ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 13, pp. 2759–2764. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © N.A. Leonenko, E.A. Vanina, E.M. Veselova, G.G. Kapustina, 2013, published in Ekologicheskaya Khimiya, 2013, Vol. 22, No. 3, pp. 162–168.

Nonlinear Effects of Laser Radiation and Physical Model of Laser Agglomeration Process

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Received August 20, 2013

Abstract—Nonlinear effects of pulsed and continuous laser radiation on mineral samples from technogenic placers in the Amur river region, containing submicron gold which cannot be extracted by modern gravity separation methods, were studied. The formation of self-organized gold structures on the surface of silicate matrix was detected, and general relations for the agglomeration and concentration of "nonrecoverable" gold species were found. The agglomeration process was simulated by a nonlinear heat conduction equation for one-dimensional case including laser radiation parameters.

Keywords: Laser radiation, ultradispersed gold, gold-bearing minerals, structural ordering.

DOI: 10.1134/S1070363213130240

Abrupt reduction of readily accessible gold stocks in ores and placers has stimulated search for novel low-waste technologies for extraction of gold and other noble metals from technogenic alluvial placers. The Russian Far East is one of the main gold mining regions of Russia, and the problem of reprocessing of technogenic gold-containing neoformations that have been accumulated over a long historical period of gold mining therein is quite important. Such alluvial deposits are generally characterized by a high clay content of sand. Gold metal in silts is mostly represented by dispersed colloidal plates or needles. Gravity concentration is accompanied loss of most gold plates and dendritic particles with the tailings, especially when their size is lower than 0.25 mm [1–3].

Unconventional methods of energy deposition include electrochemical, microwave, electric pulse, electrohydrodynamic, and magnetic pulse treatment and the action of accelerated electron beam, super-power hyper shock waves, and powerful electromagnetic pulses [4]. Nowadays, the most promising is believed to be laser irradiation of mineral concentrates. Laser radiation ensures high rate of local temperature variation in a substrate and high temperature gradients both within a narrow limited surface area and in the bulk due to low thermal conductivity. These effects could not be achieved by other methods.

On the other hand, it is known that properties of micron-sized particles and nanoparticles differ from those of larger specimens. This is related to the dependence of the specific surface area on the particle size, and hence to incomparably higher structural perfection and surface effects. Such properties include thermal, electric, and magnetic characteristics and high aggregation stability. For example, the melting point of gold macroparticles is 1064°C, whereas gold nanoparticles with a size of 4 nm melt at 427°C. The properties of nanoparticles of even the same size may differ depending on the medium. This is the result of inevitable interaction between atoms of nanoparticles and surrounding material, which is much stronger than analogous interaction involving micron-sized species. The stronger the interaction with the medium, the grater the difference in the properties of isolated particles and those placed in a certain medium. For instance, gold nanoparticles in a vacuum, in air, and in

Laser source parameters

Laser source	Laser source type (efficiency, %)	Pulse frequency, Hz	Radiant flux, W	Power input, kW	Pulse energy, J	Pulse duration
Skat 301	Solid-state pulsed Nd:YAG (3–5)	100	200	4.0	1	150 μs to 1 ms
Kvant 15	Solid-state pulsed Nd:YAG (3–5)	5	300 to 2000	7.0	8	10 μs to 100 ms
LS-06	Fiber optic continuous ytterbium (25–30)	5000	0 to 600	2.4	–	0.5–1.0 s (exposure)

association with heavy minerals in alluvial clay-rich sands should considerably differ in their properties. This is of particular importance for the solution of technological mineralogy problems and development of methods for extraction of ultradispersed minerals and nanoparticles from mineral matrices [5].

We used three sources of infrared laser radiation (see table): a Skat 301 solid-state pulsed Nd:YAG laser with a pulse frequency of up to 100 Hz and pulse duration of 150 μs to 1 ms; a Kvant-15 solid-state pulsed Nd:YAG laser with a pulse frequency of up to 5 Hz, pulse duration of 10 μs to 100 ms, and peak power of several megawatts to 1.2 GW; and an LS-06 ytterbium laser with a fiber-optic transmission system. Experiments on a new generation fiber-optic setup were carried out for the first time. Its efficiency is 30%, which is higher than the efficiency of Skat 301 and Kvant-15 pulsed lasers by almost an order of magnitude. Fiber-optic LS-06 ytterbium laser allows the radiation power to be varied from 0 to 600 W. The instrument operates in continuous mode; the modulation frequency of power output is 5 kHz, the spectral width is 10 nm, and the radiation wavelength λ is 1070 nm.

We examined the effect of laser radiation on mineral aluminosilicate samples from alluvial gold deposits containing dispersed gold particles which cannot be extracted by gravity methods.

