# Plasmachemical Process of Destruction of Sulphide Polymers

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## Abstract

The process of destruction of sulphidic polymers is investigated and mechanism of formation of laser erosive plasma is offered. The using of modulator of good quality allows obtaining of ordered structure of laser plasma, which is formed as a toroid and kept by own magnetic field. The process of plasma formation and movement over the surface of the sample proceeds in three stages.

At the first stage the dense hot nucleus of a torch absorbing laser radiation is formed. At the second stage there is a transition of thermal energy of plasma into kinetic energy of the directed dynamic movement. At the third stage – the plasmoid, having reached the maximum value of rate, is sharply hindered owing to interaction with the air medium, reorganization of the plasma dynamic movement itself takes place. Processes of plasma states under different conditions are separated both in space and in time.

## Introduction

In the past few years, a new tooling - light impulses with duration of nano, pico and femto seconds – has appeared in the laser technique [1]. Features of light pulses of so small duration determined new experimental possibilities. Alongside with small duration, narrow spectral width and coherency of a light pulse a special attention should be paid to peak power of laser impulses (high intensity at insignificant energy of the impulse). It means that it is easy to bring about multiquantum processes of absorption, *i.e.* form highly excited molecular systems and use numerous nonlinear methods of spectroscopy without heating a sample.

Specified features of a new tooling determined a new area of research in chemical kinetics, which was called "femtochemistry". The problems of femtochemistry are the research of dynamics of the intramolecular processes and a transition state, study of kinetics of ultrarate processes and regulation of chemical transformation. It is necessary to note the possibility to investigate the dynamics of the transition state in a real time. The transition state is understood as a set of configurations that are acquired by the reacting chemical system when passing from reagents to products.

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The process of dissociation can be presented as follows:

$$BC + h\nu \rightarrow [B...C]^e \rightarrow B + C \qquad (1)$$

where $[B...C]$ is a transition state, and $[B...C]^e$ is a transition state on an electron-excited surface of potential energy.

## Results and Discussion

One of the most interesting effects of interaction of laser radiation with a chemical compound is appearance of laser erosion plasma (LEP) over the surface of target materials [2]. The most important property of plasma is that it is the motion of collective particles. There are various ways of plasma retaining with the help of magnetic field: retentive magnetic field may be either external or internal, generated by its own magnetic field in plasma itself.

Under the conditions when the longitudinal current is formed by a closed circle in plasma, it is similar to a toroidal magnetic trap, for which the conditions when magnetic lines are closed and parallel to the torus axis are necessary. In this case, plasma particles should be retained inside the torus and move in a closed ring.

A plasma flow in the magnetic field may be either laminar, *i.e.* a jet flow (Figs. 1 a, b), or turbulent, *i.e.* a vortex flow (Fig. 1 a).

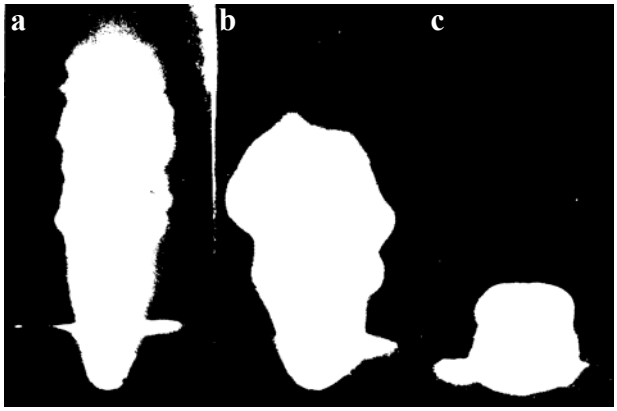


Fig. 1. Profile of a torch of a substance emission: a) Loose oscillation of radiation, $\tau_u$ = 4 ms; b) Passive modulation of quality factor, $\tau_u$ = 0.05 ms; c) Electrooptical modulation, $\tau_u$ = 30 ns

As the results of optical-spectral investigations showed, three characteristic zones differing in density of particles, their temperature and character of gas-dynamic motion, may be marked out at different distances from the surface of inorganic polymers being irradiated at flux density of laser radiation in the range of $10^3 \div 10^{10}$ W/cm$^2$ [2].

Zone 1 – a solid hot nucleus of a torch absorbing laser radiation.

Zone 2 – an acceleration zone, where the transition of plasma thermal energy to the kinetic energy of directed gas-dynamic motion takes place.

Zone 3 – a zone, where a plasmoid after reaching the maximum value of velocity is sharply hindered due to interaction with air medium. In this zone reorganization of the plasma gas-dynamic motion itself takes place.

