THE INFLUENCE OF EXOTHERMIC REACTIONS ON THE NONEQUILIBRIUM LEVEL OF DISCHARGE PLASMA

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The comparative analysis of plasma parameters of transverse arc and discharge in the gas channel with liquid wall was made for different working gas and liquids (for air, distilled water and for its mixtures with ethanol). Electronic excitation temperatures T_e^* of atoms, vibrational T_v^* and rotational T_r^* temperatures of molecules in the generated plasma were determined by optical emission spectroscopy. It was shown that both discharges generate non-equilibrium plasma in the case of working gas air and working liquid – distilled water. Adding a fuel (ethanol) into the plasma system with O_2 leads to the increasing of rotational and vibrational temperatures of molecules, which became equal to each other within the errors. This may indicate that the exothermic reactions reduce the level of non-thermality of the generated plasma as a result of additional energy supply for heavy components in the process of complete combustion of hydrocarbons.

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INTRODUCTION

It is known that using of non-equilibrium "cold" plasma, which is characterized by a high level of electrons energy and concentration of excited and charged particles at low gas temperature, takes a special place in the plasma chemical technology. The combination of these conditions allows implement the unique plasma-chemical processes. It is possible to achieve a high selectivity of the process and a product purity in that case [1].

A large number of papers devoted to the studying of chemical transformations of different substances in non-equilibrium plasma of electric discharges have appeared by now [2]. The main goal of most of these works − research of products and mechanism of its formation in order to develop technology of new substances creation, materials with new interesting properties, modifications of existing substances and materials. In most of these studies proposed mechanisms of various processes are based on the research of dependence of product yield or consumption of the initial material on the external plasma parameters - current, input power, flow rate and composition of raw materials, and based on qualitative observations [1, 2].

The quantitative measurements of the internal plasma parameters (the distribution of electric fields in the plasma, concentrations and function of the electron energy distribution, the temperature of the heavy particles, particle distribution function by levels of internal excitation, especially on the vibrational and electronic levels, the concentration of radicals), which affect the speed and the kinetics of processes in plasma, usually are not held. Nevertheless if such measurements are carried out, the measured parameters are not enough for a detailed analysis of the probable mechanisms of processes. Therefore proposed mechanisms are mostly hypothetical and its reliability is low [1]. At the same time, physicochemical processes in quasi-equilibrium and non-equilibrium plasmas are typically multichannel (in the sense that it occurs through a large number of electronic-vibrational or vibrational levels and with the formation of excited intermediate states and excited products in different quantum states). Multichannel physicochemical processes (in the case of deviations from the thermodynamic equilibrium) lead to the fact that direct and inverse processes often occur through a different quantum state. In this case the influence of chemical processes on the plasma parameters almost does not take into account that can radically change the expected result.

It should be taken into account that the influence of endothermic and exothermic chemical processes on plasma non-isothermality is fundamentally different.

The high rates of plasma-chemical reactions are often due to a high concentration of excited atoms and molecules in electric discharges. Vibrational and electronic excitations play the most important role in the stimulation of endothermic processes in plasma mainly due to the reduction of the Arrhenius activation energy E_a. and at the same this reduction E_a is practically absent for exothermic processes [3].

However, L.S. Polak [4] drew attention to an interesting relation of changes of reaction rate constants k at changes of population distribution temperature of the vibrational states − T_v and translational temperature − T_{tr} by example of experimentally studied reactions [5]: $O^+ + N^*_2(v) \rightarrow NO^+ + N$.

The reaction rate constant *k* increases up to 40 times at change T_v from 1000 to 6000 K (when T_{tr} = 300 K), and the same change of the translational temperature (not taking into account the T_v changing) leads to a significantly larger changing of *k* up to 112 times according to Arrhenius expression [6]:

$$k = AT^b e^{-\frac{E_a}{RT}}.$$

Also analysis of information about chemical lasers [7] shows that it can be expected that about half of released energy goes into increasing exactly translational temperature at the exothermic chemical reactions.

Studies of plasma assisted combustion showed that the non-equilibrium plasma can stimulate the low-temperature oxidation of the fuel, even without ignition of the combustible mixture [2].

