Working-Gas Activation in the Hollow Anode Region of Gas Low-Pressure Arc Discharge[1]

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Abstract – The results of experimental investigation of low-pressure non-self-sustained arc discharge plasma used for the process of nitriding of materials and tools are presented. The elemental composition of N_2, Ar, N_2–Ar plasmas have been determined at the pressure of $4.5 \cdot 10^{-3}$ Torr by Hiden EQP 300 mass spectrometer. In addition, the effect of low-pressure arc discharge on working-gas activation is discussed.

1. Introduction

Plasma diffusion treatment is a well known method for substantial improvement of wear, corrosion, and fatigue resistance of materials and tools. Nitrogen is widely used as an additional element to metals. Most frequently, plasma activated nitriding is performed by d.c. glow discharge in the atmosphere of dissociated ammonia or hydrogen-nitrogen mixtures. When 300–1000 V is applied between the substrate, which plays as a cathode, and the chamber walls (anode), under the pressure between 40 and 400 Pa a self-sustained glow discharge operates [1].

During, approximately, last twenty years new technologies of plasma generation were developed and made it possible to uncouple plasma formation from the substrate [2, 3]. Usually, working pressures are lower as compared to a traditional glow discharge so that ions are accelerated up to the energies equal to substrate biasing voltage and thus effectively clean the surface from dust and surface oxides.

One of the mentioned methods is plasma generation by non-self-sustained low-pressure arc discharge [4]. This method has shown better results in treatment time, operation of modified layer structure, gas consumption, and consequently, treatment cost than dc glow discharge one when nitriding [5, 6]. It should be mentioned that in the process commercial nitrogen without any hydrogen addition was used.

So, the study of plasma generated by low-pressure non-self-sustained arc discharge is necessary for understanding the benefit reasons of given gas activation method, also for modeling the plasma-surface and diffusion processes, and for scaling reasons. The knowledge of main active plasma species influencing the better results in nitrogen penetration into the substrate surface, and corresponding operational parameters, will provide the ability to extend plasma generation volumes from one to tens of cubic meters.

2. Experimental setup

Figure 1 shows a schematic view of the experimental setup.

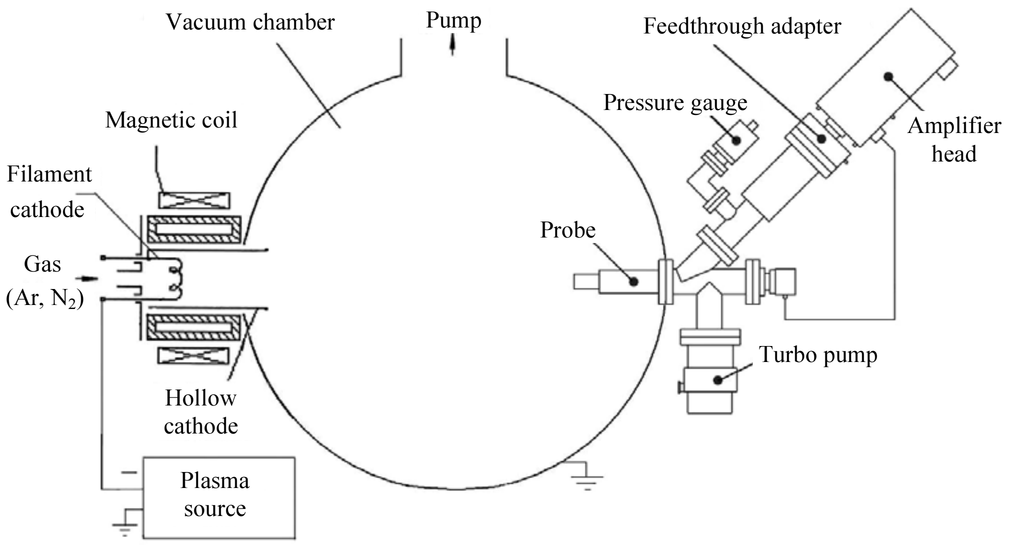

Fig. 1. Scheme of the experiments

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Plasma source with filament and hollow cathode was mounted on the vertical flange of a water-cooled experimental chamber. The plasma generator creates plasma with concentration about 10^9–10^{10} ions per cubic centimeter in the pressure range of 0.1–1 Pa in the volume of about one cubic meter.

For the work, a HIDEN EQP 300 mass spectrometer was used. A profound description of this diagnostic unit has been given by Budtz-Jorgensen [7].

The HIDEN EQP 300 consists of five main sections (Fig. 2).

