Proceedings of BALTTRIB'2024 edited by prof. J. Padgurskas
eISSN 2424-5089 (Online)

DOI: 10.15544/balttrib.2024.10.

ENHANCEMENT OF WEAR RESISTANCE OF Ti6Al4V TITANIUM ALLOY BY SURFACE MODIFICATION

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Abstract: The effect of surface modification (thermal oxidation and gas nitriding) on phase-structural state and wear resistance of Ti6Al4V titanium alloy was investigated. The wear resistance was evaluated under dry friction conditions with various loads (10 to 25 N). The friction and wear experiments demonstrated that under various loads, the wear of the surface-treated Ti6Al4V alloy decreased by 5–37% (for oxidation) and 28–47% (for gas nitriding) compared to that of the untreated one. It should be noted that the greater the load during dry sliding friction, the greater the effectiveness of the proposed surface treatments. The best wear resistance of titanium was provided by gas nitriding due to the formation of a surface compound ($TiN+Ti_2N$) layer with high hardness. To conclude, our findings indicate that surface modification is an effective approach to improving the wear performance of Ti6Al4V alloy.

Keywords: titanium, powder metallurgy, porosity, friction, boundary lubrication, wear resistance.

1. INTRODUCTION

Every year, titanium and its alloys expand their scope of application in machine building, marine engineering, and the aviation industry. This is explained by an excellent combination of their properties, such as high specific strength, corrosion resistance and low cold brittleness threshold [1–3]. However, titanium alloys have several disadvantages – high cost, low surface hardness and wear resistance. The last two disadvantages limit the use of titanium alloys for work under conditions of contact loads and friction [1–6].

Thermochemical treatment is used for titanium alloys to eliminate the mentioned disadvantages. Among the many thermochemical treatment methods for titanium alloys, diffusion saturation of the surface with the interstitial elements, such as oxygen and nitrogen, is the most widely used. During this treatment, a hardened layer of titanium oxides or nitrides is formed on the surface, with a favourable combination of mechanical (high hardness, wear resistance, heat resistance) and physicochemical (corrosion resistance, thermal conductivity, density comparable to titanium, and coefficient of thermal expansion) properties. In addition, during this treatment, a transitional diffusion layer (α-case solid solution of the interstitial elements in the titanium layer) is formed, which allows the avoidance of a sharp gradient of properties between the compound layer and the matrix and, therefore, reduces the probability of cracking and chipping of the surface layers during operation. The advantage of this method is also that it allows to process parts of complex shapes, control the composition, structure and depth of the hardened layer [3–10].

For example, H. Dong et al. showed that thermal oxidation (TO) made it possible to significantly increase the wear resistance (wear intensity is decreased by two orders of magnitude) of Ti6Al4V alloy compared to untreated (UT) one [8]. A. Maytorena-Sánchez et al. evaluated the effect of TO temperature (450–1000 °C) on the phase-structural state of the titanium surface. They established that titanium has

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the best wear resistance after TO at 750 °C, with a surface hardness of 10.6 GPa, a friction coefficient of 0.57 and a volumetric wear of $2.26\cdot10^{-5}$ mm^3/Nm [9]. Instead, Y. Mantani et al. showed that gas nitriding (GN) also, due to the formation of a nitride compound layer, allows a significant increase both the surface hardness and the wear resistance of the Ti-18Nb alloy in a tribo-pair with steel and Al_2O_3 balls [10].

This paper compares the influence of thermal oxidation (TO) and gas nitriding (GN) on the phase-structural state and wear resistance of the Ti6Al4V alloy.

2. EXPERIMENTAL

The Ti6Al4V titanium alloy was studied. TO and GN were chosen as surface modification methods. The regimes of surface modification are as follows:

- TO: The samples were heated in a vacuum (P_{vacuum} ~ $1.3\cdot10^{-3}$ Pa) to 750 °C. Then, an oxygen-containing dynamic environment (P_{O2} ~ $2.7\cdot10^{-2}$ Pa) was introduced into the reaction chamber and held for 5 hours. After an exposure, they were cooled in an oxygen-containing medium to 350°C, and an air was introduced into the reaction chamber.
- GN: The samples were heated in a vacuum (P_{vacuum} ~ $1.3\cdot10^{-3}$ Pa) to 850 °C. Then, commercial pure nitrogen (P_{N2} ~ 10^5 Pa) was introduced into the reaction chamber and held for 4 hours. After an exposure, they were cooled to 750 °C, held for 2 hours, and then furnace-cooled.

