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SPECTROSCOPY OF UNDERWATER DISCHARGE PLASMA WITH COPPER AND MOLYBDENUM VAPOUR ADMIXTURES

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This work is devoted to the investigation of plasma parameters (excitation temperature and electron density) of the underwater discharge between two types of metal granules, in particular: between single-component granules of copper or molybdenum, copperized molybdenum, and both copper and molybdenum with a volume ratio of 50%. Optical emission spectroscopy was used to study such plasma of underwater spark discharges between different types of granules. Namely, the excitation temperature was determined by the Boltzmann plot technique, and the electron density was obtained from the width of the spectral lines of hydrogen and individual lines of metal atoms, assuming that the Stark effect is the dominant mechanism of broadening.

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INTRODUCTION

Nowadays, due to the needs of the agricultural technologies, medicine, additive manufacturing [1], synthesis of nano-sized structures of metals and their oxides by erosion of electrodes in a liquid medium [2, 3], there is a growing interest in the research and development of new materials. Underwater discharge plasma is widely used for the synthesis of various nanoparticles, including metal, oxide, and carbon nanoparticles [4]. These nanoparticles, when incorporated into colloidal solutions used as fertilizers, offer numerous opportunities for improving the quantitative and qualitative characteristics of plants and seeds grown for consumption, as well as reducing production costs. Additionally, the intense ultraviolet radiation, electric field, shock waves, and active substances (such as OH radicals and atomic oxygen) generated in plasma-liquid systems are effective agents against many biological and chemical solutions.

It is known that colloidal solutions with copper nanoparticles have good antiseptic, antifungal and antiviral properties, which makes them relevant in applications in the fields of medicine, agriculture and biology [5]. Molybdenum is of practical interest due to its diverse applications and unique properties. Notably, it serves as an essential micronutrient that facilitates nitrogen fixation from the atmosphere by bacteria, aiding in the synthesis of new proteins in plants [6]. As a result, the use of molybdenum in colloidal solutions can greatly enhance the vitality of plants or seeds treated with these substances. Furthermore, molybdenum's low biological toxicity, ease of excretion, and suitability for photoacoustic imaging make it an excellent material for phototherapy, which has superior properties in the field of tumour diagnosis and treatment [7].

The additive combination of the properties of different metals, such as copper and molybdenum, in colloidal solutions of metal nanoparticles is promising. The processes of generating copper and molybdenum nanoparticles in the plasma of underwater electric spark discharges have been previously studied [8, 9]. However, the generation of colloidal solutions containing both of these metals simultaneously has not yet been investigated.

The main aim of this work is to investigate the plasma of underwater electric spark discharge with copper and/or molybdenum vapour admixtures using optical emission spectroscopy. Particular attention is paid to the assessment of the state of the plasma, namely, the realisation of local thermodynamic equilibrium.

1. INVESTIGATION METHODS

The investigations are carried out using discharge chamber specially developed for nanoparticle generation described in detail in [9]. Nanoparticles generation was performed in pulse mode with frequency of 100 Hz, duty factor of 1% and supplied voltage of approximately 30 V. Four different modes of discharge operation are considered, namely using single-component copper (Cu), single-component molybdenum (Mo), copperized molybdenum (copperized Mo), copper and molybdenum granules with volumetric ratio of 50% (Cu&Mo50). Rod granules made of copper (6 mm diameter and 4…5 mm length) and molybdenum (6 mm diameter and 6…7 mm length) were used. Copperized molybdenum granules were obtained by initiating underwater discharges in Cu&Mo50 mode. Thus, during the discharge between the two types of granules, copper (as a more fusible material) was eroded more strongly and partially remained on the molybdenum surface. After that, all copper granules were removed and only molybdenum granules covered with a copper layer remained – the so-called copperized molybdenum.

Emission spectra of underwater discharge plasma were registered using Solar LS SDH-IV spectrometer in the spectral range from 440 to 910 nm and instrumental function of 0.33 nm [9]. The emission spectra were registered over the time. The excitation temperature in plasma was determined by Boltzmann plot technique [10] based on the emission intensity of Cu I 465.1, 510.5, 515.3, 570.0, 578.2, 809.3 nm, Mo I 470.7, 473.1, 476.0, 550.7, 553.3, 557.0, 568.9, 575.1, 592.9, 603.1 nm spectral lines and hydrogen spectral lines of Balmer series, namely H_α 656.3 and H_β 486.1 nm.

