EFFICIENCY OF THE NITRIDING PROCESS IN GLOW DISCHARGE PLASMA

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The problem of determination of the content of atomic nitrogen in glow discharge plasma in a nitrogen-argon mixture is considered. The discharge in this mixture is widely applied in the technologies of metal`s surfaces modification and the atomic nitrogen is responsible for the efficiency of this technologies. Influence of mixture composition on the rate constant of dissociation of molecular nitrogen, accountable for producing of atomic nitrogen is determined by simulation way, and parameters of plasma – from an experiment, on the basis of measuring by double probes. A function of distribution of electrons on energies was founded by numerically integrating the Boltzmann equation. The last one was written in the binomial approaching for mixture of molecular nitrogen and argon. The differences between proposed and fluid models are briefly discussed.
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1. INTRODUCTION

The energy efficiency criterion for the nitriding process in glow discharge (GD) is proposed in paper [1]. There are presented also the results that allow determining quantitatively the basic parameters of GD depending on the pressure in this paper.

In recent years it became known that the atomic nitrogen is main agent responsible for the efficiency of nitriding the surface of metal products [2]. N_2-Ar mixture is the better of technological atmospheres in this connection, where active dissociation of N_2 takes place [3]. That is why the object of this study is optimization of the nitriding process from the view point of percentage composition of N_2-Ar mixture as technological atmosphere. GD plasma is sharply nonequilibrium and the strict analysis of atomic nitrogen producing is a challenge. Moreover, essential meaning have nonlocal effects in near cathode GD area which are a subject of active research during last years [4]. In turn, methods of direct experimental definition of nitrogen atoms density N_a in plasma are difficult enough, as application of vacuum spectroscopy methods [2] demands. Besides, they do not allow predicting character of dependence N_a from GD parameters.

Influence of mixture composition on the rate constant of dissociation of molecular nitrogen, accountable for producing of atomic nitrogen is determined by simulation way, and parameters of plasma – from an experiment, on the basis of measuring with double probes. A function of electrons distribution on energies is founded by numeral integration of Boltzmann equation. The last one was written in the binomial approaching for mixture of molecular nitrogen and argon.

2. EXPERIMENT

The discharge plasma is generated in N_2-Ar mixture at the central part of the vacuum camera (anode) of volume 0.1 m^3 [1]. The constructional details to be modified were placed on the metal plate (cathode) 5 cm in diameter. GD was powered by rectified voltage U up to 1500 V. The temperature of cathode was controlled by a thermocouple and maintained at the level ~ 810-820º K by heating from GD of level UI ~ 60 Wt (I – discharge current).

Actually nitriding was carried out in a N_2-Ar mixture at a pressure of 150 Pa and the pumping rate of the mixture ν = 1,5 Pa m^3s^{-1} for 30 min.

The density of charged particles N_e and the electric field E were measured by double probes, which could move along the radius of the chamber.

3. GENERATION OF ATOMIC NITROGEN

The role of atomic nitrogen was analyzed by determining its density N_a on the basis of calculating the electron distribution function (EDF) in view of its dependence on the component composition of the technological atmosphere and plasma parameters. The latter include the rate of flow ν and temperature T of the working gas, as given parameters, and two determined experimentally: the density N_e and the field E. In principle, we were simulated $N_e(r)$ and $E(r)$ also using fluid model [1]. The example of this simulation is presented in the Fig. 1.

Nevertheless, this model cannot explain the fact, that experimentally observed extension of ionization region (~ 3 cm), exceeds substantially the thickness of the calculated near-cathode layer ~ 0,5 cm as is shown in Fig. 1. That is why we proceed analogously to the paper [4], where the averaged parameters of the plasma in this region are introduced. Namely, we used the average values of N_e and E measured by double probes. It is also assumed that the temperature of the gas near the cathode is 800 K.

The positive column of the investigated spherical GD is not limited to the transverse direction as the long GD in tubes. That is why the illumination in this region is absent

(it is believed that this region corresponds to the dark part of corona discharge [4]). Actually viewable zone is concentrated near the cathode in the volume $V_d \sim 0{,}25\ dm^3$.

