The effect of plasma electrolytic polishing on the surface properties of nitrocarburised steel

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Abstract. The effect of anodic plasma electrolytic polishing on the characteristics of low carbon steel (0.2 % C) after nitrocarburising was investigated. The formation of the modified layer including a hardened diffusion layer and a surface oxide layer occurs as a result of anodic plasma electrolytic nitrocarburising in an aqueous solution of glycerol (8 %), ammonium nitrate (5 %) and ammonium chloride (15 %) at 850 °C. Conducting a plasma electrolytic polishing of the surface leads to the removal of a loose part of the oxide layer (predominantly FeO), which affects the reduction the surface roughness of 2 times. The rate of the weight loss of steel in this process is 0.5 mg/s. The corrosion current density in a 3.5 % sodium chloride solution decreases from 41.0 μA/cm² in an untreated sample to 32.6 μA/cm² in the steel after nitrocarburising and polishing during 30 s and to 2–24 μA/cm² when the second operation lasted 60–300 s due to the protective action of the nitride zone and the dense part of the oxide layer. Wear test shows that plasma electrolytic polishing enhances the wear resistance of a nitrocarburised sample by 1.8 times.

1. Introduction
Plasma electrolytic nitrocarburising (PEN/C) is one of the high-speed methods of diffusion saturation, which permits to obtain a hardened layer with a thickness of up to 0.23 mm in 5 minutes on the surface of low-carbon steel [1]. The features of PEN/C is a more complex composition of the modified layer, which depends not only on the temperature and duration of processing, but also on the composition of the electrolyte and polarity of the workpiece. Saturation with nitrogen and carbon in a vapour-gaseous medium leads to a formation of iron oxides, which are detected at cathodic PEN/C of medium-carbon steel [2]. In the case of anodic treatment, an oxide layer thickness reaches 0.2 mm [3]. In addition, quenching of sample in the same electrolyte after PEN/C ensures the formation of martensite and retained austenite [4]. The surface hardness of low-carbon steels can reach 920–930 HV both after cathodic PEN/C [1, 5] and after anodic one [3, 6].

The polarity of the workpiece has a strong influence on its surface roughness. Electrical erosion at cathodic PEN/C increases the Ra roughness parameter from 0.11 μm to 2.17 μm after treatment of Q235 steel in urea-based electrolyte [7]. On the contrary, anodic PEN/C reduces sometimes the surface roughness due to anodic dissolution [6]. Both processes enhance the wear resistance of low-carbon steels, but the results achieved depend significantly on the test conditions. For example, the lubricant wear rate of steel 20 after anodic PEN/C in a solution of ammonium nitrate, glycerol, and ammonium chloride can be reduced 14 times against a hardened steel disc [3]. Ammonium nitrate is
an effective source of not only nitrogen, but also oxygen with the formation of a porous oxide layer that has good running-in and lubricant retention. Under dry friction conditions, this composition does not increase the wear resistance of steel.

Cathodic PEN/C in urea electrolyte enhances the corrosion resistance of steel 1020 due to the formation of iron carbonitrides [1]. In this case, the corrosion current density in a 3% sodium chloride solution decreases by a factor of 1.3 compared with untreated sample, and the corrosion potential shifts in the noble direction. More significant results are shown by anodic PEN/C according to test data in solutions of sodium chloride or sulphate due to the formation of an oxide layer. The corrosion current density of steel 20 in a 1M sodium sulphate solution decreases from 97 µA/cm² for untreated sample to 4.05 µA/cm² after saturation at 850 °C in a solution of ammonium nitrate, ammonium chloride and glycerol [3]. The results of potentiodynamic measurements are confirmed by the determination of the corrosion rate by the gravity method and electrochemical impedance spectroscopy [8].

The structure of the oxide layer affecting significantly the wear and corrosion resistance of steels depends not only on the electrolyte composition, but also on the PEN/C temperature. Different coefficients of thermal expansion of iron oxides and steel matrix lead to uncontrolled peeling of the outer layer during its growth and especially after quenching in the electrolyte. The loose structure of the oxide layer can play a positive role in wear testing with lubrication, but it can inhibit the increase in wear resistance under dry friction conditions. The quality of the outer layer can be improved by polishing it. The paper [9] shows the possibility of plasma electrolytic polishing (PEP) of the steel surface after its diffusion saturation in a single technological process. Positive results of PEP are reached for medium carbon steel after its treatment in nitrate and ammonium chloride solution using its heating at 750 °C for 5 min. The reduction of the surface roughness from 4.5 µm to 1.9 µm of PEN steel by PEP using mode of current interruption for 2 min without changing the structure of the diffusion layers is shows.

The aim of this work is to study the possibility of combined processing of low-carbon steel including anodic PEN/C followed by electrolytic plasma polishing (PEP) in the same electrolyser. To achieve this goal, it is necessary to determine the time of polishing to improve the characteristics of wear and corrosion resistance.

