

# Anode Plasma Electrolytic Boronitrocarburising of Low-Carbon Steel

S. A. Kusmanov, I. V. Tambovskiy, A. R. Naumov, I. G. Dyakov, P. N. Belkin

*Nekrasov Kostroma State University,  
1 May str., 14, Kostroma, 156961, Russia, e-mail: [sakusmanov@yandex.ru](mailto:sakusmanov@yandex.ru)*

Multicomponent saturation of low-carbon steel with carbon, nitrogen, and boron was investigated under the anode plasma electrolytic treatment. Optical and scanning electron microscopes with an energy dispersive attachment were used to characterize the composition of the modified layer and its surface morphology. Surface roughness and microhardness were studied with a profilometer–profilograph and a microhardness tester; tribological properties were evaluated using a pin-on-disc tribometer at lubricated testing conditions. It has been established that the thickness of the oxide layer slowed down the diffusion of carbon, nitrogen, and boron as determined by the anode dissolution and high temperature oxidation, which are dependent on the processing temperature. Dissolution prevails over oxidation up to 850°C that results in the sample weight loss. At 900°C, the sample weight increases owing to oxidation which prevails over dissolution. The maximal boronitrocarburising layer thickness (0.11 mm) is observed at 850°C. The maximal microhardness of this layer is 880 HV after saturation at 850°C for 5 min. The friction coefficient and the wear rate of the samples treated at 850°C decrease by a factor of 2 in comparison with those of an untreated sample.

*Keywords: plasma electrolytic boronitrocarburising, oxide layer, anode dissolution, high-temperature oxidation, roughness, friction coefficient.*

УДК 621.785.53; 621.3.035.183

## INTRODUCTION

Plasma electrolytic saturation (PES) of metals and alloys with light elements has some advantages in comparison with conventional thermally activated saturation processes. PES is easily combined with hardening by disconnecting voltage and cooling in the same electrolyte without reheating. Continuous motion of the medium in the vapour-gas envelope (VGE) provides rapid supply of saturating components to workpieces and removal of reaction products. A high heating rate of workpieces (up to 100 deg/s) because of small VGE thickness allows avoiding the grain growth and the associated deterioration of the material properties. In addition, small VGE thickness contributes to rapid stabilization of conditions: the equilibrium concentration of adsorbed diffusant is achieved in several seconds. As a result, the processing time is decreased up to several minutes.

Most widely spread saturating components for PES are carbon, nitrogen, and boron. Moreover, complex diffusion processes were developed with new technological opportunities. In this article, we consider the steel saturation with boron and other elements, in parallel. Iron borides have high hardness, wear and abrasion resistance, heat resistance or corrosion resistance [1]. The main disadvantage of boronising processes is brittleness of the boriding layer, especially of FeB boride. Plasma electrolytic borocarburising process in the borax electrolyte with an additive result in the increase in the content of

Fe<sub>2</sub>B phase and decrease of FeB, iron oxides, and iron carbide phases, respectively [2]. Cathode borocarburising leads to increase in roughness because of the electrical discharges action. However, the formation of a layer with high hardness provides for a decrease of the friction coefficient and wear rate.

Decrease of FeB content can be achieved by means of steel saturation with boron, carbon, or nitrogen. The authors in [3] studied four cathode processes of the medium carbon steel modification, namely, boronitriding, borocarburising, borocarbonitriding, and nitrocarburising. The maximal surface microhardening and minimal wear rate were established to be observed after boronitriding of samples. Borocarburising and borocarbonitriding were characterized by a lower wear resistance. The minimal microhardness and maximal wear rate were obtained after nitrocarburising.

All observed structures are characterized by the different nanocrystalline grains, which contributes to wear resistance. It is also established that the simultaneous saturation of high-speed steel with boron, sulfur, carbon, and nitrogen allows to increase the tool endurance [4].

In most cases, electrolytes for PES are aqueous solutions. The first component provides a sufficiently high electrical conductivity of the solution. Other components are sources of saturating atoms. Known electrolyte compositions for the steel saturation with several elements and results obtained are shown in Table.

**Table.** Examples of PEC. Nomenclature:  $U$  – voltage;  $T$  – sample temperature;  $\delta$  – layer thickness;  $t$  – treatment time;  $R_a$  – roughness (in brackets – initial roughness).

