CONDITIONS ACCOMPANYING FORMATION OF LONG-LIVING LUMINOUS OBJECTS FROM DISSIPATING PLASMA OF ELECTRIC DISCHARGE IN WATER

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In the work we submit results of experimental research into dynamics of long-living luminous objects (LLLO) formation, spectra of radiation of dissipating plasma and calculations of time dependence of degree of ionization, pressure, temperatures and chemical compound of products of disintegration. The received data specify that LLLO consist from unusual power-consuming connections of oxygen and hydrogen.

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EXPERIMENTAL RESULTS

Long-living luminous objects (LLLO) are formed as a result of electric discharge in water [1-5].

The basic scheme of experimental installation is described in [4]. Shooting of the dynamics of luminous zones and spectra of radiation was carried out with a help of electron-optical chamber (EOC) designed on the basis of time-analyzing EOP PIM-103, supplied with amplifier of brightness PMU-2B. EOC could work in the mode of time-lapse shooting or chronography mode. Registration of spectra was carried out with the help of MUM monochromator.

In Fig.1 the photo, illustrating the formation of luminous objects inside an extending cavity, is submitted. On the photo are shown 9 frames which had been taken with the help of EOC. The exposition of each frame $-2.5 \,\mu$ s, an interval between the frames $-50 \,\mu$ s, the delay between the start of shooting and the moment of the termination of energy release $-50 \,\mu$ s. The order of following of the frames - from left to right, from top to down.



Fig.1. Result of frame-by-frame shooting of the luminous area formed inside the cavity, initiated by electric discharge in water

On the first photo two luminous zones of different sizes are visible. On the second photo the sizes of zones and their brightness have appreciably decreased. Inside the greater zone two objects with brightness appreciably higher than the surrounding are visible. On the following frame it is visible that luminous zones disappear and these two luminous objects exist up to the end of shooting (\geq 350 µs), though they have reduced size (\approx 1 mm). Thus, it is possible to speak, that in 100 µs after the termination of energy release inside the cavity extending in water we confidently registered LLLO. Hence,

the processes resulting in producing of the compounds of which these objects are formed, and the process itself occurs in the mentioned above time.

One of the important factors determining LLLO formation is duration of the discharge. In all experiments of the authors of the report it did not exceed 5 μ s. Average radiance temperature of discharge plasma did not exceed 10⁴ K. In 3 μ s time after the termination of energy release in a continuous spectrum of radiation of dissipating plasma lines of radiation of atoms O and H started to be shown. In Fig.2 the photo received at chronography of the spectrum of radiation from the cavity is presented. Time of chronography – 10 μ s, the delay between the start of shooting and the beginning of the discharge – 5 μ s. In the top and bottom part of the photo basic lines of radiation of Kr with wave-lengths $\lambda_1 = 8059.5$ and $\lambda_2 = 7694.54$ Å accordingly are visible.



Fig.2. Result of chronography of the spectrum of radiation of dissipating plasma of electric discharge in water (a) and of the spectrum of radiation of products of disintegration of water plasma (b)

On Fig.2,a the widened line is visible, the middle of which corresponds to $\lambda \approx 7773.5$ Å. In our opinion, it consists of three lines of radiation of atoms of oxygen with wave-lengths $\lambda_1 = 7775.39$; $\lambda_2 = 7774.17$; $\lambda_3 = 7771.94$ Å. It is necessary to note, that the listed above lines of radiation specify formation in the process or recombination of water plasma of O^{*} atoms in metastable state $\frac{5}{3}S_2^0$ with energy 9.146 eV and radiation life time 180 µs. Obviously, in these conditions atoms of H^{*} in a metastable condition should be formed also with $\frac{2}{2}S_{1/2}$ states, energy 12.09 eV and radiation life time 0.1215 sec.

Approximately in 40 µs after the termination of energy release we registered in the spectrum of radiation of products of disintegration of water plasma groups of lines which appear only at realization of the conditions necessary for LLLO formation. They are observed during \leq 50 µs. The found groups of lines lay in the range 7388...7450 Å and 7910...8000 Å (the error of definition \pm 2 Å). In Fig.2,b the result of chronography of one of such groups of lines is presented. The found groups of lines are similar to oscillatory molecular spectra, but do not correspond to known spectra of radiation of H₂, O₂, H₂O and radical OH.

From the above-stated follows that LLLO formation is preceded with appearance inside the extending cavity of metastable atoms O^* and H^* . Furthermore, LLLO appearance is accompanied by formation of unusual compounds of oxygen and (or) hydrogen.