Microscopic analyses were carried out using a LEO EVO 40HV scanning electron microscope (Carl Zeiss, Germany) equipped with an INCA-ENERGY energy-dispersive analyzer. It was found that laser irradiation induces formation of enlarged spherically agglomerated gold particles on the aluminosilicate matrix. The topography of mineral samples was examined with the aid of a secondary electron (SE) detector. In addition to SE detector, a backscattered electron detector (BSE) was applied. The latter ensures a higher atomic number resolution, so that phases with higher average atomic number appear in a BSE image more contrast than those with lower average atomic number. Insofar as the difference in the atomic weights of gold and other elements contained in the mineral samples under study is fairly large, gold can be visually detected in the resulting contrast images. We observed a difference in the surface topography of agglomerated gold particles obtained by the action of pulsed and continuous laser irradiation.

Local qualitative and quantitative chemical analyses were carried out with the aid of an INCA-ENERGY energy-dispersive X-ray spectrometer (EDX) (sensitivity ~0.1%, electron beam width ~20–30 nm, electron beam penetration depth ~ 1 μm). The EDX study confirmed agglomeration of gold and revealed qualitative and quantitative difference in particle surface topography (Figs. 1, 2). The observed differences originate from gas-dynamic processes initiated by short laser pulses with a millisecond duration and continuous laser irradiation over a period of 1 to 20 s. In the first case (pulsed laser radiation), the surface of agglomerated gold particles is more even (Figs. 1d–1h) than that observed after continuous laser irradiation (Figs. 2a–2f).

As a result of gas-dynamic processes occurring under the impact of pulsed and continuous laser radiation, agglomerated gold particles lose surface continuity. The shape of surface cracks depends on the conditions of laser irradiation. Pulsed laser radiation produces irregularly shaped holes (Figs. 1d, 1g) with ferruginized aluminosilicates (Figs. 1f, 1g; dark