Electrolyte composition	$U$ , V	$T$ , °C	Material and sizes sample, mm	$\delta$ , mm	$t$ , min	HV	$R_a$ , $\mu\text{m}$	Research group
Cathode process								
Borax + sodium hydroxide	233	960	H13 $\varnothing 25 \times 3$	0.18	10	1930		Taheri et al. [1]
15% borax + sodium hydroxide	600		1020 $\varnothing 8 \times 50$	–	15	1600		Bejar et al. [5]
10–15% sodium thiosulfate + 14–16% ammonium chloride + 10–15% carbamide + 10–15% borax + 8–10% sodium carbonate	150	950	R6M5	0.1	1.6	1350		Ivanov et al [4]
30% borax + carbon-containing organic additive	330	950	Q235 $55 \times 16 \times 1.5$	0.064	30	1800	1.7 (0.17)	Wang et al [2]
8% potassium carbonate + 41% glycerol + 10% boron carbide	200	900	40X	0.05	5			Terent'ev [6]
8% potassium carbonate + 41% glycerol + 10% boron carbide	200	900	40	0.12	10			Terent'ev [6]
8% potassium carbonate + 41% glycerol + 10% boron carbide	200	850	Fe	0.04	5			Terent'ev [6]
Borax + sodium nitrite	500	900	H13 $\varnothing 25 \times 3$	0.16	15	2100		Taheri et al. [3]
Borax + calcium carbonate	500	900	H13 $\varnothing 25 \times 3$	0.16	15	1900		Taheri et al. [3]
Borax + carbamide	500	900	H13 $\varnothing 25 \times 3$	0.16	15	1890		Taheri et al. [3]
Anode process								
3% borax + 10% sodium hydroxide	225	1250	45 $\varnothing 10 \times 3$	–	12	450	5.5 (6)	Kuzenkov et al. [7]
15% carbamide + 15% ammonia chloride + 10% boric acid + 10% sodium thiosulphate	230	800	20 $\varnothing 10 \times 15$	0.06	5	600		Kusmanov et al. [8]

A feature of anode PES is oxide layer formation. This fact is in detail investigated in carburizing [9, 10], nitrocarburising [11], and nitroquenching [12]. A porous oxide layer is found to slow down carbon and nitrogen diffusion; this layer thickness is determined by oxidation and anode dissolution processes. Multicomponent saturation of steel is also accompanied by the formation of an oxide layer; all diffusing elements are found below the oxide layer [8]. Carbon concentration reaches 0.8% that is consistent with pearlite structure and indicates a sufficiently high carbon potential in VGE of carbamide electrolyte. Concentrations of boron, nitrogen, and sulfur are 0.3–0.4%, therefore, their components are in the form of a solid solution.

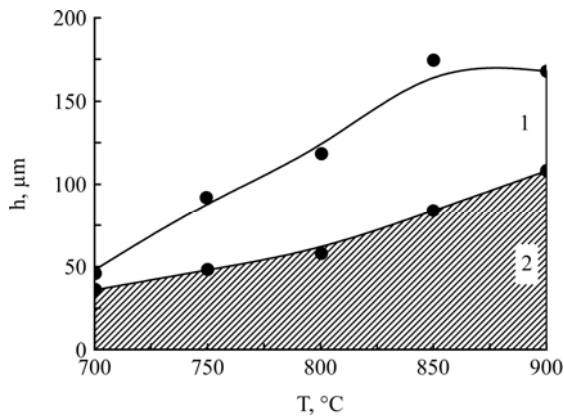
The goal of this paper is to study saturation of low-carbon steel with carbon, nitrogen, and boron in PES using aqueous electrolyte.

#### EXPERIMENTAL

Cylindrical samples ( $\varnothing 12 \times 15$  mm) of low-carbon steel (wt.%: 0.2 C; 0.38 Mn; 0.21 Si;

0.014 P; 0.013 S; 0.17 Cr; 0.09 Ni; 0.17 Cu; 0.01 As) were under anode treatment in a cylindrical working chamber with an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the chamber, as in our earlier work [13]. In the upper part of the chamber, the electrolyte overflows into the sump and is further pumped through a heat exchanger at a rate of 3 l/min. The volume flow rate was measured with a RMF-0.16 GUZ flowmeter (with an accuracy of  $\pm 2.5\%$ ). The electrolyte temperature was measured by an MS-6501 digital thermometer and rapid response thermocouples (with an accuracy of  $\pm 3\%$ ) and was maintained at  $20 \pm 1^\circ\text{C}$ . The samples were connected as the positive output and the chamber was connected as the negative output of the power supply.

