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Features of focusing of a laser beam of laser ablation in supercritical carbon dioxide

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features of the phenomena of a laser nanosecond radiation In supercritical carbon dioxide are revealed. It is shown that the presence of a supercritical fluid leads to the expansion of the structures formed on the target in comparison with the air media. It has been suggested that the resulting magnification effect is due to the defocusing of the system, which causes the formation of the lens impact. Obtaining useful results is possible with the use of various technologies of laser ablation and microstructuring in supercritical fluids.

Keywords: nanosecond laser radiation, supercritical fluid, metal target, fluctuations.

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Supercritical carbon dioxide (sc-CO$_2$) is currently being used more and more often as a medium for laser ablation and microstructuring of various targets [1–3]. The sc-CO$_2$ medium, which is unique in being highly environmentally friendly, featuring very low viscosity and high molecular mobility values, and providing an opportunity for immediate adjustment of density within a wide range, was proven efficient in production of heterogeneous catalysts [4,5], nanoparticle synthesis [6,7], production of unique polymer materials [3], and micronization of medicinal plants [8,9]. Another undeniable advantage of sc-CO$_2$ consists in the fact that carbon dioxide becomes supercritical at fairly low values of pressure (7.38 MPa) and temperature (31.1°C). At the same time, supercritical fluids (especially in the neighborhood of the critical point) are known to have strong parameter fluctuations [10,11], which induce a significant enhancement of light scattering [12]. These fluctuations may exert a significant negative influence on the parameters of laser radiation focusing in sc-CO$_2$, which are crucial for many technological processes.

The aim of the present study is to reveal the specifics of focusing of nanosecond laser radiation in supercritical carbon dioxide.

Experiments were carried out in a standard high-pressure reactor that was used in our earlier study [13]. An YLPP-1-150V-30 (IPG, Russia) fiber laser with radiation wavelength $\lambda = 1064$ nm, pulse length $\tau = 0.05-7$ ns, and pulse repetition rate $F = 2-1000$ kHz was used. The pulse energy was $E = 0.5$ mJ, and the mean power was as high as 30 W. An F-theta lens with a focal distance of 63 mm was used for focusing. The waist radius in the focal plane was $\omega_0 = 17 \pm 2\,\mu$m. The microstructuring parameters were as follows: $\tau = 5$ ns, $F = 15$ kHz for laser craters (spots) and $\tau = 2$ ns, $F = 60$ kHz for laser stripes (lines) at a scan rate of 100 mm/s. The number of pulses was varied within the $n = 1-1000$ range in the production of craters, while stripes were formed in different numbers ($N = 1-1024$) of passes. The parameters of the sc-CO$_2$ medium in the high-pressure reactor were as follows: pressure $P = 20$ MPa and temperature $T = 50°$C. An HRM-300 Series 3D microscope (Huvitz, Korea) and a PHENOM ProX (Phenom World, Netherlands) scanning electron microscope (SEM) were used to visualize laser structures formed on the target surface.

Figure 1 presents the SEM images of laser stripes formed on the surface of a silver plate in different numbers of laser passes N. It can be seen that the stripes in sc-CO$_2$ are much wider than in air, and their crosswise size exceeds considerably the laser spot diameter in the focal plane. Specifically, the width of a stripe formed in sc-CO$_2$ at $N = 64$ (inset in Fig. 1) was 200 μm, which is ~ 6 times greater than the laser spot diameter ($2\omega_0 = 34 \pm 4\,\mu$m). In the case of microstructuring in air, the stripe width at $N = 64$ is approximately equal to 70 μm.

Similar widening of microstructures in sc-CO$_2$ was observed in the case of production of craters (Fig. 2, a). It is evident that the crosswise size of craters increases rapidly with number of laser pulses.

The dependence of crater depth on the number of laser pulses in the sc-CO$_2$ medium (see Fig. 2, b) shows that the mean penetration rate decreases rapidly as n increases (from $\sim 2\,\mu$m/pulse at $n = 1$ to ~ 10 nm/pulse at $n = 1000$). At the same time, crater diameter squared D^2 increases exponentially with $\lg n$ (Fig. 2, c). Note that the dependence of D^2 on $\lg n$ is linear [14] when a similar crater is formed by a laser beam with a Gaussian intensity distribution in standard air atmosphere.

