Optical emission spectroscopy study of the influence of the low-energy electron beam parameters on the content of neutral atomic nitrogen in the beam plasma

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Abstract. Optical emission spectroscopy was used for studying the influence of plasma generation mode (continuous and repetitively-pulsed), electron beam parameters (current 2-14 A, energy of 100-300 eV) and pressure of nitrogen-argon gas mixture (0.3-3 mTorr) on the relative content of neutral atomic nitrogen in the beam plasma.

1. Introduction

Based on gas discharge plasma technologies for processing of surfaces of different materials are widely used in industry, in particular, for nitriding of steels and alloys [1]. Electron beams are currently used for generation of dense low-temperature plasma [2]. Differences in composition and parameters of plasma generated using these techniques can specify their application areas. A number of publications show that the electron beam ionizes gas more effectively, the temperature of electrons in plasma beams is significantly lower than in the plasma of gas discharges of low pressure [3]. The combination of high concentrations of nitrogen molecular ions and low electronic temperature promotes intensive dissociative recombination of molecular ions and increase in the concentration of atomic nitrogen, which plays a major role in plasma nitriding. The most detailed analysis of the results of computational simulation of generation of charged and neutral particles under the influence of electron beam in nitrogen at low pressures, as well as spectroscopic and probe measurements of plasma beams is given in [4]. Calculations and measurements carried out under conditions characteristic of plasma generation by a beam of electrons created in a high-voltage glow discharge with the hollow cathode. Electron beam energy was 2 keV at nitrogen pressure 30-90 mTorr, beam current was not precisely determined and was assessed as a percentage of full discharge current, which amounted to a few tens of mA. This source has been successfully used earlier in experimental nitriding of steels [5]. Since an independent discharge of this type exists under certain combinations of voltage across interval, discharge current and pressure of working gas, independent adjustment of these tightly interrelated parameters is impossible, limiting the scope of possible applications and making it difficult to interpret the results of the experiment.

Results of steel nitriding using more powerful electron source with beam current up to 20 A and electron energy 80 eV based on usage of discharge with thermal emission cathode are shown in [6]. Spectroscopic studies of the beam plasma in such a source have revealed that the concentration of atomic nitrogen increases linearly from $10^{11}$ cm$^{-3}$ to $10^{12}$ cm$^{-3}$ at beam current increase from 2 to 20 A.
IOP Conf. Series: Journal of Physics: Conf. Series 1115 (2018) 032010  doi:10.1088/1742-6596/1115/3/032010

[7]. At the beam current 4 A and the accelerating voltage 120 V, growth of nitrogen pressure within 0.1-0.4 Pa led to 5-fold increase in the concentration of atomic nitrogen [8]. However, the use of multi-aperture double-electrode electron-optical system for the forming of a wide beam in this source also eliminates the possibility of independent change of beam parameters at with fixed length of the accelerating gap.

In the present work to generate plasma electron source with plasma cathode based on discharge with self-heated hollow cathode (SHHC) has been used, in which the acceleration of electrons occurs in a layer of spatial charge between emissive and beam plasmas that emerges in the mesh electrode plane [9]. In direct current mode the beam current with cross-section of 80 cm$^2$ in such a source may vary within a 5-25 A, accelerating voltage – within 100-300 V, the range of working gas pressures is 0.3-3 mTorr, and all listed parameters are regulated independently [10]. In case of pulsed excitation of discharge, the source operates in a repetitively-pulsed mode with current up to 100 A, pulse repetition rate up to 1 kHz at pulse duration 0.1-1 ms [11]. Method of optical emission spectroscopy was used for studying the influence of plasma generation mode (continuous and repetitively-pulsed) and beam parameters on relative contents of neutral atomic nitrogen in the beam plasma. Comparison was performed for electron beam plasma and the anode plasma of discharge with SHHC, which is characterized by the presence of fast electrons with an energy exceeding the threshold of gas ionization by electron impact in the discharge gap [12].

2. Experimental technique

Experiments were carried out on installation with a source of the broad electron beam based on discharge with SHHC, design and scheme of which are described in detail in [13]. Since the addition of argon into the nitrogen medium increases the efficiency of nitriding due to increased concentrations of atomic nitrogen through recharge of Ar$^+$ on N$_2$ with subsequent dissociation and recombination of N$_2^+$ [14], the measurements in this work were performed in nitrogen-argon gas mixture (Q$_{N_2}$:Q$_{Ar}$=1:1). The total gas flow Q was determined given the stable burning of discharge with maximum current 100 A and amounted 50 cm$^3$/min, pressure in the chamber was controlled through changing the position of the flap in vacuum shutter.