An aqueous solution of ammonium chloride (15 wt.%), of carbamide (15 wt.%) and of boric acid (5 wt.%) was used as the working electrolyte.



**Fig. 1.** Thicknesses of modified layer (1) and oxide layer (2) vs treatment temperature.

After switching the voltage, the samples were immersed in the electrolyte to a depth equal to their height. The voltage was measured with an LM-1 voltmeter (with an accuracy of  $\pm 0.5\%$ ). The current was probed with an MS8221 multimeter. The sample temperature was measured with a second MS8221 multimeter and the M89-K1 thermocouple was inserted into the sample approximately 1 mm to the low surface by drilling a hole (accuracy to within  $\pm 2.0\%$ ).

The treatment temperature was varied from 700 to 900°C.

The structure of the surface layer of the samples was examined by an EU METAM CM 21 optical microscope after polishing and etching with a 4% nitric acid solution in ethanol for 5–10 s.

A scanning electron microscope (SEM) with an energy dispersive attachment with a silicon drift detector was used to observe the surface morphology after nitrohardening and for the subsequent elemental microanalysis.

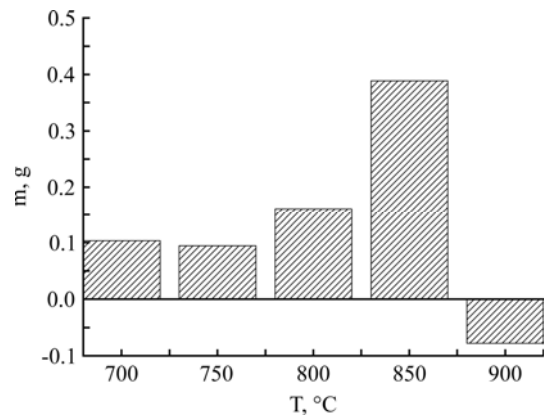
The microhardness of the sample surface layer was measured on a PMT-3M apparatus at a loading of 50 g.

The surface roughness before and after PET was investigated with the use of the 130-model profilometer–profilograph.

Sliding wear is made at the friction machine UMT-01 with schema “pin-on-disk”. A counterbody is a disk made of steel 45 (50 HRC). The Industrial facility “LITOL” is used as lubricant. The value of the normal force is equal to 315 N. A linear velocity of sliding was 0.47 m/s. The sliding distance is equal to 1000–1200 m. The sample weight loss is determined by measuring the difference of mass before and after test.

## RESULTS AND DISCUSSION

Optical microscope and SEM examinations of treated samples revealed oxide and diffusive layers. The oxide layer thickness increases with the saturation temperature in the range of 700–900°C (Fig. 1)



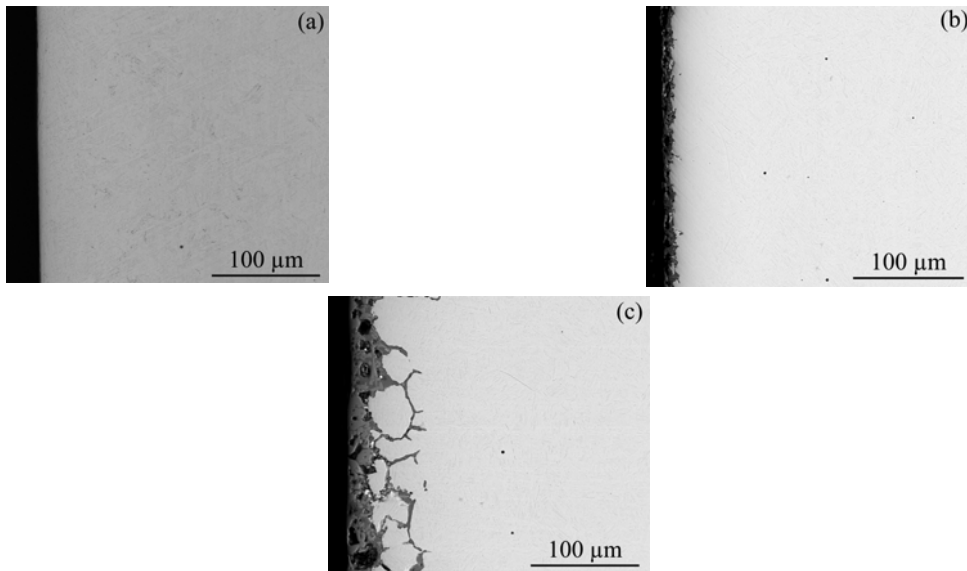
**Fig. 2.** Weight loss of anode at different treatment temperatures.

