Pulse-periodic laser action to create an ordered heterogeneous structure based on copper and zinc oxides

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Abstract. We developed a method of pulse-periodic laser action has to create an ordered heterogeneous structure of CuO / ZnO. We performed pulse-periodic irradiation of a CO\(_2\) laser ROFIN DC 010 into two types of brass samples L62: grinded and surface etched after grinding. It we found that when the beam power was increased in the range 270–330 W, the density of nanowires increased, shorter and wider nanowires formed. The synthesized nanowires reinforced on the surface had a length of ~ 0.5–3 μm, a diameter of ~ 40–90 nm. The surface of the Cu-Zn alloy subjected to etching had a clearly discernable grain boundary with a grain size in the range of ~ 40–100 μm. The surface of the samples after etching consisted of pure copper. As a result of oxidation at the grain boundaries, whose size decreases to ~ 20–30 μm, growth of ZnO nanowires was observed. When an increase in the duration of oxidation by using laser action to air, the growth of ZnO nanowires has became more intense. Obtained results are important to solve the tasks of laser information technologies. These results are a basis for software creating to control of lasers that provide required processing modes of materials.

1. Introduction

The change in the complex of physical and mechanical properties of metallic materials is an important direction in conducting fundamental research for the subsequent solution of actual applied problems in various industries. Directional regulation of the composition and structure of metals and alloys provides an opportunity to control their strength and plasticity, improve antifriction properties, vibroacoustic characteristics, and etc. For the realization of progressive methods for the structures formation of metallic materials, laser radiation is used [1, 2]. For example, for the manufacture of metallic nanoporous materials, chemical or electrochemical methods are currently used, for example electrochemical selective dealloying [3, 4], selective anodic etching [5], and preferential dissolution [6, 7]. In the latter case, the use of laser beam energy in the presence of electrolyte makes it possible to obtain the effect of selective dissolution of a certain phase of metallic material to create a permeable zone in its structure [8]. The conditions for the formation of nanoporous structures in a copper-zinc alloy by laser action were determined in Refs. [9–11]. In this case, the formation of nanopores, both single and branched channels, occurs in the material.

A method for oxidation the surface of an alloy of the Cu-Zn system at laser action was developed in [12–14]. It is known that monoclinic CuO and wurtzite ZnO are actively used in electronic and optoelectronic devices, such as solar cells and gas sensors. Studies was performed by various authors have demonstrated that heterogeneous polycrystalline microstructures consisting of CuO and ZnO micrograins can be obtained using various processing techniques such as spraying and subsequent sintering [15, 16], and deposition from the gas phase.
It was determined [17, 18] that the hetero-contact CuO / ZnO microstructures produced by sol-gel process have higher sensitivity to hydrogen in comparison with polycrystals ZnO. In addition, in the thin-film CuO / ZnO heterojunctions, the phenomena of voltage-dependent gas sensitivity [19] and selectivity for CO were observed [20]. The introduction of a heterocontact between CuO and ZnO facilitates the interaction of the analyzed gas and the two components of the heterostructure; it opens up yet another perspective for chemical sensors based on metal oxides. In particular, the distribution on the position and size of heterocontacts and grains plays a major role in the management of the charge transfer that is induced by the gas-heterocontact surface interaction [17]. Thus, ordered heterogeneous structures such as CuO / ZnO are promising materials for further improving the properties of chemical sensors and other similar devices based on heterostructures. The goal of this work is to develop a method of pulse-periodic laser action to create such structures.

2. Laser equipment and researched material
A diffusion-cooled and radio frequency excited CO2-laser ROFIN DC 010 was used for the research. The main technical characteristics of the laser: beam wavelength 10.6 μm; power control range 100–1000 W; pulse frequency 2–5000 Hz; single pulse duration 0.026–125 ms; beam aperture 20 mm. Laser action was perform on samples of L62, Cu-Zn alloy with a copper / zinc ratio of 62/38, having a thickness of 50 μm. Previously, metal foils were mechanically machined to dimensions of 20×30 mm². For the comparative study, two types of brass samples were prepared: graded and surface etched after grinding. When grinding, the grain size of the sandpaper from SiC was 80; 180; 300; 600; 800; and 1200 in series. For surface etching of samples from copper-zinc alloy, an etching solution was prepared: 5 g FeCl₃, 50 ml HCl and 500 ml H₂O. Surface etching was carried out for 30–120 s.

