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# CREATION OF METAL MATERIALS NANOPOROUS STRUCTURES UNDER THE ACTION OF LASER RADIATION

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# Creation of metal materials nanoporous structures under the action of laser radiation

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**Abstract**

The laser radiation exposure for creation of nanoporous structures in the Cu-Zn alloy was studied. Exposure to laser pulse-periodic radiation with pulse repetition rate up to 5000 Hz makes it possible to form a nanoporous structure in the near-surface layer. The modes of an increase of the area depth of such structures formation up to 40...45 µm were ascertained. The temperature and speed modes which provide predominant channel-type nanopores formation with widths of about 100 nm forming a nanoporous net were investigated.

Keywords: laser radiation; nanoporous structures; metal materials.

## Introduction

Nanoporous materials are used in filtration of gases and liquids in medicine, nuclear power engineering, microbiology, food industry and other [1-3]. The most commonly used membranes are made of nanoporous materials based on polymers, glass, ceramics and graphite. Compared with them, metal membranes have superior technological and physical-mechanical qualities, such as: mechanical durability, heat resistance, they have a long period of operation, can be cleaned by backflow of liquid and calcinations. Common used methods of making nanoporous metal materials, including electrochemical dealloying, selective anodic etching, preferential dissolution, powder compacting and film technology [4-7], have considerable technological constraints on the stability of pore sizes, and created products have decreased mechanical properties and relatively high prices. By that, problems of developing new techniques of nanoporous structures formation in metal materials have great scientific and practical interest.

The possibility of creation of nanoporous structure in the near-surface layer of a two-component alloy with type of solid solution by exposure to laser radiation with high pulse repetition frequency is described in papers [8-10]. The use of special optical systems based on the elements of computer-generated diffractive optical elements - radiation focusators [11-16] gives the ability to selectively perform processing of areas with required shape. After laser treatment nanoporous cellular structure with an average size of nanopores of 40…50 nm is created in the near-surface layer to depths of 25…30 nm. The pores have rather stable sizes and shapes, they are uniformly allocated inside subgrains. The sizes and shapes of nanopores are more irregular at the subgrain borders. It is advisable to determine the conditions for the formation of nanopores of mainly channel-type with widths greater than those obtained previously with an increase of the depth of nanoporous structures formation for the progress of practical use of the developed method.

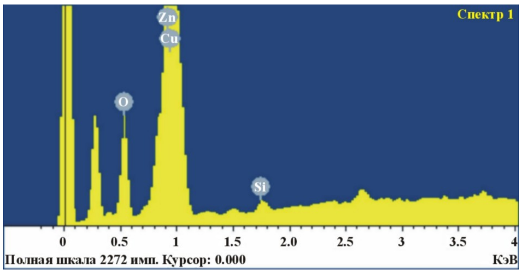
## Results and discussion

Cu-Zn alloy brass with a 60,5…63,5 % content of copper was used as the model material, which feature is a significant concentration of the component (Zn) with higher vapor pressure. In the course on experimental studies, an important advantage of the usage of the specified alloy as model material is that the reduction of Zn concentration on the surface can be visually observed, because the brass changes its color from the original yellow to red. The samples surfaces were not exposed to special treatment before exposure to laser radiation.

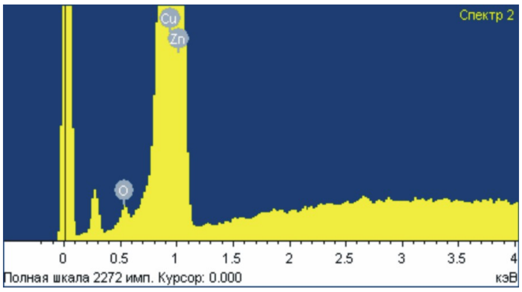
The gas $CO_2$-laser ROFIN DC 010, with output power ranging from 100 to 1000 W and the output beam diameter of about 20 mm, was applied for the laser radiation exposure. The temperature in the heating area was monitored with the use of the non-contact pyrometer Kelvin-1300 LZM. The geometric parameters of laser radiation was transformed into a light spot with uniform power density by the diffractive optical element [15, 16]. It ensures production of a desired shape of the treatment zone with a specific distribution of laser radiation density and maximum utilization of the radiated power. Said optical system comprises a diffractive optical element ensuring rotation of the laser beam, its special phase modulation, and redistribution of its power over the treatment zone having a desired shape. The diffractive optical element is made as a reflecting plate whose surface micropattern is dictated by the desired shape of the treatment zone, by the distribution of radiated intensity, and by the wavelength of laser radiation. Such optical systems make it possible to expand the rang of production operations performed by laser treatment of materials and to achieve a higher utilization factor of laser radiation by providing flexible control of geometrical characteristics of laser beams in zone of treatment on the surface of objects, while retaining radiated power and ensuring desired distribution of the laser beam density. Moreover, parameters of production processes can be regulated more easily, laser treatment becomes more accurate, the number of elements in the optical system for delivery of laser radiation to the object to be treated is reduced, and this system becomes more reliable and compact.

