Features of microrelief formation during laser treatment of Cu-Cr-Zr alloy surface for diffusion welding

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Abstract. The effect of UV laser pulses of nanosecond duration on surface of Cu-Cr-Zr alloy samples was investigated. Noticeable changes in the morphology of the surface layer after irradiation were found at pre-threshold values of the energy density of ~ 0.2 – 0.8 J/cm². Changes are traces of thermoplastic deformation resulting from influence of a concentrated energy flow and appears in irregular elevation of the irradiated surface area of the sample by up to 1 μm and in some cases – more. A developed metal surface, deformation of the crystal structure of the surface layer can support the diffusion process during diffusion welding. For energy densities of the order of 1 J/cm² or more, optical breakdown with the formation of a crater on the metal surface occurred. The mechanical impulse of a laser plasma when exposed to a metal surface prevents the thermomechanical expansion of the material, and the effect of raising the surface of the samples was not observed.

1. Introduction
Diffusion welding is a method of joining of different materials, which usually cannot be joined in another way. This process is extremely important for high-tech industries using the most advanced materials on the limit of their physical capabilities. The surface condition has an important influence on the processes of mutual adhesion of the materials being welded [1–2]. Processing with intense laser radiation actively effects on the adhesive properties of materials [3–7]. Adhesion, as is known [2], is determined primarily by diffusion phenomena, and pulsed laser irradiation contributes to a sharp change in the diffusion parameters, up to an increase in diffusion coefficient by up to 6 orders of magnitude [8–9]. These processes occur in the surface layer, the modification of which can have a significant effect on the formation of micro- and nanostructures, largely determining the adhesion properties of the surface. With this treatment, the effective surface area markedly increases.

The direct laser nanostructuring method, due to its comparative simplicity and high efficiency, is one of the most promising [4–6]. This method has only one stage, which consists in processing the surface of the material with a focused laser beam and does not require the use of any masks or other supporting means.

The main amount of work on direct laser nanostructuring was performed earlier using pico- and femtosecond lasers [10–13]. However, for practical applications, it is of interest to use cheaper and easier to use sources, such as nanosecond lasers. The papers [14–16] give examples of the formation of nanostructures on the surface of various materials: polymers, semiconductors, metals and ceramics.
obtained using these lasers; moreover, the main attention was paid to nanostructures formed as a result of optical breakdown, accompanied by ablation effects. In this paper, we studied microrelief formation features during laser surface treatment of the Cu–Cr–Zr copper alloy, which is often used for diffusion welding [17], and the main attention is paid to the pre-ablation mode of material processing, which is characterized by processes occurring in the condensed state of the metal.

2. Experimental technique
The laser source was a solid-state pulsed periodic NdYAG laser (third harmonic with a wavelength of \( \lambda = 355 \) nm). The choice of the UV radiation range is explained by the fact that in this range most construction materials have significant absorption. The magnitude of the quantum of radiation provides a slightly larger value of the depth of the processed material, compared with sources of visible and infrared radiation; at the same time, the atmosphere is transparent to UV radiation.

The pulse duration was \( \tau = 10 \) ns, and the energy in the pulse reached 8 mJ, and the pulse repetition rate was 10 Hz. In the experiment, the energy and the number of acting radiation pulses were changed. After exposure, the surface morphology of the sample was studied on an optical three-dimensional profilometer – Zygo NewView 7300 and scanning electron microscope (SEM) JEOL JSM 6610LV.

The initial content of alloying additives in the alloy (Cr ~ 1%, Zr ~ 0.1 - 0.2%) was measured by the X-ray diffraction method using an attachment to JEOL JSM 6610LV. The reflection coefficients of polished samples of copper and its low-alloy alloys were measured using a Cary-5000 UV-VIS-NIR spectrophotometer with UMA prefix. At the working wavelength, the studied samples reflected ~ 10%. The accuracy of reflection coefficient measurements was 1%.

The sample was mounted normally to the optical axis of the laser on a three-coordinate subject table. It consisted of two linear translators 8MT180 and one 8MT173, operated by the controller 8SMC1-USBhF (Standa Ltd, Lithuania). The radiation energy density on the sample was changed both by changing the energy of the exposing laser pulse and by changing the size of the laser beam cross section by shifting the surface of the sample from the focal plane of the lens. The number of laser pulses exposing on the sample was controlled by an electromechanical shutter.

3. Experimental result and discussion
In the work, two pronounced regimes of exposure of radiation on the surface of the material were observed. This is a previously relatively well-studied ablation regime [18–21] and a little-studied pre-ablation regime in which the threshold of optical breakdown is not yet reached and the main processes of exposure occur mainly without changing the phase state of the material.

In the ablative mode, the interaction of radiation with the surface of the sample occurred in the well-known mode, many times described in the literature [22]. The exposure was accompanied by optical breakdown, in which a plasma torch and crater formation on the surface of the sample occur. Figure 1a shows a microphotograph of the affected area. The profilogram (figure 1b) shows that a cavity is observed in the centre, and along the edges, there is a roller formed by the material evaporated from the crater zone and deposited onto the surface by the flow of material from the centre to the edges of the molten zone.

