SPECTROSCOPY OF PLASMA WITH METAL VAPOR ADMIXTURES

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Wide class of diagnostic techniques of plasma of electric discharges in gases and liquids is presented. The admixture of metals vapors in plasma is common feature of these discharges. This one not only changes plasma properties, but gives an opportunity for its diagnostics. Experimental techniques, which allow to define electric arc discharge plasma properties in different media, and after all, plasma composition, are described. The techniques are based on optical emission or laser absorption spectroscopies approaches.

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INTRODUCTION

Studies of properties of electric arc discharge plasma with metal admixtures attracts attention of researchers both from the point of view of scientific challenges and numerous applied problems. As known, processes of electric arc welding and cutting, plasma surface processing, operation of arc light sources and current switching in electrical devices are followed by intense evaporation of details' and electrodes' materials. The alternate application of electric arc discharge plasma is production of nanomaterials. All the mentioned applications require development of diagnostic techniques specifically for the case of electric arc discharge plasma with admixtures of metal.

It is known that during the electrical circuit switching the arc discharge may occur that may lead to contacts' erosion, which, in turn, results in decrease of service time of switches, contactors, etc. Because of this circumstance, a great interest lies in studying of physical processes, which take place in plasma media of such devices during the commutation and on working surfaces of contacts. Combination of high-melting components (for instance, molybdenum, chrome, tungsten) and component with a high electrical conductivity (copper) allows to obtain materials with high exploitation characteristics under conditions of electric arc. Results of investigation of electric arc discharge plasma with admixtures of metals of electrode origin allow to increase the erosion resistance of electrodes due to optimization of material's composition and development of new technologies of their fabrication.

Taking this into account, it presents the vital objective to develop diagnostic techniques of thermal plasma with admixture of metals vapors, which takes place in electric arc discharges, from one hand.

From other hand, there is increasing interest in plasma discharge in liquid, mostly because of its importance in electrical conductivity processes and its practical applications in biology, chemistry, and electrochemistry. Special place within the variety of its exploitations belongs to the water treatment. Due to the low efficiency of the conventional techniques, and presence of a number of disadvantages in other developing and existing methods (i.e. chlorination, ozonation, advanced oxidation processes, photocatalysis) [1-3], application of the electrical discharges in liquid has proven to be one of the most advanced and affordable methods not only for the water treatment (removal of organic compounds), but also in surface treatment and plasma sterilizations (inactivation or killing of microorganisms) [4-6]. Such discharges are the effective sources of simultaneous production of intense UV radiation, shock waves, and various chemical products, including OH, O, HO_2, and H_2O_2 from the electric breakdown in water [7, 8]. Moreover, shock waves produced by high-energy plasma discharges inside liquids are used for various applications, including underwater explosions [9], rock fragmentation [10], and lithotripsy [8]. A great deal of work has been done by Locke et al. [11], who presented the review of the current status of research on the application of high-voltage electric discharges for promoting chemical reactions in the aqueous phase, with particular emphasis on applications to water cleaning. Another important application of the underwater electric discharges, which has attracted significant attention, is the nanomaterial synthesis by plasma-liquid interactions, including plasma-over-liquid and plasma-in-liquid configurations [12].

The nature of the discharges in liquids is much less understood and may be completely different from those for discharges in gases, therefore, in all the mentioned applications, it is important to understand the mechanism and dynamics of the electric breakdown process in liquids. Unfortunately, until now there are no complete physical models of underwater discharges, which makes it of a great scientific interest to investigate plasma discharges in liquid media. Particularly, the studies, carried out in [13] and [14], still is need in the extension aiming to contribute to the better phenomenological understanding. Such investigations are of great interest due to nanoparticles interaction with biological environments. It was found that colloidal substance is the most effective biological form of nanoparticles [15]. Moreover, it is known that solutions of silver and copper have bactericidal, antiviral, pronounced antifungal and antiseptic effects [16], therefore they are considered as perspective new biocides products.

The aim of this work is to present the overview of peculiarities of spectroscopy techniques of both the thermal plasma with admixture of metals vapors, which takes place in electric arcs, and underwater discharges plasma in reactors for metal nanoparticles generation.