CONTENTS OF THE CAVITY

As it has been specified, the discharge used for LLLO formation lasts some microseconds. According to the estimations made in [6], plasma under such conditions is equilibrium. Concentration of the charged particles can be estimated by the Saha formula taking into account the effect of decrease in potential of ionization and electrons' adhesion to neutral atoms from the following system of equations:

$$\begin{vmatrix} \frac{n_e n_+}{n_a} = A \frac{g_+}{g_a} T^{3/2} exp - \left(\frac{I - \Delta I}{kT}\right) \\ \frac{n_-}{n_e n_a} = \frac{g_-}{g_a} \frac{1}{A T^{3/2}} exp \left(\frac{I_- - \Delta I}{kT}\right) \\ \Delta I = 2.73 \cdot 10^{-10} \left(\frac{n_e}{T [eV]}\right) \\ n_+ = n_e + n_- \end{vmatrix}$$

where n_e , n_a , n_+ , n_- concentration of electrons, neutral atoms, positive and negative ions of oxygen and hydrogen, accordingly; A = $4.85 \cdot 10^{21} \text{ m}^{-3} \cdot \text{K}^{-3/2}$, g_+ , g_- , g_a – statistical weights of ions of different signs and neutral atoms; *T* – temperature of plasma; *I* – potential of ionization of atoms, ΔI – decrease in potential of ionization; *I*_ – affinity of atoms to electrons; *k* – Boltzmann constant. At $n_a >> n_+$ concentration of electrons can be found from the ratio:

$$n_{e} = \left(n_{a}\frac{g_{+}}{g_{a}}\right)^{0.5} AT^{1.5}exp\left(-\frac{I-\Delta I}{2kT}\right)^{-1}$$
$$\left(AT^{1.5} + n_{O}\frac{g_{-}}{g_{a}}exp\left(\frac{I_{O}-\Delta I}{kT}\right) + n_{H}\frac{g_{-}}{g_{a}}exp\left(\frac{I_{H}-\Delta I}{kT}\right)^{-0.5},$$

where n_O , n_H , I_O , I_H – concentration and potential of ionization of atoms O and H, accordingly.

Taking
$$g_{-}/g_{a} \approx 1/2$$
, we obtain for $T = 10^{4}$ K:

 $\Delta I \sim 0.7$ eV and $n_e \approx 4 \cdot 10^{18}$ cm⁻³, $n = 10^{18}$ cm⁻³. At such degree of ionization the processes of electronic and ion – ionic recombination are determined, basically, by three-fold collisions of ions, atoms and electrons [7]. The frequency of recombination in this case is determined by the following dependencies:

$$v_{e,tr} = \frac{8.75 \cdot 10^{-27} n_e n_+}{T^{9/2} [eV]},$$
 (1)

$$v_{-} = \frac{3.05 \cdot 10^{-30} n_a \sqrt{\alpha} n_+}{\sqrt{A_a} T^3 [eV]},$$
 (2)

where $\stackrel{\wedge}{\alpha} = \alpha / a_0^3$ – atom's relative polarizability, A_a – its

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atomic weight.

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The estimation of recombination speed of the scattering plasma of the electric discharge in water, based on ratio (1) and (2) shows, that in 1.5 µs after the termination of energy release the degree of ionization falls by three orders; the temperature of contents of the cavity thus makes $\approx 6 \cdot 10^3$ K. Thus, the degree of ionization of contents of the cavity is quickly reduced, and LLLO cannot be clots of nonideal plasma.

THE MODEL OF AFTER-DISCHARGE CAVITY

The dynamics of expansion of the cavity was calculated with the help of the Keller-Miksis equation [8]:

$$\left(1 - \frac{U}{c}\right) R \frac{dU}{dt} + \frac{3}{2} \left(1 - \frac{U}{3c}\right) U^2 = \left(1 + \frac{U}{c}\right) \frac{\left(P_g - P_0\right)}{\rho} + \frac{1}{\rho} \left(\frac{R}{c} \frac{dP_g}{dt} - \frac{4\mu U}{R} - \frac{2\sigma}{R}\right),$$
(3)

where U = dR/dt, R – speed of the wall and variable radius of the cavity; c – speed of a sound in water; ρ – density of water; P_g – pressure of gas in the cavity; $P_0 = 1$ atmosphere – hydrostatic pressure in unperturbed liquid; σ , μ – factors of surface tension and viscosity of water.

