Anodic plasma-electrolyte modification of Fe and Ti-based alloys

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Abstract. The anodic plasma-electrolyte modification of titanium alloy VT1-0 and low-carbon steel 20 for improvement their properties was carried out in nitrogen- and boronitrogen-containing electrolytes, respectively. Tribological and corrosion-protective properties of formed surface layers was investigated. The data of technical tests showing increase in the operational life of threaded fastening pair subjected to plasma-electrolyte boronitriding are presented.

1. Introduction

Fastening products are necessary in almost all industries; they largely determine construction reliability and durability. In this regard, it is clear that increasing the operational life is an urgent task. Despite the increasing use of new composites and alloys, a significant proportion of fasteners are still represented by steel. The widespread use of low carbon steels in many industries is due to their relatively low cost, availability and ease of machining. Rather high durability, rigidity, not deficiency and profitability allow to consider steel of this class as the main material for production of the loaded and responsible fasteners with the raised resource to a modern oil and gas complex, as example [1]. Titanium fasteners are actively used in the aviation industry along with steel. Steel and titanium bolts and nuts are applied to make detachable connections of airframe and various aircraft systems, in carbon-composite aircraft constructions [2, 3].

Improving the performance of steels and titanium alloys is possible in various ways, but the extensive ways have almost completely exhausted themselves, giving way to modifying (i.e. purposefully changing towards improvement) the desired properties. At the same time preference is given to methods of surface treatment, as in most cases it is the surface that determines the serviceability of the product generally. In addition, surface modification seems more attractive compare with methods of changing the volume characteristics of materials and articles in terms of economics. All the above has led to the development of scientific research and technological engineering aimed to improving traditional methods and creating new methods of surface modification in order to give it the parameters specified by operating conditions. This approach makes it possible most efficient use of the combination of the properties of the base material and the modified layer; moreover, the surface treatment operations can be easily incorporated into the manufacturing or repair
technological process. Development and implementation of new environmentally friendly technologies of surface layer modification, which include plasma-electrolyte methods of surface treatment, is one of the key directions of modern science and technology [4]. In this paper we studied the possibilities of improving the tribological characteristics and corrosion resistance of titanium alloy VT1-0 and low-carbon steel 20 by modifying their surface in electrolyte plasma.

2. Experimental

Cylindrical samples of steel 20 (0.17–0.24% C) and titanium VT1-0 (99.24–99.7% Ti) having a height of 10 mm and a diameter of 11 mm were treated. Prior to treatment, a work hardening layers from the side and end surfaces of the samples was mechanically removed, and the surface roughness was adjusted to Ra=1±0.1 μm. The anodic plasma-electrolyte treatment was carried out using the installation described in detail in [5]. Electrolyte coming in working chamber through the hole in its bottom flows longitudinally around samples–anodes and outflows over edge of working chamber. The electrolyte consumption controlled by the LZT-M15 rotameter with an accuracy of 2.5% was 3.7 l/min, temperature of electrolyte measured by the thermocouple on an entrance to the working chamber and maintained at the level 20±1°C. The electrolyte of aqueous solution of ammonium chloride (10%), ammonium nitrate (5%) and boric acid (3%) was used for treatment of steel 20. When modifying the VT1-0 alloy, the electrolyte containing ammonium chloride (10%) and ammonia (5%) was used. The samples were immersed in the electrolyte to a depth equal to its height, already under a voltage (150–250 V) sufficient to form a stable vapour–gaseous envelope (VGE) and achieve the required process temperature. Treatment was continued of 5 minutes since the required temperature (750, 800 and 850 °C) of sample was reached. The process was completed by switch off the voltage, as a result of which the samples were quenched in the electrolyte. After treatment, the samples washed with running water.

Samples for full-scale tests were the threaded connection pairs (bolts and nuts) with M6 thread made of steel 20. For their plasma-electrolyte treatment, the above-described methodology and electrical mode were used, but the duration of the modification was reduced to 1 min in order to avoid violation of the aspect ratio of the thread.

The microhardness of the modified layer measured using the PMT 3M instrument at the load of 50 g and the hold of 10 s with averaging the results of 5 measurements. Tribological characteristics were determined on the TRB-S-DE tribometer according to the “finger-to-disk” scheme at dry friction conditions under 5 N load and angular rotation speed of 290 min\(^{-1}\) on the friction path of 500 m with a counter body of steel 45 hardened to 58–60 HRC. The corrosion resistance was evaluated in an aqueous sodium chloride solution (3.5%) by potentiodynamic polarization curves obtained with the aid of IPC Pro M potentiotstat–galvanostat. The standard three-electrode cell was used with the test sample as the working electrode, a graphite auxiliary electrode, and a silver-chloride reference electrode. The working electrode was kept in sodium chloride solution for 150 minutes prior to testing, after which potentiodynamic polarization curves were recorded at the scanning rate of 1 mV/s. Corrosion current density was determined from the obtained curves with the aid of Tafel extrapolation.

