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Wear Resistance Increase in Ti6Al4V Titanium Alloy Using a Cathodic Plasma Electrolytic Nitriding

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Abstract—The possibility of increase in Ti6A14V alloy's wear resistance is shown using cathodic plasma electrolytic nitriding in a solution of ammonium chloride and ammonia. A competing effect on the surface erosion was revealed under the discharges and high-temperature oxidation on the surface morphology and roughness. The complex effect was established on the surface roughness and surface layer hardness of the titanium alloy's wear resistance. It was determined that the highest decrease in the mass wear by 2.7 times was observed in the samples with a maximum microhardness of the surface layer, reaching 820 HV, and the lowest roughness of the surface. It was shown that the friction coefficient decreased proportionally to the treatment duration, when the surface layer was of not-too-high hardness that benefits the counterbody's sliding motion.

Keywords: cathodic plasma electrolytic treatment, nitriding, titanium alloy, surface roughness, microhardness, friction coefficient, wear resistance

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INTRODUCTION

The increase in titanium alloy's wear resistance is of great importance in various branches of industry. The method of plasma electrolytic treatment is used to increase the wear resistance [1]. One such technology is the diffusion saturation of a surface by the atoms of light elements, in particular, nitriding. The most investigated is the anode plasma electrolytic nitriding variant of titanium alloys' nitriding. The peculiarity of the anode nitriding in water electrolytes is the formation of the oxide layer, whose phase composition is relevant to rutile TiO_2 [2]. The outside layer, which is formed resulting from the anode nitriding of technical titanium in the solution of ammonium chloride (10%) and ammonia (5%) at 850°C for 5 min, contains 29.8% titanium and 67.9% oxygen according to the data of the energy dispersion analysis [3]. The presence of nitrogen in titanium is determined using spectroscopy of nuclear inverse scattering of protons [4]. During a 5-min treatment at 700°C, the nitrogen and oxygen surface concentrations reach 10 and 13 at %, correspondingly. The developed oxide layer has micropores through which the dilution products and diffusion of nitrogen and oxygen get out into metal [5]. The dependence of the diffusion layer thickness on temperature reflects the competition of two processes: increase in the diffusion rate at the expense of temperature growth and its decrease due to the oxide layer growth (which grows quicker when the temperature is higher, thus slowing down the process of diffusion) [6].

Within the framework of the cathodic processes, the combined nitride and carbon surface saturation are studied to a greater degree. A simultaneous diffusion of nitrogen and carbon into a technical titanium forms the zone of joinings and the diffusion layer, which in itself is a solid solution of nitrogen and carbon in titanium [7]. The phase composition of the zone of joinings depends on the electrolyte used and the treatment temperature. Titanium carbonitride $Ti(C_xN_{1-x})$ is formed resulting from nitrocementation (200–260 V, 9 min) in solutions of carbamide (120 g/L), natrium nitrate (80 g/L), or triethanolamine (180 g/L) [8]. In these compositions, almost similar nitrogen content is obtained in a nitrocementated layer (13–15 at %); however, the most intense titanium carbonitride peaks are observed in diffractogram samples that were processed in carbomide or triethanolamine. For the latter electrolyte, the titanium hydride formation TiH_2 is also characteristic. A more complex phase composition was observed after nitrocementation of Ti6A14V alloy in the water solution of formamide, calcium nitrate, potassium chloride, and sodium dihydrophosphate [9]. Not only Ti_α and Ti peaks are revealed here but also those of carbonitride Ti(C,N), titanium oxide (anatase), and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. The anatase formation implies oxygen penetration, presumably from water vapors. The maximum concentration of carbon in the layer is 66.3 at %, nitrogen is 6.5 at %, and oxygen is 33.4 at %. Calcium and phosphorus are found as well.