The laser radiation exposure for creation of nanoporous structures in the Cu-Zn alloy was being studied. The modes which provide predominant channel-type nanopores formation with an increase of the area depth of nanoporous structures formation up to 40…45 µm were being ascertained. Exposure to laser pulse-periodic radiation with pulse repetition rate up to 5000 Hz at temperature, not higher than melting temperature, makes it possible to form stable stress condition on the surface of the samples. The exposure to laser radiation with uniform power density variable in range from $3 \cdot 10^6$ to $4 \cdot 10^6$ W/m$^2$ was carried out upon a rectangular area 20×5 mm on surface of the metal material. Such treatment on the two-component metal alloy with type of a solid solution of Cu-Zn system one component of which has a higher vapor pressure, causes a change in surface relief. With the use of the temperature and speed modes, as well as the duration of exposure to laser radiation, these changes are manifested in both the development (the formation of cavities with a wedge-shaped cross-section), and smoothing of the relief. The metal alloy structure with rather evenly distributed over the area open pores of different forms, from globular to irregular, is formed on surface of the metal material after exposure to laser radiation. Ramified pores with distinctive dendritic structure are also formed.

Such laser treatment resulted in significant reduction in the concentration of the component in the alloy with a relatively high vapor pressure (Zn) was attained by. Change in the brass samples colour from original yellow to red was observed that indicated reduction in concentration of Zn on their surface during the heating process. The elemental composition analysis of the samples surface of the two-component metal Cu-Zn alloy brass after laser exposure with high pulse repetition frequency, carried out by using an analytical scanning electron microscope VEGA\\ SB, Tescan, equipped with the system of electron-probe energy-dispersive microanalysis INCA Energy SEM, Oxford Instrument, showed an increase in relative copper content from 63% to 92% and reduction of zinc fraction from 36% to 7%. Results of the analysis of elemental composition of the surface and the ratio of the alloy components in terms of compact material before and after exposure to laser radiation are shown on Figure 1 and Table 1.




a




b

Figure 1: Results of the elemental composition analysis of the surface: before (a) and after (b) the laser treatment

Table 1: Alloy component ratio before and after the laser treatment in terms of a compact material

| Component | before (weight %) | after (weight %) |
|---|---|---|
| Cu | 63 | 92 |
| Zn | 36 | 7 |
| other | 1 | 1 |

For the study of the near-surface layer structure of Cu-Zn alloy firstly the surface of the slice, which was not exposed to etching, secondly the surface of the etched and re-polished slice was examined. The study was conducted with polarization-optical microscope Neophot-30. The structure of the near-surface layer of Cu-Zn alloy after exposure to laser radiation is shown on Figure 2. In the result of the alloy structure study by the method of optical microscopy on slices with plane implemented at an angle of 5° to the processed surface, the following was ascertained. In cross-section the pores are oriented from the surface into the metal. Density of pores allocation is higher near the surface, the pores have a rather complicated form, and they occupy approximately half of the grain area. Near the material surface the pores often connect to each other through narrow spots.

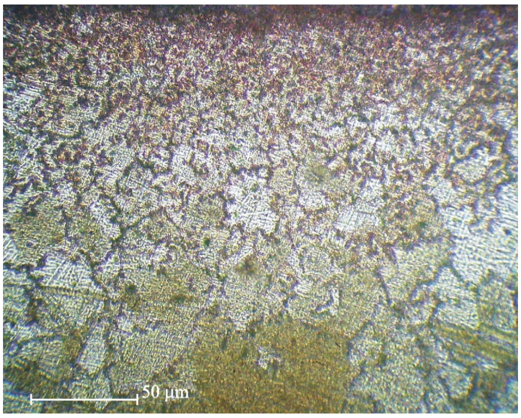



Figure 2: The structure of the near-surface layer of Cu-Zn alloy after exposure to laser radiation. Etched slice, surface of the slice is implemented at an angle of 5° to the processed surface

Pores are mainly formed along the boundaries of grains and blocks in the near-surface layer, which results in the creation of new borders and, consequently, the grain crushing. There are close pores of mainly oval form with microasperities in the form of projections and cavities inside the grains. Pores occupy smaller capacity than branched pores. The study of microstructure of the processed material showed that the concentration of pores decreases with increasing of distance from the surface into the material (Figure 3).