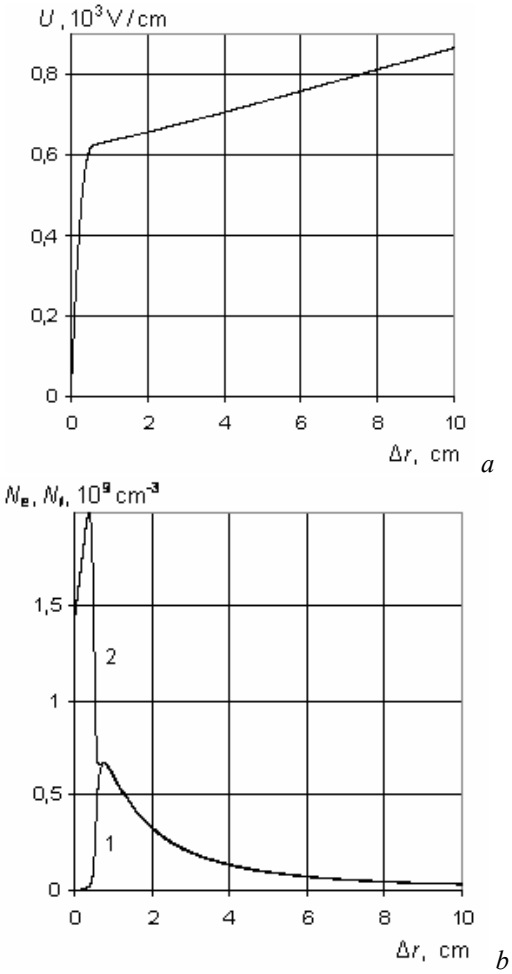

Fig. 1. The distribution of potential (a) and the density of electrons (1) and ions (2) along a radius of the spherical GD (b) at a pressure of 100 Pa: p = 150 Pa, r_K = 2 cm, r_A = 33 cm, j_K = 2 mA/ см^2, T_K = 800 K

Density of the nitrogen atoms N_a was determined from the balance between their generation in the process of N_2 dissociation by electron impact and maintenance with pumping the working gas through a vacuum chamber. The rate constant of dissociation is

$$r_d = \sqrt{\frac{2e}{m_e}} \int_0^\infty \varepsilon \sigma_d(\varepsilon) f_0(\varepsilon) d\varepsilon, \qquad (1)$$

where e and m_e – the charge and mass of the electron, ε – energy, $\sigma_d(\varepsilon)$ – cross section of dissociation by electron impact, $f_0(\varepsilon)$ – EDF. The latter was found by numerical integration of the Boltzmann equation, written in the two-term approximation [5] for a mixture of molecular nitrogen and argon:

$$\frac{1}{n_e N}\left(\frac{m_e}{2e}\right)^{1/2} \varepsilon^{1/2} \frac{\partial (n_e f_0)}{\partial t} - \frac{1}{3}\left(\frac{E}{N}\right)^2 \frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon}{\sum_i \frac{N_i}{N}\sigma_{iT}} \frac{\partial f_0}{\partial \varepsilon}\right) -$$
$$- \frac{\partial}{\partial \varepsilon}\left[2\sum_i \frac{m_e}{M_i}\frac{N_i}{N}\sigma_{iT}\varepsilon^2\left(f_0 + T\frac{\partial f_0}{\partial \varepsilon}\right)\right] = S_{eN} + S_{ee} + A(\varepsilon)\ . \qquad (2)$$

Here E – field strength; N – the total density of neutral components; M_i, N_i and σ_{iT} – mass, density of neutral components and relevant transport cross sections, T – gas temperature (eV); S_{eN} and S_{ee} – integrals of inelastic collisions between electrons and neutral particles and electrons; $A(\varepsilon)$ – ionization term. The integral of inelastic collisions between electrons and atoms and molecules has the form

$$S_{eN} = \sum_j \frac{N_j}{N}\left[(\varepsilon - \varepsilon_j)\sigma_j(\varepsilon + \varepsilon_j) f_0(\varepsilon + \varepsilon_j) - \varepsilon \sigma_j(\varepsilon_j) f_0(\varepsilon)\right], \qquad (3)$$

where σ_j – cross section of excitation of N_2 electronic and vibrational levels and Ar electronic levels, as well as the dissociation of N_2; ε_j – quantum of the appropriate reaction. Term S_{ee} has a standard form [9]. $A(\varepsilon)$ describes the ionization of N_2 and Ar:

$$A_j(\varepsilon) = \frac{N_j}{N}\{\int_{2\varepsilon+\varepsilon_i}^{\infty} \varepsilon' f_0(\varepsilon')\sigma_i(\varepsilon', \varepsilon) d\varepsilon' + \int_{\varepsilon+\varepsilon_i}^{2\varepsilon+\varepsilon_i} \varepsilon' f_0(\varepsilon')\sigma_i(\varepsilon', \varepsilon' - \varepsilon_i - \varepsilon) d\varepsilon - \varepsilon f_0(\varepsilon) \int_0^{\frac{\varepsilon-\varepsilon_i}{2}} \sigma_i(\varepsilon, \varepsilon') d\varepsilon'\}, \qquad (4)$$

where σ_i is differential ionization cross section for the component i and ε_i – ionization threshold. The next processes where taken into account to calculate the EDF:

$N_2 + e \rightarrow N_2 + e$	$N_2 + e \rightarrow N_2^+ + e + e$
$N_2 + e \rightarrow N_2(A^3\Sigma_u^+) + e$	$N_2 + e \rightarrow N + N + e$
$N_2 + e \rightarrow N_2(a^1\Pi_g) + e$	$Ar + e \rightarrow Ar + e$
$N_2 + e \rightarrow N_2(v) + e$, v=1,…,10	$Ar + e \rightarrow Ar(4s) + e$
	$Ar + e \rightarrow Ar^+ + e + e$

Links to their cross sections are presented in [5].