General shape and sizes of a torch in axial and cross-section to a great extent depend on the value of flux density of laser radiation $q_u$. Apart from $q_u$, another important factor influencing the LEP heating and scattering in air atmosphere is the relation between time of operation of laser impulse $\tau_u$ and time of gas-dynamic scattering of plasma $\tau_p$, which is determined by plasma lifetime in the field of a hot nucleus of a clot, *i.e.* value $r_0/c_s$, where $r_0$ is the initial size of plasmoid, approximately equal to the radius of a focusing spot of laser radiation, and $c_s$ is sound velocity in plasma. In the course of interaction of laser radiation impulses of nano-second duration with a substance, a gas-dynamic flow is established, when $\tau_u > \tau_p$.

Laser plasma leaves a hot field in time $\tau_p$, much less than duration of the impulse acting upon a target. Indeed, as the rate of plasma movement at the surface of target material being irradiated $\upsilon = 10^7$ cm/sec (a mode of rapidly modulated quality factor), and values of plasma radius $r_0 = 10^{-2}$ cm, the characteristic time of scattering will be equal to $\tau_p = r_0/\upsilon = 10^{-9}$ s, while $\tau_u = 3 \cdot 10^{-8}$ s, that is $\tau_p < \tau_u$ [3].

When plasma leaves the field $r < r_0$ (Zone 1), it is accelerated and its further motion is determined by the conditions of the medium. Expansion of a plasmoid in air medium occurs due to of pressure gradient (Zone 2) and is consequently characterized by a greater velocity in the direction, perpendicularly to the surface being irradiated, than in the direction parallel to it. Thus, in the first approximation, a quazi-one-dimensional model of plasma expansion with a density gradient may be used.

The transition of the absorbed energy of a laser impulse into kinetic energy of an ordered motion of particles takes place at adiabatic plasma expansion due to pressure gradient. For nano-second impulses at the flux density of radiation $q_u \approx 10^9 \div 10^{10}$ W/cm$^2$, velocity of expansion reaches the asymptotical value in time approximately equal to a half of laser impulse duration, and at distances from the place of plasma formation of about $10r_0$, where $r_0$ is the radius of a focal spot of laser radiation.

Processes of plasma states under different conditions are separated both as in space, and in time. Plasma that left the area of a hot dense nucleus, in no way influences the area of subsonic flow.

After having reached the maximum value of velocity due to acceleration the plasmoid is sharply hindered by the interaction with the atmosphere of air medium. That accounts for the appearance of a secondary zone of intensive luminescence of a torch. In this zone a gas-dynamic motion of a plasma cloud is reorganized (Zone 3).

Practically, at all stages of its scattering, laser plasma is always electricaly neutral. The motion of particles in it occurs so that electrons cannot break off from ions. Therefore, the motion of a plasmoid is a collective one.

Figure 2 shows the results, verifying the formation and reorganization of a gas-dynamic motion of a plasma torch. The pictures were taken at different distances from the target surface, which correspond to zones 1, 2, 3.

Figure 3 shows the picture of plasma formation taken at the distance > $30\text{-}40\, r_k$. The plasmoid is destructed and the temperature decreases up to the temperature of air medium.

It becomes difficult to retain plasma in a toroidal

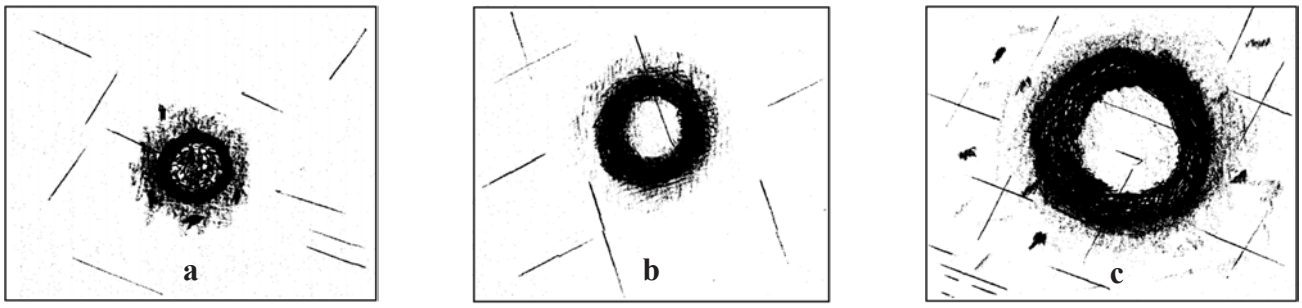


Fig. 2. Formation and restructuring of a torch above the surface of a sample: a – at a distance of ≈ $10r_k$, b – at a distance of ≈ $15r_k$, c – at a distance of ≈ $25r_k$

trap because the magnetic field in it cannot be uniform. Magnetic lines of force get thickened to the interior side of a torus. Thickness of force lines determines magnetic density and, hence, magnetic pressure, which is greater from the interior side of a torus than from the external one. This magnetic pressure gradient presses plasma out to the external side of a torus that further leads to plasma scattering (Fig. 3).

