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DYNAMICS OF PROCESSES OCCURRING IN LASER ABLATION OF METALS IN A LIQUID

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We present the results of investigations undertaken to establish relationships between certain characteristics of the disintegration of metals in air and liquid under laser radiation and their thermophysical properties, as well as between the basic parameters of a gas cavity formed in a liquid and the energy of the laser-ablation products of metals. Consideration is given to the possibilities of applying the dynamic properties of this cavity to control the time behavior of the radiation of solid-state lasers and to solve spectroanalytical problems.

Key words: *laser radiation, time characteristics, ablation, laser action, gas cavity.*

In recent years the laser technologies that employ the luminous energy of a beam acting on different materials have gained ever-increasing acceptance. In view of this of particular interest is the study of physical processes occurring under the action of laser radiation on metals that are present not only in air, but also in other media transparent to a laser beam, for example, in liquids or in chemically active gaseous media.

In contrast to the majority of works devoted to the study of optical breakdown in a liquid (see, for example, review [1]), in the present work we present the results of investigations concerned with the establishment of relationships between certain characteristics of the disintegration of metals in air and liquid under the action laser radiation and their thermophysical properties, as well as between the basic parameters of the gas cavity formed in the liquid and the energy of the laser-ablation products of metals. We also discuss the possibilities of applying the dynamic properties of this cavity for controlling the time sequences of solid-state lasers and for solving spectroanalytical problems. The experiments were carried out on neodymium glass lasers with an energy E_{gen} of from 0.5 to 1.5 J in radiation pulses τ_{pul} lasting from 150 to 900 μsec, and on ruby lasers (E_{gen} = 1-5 J, τ_{pul} = 500 μsec) operating in a free generation regime. The specimens of metals were placed in a glass cuvette filled with water (of 2.5 × 1.7 × 1.0 cm volume). A polarized lead-ceramic (TsTS-19)-based piezoelectric transducer mounted inside the cuvette ensured the recording of pressure in the water in the direction normal to the laser radiation propagation axis. It was calibrated by means of steel balls of known mass [2].

On exposure of metal in air to laser radiation of moderate power density (10^7-10^8 W/cm^2), the mass m of the erosion products, which were removed from the zone of exposure and determined in our experiments by the volume of the erosion hole, is proportional to the ratio of the absorbed energy to the magnitude of the energy expended in melting a unit mass of the substance (Fig. 1a). The diameter of the hole d, just as in other works [3], is connected in a rather complicated way with the melting temperature T_{mel}, density ρ, thermal conductivity λ, and the heat capacity c of the specimen material (Fig. 1b). The variables F_i used for obtaining the dependences in Fig. 1 are associated with the thermophysical parameters of the materials investigated in the following manner: $F_1 = (1 - R)[c(T_{mel} - T_0) + H_{mel}]^{-1}$, $F_2 = (1 - R)(T_{mel} - T_0)^{-1}(\lambda/\rho c)^{1/2}$, $F_3 = (1 - R)(T_{boil} - T_0)^{-1}(\lambda/\rho c)^{1/2}$, $F_4 = c(T_{boil} - T_0) + H_{mel} + H_{ev}$. Here R is the reflection factor; T_0, T_{boil}, H_{mel}, and H_{ev} are the initial temperature and the boiling point, the latent heat of melting and evaporation of the metal, respectively. The selection of the

