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NON-EQUILIBRIUM PROCESSES IN THE PLASMA-CHEMICAL UHF-REACTOR WITH MAGNETIK FIELD

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The work deals with inwestigations results of non-equilibrium plasma chemical UHF-discharge to carry out reactions of fusion and substance decomposition being in the gaseous phase. In particular, the fusion reactions of nitrogen oxides in the mixture N_2, O_2 and CO_2-decomposition to the elemental carbon have been considered. The experiments were carried out at the pressure of operating gas in the range 0,5-200 Torr. The break-down of gas and the heating-up plasma electrons were accomplished in the conditions of electron cyclotron resonance (λ=8mm, H=12kOe). The calculation of discharge parameters performed by means of computer has shown that in the given systems the non-equilibrium regime ($T_e \sim 2eV, T_i \lesssim 0.1eV, n_e \sim 5.10^{13} cm^{-3}$) has to be accomplished. The experimental data are in a good agreement with the calculation results. Knowing the UHF-radiation energy absorbed by plasma and the product amount one can estimate the part of energy consumed directly for the chemical reaction. This value W_{chem}/W_{abs} depends in the resonance way on the magnetic field value and reaches in the resonance the values up to 30 % for the nitrogen fixation and 60 % for the dissociation of molecules CO_2. The formation of nitrogen oxides can, probably, be connected to the generation of active particles (O, N_2^*) in discharge under the action of hot electrons. The mass-spectrometric, spectral measurements as well as the analysis throuth pressure change, the calculation and measurement of discharge parameters confirm the possibility of CO_2 decomposition in the UHF-discharge with the strong magnetic field to the elemental carbon at pressures $\sim$ 50 torr and the incomplete decomposition up to CO at the decrease in pressure. With the decrease in pressure the value T_e increases noticably and the oxidation processes become rather essential, that, evidently, results in the incomplete decomposition of CO_2 up to CO. The CO_2 decomposition process in the non-equilibrium discharge can hardly proceed according to the direct scheme :

$$CO_2 + e \rightarrow C + O_2 + e,$$

since the electron energy is not yet great. The stepped mechanism through the excited states of CO is seemed to be more probable. The fact of CO_2-decomposition to the carbon in the non-equilibrium plasma-chemical discharge may be of importance in plasma-metallurgy processes of reduction metals from its oxides.

NON-EQUILIBRIUM PROCESSES IN THE PLASMOCHEMICAL UHF-REACTOR WITH MAGNETIC FIELD

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The paper deals with investigation results of plasmochemical reactions of fusion and decomposition of substances being in a gaseous. The reactions have been performed in a non-equilibrium UHF-discharge on conditions of electron-cyclotron resonance (ECR). In particular, the fusion reactions of NO in the mixture of N_2 and O_2, and CO_2 - decomposition to the elemental carbon have been considered. Experiments were carried out at the pressure of operating gas in the range 0.5-200 Torr. The break-down of gas and heating-up of plasma electrons were accomplished under conditions of electron-cyclotron resonance. In the paper the correlation of calculated parameters with these obtained experimentally is noted. High values of energetic efficiency are accounted for by an effective pumping up UHF energy absorbed in the discharge into vibrational energy levels, When $T_v > T_{v\ min}$ the main channel of energy withdrawal is a chemical one.

NON-EQUILIBRIUM PROCESSES IN THE PLASMOCHEMICAL UHF-REACTOR WITH MAGNETIC FIELD

The work deals with investigation results of non-equilibrium plasmochemical UHF-discharge to carry out reactions of fusion and substance decomposition being in the gaseous phase.

In particular, the fusion reactions of nitrogen oxide in the mixture N_2, O_2 and CO_2 - decomposition to the elemental carbon have been considered. The characteristic property of non-equilibrium plasmochemical discharge is the distinction of electron temperature from the ion temperature and neutral gas component. In such a discharge chemical reactions are initiated by hot electrons and the gas remains relatively cold. In this case, the high energy efficiency of processes should be expected.

Experiments were carried out on the installation described in details in [1,2] . As a generator of UHF-power the magneutron with following parameters: $\lambda \sim 8$mm, the impulse power ~ 30 kw, the impulse duration 0,3 μsec, the pulse repetition frequency up to 1000 c/s was used a section of round waveguide with walls cooled by the liquid nitrogen was the reactor. The pumping out and filling the working gas were performed through connection. The magnetic field was generated within the limits from 0 to 15 kOe by means of solenoid. The experiments were carried out at the pressure of operating gas in the range 0,5-200 Torr.

The break-down of gas and the heating-up plasma electrons were accomplished in the conditions of electron cyclotron

resonance (ECR). Besides, the ECR permits to optimize the connection of reactor with the UHF-power source. At the resonance (H=12 kOe) the discharge absorbed up to 90% of power supplied. Out of the resonance the absorption dropped to 3-5%. The ECR allows to create the strongly non-equilibrium regime of discharge ($T_e \gg T_o$). The discharge non-equilibrium is sustained at the cost of heat exchange between the neutral gas and reactor wall (electrons are magnetized in this case) and the low duration of UHF - power impulse.