The electron density in such plasma was determined from FWHM (full width at half maximum) of H_α, H_β, and Cu I 515.3 nm spectral lines according to Stark mechanism of spectral lines broadening. The dependence of electron density n_e from FWHM of H_α, H_β, and Cu I 515.3 nm spectral lines can be expressed by equations (1)-(3), respectively [11, 12]:

$$n_e[m^{-3}] = 10^{23}\left(\frac{FWHM[nm]}{1.098}\right)^{1.47135}, \qquad (1)$$

$$n_e[m^{-3}] = 10^{23}\left(\frac{FWHM[nm]}{4.8}\right)^{1.46808}, \qquad (2)$$

$$n_e[m^{-3}] = 10^{23}\left(\frac{FWHM[nm]}{0.346}\right). \qquad (3)$$

2. RESULTS AND DISCUSSIONS

The excitation temperatures of underwater discharge plasma determined by Boltzmann plot technique based on the emission intensities of Cu I, Mo I and spectral lines of Balmer series are shown in Figs. 1 and 2.

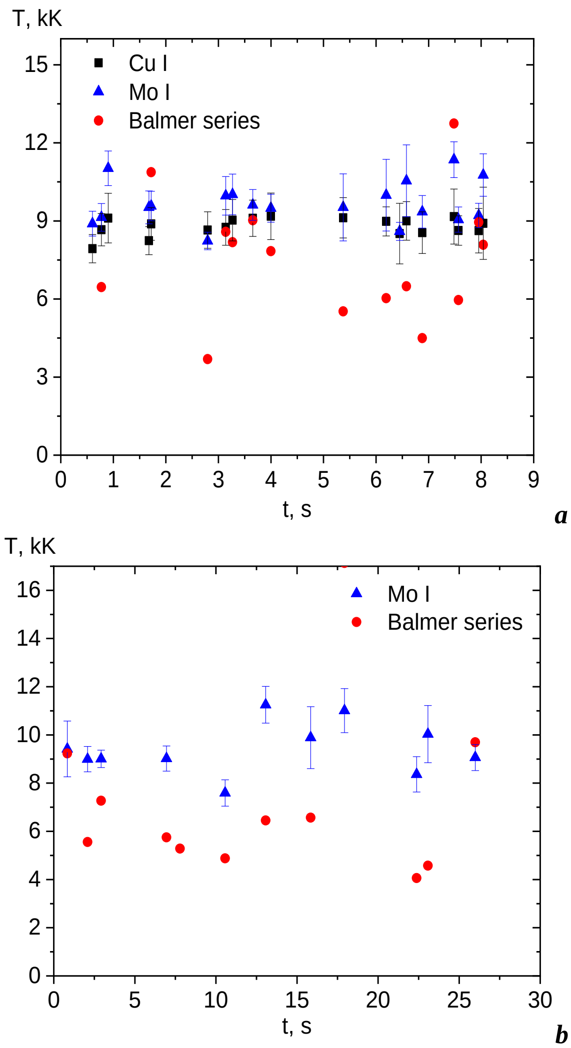

Fig. 1. Distribution of the excitation temperature over the time for the modes: a – copperized Mo; b – Mo

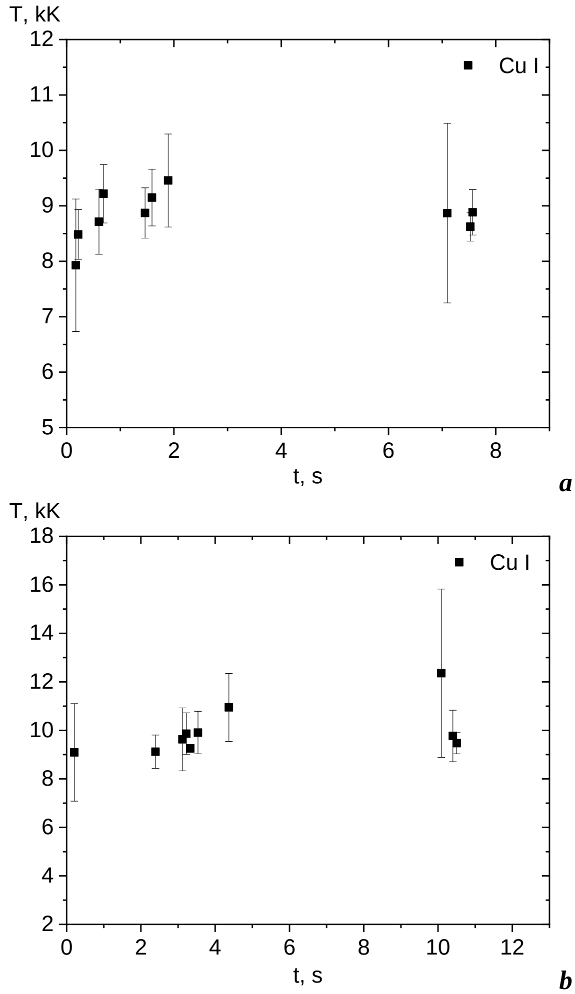

Fig. 2. Distribution of the excitation temperature over the time for the modes: a – Cu&Mo50; b – Cu