Both types of samples from the copper-zinc alloy were exposed to a pulse-periodic laser beam irradiation. During the experimental studies, the pulse frequency varied in the range 10–2500 Hz. The beam power was 270–330 W. The fine structure of previously prepared and laser beam processed samples was studied using a scanning electron microscope VEGA \ SB, Tescan. X-ray diffractometer DRON-7 with the emission of characteristic radiations of series K (λ = 1.5406 Å) was used to perform the measurements. It is used to measure the intensity and diffraction angles of X-ray that diffracted at a crystalline object in order to solve problems of X-ray diffraction and X-ray analysis of materials.

3. Results and discussion
In accordance with the diagram of the equilibrium state of the Cu-Zn system, brasses with a high copper content, including L62, have a homogeneous structure consisting of a solid solution of zinc and copper (alpha solution). In a polycrystalline alloy, α-phase is a face-centered cubic phase in which zinc atoms replace copper atoms. Two types of surface made of a metal alloy of the Cu-Zn system of brass L62 were studied: after grinding and surface etched. Thermal oxidation by using pulsed-periodic laser action suggests the growth of two types of semiconductor nanostructured heterojunctions. The first type is ZnO nanowires that evolved from nanofilms of CuO; the second type is nanofilms of CuO surrounded by a network of nanowires ZnO.

Figure 1 a, c shows the images of ZnO nanowires and nanofilms of CuO obtained using a scanning electron microscope, which are evolved on a grind ed surface of the Cu-Zn alloy after thermal oxidation using various processing parameters. Figure 1 b, d shows the images on an enlarged scale, which demonstrate a mixed nature evolved nanowires and nanofilms after thermal oxidation; this corresponds to the facts given in [21]. When the beam power is 270 W, ZnO nanowires are weakly formed on a grinded surface; when the power is increased to 330 W, the density of nanowires increases sharply. However, in this case, shorter and wider nanowires are formed. The synthesized nanowires are reinforced on a substrate and have a length of ~ 0.5–3 μm, and a diameter of ~ 40–90 nm. Clear grain boundaries after thermal oxidation, as well as on the smooth and clean surface of the grinded surface were not observed. The results of energy-dispersive X-ray spectroscopy (EDXS) study of the samples shown that nanowires on an oxidized grinded surface consist of ZnO. Figure 2 presents the results of an analysis of the elemental chemical composition of the initial structure of brass.
Figure 1. The images of ZnO nanowires and nanofilms of CuO using a scanning electron microscope, developing on a polished substrate of an alloy of the Cu-Zn system after thermal oxidation, using various parameters of the processing regime (a), (c). Images on an enlarged scale (b), (d).

The results of the analysis of the elemental chemical composition of the material surface after a pulse-periodic laser action are shown in Figure 3. It is established that the share of zinc from metal materials is up to 99%, i.e. on the surface of the material there is mainly zinc oxide ZnO. X-ray diffraction studies of the obtained samples from a copper-zinc alloy were performed. The analysis of the diffraction roentgenograms showed that thermal oxidation leads to the formation of monoclinic CuO (JCPDS 45-0937, a crystallographic group: C2/c, a = 4.6853Å, b = 3.4257Å, c = 5.1303Å, β = 99.549°), and wurtzite ZnO (JCPDS 36-1451, a crystallographic group: P63mc, a = 3.24982Å, c = 5.20661Å) on a substrate of porous Cu-Zn alloy (JCPDS 25-0322, a crystallographic group: R3m, a = 4.256Å) [21].

