NITROGEN OXIDES FORMATION IN A PULSE MICROWAVE DISCHARGE BURNING IN NITROGEN — OXYGEN MIXTURES[1])

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The starting phase of a discharge has a negative influence upon the NO_x synthesis owing to a remarkable acceleration of electrons. This effect is especially evident in the pulse regime with a short pulse duration. From the comparison of data measured in both pulse and CW regimes it clearly follows that the pulse regime is unfavourable to the NO_x synthesis.

ОБРАЗОВАНИЕ ОКИСЕЙ АЗОТА В МИКРОВОЛНОВОМ РАЗРЯДНОМ ИМПУЛЬСЕ ПРИ ГОРЕНИИ СМЕСИ АЗОТА С КИСЛОРОДОМ

Начальная фаза разряда отрицательно влияет на синтез NO_x вследствие значительного ускорения электронов. Этот эффект особенно очевиден в импульсном режиме с короткой длительностью импульса. Из сравнения данных, измеренных как в импульсном, так и в непрерывном режимах, отчетливо следует, что импульсный режим является неблагоприятным для синтеза NO_x.

1. INTRODUCTION

Pulse microwave plasma is very often used in experimental studies of plasma chemical reactions. The reasons are in that powerful magnetrons operating in a continual (CW) regime are difficult to attain as well as in different plasma parameters in the pulse and CW regimes. Some authors [1] prefer the pulse regime to the CW one because of the possibility to achieve high densities of electrons and metastable excited particles, the lifetime of which is longer compared to the pulse length.

However, the high applied pulse power results in a great increase of the electron energy, which is considerably higher than the energy of electrons in the CW plasma

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produced with the same power. Therefore it is necessary to take into account the possibility of changes in the reaction channels. This means that the choice of an operation regime must be done carefully. One must consider the type of reaction, namely the role played by every species of the excited particles involved in the plasma chemical reaction.

The aim of this study is to investigate differences in the reaction paths resulting in a nitric oxide synthesis in pulse and CW plasmas.

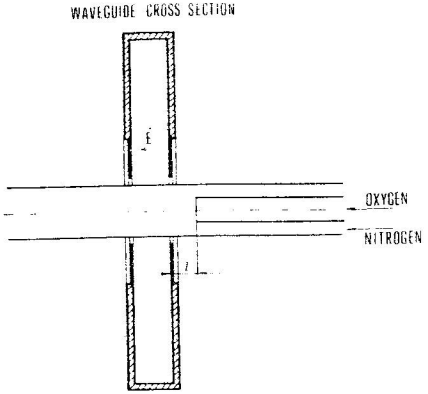

Fig. 1. The arrangement of tubes crossing the rectangular waveguide.

II. EXPERIMENTAL

The typical experimental setup is depicted schematically in Fig. 1. The reaction vessel is a 14.5 mm i.d. straight quartz tube. Reaction gases were introduced both tangentially and axially by means of a 6 mm i.d. quartz tube. The mouth of the axial tube was movable along the discharge tube as far as the discharge zone.

The discharge was generated by the absorption of microwave power inside the quartz tube passing through the centre of a rectangular waveguide in parallel to the vector of the electric field intensity **E**. The waveguide was, in the direction of **E**, narrowed to 18 mm, so that the cross section of the waveguide in the plane of the discharge tube was 109×18 mm.

Experiments were carried out at a frequency of 2.35 GHz. The repetition frequency in the pulse regime was 1 kHz. The average incidental power varied between 0 and 0.6 kW. The maximum pulse power used was 3.2 kW.

The reaction chamber was pumped by a rotary pump. The working pressure was controlled by a valve in the suction manifold and was kept at 5 kPa.

The gas flows were controlled by means of needle valves and measured by rotameters. The air taken for the experiments was dried by passing through molecular sieves. The stoichiometric nitrogen-oxygen mixture was prepared by mixing a high purity nitrogen (99.99 %, introduced tangentially) and medicinal oxygen (introduced axially) in the discharge tube.

The product analysis was performed by means of a quadrupole mass spectrometer. Absolute calibration was regularly checked by the chemical titration method [2].

Three types of nitrogen oxides, viz. NO, N_2O_3, and NO_2 were identified as the products of the reaction and the consequent oxidation. Neither ozone nor N_2O were detected.

III. RESULTS

The experiments carried out in air showed an abrupt decrease in NO_x concentration when the pulse duration fell below 100 μs (see Fig. 2). The air flow was 0.5 and 0.75 l/min.

A more complex information is obtained by the NO_x concentration vs. power dependences as it can be seen in Fig. 3 where they are given for different pulse lengths. These curves exhibit a similar behaviour: longer pulse times yield higher NO_x concentrations. The maximum product concentration was found in the CW plasma.

The NO_x plasma synthesis in nitrogen-oxygen mixtures was found to be optimum in the stoichiometric mixture for both the pulse and the CW plasmas. This is in good agreement with literature [3].

To judge if some change in the reaction mechanism takes place for pulses shorter than 100 μs, the following experiment was carried out: There was measured the dependence of the NO_x concentration on the distance z of the mouth of the inner tube, introducing oxygen, from the front wall of the waveguide, see Fig. 1. The measured curves, given in Fig. 4, have similar shapes for different pulse lengths. They are not shifted along the z axis. That means that there is no appreciable amount of hitherto absent differently reacting metastable particles that should differ in energies and lifetimes. It can be seen that under our conditions a reasonable production of NO_x proceeds only when oxygen passes through the discharge.

