Single shot femtosecond laser ablation of molybdenum

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Abstract. Molybdenum is a high-strength refractory material widely used in industry; its behavior at high temperatures causes considerable theoretical and practical interest. We present the results of experimental studies of femtosecond laser ablation of molybdenum produced by pulses with duration of 160 fs at a moderate intensity of $10^{12}$ W/cm$^2$. The values of single-shot ablation and cavitation thresholds, morphology of craters and surface expansion dynamics were measured using ultrafast chirped interferometry. The experimental data are compared to the results time-dependent heat flow calculations based on two-temperature model with the temperature dependent thermodynamic and transport coefficients in the range up to 20 kK.

1. Introduction
Today femtosecond laser is an important tool for fundamental investigations of nonequilibrium processes and metastable states in a condensed matter. The interaction of femtosecond laser pulses (FLP) with metals is described by two temperature model [1]. An ultrashort laser pulse with duration less than the heating time of the lattice can heat electrons to a high temperature while leaving the lattice relatively cool. Isochoric heating of a thin surface layer of a metal target gives rise to powerful tensile stresses and ablation of a part of the surface liquid nanolayer of the material. The nature of the fracture is a cavitation process of a formation and growth of vapor nuclei in a metastable stretched melt [2–8]. Molybdenum is a refractory metal characterized by a high modulus of elasticity, small thermal expansion coefficient and high electrical conductivity. Currently, it is widely used in the electronics industry, in particular as one of the elements of nanoscale multi-layered structures of modern electronic devices [9]. So the information on a value of ablation threshold is very important.

In this article, we continue studies of femtosecond ablation of metals [10–14]. The difference of ablation threshold values and depth of craters observed for various metals is associated with both the thermodynamic properties of the materials, as well as a strength of the condensed state, and requires an extensive study. We apply ultrafast chirped interferometry for recording of a motion of a target surface in a picosecond range with high temporal and spatial resolution. This technique allows us to record the continuous dynamics of the process in a single exposure. Novel data on ablation and cavitation thresholds, crater morphology, as well as the expansion dynamics of an ablated layer at different laser fluencies for molybdenum are experimentally obtained. These data are useful for the development of laser processing and nanostructuring of materials,
as well as for the hydrodynamic and molecular dynamic modeling of the nonequilibrium processes and metastable states mentioned above.

2. Experiment
A source radiation was CPA (chirped pulse amplification) Ti:S laser system, generating pulses of 160 fs at wavelength 795 nm. A small part of the amplified chirped pulse was taken from laser beam before the compressor and used for diagnostics. A powerful part of the pulse after the compression was applied to heat a target. The experimental scheme was described in detail in [15].

Experimental sample was a polycrystalline molybdenum film with a thickness of 1 µm deposited on polished glass substrates by magnetron sputtering.

A pump pulse of p-polarization was focused on the target surface at an angle of incidence of 55° by the lens with a focal length of 30 cm. Spatial distribution of fluence in a focal spot was Gaussian.

For the detection of the hydrodynamic motion of the ablation layer of molybdenum target frequency modulated (chirped) pulse with a duration of about 300 fs at a central wavelength $\lambda = 795$ nm and spectral width $\Delta \lambda = 40$ nm was used. The experimental scheme provides a continuous registration of process dynamics with the temporal resolution of $\delta t \approx 2$ ps in the range $\Delta t = 0–200$ ps.

The diagnostic part of the setup was a Michelson interferometer in an imaging configuration, where one of the mirrors was the surface of the tested sample. An objective with $NA = 0.3$ was used to transfer the image of interaction area to the entry slit of the imaging diffraction spectrometer Solar MS3504i. The interference patterns were recorded by 12 bit CCD camera SensiCam QE.

Fourier processing of interference patterns allows us to obtain an accuracy of measurement of phase changes of the reflected probe wave approximately $\delta \phi \approx 0.01$ rad and correspondently provides an error of the surface displacement $\delta z \approx 1$ nm.

The determination of the value of the ablation threshold $F_a$ was obtained from the measured dependence of ablation crater size on the lasers pulse energy [16]. Figure 1 shows the dependence of the squares of the radius $r_x^2$ and $r_y^2$ of the ablation crater on the logarithm of the incident energy of the laser pulse $E$. The shape of the crater in the plane of the target is elliptical because of the oblique incidence of the radiation. The intersection point of the lines, extrapolating the experimental values (markers) with the horizontal axis, corresponds to the threshold energy $E_a$. In this case, the slopes of the lines determine the spatial parameter $r_{0x}$ (line 1) and $r_{0y}$ (line 2) of Gaussian distribution in the focal spot at the level $e^{-1}$. The measured values were $r_{0x} \approx 64$ µm, $r_{0y} \approx 34$ µm and $E_a \approx 8.7 \pm 0.2$ µJ. Accordingly, the value of the ablation threshold for the incident fluence under these conditions was $F_a \approx 0.13$ J cm$^{-2}$.

Figure 2 shows the profile of the ablation crater on the surface of a molybdenum sample measured by the interferometric technique.