XRD analysis was performed using a DRON-3.0 diffractometer in CuK_α-radiation according to the Bragg-Brentano scheme. The microstructure was evaluated by an EVO 40 XVP scanning electron microscope (SEM). The hardness tests were performed by using a Hysitron TI Premier indentation device with a load of 0.5 N on a Vickers indenter. The depth of the modified layer was defined as the zone whose hardness exceeds the matrix hardness by 0.2 GPa.

The wear tests were performed using a Micro-combi tester. The tribo-test type – a steel ball dry reciprocating sliding friction on a titanium plate. The friction load varied from 10 to 25 N. The ball movement speed – 100 mm/min, the number of cycles – 5, and the track length – 6 mm. To determine the wear mechanisms, SEM and an optical imaging system with a CSM microscope and USB 2.0 CCD camera were used. The each sample was tested twice.

3. RESULTS AND DISCUSSION

3.1. Surface characterization

According to the XRD analysis, it was established that after TO, only reflections of the α-phase are observed in the diffraction spectrum, while reflections of the β- or oxide phases are absent (Figure 1). Under these TO conditions, it can be assumed that no oxide compound layer is formed on the surface, only a saturated solid-solution of oxygen in titanium. The shift of the reflections of the α-Ti matrix phases towards the smaller 2θ angles evidences the formation of a solid-solution layer. That is, during TO, oxygen atoms penetrate into the hexagonal close-packed crystal lattice of titanium, forming strain in it [11, 12]. After GN, a nitride compound layer is formed on the surface, which consists of low-valence nitride (Ti_2N) and mononitride (TiN) (Figure 1). The intensity and number of reflections of Ti_2N nitrides is greater than that of TiN in the diffraction spectrum, indirectly indicating higher content of the first phase in the layer. Predominant orientations of nitride phases: lines in the (111) and (200) directions dominate for the TiN mononitride phase and in the (002) direction for the low-valence nitride Ti_2N. Also, we observe a shift of the peaks of the α- and β-phases towards the smaller 2θ angles (Figure 1), which indicates the solid-solution penetration of nitrogen atoms in the surface layer.

The metallographic analysis confirmed that an oxide compound layer is not formed on the surface after TO (Figure 2, a). It should be noted that there are almost no β-grains in the surface layer. This can be explained by the fact that under such gas-dynamic parameters, oxygen as a strong α-stabilizer [12, 13] will dissolve in the surface layer and form a modified surface layer enriched with oxygen [14, 15]. After GN, a nitride compound layer with a thickness of 2±1 μm is formed on the surface. Due to higher GN temperature, we observe the growth of β-grains drawn out in lamellar form (Figure 2, b).