3. Results and discussion

In the above kinds of electrolytes, the surface layer was saturated mainly with nitrogen and oxygen (in the case of titanium alloy) and boron and nitrogen (in the case of steel 20). The research results are presented tables 1 and 2.

It follows from the presented data that anodic plasma-electrolyte modification allows to increase microhardness of VT1-0 alloy by two times, and although it is slightly lower than the level reached at vacuum ion-plasma saturation [6], it should be noted significant, almost two orders of magnitude reduction in wear and multiple decrease in the coefficient of friction. Probably, this is facilitated by the formation of oxide and oxide-nitride titanium phases in the surface layer, which also lead to decrease up to 40% of the corrosion current density. A similar positive effect of oxygen diffusion at plasma-electrolyte modification on titanium corrosion resistance was described in [4].
When boronitriding of steel 20, significant, five-fold increase in microhardness is observed. At the same time, forming strengthening solid nitride-boride martensitic phases increase friction coefficient 1.2–1.3 times. However, this modification total reduces wear by approximately four times compared to untreated steel. At the same time, as a result of anodic plasma-electrolyte boronitriding the corrosion resistance increases approximately three times.

Electrolyte of the above-mentioned composition and boronitriding mode at 850 °C were used to increase operational life of “nut–bolt” fastening pair made of steel 20. For full-scale tests of the fastening pairs, the cyclic technique was developed (figure 1), according to which one cycle involved screwing the bolt into the nut and then screwing out with a total operation duration of 8.5 s. The translation movement of the nut along the bolt axis was 9 mm, the returning to the initial position made by reverse motion. Each section of the friction surface passed the path of 302.4 mm and was the same for each of the cycles. The load applied to the nut during the tests along the bolt axis in the twisting-twisting direction was 14.7 N. The sliding speed was 35.6 mm/s. Changes in the weight of the bolts and nuts were measured every 240 minutes. The tests were stopped when the friction pair failed (when the bolt was jammed as a result of skew) or when the nut was wear until could not be held on the thread.

The test results were as follows. The untreated nut and bolt became inoperable after 190 test cycles, the wear resistance of the modified objects was greater in all cases. A comparison of different combinations of bolt and nut hardening showed that the greatest resource had the pair of the untreated

### Table 1. Averaged parameters for modified alloy VT1-0.

| Treatment temperature, °C | No modified | 750 | 800 | 850 |
|---------------------------|-------------|-----|-----|-----|
| Microhardness, HPa        | 2.0         | 3.2 | 3.7 | 4.1 |
| Friction coefficient      | 0.70        | 0.25| 0.22| 0.15|
| Weight loss, mg/mm²       | 0.37        | 0.018|0.005|0.009|
| Corrosion current density, A/cm² | 3.1-10⁻⁷ | 2.7-10⁻⁷|2.4-10⁻⁷|1.8-10⁻⁷|

### Table 2. Averaged parameters for modified steel 20

| Treatment temperature, °C | No modified | 750 | 800 | 850 |
|---------------------------|-------------|-----|-----|-----|
| Microhardness, HPa        | 2.2         | 9.5 | 8.2 | 10.9|
| Friction coefficient      | 0.56        | 0.72| 0.68| 0.73|
| Weight loss, mg/mm²       | 0.015       | 0.0039|0.0042|0.004|
| Corrosion current density, A/cm² | 13.4-10⁻⁶ | 6.2-10⁻⁶|4.6-10⁻⁶|4.3-10⁻⁶|

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![Figure 1. Test scheme for the pair "nut–bolt": The bolt moves only rotationally, the nut moves only translationally: (a) – the beginning and the end of the cycle; (b) – the middle of the cycle.](image-url)
bolt and nut boronitrided for 1 minute at the temperature of 850 °C (corresponding to the voltage of 190 V) (figure 2). In this case, the operational life of 9100 cycles was achieved.

4. Conclusions
1. Anodic plasma-electrolyte modification of titanium VT1-0 allows to increase microhardness of its surface by two times, reduce wear by almost two orders of magnitude and reduce the friction coefficient by several times, as well as decrease of corrosion current density up to 40%.
2. Anodic plasma-electrolyte boronitriding of steel 20 makes it possible to increase the microhardness of its surface by almost 5 times, reduce wear by about four times, despite a slight increase in the friction coefficient, and reduce the corrosion current density by about three times.
3. Modification of steel nuts at 850 °C during 1 min allows increasing the operational life of threaded pairs “untreated bolt–boronitrided nut” by about 45 times.

Acknowledgment
This work was supported by the Russian Ministry of Education and Science, the unique identifier of the Agreement is RFMEFI57718X0288.

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