that is explained by the increase of the sample weight via high-temperature steel surface oxidation [14]. Nonetheless, the sample weight decreases up to the saturation temperature 850°C due to the predominant effect of anode dissolution (Fig. 2). The modified layer thickness is determined by competition of the inhibitory effect of the growing oxide layer and the light element diffusion which increased with temperature. As a result, the diffusion layer thickness was maximal, i.e. 0.11 mm, after treatment at 850°C.

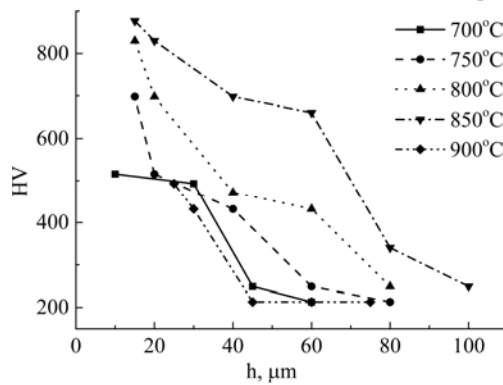
An elemental microanalysis shows that nitrogen concentration in the surface layer reaches 0.65 wt.% after treatment at 850°C. The total concentration of carbon and boron is 1.5 wt.% at the same temperature (separate identification of their elements is difficult because of peaks imposition at the EDX-analysis). Low accuracy of the light elements determination of this method does not give grounds for quantitative conclusions, still it does not contradict the well-known results according to which the anode saturation leads to the formation of iron boride  $\text{Fe}_2\text{B}$  [7] and cementite  $\text{Fe}_3\text{C}$  [15]. Fig. 3 shows the cross-sections of samples treated at different temperature. A sharp increase of the oxide layer thickness at 900°C, in comparison with other measurements, confirms that the oxidation prevails over dissolution with the sample weight increment.

The maximal surface microhardness up to 880 HV is obtained after saturation of steel with carbon, nitrogen, and boron at 850°C (Fig. 4). Significant decrease in hardness after treatment at 900°C probably is associated with areas enriched by iron oxides which penetrate to a depth of 70 μm.

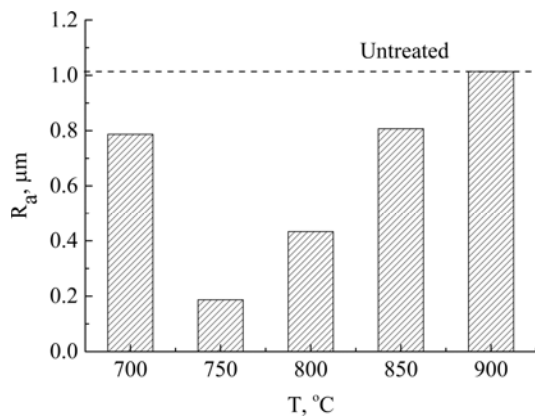
Surface roughness is minimal at 750°C (Fig. 5). The rise of the processing temperature from 750 to 900°C results in an increase in the surface roughness owing to intensification of the sample oxidizing and formation of an uneven oxide layer on the surface. The increase in roughness after treatment at 700°C may be associated with a lower rate of anodic dissolution.



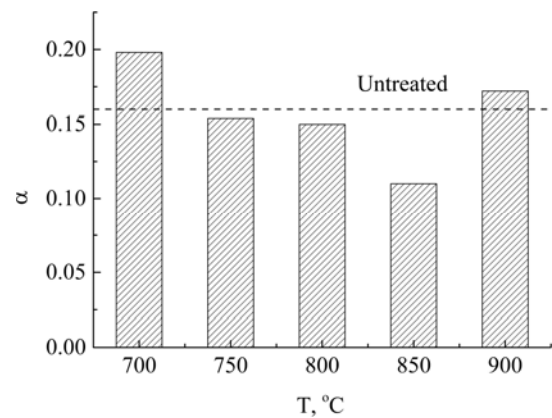
**Fig. 3.** SEM image of cross-section of steel surface after PES for different treatment temperatures: (a) 800°C; (b) 850°C; (c) 900°C.