 Plasma optical emission spectra were registered on the spectrograph ISP-30 integrated with multi-channel optoelectronic sensor MORS-6 working the spectral range of 200-950 nm. Plasma radiation was supplied to the input slit of the spectrograph using the quartz optic fiber. Registration of spectra was performed in the direction perpendicular to the discharge axis with the exposition per frame 3 s. The spectrum was registered with averaging over 25 frames. Locality of the measurement area was determined by the diameter of the collecting lens collects on the inlet and outlet of the optic fiber ~ 30 mm.

The measurements were carried out in the field, separated from plasma cathode grid by 25 cm. In order to study the composition of plasma of discharge with SHHC, the cylindrical mesh anode was substituted with the disk-shaped anode, which was located at a distance of 50 cm from the cathode, and the measurements were taken at 25 cm from the cathode. Continuous and repetitively-pulsed modes for beam generation were used. Parameters of repetitively-pulsed mode were regulated under condition of average beam current constancy (4 A) and pulse duration (200 μs), so with changing of the beam current amplitude $I_b$ the pulse repetition rate also changed within 1000-250 Hz. Initial energy of beam electrons $eU_2$ varied within 100-300 eV, nitrogen pressure $P$ was regulated within 0.3-3 mTorr.

3. Experimental results

The characteristic spectrum of the electron beam plasma in nitrogen-argon medium (figure 1) contains intense bands of excited argon atoms Ar$^+$ 750.4 nm (3p$^4$4p$^2$[1/2]$_0^0$ → 3p$^4$4s$^2$[1/2]$_1^0$) и 811.5 nm (3p$^4$4p$^2$[5/2]$_3^3$ → 3p$^4$4s$^2$[3/2]$_2^3$), molecular nitrogen ion with the most intensive line N$_2^+$ 391.4 nm (B$^2$Σ$^+$v’=0) → X$^2$Σ$^+_g$(v’=0)), first and second positive systems of molecular nitrogen, among which lines N$_2^+$ 357.6 nm and 389.5 nm (transition C$^3$Π → B$^3$Π) were reliably identified. The spectra contain lines of the excited atomic nitrogen N$^*$ 868 nm (multiplet transition 3p$^2$D$^o$ → 3s$^4$P) and 746.8 nm
(transition $3p^4S^0 \rightarrow 3s^4P$), but the latter is not always well resolved against the intense line $\text{Ar}^* 750.4$ nm.

The lack of reliably resolved lines of atomic nitrogen ions in the spectra did not allow evaluating its relative content in the plasma. Only the relative content of excited atomic nitrogen in plasma was analyzed in the experiments. It was assessed according to the ratio $I_{\text{N}^*}/I_{\text{N}_2}$ of lines of the excited atomic nitrogen $\text{N}^* 868$ nm and the neutral molecular nitrogen $\text{N}_2^* 357.6$ nm. This pair of lines was chosen because they are the most intense and are reliably detected in all modes of generation of anode and beam plasma in nitrogen and in nitrogen-argon mixtures.

$I_{\text{N}^*}/I_{\text{N}_2}$ ratio in plasma in the repetitively-pulsed beam at the constant average current of 5 A weakly depends on the amplitude of the current beam (60-100 A) at low gas pressure (0.3 mTorr). At a pressure of 3 mTorr this ratio increases by 15-20% along with increasing of amplitude current from 20 up to 100 A (figure 2). Nitrogen pressure strongly influences $I_{\text{N}^*}/I_{\text{N}_2}$ ratio, its increase by an order of magnitude results in twofold increase of $I_{\text{N}^*}/I_{\text{N}_2}$ ratio. Increase of the accelerating voltage from 100 to 300 V also leads to the increase of $I_{\text{N}^*}/I_{\text{N}_2}$ ratio (figure 3).

If the change of amplitude current at constant average beam current weakly affects $I_{\text{N}^*}/I_{\text{N}_2}$ ratio, the increase in beam current in continuous generation mode leads to a significant increase in the relative intensity of the lines of atomic nitrogen (figure 4). Ratio $I_{\text{N}^*}/I_{\text{N}_2}$ varies almost linearly with beam current at high pressures of nitrogen.

