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NITRIC OXIDE PLASMA CHEMICAL SYNTHESIS IN ARGON STABILIZED MICROWAVE DISCHARGE AT ATMOSPHERIC PRESSURE[1])

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The principle of the microwave discharge stabilization at atmospheric pressure is briefly described. It is shown that argon used for stabilization does not substantially affect the reaction course. The degree of plasma nonequilibrium is discussed.

ПЛАЗМО-ХИМИЧЕСКИЙ СИНТЕЗ ОКИСИ АЗОТА ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ В МИКРОВОЛНОВОМ РАЗРЯДЕ, СТАБИЛИЗИРОВАННОМ АРОГОНОМ

В работе кратко описан принцип стабилизированного микроволнового разряда при атмосферном давлении. Показано, что аргон, который использовался для стабилизации, не влияет существенным образом на ход реакции. Обсуждается также степень неравновесия плазмы.

I. INTRODUCTION

In studies of plasma chemical reactions at medium (some kPa) or atmospheric pressures a suitable method of the plasma stabilization is of particular importance. It may become inevitable in cases when the energy absorbed in a plasma grows up to joules per milliliter and a cooling of the discharge tube inside the wavequide, usually very complicated, is necessary.

A possibility of maintaining a stable microwave discharge even at low gas flows is to create an axial channel by an easy ionizing medium [1]. If one initiates the discharge in such a channel, it keep burning in this channel. At the boundary of the channel the discharge may proceed into the surrounding gas, owing to the radial diffusion of the free charge carriers (electrons, ions) out of the ionized channel or thanks to ion-molecule reactions.

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It is apparent that the geometric factors are considerably important. The scheme of the setup is in Fig. 1.

II. EXPERIMENTAL RESULTS

As it has been outlined, the stabilizing gas transfers a certain amount of microwave energy to the surrounding molecular gas. For this reason it is interesting to know to what extent the reaction under study is being altered by the inert stabilizing gas admixture. The dependence of the NO concentration built up in the stoichiometric mixture upon the argon flow was studied for this purpose. The results are given in Fig. 2, together with the theoretical curves based on the assumption that the argon is merely an inert diluent.

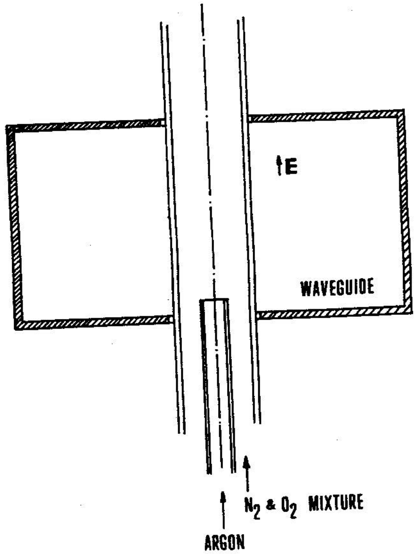

Fig. 1. The scheme of the setup for microwave discharge stabilization by argon.

The NO concentration was determined by means of the infrared spectrophotometer SPECORD 75 IR (Carl Zeiss, Jena), the calibration of which was checked chemically [2, 3]. It can be seen that the NO concentration roughly follows the theoretical curves, the deviations being within the experimental errors. This means the argon admixture up to 15 % does not substantially change the plasma chemical synthesis mechanism (in the range of our experimental conditions).

The NO concentration vs. input gas composition dependence was also measured. The typical results are shown in Fig. 3. The theoretical curves (solid lines) are the functions of the type

$$c_{NO} = k_1 c_{N2}^a c_{O2}^b \qquad (1)$$

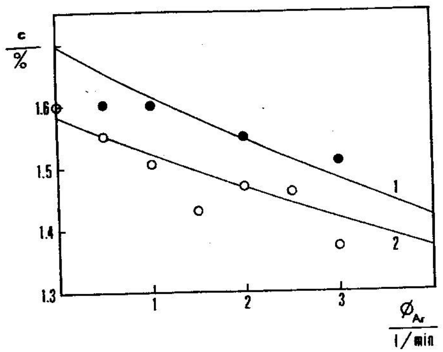

Fig. 2. Nitric oxide concentration as the function of the argon flow. Curve 1: stoichiometric mixture, flow 20 l/min, $P = 1$ kW; curve 2: air, flow 26 l/min, $P = 1.6$ kW.