There exist appreciable differences in reactions in pulse and continually generated plasmas. An elucidation of these differences demands to take into consideration not only higher electron and ion densities in the pulse regime but, moreover, the high electron energy at the beginning of a pulse. A rough illustration of the conditions mentioned can be found in Fig. 5 where the time dependence of the electron density and energy for hydrogen magnetoactive plasma is depicted [4]. Although the experimental conditions are not comparable, the existence of the first phase of the discharge (with electron energies higher than 10 eV and a low electron density) is quite real even in the case of nitrogen-oxygen mixtures. It is fairly probable to be the main reason for the observed decrease in reaction products concentrations in the case of short pulses. (Possible direct radiolysis by fast electrons has not been proved yet).

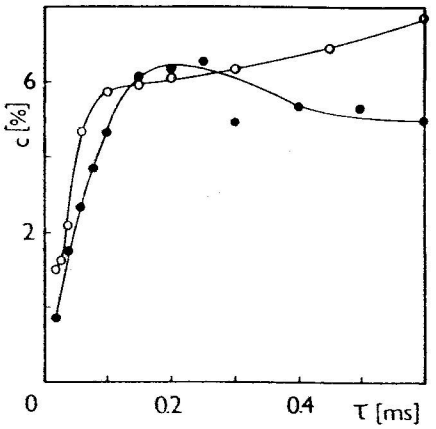

Fig. 2. The NO_x concentration dependence on the pulse length. Average incidental power for $\tau > 50$ μs was $P_{inc} = 160$ W. Air flows: 0.5 l/min ... ○, 0.75 l/min ... ●.

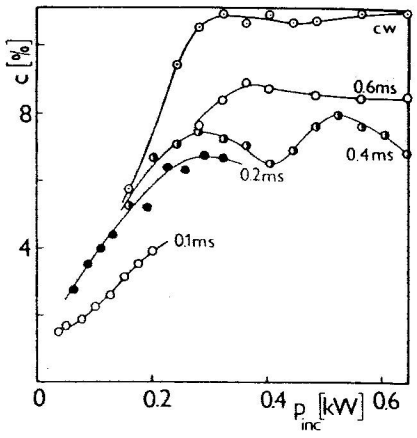

Fig. 3. The NO_x concentration vs average incidental power dependence for various pulse lengths. The flow of stoichiometric mixture 0.5 l/min.

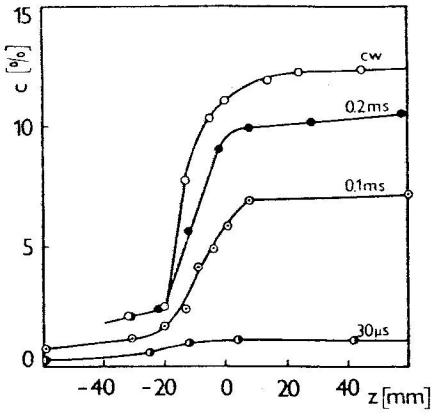

Fig. 4. The NO_x concentration dependence on the position of the inner tube orifice. Nitrogen introduced tangentially, oxygen axially, each gas flow 0.25 l/min.

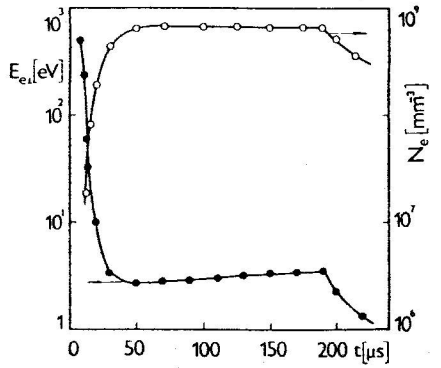

Fig. 5. The time dependence of electron density and electron energy in a pulse hydrogen magnetoactive plasma. $P_{inc} = 2$ kW, $p_{H_2} = 8 \times 10^{-2}$ Pa, $\tau = 190$ μs, $\omega_{ce}/\omega = 1.02$.

Consequently, under the conditions discussed above (especially high electron energies) the generation of atomic nitrogen increases whilst the densities of vibrationally and electrically excited molecules ($X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states) decrease. As the nitrogen atoms react with NO molecules, according to Eq. 1

$$N + NO \rightarrow N_2 + O, \qquad (1)$$

for about four orders faster than with oxygen molecules [5], according to the equation

$$N + O_2 \rightarrow NO + N \qquad (2)$$

it is clear that very short pulses, when only the first stage of discharge develops, are unfavourable for the NO_x production. It is worthwhile to note that in the case of short pulses two undesired effects combine, namely a high electron energy in the first stage and a raise of the average electron energy due to a high pulse power (at the average power kept constant).

IV. CONCLUSION

The comparison of NO_x plasma synthesis parameters in pulse and CW discharges shows that the pulse regime is not suitable for this purpose. The experimental results are in agreement with molecular reaction models in literature [6, 7]. Besides, they demonstrate a negative influence of fast electrons, which is of importance especially in the pulse regime with a short pulse time.

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