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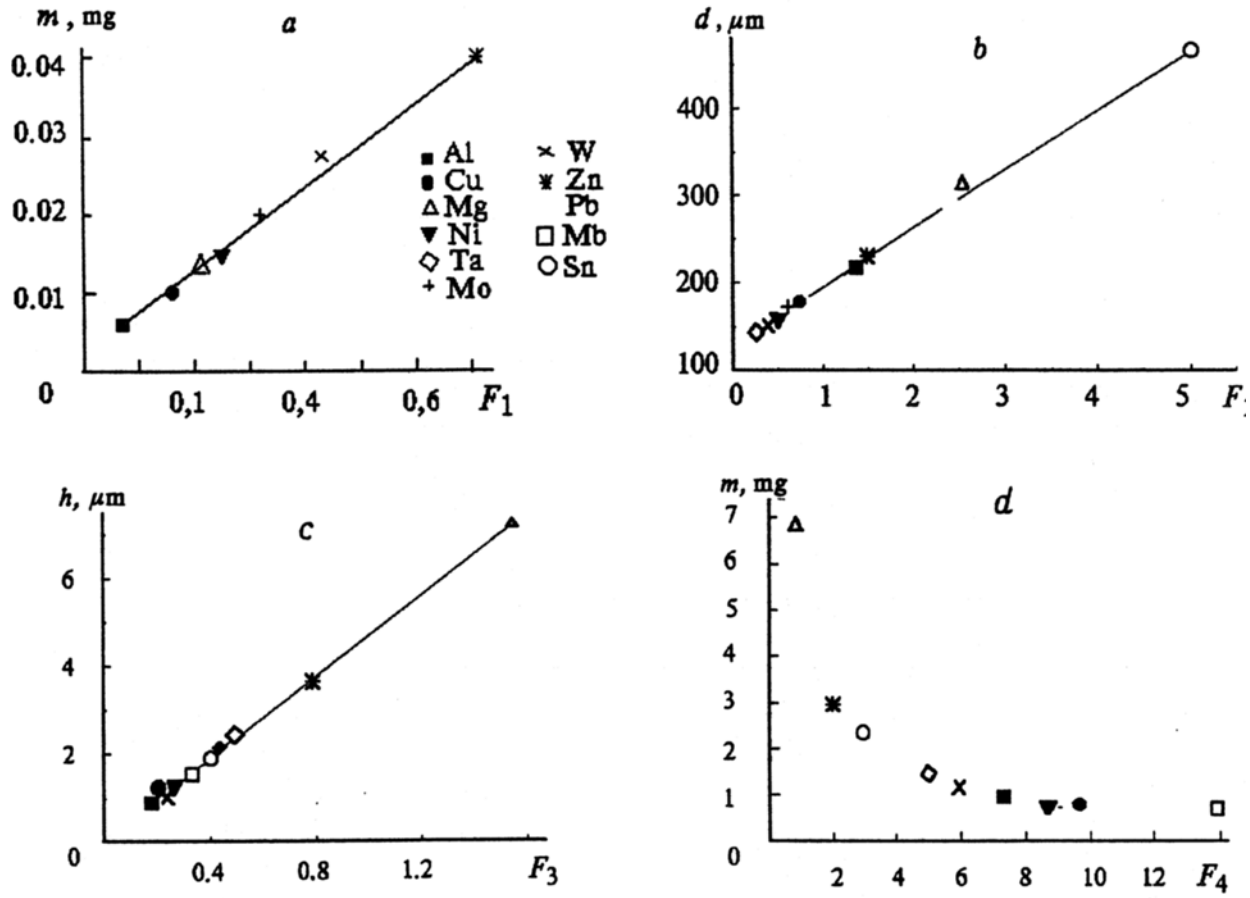

Fig. 1. Dependences of mass of light erosion products (a, d), diameters (b), and depth (c) of disintegration of metals on their thermophysical properties when the metal surface is exposed to laser radiation of power density $1.2 \cdot 10^7$ W/cm^2 in air (a, b) and distilled water (c, d).

arguments $F_1 - F_4$ in Fig. 1 indicates the possibility of obtaining practically suitable linear (Fig. 1a-c) and exponential (Fig. 1d) functional dependences of the parameters of the hole erosion on the properties of metals.

When laser radiation is focused on the surface of a specimen placed in water, it also forms a hole, whose depth h amounts to several microns (Fig. 1c), which is approximately by two orders of magnitude smaller as compared to the case of exposure of the specimen to radiation in air. Here, the mass of the metal erosion products also depends on the constants of evaporation (Fig. 1d). The hole is formed in the metal because heat removal into a specimen exposed to pulsed local heating is much greater than the heat transfer to the surrounding medium, and a portion of the metal is converted into a melted state. Intense evaporation of the substance from the melt surface leads to the formation in the liquid of a gas cavity with an elevated pressure. Due to laser-radiation scattering by the gas cavity, the diameter of the spot of metal damage in the liquid is usually larger (by about 1.5-2.0 times) than in the case of erosion by light in air [4]. The data in Fig. 1 are obtained by averaging over 50 measurements.