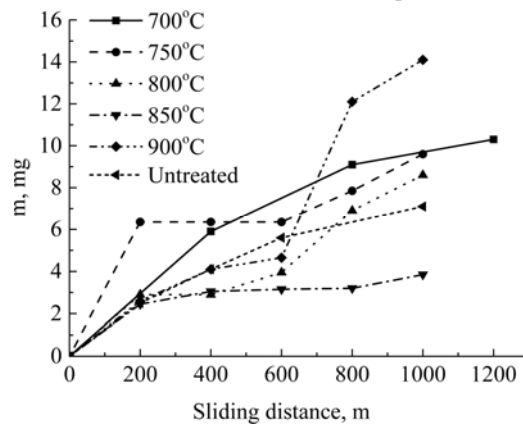
**Fig. 4.** Microhardness distribution in the surface layer after PES at different treatment temperatures.



**Fig. 5.** Surface roughness ( $R_a$ ) of untreated and treated samples at different treatment temperatures.



**Fig. 6.** Average friction coefficient ( $\alpha$ ) of the untreated and treated samples at different treatment temperatures.



**Fig. 7.** Weight loss of the samples treated at different temperatures or untreated after sliding test.

The rise of the processing temperature from 700 to 850°C results in the microhardness increase and friction coefficient decrease (Fig. 4 and Fig. 6). The treatment at 900°C leads to an increase of the friction coefficient up to 0.17 which is higher than that of the untreated sample. This fact may be associated with deep penetration of oxides destroying the metal structure during friction.

The minimal wear rate is observed after treatment at 850°C (Fig. 7). A high wear rate is observed at the beginning of the sliding test because of the adjustment of a soft oxide layer on the sample treated at 850°C. After that, the weight loss of the samples is almost unchanged during the sliding test. The maximal wear rate of the samples treated at 900°C may be associated with the destruction of the surface layer that is weakened by oxides.

### CONCLUSIONS

1. Simultaneous diffusion of carbon and boron in the anode PES is significantly dependent on the oxide layer thickness which is determined by oxidation and anode dissolution processes similar to carburizing. The effect of the anode dissolution on the samples weight prevails over the oxidation one at the temperature below 850°C according to data measuring.

2. The carbon and boron diffusion through the oxide layer is retarded. The rise of the treatment temperature results in not only diffusion acceleration but also in the growth of the oxide layer thickness that inhibits diffusion. As a result, the maximal thickness of a boronitrocarburising layer (0.11 mm) is observed at 850°C.

3. The maximal microhardness of a boronitrocarburising layer is 880 HV after saturation at 850°C during 5 min. The minimal friction coefficient and wear rate are obtained under these conditions. The iron oxide penetration increases with the processing temperature, which leads to reduced microhardness and a higher friction coefficient.

### ACKNOWLEDGEMENTS

This work was supported by the research program of the Ministry of Education and Science of the Russian Federation.

Electron microscopic studies were performed at the Facilities Sharing Centre "Diagnostics of Micro- and Nanostructures" (Yaroslavl) with the financial support of the Ministry of Education and Science of the Russian Federation.

