Optical radiation from plasma of abnormal glow discharge in various gas mixtures.

T V Stepanova*, Yu V Borisuk1, D V Mozgrin1, P S Nenashev1, V S Norakidze1, N M Oreshnikova1, T. Müller2, L. Misozhnikov3, and A A Pisarev1

1 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, 115409 Moscow, Russia
2 Rübig GMBH, Rübig GmbH&CoKG, Durisolstrasse 12, 4600, Wells, Austria
3 SKTB KASKAD, 109147, Marxist street, 34/4, Moscow, Russia
E-mail: shtanya@mail.ru

Abstract. Optical radiation from plasma of abnormal glow discharge in Ar+N2, He+ N2, and N2+H2 was investigated. Lines of N2 N2+, N, N+, Ar+, Ar, He, Fe, H, H2 and OH were detected by optical spectrometry. Discharge current and intensities of spectral lines of N2, N2+, N, and N+ versus the concentration of Ar, He, and H2 in the gas mixtures were measured at various compositions of the working gas.

1. Introduction
Abnormal glow discharge is often used for plasma nitriding [1,2] to improve mechanical and chemical sustainability of parts of various machines. Well-known drawback of the glow discharge at elevated pressures is its sudden transition in the arc mode. Nevertheless, if to operate the discharge at impulse-periodical regime at a high frequency, the arc has no time to develop [3], which makes this regime attractive for technological applications.

Nitriding is usually performed in mixtures of gases, which are added to nitrogen to accelerate the process of nitriding and control the structure of the nitrided layer. For example, addition of hydrogen removes oxides due to chemical interaction, while addition of argon cleans the surface due to physical sputtering, and both activate nitrogen penetration into the material. Some authors suggest using helium instead of argon in the process of nitriding [4]. The addition of helium leads to a smooth heating of the sample surface without local overheating and surface destruction. However, the composition of plasma, particularly the concentration of ions and exited neutrals, which participate in nitriding, depend on the composition of the working gas, and this is also a factor of significant influence on the characteristics of the nitrided surface. Therefore, various investigations of the discharge are performed to choose optimum processing parameters and plasma composition.

This work describes results of investigation of discharge current and content of nitrogen ions (N2+, N+) as well as excited atoms and molecules (N2, N) in plasma of abnormal glow discharge in various N2+Ar, N2+He, and N2+H2 gas mixtures.

2. Experimental setup
The scheme of the installation operating with the abnormal glow discharge is shown in Figure 1a. It consists of a vacuum chamber, a pumping system, a gas inlet system, and a power supplier [1,2]. The
The cathode is a rod 100 mm in length and 12 mm in diameter coaxially installed inside a cylindrical anode 180 mm in diameter and 420 mm in length. The cathode was made of stainless steel AISI 321.

The discharge is powered by a generator of rectangular pulses with the amplitude of 400-650 V, maximum power of 12 kW, pulse repetition frequency 1 - 100 kHz, and the pulse duty factor 10 - 80%. The discharge voltage and current are measured by a four-channel digital oscilloscope Tektronix TPC 2024B using a voltage divider and a shunt. Typical dependencies of the discharge voltage and current are shown in Figure 1b.

Figure 1. a) Scheme of the experimental installation, b) An example of the time dependencies of the discharge voltage and current for the discharge ignited in N₂ at 1 Torr, 600 V, 3 kHz.

Discharges in Ar, N₂, H₂, He, Ar+N₂, N₂+He, and N₂+H₂ at a pressure of 1.0, 1.5, and 2.0 Torr were investigated. The electron temperature of the discharge and the plasma density were previously measured to be 2-5 eV and 1-3×10¹⁶ cm⁻³, respectively [5].

Optical radiation from plasma was measured through a quartz glass window and neutral grey light filter by a 3-channel spectrometer AvaSpec-ULS2048L-USB2-RM. The wavelength ranges and optical resolutions of the three channels are: 200-365 nm and 0.12 nm for the first channel, 364-603 nm and 0.18 nm for the second channel, and 600-810 nm and 0.15 nm for the third channel. The integration times used for data accumulation were 400 ms, 50-200 ms, and 40-100 ms for the three channels, respectively. The signal was analyzed by a standard software package Avantes and identified using data bases [6-8]. The start of spectroscopic measurements was synchronized with application of the discharge voltage.