Comparison of the results obtained in continuous and repetitively-pulsed modes of beam generation at the same values of average beam current, pressure and accelerating voltage was performed for nitrogen-argon plasma obtained at a ratio $\text{N}_2/\text{Ar}=1$ (figure 5). Repetitively-pulse mode achieves higher $I_{\text{N}^*}/I_{\text{N}_2}$ ratio, and this difference increases with increasing pressure. Relative N content was lower in nitrogen plasma than in nitrogen-argon plasma.

Figure 6 shows dependencies of intensity ratios relations of intensities of lines $I_{\text{N}^*}/I_{\text{N}_2}$ and $I_{\text{N}_2^+}/I_{\text{N}_2}$ on the nitrogen pressure obtained for the plasma of discharge with self-heated hollow cathode with 60 A current and the plasma of continuous electron beam (10 A, 200 eV). Line $\text{N}_2^+ 391.4$ nm was used for calculation of $I_{\text{N}_2^+}/I_{\text{N}_2}$ ratio. With the 6-fold difference in the current, the relative content of atomic nitrogen in the beam plasma $I_{\text{N}^*}/I_{\text{N}_2}$ appeared to be roughly twice higher and the ionization degree of
the beam plasma $I_{N_2^+}/I_{N_2}$ appeared to be an order of magnitude higher compared to the anodic discharge plasmas.

Figure 3. Dependencies of intensity ratio $I_{N}/I_{N_2}$ in the beam plasma from the acceleration voltage in the DC mode. Beam current 10 A. Pressure of the N$_2$-Ar mixture P: 1 – 0.3, 2 – 0.75, 3 – 3 mTorr.

Figure 4. Dependencies of intensity ratio $I_{N}/I_{N_2}$ from the beam current amplitude in the DC mode. Accelerating voltage 200 V. Pressure of the N$_2$-Ar mixture P: 1 – 0.3, 2 – 0.75, 3 – 1.5, 4 – 3 mTorr.

Figure 5. Dependencies of intensity ratios $I_{N}/I_{N_2}$ in the spectra of electron beam plasma on the pressure in a vacuum chamber in the pulse DC (1) and DC (2, 3)-modes and in N$_2$-Ar gas mixture (1, 2). Beam current 10 A, accelerating voltage 200 V.

Figure 6. Dependencies of intensity ratios $I_{N^*}/I_{N_2}$ and $I_{N_2^+}/I_{N_2}$ in the spectra of plasma of direct discharge (60 A) and electron beam (10 A, 200 V) in DC mode from nitrogen pressure.
4. Discussion

The occurrence and the departure of particles in plasma are described by a kinetic equation:
\[ \frac{dn}{dt} = N_0 \sigma_{i\gamma} n \tau_i \]
(1), where \( N_0 \) is the concentration of a particle in the main state, \( \sigma_{i\gamma} \) – cross-section of excitation of the energy state, \( v_e \) – velocity of electrons, \( \tau_i \) – lifetime of the state. The concentration of particles in the excited state \( n \), is related to the intensity of radiation in the spectrum through Einstein relation: 
\[ I = a \hbar v_e n_i A_{i\gamma} \]
(2), where \( I \) is the intensity of spectral lines, \( a \) – correction factor (defined by the optical system properties), \( \hbar \) – transition energy, \( A_{i\gamma} \) – Einstein coefficient [8].

As it was already mentioned, the main mechanism of generation of neutral nitrogen atoms in the beam plasma is the direct ionization of nitrogen molecules by electron impact with the formation of molecular ion and subsequent dissociative recombination of molecular nitrogen ions involving low-energy plasma electrons. Along with the dissociative recombination, reaction of dissociative excitation of nitrogen molecules by fast electrons beam is the most probable for the appearance of excited nitrogen atoms. Cross-section of nitrogen ionization by electrons has maximum \( \sim 2 \times 10^{-16} \text{ cm}^2 \) at electron energy 70-90 eV [10]. The reaction constant for the dissociative recombination is \( 1 \times 10^{-8} \text{ cm}^3/\text{s} \) at the electron energy 0.5 eV [10]. Neutral atomic nitrogen also results from dissociative ionization, cross-section of which is about \( 1 \times 10^{-16} \text{ cm}^2 \) within electron energy range 100-300 eV [3].