Fig. 2 shows a view of the EDF, calculated according to (2) for various compositions of the mixture. As it may be concluded, even a small addition of nitrogen leads to significant changes in the EDF, namely its incidence in the energy range 3...4 eV and above. This leads to an increase in the proportion of electrons with energies up to 2 eV, decreases, respectively, share of more energetic electrons.

Since the dissociation reaction has a threshold $\varepsilon_d \approx 9{,}76$ eV, and the EDF decreases rapidly with increasing energy, crucial for rate constant r_d (1) is the value of the function at the energy ε_d, marked by the vertical dashed line in Fig. 2. Thus, the increase of N_2 in the mixture leads to a decrease in the proportion of electrons with energies greater than ε_d and, in turn, – to reduction of the constant r_d. It decreases almost 90 times when changing the proportion of N_2 in the mixture from 0 to 100% [5].

As is shown in the result of calculation, the dependence of N_a from the density N_2 in the discharge plasma of the mixture leads to the presence of the maximum values of N_a. Concerning our experiment [6], it is reached at the N_2 content ~ 25%. In this case N_a in the discharge is more than 20 times higher than in the case of a discharge in pure nitrogen. The results of determining the microhardness of the nitrided layer on the composition of the working mixture of argon/nitrogen are clearly

correlated with the nature of the dependence N_a from N_2 content. Thus, the results obtained, on the one hand, confirm the determining role of atomic nitrogen in the process of nitriding of metal surfaces and on the other - can be used to simulate these processes and their optimization.

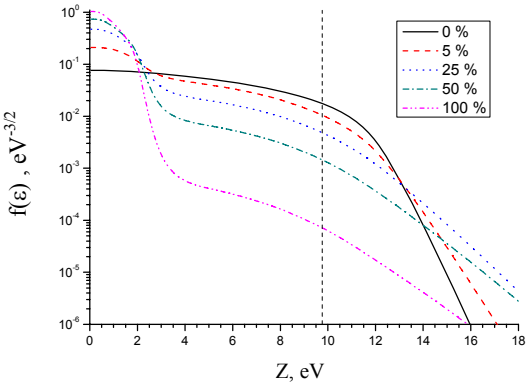

Fig. 2. View of the EDF for different nitrogen content in the plasma of nitrogen-argon glow discharge

4. LUMINOUS OF THE SPHERICAL GD

We were studied by spectroscopy method the mentioned above ionization region. The spectra of luminous from GD plasma were recorded with spectrometer S100-2048. In this case molybdenum and cooper were used as material of cathode, and nitrogen and argon – as plasma forming technological atmospheres. The specific result is that in the spectra of gases and metals mentioned only spectral lines from high exited states of atoms were observed. This feature may be used in further quantitative study GD plasma by spectral method.

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ЭФФЕКТИВНОСТЬ ПРОЦЕССА АЗОТИРОВАНИЯ В ПЛАЗМЕ ТЛЕЮЩЕГО РАЗРЯДА

В.А. Жовтянский, В.Г. Назаренко, В.А. Хомич, А.В. Рябцев, О.В. Анисимова, И.О. Невзгляд, А.Я. Шныт

Рассмотрена задача определения содержания атомарного азота как активной компоненты, ответственной за эффективность технологий модификации поверхности металлов в плазме стационарного тлеющего разряда низкого давления в смеси азот-аргон, широко применяемой в этих технологиях. Влияние состава смеси на скоростную константу диссоциации молекулярного азота, ответственной за продуцирование атомарного азота, определено расчетным путем, а параметры плазмы – экспериментально, на основе измерений двойными зондами. Функция распределения электронов по энергиям находилась путем численного интегрирования уравнения Больцмана, записанного в двучленном приближении для смеси молекулярного азота и аргона. Кратко обсуждены различия обсуждаемого подхода с решением задачи в гидродинамической модели.

ЕФЕКТИВНІСТЬ ПРОЦЕСУ АЗОТУВАННЯ В ПЛАЗМІ ЖЕВРІЮЧОГО РОЗРЯДУ

В.А. Жовтянський, В.Г. Назаренко, В.А. Хомич, А.В. Рябцев, О.В. Анісімова, І.О. Невзгляд, О.Я. Шнит

Розглянуто задачу визначення вмісту атомарного азоту як активної компоненти, відповідальної за ефективність технологій модифікації поверхні металів у плазмі стаціонарного жевріючого розряду низького тиску в суміші азот-аргон, що широко застосовується в цих технологіях. Вплив складу суміші на швидкісну константу дисоціації молекулярного азоту, відповідальну за продукування атомарного азоту, визначено розрахунковим шляхом, а параметри плазми – експериментально, на основі вимірювань подвійними зондами. Функція розподілу електронів по енергіях визначена на основі чисельного інтегрування рівняння Больцмана, записаного в двочленному наближенні для суміші молекулярного азоту і аргону. Коротко аналізуються відмінності обговорюваного підходу та розв'язку задачі в гідродинамічній моделі.