Expansion of the cavity is accompanied by sharp reduction in density of its contents. The analysis has shown that for such process the pressure of gas-steam mixture (GSM) can be found by Van der Waals equation without taking into account interaction of molecules:

$$P_g = \frac{v_m R_g T}{V - v_m b_m}, \quad v_m = \sum_i v_i, \quad b_m = \sum_i x_i b_i,$$

where v_m – amount of moles of gas-steam mixture in the cavity; R_g – absolute gas constant; T, V – temperature of contents and volume of the cavity; b_m – Van der Waals coefficient for the mixture; v_i , x_i , b_i – the number of moles, molar ratios and Van der Waals constants for components of the mixture.

Heat exchange between the cavity and liquid was taken into account with the help of boundary layer model [9], however, not like in the specified work, we attributed to the transitive layer effective temperature $T_{th} = (T_0 + T)/2$, where T_{θ} – temperature of water. The equation of heat flux through the wall of the cavity in this model has the form:

$$\frac{dQ}{dt} = 4\pi R^2 k_m \frac{(T_0 - T)}{l_{th}}$$

where k_m – heat conductivity of the mixture in thermodiffussion layer; l_{th} – thickness of this layer which was estimated with the formula [10]:

$$l_{th} = \sqrt{\chi_m t},$$

where $\chi_m = \kappa_m/c_p$ – temperature conductivity of the mixture mixes in the boundary layer.

Processes of evaporation and condensation of molecules of steam on the wall were calculated in accordance with Hertz-Knudsen-Langmuir formula which for a flux of molecules through the surface gives:

$$\frac{dN_{\nu}^{d}}{dt} = \sqrt{\frac{8\pi R_{g}T_{0}}{M_{\nu}}R^{2}\alpha_{k}\left(n_{\nu0}-n_{\nu}\right)},\qquad(4)$$

where a_k – factor of accommodation of steam molecules on the wall of the cavity (in the given work it was equal to 0.075 [11]); M_v – water's molar mass; n_{v0} – equilibrium steam concentration at temperature T_0 ; $n_v = n_{H,O}$ –

current concentration of the steam in the cavity. Thermodynamic conditions inside the cavity will be influenced also with chemical transformations of components of the mixture. In the given work the reactions resulting in formation of H, O, OH, H₂, O₂, H₂O, O₃ μ H₂O₂ were considered, too. Speeds of direct and reverse reactions were described by the kinetic equations:

$$r_{f,j} = k_{f,j} n_{tot} n_A, \quad r_{b,j} = k_{b,j} n_{tot} n_B n_B, \quad (5)$$

where k_{fj} , k_{bj} – parameters of speed of direct and reverse reaction; n_{tot} – full concentration of particles in the cavity; n_A , n_B , n_C – concentration of particles of grade A, B and C, participating in the reaction.

Parameters of speed of the reactions were determined with the help of modified Arrenius equation:

$$\begin{aligned} k_{f,j} &= A_{f,j} T^{cf,j} \exp\left(-\frac{E_{f,j}}{kT}\right), \\ k_{b,j} &= A_{b,j} T^{cb,j} \exp\left(-\frac{E_{b,j}}{kT}\right), \end{aligned}$$

where $A_{f,j}$, $A_{b,j}$, $c_{f,j}$, $c_{b,j}$ – parameters of Arrenius equation which had been taken from the work [12]; $E_{f,j}$, $E_{b,j}$ – energy of activation of direct and reverse reaction. For finding the temperature in the cavity in view of the processes described above, we used the equation:

$$\frac{dT}{dt} = \frac{1}{C_{v}} \left\{ \frac{dQ}{dt} - P_{g} \frac{dV}{dt} + \left[4T_{0} - 3T - \sum_{i} \left(\frac{\theta_{i}}{exp(\theta_{i}/T) - I} \right) \right] k \frac{dN_{v}^{d}}{dt} + V \sum_{j} r_{j} \Delta E_{j} \right\},$$
⁽⁶⁾

where C_v – thermal capacity of GSM in the cavity (it is equal to the sum of thermal capacities components of the mixture in view of oscillatory components); θ_i – characteristic oscillatory temperatures of water molecule (5262.4 K, 5404.6 K, 2294.9 K); $r_j = r_{f,j} - r_{b,j}$ and ΔE_j – speeds and thermal effects of the chemical reactions.

In Fig.3 and 4 the results of the numerical calculation of the equations (3), (4), (6) and eight equations describing chemical kinetics in the cavity are submitted. They were made with the help of expressions such as (5).

