Modification of the Cu-Zr bronze surface by exposure to powerful UV laser pulses

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Abstract. The laser pre-treatment of Cu-Zr alloy surface for diffusion welding, which is used in the aerospace industry, has been investigated. The effect of a nanosecond UV laser pulse on the surface of Cu-Zr alloy samples was studied. It was found that at a pulse energy density $E \sim 0.2$-1 J/cm² pre-ablative microscopic effects of mainly thermal nature were observed in the metal, also there were uplifts of material in the irradiated zone. The surface profile of the sample in the irradiated zone corresponds to the energy distribution of the laser beam. Significant deformations occurred in the crystal structure of the surface layer, and an irreversible configuration of the metal surface was created. At $E \geq 1$ J/cm² an optical breakdown with the formation of a plasma torch and with the appearance of a classical laser crater was observed. The arising erosion of the surface prevented registration of this effect. Microanalysis showed that the concentration of zirconium in the surface layer of the metal after exposure decreased.

1. Introduction
In the aerospace industry, various materials are used to the limit of their physical capabilities. Therefore, diffusion welding of dissimilar materials is highly relevant [1]. In particular, diffusion welding of nickel-based heat-resistant alloys with bronze is often used. Nickel alloy provides high heat resistance, and bronze promotes heat removal from the part. The paper [2] reports on the efficiency of preliminary processing of these materials by laser pulses in the plasma formation mode before diffusion welding. However, along with the positive effect of such processing, it was found that in this case oxides of these metals appear in the surface layers of the parts being welded, partially reducing the processing efficiency. The works [3-6] report the discovery of a new, more efficient method of laser processing of these materials, which significantly reduces the process of oxidation of the surfaces to be welded before diffusion welding. This work is one of the sections of the research cycle of laser preparation of these alloys for diffusion welding.

The interaction of a nanosecond laser radiation (LR) with various materials has been studied in great detail [7-9]. This is largely due to the use of the most common solid-state laser [10,11] on a garnet crystal doped with rare earth elements, emitting pulses with a duration of the order of 10-20 ns at a wavelength of $\lambda \sim 1.06$ µm in the modulated Q-switched mode. Due to the use of nonlinear optical converters, it is possible to obtain the 2-nd, 3-rd, and 4-th harmonics ($\lambda = 0.532; 0.355; 0.266$ µm,
respectively). These lasers are commercially available in various configurations [12-14] for a long time.

However, the main attention of researchers was paid to the study of laser plasma arising from the interaction of radiation with the surface of a solid, the processes of its melting and evaporation, as well as the processes occurring in the material as a result of the secondary effect of the plasma torch on the target [9,11]. In [3-6], we report on a new mechanism of subthreshold modification of the surface of metals and semiconductors by the radiation of a nanosecond ultraviolet laser. Traces of high-temperature plastic deformation of the near-surface layer were observed in the absence of melting processes.

This paper reports on the results of high-temperature plastic deformation observed after exposure to a UV (λ = 0.355 μm) laser pulse with a duration of τ = 10 ns on the polished surface of the Cu-0.5% Zr alloy.

2. Methods and materials
A pulsed periodic NdYAG laser (Opotek, Carlsbad, CA, USA, 2012) at the third harmonic was used for exposure. The pulse energy reached 8 mJ at a repetition rate of f = 10 Hz. The use of UV radiation is justified by the fact that polished Cu-Zr samples, as well as pure copper, absorb nearly 90% of the radiation at the wavelength λ = 0.355 μm, whereas at λ = 1.06 μm this value was 3-4%. This fact compensates energy losses when converting radiation into the 3-rd harmonic.

In continuation of our work [3], in which pure oxygen-free copper was irradiated, in this work, the heat-resistant Cu-Zr alloy was chosen in order to reveal differences in the reaction of this material to laser radiation. The experimental technique was described in detail in [3]. Industrial grade alloy contained 0.5% of zirconium that allows one to improve the mechanical properties of the material without significant changes in thermal conductivity, electrical conductivity and optical properties [15]. Samples were polished. The initial surface roughness on the region comparable to the area of the laser spot was approximately 10-15 nm.

At the experiment, pulse energy and a number of pulses of LR were changed. After interaction the morphology of the samples was studied on an optical profilometer NewView 7300 (Zygo, Middlefield, CT, USA, 2012) and on a scanning electron microscope JSM 6610LV (JEOL, Tokyo, Japan, 2011). Using the prefix to the scanning electron microscope (SEM) before and after exposure, the elemental composition of the samples was studied.