3. Experiment results

Figure 2 shows examples of panoramic optical radiation spectra from the discharges in Ar+N₂ (1:1), N₂+H₂ (1:1), and N₂+He (1:1), ignited at a pressure of 2.0 Torr, voltage of 600 V, pulse frequency of 3 kHz, and pulse duty factor of 80%. Panoramic optical radiation spectra ignited at a pressure of 1.0 and 1.5 Torr are similar but differ in the intensity of spectral lines and band of lines. Intensities of spectral lines increase with the gas pressure. By comparison of the experimental spectra with reference spectra, the following lines and bands of lines were identified in the Ar+N₂ discharge: Ar⁺, Ar, N₂, N₂⁺, N, N⁺, Fe, H, OH. Lines and bands of lines in mixture of N₂+H₂ were identified as N₂, N₂⁺, N, N⁺, Fe, H, H₂, and OH. Similar results were observed in [3]. Lines and bands of lines in mixture of N₂+He were identified as N₂, N₂⁺, N, N⁺, He, H, Fe, and OH. The intensity of radiation depends on the pressure and the applied voltage. The energy of electrons mainly depends on the applied potential and on the gas pressure. Optical emission increases with the gas pressure due to increase of the probability of inelastic collisions [9]. Lines OH and H in nitrogen plasma appear due to water vapor, while lines of Fe appear due to sputtering of the cathode.
Figure 3 shows dependencies of intensities of several optical lines (in arbitrary units) on gas composition, and the discharge current as a function of the composition is given for comparison. These dependencies were obtained at a pressure of 1.0 Torr, voltage of 600 V, pulse frequency of 3 kHz, and a pulse duty factor of 80%. The intensities of the following lines and bands of lines are shown: Hα (656.1 nm), N₂ (C^3Πₓ→B^3Πₓ, 380.5 nm), N (2p3s→2p3p, 648.4 nm), N₂^+ (B^2Σₓ⁺→X^2Σₓ⁺, 391.4 nm), N⁺ (2p3s→2p3p, 566.6 nm), Ar (3s^23p^2(3P½)4s→3s^23p^2(3P½)4p, 696.4 nm), Ar⁺ (3s^23p^2(3P½)4s→3s^23p^2(3P½)4p, 488.0 nm), and He (1s2p→1s3d, 587.5 nm). Intensities of molecular lines N₂ (C^3Πₓ→B^3Πₓ, 337.1 nm) and N₂⁺ (B^2Σₓ⁺→X^2Σₓ⁺, 427.8 nm) were also measured, and their features were the same as those of the intensities of respective neutral and ion lines given in the figure. Experiments at the gas pressures of 1.5, and 2.0 Torr demonstrated similar tendencies.

Figure 3a is given for the discharge in the N₂+Ar mixture. One can see that the discharge current and intensity of Ar radiation (both ions and neutrals) increase with increase of the Ar content at the fixed total pressure of the N₂+Ar mixture. The discharge current increases with the pressure of Ar due to the increase of the secondary electron emission from the cathode under impact of heavier Ar ions and due to increase of ionization degree in plasma with increase of the electron emission. The concentration of Ar⁺ ions increases due to increase of the number of electrons that ionize neutrals. The concentration of N₂⁺ and N⁺ increases with increase of nitrogen content in mixture, though the current decreases, and this may be connected with smaller ionization potential of N₂ (14.53V) with respect to argon (15.76V). N₂ and N radiations have maxima: a faint maximum for atoms and a bright maximum for molecules (right branch is due to decrease of the N₂ concentration, while the left branch is due to variation of the N₂ concentration with Ar pressure). The intensities of excited N₂ and N have maxima (the right branch decreases due to a decrease of N₂ content in mixture, and left branch increases due to Penning excitation [10] where excited Ar transfers its energy to N₂ molecule in inelastic collision and excites it. So, general trends in the current and line intensities in Ar+N₂ mixture are qualitatively described by features of electron emission from the cathode and ionization and excitation of gas components by electron impact. Penning excitation of N₂ by exited Ar atoms is important at Ar content below 50%.

![Figure 2](image)

**Figure 2.** Emission spectra of an abnormal glow discharge in: a) Ar +N₂ (1:1), b) N₂+H₂ (1:1), c) He+N₂(1:1)

Figure 3b is given for the discharge in the N₂+H₂ mixture. One can see that the current decreases at high and low concentrations of H₂ content in mixture. The increase of left branch of the current is due to smaller ionization potential of H₂ (13.6 eV for H instead of 14.53 eV for N), while the decreasing right branch is due to decrease of the secondary electron emission from the cathode. H lines follow the current qualitatively as the dissociation, excitation, and ionization are proportional to electron density in plasma. Besides, the increasing left branch is associated with increase of H₂ content in the gas, and therefore increase of the H line is faster than increase of the current. All nitrogen lines (N, N⁺) and
bands ($N_2$, $N_2^+$) behave similarly to each other. A small increase of intensity is observed at 10-20% $H_2$ content. Then intensity of all lines and bands decreases with the increase of the $H_2$ content in mixture. Increasing left branch of all nitrogen lines is due to smaller ionization potential of hydrogen. Fast general decrease of nitrogen lines at the $H_2$ concentration above 20% is due to two factors: decrease of $N_2$ content in gas and decrease of the current, which is connected with the decrease of the secondary emission from the cathode. The nitrogen lines decrease faster than the current because of the contribution of the first factor.