2. Experimental

Cylindrical samples (⌀ 10×15 mm) of low carbon steel (0.20 wt. % C) were ground with SiC abrasive paper grit size P320 to Ra ~1.0 µm and ultrasonically cleaned with acetone. Plasma electrolytic nitrocarburising (PEN/C) was carried out in a cylindrical electrolyzer with an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the electrolyzer. The solution temperature was measured using a thermocouple placed at the bottom of the chamber and maintained at 20 ± 2 °C. The samples were connected as the positive output, and the electrolyzer was connected as the negative output of the 15 kW DC power supply. An aqueous solution of glycerol (8 %), ammonium nitrate (5 %) and ammonium chloride (15 %) was used as working electrolytes. The PEN/C time was 5 min. The treatment temperature was 850 °C. After PEN/C the samples were quenched in the electrolyte (hardening).

PEP of nitrocarburised samples was carried out in an aqueous solution of ammonium sulphate (5 wt. %) under conditions of natural convection of an electrolyte at a voltage of 300 V. The electrolyte temperature was kept at 90 ± 2 °C. The PEP time varied from 30 to 300 s.

The structure of the surface layer of the samples was studied by scanning electron microscopy Quanta 3D 200i after polishing and etching of samples with the use of a 4 wt. % nitric acid solution in ethanol for 5–10 s as well as optical microscope. Microhardness of the sample’s surface layer after PEN/C and PEP was measured on a Falcon 503 (Innovatest) apparatus at a loading of 50 g. Surface roughness before and after PEN/C and PEP was investigated using a TR200 roughness tester.

Dry wear testing of the samples was carried out against a Al₂O₃ ball (6.35 mm in diameter) with a 10 N normal load, a 0.4 m/s sliding speed, and a 240 m sliding distance (diameter of track is 9 mm) at
room temperature using a ball-on-disk tribometer. The weight loss of the tested samples was measured using a Citizen CY224C balance after preliminary degreasing in acetone solution with an accuracy ±0.0001 g.

The corrosion resistance of the samples was determined by potentiodynamic polarization curves using a Biologic SP-150 potentiostat-galvanostat (Biologic Science Instruments) with a standard three-electrode cell in a 3.5 % solution of sodium chloride. Graphite served as the auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode. Potentiodynamic polarization curves were taken with a sweep speed of 1 mV/s. The corrosion current density was determined by Tafel extrapolation in the range of 50 to 250 mV with respect to the open circuit potential.

3. Results and discussion
Anodic PEN/C of steel results in the formation of a structure including oxide and modified layers (figure 1). X-ray analysis was found oxide layer (FeO, α-Fe₂O₃, and Fe₃O₄) and modified layer contains martensite, retained austenite and solid solution of nitrogen and carbon in iron. Oxide layer is formed due to the samples’ oxidation, solid solutions are the results of nitrogen and carbon diffusion into material structure. Martensite, and retained austenite are the results of incomplete hardening in electrolyte.

The study of the morphology of the steel surface after PEN/C shows the presence of microcracks and peeling of the outer part of the oxide layer. After PEP of the treated surface its morphology changes. The loose outer part of the oxide layer containing microcracks and pores is removed. The removal of the outer part of the oxide layer as a result of polishing is reflected in the linear dependence of the weight loss of samples on the processing time (figure 2).

The surface roughness of nitrocarburised samples decreases only after PEP during 30 s and then increases (figure 2). After PEN/C the surface roughness decreases by 2.5 times and further leveling of the surface profile occurs only within 30 s. After 30 s polishing of PEN/C-samples a local etching of the material begins to occur and the surface roughness becomes approximately equal to the roughness of untreated sample.

Figure 1. SEM image of cross-section of low-carbon steel surface after PEN/C: 1 – oxide layer; 2 – modified layer; 3 – initial structure.

Figure 2. Surface roughness and material removal weight of steel samples vs PEP time.

The PEP of the PEN/C sample during 30 s leads to an increase in its wear rate (figure 3). With a rise in PEP time the wear rate becomes lower than that of PEN/C-samples and untreated ones. From the results obtained, it follows that the additional polishing of the hardened surface can increase the wear resistance.

Corrosion tests show that the PEN/C and PEP of steel samples can improve its corrosion resistance (figure 4). The corrosion current density decreases by 1.9 times after PEN/C. However, corrosion current density increases significantly after 30 s of PEP, probably due to uneven removal of the oxide.
layer. With increasing PEP time, the corrosion current density decreases as the loose part of the oxide layer is removed and the nitride zone remains.

![Figure 3. Wear rate of steel samples vs PEP time.](image1)

![Figure 4. Corrosion current density of steel samples vs PEP time.](image2)

**4. Conclusions**

The opportunity of increasing the wear and corrosion resistance of steel by combining anodic plasma electrolytic saturation of the surface with interstitial elements and quenching followed by plasma electrolytic polishing is shown.

The surface roughness after the PEN/C decreases from the initial value $R_a = 1.00 \, \mu m$ to $0.38 \, \mu m$, and to $0.17 \, \mu m$ after PEP for 30 s. At the same time, the wear rate and corrosion current density are minimal after polishing for 3 min.

PEP after PEN/C is advantageous during 3 min in a 5 wt. % solution of ammonium sulphate at electrolyte temperature of $90 \, ^\circ C$ and a voltage of $300 \, V$.

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