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05

Prethreshold effects, when copper and its alloys were impacted to ultraviolet laser pulses

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The prethreshold processes on the surface of copper and its alloys are investigated. In the absence of obvious traces of melting, while preserving the metal in a condensed state, under a nanosecond ultraviolet laser radiation energy density of $0.1-1.0\,J/sm^2$, manifestations of high-temperature plastic deformation were observed. These are sliding and cracking along grain boundaries, within which crystallographic slipping was observed. A microprotrusion was formed on the surface of the irradiated zone, which was outwardly similar the distribution of laser radiation in the spot. The height of the microprotrusion reached $1\,\mu m$, and sometimes even more. An increase in the number of impacting impulses led to the accumulation of damage. The data obtained are in many ways similar to the acoustoplastic, electroplastic, and magnetoplastic effects. By analogy, we consider it possible to call the discovered effect optoplastic.

Keywords: plastic deformation, optoplastic effect, crystallographic slip, laser.

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Introduction

Soon after the creation of lasers, an optical damage effect was found and studied in detail in tens of thousands of publications [1]. This effect was found to have much in common with the electric breakdown. An optical damage results in a plasma plume in the air near the surface and a crater on the material surface. This phenomenon in metals has been studied thoroughly, suffice it to read the classical monograph [2]. However, the prevailing opinion is that this is a threshold effect occurring stepwise when a certain value of laser radiation power (energy) is exceeded. This is a vivid phenomenon that outmatches the less evident processes in solid bodies that accompany or precede a damage.

Nevertheless, though these phenomena were sometimes observed in condensed bodies they passed almost unnoticed, due to a lack of proper theoretical understanding, e.g., [3–6]. These are disparate results obtained on laser units having different wavelengths, pulse duration, spot size, energy density, therefore, they are incomparable. Prethreshold processes are significantly smaller in scale than the optical damage, probably that's why they were virtually neglected.

It is very interesting to read the theoretical studies by F.Kh. Mirzade, dealing with „nonlinear deformation waves interacting with laser-induced carriers of local disorder", summarized in Chapter 7 monograph [7]. Unfortunately, in our opinion, these works have not yet been sufficiently confirmed by experiments.

This paper summarizes the results of our study of the metal surface under the impact of pulses of a nanosecond repetitively-pulsed UV laser. Experiments were carried out on polished specimens of copper and its alloys. Main attention was paid to the prethreshold impact period. Some fragments of this study have been published in brief reports [8–10].

1. Studied materials and experimental technique

The specimens were polished disks made of oxygen-free copper (MOB) and its bronze Cu−Cr, Cu−Zr and Cu−Cr−Zr low alloys, as well as brass containing, in addition to copper, approximately 36% of zinc and a small amount of lead (maximum 0.3%). Lead does not dissolve in brass and has the form of disordered inclusions of micron and submicron dimensions, and is used to improve alloy machinability [11]. The bronzes contained maximum 0.5% of alloying additives. This little affected their optical and thermophysical properties, but considerably enhanced their mechanical properties [11].

The specimens were preliminarily polished using the standard optical technology [12]. Then, before and after the laser impact, the specimens were studied on the Zygo New View 7300 optical profiler and the JEOL JSM 6610LV scanning electron microscope (SEM). The initial roughness on a surface area, comparable to a laser spot (sized $100-200\,\mu m$), was approximately $15-20\,nm$.

Given the fact that absorption of most metals increases considerably with a decrease in the radiation wavelength, we chose a pulsed-periodic Nd:YaG-laser Opolette HR 2731 (OPOTEC Inc., USA) for the impact, third harmonic, wavelength $\lambda = 355\,nm$, pulse energy up to 8 mJ at duration $\tau = 10$ ns, repetition rate f up to 100 Hz, laser beam diameter — 3 mm, divergence — $1-2$ mrad.

At $\lambda = 355$ nm, copper and bronze low alloys reflect about 10% of radiation, while at $\lambda = 1.06\,\mu$m — more than 95% [8]. Thus, when wavelength decreases, a decrease in laser efficiency due to the use of a nonlinear-optical converter is compensated by a rise in the absorbed radiation dose.

The beam was focused onto the specimen by a quartz glass lens with the focal distance of 250 mm into a spot sized $100-200\,\mu$m. Radiation energy was recorded using the Nova II meter (Ophir Optronics Solutions Ltd., Israel) with a pyroelectric sensor. Quantity of pulses reaching the specimen was adjusted by means of an electromechanical gate. In most experiments, a specimen was exposed to 30 radiation pulses. For averaging, the readings of Nova II were divided by the number of pulses. The experimental technique and unit description are given in detail in [8–10].

