PLASMA DIAGNOSTICS

EMISSION SPECTROSCOPY OF TRANSVERSAL ATMOSPHERIC PRESSURE DISCHARGES

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Plasma properties of the transversal discharges (transverse arc and the discharge in gas channel with liquid wall) were investigated by optical emission spectroscopy. Population distribution temperatures of excited states of atoms and molecules in generated plasmas were determined. Relative concentrations of radiating plasma components were estimated by using method suggested in this work. The comparative analysis of plasma parameters of different transversal atmospheric pressure discharges was made.
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1. INTRODUCTION

One of the main approaches to solve the selectivity problem in plasmachemistry is to use nonequilibrium plasma. A great interest today is given to the plasma systems based on the transversal atmospheric pressure discharges such as: gliding arc *GA* [1], gliding arc in tornado *GAT* [2], transverse glow discharge *TGD* [3], transverse arc *TA* [4], discharge in gas channel formed by gas flows immersed into the liquid (discharge in the gas channel with liquid wall *DGCLW* [5]). Presence of transverse blowing gas flows provides the increasing of the heat- and mass exchange between plasma and environment. It also leads inhibits the development of the overheated ionization instability. That is why plasma of such discharges occupies a sizeable volume.

The main results of researching of plasma properties of the *TA* and the *DGCLW* at atmospheric pressure are presented in this work.

2. EXPERIMENTAL SETUP

The scheme of the *TA* discharge in gas flow was described in detail in our previous works [4]. It consists of two rod copper electrodes of 6-mm diameter placed aflat opposite to each other with 1.5 mm of nominal gap between them. The atmospheric airflow was directed from the stainless steel nozzle across the electrodes and formed a bright crescent-shaped electric arc. Since it is a free arc jet it has a convective cooling of the plasma column by the airflow without conductive heat losses at walls. *TA* differs from the non-stationary *GA* of Czernichowski type by the fixed arc length.

Investigated *TA* discharge was powered by the DC source at the ballast resistance R = 2 kΩ in the circuit. To regulate the airflow rate G a standard dry air system supplied with the flow meters was used. The gas flow rates $G = 0…110$ cm^3/s and discharge current I_d (330…660 mA) were kept constant.

The second transverse discharge, which was investigated in this work, is *DGCLW* [6]. It has principal discrepancy from diaphragm and capillary gas-liquid discharges operating in DC mode. Its main advantages are: (i) large ratio of the plasma-liquid contact surface to the plasma volume; (ii) wide variation of gas discharge reactivity; (iii) selectivity of plasma-chemical processes during the treatment. The schematic diagram of *DGCLW* reactor was thoroughly described in [5]. It consists of quartz cylindrical tank. Rod copper electrodes of 3-mm diameter were placed inside glass tubes narrowed to the end, which were installed coaxially nozzle-to-nozzle. The nominal gap between electrodes was 10 mm. The air directed through the tubes along the top and bottom electrodes and formed gas channel connecting both electrodes. The level of the distilled water was kept constant by using the system of communicating vessels. All gaseous products produced during the plasma treatment of the working liquid were output. The water-cooling system was used to cool reactor walls. The discharge was powered by the DC power supply. The current I_d varied from 100 up to 400 mA, the airflow rate $G = 110$ cm^3/s was kept constant during the experimental run.

Diagnostics of plasma parameters of both discharges was made by optical emission spectroscopy (OES). Computer operated CCD-based spectrometer SL40-2-3648USB with spectral resolution ~ 0.73 nm was used for spectra registration in the range of 210…100 nm. Temperatures, which correspond to the population distribution of the excited electronic states of atoms (electronic temperature T^*_e), vibration and rotational levels of molecules (vibration T^*_v and rotation T^*_r temperatures) in investigated plasmas, were determined.

3. METODOLOGY

Determination of mole fractions of the radiating components of nonequilibrium plasma at atmospheric pressure in the case of weakly known composition of plasmaforming gas is very interesting and actual problem. Method of evaluation of relative concentration of neutral and ionic components in generated plasma by using SPECAIR [7] was suggested in this work.

