CHANGES IN THE CRYSTAL STRUCTURE
OF METALS UNDER LASER RADIATION

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The change in the crystal structure of a number of metals (Cu, Al, Ag) under laser radiation of power density 10^4–10^5 W/cm^2 was detected by the method of x-ray diffractometry. It was suggested that this effect is due to the large microstresses arising in the zone of rapid anisotropic heating of the metal under irradiation.

An efficient method of hardening of metals is the treatment of them by an impulse laser radiation of definite duration and power. Under this radiation, clearly defined changes arise in certain physical properties of the metals [1–3]. For example, the hardness of many metals increases by 10–30% as a result of the exposure of them to laser radiation. In this case, neither the composition of these metals changes nor pronounced first-kind phase transitions happen in them, even though thin oxide and nitride films can appear on their surface under irradiation in air (especially in the case where each region of the metal surface is irradiated for ~1 msec); these films have such a small thickness that they cannot substantially change the hardness of the metals. In the bulk of a metal exposed to laser radiation, the composition does not change and phase transitions do not happen; however, the concentration of point and linear defects can be increased. A change in the defect structure of the metal can decrease the degree of its atomic ordering, i.e., can cause a distortion of its crystal structure. This changes can be explained by the structural transformations of the metal under laser radiation.

Since laser radiation possesses not only a power, but also a complex space-time structure and a spectral structure that can also be complex in a number of cases, its action on an object can give rise to not only heat (energy) effects but also various selective physical and physicochemical processes [4]. This makes it possible to control certain processes arising in solid bodies under laser radiation by selection of the laser-radiation parameters in the required way and changing them purposefully. One of the most important of these processes is the transformation of the crystal structure of a metal under laser radiation and after the termination of irradiation. The interest shown in this phenomenon is explained by the fact that the mechanical, electrical, magnetic, and optical properties of solid bodies are substantially dependent on their microstructure.

To date, the structural-phase transformations of steels and ferriferous alloys under laser radiation have been extensively investigated by many authors [5–9]; however, these transformations of "pure" (monatomic) metals are as yet imperfectly understood.

Because of this, the aim of the present work is to investigate the structural transformations of certain metals (Cu, Al, Ag) under laser radiation of power density 10^4–10^5 W/cm^2, the relaxation of these metals with time after the termination of irradiation, and the physical processes arising in this case.

Experimental Setup and Experimental Results. As an exciting-radiation source, we used a GOR-100M laser (with a wavelength of 0.69 μm) operating in the free oscillation regime and generating pulses of duration ~1.2 μsec with an energy varying within the range 5–50 J. The laser beam was focused to a relatively homogeneous spot with clearly defined boundaries on a sample with the use of a diaphragm and a focusing system. The diameter of the irradiation zone was varied from 2 to 5 mm; in this case, the laser-radiation power density q was charged from 10^4 to 10^6 W/cm^2. A portion of laser radiation (~5%) was directed by the front face of a glass wedge to an IMO-2N energy meter with an entrance pupil located in the focal plane of a lens. The radiation reflected by the back face of the
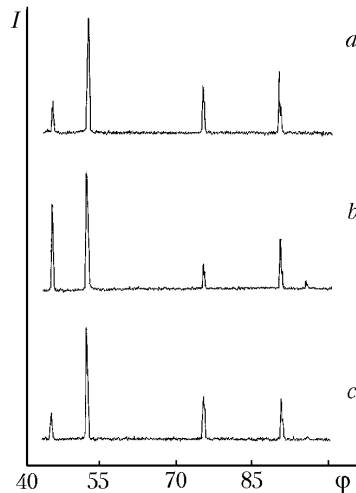
Fig. 1. X-ray diffractograms of copper samples: a) before irradiation; b) after the exposure to laser radiation with $q \sim 5 \cdot 10^4$ W/cm^2; c) within 30 days after the exposure to laser radiation with $q \sim 5 \cdot 10^4$ W/cm^2. I, rel. units; φ, deg.

wedge was directed to a coaxial FÉK-14 photocell, the signal from which was fed to the input of an S8-13 oscilloscope and was used for recording of the time shape of a laser pulse.