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1. OPTICAL EMISSION SPECTROSCOPY OF THERMAL ELECTRIC ARC PLASMA

Vertically oriented electrical arc was initiated between end-surfaces of non-cooled electrodes (Fig. 1). Two types of composite Cu-Mo or Cu-Cr electrodes were used, which were mounted into setup by draw bolt holders.

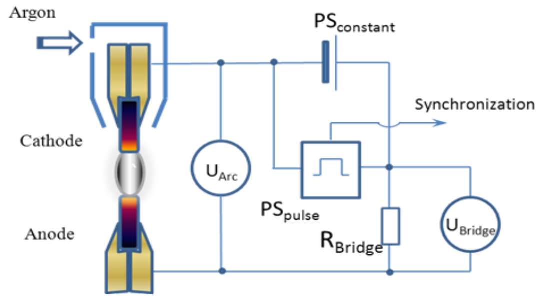


Fig. 1. Electrode assembly, scheme of power supply and electrical parameters measurement

Discharge gap in all the experiments was 8 mm. Electrodes were arranged vertically with their ends opposite to each other. Cathode was installed above and anode – at the bottom. Electric arc plasma parameters were studied at values of discharge currents of 3.5 and 30 A in argon flow. The arc was blown by the working gas flow along the discharge axis using the nozzle. Working gas flow-rate was 6 l/min and was controlled using rotameter. Investigation of flows of different gases shows that in such configuration and gas flow-rate, the flow still remains laminar.

Electrical arc was powered by stabilized power source $PS_{constant}$ of a direct current of 3.5 A. Impulse power source was connected in parallel PS_{pulse} with a microprocessor control. In order to prevent excessive evaporation and electrical erosion of electrode material, impulses of 30 A current and duration of 30 ms were imposed on "regular" current of 3.5 A (Fig. 2). Emission registration starts at 7 ms after high-current pulse initiation and remains near 3 ms.

Since electric arc in the given configuration of the electrode arrangement can easily change its position in the discharge gap, it is reasonable to use method of the rapid-series tomographic registration of plasma emission.

For registration of spatial distribution of spectral lines' intensities of plasma emission, optical scheme based on the MDR-12 (Čzerny-Turner) monochromator was used (Fig. 3). Image of the electrical arc was focused in the plane of the vertical entrance slit of monochromator using long focal lens. In order to study the transversal (radial) cross-sections of arc, the scheme implements a Dove prism, which turns the image through 90°.

Rapid-series scanning of spatial distributions of spectral lines' intensities was ensured by linear CDD sensor Sony ILX526A (B/W) containing 3000 pixels. Specifics of the given scheme is the location of CCD sensor in a sagittal focal plane of an astigmatic spectral device, which allows to avoid the use of additional optical devices.

Typical registered spatial distribution of spectral line intensity (1 in Fig. 4) has a symmetrical shape and is well approximated by Gaussian curve (2 in Fig. 4).

X-coordinate in Fig. 4 corresponds to distance along the entrance slit of a monochromator.

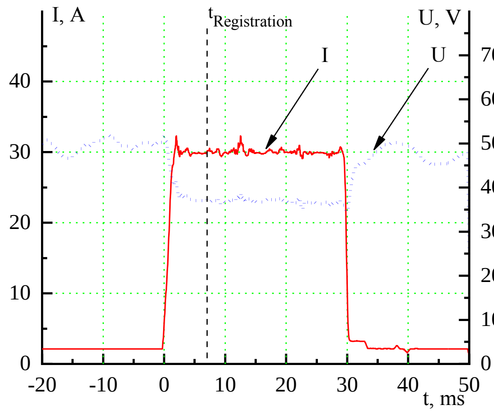


Fig. 2. Current and voltage oscillogram during the impulse (Cu-Cr electrodes)

In order to process spatial distributions of intensities the specially created software interface was used. Since electric arc discharge plasma is non-stabilized in space and time, for every spectral line the registration of 30-40 intensity distributions was performed with their following statistical treatment. The interface allows to exclude from consideration the unsymmetrical distributions and distributions that exceeds the CCD sensor's dynamic range. Afterwards, approximation of distribution by Gaussian function and normal averaging of distribution series were performed.

Calculation of the spectral sensitivity was performed exploiting the standard radiation source – calibrated tungsten ribbon lamp. The emission spectrum was registered using the experimental setup (see Fig. 3), wherein instead of the electrode assembly the given calibration lamp was installed. Spectral sensitivity of the experimental setup (Fig. 5) was obtained by taking into account the lamp radiation distribution and lamp's glass window transmission coefficient.