It is know that concentration of emitters (population of the excited state $N_n(T)$) in LTE plasma can be expressed by the total atom concentration of given component $N(T)$, by the excitation energy E_n and partition function $Z(T)$:

$$N_n = \frac{N(T)}{Z(T)} g_n \cdot \exp\left[-\frac{E_n}{kT}\right]. \quad (1)$$

In general case expression for intensity of the electronic-vibrational-rotatonal band observed in emission spectrum of optically thin plasma could be written as following:

$$I_{nm\nu'\nu''J'J''} \approx const \cdot \nu^4 \cdot \frac{N(T)}{Z(T)} \cdot f_{nm} \cdot g_m \cdot q_{\nu'\nu''} \cdot S_{J'J''} \times \quad (2)$$
$$\times \exp\left[-\frac{E_n}{kT_e^*} - \frac{E_v(\nu')}{kT_v^*} - \frac{E_r(J')}{kT_r^*} \right],$$

where ν is a frequency of the spectral transition; $N(T)$– full atom′s concentration of the component; $Z(T)$– partition function; f_{nm}– oscillator strength; g_m and g_n– statistical weight of the lower m and upper n levels correspondingly; $q_{\nu'\nu''}$– Franck-Kondon factor ($\nu'$and ν'' are vibrational quantum numbers of the upper and lower levels corresponding); $S_{J'J''}$– Höhnel-London factor (J' and J'' are rotational quantum numbers of the upper and lower levels corresponding); E_n–energy of the upper excited electronic level n; $E_v(\nu')$ is vibrational term of the excited electron level; $E_r(J')$ is rotational term of the excited electron level; T^*_e, T^*_v, T^*_r are electronic, vibrational and rotational temperatures correspondingly; k–Boltzmann constant.

Then the ratio of molecular band's intensities of two radiating plasma species A_1 and A_2 is proportional to the concentration ratio of these components (N_{A1} and N_{A2} correspondingly) under fixed pressure and temperatures (T^*_e, T^*_v, T^*_r) and to the ration of values, which defines probability of the corresponding spectral transitions:

$$\frac{I_{A1}}{I_{A2}} \approx const \cdot \frac{\nu_{A1}^4}{\nu_{A2}^4} \cdot \frac{N_{A1}(T)}{N_{A2}(T)} \cdot \frac{Z_{A2}(T)}{Z_{A1}(T)} \cdot \frac{f_{nmA1} \cdot g_{mA1}}{f_{nmA2} \cdot g_{mA2}} \cdot \frac{q_{A1}}{q_{A2}} \cdot \frac{S_{A1}}{S_{A2}} \times \quad (3)$$
$$\times \exp\left[-\frac{E_{nA1} - E_{nA2}}{kT_e^*} - \frac{E_{vA1} - E_{vA2}}{kT_v^*} - \frac{E_{rA1} - E_{rA2}}{kT_r^*} \right].$$

Since SPECAIR code uses database of an initial LTE species distribution in air and allows modeling the absolute intensity of spectral radiation emitted by gases and plasmas of various compositions (*N, O, C, NO,* N_2, N_2^+, *OH, NH,* C_2, *CN, CO*) in the wide spectral range for different pressures we proposed method for determining relative concentrations of radiating species in generated plasma in the case of weakly known compound of plasmaforming gas.

At the first stage the identification of emission spectra was made and electronic temperature T^*_e was estimated from Boltzmann plot by using relative intensities of emission lines of blowing gas atoms (*H* and *O*) [4]. T^*_v and T^*_r temperatures were determined by fitting experimental spectrum of the 2nd positive system of N_2 with results of SPECAIR simulation [8]. At the next step the intensity (signal) of each radiating species I_{expAi} was determine from experimental spectrum and corresponding to them wavelengths λ_i were fixed. It is better to carry out this procedure of signal determination in the range free from overlapping spectral bands and lines. After that we simulated emission spectrum of each radiating compound separately by using SPECAIR at previously determined T^*_e, T^*_v, T^*_r temperatures. The absolute intensities of calculated spectrum I_{calAi} at wavelength (where the corresponding experimental signals I_{expAi} were estimated) were determined under fixed pressure (atmospheric in our case). Then the concentration ratio of two radiating species A_1 and A_2 can be evaluated by following formula:

$$\frac{[A_1]}{[A_2]} = \frac{N_{A_1}}{N_{A_2}} = \frac{I_{\exp A1} \cdot I_{calA2}}{I_{\exp A2} \cdot I_{calA1}}. \quad (4)$$