If the magnitude of the tensile stresses arising after isochoric heating exceeds the strength of the condensed state, then in the stretched melt a cavitation process of formation and growth of vapor bubbles develops, leading to further spalling of a superficial layer. Cavitation in the melt occurs at an energy density exceeding the cavitation threshold $F_c$ that is greater than the melting threshold $F_m$, but smaller than the ablation threshold $F_a$. In the event that the freezing time of the melt is shorter than the time for the collapse of the cavitation bubbles, then in the annular region around the crater on the target, where $F_c < F < F_a$, the rim appears due to the formation of a subsurface porous structure [4]. The such rim around the crater with a height of 3–5 nm is clearly seen in figure 2. The value of the cavitation threshold for molybdenum is equal to $F_c \approx 0.7F_a$. The ablation crater has sharp vertical boundaries, and its shape differs significantly from the laser Gaussian intensity distribution in the focal spot. The depth of the
Figure 1. Determination of the ablation threshold for molybdenum; $E_0 = 1 \mu$J.

Figure 2. Profile of the ablation crater 1; spatial distribution of fluence in the focal spot 2.

crater $h$ near the threshold $F_a$ is approximately 15 nm and increases up to maximum value $h \approx 20$ nm at the center of the spot where $F_0 \approx 1.5F_a$.

Figure 3 represents the recorded motion of the surface of Mo sample after laser exposure with $F_0 = 0.19$ J cm$^{-2}$. Figure 4 shows the time dependences of the displacement $z(t)$ of the sample surface at different fluencies, measured in a single shot. The cross sections are plotted for the central and peripheral regions of the focal spot, corresponding to different fluencies.
Figure 3. Spatial-temporal distribution of phase shift of the diagnostic pulse during surface expansion: color bar is in radians; $F_0 = 0.19 \text{ J cm}^{-2}$.

Figure 4. Surface displacement profiles $z(t)$ for the different fluencies: 1—$F_0 = 1.57F_a$; 2—$F_0 = 1.4F_a$; 3—$F_0 = 1.3F_a$; 4—$F_0 = 1.2F_a$; 5—$F_0 = 1.1F_a$.

Noticeable movement of the surface of the sample appears several picoseconds after the action of FLP. At a smaller time $t \approx 10^{-12} \text{ s}$, the recorded small phase changes comparable with the measurement error coincide with a sharp increase in the reflectivity and are obviously a
Figure 5. The dependence of the expansion velocity on the normalized fluence.

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consequence of the change in the optical constants of molybdenum due to heating. The problem
of measuring of optical constants of matter [10,17], which is in a strongly nonequilibrium state,
requires additional investigations and is not considered in the present paper.

Figure 5 shows the dependence of the averaged expansion velocity in the temporal range
$\Delta t = 30–80 \text{ ps}$ on the excess of fluence above the ablation threshold. In this interval $\Delta t$, the
expansion rate is approximately constant.

However, after 100 ps the rate of motion decreases. The decrease in speed is evidently due
to the resistance of the foamed melt to stretching [3]. And this slowdown is stronger near the
ablation threshold (figure 4, curves 4 and 5). This, apparently, is connected with the greater
resistance to stretching of less heated foam.

3. Discussion

The dynamics of the electron $T_e$ and ion $T_i$ temperatures in metals, heated by FLP is described
by the equations [1]:
\[
C_e \frac{\partial T_e}{\partial t} = - \frac{\partial}{\partial z} \left( \kappa \frac{\partial T_e}{\partial z} \right) - \alpha (T_e - T_i) + Q(z,t),
\]
\[
C_i \frac{\partial T_i}{\partial t} = \alpha (T_e - T_i). \tag{2}
\]

Here the laser source of heat is represented as
\[
Q(z,t) = \frac{(1 - R)F}{\sqrt{\pi \delta \tau_L}} \exp \left( - \frac{t^2}{\tau_L^2} \right) \exp \left( - \frac{z}{\delta} \right). \tag{3}
\]

Figure 6(a) shows the electronic heat capacity was calculated using a polynomial of the fifth
degree $C_e(T_e) = \sum a_i T_e^i$, which approximated the data from [18]. For comparison also is plotted
the linear dependence $C_e(T_e) = \gamma_e T_e$ (dashed line), where $\gamma_e = 0.1947 \text{ mJ cm}^{-3} \text{ K}^{-2}$ [19].
Figure 6. Specific electron (a) and ion (b) heat capacity versus temperature. The circles denote the data from [18], triangles—[20] and squares—[21]; solid lines—approximating curves.

The specific ionic heat capacity $C_i(T_i)$ is given by the interpolation expression $C_i(T_i) = C_{i,0}T_i^m$, solid line in figure 6(b), where $T_i$ is given in [kK], and $C_{i,0} = 3.1 \text{ J cm}^{-3} \text{ K}^{-1-m}$, $m = 0.2$ are the fitting parameters approximating the experimental data [20] and [21].