Since the setup in Fig. 3 allows only for the side observation of the plasma object, the Abel inversion technique [17] was performed for determination of local emissivity values from the registered intensity distributions.

Subsequently, local emissivity distributions were used for a plasma temperature determination by Boltzmann plot technique (Fig. 6). This technique is based on measurement of intensities of spectral lines emitted by a separate element, for instance, copper atom or/and molybdenum. Therefore, significant attention is paid to peculiarities of intensity registration taking into account the spectral sensitivity of the registering device.

Further plasma diagnostics aiming the measurement of plasma temperature by Boltzmann plot technique can be complicated due to possible deviation from local thermodynamic equilibrium (LTE).

One can see, that at the arc periphery (in contrast to axial point) in plasma column of electric discharge in argon flow between copper electrodes at current 3.5 A two groups of atom energy levels are populated with different excitation temperatures (Fig. 7).

So, obviously, the deviation from Boltzmann distribution of energy level populations takes place in this case just for copper atom in the investigated mode of arc discharge plasma (see Fig. 7,b).

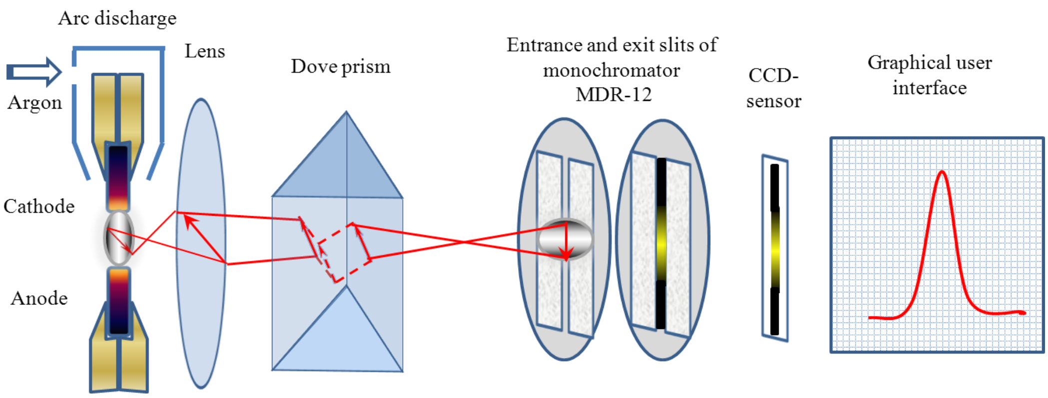


Fig. 3. Optical scheme of setup for registration of spatial distributions of spectral lines' intensities

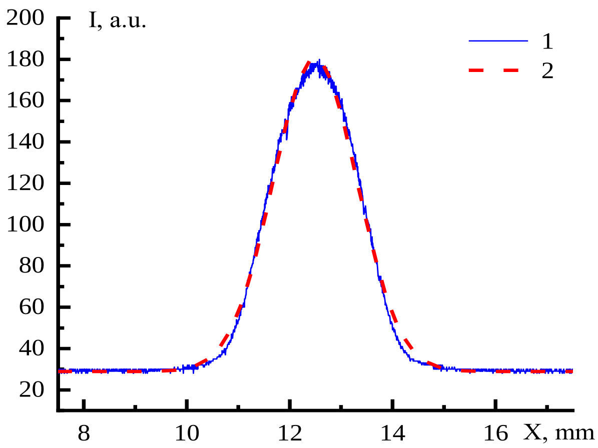


Fig. 4. Spatial distribution of Cu I 510.5 nm spectral line intensity in middle cross-section of electric arc discharge at 3.5 A between Cu-Cr electrodes: 1 – registered spatial distribution of spectral line intensity; 2 – approximation by Gaussian curve

