Pulsed abnormal glow discharge with hollow cathode for nitriding of internal cylindrical surfaces

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Abstract. Possibility of nitriding of internal cylindrical surfaces in plasma of abnormal glow discharge with hollow cathode in the pulse-periodic mode in N₂+H₂ was investigated. Tubes with internal diameters of 6, 8, and 9 mm and with the aspect ratio from 12 to 50 were made of low carbon steel were used. Regimes of the discharge were investigated. Nitrided layers in different parts of the tubes were analyzed.

1. Introduction
Plasma nitriding is a method of thermochemical treatment, which is widely used to enhance surface hardness, fatigue strength, and corrosion resistance of steels [1, 2]. In industry, abnormal glow discharge is commonly used for this purpose. The specific technological task is treating of cavities, which are usually inaccessible for plasma. Still, the need to modify cavities and tubes of small diameters and large aspect ratios exists. In [3], it was proposed to use the abnormal glow discharge (AGD) with hollow cathode in the pulse-periodic mode for this purpose. The present work is devoted to investigation of ignition and properties of the abnormal glow discharge in tubes and demonstration of nitriding of internal surfaces of the tubes.

2. Discharge features
Experiments were performed in the experimental set up described in details in [4]. The treated tube served as the cathode, and vacuum wall served as the anode. Nitriding was performed in plasma of the abnormal hollow cathode discharge. Tubes with the internal diameter of 6, 8, and 9 mm and with the aspect ratio from 12 to 50 were used as the cathode. Tube dimensions are denoted in the text below by three numbers in mm (external diameter × internal diameter × length). The tubes were made of Russian low-carbon steel 30XH2MФA (its analogues in Poland and Bulgaria are 30HN2MFA and 30ChN2MFA, respectively). Before nitriding, the samples were cleaned in an ultrasonic bath and then in a glow-discharge plasma to remove oxides (discharge in argon, pressure 0.5–0.8 mbar, voltage 450–500 V, duration 15–30 minutes). Plasma nitriding was performed in the 50–50% mixture of nitrogen and hydrogen. Plasma parameters during nitriding were the following: voltage 450–650 V, frequency 1–100 kHz, duty cycle 25–85%, pressure 0.6-6.6 mbar, duration 4–4.5 hours. Voltage and discharge current as well as the temperature of samples were monitored.

The discharge was initiated on the outer surface of the tube at the voltage of 600 V, and then it propagated into the tube. Penetration into the tube was accompanied by sharp increase in the discharge
current and decrease in the voltage to 450 V (mention that the voltage is negative). The current and voltage oscillograms of the discharge are shown in figure 1. Discharge transition into the tube is shown on a larger scale in the circular inset. The small initial step of the current of the order of 0.1 A is connected with the discharge on the outer surface, while the following sharp increase of the current up to 1.7 A is due to transition of the discharge into the tube. Typical final volt-ampere characteristics of the discharge are shown in figure 2. The rising dependence is typical for the abnormal discharge [5].

![Figure 1. Current and voltage oscillograms of the discharge (gas argon, pressure 4 mbar, frequency 1 kHz, duty cycle 50%, the tube 20×8×100 mm). The time of ignition and transition inside the tube are shown by vertical lines. Transition of the discharge into the tube is shown in the circle insert.](image1)

![Figure 2. Volt-ampere characteristics of the discharge in mixture of nitrogen and hydrogen 50–50% at a pressure of 4.0 mbar, frequency of 25 kHz, and duty cycle of 50%](image2)

3. Nitriding results
After nitriding, the samples were cut perpendicular to the axis in several parts, and the cross sections were polished and investigated under the electron microscope. Microhardness over the cross-section was measured using a FM-ARS 9000 hardness tester. The load on the indenter was 10 g, and it was applied perpendicular to the cross section at different distances from the tube surface. The respective depth profiles of three nitrided and one not nitrided sample are shown in figure 3 for the cross section near the central part of the tube between its edges (figure 3a) and in the cross section near the tube edge (figure 3b). After nitriding, the microhardness close to the surface increased 1.5–2.5 times. The thickness of the hardened layer was 300–400 μm. Tube 14×9×150 (green line) was overheated, and therefore the hardness of its core decreased compared to that of the virgin sample.

Microstructure of samples was analyzed using a TESCAN VEGA3 scanning electron microscope. Polished cross sections were chemically etched in the 16:3:1 solution of hydrogen peroxide, water, and hydrofluoric acid (H₂O₂+H₂O+HF) prior to the analyses. Elemental composition in the cross section was measured by energy dispersive analyses (EDS) as it was made in [6].

Figure 4 shows typical SEM images of the cross-sections of treated samples. The samples were nitrided at a temperature of 450 °C. After plasma nitriding at temperatures below 500 °C the samples still have their original ferrite-pearlite structure with distinct grain boundaries. The compound layer was about 2–5 μm thick. One can see that both the white layer and the structure of the diffusion zone are similar for the external and internal surfaces of the tube, though currents and therefore fluxes of active nitrogen were very different outside and inside the tube.
Figure 3. Hardness as a function of the distance from the internal surface of the tubes nitrided at 450–500 °C measured in two cross sections: (a) in the middle area of the tube between its edges, (b) near the edge of the tube.

Figure 4. The microstructure of a cross-section in the middle area between the edges of the tube nitrided at 450 °C. The cross sections are shown near: (a), (c) internal surface, (b), (d) external surface.

Figure 5 shows the distribution of elements through the depth near the internal surface of samples after the plasma modification. The nitrogen concentration is high within 5 µm, which correlates with the thickness of the compound layer. Although the hardness is high within 150–200 µm, the nitrogen concentration is small behind the compound layer and only slightly exceeds the background at these
depths. It is usually suggested that hardening at large depths is due to nitrogen in solid solution where nitrogen concentration is low.

![Figure 5. EDS distributions of elements as a function of the distance from the internal surface of the tube nitrided at 450 °C. Measurements were made in the middle part between the edges of the tube 20×8×100 mm.](image)

4. Conclusion
Hardening of the internal surfaces of tubes by nitriding at 400-550°C in abnormal glow discharge with hollow cathode was investigated for tubes with internal diameter from 6 to 9 mm and the aspect ratio from 50 to 12 respectively. Hardening was observed all through the length of the tubes both on the external and internal surfaces. The compound layer was about 2-5 µm thick, and the hardened zone was about 300–400 µm thick. The hardness of close to the internal surface below the compound layer increased 1.5–2.5 times after nitriding.

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