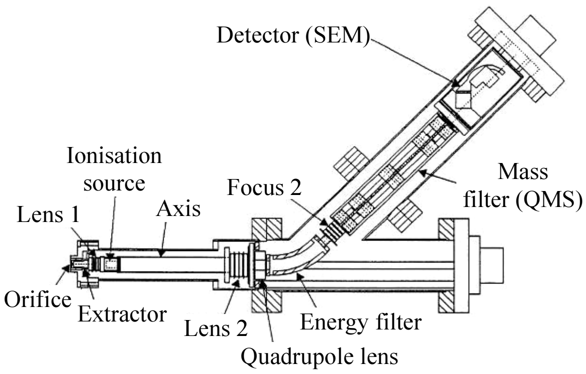

Fig. 2. Diagram of the HIDEN EQP [7]

The functions of these sections shall be explained briefly. The extraction section consists of the extractor and lens 1. In this part, the ions and neutrals that pass the orifice must be directed towards the detector. The ionization source is only needed when measurements in the RGA mode must be conducted. Neutral particles are then ionized by a dual-filament electron impact ionization source. The deceleration section consists of the axis, lens 2 and the quadrupole lens. This section is needed to decelerate the ions to an energy of approximately 40 eV. Only this low kinetic energy ions can pass the 45° bend to the analyzer. The energy filter is a 45° sector field energy analyzer, where ions are deflected by an electric field. Depending on the kinetic energy, the particles enter the section field. The last section of the HIDEN EQP 300 is the mass filter. This filter is a quadrupole mass spectrometer consisting of four metal rods with a superposed d.c. and rf voltage. Only particles with a special mass-to-charge ratio can pass this filter and are detected, while the other mass-to-charge ratios are removed by the r.f.-field, respectively.

3. Investigation method

The vacuum chamber was evacuated by turbo molecular pump down to a pressure of $4 \cdot 10^{-5}$ Torr. Before each of the experiments for different gases about 5–7 h of pumping took place. The argon, nitrogen, and 50% argon – 50% nitrogen gas mixture were introduced throughout a manual leak valve. The experiments were held at the pressure of $4.5 \cdot 10^{-3}$ Torr.

To reveal changes of ion plasma composition versus discharge current, two values of 50 and 100 A have been chosen. The current was tuned by electron emission of filament cathode. To stable the system parameters after switching on the discharge it was remained working for an hour.

The mass spectrometer was differently pumped to a pressure of $8.5 \cdot 10^{-8}$ Torr. During the experiments its pressure was $1 \cdot 10^{-6}$ Torr. For ion mass scans, parameters of the HIDEN EQP were tuned to obtain the maximum signal.

4. Results and discussion

Figure 3 shows two spectra of ions of an argon plasma for 50 and 100 A of discharge current, respectively. In order to interpret the results, a spectrum was always scanned before turning on the discharge to check the initial neutral gas composition. It was revealed that gas impurity and "residual" water in the experiment volume form about 1% of H_2O.

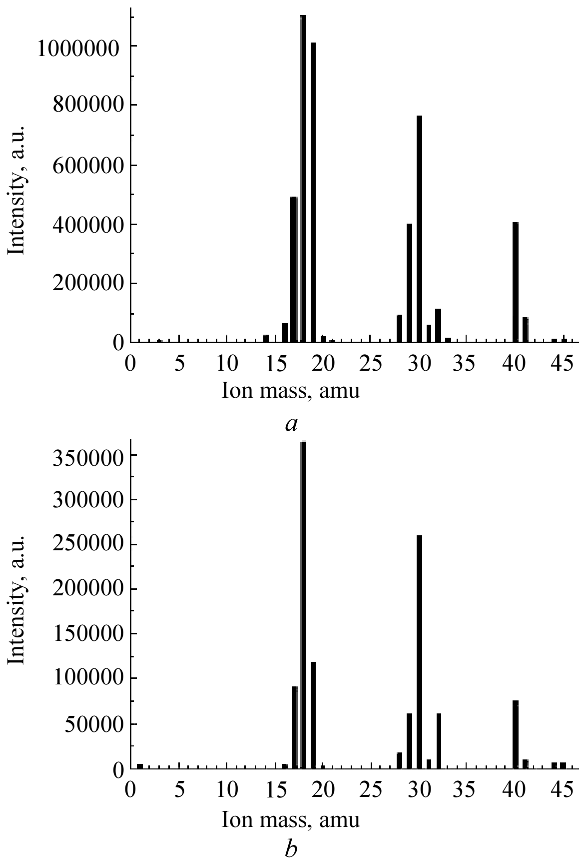

Fig. 3. Mass spectra of Ar plasma. The discharge current is: *a* – 50; *b* – 100 A

So, peaks with $m/z = 17$ and 18 correspond to ions from the residual water (OH^+ and H_2O^+). Peaks of residual nitrogen ions is also presented as $m/z = 14$ and 28 (N^+, N_2^+). As a result of plasma-chemical reactions NO ions are formed (intense peaks, $m/z = 30$). A considerable amount of argon ions is detected, but with the discharge current increased from 50 A

(Fig. 3, *a*) to 100 A (Fig. 3, *b*), its relative value in the plasma decreases, and simultaneously, peaks of H_2O and NO become more pronounced. A small hydrogen atoms peak is observed when the discharge power is increased.

In the case of nitrogen (Fig. 4), there are two distinguished ion peaks of molecular and atomic nitrogen. As in the previous case, there are a number of oxygen-containing complexes with high signals. Peak with $m/z = 17$ is higher than for argon in both 50 and 100 A cases. It may contain NH_3 as well as OH ions but their proportions are not estimated in present work.