In NO fusion experiments the mixture N_2, O_2 is used in proportion of 1 within the pressure range of 30-200 Torr. The calculation of discharge parameters performed by means of computer has shown that in the given system the non-equilibrium regime ($T_e/T_o \sim 20$) has to be accomplished. In particular, the calculation for the initial pressure P=50 Torr has given the next values: T_e=1.8eV, T_o=0.09eV, $n_e = 8\ 10^{12}\ cm^{-3}$. The experimental data are in a good agreement with the calculation results. For example: the temperature of neutrals T_o defined from analysis of structure of bond rotational components N_2 in the discharge spectrum equals to 0.08 eV. When studying the radiation spectrum of discharge the emissive lines N_2, N_2^+, N, NO were found. The mass-spectral analysis of the obtained product has shown mainly the presence of NO and small amount of NO_2 in it.

The selection of product for analysis was performed by meand of control collector cooled by the liquid nitrogen. The reactor system was not flowing that allowed to check the product build-up through the decrease of pressure in the reactor du-

ring the operation process at the cost of freezing the nitrogen oxides on the reactor cold wall. The relative yield of product ($P_{prod.}/P_{N_2,O_2}$) amount to 2%. In the case of conflowing reactor system the value of product relative yield is limited by reverse reactions and is the characteristic of the system rather than the process. However, it is clear that the obtained relative yield value exceeds significantly the equilibrium value which is vanishingly small at $T_0 \sim 0.1$ eV [3].

The formation of nitrogen oxides can, probably, be connected to the generation of active particles (O, N_2^*) in discharge under the action of hot electrons:

$$O_2 + e \rightarrow O + O^-$$

$$N_2 + e \rightarrow N_2^* + e$$

The formation of nitrogen oxide can now proceed accroding to the following scheme [4]

$$O + N_2^* \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

Knowing the UHF-radiation energy absorbed by plasma and the product amount one can estimate the part of energy consumed directly for the chemical reaction. This value W_{chem}/W_{abs} depends in the resonance way on the magnetic field value and reaches in the resonance the values up to 30%. It should be noted that at the nitrogen fixation, in the resonance case, about 1,5% of energy is consumed directly for NO fusion at the atmosphere pressure and optimum gas temperature ($\sim$ 4000°K).

Let's consider the dissociation process of molecules CO_2. The CO_2 decomposition can proceed through two possible channels (only initial and final reaction products are taken into ac-

count):

$$CO_2 \longrightarrow C + O_2 \qquad (1)$$

and

$$2CO_2 \longrightarrow 2CO + O_2 \qquad (2)$$

The first reaction proceeds without change in gas pressure and at the second - the pressure increases by a factor of 1,5. The experiment was carried out according to the following scheme: The CO_2 filling into the reactor, the switch on the discharge, the measurement of pressure change in the process of operation, the switch off of the discharge. Then the remaining CO_2 was frozen off by the liquid nitrogen and the total press sure of non-frozen gaseous product of reaction (O_2 and CO) was measured. After this the mass-analysis of these products was performed.

Such a procedure of measurement of pressure change allowed to determine the ratio of finite products of reaction C/CO. Practically only the process (1) of complete CO_2 decomposition turned out ot proceed in the reactor at the CO_2 pressure 50 Torr. In this case 10% of CO_2 was decomposed per one operation cycle of the reactor.

At the decrease in pressure of working gas the effectiveness of channel (2) of CO_2 incomplete decomposition increase. At the pressure 0,5-2 Torr the carbon was practically not produced, in the gas phase of reaction products the component CO became prevalent. Nevertheless, the total output increased. Thus, at the pressure 0,5-5 Torr 25-50% of CO_2 was dissociated. The mass-spectrometry of product gas phase confirms conclusions of analysis through the pressure difect change (Fig. 1)

The spectral measurements of discharge radiation in the visible region of spectrum were also carried out at various pres-

sures (0,5-50 Torr). The distinctive characteristic of spectra at pressures 20-50 Torr is the availability of Swan band system (cluster C_2) and Anystrom system (CO). With the pressure drop up to 0,5 - 2 Torr Swan bands vanish not completely but the intensity of Angstrom system grows.