The anode nitriding of highly alloyed VT22 (4–5.5% Mo, 4–5.5% V, 4.4–5.9% Al, 0.5–1.5% Fe, 0.5–2% Cr) results in hardening with a martensite semitransformation [2]. The anode treatment of low-alloyed titanium alloys increases markedly their surface hardness owning to saturation of the surface layer with nitrogen and oxygen, and, possibly, due to a fast cooling in the electrolyte [10]. Similar results were obtained at nitriding low-alloyed alloys Ti–3Al–2.2Zr and Ti–3.5Al–1.2Mn in an ammoniac solution at 950–1000°C [11]. Metallographic analyses showed that the recrystallization took place in the surface layers of the nitrided titanium alloys, with the grain size being enlarged by 20 times. A gradual transition from recrystallized to the initial fine-grain structure was observed with the removal from the surface to the depth of the sample. The treatment in accordance with the above modes results in a certain increase in microhardness of the surface layer up to a 1-mm thickness, which is facilitated by the accelerated cooling in the solution after the nitriding.

The advantage of the cathodic processes is a higher surface microhardness, which is reached due to a brief local temperature increase under the electric discharges. For instance, during the cathodic nitrocarburizing of technical titanium [7] or Ti6A14V alloy, titanium carbonitrids are formed; however, they are not revealed at the anode treatment.

The tribologic properties of the technical titanium increase after the anode nitriding in the solution that contains 5% ammonia and 10% ammonium chloride [6]. The friction coefficient decreases by 4.7 times with an increase in the treatment temperature to 850°C, which can probably be attributed to the growth of the oxide layer. A minimum wear intensity is reached after the treatment at 800°C: the mass wear is reduced to 71 times. After the anode nitriding of VT22 (4–5.5% Mo, 4–5.5% V, 4.4–5.9% Al, 0.5–1.5% Fe, 0.5–2% Cr) alloy in the same electrolyte, the friction coefficient decreases from 0.53 in the control sample to 0.12–0.18, and the wear intensity of the nitride alloy of the quenched steel decreases by four orders compared to the control untreated sample [2]. The wear resistance increase is assumed to be obtained as a result of the combined action of the oxide layer and sublayer with a higher hardness, which ensure the friction localization in a thin surface layer.

The decrease in the mass wear by 15 times during the cathodic nitricarburising of the technical titanium in carbamide electrolyte is facilitated by an increase in the treatment duration to 9 min at 700°C and hardness of the layer of 800 HV [7]. The effect of the treatment temperature on the wear intensity is not determined. Also, the possibility of the Ti6A14V titanium alloy wear resistance increase after the nitrocarburizing in the solution of formamide and formaline during friction with lubrication is shown to be by three orders [12]. The Ti6A14V alloy wear resistance is increased by an order after the nitrocarburizing in the solution of formamide (50%) with kalium chloride [13]. The correlation of the wear resistance of Ti6A14V nitrocarburized alloy is shown with a surface roughness, its microhardness and friction coefficient.

The aim of this work is to reveal the possibility of increasing the wear resistance of the alloyed Ti6A14V titanium alloy using the cathodic nitriding in the electrolyte based on ammonia and ammonium chloride, which recommended itself for the anode treatment both of titanium alloys and steels.

MATERIALS AND RESEARCH METHODS

The cylinder Ti6A14V titanium alloy samples (86–90% Ti, 5.3–6.8% Al, 3.5–5.3% V) with a diameter of 10 mm and length of 15 mm were exposed to the cathodic plasma electrolytic nitriding after their being sanded up to R_a, equal to 1.0 ± 0.1 μm and rinsing with acetone in an ultra-sound bath. The treatment was performed in a cylinder electrolyzer with the electrolyte longitudinal flow-past of the sample, supplied via the branch pipe in the electrolyzer bottom [14]. At the electrolyzer top, the electrolyte was poured into a catcher, from which it was supplied using a pump into a heat exchanger at a rate of 2.5 L/min, under control of a PMF-0.16 ZHUZ rotameter at an accuracy of 2.5%. The electrolyte temperature was measured with a thermal couple that was located at the electrolyzer bottom and was maintained equal to 30 ± 2°C. As the electrolyte, a water solution of ammonium chloride and ammonia was used, with the concentration of each of the components equal to 5% (here and further, the mass percent is used). After supplying the voltage of 230 V, the samples were immersed into the electrolyte at the depth similar to their height. The voltage and current were measured using a DP6-DV voltmeter and a DP6-DA ammeter. The samples' temperature was measured by a MY-K2 thermal couple with an APPA109N multimeter (3% accuracy in the temperature range of 400–1000°C). The thermal couple was mounted in the sample aperture at a 2-mm distance from the flange. Upon a sample's full immersion, the voltage was gradually decreased to the value in the interval of 100–135 V, which was relevant to the temperature of saturation that ranged from 600 to 850°C. The nitriding duration was 5–30 min, after which the voltage was switched off and the sample was quenched in the electrolyte.