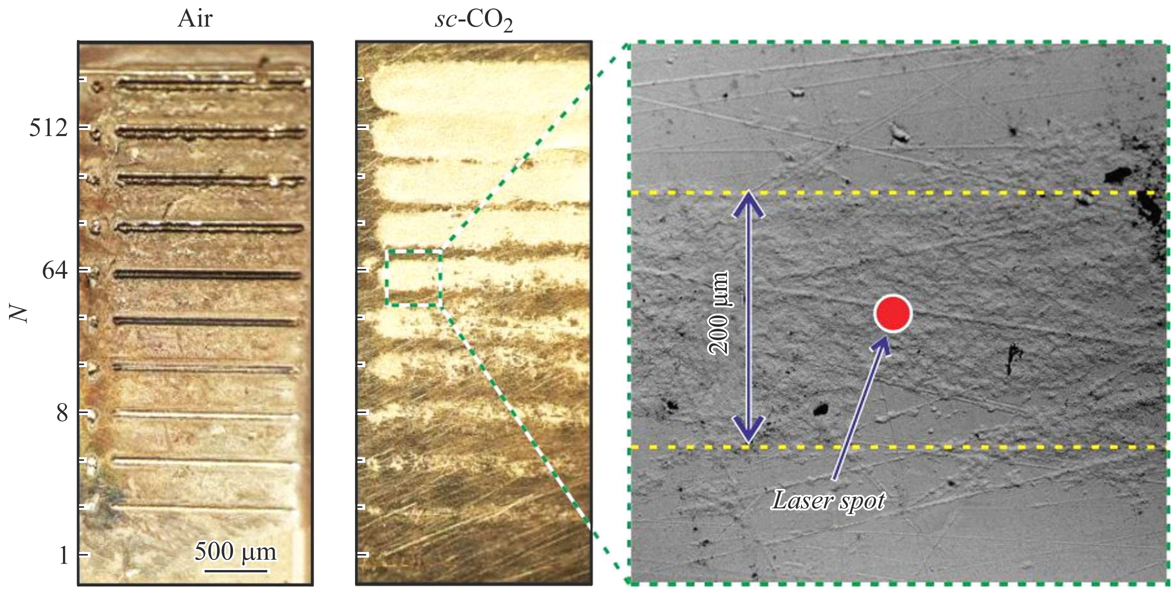

Figure 1. SEM images of laser stripes formed on the surface of silver in air and *sc*-CO$_2$ in different numbers of laser passes N. An enlarged fragment of a stripe 200 μm in width is shown in the inset. A laser spot is indicated.