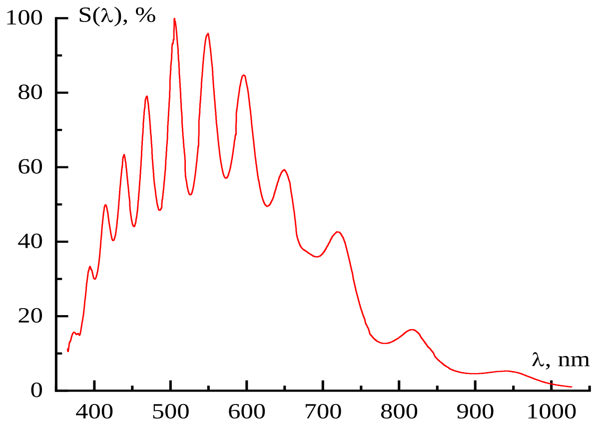


Fig. 5. Normalized spectral sensitivity of the experimental setup

Determination of electron density of thermal electric arc plasma in optical emission spectroscopy (OES) commonly uses dependency of spectral lines' profile broadening on N_e as a result of the quadratic Stark effect [18]:

$$N_e = K \cdot \Delta\lambda \,,$$

where K – Stark broadening parameter which defines the electron density normalized by a line half-width, $\Delta\lambda$ – half-width of a spectral line. Hence, for N_e determination it is required to pick up the spectral line mechanism of broadening of which is a quadratic Stark effect and to study its line profile.

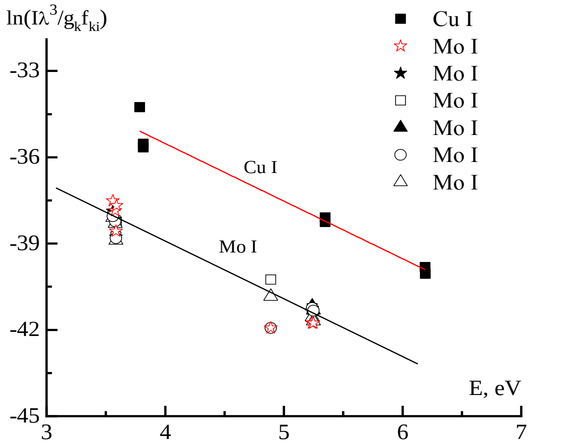
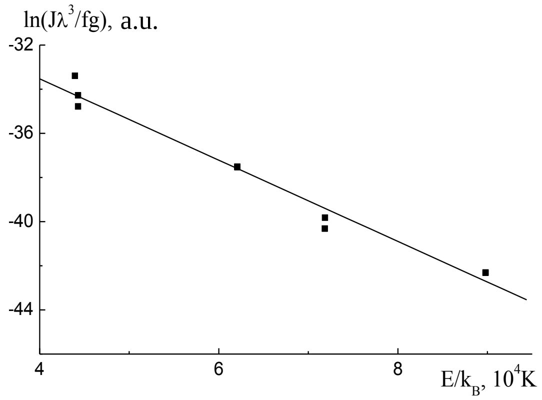


Fig. 6. Boltzmann plot involving Cu I and Mo I spectral lines for the axial point of the middle cross-section of plasma of electric arc discharge between Cu–Mo electrodes at current 3.5 A in argon flow

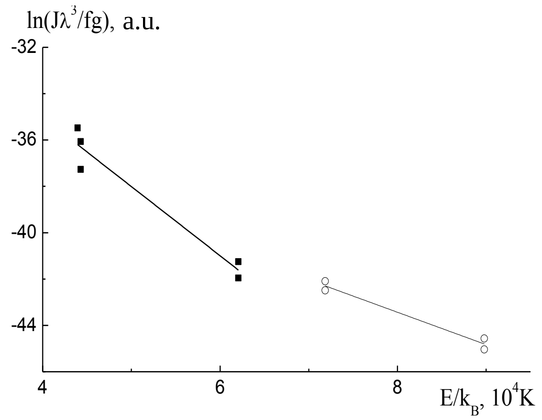
The experimental setup for line profiles' registration consists of a Fabry-Perot interferometer and MDR-12 monochromator (Fig. 8). Transversal cross-section of the electric arc discharge plasma channel was placed in the focal plane of a collimator lens, which forms a parallel beam. Interferometer plays a role of a device with a high resolution. The second lens focuses image (turned through 90° using Dove prism) and forms interferential pattern on the vertical entrance slit of monochromator.

Since spectra of plasma with metal vapour admixtures contain a big amount of spectral lines, therefore, experimental setup includes a monochromator, which separates the necessary system of interferential maximums out of the general picture. Direction of the interferometer's dispersion is oriented perpendicularly to the monochromator's dispersion direction, i.e. along its entrance slit.