With taking into account the extremely high level of energy release during the exothermic chemical reactions (≥ 1 eV/mol) all saying above indicates that influence of chemical reactions on the level of non-isothermality of plasma itself can be extremely high. And in the development of plasma-chemical technologies with using exactly non-equilibrium plasma it should to be taken into account.

In this paper were studied the influence of the presence of a small addition of lean burn in plasma gas on non-isothermality of transversal arc plasma (TA) and plasma of discharge in the gas channel with liquid wall (DGCLW). The mixture of ethanol with oxygen of air was used as fuel.

1. EXPERIMENT

Experimental schema of the electro arc discharge in the transverse blowing gas flow (transverse arc – TA) and discharge in the gas channel with liquid wall (DGCLW) were considered in details in [8, 9] correspondingly.

Two copper horizontal electrodes were placed opposite each other and gas flow was directed perpendicular to the electrode axis. TA discharge was powered by the DC source. All measurements were carried out for the discharge currents I_d=0.1…1 A and gas flow G=110 cm^3/s. Different working gases (air and mixture air/ethanol) were used.

For realization the second discharge two copper electrodes were placed inside glass tubes, along which gas flows. Two contrary gas flows immersed into the liquid collide and form the gas channel where discharge burns. Since gas flows through the bubble-liquid interface (outside the gas channel) and evaporation from the liquid is directed inside the bubble (gas channel), thus the intensive transversal heat and mass exchange occurs in this discharge. Discharge current I_d for each regime was varied from 60 to 400 mA. Airflow rate G=55 cm^3/s was maintained constant.

Working gas (air) and different liquids (distilled water, its mixture with ethanol and pure ethanol) were used for DGCLW. Different regimes of the discharge were studied: (i) both Cu electrodes; (ii) one “liquid” electrode with positive polarity – “liquid” anode (LA); (iii) with negative polarity of one “liquid” electrode – “liquid” cathode (LC).

2. METHODS AND RESULTS

Emission spectra of TA plasma were measured by CCD based spectrometer SL 40-3648 *Solar TII* in the range of 200…1100 nm with spectral resolution ~ 0.7 nm.

Population distribution temperature of the electronic states of atoms (electronic temperature T_e^*) in plasma were determined by the relative intensity of the cooper (material of electrodes), oxygen (777.2, 844.6, 926.6 nm), hydrogen (656.1, 486.2 nm) spectral lines by Boltzmann plots. Vibrational T_v^* and rotational T_r^* temperatures of molecules were evaluated by relative intensities of the emission bands of N_2(C-B), OH (A-X) (in the case of air for TA and distilled water for DGCLW), CN(B-X), C2(A-X) (in the case of using mixture air/ethanol, water/ethanol) by using SPECAIR [10] simulation.

Population temperatures distribution along the gas flow in the TA plasma for different working gas is shown on Fig. 1.

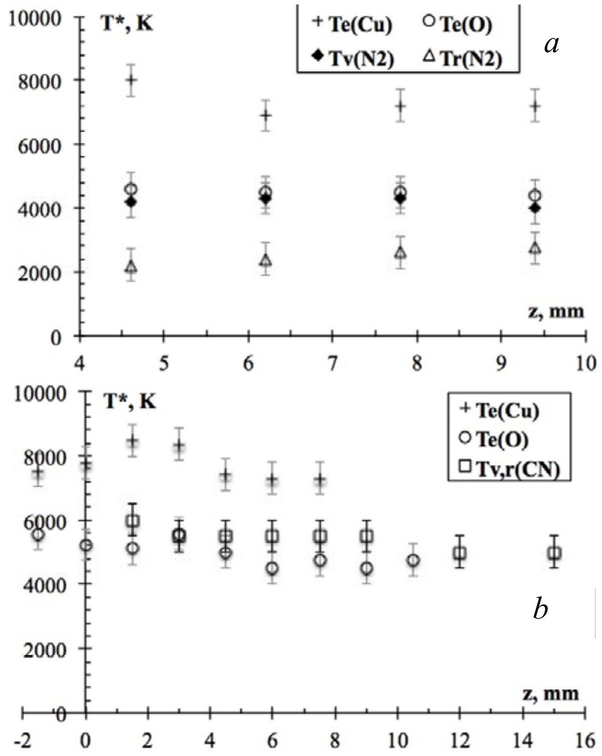

Fig. 1. Distribution of the population distribution temperatures of atoms and molecules in TA plasma along the gas flow z for different working gas: a − air (discharge current I=480 mA); b − mixture air/ethanol=30/1 (I=400 mA). Flow rate G=110 cm^3/s, z = 0 the middle of electrodes for both cases

