Increasing wear resistance of austenitic stainless steel by anodic plasma electrolytic nitrocarburising

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Abstract. The effect of plasma electrolytic nitrocarburising on the wear resistance of 12Cr18Ni10Ti steel was investigated. The phase composition of the modified layer and the surface morphology were studied using X-ray analysis and scanning electron microscope. The wear of the specimens was determined with dry friction of the lateral surface of a cylindrical specimen against a bearing steel disc (60 HRC). It is shown that anodic PEN/C of steel samples results in the formation of a hardened layer with a microhardness up to 370 HV due to its saturation with nitrogen and carbon followed by quenching. The wear resistance of steel enhances by 8.5 times after treatment in a solution of carbamide (12 wt. %) and ammonium chloride (10 wt. %) at 800 °C for 5 min with quenching in an electrolyte.

1. Introduction
Austenitic stainless steels are widely used due to their anti-corrosion properties in a variety of industries but the mechanical properties of these steels are an urgent problem. A positive result is achieved by using plasma electrolytic nitrocarburising (PEN/C) by means of formation a modified layer with improved characteristics. Cathodic PEN/C of 316L steel in carbamide-based electrolyte leads to the formation of a surface layer up to 60 μm thick, containing austenite, Fe,Cr(N,C)x, carbonitride and Fe(Fe,Cr)2O4 oxide [1]. This treatment increases the surface microhardness up to 1200 HV and promotes some reduction in the coefficient of friction. The main result is a 50-fold reduction in the wear rate after PEN/C of 316L steel at a voltage of 250 V for 60 s. The results are obtained under conditions of natural convection of the electrolyte without its cooling; therefore, maintaining a constant temperature inside the sample required a change in voltage. The local temperature in the areas of the layer formation is not controlled.

Processing of 316L steel in a flowing electrolyte is shown to be more stable and results in the formation of iron nitrides and oxides [2]. A significant increase in wear resistance is also found after treatment in a solution of carbamide or ammonium nitrite. The best results are obtained after PEN/C for 30 minutes. In addition, it is established that cathodic PEN/C of steel 316L in an electrolyte with carbamide and other additives enhances wear resistance during fatigue-wear tests [3]. The wear mechanism of nitrocarburised samples against 52100 steel is shown to become abrasive. In this case, the wear products are sintered and fill the craters between the protrusions of the worn surface without leaving the system, which increases the wear resistance of the material [4]. The disadvantage of cathodic PEN/C is an increase in surface roughness under the influence of electrical discharges.
Anodic PEN/C in a stationary heating mode is characterized by a decrease in roughness due to anodic dissolution [5]. However, an increase in voltage up to 450 V leads to appearance of electric discharges in the vapour-gaseous envelope. In this case, the anodic PEN/C of medium-carbon steel is also accompanied by a growth in the surface roughness and even a decrease in its wear resistance [6]. Therefore, a positive result is achieved by polishing the samples after PEN/C.

The noted results indicate that anodic PEN/C of austenitic steels is promising, but the information obtained is very small. Therefore, the purpose of this work is to study the characteristics of 12Cr18Ni10Ti stainless steel after its PEN/C in carbamide-based electrolyte. These characteristics include the analysis of the resulting structure and phase composition, distribution of microhardness in layer, and surface roughness under various processing conditions as well as measurements of the coefficient of friction and wear rate.

2. Experimental
Cylindrical samples of austenitic stainless steel 12Cr18Ni10Ti with 8–12 mm in diameter and 15 mm in length were subjected to PEN/C in a cylindrical working chamber. The samples were connected to the positive outlet of the power supply, and the electrolysers to the negative. After applying voltage to the system, the samples were immersed in the electrolyte to a depth equal to their height. The voltage was measured with an LM-1 voltmeter (accuracy ±0.5 %); the current was controlled with an MS8221 multimeter. The sample temperature was measured with a second MS8221 multimeter using an M89-K1 thermocouple with an accuracy of 2 °C in the temperature range from 400 to 1000 °C. A thermocouple was placed in the axial hole and directly contacted the sample at a point 2 mm from its end. The processing time was 5 minutes. After saturation with carbon and nitrogen the samples were either quenched from the processing temperature or cooled in air.

The first part of samples was processed in an electrolyte containing 10 wt. % ammonium chloride and 10 wt. % carbamide. This composition has shown good results and a sufficiently high saturating capacity, both at cathodic [7] and at anodic PEN/C [8]. The processing temperature was varied from 750 to 950 °C with a step of 50 °C. The second part of samples was treated at a fixed temperature of 800 °C, but the concentration of carbamide in the solution varied from 6 wt. % to 18 wt. % with a step of 3 %. The phase composition was determined using an ARL X'tra X-ray diffractometer (Thermo Fisher Scientific) with Cu-Kα copper radiation and a scanning rate of 2 °C/min. The microhardness of the surface layer of the samples was measured by a Falcon 503 (Innovatest) apparatus at a loading of 50 g.

The concentration of nitrogen and carbon were determined over the thickness of the modified surface layer on thin sections of the end part of the samples by EDX analysis on the same microscope. The roughness value was determined using a TR-200 device.

Wear tests were carried out with dry friction of the lateral surface of a cylindrical specimen against a bearing steel disc hardened to 60 HRC. The friction path of the sample being 2 mm in wide was also removed from its end by 2 mm. The linear sliding speed of the sample varied from 0.4 m/s to 1.5 m/s, the normal load varied from 1.02 N to 13.7 N. The change in the weight of the samples was determined on an electronic analytical balance CitizenCY224C with an accuracy of ±0.1 mg after washing the samples with distilled water to remove traces of salts.