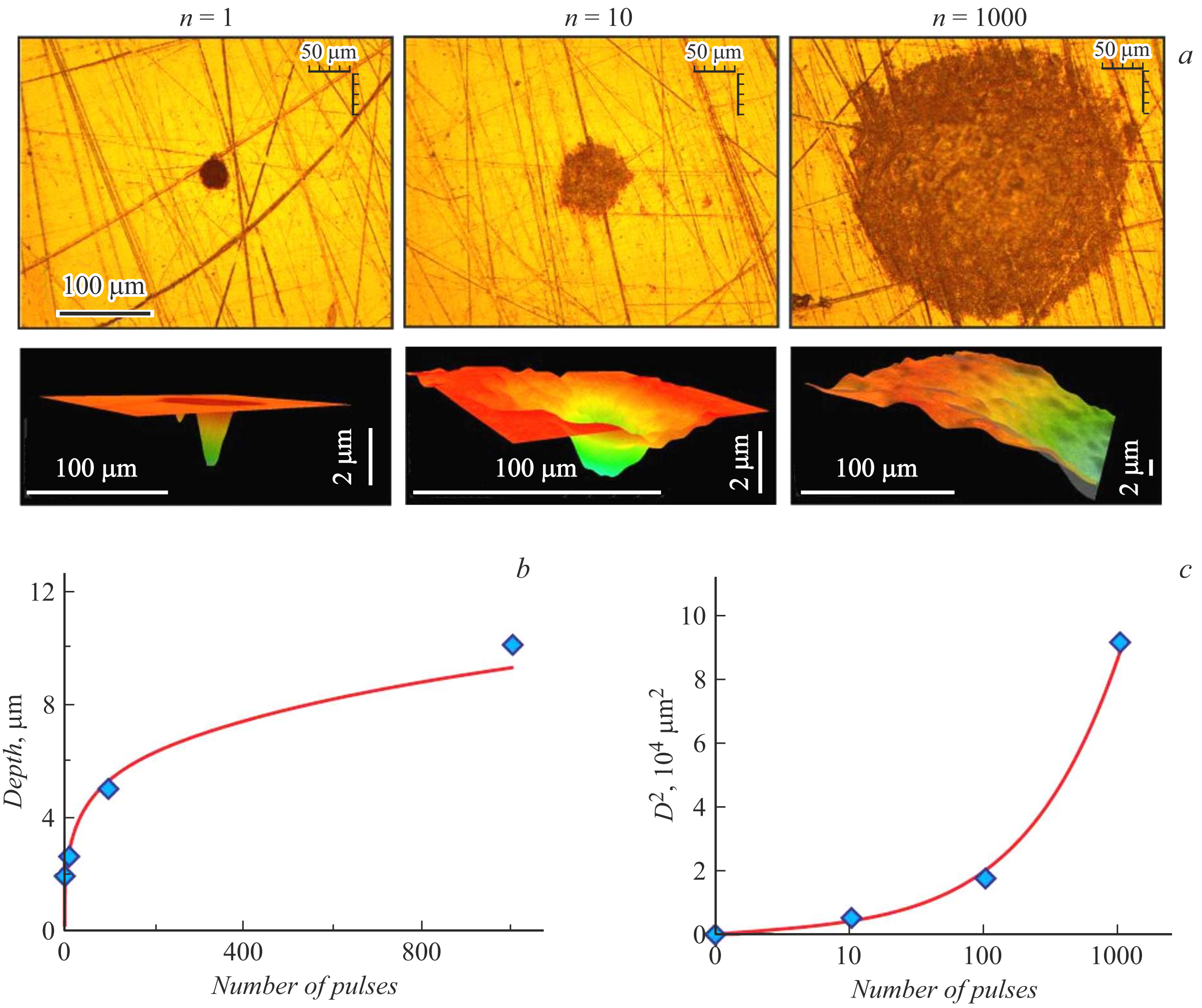

Figure 2. *a* — 2D and 3D images of laser craters formed on the surface of silver in*sc*-CO$_2$ at different numbers of laser pulses n. *b* and *c* — Dependences of the depth and the diameter squared, respectively, on number of laser pulses n.

The observed widening of microstructures in the sc-CO_2 medium (Figs. 1, 2) may be attributed to the formation of a thermal lens in the region of laser irradiation. In the classical case, the thermal lens effect is produced when laser radiation is absorbed in the bulk of a fluid. A temperature gradient associated with the spatial distribution of light intensity forms in this case and induces a refraction-index gradient in the medium [15]. Different approximations („parabolic lens“ [16] and „aberrant lens“ [17]) are used to solve the diffraction equations characterizing the influence of the refraction-index gradient on the output beam.

It may be assumed that laser radiation in our experiments is absorbed not in the sc-CO_2 medium itself, but in the metal target only. This stems from the fact that the coefficients of light absorption for metals and dielectrics (sc-CO_2) differ significantly. In addition, the absorption bands of carbon dioxide [18] lie outside the used wavelength range. In the process of ablation, a fluid column above the ablated target surface is heated (in the vicinity of the target) by an ablation plume. The entire reactor region above the target near the optical axis is also heated by the emerging convective flows, inducing temperature gradients. It is known that the critical region of a fluid is characterized by the values of isobaric thermal coefficient $\rho^{-1}(\partial\rho/\partial T)_P$ (ρ is density, T is temperature, and P is pressure), which increase greatly on approach to the critical point [15]. Therefore, temperature gradients may be induced in the present case by strong convective flows.

Using the temperature dependence of the refraction index of the sc-CO_2 medium [19] and tabular data [20], one may estimate the temperature coefficient of the refraction index in the supercritical region: $\sim 0.03\,\mathrm{K}^{-1}$ (for the parameters set in our study). A thermal lens forms above the laser irradiation region as a result; in our view, this lens is the cause of defocusing and effective widening of laser microstructures.

Since the defocusing effect should depend on the power of the formed thermal lens, the effective spot size should depend on the degree of heating of the target surface and, consequently, on the duration of laser treatment. This is what was observed in experiments. In the case of a single exposure ($n = 1$ in Fig. $2, a$), the thermal lens effect is zero and the crosswise size of a crater is comparable to the laser spot diameter. As n increases, the thermal lens effect becomes stronger, inducing fast growth of the crater diameter (Fig. 2).