From Fig. 1,a can be seen that TA in air generates non-thermal plasma

$$(T_r^*(N_2) < T_v^*(N_2) = T_e^*(O)<T_e^*(Cu)).$$

The difference between the temperatures $T_e^*(Cu)>T_e^*(O)$ was explained by different mechanism of population of the excited electronic states of these atoms. Since main positive ions in electroarc discharges with copper electrodes are copper atomic ions and the characteristic time of the ion-ion recombination is comparable with the time of optical transitions in Cu I the additional mechanism of the population of the excited electronic states of cooper atoms occurs due to the ion-ion recombination, which is almost absent for the blowing gas atoms [11].

Increasing of the arc length was observed in the case of adding fuel into the plasma forming gas at fixed discharge current and gas flow. In the case of working with mixture air/ethanol the degree of non-equilibrium of the generated plasma significantly reduces (absolute values of vibrational and rotational temperatures of molecules increase and became equal to each other (see Fig. 1,b). The values electronic population temperatures of copper and oxygen atoms, as well as its distributions along the gas flow, remain the same within the error (see Fig. 1).

Dependences of population distribution temperatures of atoms, molecules and radicals on the discharge current for the DGCLW are represented on Fig. 2.

As can be seen from Fig. 2,a DGCLW generates non-thermal plasma (with noticeable difference between vibrational and rotational temperatures of N_2 molecule).

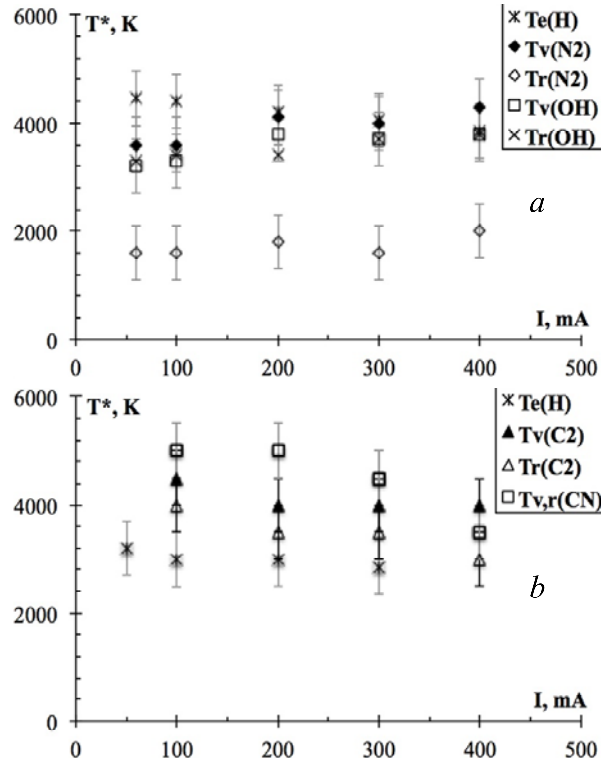

Fig. 2. Dependences of population distribution temperatures of atoms and molecules in the plasma of DGCLW on the discharge current. Discharge mode - "LA", air flow G=55 cm^3/s: a) - distilled water; b) - solution of water/ethanol (1/5)

At the same time $T_v^*(N_2) \approx T_v^*(OH) \approx T_r^*(OH)$ within the marked error and $T_v^*(N_2) < T_e^*(H)$ at low currents ($I \leq 100$ mA). With discharge current increasing the level of non-equilibrium decreases, but the difference between all determined temperatures and rotational temperature of nitrogen remains noticeable (see Fig. 2,a).

Intensive bands of CN and C_2 molecules were observed in emission spectra of plasma in the case of adding the fuel mixture into the working liquid or working gas. At that time diagnostics by the N_2 bands of the 2^+ system was impossible because of its overlapping with CN bands (B-X transition). In this case vibrational and rotational temperatures were determined by the emission bands of CN and C_2 molecules.