The repetition rate of $f = 10$ Hz was used in the described experiments. The specimen surface completely cooled down within the inter-pulse time [8–10].

2. Experimental results

The threshold of laser crater formation, which in this case coincides with the optical damage threshold, has occurred on specimens of copper and its alloys at energy density $W \approx 1.0\,\mathrm{J/cm^2}$. The used devices, however, made it possible to observe the radiation impact results already at $W \sim 0.1\,\mathrm{J/cm^2}$. These are traces of a high-temperature plastic deformation: sliding along grain boundaries which turns into cracking as the number of absorbed pulses increases. Crystallographic slipping was observed inside many grains.

However, the most vivid manifestation is swelling, seen very well on a polished surface (see the figure). The shape and dimensions of the formed protrusion qualitatively match the radiation distribution in the spot. An increase in the number of impacting impulses led to the accumulation of damage. The height of the formed microprotrusion reached $1\,\mu$m, and sometimes even more. Microprotrusions are stable formations. We analyzed the profilogram of the microprotrusions on the copper specimen measured on the day of the impact and after 6 months of specimen storage in a laboratory room. They turned out to be identical.

Figure a shows a microphotograph of the copper specimen surface after the impact of a single laser pulse with the energy density of $W \sim 0.82\,\mathrm{J/cm^2}$. A microprotrusion of height $\sim 0.1\,\mu$m can be seen well. Small scratches in the microprotrusion zone usually healed. After the impact of three pulses (see Figure *b*), the grain boundaries appeared in some places, and they became more distinct after five pulses (see Figure *c*). After the impact of 30 pulses (see Figures *d, e*), surface degradation of the irradiated microprotrusion became much more noticeable, there were traces of crystallographic slipping in the grains, height of some microprotrusion areas was close to $1\,\mu$m. Boundaries between grains became more distinct. Sometimes the grains began diverging so much that material continuity was disrupted in the boundary region.

Similar phenomena were also observed in the bronze and brass specimens irradiated according to the same procedure.

3. Discussion of results

Since the average laser power was insignificant (below 1 W), this impact virtually did not affect the properties of the specimen volume. However, intensive heat treatment by the pulsed component of radiation caused noticeable changes in the specimen's near-surface layers.

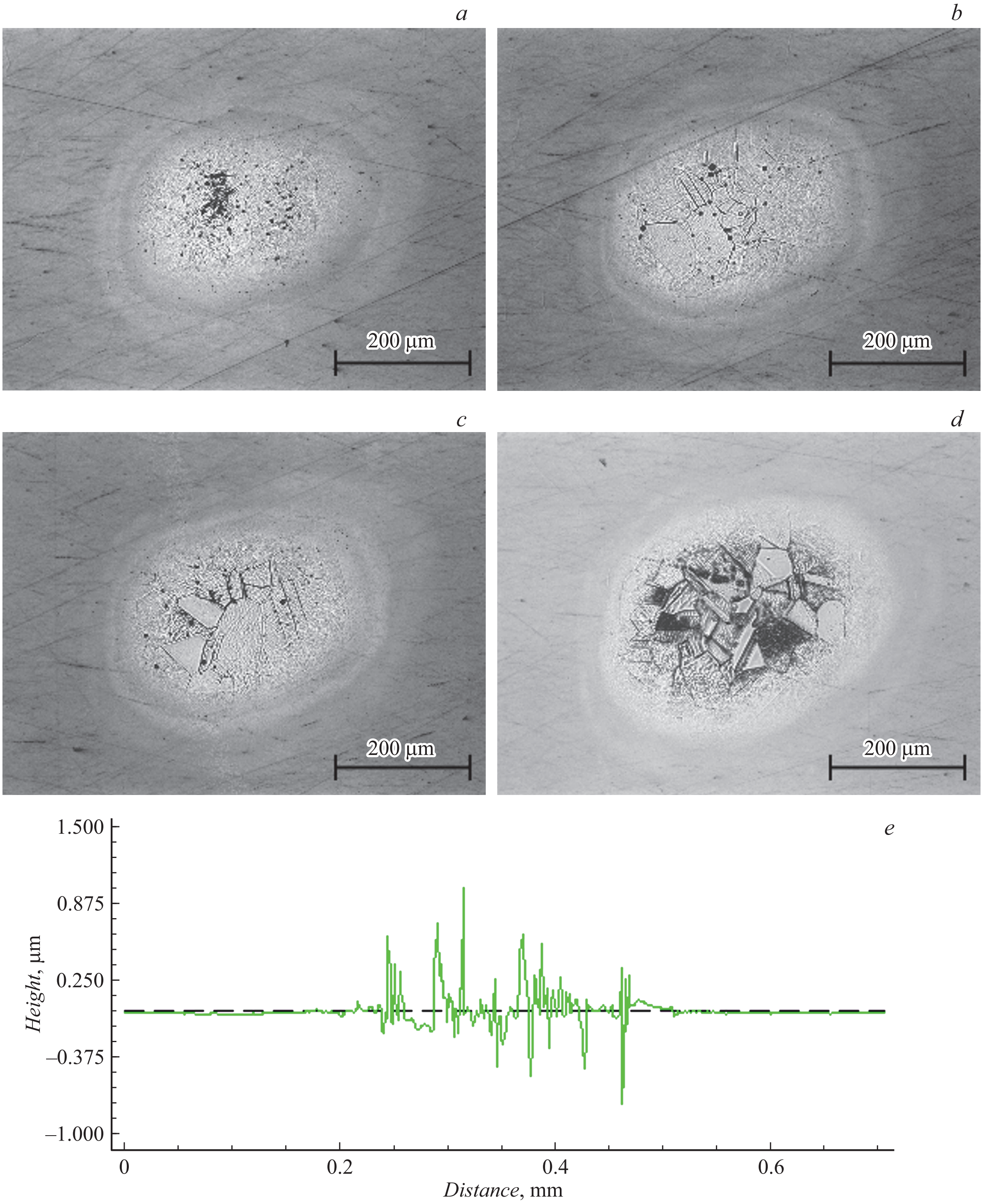
An interesting solution applied in the laser marking of metals is the exposure of a metal surface to focused nanosecond radiation [13]. In this work marking by laser spots with pronounced crater formation. In our case, the condition of maintaining the metal in the condensed state was strictly observed.