Thus, it was demonstrated experimentally that the crosswise size of microstructures forming on a target increases in the process of ablation under the given parameters of temperature and pressure in the reactor, which correspond to a supercritical fluid. It was established that this effect is associated with defocusing due to the formation of a thermal lens. Further studies in other phase states of carbon dioxide are needed in order to prove that the effect is related specifically with the supercritical state of carbon dioxide.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K. Saitow, T. Yamamura, T. Minami, J. Phys. Chem. C, **112**, 18340 (2008). DOI: 10.1021/jp805978g

[2] D. Sanli, S.E. Bozbag, C. Erkey, J. Mater. Sci., **47**, 2995 (2012). DOI: 10.1007/s10853-011-6054-y

[3] A. Rybaltovskii, N. Minaev, S. Tsypina, S. Minaeva, V. Yusupov, Polymers, **13**, 3525 (2021). DOI: 10.3390/polym13203525

[4] O. Parenago, A. Rybaltovsky, E. Epifanov, A. Shubnyi, G. Bragina, A. Lazhko, D. Khmelenin, V. Yusupov, N. Minaev, Molecules, **25**, 5807 (2020). DOI: 10.3390/molecules25245807

[5] M. Labusch, S. Puthenkalam, E. Cleve, S. Barcikowski, S. Reichenberger, J. Supercrit. Fluids, **169**, 105100 (2021). DOI: 10.1016/j.supflu.2020.105100

[6] A. Rybaltovsky, E. Epifanov, D. Khmelenin, A. Shubny, Y. Zavorotny, V. Yusupov, N. Minaev, Nanomaterials, **11**, 1553 (2021). DOI: 10.3390/nano11061553

[7] S. Nakahara, S. Stauss, T. Kato, T. Sasaki, K. Terashima, J. Appl. Phys., **109**, 123304 (2011). DOI: 10.1063/1.3599887

[8] R.D. Oparin, Y.A. Vaksler, M.A. Krestyaninov, A. Idrissi, S.V. Shishkina, M.G. Kiselev, J. Supercrit. Fluids, **152**, 104547 (2019). DOI: 10.1016/j.supflu.2019.104547

[9] R.D. Oparin, K.V. Belov, I.A. Khodov, A.A. Dyshin, M.G. Kiselev, Russ. J. Phys. Chem. B, **15**, 1157 (2021). DOI: 10.1134/S1990793121070101

[10] J.A. White, B.S. Maccabee, Phys. Rev. Lett., **26**, 1468 (1971). DOI: 10.1103/PhysRevLett.26.1468

[11] B. Sedunov, Am. J. Anal. Chem., **3**, 899 (2012). DOI: 10.4236/ajac.2012.312A119

[12] E. Mareev, V. Aleshkevich, F. Potemkin, V. Bagratashvili, N. Minaev, V. Gordienko, Opt. Express, **26**, 13229 (2018). DOI: 10.1364/OE.26.013229

[13] E.O. Epifanov, A.G. Shubnyi, N.V. Minayev, A.O. Rybaltovskiy, V.I. Yusupov, O.P. Parenago, Russ. J. Phys. Chem. B, **14**, 1103 (2020). DOI: 10.1134/S1990793120070052

[14] V. Zhigarkov, I. Volchkov, V. Yusupov, B. Chichkov, Nanomaterials, **11**, 2584 (2021). DOI: 10.3390/nano11102584

[15] D.E. Wetzler, P.F. Aramendía, M.L. Japas, R. Fernández-Prini, Int. J. Thermophys., **19**, 27 (1998). DOI: 10.1023/A:1021442901002

[16] C. Hu, J.R. Whinnery, Appl. Opt., **12**, 72 (1973). DOI: 10.1364/AO.12.000072

[17] S.J. Sheldon, L.V. Knight, J.M. Thorne, Appl. Opt., **21**, 1663 (1982). DOI: 10.1364/AO.21.001663.
[18] G.B. Rieker, J.B. Jeffries, R.K. Hanson, Appl. Phys. B, **94**, 51 (2009). DOI: 10.1007/s00340-008-3280-3.
[19] E.I. Mareev, V.A. Aleshkevich, F.V. Potemkin, N.V. Minaev, V.M. Gordienko, Russ. J. Phys. Chem. B, **13**, 1214 (2019). DOI: 10.1134/S1990793119070261
[20] *Search for species data by chemical formula* [Electronic source]. https://webbook.nist.gov/chemistry/form-ser/