Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2013, **23**, 226–228
Mendeleev Communications

Pulsed laser heating of a metal surface confined by a thin layer of transparent dielectric: an experimental approach to the creation of a chemical reactor on supercritical metals

Dmitriy M. Ksenofontov,*[a] Alexander A. Karabutov,[a] Alexander G. Kaptilniy[b] and Alexander Yu. Ivochkin[a]

[a] *Department of Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 5309; e-mail: ksenofontov@physics.msu.ru*
[b] *Joint Institute for High Temperatures, Russian Academy of Sciences, 125412 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2013.07.017

An experimental approach to the near- and supercritical thermodynamic states of metals under dynamic control over a thermodynamic trajectory of pulsed laser heating was developed. Proof-of-concept experiments on aluminum confined by organic and nonorganic films were conducted, and high-energy states with temperatures up to 10^4 K and pressures up to 600 MPa were obtained.

Metal nanoparticle technology based on the specific properties of supercritical matter is of great current interest.[1,2] Continuous production processes in which a metal interacts with a supercritical solvent typically occur under a pressure of several hundred bars at a temperature of up to hundreds of kelvin.[3] These relatively low thermodynamic parameters allow controlling a thermodynamic trajectory in the course of the process and adjusting it for achieving desired particle size, geometry and distribution. Other methods imply the existence of a metal in near- and supercritical states. The critical points of metals have high thermodynamic parameters (a pressure of several GPa units and a temperature of dozens of kilokelvin) unachievable under static conditions. Therefore, these methods are nonstationary, and they are usually based on material ablation during pulsed heating, which may occur due to laser irradiation.[4,5] The pulsed laser ablation of metals in condensed media was described previously.[6,7] This approach is based on the fact that the mechanical confinement of a heated metal surface (*i.e.*, when a heated metal region contacts with a liquid or solid) leads to a significant pressure and temperature increase, as compared to the pulsed laser heating of a free surface (*i.e.*, contacting with a gas or vacuum). In comparison with the continuous production of nanoparticles, pulsed laser ablation in a condensed medium offers several advantages, for example, a simple experimental setup (no need for high pressure equipment) and the on-line optical diagnostics of produced particles. Nevertheless, pulsed laser ablation has a serious disadvantage in comparison with a continuous production process – the absence of control over a thermodynamic trajectory other than the alteration of laser radiation pulse duration and intensity. To avoid this disadvantage, we developed an experimental approach.

We consider the pulsed laser heating of a metal confined by a transparent dielectric: laser radiation falls on a metal/dielectric interface at an incidence angle of 45°, and it is absorbed and partly reflected by the metal. Due to nonstationary heating stress acoustic waves are generated in both the metal and transparent dielectric. This process has several spatial scales: $L_0 = 1/\alpha$ is the optical penetration depth, $L_T = \sqrt{\chi\tau_L}$ is the thermal diffusion length and $L_A = C_L\tau_L$ (α is the optical absorption coefficient, χ is the thermal diffusivity, τ_L is laser pulse duration and C_L is the sound velocity). For the majority of metals, the following relations between the mentioned spatial scales are satisfied for nanosecond laser pulse duration: $L_0/L_T << 1$, $L_T/L_A << 1$. These relations represent surface heating conditions and show that heating and pressure generation is sensitive to conditions at the metal/dielectric boundary;[8,9] thus, one can control the thermodynamic trajectory of pulsed laser heating altering metal surface confinement properties in the course of the process. Here, we propose to alter boundary conditions at the metal/dielectric interface using an acoustic pulse reflected from the free dielectric surface. It is well known that an acoustic pulse changes its sign after reflection from a softer medium,[10] so after round trip time of the acoustic pulse in confining dielectric rarefication wave with absolute amplitude comparable to pressure in metal reaches metal surface. It leads to rapid pressure release and may result in the breakdown of the dielectric from the metal. In other words, the transition between confined and free surfaces of the metal

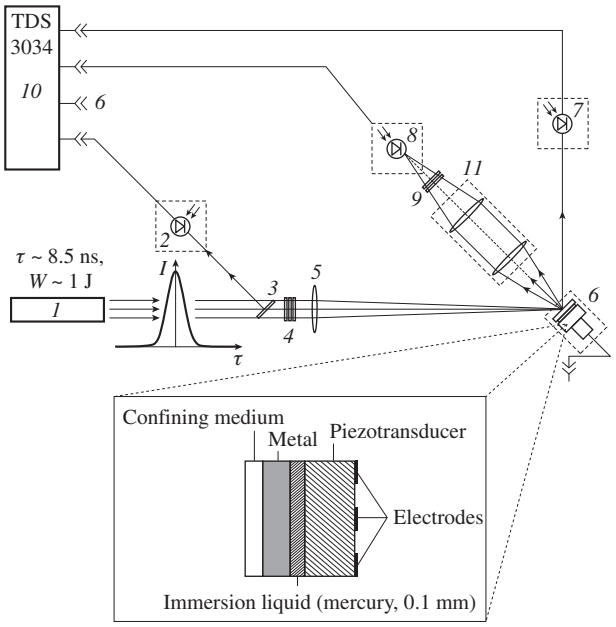

Figure 1 Experimental setup. (*1*) Q-switched YAG:Nd laser, (*2*) trigger photodetector (Thorlabs DET10), (*3*) beamsplitter, (*4*) neutral optical filters, (*5*) focusing lens, (*6*) pressure measurement cell, (*7*) reflected radiation photodetector (Thorlabs DET10), (*8*) thermal radiation photodetector (Thorlabs DET10), (*9*) BGG optical filters, (*10*) TDS3034B digital oscilloscope, (*11*) thermal radiation collimator.

occurs. The initial thermodynamic state for pressure release is defined by confining dielectric layer, and it can be adjusted by altering dielectric thickness and material.