The structural changes in solid polycrystalline metal samples, having a face-centered cubic lattice in the equilibrium state, were detected before and after the exposure of them to laser radiation with the use of an x-ray DRON-2.0 diffractometer. The K_α-line radiation of a tube with a copper anticathode, filtered by a nickel standard filter at a wavelength of 154.050 pm, was used in the diffractometer. Figure 1 presents x-ray diffractograms of a copper sample before (a) and after (b) the exposure of it to laser radiation of power density $q \sim 5 \cdot 10^4$ W/cm^2. In Fig. 1c, the diffractograms of this sample, made within 30 days after its irradiation, are shown. It is seen that the diffractograms presented in Fig. 1a and b are very different, and the difference the between the diffractograms presented in Fig. 1a and c is not so large. Similar results were obtained for Al and Ag samples exposed to laser radiation with q varying from 10^4 to 10^5 W/cm^2; in this case, melting or destruction of the metal zones irradiated were not detected visually. Since the differences obtained are explicitly beyond the experimental error, they, in our opinion, deserve consideration.

Processing and Discussion of Results. As is known, structural defects existing in crystals cause deformations of their unit cells. If, in an ideal cubic crystal, the distribution of the a-parameter (cube-edge length) of a cell is determined by the delta function, in real (defect) crystals the statistical distribution $P(a)$ is described by a function with a nonzero dispersion. The change in the position of refections in an x-ray diffraction pattern, caused by the shift of the reciprocal-lattice sites from their ideal positions, can be illustrated with the following model.

Let us consider a crystal with a fairly perfect cleavage, in which the layers of thickness d_i (i = 1, 2, ..., N) alternate in a random manner. Such a structure is called the mixed-lattice structure; it is characteristic, e.g., of certain agrillaceous minerals [10]. As an example, we will consider a crystal with layers of two types (n = 2), namely, a hydrated mica containing nonhydrated layers of thickness d_1 and hydrated layers of thickness d_2. The indicated layers will be considered as scattering objects. It is common practice to bring the perfect-cleavage planes of a crystal into coincidence with the xy plane of the crystallographic coordinate system. Consequently, these reflections have crystallographic indices 001. Let us assume that their scattering abilities satisfy the condition

$$F_1(001) = F_2(001) = F(001).$$

(1)

In a perfect layered crystal (n = 1), the layers of thickness d (001) form integral series. However, this condition is not fulfilled as a rule. The intensity of x-ray reflections is defined, with an accuracy to the multipliers PLG and K, by the structural factor

$$I(S) \sim \left| F \right|^2 = F \cdot F^*. \tag{2}$$

In the case being considered, the layers differ insignificantly in their scattering power; therefore, it may be assumed that $F_1 = F_2$. In this case, the intensity $I(S)$ is equal to the real part of the expression

$$I_c(S) = \left| F \right|^2 \sum_\alpha \sum_\beta W_{\alpha\beta} \exp 2\pi i S (\alpha d_1 + \beta d_2), \tag{3}$$

where $S = 2 \sin 2\theta / \lambda$ and $W_{\alpha\beta}$ is the probability that the radiation will reach the layer of thickness $\alpha d_1 + \beta d_2$. If the concentration of the layers with a thickness d_1 is equal to P, the concentration of the layers with a thickness d_2 is equal to $(1 - P)$. In this case,

$$W_{\alpha\beta} = C_{\alpha+\beta}^\alpha P^\alpha (1 - P)^\beta = C_{\alpha+\beta}^\beta P^\alpha (1 - P)^\beta. \tag{4}$$

Let $P \exp 2\pi i d_1 S = A$, $(1 - P) \exp 2\pi i d_2 S = B$, and $\alpha + \beta = n$; in this case, the condition (3) will take the form

$$I_c(S) = \left| F \right|^2 \sum_n \sum_\alpha C_n^\alpha A^\alpha B^{n-\alpha}. \tag{5}$$

This expression is the expansion of the binomial theorem; consequently,

$$I_c(S) = \left| F \right|^2 \sum_n (A + B)^n = \left| F \right|^2 \sum_n [P \exp 2\pi i d_1 S + (1 - P) \exp 2\pi i d_2 S]^n. \tag{6}$$