Interferogram (1 in Fig. 9) presents a combination of line profiles of the selected spectral lines in different spatial points of plasma object. Interval δλ contains region of the emission spectrum formed by Fabry-Perot interferometer and is called free spectral range of this device. Intrinsic curve (see 2 in Fig. 9), plotted through the maximums of interferogram characterises the spatial distribution of plasma source emission intensity on the given wavelength. In case of the arc channel's symmetry in relation to longitudinal axis, such intrinsic curve is also symmetrical and has an axial maximum. X-axis (see Fig. 9) corresponds to the spatial point on the segment along the monochromator's entrance slit. In such a manner, every interferential maximum can be associated with its distance from the arc axis.



a



b

Fig. 7. Boltzmann plot involving Cu I spectral lines for the axial (a) and periphery (b) points of the middle cross-section of plasma of electric discharge between Cu electrodes at current 3.5 A in argon flow

In addition, note that such technique of line profiles' registration with Fabry-Perot interferometer in optical scheme can be used as a convenient tool for testing of possible self-absorption of spectral lines and, furthermore, for estimation of atom concentrations in arc plasma [19].

At the next step the calculation of equilibrium plasma composition can be carried out and, as a result, the content of different metal vapors in plasma can be determined.

If plasma resides in the state of LTE, it can be characterised by the set of equations which, primary, depend on the particles which are contained in plasma volume [18]. Experimentally determined radial profiles of temperatures, electron density and ratio of emission intensities of spectral lines are the initial parameters of the system. In case of electric arc discharge plasma between composite Cu-Mo electrodes in argon flow, the attention is paid to argon atoms and ions. Besides, due to the thermal effect of discharge on electrodes and their further evaporation, plasma will contain atoms and ions of copper and molybdenum.

The laser absorption spectroscopy can be used for verification of results, obtained by OES, namely, of metal vapor distribution in electric arc plasma [20].

The laser absorption spectroscopy technique was realized in the experimental setup wherein electric arc discharge plasma was examined by laser beam at wavelength of Cu I 510.5 nm. Degree of absorption of such emission in plasma is defined by population of $^2D_{5/2}$ energy level of copper atom.

So, two-dimensional spatial distribution of this level populations and, finally, copper vapor distribution in discharge gap can be obtained in LTE assumption.

The measured distribution of copper atom concentration by this technique is possible to compare with results obtained using the optical emission spectroscopy (Fig. 10). One can concludes that the results coincide within the range of an expected accuracy; therefore, it means that assumption of a plasma thermodynamic equilibrium is correct.

2. OPTICAL EMISSION SPECTROSCOPY OF UNDERWATER ELECTRIC SPARK DISCHARGE PLASMA

Colloid solutions of metal particles are obtained by volumetric electric spark destruction of metal granules. This method lies in simultaneous formation of spark channels in contacts between the metal granules immersed in a liquid. A pulsed voltage supply was used on the base of the specially developed generator [13]. As a result of spark erosion, the part of metal of granules evaporates and, being tempered into a liquid, forms fine dispersion fraction of spark-erosive particles.

Optical emission spectroscopy methods were used for diagnostics of underwater electric spark discharge plasma between metal granules. Plasma emission was registered by the SDH-IV (SOLAR Laser Systems) spectrometer. Toshiba TCD 1304 AP linear image sensor was used as CCD detector. Spectral sensitivity of spectrometer is determined (Fig. 11) and was taken into account in all obtained results. The entrance slit of spectrometer was installed directly towards the quartz window mounted in the bottom of the discharge chamber, which allowed to register the integral spectrum of discharges within 8 ms acquisition time. Experiments with granules of Cu, Al, Mo, Cr, Mg, Ag, Fe, Mn, Co, and Si were performed.

An estimation of plasma parameters was realized for case of copper granules. This is due to the fact that Cu has been thoroughly studied and Cu I spectral lines and their spectroscopic data, that can be recommended for diagnostics of plasma with addition of copper, have been previously selected [18]. The emission spectrum of the discharge between copper granules registered in spectrum range 440…900 nm is shown in Fig. 12.

