Plasma electrolytic polishing of nitrided steel under force convection condition

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Abstract. The effect of plasma electrolytic polishing in an ammonium chloride electrolyte under force convection condition on the characteristics of medium carbon steel after anodic plasma electrolytic nitriding was investigated. The morphology of the steel surface was studied using a metallographic microscope. The phase composition of the surface layers was studied using an X-ray diffractometer. Treatment specimens were tested under dry friction conditions with a counter body made of bearing steel. Corrosion studies were performed using potentiodynamic polarization curves in a 3.5% sodium chloride solution. Nitriding increased the surface hardness up to 1130 HV due to the formation of a nitride-martensite layer with an outer oxide layer. After polishing of the nitrided surface, the loose outer part of the oxide layer containing microcracks and pores is removed, surface lightening has occurred. The reduction of the wear rate of 45-fold and the corrosion current density of 4.8-fold of nitrided steel by plasma polishing without changing the structure of the diffusion layers was shown.

1. Introduction
Plasma electrolytic technologies have a wide potential usage in various industries. These include the aerospace and oil industries, tool and electrical ones [1], as well as biomedical applications in surgery [2], disinfection of solutions [3], etc. Plasma electrolytic nitriding (PEN) increases significantly the wear and corrosion resistance of some structural steels due to the rise in the hardness of the surface layer and the protective action of nitrides and iron oxides. There are examples of PEN of S0050A medium carbon steel in a carbamide-based electrolyte [4], 316L steel in a solution of ammonium carbonate [5], and low-alloy steel 40Cr in electrolyte contained ammonia and ammonium chloride [6]. The disadvantage of the cathode PEN is the erosion of the surface due to electrical discharges. Anodic PEN is accompanied by anodic dissolution [3], which reduces the surface roughness of the treated steel. In addition, the anodic process leads to the formation of an oxide layer with protective properties under the conditions of atmospheric corrosion [7], but not always having good behavior in friction pairs [8]. The likely reason is the presence of a loose part of the oxide layer.

An effective method of the enhancement of metal surfaces is plasma electrolytic polishing (PEP), also implemented in aqueous electrolytes, but with use of other current passing modes. PEP is characterized by high processing speed, low surface roughness of the polished layer, the absence of aggressive and toxic reagents. This method has been successfully used for polishing knee caps, titanium micro implants [9], etc. This process reduces the surface roughness of nitrided steel without
removing the hardened layer [10]. Therefore, the purpose of this work is to increase the wear and corrosion resistance of nitrided steel by means of its additional PEP, which can be performed in the same electrolyzer.

2. Experimental

Cylindrical samples (a diameter of 10 mm, a length of 15 mm) of medium carbon steel (0.45 wt.% C) were subjected to plasma electrolytic nitriding in a cylindrical electrolyzer under force convection condition. There was an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the electrolyzer. In the upper part of the electrolyzer, the electrolyte was overflowing into the sump and was further pumped through a heat exchanger at a rate of 2.6 l/min. The solution temperature was 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 ammonium nitrate NH₄NO₃ (5 wt.%) with ammonium chloride NH₄Cl (15 wt.%) was used as the working electrolyte. After switching the voltage to 200 V, the samples were immersed in the electrolyte at a speed of 1–2 mm/s. Once the sample was immersed at a depth equal to its height, the voltage was decreased to 135 V in order to reach the prescribed temperature of the sample – 850°C, the current was 8.2±0.2 A. The PEN time was 5 min and after that, the samples were quenched in the electrolyte (hardening). PEP was carried out in an aqueous solution of ammonium chloride (3 wt.%) with added glycerol or oxalic acid (5 wt.% each) at a voltage of 275 and 300 V. The immersion depth of the upper end was 5 mm. The electrolyte was pumped through a heat exchanger at a flow rate of 1 l/min. The electrolyte temperature was kept at 80±2°C. In this case, the sample temperature was known to be 110–120°C while the PEP time was 1 min.

The phase composition of the surface layers after PEN was investigated with the use of an X-ray diffractometer with Co Ka radiation by a simple scanning mechanism in the theta-2theta-mode with a step of 0.1° and a scanning rate of 1.25°/min. The morphology of the steel surface was studied using a metallographic microscope. Microhardness of the surface layer of the sample after PEN+PEP was measured on a Falcon 503 apparatus at a loading of 50 g. The corrosion resistance of the samples was determined by the potentiodynamic polarization curves using an SP-150 Biologic potentiostat-galvanostat with a standard three-electrode cell in a 3.5% solution of sodium chloride at a sweep rate of 1 mV/s. Dry wear testing of the samples was carried out against a bearing steel disk with a normal load of 10.4 N, a sliding speed of 1 m/s, and a sliding distance of 1000 m at room temperature using a laboratory unit.