From graphs in Fig.3 it is visible, that the temperature of contents of a cavity sharply falls in the first 10 μ s of expansions of the cavity, reaching the size $\approx 4 \cdot 10^3$ K. Further, on account of exothermal chemical reactions, the rate of its fall is slowed down and by the moment of confident LLLO registration (see Fig.1), the temperature is $\approx 3 \cdot 10^3$ K. Pressure inside the cavity at this moment is ≈ 0.4 atmosphere. According to graphs in Fig.4 the cavity by this time is filled basically by H, O, OH, H₂, O₂ and H₂O. Concentrations of O₃ and H₂O₂ are negligently small.



Fig.3. Parameters of the cavity at initial stage of expansion; Curves: 1 - radius of the cavity; 2 - temperature of contents of the cavity; 3 - pressure in the cavity



Fig.4. Kinetics of the chemical compound of afterdischarge cavity: 1 - H, 2 - O, $3 - H_2O$, $4 - H_2$, 5 - OH, $6 - O_2(a)$; $1 - H_2O_2$, $2 - O_3(b)$

DISCUSSION

As it was specified in works [1,2] LLLO cannot be the heated up particles consisting of a material of electrodes as the sizes of luminous objects are rather great, and the spectrum of radiation sharply differs from the spectrum of absolutely black body. The material of electrodes cannot play the basic role during LLLO formation as the latter appear only at discharges in distilled water (discharges in hydrocarbons, spirits, etc. do not lead to formation of luminous objects) with the use of refractory electrodes (tungsten, molybdenum, graphite). Thus the spectrum of LLLO radiation does not depend on material of electrodes. The temperature and pressure in the cavity when luminous objects are registered by EOC are such that any condensation of water is impossible. Formation of clots of nonideal plasma as it was specified above is impossible, too. LLLO cannot be simple association of the excited atoms or molecules as they keep integrity and form as at its exit from the cavity to surrounding water [1,2], as at its movement in air with speed up to 50 m/s [3].

All the aforesaid allows us to speak that LLLO are formed of unusual power-consuming compounds of oxygen and (or) hydrogen. In formation of such compounds metastable atoms of hydrogen and oxygen can play an important role. Their formation is evidenced by spectra of radiation of dissipating plasma. Reactionary ability of the excited atoms is much higher, than of not excited ones. Hence, not excited atoms of oxygen and radicals OH, whose concentration is great within the contents of the cavity at a stage of LLLO formation (see Fig.4) will react first of all with metastable atoms. By virtue of significant affinity to electron of atomic oxygen and OH, and to small potential of ionization of metastable oxygen and hydrogen the excited molecules with ionic and not covalent linkage will be formed. The geometry of such molecules will differ from a spatial arrangement of atoms in not excited molecules. For example, atoms of hydrogen and oxygen in a usual molecule of water settle down in tops of a triangle with an angle $\angle HOH = 104.5^{\circ}$. Metastable atom in a state ${}_{2}^{2}S_{1/2}$ will react with radical OH just like atom of an alkali element. In such case $\angle H^*OH = 180^\circ$. Another combinations of the compound are possible, for example O*OH, O*O₂, H*O₂, H₂*O₂, O₂*O₂ etc. Such molecules will possess a stock of energy approximately equal to energy of excitation of metastable atom. Properties of the condensed phase formed from such compounds will sharply differ from properties of water or ice. Release of energy reserved in such excited molecules can lead to fluorescence or luminescence and other effects. The question on life time of such compounds in a gas or condensed phase remains open.

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УСЛОВИЯ ОБРАЗОВАНИЯ ДОЛГОЖИВУЩИХ СВЕТЯЩИХСЯ ОБЪЕКТОВ РАСПАДАЮЩЕЙСЯ ПЛАЗМЫ ЭЛЕКТРИЧЕСКОГО РАЗРЯДА В ВОДЕ

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Представлены результаты экспериментальных исследований динамики образования долгоживущих светящихся объектов (ДСО), спектров излучения распадающейся плазмы и расчеты временных зависимостей степени ионизации, давления, температуры и химического состава продуктов распада. Полученные данные указывают, что ДСО состоит из энергоемких соединений кислорода и водорода.

УМОВИ УТВОРЕННЯ ДОВГОІСНУЮЧИХ СВІТНИХ ОБ'ЄКТІВ РОЗПАДНОЇ ПЛАЗМИ ЕЛЕКТРИЧНОГО РОЗРЯДУ У ВОДІ

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Представлені результати експериментальних досліджень динаміки утворення довгоіснуючих світних об'єктів (ДСО), спектрів випромінювання розпадної плазми та розрахунки часової залежності ступеня іонізації, тиску, температури та хімічного складу продуктів розпаду. Отримані результати вказують, що ДСО складаеться з енергоємних сполук кисню та водню.