We have chosen aluminum as a sample material due to its relatively low critical point theoretical parameters (T_c = 7970 K, P_c = 350 MPa).[11] Thin layers of PET (40 μm) and sodium silicate (60–200 μm) were used as confining dielectric layers. Solid confining media were chosen for the simplicity of layer thickness control. The target and the experimental setup are shown in Figure 1. The simultaneous measurements of metal temperature, pressure and reflectivity with a nanosecond time resolution, which was successfully used for studying first-order phase transitions in lead and mercury,[12] were performed. Pressure was measured with a calibrated wideband piezotransducer (bandwidth of 100 MHz). Temperature was measured with a full-flux high-speed optical pyrometer. Laser radiation energy density (fluence) was varied from 80 mJ cm^{-2} to 5 J cm^{-2} with neutral optical filters; the laser pulse duration (τ_L) was 8.5 ns. Synchronous measurements of the pressure and temperature dynamics allowed us to plot the thermodynamic trajectory of pulsed laser heating in the *P*–*T* coordinates.

Figure 2 shows the dynamics of pressure and surface temperature in aluminum confined by a PET film within the incident laser radiation energy density range from 0.08 to 1 J cm^{-2}. The negative pressure pulse, which is reflected from confining dielectric free surface, is marked with an arrow in Figure 2. It can be seen that, with increasing laser radiation fluence, the relative amplitude of rarefication wave that pass into metal decreases

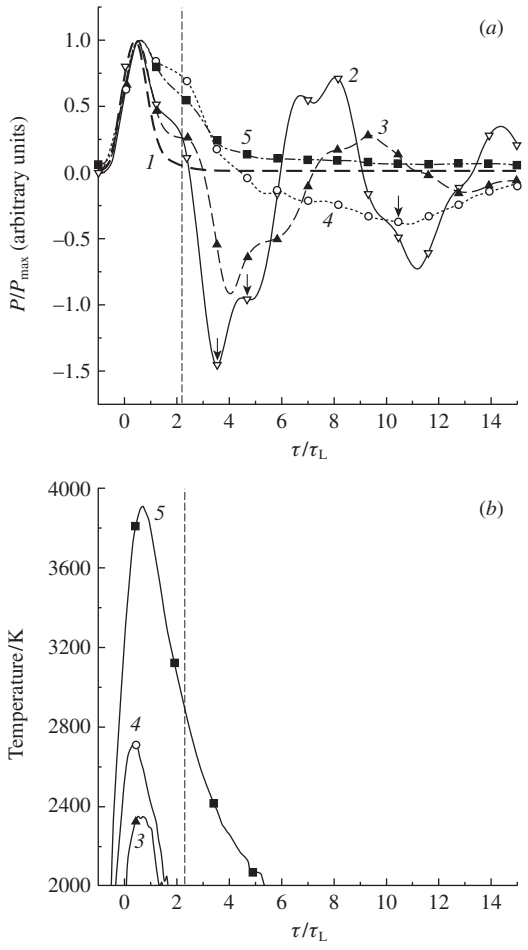

Figure 2 The time dependence of (*a*) pressure normalized to its maximum and (*b*) temperature for aluminum confined by a PET film. (*1*) Laser pulse, (*2*) E = 0.08 J cm^{-2}, P_{max} = 1.5 MPa, (*3*) E = 0.26 J cm^{-2}, P_{max} = 9 MPa, (*4*) E = 0.5 J cm^{-2}, P_{max} = 15 MPa, (*5*) E = 1 J cm^{-2}, P_{max} = 50 MPa. Arrows indicate pressure release pulse. Dashed vertical line indicates the start of pressure release.

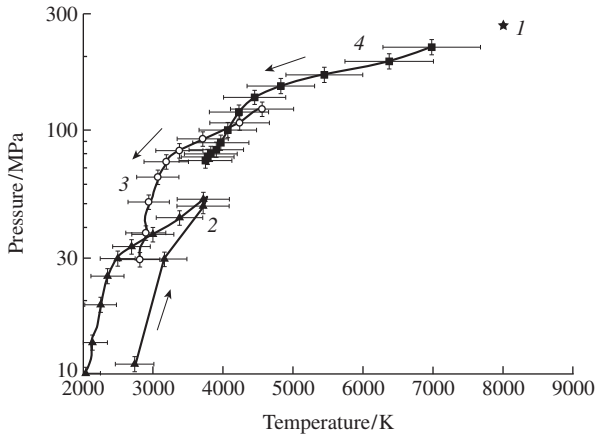

Figure 3 Thermodynamic trajectories of the pulsed laser heating of aluminum confined by a PET film: (*1*) theoretical critical point,[11] (*2*) 1 J cm^{-2}, (*3*) 2 J cm^{-2} and (*4*) 3 J cm^{-2}. Timespan between two sequential points is 4 ns.