3. Results and discussion

The anodic PEN results in the formation of a surface layer of oxides (FeO and Fe₃O₄) and a modified layer underneath containing nitrices (Fe₃N), martensite and retained austenite. The morphology study of the steel surface after PEN shows the presence of microcracks and peeling of the outer part of the oxide layer (figure 1a). This morphology changes after PEP of the nitride surface. The loose outer part of the oxide layer containing microcracks and pores is removed (figure 1b). Table 1 shows the weight loss of the samples on the processing PEP. Moreover, X-ray analysis confirms the decrease in the intensity of the peaks of oxides after PEP, while the peaks of nitrides are maintained. Fe₃O₄ is not detected after PEP in the chloride electrolyte with the addition of glycerol at 275 V and oxalic acid at 300 V. In the latter case, FeO is not also found. At the same time, these additives lead to a decrease in the weight loss of the samples and the current yield (Table 1). This is due to the surface passivation by the interaction products of functional groups of organic molecules with the metal, which leads to a current consumption. This process can be carried out according to the following scheme:

(n+1)Fe³⁺ + mH₂O_ads + xOH⁺(•OH)ads → [Fe(Fe₃O₄m)(OH)ₓ]ads + 3(n+1)H⁺
[Fe(Fe₃O₄m)(OH)ₓ]ads → Fe₃O₄m + Fe(OH)ₓ

The microhardness of the diffusion layers reduces slightly when these additives are used, except for PEP with glycerol at 275 V (figure 2), which makes it possible to use these additives in the electrolyte for polishing.
Figure 1. Morphology of steel surface after PEN (a) and PEP (b) in an electrolyte containing NH₄Cl.

Table 1. The characteristics of PEP and surface properties

| Electrolyte composition | Voltage (V) | Sample weight loss (mg) | Current yield | Corrosion current density (µA/cm²) | Wear rate (ng/N·m) | Friction coefficient |
|-------------------------|-------------|-------------------------|---------------|------------------------------------|---------------------|---------------------|
| Not treated             | –           | –                       | –             | 39.5                               | 1327                | 0.61                |
| NH₄Cl                   | 300         | 38.3                    | 0.68          | 30.2                               | 48                  | 0.58                |
| NH₄Cl + Gl              | 275         | 29.3                    | 0.47          | 8.2                                | 29                  | 0.57                |
| NH₄Cl + Gl              | 300         | 27.7                    | 0.49          | 13.7                               | 38                  | 0.54                |
| NH₄Cl + Ox              | 275         | 27.5                    | 0.54          | 25.5                               | 38                  | 0.54                |
| NH₄Cl + Ox              | 300         | 28.9                    | 0.56          | 22.7                               | 29                  | 0.52                |

Gl is glycerol and Ox is oxalic acid.

Figure 2. Microhardness distribution in the surface layer of steel after PEN+PEP.

Corrosion tests show that the PEP of PEN-treated steel can improve the corrosion resistance of the steel (Table 1). The contact of the surface with the corrosion media occurs through a modified layer enriched with iron oxides and nitrides, which play a positive role in increasing the corrosion...
resistance. The maximal decrease in the corrosion current density occurs after PEP in an electrolyte containing glycerol and oxalic acid owing to the additional surface passivation.

Tribological tests show that friction coefficient of samples treated is always lower than that of untreated sample (Table 1). PEN provides the formation of a hardened sublayer in which mainly elastic deformations occur. The outer layer containing iron oxides and retained austenite, has good behavior, since plastic deformations are localized in this layer. PEP slightly affects the hardness of the layer, but it reduces the wear rate (Table 1). The maximal reduction of the friction coefficient and wear rate is observed with use of glycerol and oxalic acid as the electrolyte components for PEP. This may also be associated with additional surface passivation and improved plasticity of the contact of friction pairs.

4. Conclusions
An increase in the wear and corrosion resistance of medium carbon steel can be achieved by means of PEN, followed by PEP in the same electrolyzer. Anodic PEN is carried out in an aqueous solution of ammonium nitrate (5 wt.%) and ammonium chloride (15 wt.%) with the following quenching. The temperature of the sample is 850 °C and the electrolyte temperature is 20 °C during PEN. PEP is advantageous in a 3% solution of ammonium chloride with glycerol or oxalic acid (5 wt.% each) at electrolyte temperature of 80 °C and a voltage of 275 and 300 V for 1 min. The corrosion current density in a 3.5% sodium chloride solution reduces from 39.5 μA/cm² in the untreated sample to 8.2 μA/cm² in steel after PEN and PEP in an ammonium chloride electrolyte with glycerol due to the protective action of the nitride zone and the dense part of the oxide layer. The dry friction coefficient with a counter-body of bearing steel slightly decreases from 0.61 in the untreated sample to 0.52 after PEN and PEP in an ammonium chloride electrolyte with oxalic acid. The weight wear rate being 1327 ng/(N·m) in the untreated sample is reduced to 29 ng/(N·m) after PEN and PEP in an ammonium chloride electrolyte with glycerol or oxalic acid. The structure of diffusion layers does not change.

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