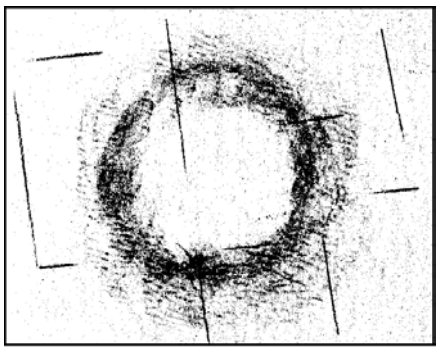

Fig. 3. Structure of a torch above the surface of a target at a distance of > 40.

The possibility of gas-plasma cloud formation in the form of a toroidal vortical ring, which moves in the air medium according to the laws of quasi-elastic body, experimentally determined by us, is of considerable interest for controlling the behavior of a gas-plasma cloud motion in the air medium (Figs. 1 c, 2 b, c and 3) [2].

The obtained result is in a good agreement with the data of the work [4], obtained at erosion of metals by a high-frequency spark: in 25 μs after chopping of a spark discharge, metal fmes form a toroidal cloud.

Mathematical description of ordered motion of gas-plasma formations in the air may be made by analogy with the models of vortical rings formed with the help of impulse generators of vortexes [5]. The method of obtaining and development of ordinary fume rings (Reynolds number Re >> $10^3$) may serve as one of the most simple dynamic models to account for the peculiarities of the formation and behavior of coherent gas-plasma formation.

The velocity of a general translational motion of a ring vortex in the air atmosphere is less than that of a plasma jet one (Fig. 1 a), which is characteristic of the effect of millisecond laser impulses with irregular spikes, when destruction of samples is accompanied by formation and interaction of a series of separate plasmoids with each other and the environment. That is why in the formation of separate erosive plasmoids in the air environment with the help of pulsing-periodic lasers it is necessary to take into account the frequency of recurrence of impulses. The results showed that the frequency of sequences of nanosecond impulses being equal to 2 Hz, provides a good reproducibility of dynamic and spectral characteristics of plasma torches.

Optimum value of flux density of laser radiation is $q_u \approx 10^{10}$ W/cm$^2$. This mode provides a stable character of gas-dynamic movement of LEP torch in the air atmosphere and the best reproducibility of plasma spectral characteristics.

The process of destruction of inorganic polymers under the influence of laser radiation is very complex and multistage. However, the study of kinetics of laser destruction process of sulfide polymers and LEP occurrence, LEP structure and parameters are of a great scientific-practical interest for development of new technological schemes of mineral raw material processing.

As all major natural polymers are obtained by polycondensation, destruction being an inverse process takes place due to pyrolysis of these polymers. The process of laser destruction takes place in an open system at atmospheric pressure in the air and is as follows:

- for chalcopyrite monomineral:

$$2CuFeS_2 \rightarrow Cu_2S + Fe_2S_3 \rightarrow 2Cu + 2Fe + 4S \quad (2)$$

- or in the presence of impurities in chalcopyrite:

$$CuFeS_2 + O_2 + Me \rightarrow Cu_2S + \ldots + Fe_2S_3 + \ldots + SO_2 + \ldots + Me \rightarrow$$
$$\rightarrow Cu + \ldots + Fe + \ldots + Me + \ldots + O_2 + \ldots + S \quad (3)$$

where *Me* - different impurities in a sample of mineral raw material.

In a real situation, the process is much more complex. Destruction in a plasma-chemical process goes on until the matrix of chalcopyrite breaks up completely to neutral atoms and ions.

Atoms, molecules, or ions can take part in elementary acts of reactions depending on the nature of reacting systems and conditions of their interaction. According to this, there are simple, ionic and radical reactions.

Probability of simple (between molecules) reactions is very small, high energy of activation (150-450 kJ/mol) is required. Reactions with participation of charged particles (ions, electrons) or those proceeding with intermediate formation of free radicals are more probable. Activation energy of ion-ion or ion-molecular interactions is very low (80 kJ/mol). Free radicals, atoms being among them, are extremely reactive, and activation energy of radical reactions is even lower, than that of ionic ones – 0-40 kJ/mol [1].

One more feature of radical reactions is that it is a chain reaction. One primary act of activation results in disintegration of a great number of molecules of initial substances. This or that way, molecules acquire excess energy and undergo deformation (valence angles, interatomic distances change) and disintegrate to ions and radicals (atoms). In the latter case, the reaction is of a chainomatic character and is frequently accompanied by an explosion, *i.e.* occurs instantly.

## Conclusions

The problem of obtaining steady gas-plasma formations in the air atmosphere under the influence of single impulses of laser radiation on a sample is studied little at present.

It represents a great interest of fundamental character for the processes of LEP formation and needs additional special researches.

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