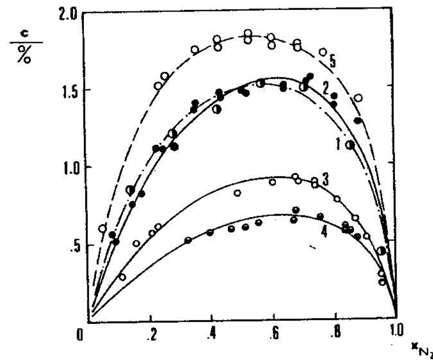

Fig. 3. The NO concentration vs. nitrogen molar fraction dependence for various experimental conditions (see Table 1).

the parameters of which were set so as to fit the experimental data. The NO concentration was measured by infrared spectrophotometry (curve 1) and by means of the quadrupole mass spectrometer Balzers QMG 511 (curves 2—5). The use of the quadrupole mass spectrometer has a great advantage in the possibility of an accurate control of the actual concentrations of all the components of the system, incl. N_2 and O_2. The parameters obtained are given in Table 1.

Table 1

Experimental conditions and parameters a, b from Eq. (1)

Curve	P/kW	Φ/l/min	a	b
1	1.0	17	0.7	0.5
2	1.0	15.3	0.8	0.5
3	1.0	40	0.9	0.6
4	1.0	54.6	0.7	0.4
5	1.5	54.6	0.5	0.4

III. DISCUSSION

In the case of the generated plasma in complete thermodynamic equilibrium both parameters should be 0.5. This follows from the equilibrium constant (K) relation:

$$K = \frac{c_{NO}^2}{c_{N2} c_{O2}}, \qquad (2)$$

corresponding to the chemical equilibrium

$$N_2 + O_2 \rightleftarrows 2\,NO. \qquad (3)$$

Under considerations far from the chemical equilibrium (NO concentration being low compared to its equilibrium value), the following relation may be used (4):

$$\frac{dn_{NO}}{dt} = kc_{N2}c_{O2}^{0.5}. \qquad (4)$$

Here, dn_{NO}/dt is the NO production rate. In Eq. (4), only the (equilibrium) dissociation of oxygen

$$O_2 + M \rightleftarrows O + O + M \qquad (5)$$

and the reaction of vibrationally excited molecular nitrogen with atomic oxygen

$$N_2 + O \rightarrow NO + N \qquad (6)$$

are included (M represents an arbitrary particle).

Rusanov et al. [5] considered all the chain reactions and found theoretically an outstanding NO concentration maximum for the oxygen concentration at approx. 10 %. Their experimental conditions were: non-self sustained discharge initiated by the relativistic electron beam ($\tau = 10^{-6}$ s), atmospheric pressure, $T_e/T_0 \geqq 10$.

The plasma — gas interaction time in our experiments was in the range of 10—100 ms. In the case of equilibrium plasma the temperature should be at least 2600 K to produce up to 1.8 % NO. However, under these conditions the equilibrium ($c_{NO}^{actual}/c_{NO}^{equil.} > 9$) should be achieved in 20 ms [6]. The exponents *a*, b (defined in Eq. (1)) found in our measurements indicate that the microwave plasma is probably near equilibrium. The equilibrium parameters are not precisely established in spite of the complex character of all the effects that have influence upon the overall compound balance.

Although the specific absorbed energy varies from 1.1 J/ml to 8.6 J/ml, no significant shift in the coefficients was observed.

IV. CONCLUSION

The system of plasma stabilization by an inert gas channel may be of great practical importance in low-flux systems. Though the discharge burns partially in inert gas, the reaction occurs in the same mechanism as without the inert admixture (up to 15 %). The analysis of the NO concentration dependence upon the composition of the inlet gas indicates that the microwave plasma is not far from thermodynamic equilibrium. A more detailed analysis of the problem (measurements of vibrational and translational temperatures and of other plasma parameters) is under study.

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