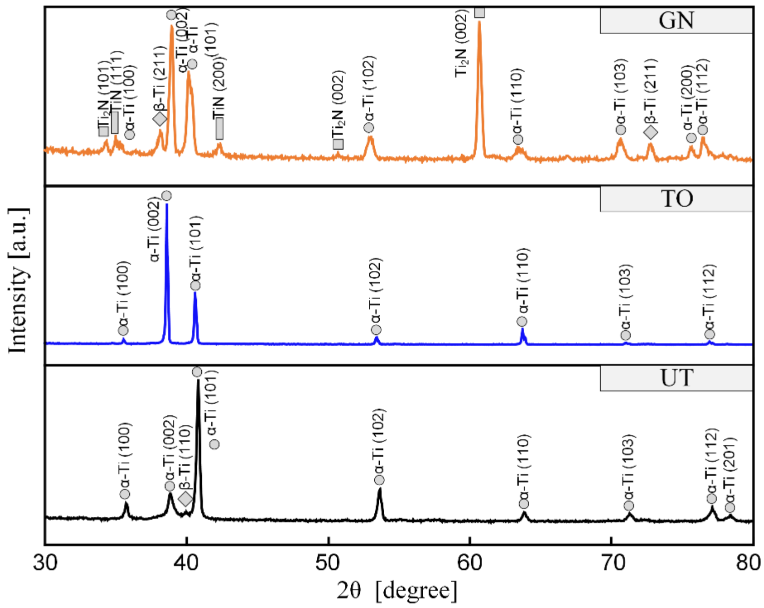

Figure 1. XRD analysis of Ti6Al4V alloy after surface modification

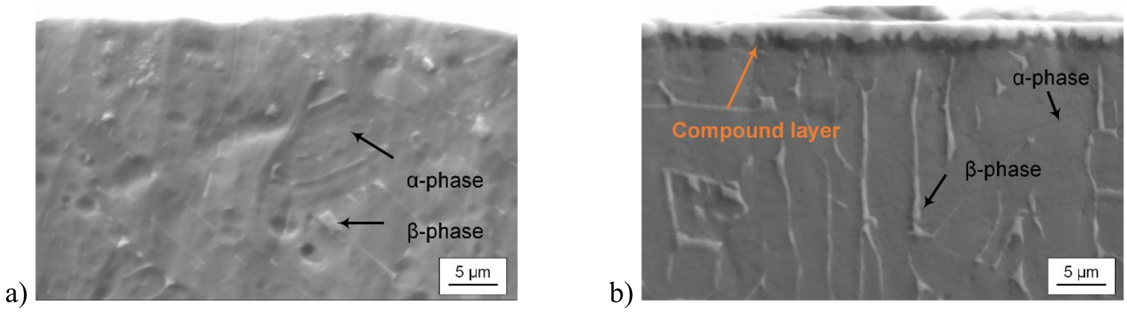

Figure 2. Microstructure of Ti6Al4V alloy after TO (a) and GN (b).

The durometric analysis results show that surface modification effects on the surface hardening of the Ti6Al4V alloy (Figure 3). TO and GN allow to increase of the surface hardness by ~ 1.8 and 2.6 times, respectively. The most significant increase of the surface hardness was observed after GN, which is explained by forming a nitride compound layer consisting of the nitride phases. Also, a diffusion layer with increased microhardness is formed due to the diffusion of the interstitial oxygen and nitrogen atoms deep into the Ti6Al4V alloy (solid-solution phenomena [16]). The character of the microhardness distribution curves in the surface layer is gradient. As the distance from the surface increases, the hardness decreases, which is explained by lower content of the interstitial elements (oxygen or nitrogen) [12–16]. The depth of the diffusion zone is ~ 30 and 45 μm for TO and GN, respectively. It should be noted that oxygen atoms, due to their smaller size and higher diffusion mobility than nitrogen atoms, should provide deeper penetration into the surface layer. However, we record greater depth after GN, which is explained by higher temperature of a treatment and, as a consequence, higher diffusion mobility.

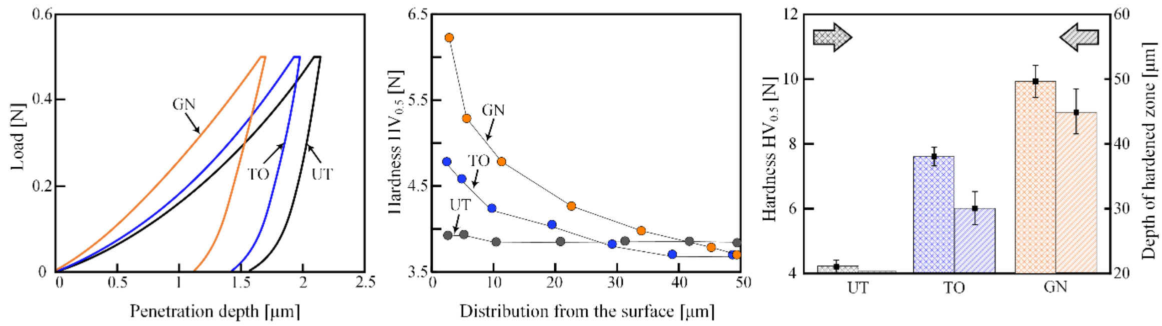

Figure 3. Durometric analysis of Ti6Al4V alloy after surface modification

3.2. Tribological characterization

The profilometric analysis established that as the load during friction increases, the roughness of the modified surface increases due to the formation of a wear track. The minor changes in surface relief were observed after GN, which indirectly indicates better wear resistance (Figure 4).