The real side of this expression, which is of interest for us, has the form

$$I(S) = \left| F \right|^2 \sum_n [P \cos 2\pi S d_1 + (1 - P) \cos 2\pi S d_2]^n.$$

The extremum value of $I(S)$ is determined on the condition that

$$\frac{dI}{dS} = -2\pi \left| F \right|^2 \sum_n n [P \cos 2\pi S d_1 + (1 - P) \cos 2\pi S d_2]^{n-1} \times$$

$$\times [d_1 P \sin 2\pi S d_1 + d_2 (1 - P) \sin 2\pi S d_2] = 0,$$

and this equation is solved on the condition that

$$\cos 2\pi S d_1 = -\frac{(1 - P)}{P} \cos 2\pi S d_2 \quad \text{or} \quad \sin 2\pi S d_1 = -\frac{(1 - P) d_2}{P d_1} \sin 2\pi S d_2. \tag{7}$$

In the case being considered, the concentration of the nonhydrated layers P substantially exceeds the concentration of the hydrated layers, i.e., $1 - P \ll P$. In this case, the points of intersection of the functions (and, consequently, the solution of Eq. (7))

$$y_1 = \sin 2\pi S d_1, \quad y_2 = \frac{(1 - P)}{P} \frac{d_2}{d_1} \sin 2\pi S d_2 \tag{8}$$

or

TABLE 1. Parameters of Metals Calculated by the X-Ray Diffraction Patterns Obtained before (Numerator) and after (Denominator) Exposure to Laser Radiation with $q \sim 5 \cdot 10^4$ W/cm^2

Metal	$\bar{a}$	a_{min}	a_{max}	Δa	σ
Al	$\dfrac{4.041}{4.038}$	$\dfrac{4.036}{4.020}$	$\dfrac{4.046}{4.059}$	$\dfrac{0.010}{0.039}$	$\dfrac{0.004}{0.037}$
Cu	$\dfrac{3.597}{3.600}$	$\dfrac{3.589}{3.587}$	$\dfrac{3.605}{3.625}$	$\dfrac{0.016}{0.038}$	$\dfrac{0.006}{0.026}$
Ag	$\dfrac{4.086}{4.087}$	$\dfrac{4.082}{4.072}$	$\dfrac{4.090}{4.105}$	$\dfrac{0.008}{0.033}$	$\dfrac{0.003}{0.010}$

$$z_1 = \cos 2\pi d_1 , \quad z_2 = \frac{(1-P)}{P} \cos 2\pi S d_2 \tag{9}$$

are positioned near $\dfrac{m}{2d_1}$ or $\dfrac{m+1/2}{2d_1}$, where m is an integer; however, they do not coincide exactly with $\dfrac{m}{2d_1}$.

Thus, the interplanar distances obtained experimentally for the mixed-lattice structures do not form an integer-valued series:

$$\frac{1}{d\,(001)} : \frac{1}{d\,(002)} : ... : \frac{1}{d\,(00l)} \neq 1 : 2 : ...$$

and the higher the degree of the structure imperfection, the larger the deviation of the indicated inequality from an equality. Consequently, the degree of the structure imperfection can be estimated by the distribution of the quantity $d(00l) \cdot l$. In this case, because of the small concentration of the layers of thickness d_2, the experimental values of $d(00l)$ will fluctuate about the ideal values of $d_i(00l)$ determining the integer-valued series of the ratios between the reciprocal interplane distances.

The influence of the three-dimensional disordering on the positions of the reciprocal-lattice sites can be investigated analogously on the assumption that an individual crystal-lattice cell is a scattering center. In this case, as in formula (2), the intensity of a reflection, determined accurately to a constant multiplier, will take the form

$$I_c\,(\mathbf{S}) = \sum_j \sum_k A_{jk} F_j F_k^* \exp 2\pi i \mathbf{S} \mathbf{r}_{ik} . \tag{10}$$

Consequently, analysis of the structure of a crystal by the distribution of the crystal-lattice cell parameters, determined by different reflections, i.e., having different values of $\mathbf{S}$, with the use of the method of x-ray diffractometry, allows one to obtain a qualitative criterion for estimation of the degree of deviation of the crystal structure from the ideal one [11].