The surface morphology and structure of the modified surface layer were examined using a Micromed MET optical metallographic microscope. The microhardness of the samples was measured at a Falcon 503 microhardness tester at a load of 50 g. The surface roughness was studied at a TR200 device. The change

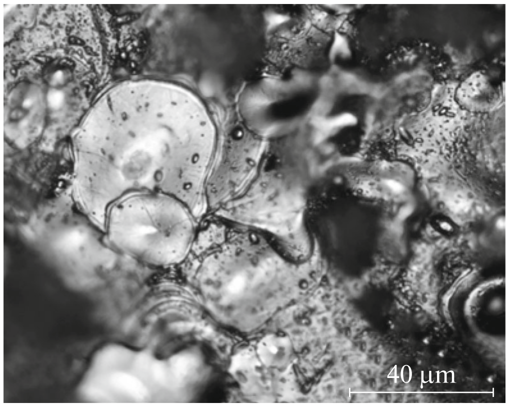

Fig. 1. Morphology of titanium Ti6A14V alloy's surface of after each cathodic nitriding at 750°C for 10 min.

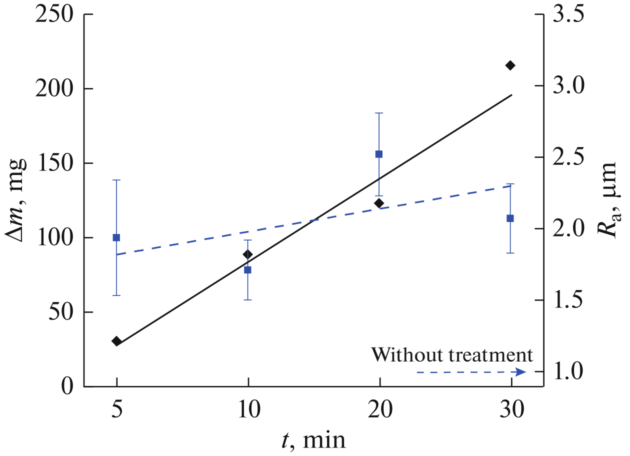

Fig. 2. Dependence of mass loss and roughness of sample surface from Ti6A14V titanium alloy after cathodic nitriding at 750°C on the treatment duration.

in mass of the samples was defined using a Citizon-CY224C electronic analytic balance with an accuracy of ±0.0001 g after their being rinsed with distilled water for removing salts.

The tribological experiments were carried out at a dry friction of a side surface of the cylindric sample over the bearing steel disk hardened up to 60 HRC under the load of 10 N. The sample's linear sliding rate was 1.555 m/s, and the friction distance was 1 km. The friction coefficient was determined at the last 100 m after the friction couple aging.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the titanium alloy surface morphology after the cathodic nitriding. The revealed developed surface was determined by the action of the physical and chemical processes characteristic for the cathodic treatment. In particular, during the cathodic plasma electrolytic treatment in water electrolytes, a simultaneous surface oxidation with the oxide layer formation occurs. The latter primarily consists of rutile TiO, and the surface erosion results from the electric discharges effect. The formed surface morphology will be determined by its roughness.

Profilometry measurements showed an increase in roughness by 1.7–3.1 times caused by nitriding. With an increase in the treatment duration, the linear loss in the samples' mass resulting from the surface erosion is observed, which induces the growth in its roughness (Fig. 2). Nitriding temperature variation shows minimum for the roughness value and maximum for the sample mass loss at 750°C (Fig. 3). These results can be attributed to competing effects of oxidation and erosion of the surface. Upon the treatment temperature increase ranging from 600 to 700°C, the growth in the sample mass loss and surface roughness is observed, when the erosion almost wholly determines the change in the treated surface and is intensified proportionally to the power released in a vapor-gas shell (temperature increase in the studied range occurs with a voltage increase from 100 to 135 V, while registered current density hardly changes in this case and is in the interval of 2.0–2.5 A/cm^2). Further on, upon temperature increase to 750°C the mass loss continues to be observed; however, the roughness is considerably decreased. Most likely, the forming pores and craters from the discharges are seen to be filled in with oxides, which leads to passivation of these zones and more intense destruction of the protruding sites of the surface, which reduces the roughness. Upon further temperature increase, the oxidation intensification compensates the mass loss due to the erosion effect, and the roughness growth during the temperature increase from 800 to 850°C can be explained by the erosion intensification, which dominates the oxidation.