3. Result and discussion
It is known that when exposed to nanosecond pulses of UV laser radiation, the metal surface is modified, however, ablation effects were usually observed, and in the surface layer, there was a rapid evaporation and crystallization of the material [9,16,17].

In contrast to the results of [9,16,17], the effects described in this paper occurred in the mode before ablation, that is without changing the state of aggregation, while maintaining the condensed state of the material.

Figure 1a shows an optical microphotograph of the sample surface after exposure to 25 pulses with E ~ 0.6 J/cm², and figure 1b shows a surface profile of the irradiated region. Figure 2 shows a SEM microphotograph of the sample after exposure to 25 pulses with E ~ 0.3 J/cm².
Figure 1. Cu-Zr alloy surface after exposure of UV pulse ($\lambda = 355$ nm, $\tau = 10$ ns, $E \sim 0.6$ /cm², 25 pulses, $f = 10$ Hz): (a) microphotograph by optical microscope; (b) surface profile by optical profilometer.

It was found that at subthreshold (optical damage is not observed) energy densities (at $E \sim 0.6$ J/cm²) in the absence of any visible traces of ablation, as in [3-5], in addition to cleaning the surface from impurities and oxides, there was a permanent lifting of the metal surface in the irradiation zone. It approximately corresponds to the distribution of laser energy in the spot. This effect is cumulative despite the fact that the sample surface completely cooled down to room temperature during the time between pulses [18]. With an increase in power density to the level ($E \sim 0.8$ J/cm²), the effect of exposure becomes more noticeable already after a single pulse. Small scratches in the spot area become invisible. With a further increase in energy densities (to a level of $E \geq 1$ J/cm²) ablation processes level out the lifting effect due to a noticeable redistribution of material in the spot. When analyzing microphotographs (figures 1, 2) and below estimates, it becomes clear, that the observed process of plastic deformation is predominantly thermal in nature. Point traces of melting were observed. When taking into account the specific heat of fusion, the threshold energy density [17] is (equation (1)):

$$E_m(\tau) = \delta(\tau) \rho \left[ C(T_m - T_{in}) + L_m \right]$$

where $\delta(\tau)$ is the effective thickness of the layer, in which energy is released during laser pulse $\tau$; $\rho$ is the material density, $C$ is the specific heat, $T_m$ is the melting temperature, $T_{in}$ is the initial temperature, and $L_m$ is the specific heat of fusion of the material. In a case of surface heating (equation (2)):

$$\delta(\tau) = \frac{1}{2} (\pi a \tau)^{1/2}$$

where $a$ is the thermal diffusivity of the material.

The threshold energy density and effective layer thickness were estimated for copper (the constants used for copper slightly differ from the corresponding values for the Cu-Zr alloy). Taking into account equations (1) and (2) at $C = 385$ J/kg K, $\rho = 8920$ kg/m³, $a = 1.2 \cdot 10^{-4}$ m²/s, $T_m = 1356$ K, $T_{in} = 293$ K, $L_m = 204.7 \cdot 10^3$ J/kg [15], for $\tau = 10$ ns we have: $\delta(\tau) = 971$ nm, $E_m(\tau) = 0.53$ J/cm².

In addition, the height of surface lifting was evaluated. It is based on an analysis of the process of irreversible thermal deformation of the heated sample area at an average temperature of the surface layer $T \sim 1350$ K. During time $\tau$ heat spreads to depth (equation (3)):

$$h = 2 \cdot \sqrt{a \cdot \tau} = 2.2 \text{ (um)}$$

where $a$ is the thermal diffusivity of copper ($1.2 \cdot 10^4$ m²/s [15]), $\tau = 10$ ns.
Figure 2. SEM microphotograph of irradiation spot on the surface of a Cu-Zr alloy (E ~ 0.3 J/cm$^2$, 25 pulses).

Since there was a rapid heating of the local irradiated volume in the cold matrix, its thermal expansion should occur mainly in the direction of the free surface. In this case, the magnitude of the rise $\Delta h$ is (equation (4)):

$$\Delta h = K_{LE} \cdot h \cdot (T - T_{in}) \approx 40 \text{ nm}$$ (4)

where $K_{LE}$ is the coefficient of thermal expansion (for copper $\sim 17 \times 10^{-6} \text{ K}^{-1}$), $T_{in}$ is room temperature (300 K).