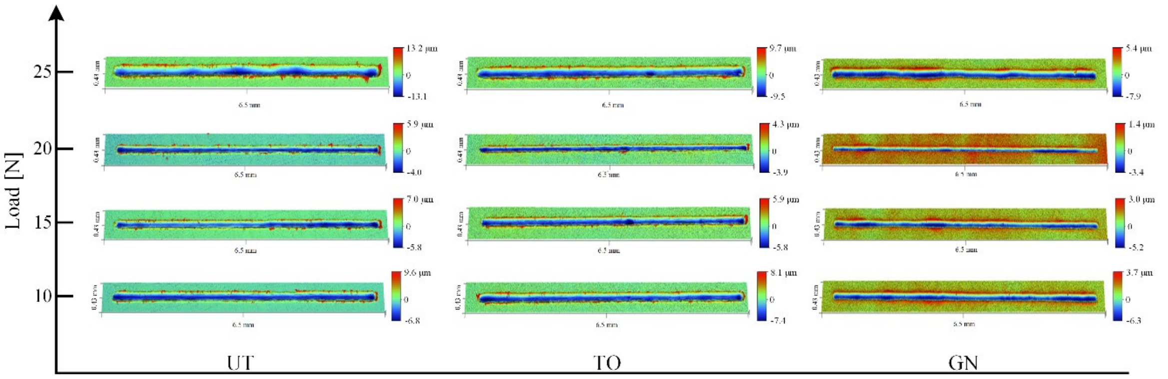

Figure 4. Three-dimensional morphologies of untreated and surface modified Ti6Al4V alloy after friction with steel ball under different load

Figure 5 shows the wear volume and the wear track cross-sectional profile. The UT Ti6Al4V alloy had the highest wear volume in the entire load range. TO and GN reduce the wear volume of the Ti6Al4V alloy by 7–37 and 33–47%, respectively. It should be noted that the best effect of improving wear resistance after surface modification is observed at higher loads. The width and depth of the wear scar for the UT Ti6Al4V alloy are the largest (Figure 5), especially after friction under a load of 25 N, which is associated with low hardness and, therefore, a high tendency to the adhesion junction and shear resistance. The increase of the surface hardness after TO and GN makes the Ti6Al4V alloy capable of withstanding shear forces arising during dry reciprocating sliding friction and leads to less accumulation of wear products and, as a result, to higher wear resistance [17, 18]. The lowest amount of wear (0.1–0.45·10^3 μm^3) is fixed for the GN Ti6Al4V alloy in the entire range of loads (10–25 N). However, the apparent differences in the performance of the nitrided layer during friction under different loads cannot be ignored. Thus, starting with a load of 15 N and above, the depth of the wear scar is larger than the thickness of the nitride compound layer, indicating its destruction. For both TO and GN, the effect of increased wear resistance is associated with forming a diffusion zone, which has higher hardness due to forming a solid-solution of oxygen or nitrogen in Ti6Al4V alloy. A deeper diffusion layer with higher hardness (Figure 3) provides the Ti6Al4V alloy with better wear resistance (Figure 5).