As can be seen from Fig. 2,b, adding the fuel into the plasma system leads to the increasing of rotational and vibrational temperatures of molecules, which became equal to each other within the errors for each molecule (CN or C_2). This may indicate that the exothermic reactions reduce the level of non-thermality of the generated plasma as a result of additional energy supply for heavy components in the process of complete combustion of hydrocarbons. Beside that, the decreasing of non-thermality level of plasma was observed with discharge current increasing. It was founded that $T_e^*(H) < T_r^*(C_2) \leq T_v^*(C_2) < T_r^*(CN) = T_v^*(CN)$ (see Fig. 2,b).

Lower temperatures $T_e^*(H)$ in comparison with rotational and vibrational temperatures of CN and C_2 molecules can be explained by the fact that exothermic reactions lead to the energy release, which is basically spent for changing the thermal energy of heavy particles and for the excitation energy of rotational and vibrational levels of molecules without changing the thermal energy of electrons.

CONCLUSIONS

- TA and DGCLW generate non-equilibrium plasma in the case of working gas air and working liquid – distilled water.
- Adding the fuel into the plasma system leads to the increasing of vibrational and rotational temperatures of molecules, which became equal to each other within the errors. This may indicate that the exothermic reactions reduce the level of non-thermality of the generated plasma as a result of additional energy supply for heavy components in the process of complete combustion of hydrocarbons.
- It was founded that electronic temperature of hydrogen is lower than vibrational and rotational temperatures of cyan and carbon molecules. It was supposed that energy release as result of exothermic reactions is basically spent for changing the thermal energy of heavy particles and for the excitation energy of rotational and vibrational levels of molecules without changing the thermal energy of electrons и excitation energy of electronical levels of molecules.

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ВЛИЯНИЕ ЭКЗОТЕРМИЧЕСКИХ РЕАКЦИЙ НА УРОВЕНЬ НЕРАВНОВЕСНОСТИ РАЗРЯДНОЙ ПЛАЗМЫ

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Сравнительный анализ параметров плазмы поперечной дуги и разряда в газовом канале с жидкой стенкой проведен для различных рабочих газов и жидкостей (для воздуха, дистиллированной воды и их смеси с этанолом). Электронные температуры заселения T_e^* атомов, колебательная T_v^* и вращательная T_r^* температуры заселения молекул в генерируемой плазме определены с помощью оптической эмиссионной спектроскопии. Показано, что оба разряда генерируют неравновесную плазму в случае рабочего газа – воздуха, и рабочей жидкости – дистиллированной воды. Добавление топлива (этанола) в плазменную систему приводит к увеличению вращательной и колебательной температур заселения молекул, которые становятся равными друг другу в пределах погрешности. Это может свидетельствовать о том, что экзотермические реакции уменьшают уровень неравновесности генерируемой плазмы в результате подачи дополнительной энергии тяжелой компоненте в процессе полного сгорания углеводородов.

ВПЛИВ ЕКЗОТЕРМІЧНИХ РЕАКЦІЙ НА РІВЕНЬ НЕРІВНОВАЖНОСТІ РОЗРЯДНОЇ ПЛАЗМИ

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Порівняльний аналіз параметрів плазми поперечної дуги та розряду в газовому каналі з рідкою стінкою проведений для різних робочих газів та рідин (для повітря, дистильовоної води та їх суміші з етанолом). Електронні температури заселення T_e^* атомів, коливальна T_v^* і обертальна T_r^* температури заселення молекул у плазмі, що генерується, визначені за допомогою оптичної емісійної спектроскопії. Показано, що обидва розряди генерують нерівноважну плазму у випадку робочого газу – повітря та робочої рідини – дистильованої води. Додавання палива (етанолу) в плазмову систему призводить до збільшення обертальної та коливальної температур заселення молекул, які стають рівними одна одній у межах похибки. Це може свідчити про те, що екзотермічні реакції зменшують рівень нерівноважності плазми, що генерується, внаслідок подачі додаткової енергії важкій компоненті в процесі повного згорання вуглеводнів.