Table 1 presents the results of processing of the x-ray diffractograms of polycrystal samples of Al, Cu, and Ag before and after the exposure of them to laser radiation. It is seen from the table that, after the irradiation of these samples, the deviations of the reciprocal-lattice sites from their ideal positions increase reliably, even though the average values of the parameters remain practically unchanged.

To investigate the structural transformations being considered in more detail, it is necessary to determine not only the positions of x-ray reflections, but also their intensities; for this purpose, we will use the method proposed in [11, 12]. The essence of this method is that the Paterson function P(**u**) is calculated, i.e., the self-convolution of the relative electron-density function is performed [13]:

$$P\,(\mathbf{u}) = \frac{1}{V} \int \rho\,(\mathbf{r})\,\rho\,(\mathbf{r}-\mathbf{u})\,d\mathbf{r} . \tag{11}$$
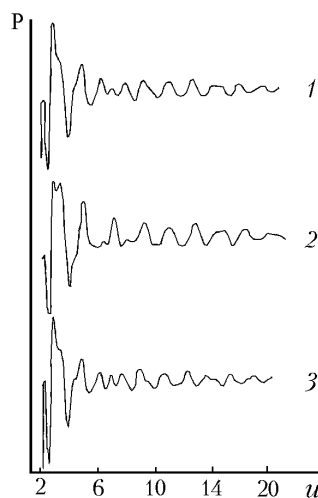
Fig. 2. Correlation functions P(u) of copper samples: 1) before irradiation; 2) after the exposure to laser radiation with $q \sim 5 \cdot 10^4$ W/cm^2; 3) within 30 days after the exposure to laser radiation with $q \sim 5 \cdot 10^4$ W/cm^2. P, rel. units; u, Å.

It is apparent that

$$P(\mathbf{u}) = \int F^2(\mathbf{S}) \cos 2\pi \mathbf{S} \mathbf{u} \, d\mathbf{S} . \tag{12}$$

In the case where the polycrystal x-ray diffractometry is used, the function P(u) should be averaged over the sphere of radius S in the reciprocal space. In this case,

$$\langle P(\mathbf{u}) \rangle = \int_S F^2(\mathbf{S}) \frac{\sin 2\pi \mathbf{S} \mathbf{u}}{2\pi \mathbf{S} \mathbf{u}} \, d\mathbf{S} . \tag{13}$$

This formula was used for calculating the correlation components of the atom-density radial distribution functions [13]. These functions for copper crystals are presented in Fig. 2. It is seen that the first three maxima for an unirradiated crystal correspond to the theoretical maxima for the interatomic vectors (a = 3.62 Å for copper), even though their heights (areas) differ from the theoretical ones. The smearing of the maxima is explained by the fact that polycrystals and not single crystals were considered, which leads to a larger spread in the values of the parameter u as compared to its ideal values.

For the Cu samples irradiated, we obtained not only fuzzy distributions, but also split ones. Analogous results were obtained for Al and Ag. It was established that the face-centered cubic lattice of the irradiated zone of these metals is distorted, i.e., a unit cell takes the form of a parallelepiped differing from a cube.

It is our opinion that the mechanism of the above-described transformation is as follows. In the conditions being considered, the time form of a pulse represent a chaotic set of spikes of duration ~1 μsec each (Fig. 3). As the calculations, similar to the calculations done in [14], show, each of these spikes, acting for ~1 μsec, causes an increase in the temperature of the laser-radiation focus spot on the surface of a metal sample by several hundreds of kelvins (about 150 K for copper). Since the main mass of the sample is not heated, the zone irradiated is expanded mainly in the direction of the laser beam. The zone heated is cooled also fairly rapidly [14] (~1 μsec for copper), i.e., before the next laser-radiation spike begins to act on the sample. For this time, the distorted form of the deformation zone has not managed to restore, i.e., the form of the zone irradiated is "frozen". This effect can be enhanced by the internal stress arising in the zone irradiated in the process of formation of acoustic waves in the sample [15, 16].