Titanium alloy surface nitriding forms a hardened diffusion layer: a solid solution of nitride in the initial alloy structure. The hardened layer thickness that is defined according to the microhardness grows with an increase in the duration of the treatment from 5 to 10 min, and it decreases further on with the treatment during 20 and 30 min (Fig. 4). Similarly, the highest microhardness of the diffusion layer is observed after 10 min of nitriding and is 820 HV. Upon treatment temperature variation, a marked effect of hardness occurs only after 750°C (Fig. 5). This is explained by the fact that, at temperatures higher than 750°C at a further hardening, the titanium alloy is exposed to martensite aging with an α-phase release [2]. The reason for the microhardness and hardened layer thickness reductions with an increase in duration (more than 10 min) and temperature (higher than 750°C) of the treatment is the thickening of the oxide layer, which restrains the nitrogen diffusion shown by the example of anode nitriding [6].

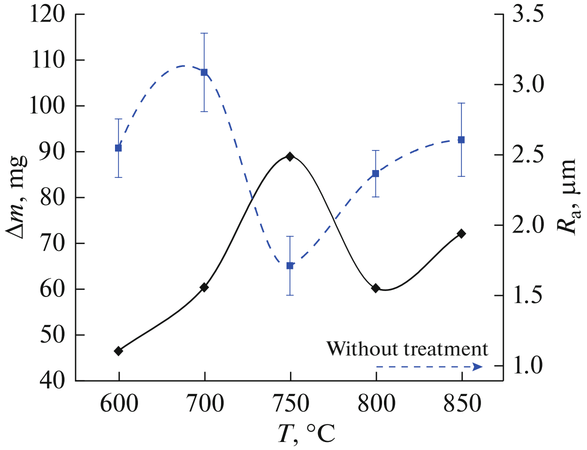

Fig. 3. Dependence of mass loss and roughness of sample surface from Ti6A14V titanium alloy after cathodic nitriding for 10 min on the treatment temperature.

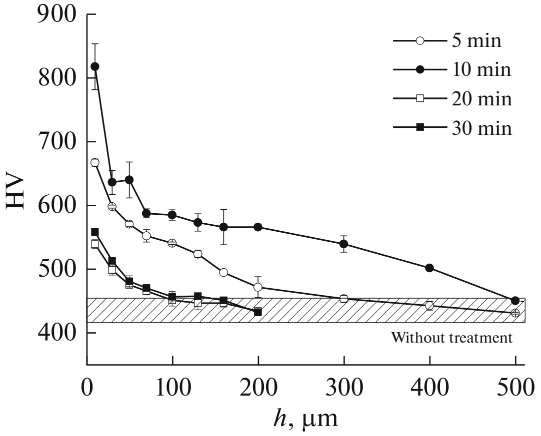

Fig. 4. Microhardness distribution in surface layer of Ti6A14V titanium alloy after cathodic nitriding at 750°C of different treatment duration.

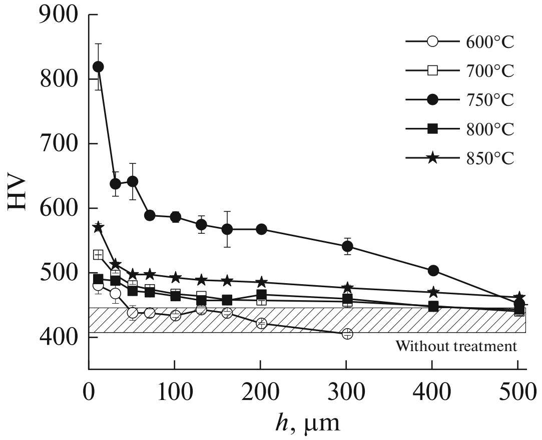

Fig. 5. Dependence of microhardness in sample surface from Ti6A14V titanium alloy after cathodic nitriding for 10 min at different the treatment temperature.