At lower, subthreshold values of the radiation power density (\( E < 0.8 – 0.9 \) J/cm\(^2\)), an irregular lifting in the sample surface was observed in the exposure zone. After a single exposure at a power density (\( E = 0.2 – 0.3 \) J/cm\(^2\)), it was not possible to detect surface lifting. However, because the effect is cumulative in nature, after exposure to 30 laser pulses, this was recorded. Figure 2a shows a microphotograph of the surface area of the sample after exposure. It can be seen that in addition to cleaning the surface, at the centre of the spot irregular rise of the surface level with a maximum of 30 nm was observed (the profile is shown in figure 2b). It is clearly visible that the scratch, remaining after polishing, and passing through the centre of the spot is almost invisible in the exposure zone. With increasing power density, this effect becomes more noticeable.

With an increase in power density to a level (\( E \sim 0.8 \) J/cm\(^2\)), the effect of exposure becomes more noticeable even after a single exposure (figure 3). In this case, the lifting height of some surface areas
already reached the level of 1 μm, sliding along grain boundaries, which is characteristic of plastic deformation at elevated temperatures was observed [23]. At the same time, traces of boiling of a thin layer of instantly solidifying liquid metal appeared on the surface, manifesting themselves in the form of characteristic microcraters ~ 1–3 μm in size. Noticeable changes have also occurred in the elemental composition of the surface layer — the presence of oxygen was revealed. In the centre of the spot, its share was ~ 1% by weight, and up to ~ 4–5% along the edges. Accordingly, the relative concentration of the main element of the alloy, – copper, slightly decreased. However, a significant dispersion was observed in different spots.

Figure 1. Cu-Cr-Zr alloy surface after exposure to a UV pulse (λ = 355 μm, 10 ns, E = 2.15 J/cm², 30 pulses, f = 10 Hz): a) microphotograph, optical microscope, Zigo; b) surface profile, Zigo.

Figure 2. Cu-Cr-Zr alloy surface after exposure to a UV pulse (λ = 355 μm, 10 ns, E = 0.2 J/cm², 30 pulses, f = 10 Hz): a) microphotograph, optical microscope, Zigo; b) surface profile, Zigo.

An increase in the number of exposing pulses led to a noticeable intensification of the observed effect (figure 4). Faults distinctly appeared in the exposing zone along the boundaries of grains unevenly extruded from the mass of the sample. Inside some of them, traces of crystallographic sliding, noticeably changing the slope when passing through the grain boundary, were clearly observed. The height of some sections of uplift also reached ~ 1 μm. In the region of slide bands and grain boundaries, the material was “laser etched” by subsequent pulses, that is, the initially sharp edges of slide bands and grain boundaries seemed to melt slightly, obtaining round shape, but the character of the picture was not distorted. However, the proportion of oxygen in the composition of the surface layer of the alloy did not noticeably increase.
Figure 3. Cu-Cr-Zr alloy surface after exposure to UV pulse ($\lambda = 355 \mu m$, 10 ns, $E = 0.8 J/cm^2$, 1 pulse):
   a) microphotograph, optical microscope, Zigo; b) SEM, c) surface profile, Zigo.

Figure 4. These Cu-Cr-Zr alloy surface after exposure to a UV pulse ($\lambda = 355 \mu m$, 10 ns, $E = 0.8 J/cm^2$, 25 pulses, $f = 10$ Hz): a) microphotograph, optical microscope, Zigo; b) SEM, c) surface profile, Zigo; d) 3D image.
Figure 5. SEM microphotograph of a fragment of a portion of the exposure zone, shown in figure 4.

This picture is clearly visible on the periphery of the exposure zone, where the radiation power density was naturally slightly lower than in the centre of the spot, which was densely dotted with continuous microcrater formations, masking the traces of plastic deformation. This is clearly seen in figure 5, which shows a SEM microphotograph of a fragment of the exposure zone shown in figure 4.

4. Conclusions
On the samples of Cu-Cr-Zr alloy, after exposure with a UV laser pulse of nanosecond duration at pre-threshold values of the energy density of ~ 0.2 – 0.8 J/cm², noticeable changes in the morphology of the surface layer were found. They are traces of thermoplastic deformation that has occurred as a result of exposure to a concentrated energy flow, and appear in the irregular rise of the exposed region of the surface of the sample by up to 1 μm, and in some cases – more. In the exposure zone, classical manifestations of high-temperature plastic deformation are observed – grain-boundary sliding and traces of crystallographic slip. The effect is cumulative in nature, that is, the height of the uplifts increases with increasing number of exposing pulses. It is assumed that the obtained metal-developed surface should be very attractive for subsequent diffusion welding. Significant distortions of the crystal structure of the surface layer of the metal, which have arisen, should support diffusion process.

Traditionally, in experiments on laser exposure on the surface of solids the focus was on the phenomenon of optical breakdown of the material and its consequences. For energy densities of the order of 1 J/cm² or more, optical breakdown with the formation of a crater on the metal surface occurred. The mechanical impulse of a laser plasma, when exposed to a metal surface, prevents the thermomechanical expansion of the material, and therefore, similar effects were not previously observed. And the appearance of a laser crater accompanying an optical breakdown, the depth of which is noticeably higher than the lifting height, excludes the detection of these effects.

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