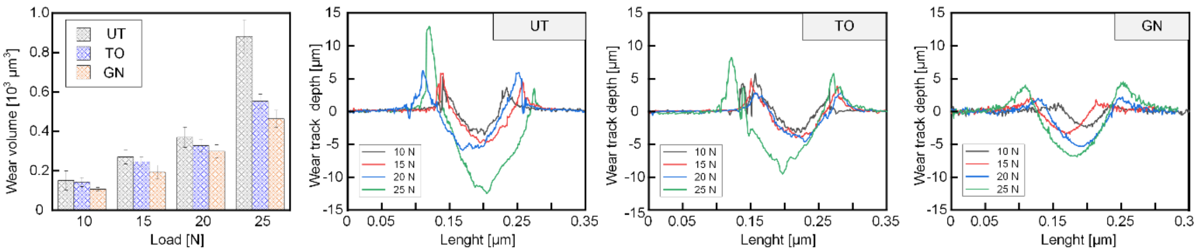

Figure 5. Wear volume and cross-sectional profile of wear track of UT and surface modified Ti6Al4V alloy after friction with steel ball under different load

Regardless of the modification, on the surface of the steel ball after friction, we observe round, flat spots, which indicates its wear (Figure 6). As the load increases, the worn spot's diameter increases, indicating more intense wear of the steel ball. TO and GN of the Ti6Al4V alloy increase the worn spot of the steel ball during friction by 80–90 and 115–125 µm, respectively. It should also be noted that on the surface of the steel ball that friction with the GN Ti6Al4V alloy, we observe a furrowed relief, characteristic of the abrasive wear mechanism. On the other hand, on the surface of the steel ball that friction with the UT and TO Ti6Al4V alloy, in addition to the furrowed relief, we note minor adhesive smearing. Such adhesive junction can be explained by high chemical activity and low thermal conductivity of Ti6Al4V alloy [7]. This will lead to the appearance of cold micro-welding and traces of material transfer, which is characteristic of the adhesive mechanism [19]. GN provides higher surface hardness, which, like an abrasive, will more intensively wear the steel ball and increase the diameter of the worn spot. Taking into account the wear volume of the surface modified alloy (Figure 5) and the corresponding wear spot of the steel ball (Figure 6), we observe a dependence: surface modification increases the hardness of the Ti6Al4V alloy, which contributes to improving its wear resistance and reducing the wear resistance steel ball.

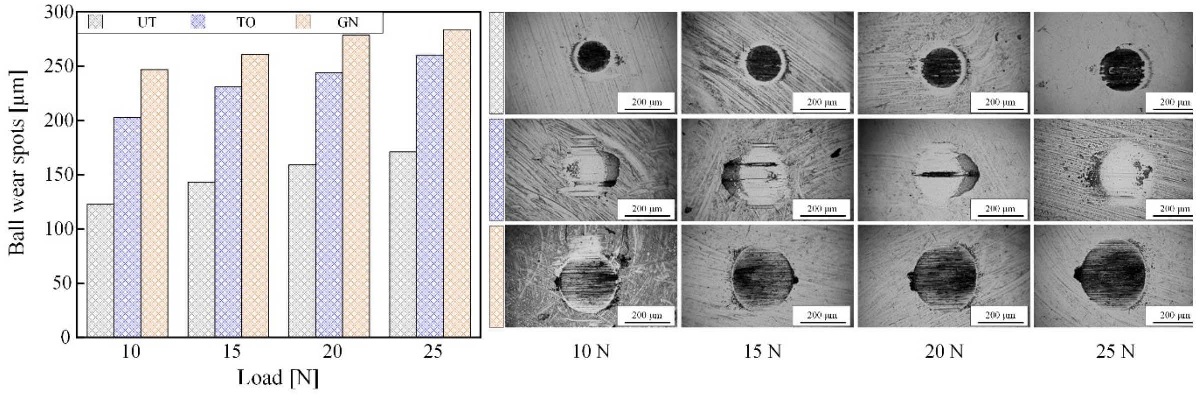

Figure 6. Ball wear spots and optical image of wear spots of steel ball after friction with UT and surface modified Ti6Al4V alloy under different load