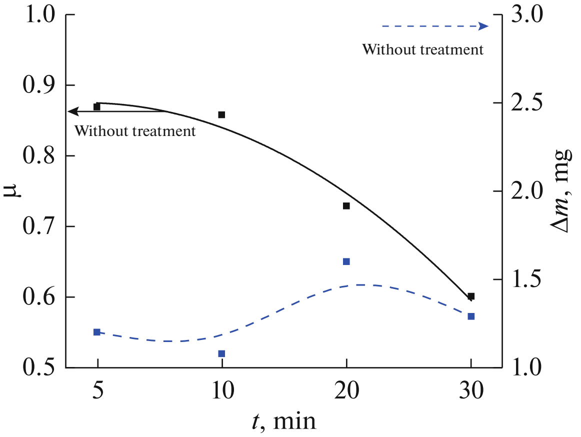

Fig. 6. Dependence of friction coefficient and mass wear of Ti6A14V titanium alloy sample after cathodic nitriding at 750°C on treatment duration.

The tribological experiments revealed a positive effect of the cathodic nitriding on the decrease in the friction coefficient and mass wear of the Ti6A14V titanium alloy surface (Figs. 6, 7). It was shown that the friction coefficient upon the friction couple aging decreases monotonously with an increase in nitriding duration and grows with a temperature increase. Under these conditions, the surface layer has a low hardness, contributing to the counterbody's sliding. The dependence of the mass wear on the treatment duration is not found; this index decreases by 1.8–2.7 times compared to the untreated sample. The increase in the treatment temperature to 750°C benefits the wear decrease; an insignificant wear resistance decrease occurs at a high temperature. The highest mass wear reduction takes place after the cathodic nitriding at 750°C during 10 min, which is by 2.7 times less compared to the untreated sample. Under the above conditions, the least surface roughness and highest surface layer microhardness are observed. Thus, the complex effect of the surface roughness and surface layer hardness on the material wear resistance is clearly seen.

CONCLUSIONS

(1) The possibility is shown of strengthening titanium Ti6A14V alloy's surface and improving its wear resistance using the cathodic plasma electrolytic nitriding in the water electrolyte based on ammonia (5%) and ammonium chloride (5%).

(2) Increase in surface roughness resulting from the cathodic nitriding application by 1.7–3.1 times caused by the competing effect of nitriding and surface erosion is found.

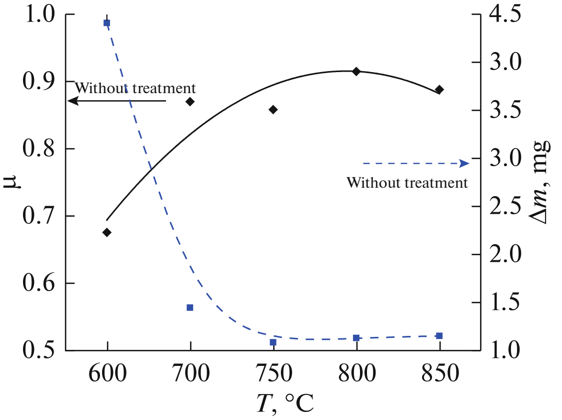

Fig. 7. Dependence of friction coefficient and mass wear of sample surface of Ti6A14V titanium alloy after cathodic nitriding for 10 min on the treatment temperature.

(3) The formation of the hardened surface layer is revealed as a result of the nitride diffusion and martensite aging at temperatures higher than 750°C with a consequent quenching. The inhibitory effect of oxidation is shown on the thickness and microhardness of the hardened layer similarly to the anode nitriding.

(4) A complex effect is determined of the surface roughness and surface layer hardness on the titanium layer's wear resistance. The highest decrease in the mass loss occurs at the lowest roughness and the greatest microhardness of the hardened layer. At the same time, the friction coefficient decreases at a low hardness of the surface layer, which benefits the counterbody's sliding.

(5) The Ti6A14V titanium alloy's cathodic nitriding optimal mode in the water electrolyte based on ammonia (5%) and ammonium chloride (5%) is determined at the treatment temperature of 750°C and duration of 10 min, which makes it possible to increase microhardness of the surface layer to 820 HV and to decrease the mass wear by 2.7 times.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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