3. Results and discussion
Metallographic and X-ray analyzes reveal the formation of a standard structure which is characteristic for anodic PEN/C. The outer part of the modified layer consists mainly of iron oxides Fe₂O₃ and Fe₃O₄. There is also a peak corresponding to both iron oxide FeO and its nitride FeN. Nitrogen diffusion is confirmed by the elemental analysis of the layer, according to which the highest nitrogen concentration of 2.7 wt. % is achieved at 750 °C at a depth of its penetration of at least 10 μm. A further increase in the PEN/C temperature reduces the nitrogen concentration, but increases its penetration depth from 10 μm at 750 °C to 20 μm at 900 °C. According to EDX analysis, no dependence of carbon concentration on saturation temperature is found. On average, the weight...
fraction of carbon slightly increases to 0.2 wt. %. The penetration of nitrogen lowers the temperature of austenitisation, too. Therefore, the martensite lines appear in the diffraction patterns after PEN/C at temperatures above 850 °C followed by quenching in the electrolyte. At lower saturation temperatures, this phase does not form. The pattern of the samples cooled in air does not differ in phase composition, but the peaks related to the Fe₂O₃ oxide appear more intensely in it. At all temperatures, the austenite phases Fe₀.₉₈C₀.₀₁₈ and Fe₀.₉₉₂C₀.₀₀₈ are found.

The highest microhardness of the 370 HV layer is observed for samples treated at 850 °C with subsequent quenching. Cooling nitrocarburized samples in air leads to lower microhardness values of 280–290 HV, which exceed the initial 180 HV. In the case of samples cooled in air from high temperatures, the peaks corresponding to martensite also appear in the pattern which indicates incomplete quenching. The temperature rise leads to the formation of a thicker and less rough oxide layer both during quenching in the electrolyte and upon cooling in air.

Figure 1 shows the dependence of the friction coefficient on the PEN/C temperature for samples quenched in the electrolyte and cooled in air. The smallest value of the friction coefficient is observed after PEN/C at 850 °C, which corresponds to the highest microhardness of the surface layer. Correlation of a lower coefficient of friction with a higher surface hardness is characteristic of the austenitic steels. When the PEN/C temperature rises, the lateral surface of the sample becomes smoother, which leads to an increase in the friction coefficient. The differences in the values of the friction coefficients after quenching in solution and cooling in air are not significant. The friction coefficient grows after the first kilometer of the sliding distance after removal of the nitrogen-rich layer (figure 2). The maximum depth of the friction track along this path is 12 μm.

Figure 1. Effect of the PEN/C temperature on the friction coefficient where sliding distance is 1 km, sliding speed is 1.059 m/s, and normal load is 10.28 N. The PEN/C time is 5 min (1 – quenching in the electrolyte, 2 – air cooling).

An increase in the sliding speed reduces the friction coefficient due to the localization of plastic deformation in a smaller volume (figure 3). The friction coefficient grows with a rise of the applied load, which is typical for the plastic contact of the sample with the counter-body (figure 4).

No explicit dependence of the friction coefficient of the samples on the carbamide in the electrolyte is found. The smallest values of weight wear are observed after PEN/C in electrolyte solutions with a 12 wt. % carbamide. A further increase in the carbamide concentration decreases the wear resistance of the steel, probably due to the intensification of steel oxidation without a rise of the nitrogen potential. The weight loss of sample is established to increase from 0.3 mg to 0.5 mg, when the normal load rises from 1 N to 8 N. An increase in the sliding speed of the sample from 0.4 m/s to 1.5 m/s slightly reduces the sample weight loss within 0.1 mg.
Figure 3. Effect of the sliding speed on the friction coefficient where sliding distance is 1 km and normal load is 10.28 N. The PEN/C temperature is 800 °C with quenching in the electrolyte.

Figure 4. Effect of the normal load on the friction coefficient where sliding distance is 1 km and sliding speed is 1.059 m/s. The PEN/C temperature is 800 °C with quenching in the electrolyte.

Figure 5 shows the dependence of the weight loss of samples during wear testing on the PEN/C temperature. Higher wear resistance is characteristic of samples quenched in electrolyte due to their higher hardness compared to samples cooled in air. The weight loss of the sample in wear tests begins to increase significantly after the second kilometer of the sliding distance, which is associated with the removal of a harder layer saturated with nitrogen and carbon (figure 6).

Figure 5. Dependence of the sample weight loss during testing on the PEN/C temperature. Sliding distance is 1 km, sliding speed is 1.059 m/s, normal load is 10.28 N (1 – quenching in the electrolyte, 2 – air cooling).

Figure 6. Dependence of the sample weight loss on the sliding distance. The PEN/C temperature is 800 °C followed by quenching, sliding speed is 1.059 m/s, and normal load is 10.28 N.

The results obtained reveal that the leading parameter for enhancing the wear resistance of steel under the studied conditions of wear tests is the microhardness of the modified layer containing martensite with iron nitrides and retained austenite.

4. Conclusions

Treatment of austenitic steel by PEN/C increases in the microhardness of the boundary layer samples from 200 HV$_{50}$ to 300 HV$_{50}$ or more, depending on the processing mode.

The dependence of distribution of nitrogen at the diffusion layer was determined. Decreasing treatment temperature from 900 to 750 °C was leaded to increase nitrogen concentration at the edge of sample from 0.4 to 2.8 wt. %.
It is shown weight loss on the order of friction compared to untreated steel in any of the discussed processing conditions. The dependence of the friction coefficient and weight loss on the processing modes is not detected, so the choice of processing conditions can be determined by the requirements for surface hardness and corrosion resistance of the samples. An increase in the proportion of urea solution reduces the coefficient of friction of 0.155 to 0.12 and the weight loss of 17 to 2 mg.

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