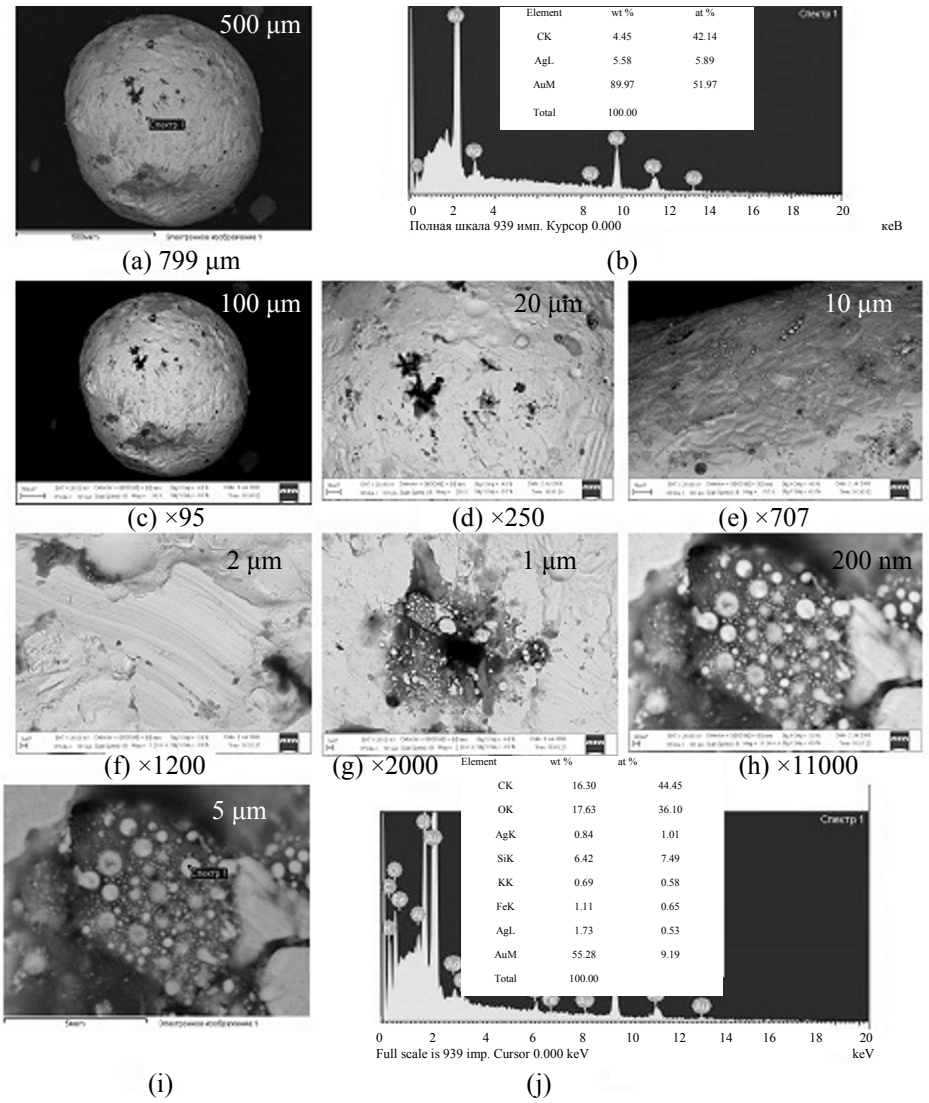

Fig. 1. SEM images of a spherical agglomerated gold particle formed as a result of pulsed laser irradiation and some parts of its surface: (a) a 700-μm gold particle with the elemental analysis area marked with a dark rectangle; (b) spectrogram and EDX elemental analysis data for the marked area in (a); (c–h) different parts of the gold particle surface at magnifications of (c) ×95, (d) 250, (e) ×707, (f) ×1200, (g) ×2000, and (h) ×11 000; (i) nanosized objects with the elemental analysis area marked with a dark rectangle; (j) spectrogram and EDX elemental analysis data for the marked area in (i).

background) and nanosized gold inclusions at the edge. Continuous laser irradiation leads to the formation of rounded gas holes. The surface of agglomerated gold particles is characterized by a high roughness (Figs. 2a, 2d); in addition, structural ordering of the resulting ridged surface is observed, presumably due to high-temperature gas-dynamic flows (Fig. 2f). Thus, laser treatment of gold-bearing mineral samples in both pulsed and continuous modes gives rise to fast processes leading to the formation of different gold surface structures; general relations holding in agglomeration and concentration of ultradispersed gold which cannot be extracted by gravity methods were also revealed. As shown in [6], thermocapillary forces provide the main contribution to the laser-induced enlargement of gold particles from nanoscale to a practically significant level (hundreds of microns).

The agglomeration process can be described by a nonlinear thermal conduction equation for one-

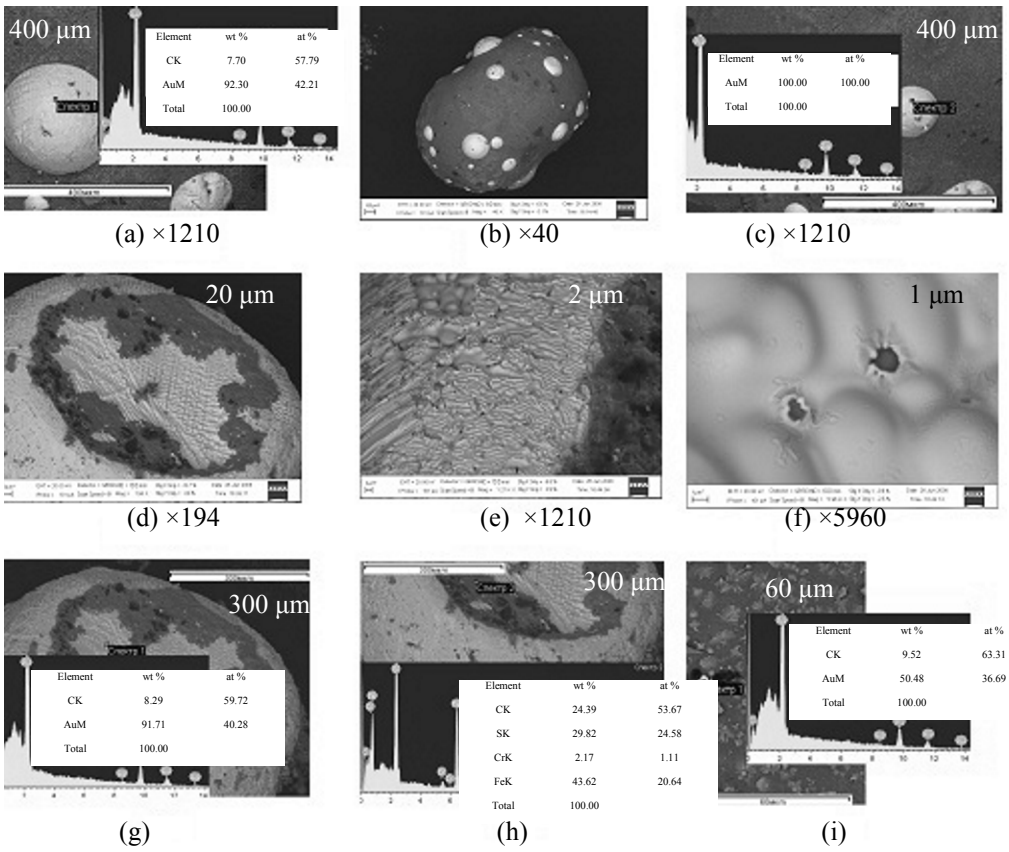

Fig. 2. SEM images of a spherical agglomerated gold particle formed as a result of continuous laser irradiation (LS-06) and some parts of its surface at magnifications of (a, c, e) ×1210, (b) ×40, (d) ×194, (f) ×5960, (g, h) 300 μm, and (i) 60 μm. Elemental analysis (EDX) areas are marked with dark rectangles.

dimensional case with account taken of laser radiation parameters. The efficiency of this process is largely determined by temperature distribution in the irradiated sample, which depends in turn on the laser irradiation parameters.