It can be seen that for mode copperized Mo the excitation temperatures determined based on the emission intensities of Cu I, Mo I and hydrogen spectral lines of Balmer series coincide within the error (see Fig. 1,a). Thus, it can be assumed that the local thermodynamic equilibrium (LTE) can be realised in the plasma of underwater discharges between copperized molybdenum granules. For mode Cu&Mo50 (see Fig. 1,b), the excitation temperature based on emission intensity of Mo I spectral lines was not calculated due to the absence of low-intensive Mo I spectral lines (470.7, 473.1, 476.0 nm). Therefore, one can conclude, that at such a ratio (1:1) of granules, those that have a lower melting point and better electrical conductivity (in this case, copper) erode more intensively.

The obtained by equations (1)-(3) electron density in plasma of underwater discharge of all modes are shown in Fig. 3.

One can see, both excitation temperature and electron density do not change significantly with time, at the level of fluctuations. Moreover, the average value of both temperature and electron density remains the same for all modes. Thus, one can conclude that the average value of the excitation temperature (which equals to the plasma temperature under the assumption of LTE realisation) and electron density in such types of plasma do not depend on the type of granules immersed in the discharge chamber. The difference can be seen only in the intensity of erosion of materials and, accordingly, in the absolute emission intensity of the corresponding spectral lines.

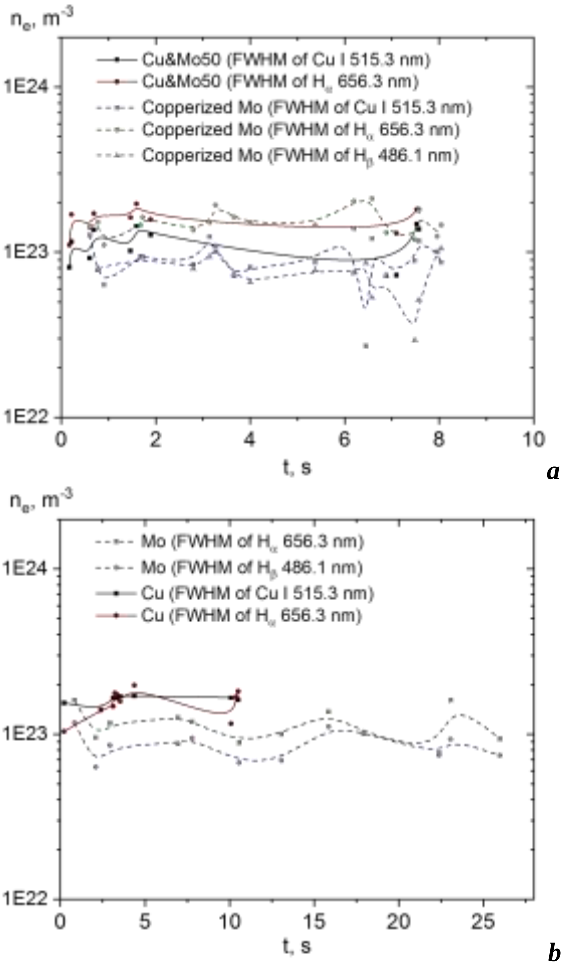

Fig. 3. Distribution of the electron densities over the time for the modes:
a – Cu&Mo50 and copperized Mo; b – Mo and Cu

In order to investigate the dissipation channels in all investigated discharge modes, the number density ratio of atoms of metals and hydrogen was calculated. Based on the experimentally determined excitation temperature and emission intensity of Cu I 510.5 nm, Mo I 553.3 nm and H_α 656.3 nm spectral lines the ratio can be expressed by equation (4):

$$\frac{n_i}{n_k} \propto \frac{I_i \lambda_i^3 \Sigma_i f_k g_k}{I_k \lambda_k^3 \Sigma_k f_i i} e^{\frac{E_i - E_k}{k_B T}}, \qquad (4)$$

where n is the number density of kind i or k; I is the emission intensity of spectral lines with wavelength λ; Σ is the partition function of atoms of kind i or k; f is the oscillator strength of lower energy level of the corresponding spectral transition with statistical weight g; E is an energy of upper energy level; k_B is the Boltzmann constant; T is the obtained temperature. The obtained ratio of n_{Cu}/n_{Mo}, n_H/n_{Cu}, and n_H/n_{Mo} are shown in Fig. 4.

One can see, the number density of copper atoms is approximately 30-50 times greater than that of molybdenum atoms when equal volumes of copper and molybdenum granules are used. In the case of using copperized molybdenum, the number density of copper atoms is still higher (by a factor of about 3). It can be noted that energy in all modes is mostly spent on hydrogen atomization as a component of water, which is indicated by the concentration of hydrogen atoms (4-7 orders of magnitude higher than the concentration of metal atoms).