### REFERENCES

1. Taheri P., Dehghanian Ch., Aliofkhaezrai M., Rouhaghdam A.S. Evaluation of Nanocrystalline Microstructure, Abrasion, and Corrosion Properties of Carbon Steel Treated by Plasma Electrolytic Boriding. *Plasma Process Polym.* 2007, **4**, S711–S716.
2. Wang B., Jin X., Xue W., Wu Z., Du J., Wu J. High Temperature Tribological Behaviors of Plasma Electrolytic Borocarbured Q235 Low-Carbon Steel. *Surf Coat Technol.* 2013, **232**, 142–149.
3. Taheri P., Dehghanian Ch., Aliofkhaezrai M., Rouhaghdam A.S. Nanocrystalline Structure Produced by Complex Surface Treatments: Plasma Electrolytic Nitrocarburizing, Boronitriding, Borocarburing, and Borocarbonitriding. *Plasma Process Polym.* 2007, **4**, S721–S727.
4. Ivanov S.V., Salmanov N.S., Salmanov M.N. Borosulfocarbonitriding of Cutting Tools in Electrolyte Plasma. *Met Sci Heat Treat.* 2002, **44**(9–10), 405–406.
5. Bejar M.A., Henriquez R. Surface Hardening of Steel by Plasma-Electrolysis Boronizing. *Mater Design.* 2009, **30**, 1726–1728.
6. Терентьев С.Д. Интенсификация химико-термической обработки металлов. *ЭОМ.* 1982, (2), 83–84.
7. Kuzenkov S.E., Saushkin B.P. Borating of Steel 45 in Electrolyte Plasma. *Surf Eng Appl Electrochem.* 1996, (6), 10–15.
8. Кусманов С.А., Наумов А.Р., Тамбовский И.В., Белкин П.Н. Анодное электролитно-плазменное насыщение малоуглеродистой стали углеродом, азотом, бором и серой. *Письма о материалах.* 2015, **5**(1), 35–38.
9. Kusmanov S.A., Belkin P.N., D'yakov I.G., Zhironov A.V., Mukhacheva T.L., Naumov A.R. Influence of Oxide Layer on Carbon Diffusion during Anode Plasma Electrolytic Carburizing. *Prot Met Phys Chem.* 2014, **50**(2), 223–229.
10. Kusmanov S.A., Shadrin S.Yu., Belkin P.N. Carbon Transfer from Aqueous Electrolytes to Steel by Anode Plasma Electrolytic Carburizing. *Surf Coat Technol.* 2014, **258**, 727–733.
11. Smirnov A.A., Mironova O.A., Barashkov V.N., Kusmanov S.A. Features of Anode Plasma Nitrohardening of Steel. *Abstracts 7<sup>th</sup> International conference on material science and condensed matter physics.* 16–19 September 2014. Chisinau, 2014, P. 280.
12. Кусманов С.А., Наумов А.Р., Паркаева Ю.В., Белкин П.Н. Анодное электролитно-плазменное насыщение малоуглеродистых сталей азотом и углеродом. *Физика и химия обработки материалов.* 2013, (6), 47–53.
13. Belkin P.N., Dyakov I.G., Zhironov A.V., Kusmanov S.A., Mukhacheva T.L. Effect of Compositions of Active Electrolytes on Properties of Anodic Carburization. *Prot Met Phys Chem Surf.* 2010, **46**(6), 715–720.
14. Жиров А.В., Дьяков И.Г., Белкин П.Н. Растворение и окисление углеродистых сталей при анодном нагреве в водных электролитах. *Известия вузов. Химия и химическая технология.* 2010, **53**(2), 89–93.
15. Шкурпело А.И., Белкин П.Н., Пасинковский Е.А. Фазовый состав и структура поверхностного слоя

армко-железа и аустенитной нержавеющей Cr-Ni-стали 12X18H10T после нитроцементации при анодном электролитном нагреве. *Физика и химия обработки материалов*. 1993, (2), 116–125.

*Поступила 30.10.14*

*После доработки 24.03.15*

### **Реферат**

Исследовано многокомпонентное насыщение малоуглеродистой стали углеродом, бором и азотом в условиях анодной электролитно-плазменной обработки. Для изучения состава и морфологии поверхностного слоя использовались оптический и электронный микроскопы с приставкой для элементного микроанализа. Поверхностная шероховатость и микротвердость измерялись с помощью профилографа-профилометра и твердомера, трибологические свойства образцов изучались на машине трения по схеме «палец по диску» со смазкой. Установлено, что при насыщении стали толщина оксидного слоя, тормозящего диффу-

зию углерода и бора, определяется процессами анодного растворения и высокотемпературного окисления, зависящих от температуры обработки. Преобладание растворения над окислением наблюдается до 850°C, что приводит к убыли массы образца. При температуре 900°C масса образца увеличивается за счет окисления, более интенсивного, чем растворения. Максимальная толщина боронитроцементованного слоя (0,11 мм) наблюдается при температуре 850°C. Максимальная микротвердость этого слоя составляет 880 HV после насыщения при 850°C в течение 5 мин. Коэффициент трения и скорость износа образцов, обработанных при температуре 850°C, снижается в два раза относительно необработанного образца.

*Ключевые слова: электролитно-плазменная боронитроцементация, оксидный слой, анодное растворение, высокотемпературное окисление, шероховатость, коэффициент трения.*