When different materials located in water were exposed to laser radiation of power density $1.2 \cdot 10^7$ W/cm^2, we found that $m[c(T_{boil} - T_0) + H_{mel} + H_{ev}] = Qm \cong$ const and was equal to 0.008 J. Consequently, the energy of erosion products in a gas cavity formed in the zone of the surface of different metals subjected to laser irradiation is virtually a constant value. It determines the possibilities for the development of a gas cavity, since it is the potential energy E_{pot} accumulated in expansion of the cavity to a maximum size. It might be expected that under our experimental conditions this size must not be dependent on the properties of the metal exposed to radiation,

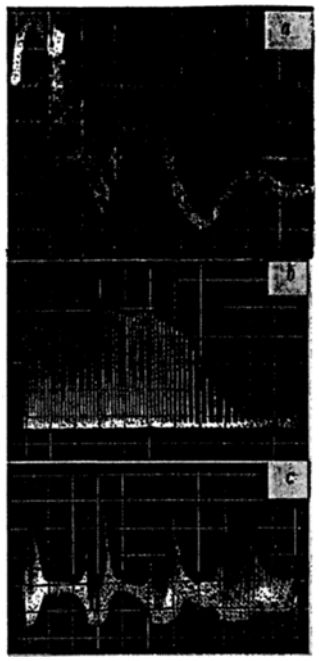

Fig. 2. Oscillograms of pressure (a) developed in distilled water with aluminum surface exposed to neodymium-glass laser radiation of power density $1.2 \cdot 10^7$ W/cm and to ruby laser radiation with Q-switching by erosion products of specimens in air (b) and water (c), (a) 250, b) 50, c) 25 μsec/div).

since the maximum radius of the cavity r is determined by the expression [5]: $r = (3E_{pot} \mid 4\pi P_0)^{1/3}$ (where P_0 is the hydrostatic pressure). From this, at $P_0 = 9.8 \cdot 10^4$ N/m^2 and $E_{pot} = 0.008$ J we obtain $r = 0.27$ cm. From the phototraces of the shadow graphs that show the dynamics of the development of the gas cavity in water and that were obtained by means of an SFR-2 M high-speed photorecorder it follows that in the case of laser irradiation of metals with a power density of $1.2 \cdot 10^7$ W/cm the maximum diameter of the gas cavity is 0.55-0.58 cm, which agrees satisfactorily with the prediction.

The high rate of energy liberation in the zone on the metal surface exposed to laser radiation is accompanied by a considerable local increase in pressure with the formation of a shock wave that propagates in the liquid. The interrelation between the magnitude of the pressure and the pulsation period of the vapor-gas cavity is established from pressure diagrams. These characteristics, in turn, are associated with the maximum size of the gas cavity and with the magnitude of the energy released at the point of laser irradiation (at the point of "explosion"). A pressure pulse forms in the liquid a series of compression waves that correspond both to the moment the gaseous cavity starts to formation and to its subsequent pulsations with a perod of ~ 750 μsec. The first compression wave is characterized by a sudden increase in pressure, whereas the subsequent pulses, as a rule, are characterized by a smoother increase in pressure. When a compression wave passes through the liquid layer, we note a decrease in the pulse amplitude. The pulsation period τ of the gas cavity was estimated also from the formula [6]: $\tau = 1.14\rho^{1/2}E^{1/3}P^{-5/6}$ (where P is the pressure jump at the shock wave front, $E = 0.008$ J is the energy released in explosion) and amounted to 750 μsec.

Figure 2a presents a typical oscillogram of the pressure developed in distilled water with an aluminum surface exposed to laser radiation. The values for the pressure P obtained in processing of oscillograms at the shock wave front depending on the distance l to the point of the effect of laser radiation ($1.2 \cdot 10^7$ W/cm^2) on the aluminum agree satisfactorily with the data predicted by the approximate formula [7]:

$$\frac{P}{A} = \frac{8}{25}\frac{n}{n+1}\left\{0.611\left[\left(1 + 0.16\frac{nA}{E}r_{fr}^3\right)^{5/8} - 1\right]\right\}^{-1}, \quad (1)$$