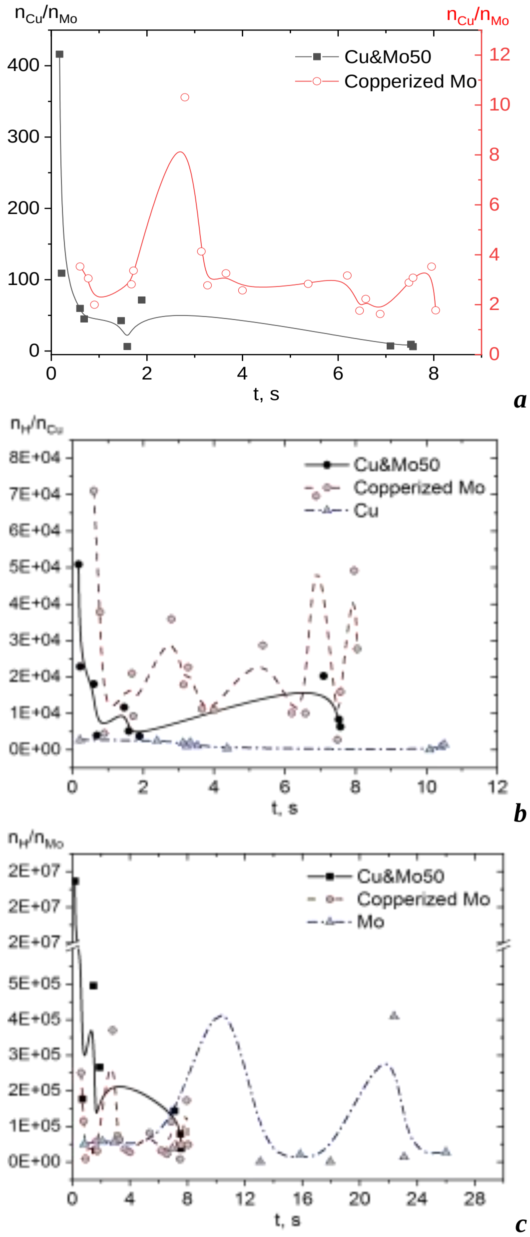

Fig. 4. Distribution of the number density ratios of atoms over the time for the different modes:
a – n_{Cu}/n_{Mo}; b – n_H/n_{Cu}; c – n_H/n_{Mo}

CONCLUSIONS

Plasma of underwater electric discharges between metal granules was investigated. Four different granule materials were used, namely copper with molybdenum granules (50 vol.%), copperized molybdenum granules, copper granules, and molybdenum granules.

Special attention was paid to the thermodynamic state of the plasma of such underwater discharges. It has been found that local thermodynamic equilibrium can be realized in the plasma of discharges between copperized molybdenum granules. This is indicated by the coincidence (within an error) of the excitation temperatures determined by the Boltzmann plot technique based on the emission intensities of Cu I, Mo I and hydrogen spectral lines of Balmer series.

One can conclude that neither the average value of the excitation temperature (9000 K) nor the electron density ($1 \cdot 10^{23}$ m^{-3}) in the plasma of such underwater discharges depend on the type of granules immersed in the discharge chamber. The difference can be seen only in the intensity of erosion of materials and, accordingly, in the absolute emission intensity of the corresponding spectral lines.

It has been found that when using equal volumes of copper and molybdenum granules, the number density of copper atoms is approximately 30–50 times greater than that of molybdenum atoms. In the case of using copperized molybdenum, the number density of copper atoms is still higher (by a factor of about 3). It can be concluded that the granules made from materials with a lower melting point and better electrical conductivity (in this case, copper) are subject to more intense erosion even with very small amounts in the composition of the metal granules.

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СПЕКТРОСКОПІЯ ПЛАЗМИ ПІДВОДНОГО РОЗРЯДУ З ДОМІШКАМИ ПАРІВ МІДІ ТА МОЛІБДЕНУ

А. Веклич, О. Мурманцев, В. Борецький

Досліджено параметри плазми (температури заселення та концентрації електронів) підводного розряду між двома типами металевих гранул, зокрема: між однокомпонентними гранулами міді або молібдену, омідненого молібдену та одночасно міді і молібдену з об'ємним співвідношенням 50%. Для дослідження такої плазми підводних електроіскрових розрядів між різними типами гранул використана оптична емісійна спектроскопія. А саме температура заселення визначалась методом діаграм Больцмана, а концентрацію електронів одержували із ширини спектральних ліній водню та окремих ліній атомів металів у припущенні, що ефект Штарка є домінуючим механізмом розширення.