This spectrum contains not only Cu I spectral lines, but also oxygen triplet (λ=777 nm), and hydrogen Balmer H_α and H_β lines, which is typical for emission spectrum of electric discharge plasma in water [21]. Similar to the case of thermal arc plasma discharge, Boltzmann plot method was implemented as a tool for excitation temperature determination [18] using spectral lines of copper atom. The excitation temperature of plasma in discharge between copper granules at 150 A current was measured as T=(10600±1200) K.

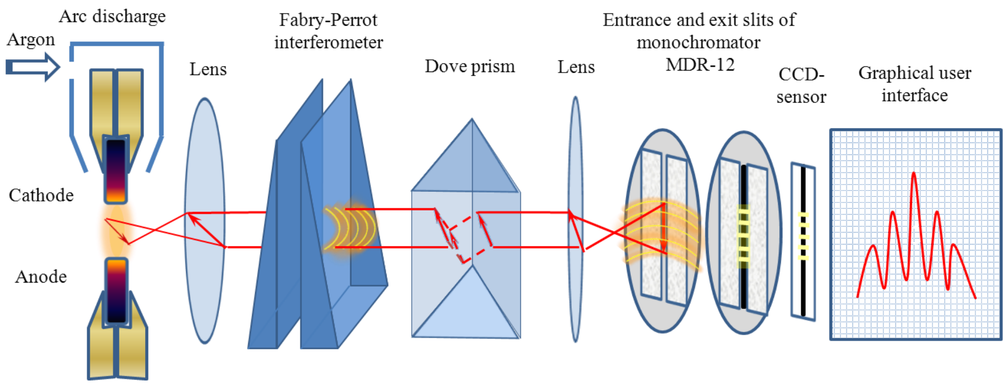


Fig. 8. Optical scheme of the setup for spectral line profiles' registration

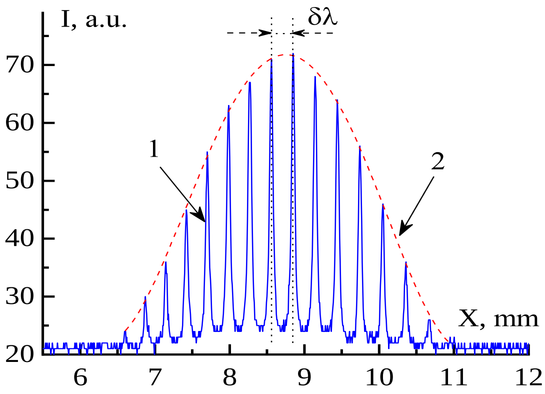


Fig. 9. Interferogram of Cu I 515.3 nm spectral line which is emitted in the average cross-section of the discharge at current of 30 A between Cu-Mo electrodes

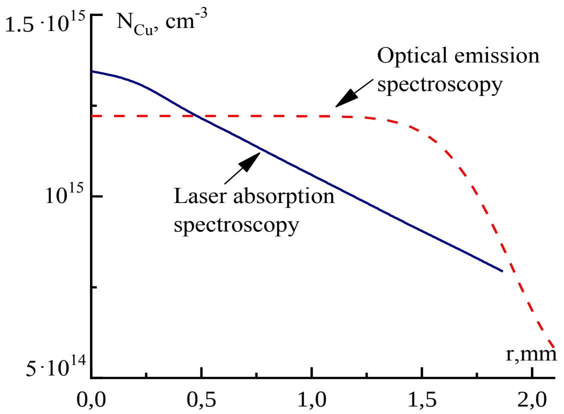


Fig. 10. Comparison of copper atoms' concentration determined by two independent techniques

The values of electron density were obtained using H_β, H_α lines from the following equations presented in [21], which takes into account the ion dynamic effects:

for H_β: $$N_e\left[m^{-3}\right]=10^{23}\times(w_S[nm]/4.8)^{1.46808},$$

for H_α: $$N_e\left[m^{-3}\right]=10^{23}\times(w_S[nm]/1.098)^{1.47135}.$$

Electron density for Cu I 515.3 nm line is obtained from the linear interpolation from the table presented in [22], whereas the theoretical and experimental Stark widths of Cu I lines are listed for $N_e = 10^{17}$ cm^{-3} and $T_e = 10000$ K. These values were assumed as parameters for the estimations presented in this work. In the frame of presented experiments, weak temperature dependence of these constants is neglected. For the selected lines, the influence of all other broadening mechanisms (Doppler, Van der Waals) under these experimental conditions (atmospheric pressure, temperature around 10000 K) is not essential. The half-width of the corresponding lines was determined from the experimentally registered spectra. Electron density is $1.56\cdot10^{17}$ cm^{-3} in electric spark discharge plasma between copper granules at current of $I = 150$ A.