That makes possible to determine relative concentration of each component in the investigated plasma:

$$[A_1]^* = \frac{[A_1]}{\sum_i [A_i]}. \quad (5)$$

4. RESULTS

Emission spectra of *TA* and *DGCLW* plasmas are multi-component and contain 2nd positive system of N_2 ($C^3\Pi_u$-$B^3\Pi_g$), atomic lines *H* (λ=656.3;486.1; 434.05 nm), *O* (λ=777.2; 844.6; 926.6 nm), *Cu* (electrode's material) (λ=324.75; 327.4; 465.1; 510.5; 515.3; 521.8; 578.2 nm). Besides 1st negative system of N^+_2($B^2\Sigma^+_u$-$X^2\Sigma^+_g$), *NH* band ($A^3\Pi^+$-$X^3\Sigma^-$), *NO* γ system ($A^2\Sigma^+$-$X^2\Pi$) and weak *OH* bands ($A^2\Sigma^+$-$X^2\Pi$) were observed in plasma of the *TA* in air. Intensive UV system of OH ($A^2\Sigma$-$X^2\Pi$: (0-0) 306.4-308.9 nm) presents in the spectrum of plasma of the *DGCLW*.

It was shown that population distributions of the excited electronic states of *Cu*, *O* and *H* atoms and of excited vibration levels of N_2 molecule in the investigated plasma are close to Boltzmann for used regimes of both discharges [4]. Thus, for *TA* plasma $T^*_e(O)$≈4200-4600K and $T^*_e(Cu)$≈6800-8200K was determined from corresponding Boltzmann plots, T^*_v≈4000-4600 K and T^*_r≈2000-2800K were estimated from 2nd positive system of N_2 by fitting the experimental spectra with the simulated ones. $T^*_e(O)$≈3700-4300K, $T^*_e(H)$≈3800-4900K, $T^*_e(Cu)$≈6700-7000K, T^*_v≈3500-4200K and T^*_r≈3500-4000K were determined in the investigated plasma of *DGCLW*.

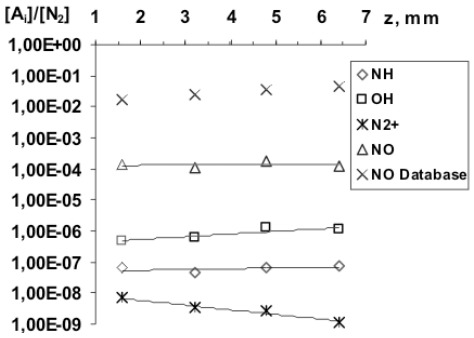
The comparative analysis of plasma parameters of investigated *TA* discharge in airflow with other known sources of non-equilibrium atmospheric pressure plasma was made and the main results are presented in the Table.

Parameters of non-equilibrium atmospheric pressure plasma sources
($^*T$ ($^*NT$) - thermal (non-thermal) regime of GA [1])

Type	*GA* [1]	*GAT* [2]	*DGCLW* [5]	*TA* [4]
Power *P*, W	200-1000	90-300	260-300	220-330
Gasflow rate *G*, cm^3/s	(2-50)×10^3	(0.5-2.5) ×10^3	0.11×10^3	(0.04-0.2) ×10^3
T^*_e, eV	$^*T$: 0.52 $^*NT$: 0.86	> 0.9	(Cu) 0.6 (O) 0.35 (H) 0.35	(Cu) 0.6 (O) 0.35 (H) 0.35
T^*_v, eV	$^*T$: 0.27-0.34 $^*NT$: 0.17-0.26		(N_2) 0.3-0.35	(N_2) 0.35
T^*_r, eV	$^*T$: 0.2-0.34 $^*NT$: 0.07-0.18	0.17-0.34	0.35-0.4	(N_2) 0.1-0.2