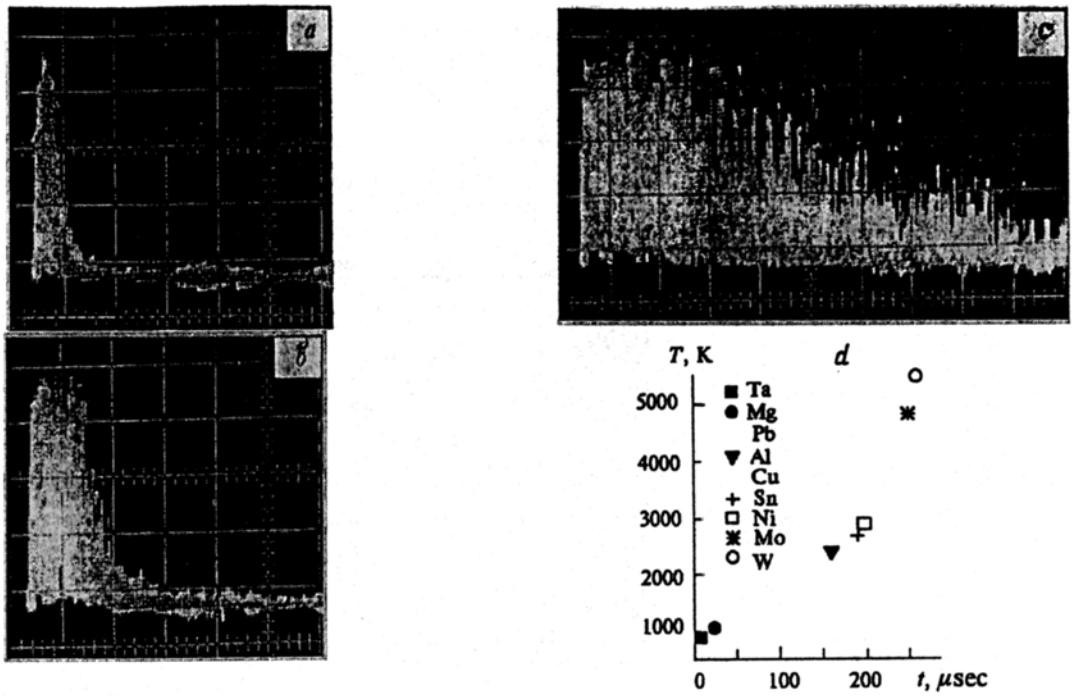

Fig. 3. Oscillograms of the neodymium glass laser radiation (100 μsec/div) that has passed through an optical shutter with lead (a), molybdenum (b), and without a target (c) in the cuvette. There is relationship between the laser radiation duration and the evaporation temperature of metals (d) in the cuvette filled with water.

where r_{tr} is the shock wave radius; $A = 3001$ atm, $n = 7$ (for water). When the distance l increased from 1 to 5 mm, the value of P changed from $6 \cdot 10^7$ to $5 \cdot 10^6$ N/m^2.

The satisfactory agreement between the experimental and calculated values for the basic parameters of the gas cavity indicates that they are determined by the total energy of evaporation of the substance removed from the zone of laser radiation action on metals in a liquid, whereas the dynamics of the cavitational cavity can be considered on the basis of the concepts of the point explosion physics.

Proceeding from the dynamic characteristics of the development of a bubble, it is of interest to estimate the magnitude of pressure developed on the surface of the metal in the zone of its exposure to laser radiation. This can be done using, for example, the dependence of the expansion of a spherical cavity filled with a gas in an ideal incompressible liquid on the initial bubble radius r_0, hydrostatic pressure at the explosion depth P_0, and the initial pressure P_1 in the incipient bubble [5]

$$P_1 = \frac{P_0 \left[1 - (r_0/r)^3\right]}{3 (r_0/r)^3 (1 - r_0/r)}, \tag{2}$$

Substituting experimental values and identifying the initial bubble radius with the light spot radius, we obtain a value of the order of 10^9 N/m^2. As noted in [5], such an estimate is known to be inaccurate, since the liquid compressibility is not taken into account and the precise initial bubble radius (which may not be identical to the light-spot radius) is also unknown. Moreover, the relation used was obtained for a sphere filled with an ideal gas with known thermodynamic properties. As the photographs of the radiation spectra of the plasma in the bubble show, in our case a vapor-gaseous medium is formed that along with the light-erosion products of metal also contains the products of liquid dissociation. However, despite the roughness of the estimate of the pressure magnitude, this result may turn to be useful, because it indicated the order of the magnitude of pressure that can be attained in

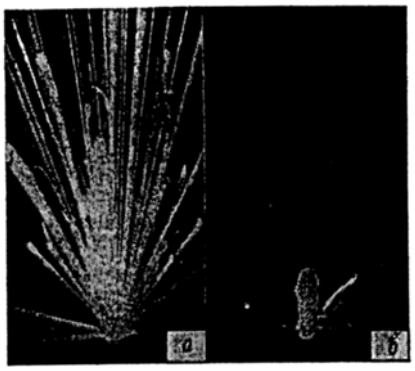

Fig. 4. Photographs of escape of aluminum erosion products formed on exposure to laser radiation ($6 \cdot 10^6$ W/cm^2) in a regime of free generation (a) and of a short pulse formed by an optical shutter with aluminum in distilled water (b).

the zone of laser radiation effect on metals. Nearly the same pressure (~1 GPa) was obtained in [8] when metals in chemically active liquids with water as a solvent were exposed to nanosecond laser radiation pulses.