Light is initially absorbed by metals due to transfer of photon energy to the electron component of the skin layer ~ 15 nm [14]. Naturally, in our case this causes a considerable overheat of the electron subsystem. Relaxation of this process occurs with a time of approximately $2-3$ ps. Electrons transfer the excess energy to the phonon subsystem. Thus, the metal near-surface layer is heated within the laser pulses action time of 10 ns. This layer fully cools down within ~ 20 ns. Moreover, thermal expansion of the spot zone takes placed under abrupt heating of the metal surface layer.

Such an abrupt thermomechanical impact leads to a significant increase of the concentration of point defects which are caused by the dislodging of a part of metal ions into the interstice by an electron flow and do not manage to return to the lattice due to fact cooldown. The so-called Fraenkel pair is formed (vacancy + interstitial atom). This phenomenon is well-known in radiation physics (see, for instance, monographs [15,16]) and has an established term — irradiation-induced swelling of metals. In our opinion, the formation of a microprotrusion on the metal surface after laser pulses impact can be similar in nature. However, differences also exist.

In radiation physics, a metal is usually exposed to rather a long radiation impact. Interstitial atoms, as significantly more mobile defects, are absorbed by dislocation, grain boundaries etc. Vacancies, due to diffusion interaction, coagulate with the formation of micropores. While the micropores in our case do not manage to originate due to the short time of the process, and point defects are fixed in the crystalline structure near the place of origination.

Nevertheless, the impact of powerful femtosecond radiation on the metal has enabled the formation of micropores in the subsurface layer, but, to do so, the material surface had to be melted [17]. In this case the vapor bubbles „froze" in the extremely rapidly congealing melt.



Impact traces of the laser pulses with $W \sim 0.82\,\mathrm{J/cm^2}$ on the surface of the copper specimen ($\lambda = 355\,\mathrm{nm}$, $\tau = 10\,\mathrm{ns}$, $f = 10\,\mathrm{Hz}$); *a* — one pulse, *b* — 3 pulses, *c* — 5 pulses, *d* — 30 pulses, *e* — profilogram of the specimen shown in Figure *d*.

The analysis of the microphotographs in the figure and the simple estimates made in [8] using formula (1) have demonstrated the achievement of the pre-melting temperature in a thin near-surface layer of copper due to heating by a laser pulse at $W \sim 0.6{-}1.0\,\mathrm{J/cm^2}$.