The above-described processes, along with the local heating, can result in the cubic cells of a crystal with a point group $m3m$ [17] being distorted; in this case, the sizes of the cells in the zone exposed to laser radiation increase to a larger degree in the direction perpendicular to the surface of the polycrystal and to a lesser degree in the direction
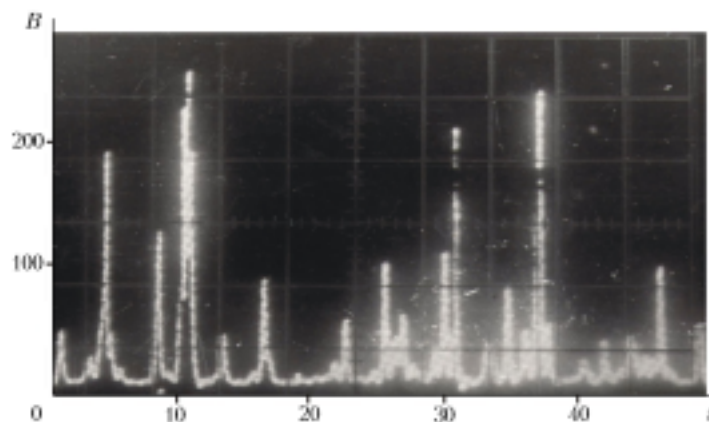
Fig. 3. Form of a laser pulse. The multilayer factor of the ordinate axes is 50 kW. The rate of scan is 5 μsec/div.

parallel to the polycrystal surface. It is known that, only for ideal crystals the cell-parameter value, determined by the quadrature formula, is independent of the crystallographic index of the reflections obtained by the x-ray radiography method [10]. In real crystals (with a defect structure) the fluctuations of the cell parameters $a(hkl)$ can significantly exceed the experimental errors. The mechanical microstresses appearing in a metal sample under laser radiation can also cause changes in the microrelief of its surface (corrugation); this effect was detected in a number of cases with the use of the atomic-force microscopy method.

Since the distorted cubic crystal structure of the metals being considered is not in equilibrium, it relaxes at room temperature (~300 K), i.e., the crystal cells are transformed into the equilibrium face-centered cubic cells, which manifests itself as an approach of the x-ray diffractograms (Fig. 1c) and the correlation functions (Fig. 2) of the samples exposed to laser radiation to the initial ones obtained for these samples before their irradiation.

Our investigations have shown that, in the case where the surface of a number of metals (Cu, Al, Ag) is exposed to laser radiation, the face-centered cubic structure of the irradiation zone is distorted and takes the form of a parallelepiped differing from a cube. This effect can be due to the anisotropy of the heat expansion of these metals. At a temperature of ~300 K, the structure of the metals being investigated relaxes to the initial state within approximately 30 days.

NOTATION

a-parameter, length of the crystal-lattice cube edge, m; $\bar{a}$, $a_{\min}$, $a_{\max}$, medium, smallest, and largest values of the cell parameters determined by the experimental reflections; $\Delta a = a_{\max} - a_{\min}$; A_{jk}, probability of the vector $\mathbf{r}_{jk}$; B, laser-radiation power, kW; C_n^m, number of combinations of natural numbers n with respect to m; d_i, thickness of a crystal layer, m; F, scattering power of crystal layers; F^*, value of the conjugation F; F_j, structural amplitude of the jth cell; $I(S)$, intensity of x-ray reflections; K, multiplier including the absorption, extension, and temperature factors; N, number of different values of the thickness of a crystal layer; P, concentration of crystal layers; PLG, multiplier including the polarization, Lorentz, and geometric factors; P($\mathbf{u}$), Paterson function; q, laser radiation power density, W/cm^2; $\mathbf{r}_{jk}$, vector connecting the centers of the jth and kth cells; $\mathbf{S}$, vector of the reciprocal space, m^{-1}; S, magnitude of the vector $\mathbf{S}$; $\mathbf{u}$, vector connecting two scattering centers with a radius-vectors $\mathbf{r}$ and ($\mathbf{r}-\mathbf{u}$); u, magnitude of the vector $\mathbf{u}$; V, scattering volume, m^3; x, y, space coordinates; α, β, integers with identical signs; λ, wavelength of x-rays, m; σ, roof-mean-square deviation of the a-parameter from the average value; θ, Wulf–Bragg angle, rad; ρ, atoms density; φ, diffraction angle. Subscripts: i, j, n, m, natural numbers; h, k, l, crystallographic indices.

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