Realization of such pressures and rather high temperatures in the zone of exposure intensifies the processes of the synthesis of new compounds. We obtained titanium nitride of stoichiometric composition and of traditional yellow-green color by exposing a freshly spray-coated (in a magnetron discharge) pure titanium in ammonia to ~2 msec-duration neodymium-glass laser radiation with a power flux density of $\sim 10^5$ W/cm^2.

The formation of a gas cavity in the liquid very substantially changes the conditions of laser energy supply to the target. In this case one should expect additional losses of energy by the substance erosion products and due to reflection and scattering by the cavity-liquid interface.

Figures 3a and 3b illustrate oscillograms of laser radiation that has passed through a liquid (distilled water) at a distance of 0.1 cm from the target surface exposed to laser radiation with a power density of $1.2 \cdot 10^7$. W/cm^2. For comparison, in Fig. 3c we have an oscillogram of laser generation (free regime) obtained in the absence of a bubble on the route of radiation propagation. It is seen that the gas cavity formed, having the properties of an optical shutter, leads to attenuation of probing radiation. The duration of the stage of gas cavity development to sizes that are sufficient for virtually complete attenuation of radiation is determined by the thermophysical properties of the target substance and changes with the substance. In particular, the gas cavity increases with an increase in the evaporation temperature of the substance (Fig. 3d).

Our experiments also showed that the use of an optical shutter based on the intersection of the laser radiation by an incipient bubble, makes it possible to decrease considerably in erosion products the amount of the liquid-droplet phase, which is dispersed from the analyzed sample surface located in air (Fig. 4b). This is achieved by using only the initial stage of the disintegration of the specimen, when mainly a vapor phase is present in erosion products. As the effect of laser radiation lasts for comparatively a short time, the melt has no time to develop processes leading to ejection of droplets. This reduces the background and increases the accuracy and absolute sensitivity of laser spectral analysis as well as the effectiveness of the use of the specimen substance. In the absence of an optical shutter on the path of laser irradiation of the specimen material in air, the phase composition of the erosion products of the specimen changes sharply (Fig. 4a). In this case the part played by the liquid phase becomes more substantial. By changing the conditions for the formation of a gas cavity in a liquid, it is possible to vary the phase composition of the light erosion products.

In the experiments described the cuvette with liquid and the target were placed outside of the laser cavity. Of certain interest is investigation of the possibility of using such a device as a Q-modulator for the laser cavity. For this purpose, we placed a cuvette with a liquid inside a ruby laser cavity between the end of the active element and output mirror. At the bottom of the cuvette near the cavity caustic we fastened specimens made of different materials. Using prisms with total internal reflection we turned the laser beam, and a lens with a focal length of 6

cm focused it on the specimen surface. In this case the gas cavity in the liquid did not shut off the laser radiation beam in toto. However, perturbations created in the liquid during the formation of the gas cavity led to a change in the time behavior of the laser generation: the laser radiation was modulated by low-frequency oscillations (Fig. 2c). The period of pulsations for a carbon target in water and a generation energy of 1.5 J was 70 μsec, whereas for a molybdenum target it was 55 μsec.

In the absence of liquid, but in the presence inside the cavity of a cuvette with metal on whose surface a portion of laser radiation was focused, the formation of a torch of light-erosion products that crossed the cavity caustic led to the onset of the so-called "self-consistent" generation regime, which was first observed in [9] (Fig. 2b). The specific features of the temporal behavior of generation in both cases are due to the difference in the rates of development of inhomogeneity in the cavity. In the case of the "self-consistent" generation regime, the inhomogeneity is formed by a plasma. When the cuvette is filled with liquid, the formation of low-frequency modulation is caused by a rather complex structure of compression waves formed in the cuvette during the formation and pulsations of the gas cavity.

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