Problems related to determination of the temperature field are solved with the use of the heat conduction equation (1):

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) = a\nabla^2 T, \qquad (1)$$

where

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplace operator,

$a = \frac{\lambda}{c\rho}$ is the thermal diffusivity, λ is the thermal conductivity, c is the specific heat capacity, and ρ is the density of the irradiated material.

The specific power of laser source is denoted as ω (W m^{-3}). Then the amount of heat liberated in a unit volume per unit time is equal to $\omega \partial x \partial y \partial z$; this amount of heat fits Eq. (1). After analogous transformations, the differential thermal conduction equation with heat sources will be as follows:

$$\frac{\partial T}{\partial t} = a\nabla^2 T + \frac{\omega}{c\rho}. \qquad (2)$$

If a laser hot spot on a sample surface is much larger than the laser penetration depth (as in our experiments), thermal field distribution in the irradiated sample may be described by the thermal conduction equation for one-dimensional case:

$$\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial x^2} + \frac{1}{\rho c} q(x, t), \qquad (3)$$

where $q(x, t)$ is the flux density of the absorbed light:

$$q(x, t) = \frac{P}{S} = \frac{W}{S\tau}, \qquad (4)$$

where P is the laser radiant flux, W is the pulse energy, S is the hot spot area, and τ is the duration of laser impact. The duration of continuous laser irradiation depends on the laser beam scan rate v over the surface, $\tau = (2r)/v$.

Thus the agglomeration process may be described by non-linear thermal conduction equation for one-dimensional case, which includes laser radiation parameters:

$$\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial x^2} + \frac{Wv}{2\rho cSr}. \quad (5)$$

With a view to define the problem in more detail, let us formulate single-valuedness conditions, i.e., the initial and boundary conditions. The initial condition is defined by setting the temperature distribution law inside the sample in the initial moment. In our case we assume that the temperature in all points before irradiation (T_0) is the same and equal to ambient:

$$T(x, 0) = T_0 = \text{const}. \quad (6)$$

While considering nonstationary temperature field ($\partial T/\partial t \neq 0$), it is necessary to apply conjugating boundary conditions in order to define the problem in detail. Throughout the irradiation process, a rounded heat source with a specific power q operates on the sample surface, and the supplied energy is completely consumed for heating of the sample.

Then, the boundary condition for the thermal conduction equation is given by

$$\lambda\frac{\partial T}{\partial x}\Big|_{x=0} = q. \quad (7)$$

As analytical solution of nonstationary thermal conduction equation (5) for one-dimensional case with the initial and boundary conditions set by Eqs. (6) and (7), respectively, we obtain

$$T(x, t) = \frac{q}{c\rho L}\left[1 + 2\sum_{n=1}^{x}\cos\left(\frac{n\pi x}{L}\right)\exp\left(\frac{n^2\pi^2}{L^2}\right)at\right], \quad (8)$$

where L is the sample dimension characteristic which determines the range of variation of x ($0 \le x \le L$).

The obtained temperature field distribution [Eq. (8)] can be used to optimize the parameters of laser irradiation (duration, pulse energy, beam diameter, focal length) with a view to obtain gold particles as large as possible, which should facilitate their sub-sequent extraction.

In summary, the process of laser-induced agglomeration of gold particles has been described in terms of a non-linear thermal conduction equation for one-dimensional case with account taken of such parameters as irradiation duration and intensity, diameter of beam defocusing, and thermal characteristics of substrate. The initial and boundary conditions have been formulated, and an analytical solution of the non-stationary thermal conduction equation has been obtained.

The physical model of temperature field distribution developed on the basis of the generalized thermal conduction law [7–9] can be successfully used in numerical studies of laser-induced agglomeration of ultradispersed gold and selection of optimal thermal exposure modes. Structural modification of gold-containing materials by the action of laser irradiation, specifically concentration and enlargement of submicron gold particles on silicate surface, makes it possible to extract gold at the submicron level [10, 11].

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 13-05-00586) and by the Far Eastern Branch of the Russian Academy of Sciences (project no. 12-III–A-08-179).

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