Figure 3c is given for the discharge in the $N_2$+$He$ mixture. One can see that the current decreases rather rapidly with increase of $He$ content in the mixture due to very high ionization potential of $He$ (24.58 eV) and decrease of the secondary electron emission from the cathode. All nitrogen lines and bands generally follow the decrease of the current with increase of $He$ content. Increase of $He$ content leads to increase of the number of $He$ atoms in metastable state in plasma. According to [11], the faint increase in the intensity of $N_2^+$, which is observed at low concentration of $He$, can be due to the Penning ionization process where $He$ in metastable state transfers its energy to $N_2$ molecule in inelastic collision and ionizes it.

Figure 3. Discharge current and intensities of selected optical lines at various compositions of the working gas: a) Ar+$N_2$, b) $N_2$+$H_2$, c) $He+N_2$ at $U=600V$, $v=3$ kHz, $D=80\%$, $p=1$ Torr

Figure 4 shows the compilation of the dependences of the discharge current and line intensities (in arbitrary units) of ions $N^+$ and excited neutrals $N$ on the pressures of $N_2$ and supplementary gases in various gas mixtures at $U=600V$, $v=3$ kHz, $D=80\%$, $p=1$ Torr.

Figure 4. Discharge current and radiation of a) neutrals $N$ (648.4 nm) and b) ions $N^+$ (566.6 nm) in various gas mixtures at $U=600V$, $v=3$ kHz, $D=80\%$, $p=1$ Torr
One can see that with increase of the N\textsubscript{2} content, the discharge current decreases in mixture with Ar, increases in general in mixture with He, and has an intermediate behavior in mixture with H\textsubscript{2}. In the technologically useful region of N\textsubscript{2} content below 40%, the current is approximately constant in mixture with Ar, and increases with increase of N\textsubscript{2} content in mixtures with H\textsubscript{2} and He. With increase of N\textsubscript{2} content in gas mixtures, intensities of neutral lines generally increase in mixtures with light gases following the current trends, but in mixture with heavy Ar they have flat maxima. Concentrations of N\textsuperscript{2+} and N\textsuperscript{-} generally increase with increase of N\textsubscript{2} content in all gas mixtures. In the technologically useful region of N\textsubscript{2} content below 40%, all neutral and all ion lines increase with increase of the N\textsubscript{2} content in all working gases. At high concentrations of N\textsubscript{2} above 90%, concentrations of N\textsuperscript{2+} and N\textsuperscript{-} decrease in mixture with light gases (H\textsubscript{2} and He) and increase in mixture with heavy Ar. Maximum current at 90% N\textsubscript{2} content is in mixture with H\textsubscript{2}.

4. Conclusion

Variation of the current and optical plasma radiation of neutrals and ions in the abnormal glow discharge powered with the frequency of 3 kHz in N\textsubscript{2}+Ar, N\textsubscript{2}+He, and N\textsubscript{2}+H\textsubscript{2} were investigated at pressures of 1.0 - 2.0 Torr. All main lines of N\textsubscript{2}, N\textsuperscript{2+}, N, and N\textsuperscript{-} particles, which are active in nitriding of steels and alloys, have been found in optical spectra. At the N\textsubscript{2} content in the working gases below 40%, which is important for technological applications, the discharge current is invariable in mixture N\textsubscript{2}+Ar, while it decreases with decrease of the N\textsubscript{2} pressure in mixtures N\textsubscript{2}+He, and N\textsubscript{2}+H\textsubscript{2}. Concentrations of all exited nitrogen neutrals and nitrogen ions decrease with decrease of the N\textsubscript{2} pressure in this pressure range in all gas mixtures. In the region of high N\textsubscript{2} content, behavior of line intensities is rather complicated, but in general, increase of the N\textsubscript{2} pressure leads to the following features: the neutral lines (N) in mixture N\textsubscript{2}+Ar slightly decrease, while neutral lines in N\textsubscript{2}+He, and N\textsubscript{2}+H\textsubscript{2}, increase and have a not well pronounced maximum at about 90%N\textsubscript{2}. All ion lines at high N\textsubscript{2} concentration increase with the N\textsubscript{2} pressure in general, and lines in mixtures N\textsubscript{2}+He, and N\textsubscript{2}+H\textsubscript{2} have a not well pronounced maximum at about 90% N\textsubscript{2}.

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