until the moment of confining film breakdown from the metal surface (regime *5* in Figure 2). Note that, in this regime, the surface temperature in the moment of pressure release is higher than the boiling temperature of aluminum, and a long tail of the acoustic pulse with a relatively low amplitude (up to 5 MPa) can be explained by the recoil pressure due to evaporation. The experimental results show that the proposed approach can be used to control pressure release in the course of pulsed laser heating.

This approach was applied to study a near and supercritical region of the aluminum phase diagram. Despite the low optical durability of PET film, which limited incident radiation fluence at 3 J cm^{-2}, high energy states of aluminum were obtained. The measured thermodynamic trajectories are presented in Figure 3 (here and below the part of the trajectory corresponding to rising edge of pressure pulses greater than 100 MPa is not shown due to the unrestorable nonlinear distortion). Arrows in Figure 3 indicate the direction of the process.

In order to increase the acceptable laser radiation fluence and to achieve near- and supercritical states of aluminum, sodium silicate films were used due to their higher optical durability. Different acoustic impedances ($Z = \rho C_L$, where ρ is the material density and C_L is the sound velocity) of films were used in order to have fine control over the maximum thermodynamic parameters achievable under a constant incident radiation fluence (5 J cm^{-2}). Thermodynamic trajectories of the pulsed laser heating of aluminum confined by sodium silicate films are presented in Figure 4. It can be seen that the maximum pressure was 600 MPa and the corresponding temperature was 10^4 K, which means that supercritical states of aluminum were obtained.

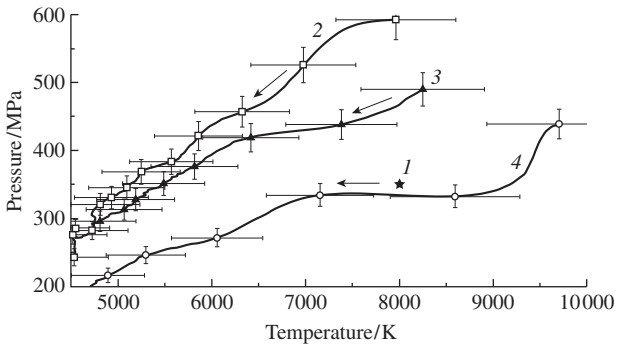

Figure 4 Thermodynamic trajectories of the pulsed laser heating of aluminum confined by sodium silicate films with different acoustic impedances. Laser radiation fluence, 5 J cm^{-2}: (*1*) theoretical critical point,[11] Z_{Al}/Z = (*2*) 2.0, (*3*) 2.2 and (*4*) 2.6, where Z is the acoustic impedance of the confining film and Z_{Al} is that of aluminum. Timespan between two sequential points is 4 ns.

The experimental results allow us to conclude that the above technique is applicable to the study of the high energy states of metals with the ability of controlling the thermodynamic trajectory of the process. This approach can be used for conducting chemical reactions under high pressure and temperature conditions with a supercritical metal under the control over reaction course by controllable pressure release.

References

1 E. Reverchon and R. Adami, *J. Supercrit. Fluids*, 2006, **37**, 1.
2 F. Cansell and C. Aymonier, *J. Supercrit. Fluids*, 2009, **47**, 508.
3 B. Veriansyah, H. Park, J-D. Kim, B. Min, Y. Shin, Y-W Lee and J. Kim, *J. Supercrit. Fluids*, 2009, **50**, 283.
4 T. Seto, M. Hirasawa, N. Aya, N. Suzuki, T. Yoshida, Y. Kawakami and E. Ozawa, *J. Aerosol Sci.*, 2000, **31**, 628.
5 J. C. Alonso, R. Diamant, P. Castillo, M. C. Acosta–García, N. Batina and E. Haro-Poniatowski, *Appl. Surf. Sci.*, 2009, **255**, 4933.
6 Y. Zijie and B. D. Chrisey, *J. Photochem. Photobiol. C*, 2012, **13**, 204.
7 P. V. Kazakevich, A. V. Simakin, V. V. Voronov and G. A. Shafeev, *Appl. Surf. Sci.*, 2006, **252**, 4373.
8 H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, 1986.
9 V. E. Gusev and A. A. Karabutov, *Laser Optoacoustics*, AIP Press, New York, 1993.
10 M. A. Isaakovich, *Obshchaya akustika (General Acoustics)*, Nauka, Moscow, 1973 (in Russian).
11 G. Faussurier, C. Blancard and P. L. Silvestrelli, *Phys. Rev. B*, 2009, **79**, 134202.
12 A. Yu. Ivochkin, A. A. Karabutov, A.G. Kaptilniy and D. M. Ksenofontov, *Laser Phys.*, 2012, **22**, 1220.

Received: 8th April 2013; Com. 13/4099