Figure 2. The results of the analysis of the elemental chemical composition of the initial structure of brass.
The surface of the Cu-Zn alloy, subjected to etching, has a clearly discernable grain boundary with a grain size in the range of ~ 40–100 μm. The results of analysis of the elemental chemical composition by the method of energy dispersive X-ray spectroscopy demonstrate that the surface of samples after etching consists of pure copper. As a result of oxidation at the grain boundaries, the size of which decreases to ~ 20–30 μm, growth of ZnO nanowires is observed (Figure 4).

![Figure 3. The results of the analysis of the elemental chemical composition of the surface of the treated material after a pulse-periodic laser action.](image)

![Figure 4. The growth of ZnO nanowires as a result of oxidation at the grain boundaries, whose size decreases to ~ 20...30 μm.](image)

The bundles of nanowires are clearly distributed over the region of grain boundaries, while the rest of surface is observed only a certain amount of nanowires. ZnO is dominant in the boundary region, while CuO predominates on the rest of surface. The formation of ZnO is dominant due to a higher rate of external diffusion and oxidation than copper, while Zn can penetrate through the surface pores of copper, and then through the CuO layer. In addition, the growth of ZnO nanowires may be due to the lower melting point and higher vapor pressure of zinc than copper under the same conditions. Thus, it is obvious that the bunches of ZnO nanowires grow in the region of intergranular boundaries, while the CuO film grows on the rest of the surface, forming a network of nanowires / film junctions on the surface of the copper-zinc alloy.

When the oxidation time by laser action to air is increased, the growth of ZnO nanowires becomes more intense, suggesting a further predominance of zinc diffusion and oxidation on the entire surface during longed thermal oxidation. As a result, a relatively dense porous metal oxide layer is formed on the surface of the porous copper-zinc substrate. Further increase in the duration of laser action leads to intense cracking of the oxide layer (Figure 5). It should be noted that after intense cracking, spalling, and exposing the almost non-oxidized surface of the Cu-Zn grains, the region of grain boundaries contains an inseparable intermediate ZnO layer as a result of the presence of broken ZnO nanowires.
4. Conclusion
A method of pulse-periodic laser action has been developed to create an ordered heterogeneous structure of CuO / ZnO. The laser action by using of a CO₂-slab ROFIN DC 010 was performed on two types of brass samples L62: grinded and surface etched after grinding. For surface etching of surface of copper-zinc alloy, an etching solution was used: 5 g FeCl₃, 50 ml HCl and 500 ml H₂O. During the experimental studies, the pulse frequency varied in the range of 10–2500 Hz. The beam power was 270–330 W.

It was found that with increasing beam power, the density of nanowires increased, shorter and wider nanowires was formed. The synthesized nanowires are reinforced on a samples surfaces and have a length of ~ 0.5–3 μm, and a diameter of ~ 40–90 nm. The surface of the Cu-Zn alloy, subjected to etching, has a clearly discernable grain boundary with a grain size in the range of ~ 40–100 μm. The samples surfaces after etching are consisted of pure copper. As a result of oxidation at the grain boundaries, whose size decreases to ~ 20–30 μm, growth of ZnO nanowires was observed. When an increase in the duration of oxidation by using laser action to air, the growth of ZnO nanowires became more intense. A further increase in the duration of the laser action led to an intense cracking of the oxide layer.

The developed method of pulse-periodic laser action implements a new approach to the creation of ordered networks of heterojunctions based on semiconductor nanowires ZnO and nanofilms CuO by laser-induced selective thermal oxidation of the surface of a de-zinced surface of a polycrystalline alloy of the Cu-Zn system. Specially designed structured materials from such alloys can provide an opportunity to create promising assemblies from heterogeneous nanostructures. This approach allows us to open new prospects for the formation of complex nanostructures and the use of heterogeneous nanodevices. Obtained results are important to solve the tasks of laser information technologies. These results are a basis for software creating to control of lasers that provide required processing modes of materials.

5. References
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