The morphology of the worn surface together with low and high magnification (highlighted in red area) images after dry sliding under a load of 25 N for UT and surface modified Ti6Al4V alloy is shown in Figure 7. In general, parallel wear tracks along the sliding direction formed by frictional interaction with the steel ball are observed. In addition, all worn surfaces show signs of plastic deformation and ridges along the sliding direction due to the accumulated removed material. Depending on the surface treatment, the size and volume of such protrusions will alter the frictional behaviour during sliding due to material deposition on the ridges. In addition, the track width and wear damage for all samples differ, indicating different wear mechanisms. For example, on the surface of the UT alloy, we fix numerous furrows and wear debris on the surface of the scar, which are characteristic features of the abrasive mechanism. Zones of plastic deformation at the edges of the scar, accompanied by delamination of the surface layers, the appearance of micro-cracks, and the accumulation of removed material, were observed. (Figure 7, a). The worn surface of the TO Ti6Al4V alloy shows the same signs of wear as the UT one, which indicates the implementation of the same wear mechanisms – abrasive and delamination. However, the number and size of furrows and wear debris on the scar surface are smaller, indicating less abrasive wear [19, 20]. We note smaller ridges at the edges of the TO Ti6Al4V alloy scar than for the UT one, which means that smaller fraction of the accumulated material in these areas was released. More excellent surface resistance to plastic deformation (Figure 7, b) can explain the less accumulation of removed material at the edges of the scar. This is confirmed by the fact that modifying (saturation) the surface layer of the Ti6Al4V alloy with oxygen increases the crack propagation energy [21, 22], thereby increasing the resistance to delamination and wear. GN provides the narrowest and the smoothest wear track. At the edges of the scar, we observe minor zones of plastic deformation and accumulation of material. In general, we do not observe the characteristic features of the abrasive wear (furrows or debris), which indicates the high wear resistance of the nitride compound layer. Unlike UT and TO Ti6Al4V alloy, a nitride compound layer with high hardness and chemical inertness acts as an abrasive, contributing to the counterbody wear. However, it should be noted that we observe a micro-cracks network on the scar surface. Such a micro-cracks network is formed because, despite the high hardness of the nitride compound layer, its thickness is not enough to resist brittle destruction under the action of tangential loads during friction. However, due to the underlayer diffusion zone, which performs the role of mechanical support [23], the nitride compound layer has good adhesion with the alloy matrix. It helps with resistance to remove the nitride compound layer from the contact zone (Figure 8). Therefore, surface modification improves the wear resistance of Ti6Al4V alloy by reducing the intensity of the abrasive wear and delamination. Forming a solid-soluble oxygen-hardened layer (in the case of TO) or a nitride compound layer (in the case of GN) increases wear resistance (Figure 8). The best improvement is obtained after GN.