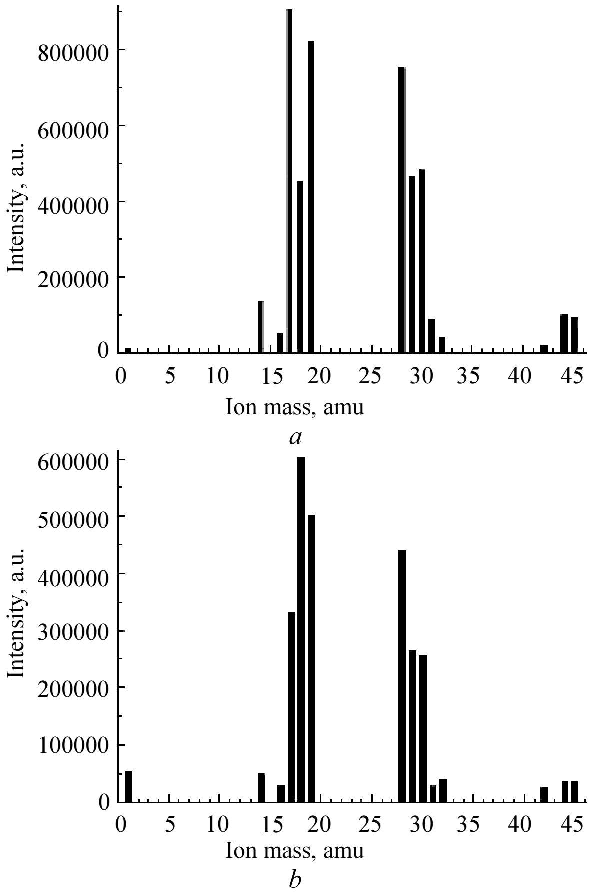

Fig. 4. Mass spectra of N_2 plasma. The discharge current is: *a* – 50; *b* – 100 A

Figure 5 shows mass spectra from 50% Ar – 50% N_2 mixture plasma at the discharge current of 50 and 100 A, respectively. At a discharge current of 50 A (Fig. 5, *a*), nitrogen atom ions ($m/z = 14$) are prevail over the molecule ions ($m/z = 28$) and argon ions ($m/z = 40$). Increasing the current to 100 A, molecule nitrogen ions become dominating, but nitrogen atoms amount decreases. As in the case of Ar and N_2, the ionization of gas impurities and residual atmosphere occur more effective in the Ar–N_2 mixture.

In spite of the presence of oxygen-containing impurities in N_2 case, it was previously shown that nitriding processes in the plasma of low-pressure non-self-sustained arc discharge is effective [5].

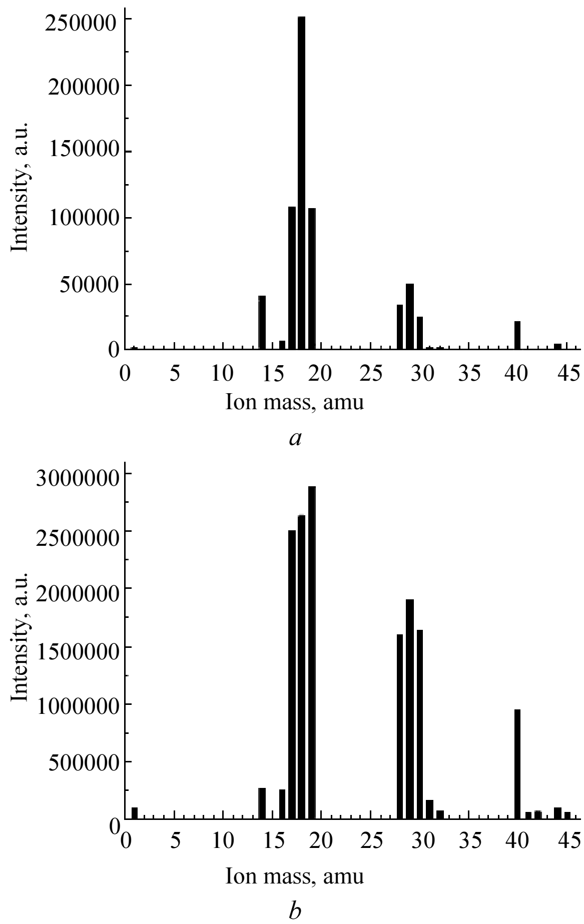

Fig. 5. Mass spectra of 50% Ar – 50% N_2 plasma. The discharge current is: *a* – 50; *b* – 100 A

For all three gases $m/z = 19$ was observed. It can be H_3O or F ions. However, it was not checked in this work.

Thus, by the method of mass spectrometry in the hollow anode region it was shown that low-pressure non-self-sustained arc discharge is a good gas activator. It appeared that oxygen-containing complexes compose a considerable part of ion component of plasma. To decrease its presence, long pumping is required. For better understanding the gas activation processes and precise plasma components detection, next work should involve probe and plasma spectroscopy methods. In addition, neutral components of plasma should be detected.

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