backscattered electron (right) images of the treatment zone of the sample.



**Figure 5.** Zones with different oxygen content on the surface: 1 – minimum oxygen content (dark purple-red region); 2 – maximum oxygen content (turquoise region).

### 3. Conclusions

A colorization of copper surfaces by nanostructure modifications with ultrashort laser pulse was studied. Femtosecond laser was used for experiments. A relative motion on the material of the laser beam in a multi-pulse mode with an energy density lower than the threshold ablation led to formation of low-spatial frequency periodic surface structures. By the surface treatment with a laser pulses duration smaller than 30 fs, almost-wavelength periodic structures were formed and finally the surface brightness was increased. To determine the possible dependence of the visible colour on the surface topology, regions of different colours were studied using atomic force microscopy. The average length of the microrelief period on the sample surface turned out to be almost the same for all examined regions and was in the range 600–630 nm. The average height of the microrelief was showed maximum values in a turquoise region and was 1.7 times greater than in the dark purple-red region. Grey-green and yellow-orange regions were characterized by an average height in the interval between

those two values, and their average heights were closer to the value of the dark purple-red region. It has been demonstrated that small nanostructure modifications changed the surface colour significantly.

Using backscattered and secondary electron modes of scanning electron microscopy images were obtained from four sample regions that showed different colours, such as dark purple-red, turquoise, yellow-orange and grey-green. It was revealed that visible turquoise regions have more numerous and large adhering particles than dark purple-red regions. Obtained backscattered electron images show dark regions with clearly defined borders on a brighter background. Dark regions are regions contain lighter atoms, from which electrons of the beam are reflected worse than from heavier chemical elements. Results indicate that the sample material shows a certain heterogeneity in its composition, since regions with a light element – that is oxygen in the common copper matrix – can be detected. A surface chemical analysis allowed to determine that the content of oxygen in turquoise regions is much higher than in dark purple-red region. Thus, it was found that one of the main reasons for the difference in colour of images is the oxidation degree.

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