In this work we succeeded in fixing the traces of the surface lifting at the energy density exceeding 0.2-0.3 J/cm$^2$. It is possible, that such effect could also be observed at slightly lower energies, if the initial surface roughness would be less. The lifting effect was observed up to the value of E ~ 1 J/cm$^2$, at which optical damage and crater occurred. Figure 3 shows a typical result of exposure to 25 laser pulses of superthreshold intensity of E ~ 1.75 J/cm$^2$. It can be seen that, because of exposure, a classical laser crater having a depth of almost 2000 nm with a height of the surrounding barrier of deposited material nearly 1000 nm was formed. It is clear that against the background of such damages, a possible lifting will be invisible. The process of laser cratering in metals and semiconductors has been thoroughly investigated quite a long time ago [19] and, although it was recently studied in papers [20,21], this phenomenon is not a priority topic of our research.

Figure 3. Cu-Zr alloy surface after exposure to 25 laser pulses with E ~ 1.75 J/cm$^2$ ($\lambda = 355$ nm, $\tau = 10$ ns, $f = 10$ Hz): (a) microphotograph by optical microscope; (b) surface profile by optical profilometer.
Figure 4 shows a SEM microphotograph of the laser crater after exposure to 25 pulses with \( E \sim 15 \text{ J/cm}^2 \), and Table 1 shows data from a study of the elemental composition in different parts of the spot. Inside the crater, you can see rounded veriform grooves and canals with a width of 1 to 5 \( \mu \text{m} \) and various lengths. Moreover, in the center of the spot, they have a concentric radial character, and closer to the periphery the location of such structures becomes circular. Also, on SEM microphotograph spot regions were noted, in which the elemental composition averaged over the area of the region was recorded.

Unfortunately, the data on the elemental composition are qualitatively illustrative, since the initial zirconium concentration was only 0.5%, and the error in measuring the elemental composition of the alloy in the JSM 6610LV SEM used by us was 0.5%.

The composition of the material (Table 1) was studied in three zones: 1) outside the main damage zone (on SEM microphotograph traces of condensed material from vaporations of the crater are observed on the surface); 2) the barrier region; 3) the central zone of the crater. One can see that the elemental composition of the material in the exposure zone has changed. The concentration of zirconium in the alloy in crater zone is significantly decreased. In the barrier zone of the crater the zirconium was completely absent, since the barrier is formed by material ejected from the crater and mainly formed from liquid and gaseous phases. Oxygen appeared, moreover, it was not observed in the central zone of the spot, but was concentrated in the barrier zone from the deposited material.

![Figure 4](image.jpg)

**Figure 4.** SEM microphotograph of the crater after exposure of 25 laser pulses on the surface of the Cu-Zr alloy (\( \lambda = 355 \text{ nm}, \tau = 10 \text{ ns}, E \sim 15 \text{ J/cm}^2, f = 10 \text{ Hz} \)).

**Table 1.** Elemental composition in different parts of the spot.

| Spectrum region | O (oxygen) | Cu (copper) | Zr (zirconium) |
|-----------------|------------|-------------|----------------|
| Zone 1          | 0.6        | 99.1        | 0.2            |
| Zone 2          | 2.0        | 97.9        |                |
| Zone 3          | -          | 99.9        | 0.1            |

Note. In the results of spectral analysis, carbon in some amounts is present. In SEM it is known the problem of the formation of ‘soot’ on the surface of investigated object, as a result of the impact of the electron probe [22]. ‘Soot’ is formed due to the decomposition of hydrocarbons, which are inevitably present in the microscope chamber. The growth of ‘soot’ is mainly due to the action of secondary electrons. It increases with increasing dose of primary exposure. Even after a short exposure (a single accumulation of the x-ray spectrum at a point) when analyzing the composition, carbon appears in samples that do not contain it, which leads to errors in determining the elements in the object under study. In this case, since the presence of carbon in the alloy is not assumed, the data of spectral analysis were corrected.
4. Conclusion

Thus, it was found that the pre-ablation microscopic effects in the Cu-Zr alloy, arising as a result of the action of a nanosecond UV laser pulses with energy densities of $E \sim 0.2 - 1$ J/cm$^2$ most likely have a predominantly thermal nature. The surface profile of the sample in the irradiated zone corresponds to the distribution of the energy in the laser beam. Significant distortions occurred in the crystal structure of the surface layer, and an irreversible configuration of the metal surface was created.

At $E \geq 1$ J/cm$^2$ an optical damage with the formation of a plasma torch was observed. The resulting surface erosion prevented the registration of the effect of surface lifting. Microanalysis showed that the concentration of zirconium in the surface layer after exposure decreased.

It is assumed that the use of surface treatment of the bronze Cu-Zr alloy by the frequency-pulse radiation of a nanosecond UV laser at energy densities $E \sim 0.7-1$ J/cm$^2$ will facilitate its use in diffusion welding.

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