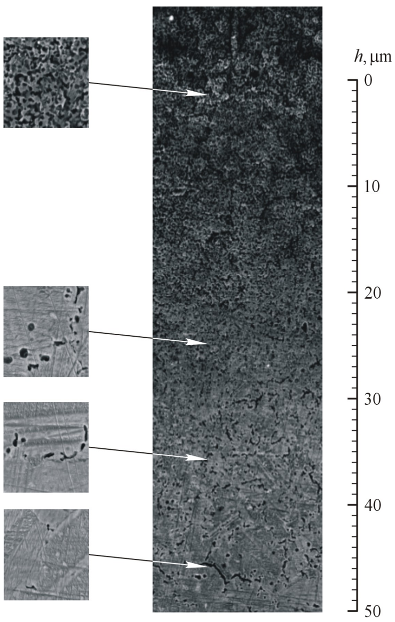



Figure 3: The distribution of pores in the depth of the processed material

The temperature and speed modes which provide predominant channel-type nanopores formation with widths of about 100 nm forming a nanoporous net were investigated. The uniformly allocated on the surface of subgrains nanopores have relatively stable sizes and shapes. Figure 4 shows the scheme of research of nanoporous structure of the processed material. Figure 5 shows the image of typical channel-type nanopores with widths up to 100 nm.

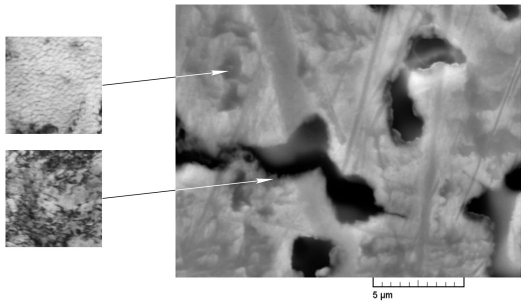



Figure 4: Scheme of research of the processed material nanoporous structure

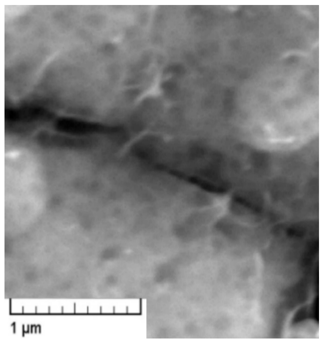



Figure 5: Image of a typical channel-type nanopore of about 100 nm wide

It is assumed that the principal mechanism of nanoporous structure creation is the sublimation of the alloy component with higher vapor pressure (Zn). Concentration gradient is created in the material, subsequently this component sublimates to the extent to which its diffusion delivery to the surface is ensured. In the course of time the thickness of the zinc-depleted layer increases, and diffusion becomes the limiting factor of the process of sublimation. The condition for the intensification of mass carry in the solid phase of metal materials is non-stationary local deformation caused by high-energy external action. This patented technology [17, 18] is perspective for production of catalysts and ultrafiltration membranes.

## Conclusion

The laser radiation exposure for creation of nanoporous structures in the Cu-Zn alloy was studied. The modes which provide predominant channel-type nanopores formation with an increase of the area depth of such structures formation up to 40…45 μm were ascertained. The exposure to laser radiation with uniform power density variable in range from $3 \cdot 10^6$ to $4 \cdot 10^6$ W/m$^2$ was carried out upon a rectangular area 20×5 mm on surface of the metal material. It was established that exposure to laser pulse-periodic radiation with pulse repetition rate up to 5000 Hz makes it possible to form a structure with rather evenly distributed over the area open pores of different forms, from globular to irregular, on surface of the metal material. Ramified pores with distinctive dendritic structure are also formed.

Significant reduction in the concentration of the component in the alloy with a relatively high vapor pressure (Zn) was attained by such laser treatment. The elemental composition analysis of the samples surface of the two-component metal alloy with type of solid solution of Cu-Zn alloy brass after laser exposure with high pulse repetition frequency showed an increase in relative copper content from 63% to 92% and reduction of zinc fraction from 36% to 7%. The study of the structure of the near-surface layer of Cu-Zn alloy after exposure to laser radiation showed that in cross-section the pores are oriented from the surface into the metal, the concentration of pores decreases with increasing of distance from the surface. Laser treatment creates a nanoporous structure in the near-surface layer. The temperature and speed modes which provide predominant channel-type nanopores formation with widths of about 100 nm forming a nanoporous net were investigated.

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