For a two temperature thermal conductivity $\kappa(T_e,T_i)$ the dependence in the form $\kappa(T_e,T_i) = (k_1 + k_2T_i)(T_e/T_i)$ was used at $0.3 < T_e < 20 \text{ kK}$, $0.3 < T_i < 4 \text{ kK}$. According to the literature data [19], the coefficients $k_1 = 143.6 \text{ W m}^{-1} \text{ K}^{-1}$, $k_2 = -18.5 \text{ W m}^{-1} \text{ K}^{-2}$. The dependence of electron-phonon coupling parameter on $T_e$ (figure 7) was taken from [18].
Figure 7. Parameter of electron-phonon coupling as a function of electron temperature. The circles denote the data from [18]; solid line—approximating curve.

Figure 8 shows the result of calculating temperature profiles $T_i(t)$ near the ablation threshold of $F_a = 130$ mJ cm$^{-2}$ using two temperature model (1)–(3). To calculate the absorbed fluence, the value of the reflection coefficient $R = 0.4$ is taken according to [22].

The purpose of the numerical calculation was to estimate the heating depth, where $T_i$ exceeds the melting point. It follows from the calculation that the electron temperature at the surface of the sample at the end of the laser pulse is $T_{i}^\text{max} \approx 9$ kK. The temperature $T_{i}^\text{max}$ on the surface ($z = 0$) is approximately 1.5 times the melting point of molybdenum under normal conditions $T_m = 2893$ K [19], and the heating time of the ion subsystem up to $T_m$ is less than a picosecond.

From the spatial profiles of ion temperature in figure 9 it follows that near the threshold $F_a$ after the heat transfer from electrons to lattice $T_i > T_m$ in the superficial layer 20–30 nm in thickness.

Note that, for high overheating of the lattice, realized in experiments with FLP, the melting of the surface layer takes place through homogeneous nucleation during $\sim 10^{-12}$ s [23]. This time is shorter than the characteristic time for unloading and forming a tensile stress wave $t^* = d_T/c_s \approx 10-15$ ps (where $d_T \approx 50-70$ nm is the depth of heating at the end of two-temperature stage, $c_s \approx 5$ km s$^{-1}$ is speed of sound [19]). As a consequence, destruction occurs in a metastable stretched melt as a result of the cavitation process of formation and growth of the nuclei of vapor, followed by the separation of a part of the melt in the form of a spalling nanoplate. As noted above, the spallation regime of destruction is indicated by the characteristic shape of the crater, as well as the presence of a cavitation zone around it, which is a consequence of tensile stress acting on the melt. It should be noted that the depth of the ablation crater near the threshold is $h \approx 15$ nm and less than the depth of the melt. The above experimental and calculated data are in good agreement with the general performances on the mechanism of thermomechanical laser ablation of metals available today [7].

The simple two-temperature model (1) and (2) does not describe the melting process of the heated layer. The loss of energy density for melting in vicinity $F_a$ in the layer of $h_m \approx 20-25$ nm in thickness can be estimated as $\Delta H h_m \approx 0.01$ J cm$^{-2}$ (here $\Delta H = 3.8$ kJ cm$^{-3}$ [19] is the
Figure 8. Temporal profiles of electron (red) and ion (blue) temperatures near the ablation threshold on the surface.

Figure 9. Spatial profiles of ion temperature near the ablation threshold for different time after exposure.

specific heat of melting of molybdenum). This is approximately 12% of the absorbed energy density of $F_{abs} \approx 0.08$ J cm$^{-2}$ contained in the layer $h_m$. Those the inclusion of melting should reduce by a commensurate magnitude the value $T_i$, which does not significantly vary the ablation regime considered above.
Furthermore, the two-temperature model (1) and (2) does not describe the substance motion, which leads to a change in density. However, according to figure 4 at the early stage $t \leq 10$ ps, considered in the model, near the ablation threshold the displacement of the boundary is negligible compared to the thickness of the heated layer. This confirms the applicability of the model for estimates of the temperature distribution in the case under consideration (see also, for example, [24]). However, for a rigorous description of the ablation process, including the kinetics of melting, nucleation in a melt and matter expansion, it is necessary to use more complicated hydrodynamic models [8, 10, 11, 25, 26], that in particular is a further development of this work.

4. Conclusions

The values of the spallation and cavitation thresholds for laser pulses of 160 fs duration were experimentally determined. Using chirped pulse interferometry, data on the dynamics of motion of the target surface in a picosecond range and fluences up to $1.5 F_a$ were obtained in a single exposure with the temporal resolution 1 ps. The ablation crater has the sharp boundaries and its depth near the threshold $F_a$ is 15 nm. The results of calculations of the electron and ion temperature distributions are in good agreement with experimental data, including the ratio of the temperature reached at the ablation threshold with the melting temperature, as well as the size of the melting zone and the depth of the crater.

The data obtained are important for improving the technology of laser processing of materials and nanoparticles formation. They are also relevant for the development of methods of molecular dynamics and hydrodynamic simulations, testing of interaction potentials, and also refinement of the thermodynamic and kinetic parameters of metals in the region of high electron temperatures up to 20 kK.

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