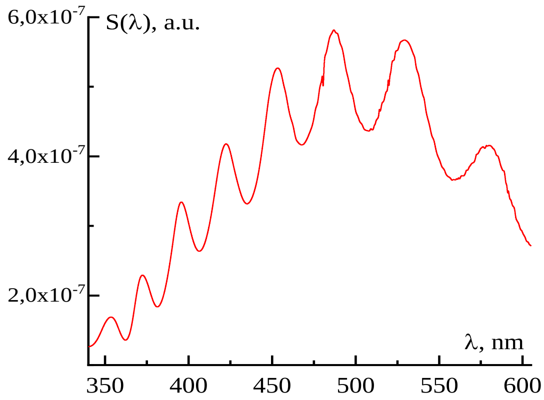


Fig. 11. Spectral response of SDH-IV spectrometer calculated using tungsten ribbon lamp as a standard source of emission in a spectral range λ = 345…605 nm

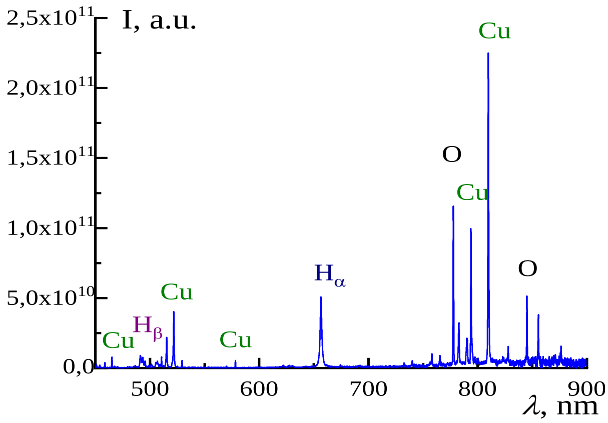


Fig. 12. Emission spectra of electric spark discharge plasma between copper granules: I = 150 A

CONCLUSIONS

Spectroscopy techniques of plasma with metal vapor admixtures are developed. Namely, inhomogeneous and non-uniform thermal plasma in gaseous media and underwater point plasma source are considered.

The Boltzmann plot method is developed to use not only for temperature measurement but for examination of local thermodynamic equilibrium in different spatial points of both types of considered plasma sources as well. The electron density is measured from width of spectral lines broadened by both quadratic (copper) and linear (H_α and H_β) Stark effects in thermal and underwater plasma.

Combination of optical emission and laser absorption spectroscopies is recommended to validate the thermodynamic equilibrium state in studied plasma objects.

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СПЕКТРОСКОПИЯ ПЛАЗМЫ С ПРИМЕСЯМИ ПАРОВ МЕТАЛЛОВ

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Рассматриваются методы диагностики плазмы электрических разрядов в газах и жидкости, отличительной особенностью которых является наличие примесей паров металлов. Свойства исследуемой плазмы, а также особенности ее диагностики полностью определяются такими примесями. Описанные экспериментальные методики позволяют определять не только параметры, но и состав плазмы электрических разрядов в различных средах. В работе использованы методы оптической эмиссионной или лазерной абсорбционной спектроскопии.

СПЕКТРОСКОПІЯ ПЛАЗМИ З ДОМІШКАМИ ПАРІВ МЕТАЛІВ

А.М. Веклич, М.М. Клешич, С.О. Фесенко, В.Ф. Борецький, В.Є. Осідач, А.В. Лебідь, А.І. Іванісік, Т.А. Тменова, Я. Кресо, Ф. Валенсі, К.Г. Лопатько, Є.Г. Афтанділянц

Розглядаються методи діагностики плазми електричних розрядів у газах і рідині, відмінною рисою яких є наявність домішок парів металів. Властивості досліджуваної плазми, а також особливості її діагностики повністю визначаються такими домішками. Описані експериментальні методики дозволяють визначати не лише параметри, але і склад плазми електричних розрядів у різних середовищах. У рамках цього дослідження використані методи оптичної емісійної або лазерної абсорбційної спектроскопії.