Relative concentrations of radiating plasma components of the investigated *TA* in airflow (*G*=75 cm^3/s and I_d=480 mA) were calculated by using suggested method of working with SPECAIR. Calculated relative

concentrations should be taken as a very rough estimate, just indicating the order of magnitude. Distribution of the relative mole fractions of radiating species in the investigated plasma is represented on Figure.



Distributions of relative concentrations of radiating plasma components in TA along the gasflow z (I_d=480 mA, G=75 cm^3/s)

Decreasing of $[N_2^+]$ concentration with increasing of distance from electrodes (z) is in good correlation with excitation temperature distributions. It is clear that ionization processes decreases at the periphery of the discharge. As can be seen from the Figure, amount of *NO* radicals in plasma of the transverse arc is much lower than corresponding values in SPECAIR database for LTE air plasma at the same temperatures. We supposed that it could be explained by the following: the characteristic time of *NO* producing reaction is larger than transit time of initial components (N_2^*, O_2^* and *etc.*) through plasma column.

Regime of the arc in air (at the same geometry but with G=0 cm^3/s) with discharge current I_d=660mA was investigated and the excitation temperatures were determined ($T^*_e \approx T^*_v \approx$6950K, $T^*_r \approx$1750K). Relative concentration of the *NO* radicals in generated plasma was evaluated in this case ($[NO]/[N_2] \approx 4{,}5 \cdot 10^{-3}$). Obtained value is comparable with $4{,}38 \cdot 10^{-3}$ which is represented in SPECAIR database under similar temperature $T \approx$1800K. It can be considered like one more confirmation of our assumption.

CONCLUSIONS

TA generates non-thermal plasma with noticeable increasing of T^*_r along the gas flow. It was shown that level of nonequilibrium of the *TA* plasma is higher then in the *DGCLW*.

Obtained T^*_e of blowing gas atoms (*O* and *H*) are smaller than corresponding values of *Cu* atoms (material of electrodes) due to the additional electron-ion recombination mechanism of excited electronic states population of copper atoms, which is almost absent for atoms of a blowing gas.

The relative concentrations of radiating plasma species (N_2, N_2^+, *NO, OH, NH*) in *TA* were estimated by using SPECAIR. It was shown that relative concentration of [*NO*] evaluated from experimental emission spectra of *TA* plasma is significantly lower then data in LTE air plasma of atmospheric pressure at the same temperatures.

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ЭМИССИОННАЯ СПЕКТРОСКОПИЯ ПОПЕРЕЧНЫХ РАЗРЯДОВ АТМОСФЕРНОГО ДАВЛЕНИЯ

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Методом оптической эмиссионной спектроскопии исследованы свойства плазмы поперечных разрядов (поперечной дуги и разряда в газовом канале с жидкой стенкой). Определены температуры заселения возбужденных уровней атомов и молекул в генерированных плазмах. С помощью предложенного в данной работе метода оценены относительные концентрации излучающих компонент плазмы исследуемых разрядов. Проведен сравнительный анализ параметров плазмы различных поперечных разрядов атмосферного давления.

ЕМІСІЙНА СПЕКТРОСКОПІЯ ПОПЕРЕЧНИХ РОЗРЯДІВ АТМОСФЕРНОГО ТИСКУ

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Методом оптичної емісійної спектроскопії досліджено властивості плазми поперечних розрядів (поперечної дуги та розряду в газовому каналі з рідкою стінкою). Визначені температури заселення збуджених рівнів атомів та молекул у генерованих плазмах. За допомогою запропонованого в даній роботі методу оцінені відносні концентрації випромінюючих компонентів плазми досліджених розрядів. Проведено порівняльний аналіз параметрів плазми різних поперечних розрядів атмосферного тиску.