The threshold density of melting energy, taking into account the specific heat of melting, is [18]:

$$W_m(\tau) = \delta(\tau)\rho[C(T_m - T_{\mathrm{in}}) + L_m], \qquad (1)$$

where $\delta(\tau)$ is effective thickness of the metal layer where the energy of a laser pulse of duration τ is absorbed. Density, specific heat capacity, melting temperature, initial temperature and latent heat of melting of the material are denoted with symbols ρ, C, T_m, T_{in}, L_m respectively. During surface heating

$$\delta(\tau) = \sqrt{2\alpha\tau}, \tag{2}$$

where a is thermal diffusivity of the material.

Qualitative assessments have been made for copper based on equations (1) and (2) with the values $C = 385$ J/kg·K, $\rho = 8920$ kg/m^3, $a = 1.2 \cdot 10^{-4}$ m^2/s, $T_m = 1356$ K, $T_{\text{in}} = 293$ K, $L_m = 204.7 \cdot 10^3$ J/kg [11]. The following values have been obtained for $\tau = 10$ ns: $\delta(\tau) = 1.5\,\mu$m, $W_m(\tau) = 0.85$ J/cm^2. The result is almost the same for the copper alloys studied in the present paper.

Thus, the obtained results (see the figure) clearly show that traces of high-temperature plastic deformation were observed in the near-surface layer of specimens made of copper and its alloys due to the impact of nanosecond UV laser pulses.

The fundamental property of plasticity (the capability to deform irreversibly under applied stresses) is used for metal working during rolling, forging, die stamping etc. Therefore, various methods of impact on this phenomenon are rather topical for practical applications.

Various high-power pulsed devices have enabled experimental studies of pulse impacts on the process of plastic deformation in metals [18–22]. The acoustoplastic effect was found [18]. Irradiation with intensive ultrasonic oscillations selectively acts on structural defects of the crystalline lattice (point, linear defects, grain boundaries, emissions of various phases etc.). This results in movement and redistribution of these defects, thus noticeably facilitating the plastic deformation process.

Further development of this phenomenon was the discovery of the electroplastic and magnetoplastic effects [19–22]. It has been found that the impact of pulsed electric and magnetic field, which excites the electron subsystem and quickly transfers the energy to the phonon subsystem, also generates a large number of short-wavelength phonons. They, in their turn, due to microprocesses eventually accelerate the macroprocess of plastic deformation.

Nowadays more than ten different electric, magnetic and electronic phenomena, which directly affect the processes of plastic deformation, are known.

The reverse phenomenon also exists [23]. The photoplastic effect was discovered in 1968: non-equilibrium defects originate in a semiconductor when exposed to light. They are caused by a redistribution of electric charges in the bulk, [1] and lead to a decrease in the speed of dislocation drift and crystal compaction.

Papers [8–10] report an experimental detection of traces of high-temperature plastic deformation in the near-surface layer of copper and its allows, caused by the impact of nanosecond UV laser pulses. In the present paper we complement and summarize the obtained results and make a conclusion on observation of processes which are directly similar to acoustoelastic, electroplastic, magnetoplastic and other effects. Therefore, by analogy, the discovered effect of prethreshold damage of a metal caused by laser pulses can be rightfully called optoplastic.

The optoplastic effect, despite the evident similarly to the above-mentioned phenomena, has its own peculiarities, namely, it manifests itself, first of all, in the near-surface layer of the metal. It is not improbable, however, that a thermomechanical wave caused by a laser impact can affect the metal's bulk properties when propagating deep into the specimen (see, for instance, [5]). In this case there can be resonance phenomena caused by selective absorption of the wave energy on different defects in the metal structure, such as inclusion of the second phase, dislocations, grain boundaries etc. These processes are a manifestation of internal friction in the metal [24].

Conclusion

Traces of high-temperature plastic deformation have been found during the study of prethreshold processes on the surface of copper and its alloys (in the absence of evident melting traces); radiation energy density of the nanosecond UV laser was $0.1-1.0$ J/cm^2. A microprotrusion forms on the metal surface in the irradiated zone; outwardly it resembles the distribution of laser radiation in a spot. An increase in the number of impacting pulses and energy density led to the accumulation of damage. Height of the formed microprotrusion can reach $1\,\mu$m, and sometimes slightly more. This formation is stable. After 6 months of the storage at the laboratory room temperature, no changes on the measured profilogram have been found on the copper specimen. Sliding and cracking along the grain boundaries, inside which traces of crystallographic slipping occurred, have been observed in the microprotrusion.

The obtained results are similar to the acoustoplastic, electroplastic, and magnetoplastic effects. By analogy, we consider it possible to call the discovered effect optoplastic.

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Conflict of interest

The authors declare that they have no conflict of interest.

[1] This scientific discovery is listed in the State Register of Discoveries of the USSR under № 93.

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