According to the model of the electron beam plasma generation by electron beam proposed in [3], increasing of gas pressure and electron beam current results in the accelerated generation of molecular nitrogen ions and neutral atoms. The increase in the concentration of these particles in the volume will be limited by their recombination, also on the walls.

The influence of the accelerating voltage on atomic nitrogen content is due to a change in the ionization frequency in volume by the beam electrons and high-energy secondary electrons that emerge in the process of gas ionization and may have energy up to \( \frac{1}{2} \) of ionizing electron energy [3]. Since the average energy cost of the electron beam for the formation of electron-ion pair in nitrogen is much lower than in discharge and is \( \sim 36 \text{ eV} \) [3], the increase in energy of primary electrons from 100 to 300 eV results not only in compensation for the decrease of ionization cross-section of the primary electrons by energy increase in rapid secondary electrons, but also provides an increase in ionization frequency.

A known cause of differences in atomic nitrogen generation rate for continuous and repetitively-pulsed modes at the same average beam current is decreasing temperature of electrons in the decaying plasma, which promotes the dissociative recombination of molecular nitrogen ions in the plasma [7]. This effect plays a significant role in gas discharges, in which the energy of electrons is considerably higher than in beam plasma. According to the calculations, maximum ratio of the nitrogen atom flow to ion flow is achieved at frequencies around 1 kHz and filling factor \( \sim 30-40\% \) [7]. However, in experiments with pulse electron beam with pulse duration 2 ms and filling factor 10-40\%, there was almost no impact of relative pulse duration on the relative content of N in beam plasma [3]. This can be explained by the lower temperature of electrons in the beam plasma and lesser absolute temperature change in process of plasma decay. However, the data shown in figure 5 indicate a more efficient generation of atomic nitrogen in the repetitively-pulsed mode, and this difference increases with increasing pressure of the nitrogen-argon mixture. A possible reason for the increase in the relative content of \( N^* \) in nitrogen-argon plasma compared to the pure nitrogen could be recharging of argon ions on nitrogen molecules with the formation of \( N_2^* \) and subsequent dissociative recombination of molecular ion.

Quantitative assessment of the relative content of excited atomic nitrogen in the plasma was done using the relations (1) and (2) relative to the ratios of intensities of the corresponding lines in the spectra. Since the cross-section of the particular process substantially depends on the incident electron energy, the values of corresponding cross-sections were calculated based on the results of studies of the electron beam energy spectrum [15]. It is estimated that the relative content of excited atomic nitrogen \( n(N^*)/n(N_2^*) \) in the high-current electron beam in the mode of continuously burning discharge \( (I_0=10 \text{ A}, U_2=200 \text{ V}) \) in nitrogen-argon medium (\( P=3 \text{ mTorr} \)) reaches \( \sim 5-6\% \). Unfortunately, AES method does not reveal non-excited atomic nitrogen, which, according to various sources, can be from \( \sim 2-3\% \) [16], to \( \sim 15-6\% \) [17]. However, as noted above, the formation of excited and non-excited
nitrogen atoms in the beam plasma occurs mainly in the same reactions, and the number of excited atoms correlates well with the overall content of atomic nitrogen, so the obtained qualitative dependencies are likely to be valid for non-excited atomic nitrogen as well.

The results shown in figure 6 were obtained at electron beam power 2 kW and the discharge power consumption 6 kW. The proportion of molecular nitrogen ions of nitrogen ions n(N_2^+)/n(N_2^+) in the beam plasma is six times higher and reaches ~2-3% and relative content of neutral nitrogen atoms is 1.8 times higher. This result illustrates the higher efficiency of nitrogen ionization and generation of atomic nitrogen by the electron beam compared to the gas discharge, which is explained by the greater beam energy consumption for the ionization of nitrogen, when mainly molecular ions are created, and by the lower temperature of electrons in the beam plasma.

5. Conclusion

Increase in pressure of the nitrogen-argon gas mixture, accelerating voltage and discharge current lead to an increase in the content of atomic nitrogen in the electron beam plasma, with the pressure of gas mixture and the average current value being the most significant parameters. Application of repetitively-pulsed mode does not accompanied by a significant increase in atomic nitrogen content characteristic of the discharge plasma. Electron beam much more effectively generates atomic nitrogen compared to the discharge with the self-heated hollow cathode.

Acknowledgments

This work was performed in the frame of State Task No. 0389-2015-0023 and was supported in part by RAS Program (Project No. 18-2-2-7).

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