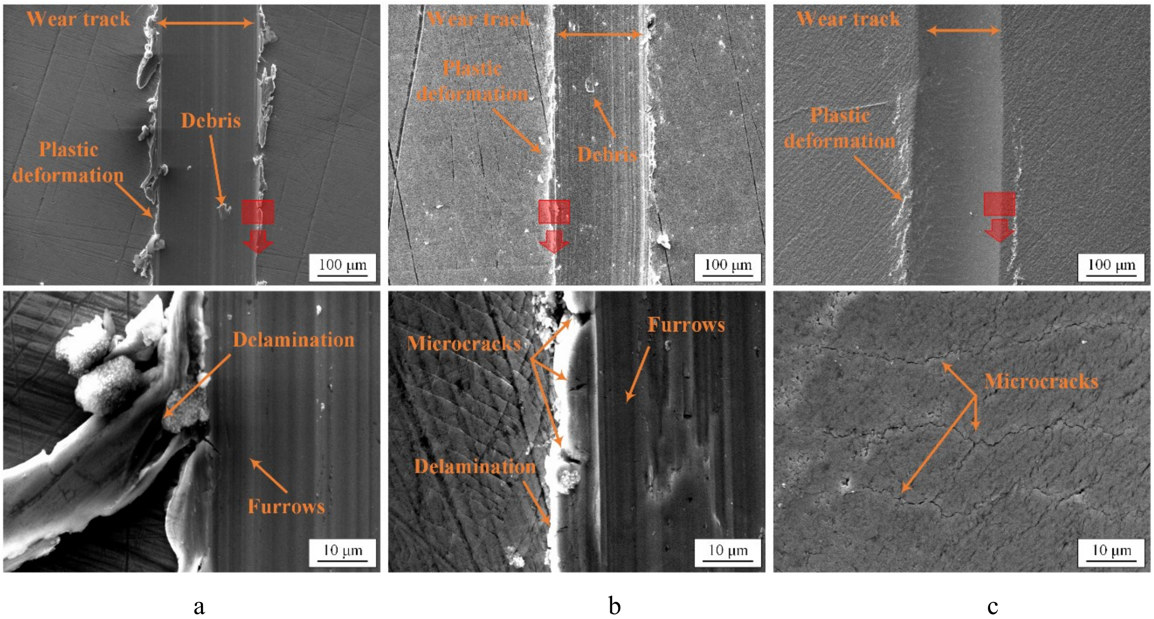

Figure 7. Worn surface of UT (a), TO (b) and GN (c) titanium alloy after friction with steel ball alloy under load of 25 N

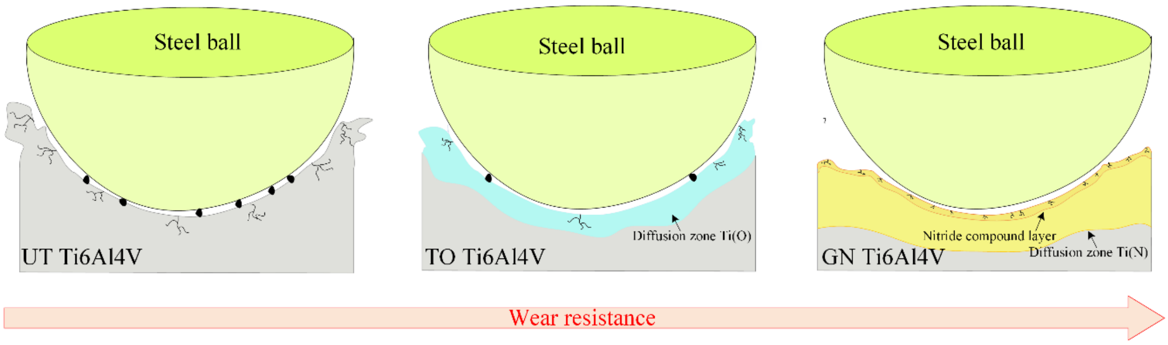

Figure 8. Schematic of wear mechanism of untreated and surface modified Ti6Al4V alloy with steel ball.

CONCLUSIONS

The effect of surface modification (thermal oxidation and gas nitriding) on the phase-structural state and wear performance of Ti6Al4V titanium samples was studied. Based on the findings of the aforementioned research, the following conclusions have been reached.

1. According to XRD and SEM analysis, TO ensures the formation of a solid-solution diffusion layer of Ti(O) oxygen in the alloy. Instead, GN, apart from the Ti(N) diffusion zone, forms a nitride compound layer consisting of mononitride (TiN) and low-valence nitride (Ti_2N).
2. The hardness test showed that TO and GN increase the surface hardness by ~ 1.8 and 2.6 times, respectively. Due to the diffusional penetration of O or N elements into the surface layer, a hardened diffusion layer with a thickness of 30 and 45 µm, respectively, is formed.
3. The wear resistance of the surface-modified Ti6Al4V alloy under conditions of dry sliding with a steel ball under different loads (10–25N) was evaluated. TO and GN allow to reduce the wear volume of Ti6Al4V alloy in the load range of 10–25 N from 0.15–0.85·10^3 µm^3 to 0.13–0.55·10^3 µm^3 and 0.10–0.45·10^3 µm^3, respectively.
4. Based on SEM analysis of the worn surface, the main wear mechanisms of the surface-modified Ti6Al4V alloy were investigated. It was shown that surface modification increases the wear resistance of the Ti6Al4V alloy by reducing the intensity of the abrasive wear and delamination. The increase of the wear resistance is achieved due to the formation of a solid-soluble oxygen-reinforced

layer (in the case of TO), or a nitride compound layer (in the case of GN). The best effect of improving wear resistance is obtained after GN.

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