To find the dependence of CO_2 decomposition reaction character on the pressure the calculation and experimental measurement of discharge parameters were carried out. The essential result of calculation can be believed the demonstration of strong non-equilibrity of the system (T_e/T_0=10-30) which increased at the pressure growth. However, the neutral gas temperature T_0 depends upon pressure even stronger. At P=50 Torr T_0 during the discharge increases only by ΔT=300° and attains 600°K, i.e. the gas remains practically cold. With the decrease in pressure the value ΔT increases noticably (at P=2Torr, $\Delta T \sim$ 1500°) and the oxidation processes become rather essential, that, evidently, results in the incomplete decomposition of CO_2 up to CO according to the scheme (2). The experimental results are in agreement with calculation data. To determine the temperature of neutral component nitrogen was injected into the discharge together with CO_2. The structural analysis of rotational component of bands N_2 permitted to evaluate the neutral gas temperature T_0(Fig.1)

So, the mass-spectrometric, spectral measurements as well as the analysis through pressure change, the calculation and measurement of discharge parameters confirm the possibility of CO_2 decomposition in the UHF-discharge with the strong magnetic field to the elemental carbon at pressures ~50 Torr and the incomplete decomposition up to CO at the decrease in pressure.

The CO_2 decomposition process in the non-equilibrium discharge can hardly proceed according to the direct scheme:

$$CO_2 + e \longrightarrow C + O_2 + e$$

since the electron energy is not yet great. The next stepped mechanism through the excited states of CO is seemed to be more probable:

$$CO_2 + e \rightarrow CO_2^* + e$$
$$CO_2^* + CO_2^* \rightarrow 2CO + O_2$$
$$CO + e \rightarrow CO^* + e$$
$$CO^* + CO^* \rightarrow C + CO_2$$
$$CO^* + O \rightarrow C + O_2$$

In conclusion it should be noted the high energy efficiency of CO_2 dissociation process in the non-equilibrium UHF & reactor. At the pressure 50 Torr the value W_{chem}/W_{abs} reaches 60%.

It is known that for the reaction to proceed through vibrationally excited states the mean vibrational temperature T_v should exceed a threshold temperature $T_{v\ min}$ for the reaction in question. This threshold temperature is readily determined by a formula [5]

$$T_{v\,min} = \frac{E_a}{\ln Z_{VT}(T_0)}$$

where E_a is the activation energy, $Z_{VT}(T_0)$ is the inverse probability of the vibrational relaxation.

In our case $T_{v\ min}$ equals 0.18eV for the limiting reaction $N^* + O \rightarrow NO + N$ and changes from 0.2 to 0.4 eV for the CO_2 dissociation depending upon realizable elementary processes.

Taking into account that the vibrational excitation is ta-

ken off both at the expense of chemical reaction and during V-T relaxation, it is interesting to note that there is no strict demands in our set-up to exceed $T_{v\ min}$ immediately after the first UHF power impulse. Because of high values of V-T relaxation time (~ 0.1s) at our parameters (the impulse repetition frequency being 500 $\frac{c}{s}$) the vibrational temperature of molecules practically does not change up to the influence of the following HUF-radiation impulse, that is, a constant energy pumping into vibrational states occurs. And only when $T_v > T_{v\ min}$ the non channel of energy withdrawal appears which is a chemical one. When influenced by every successive impulse the UHF-radiation energy is effectively pumped up into vibrational states of molecules and, in the long run, is utilized in the dissociation process. (CO_2 being the operating gas) or in the reaction $N_2^* + O \rightarrow NO + N$ when the mixture of N_2 and O_2 is employed.

Plasmochemical reactions proceeding according such a scheme are bound to have high energetic efficiency since they have no side channels of energy withdrawal, the fact confirmed by our experiments.

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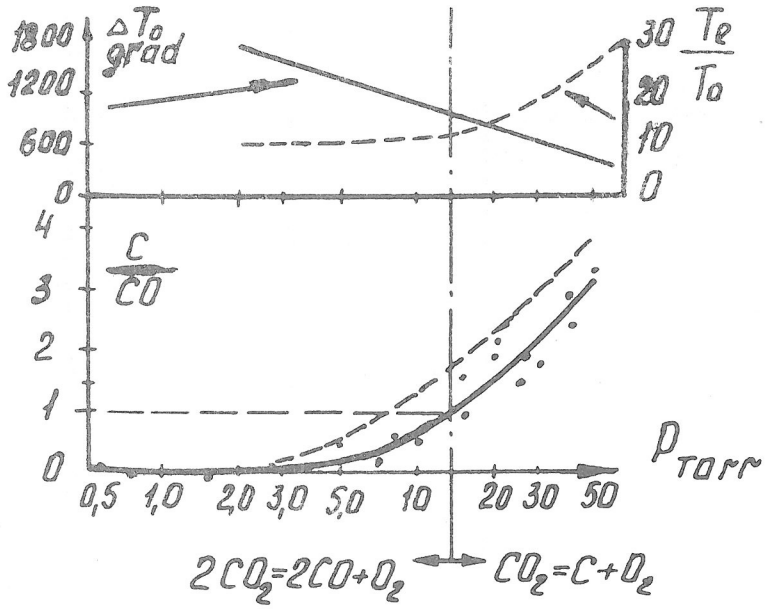

Fig. 1.