International Tribology Council
Aleksandras Stulginskis University
Lithuanian Scientific Society Department „Tribologija"

The 9th International Conference BALTTRIB'2017
16–17 November 2017
Akademija, Kaunas, Lithuania

Proceedings of BALTTRIB'2017 edited by prof. J. Padgurskas
eISSN 2424-5089/eISBN 978-609-449-127-6

https://doi.org/10.15544/balttrib.2017.09

TOPOGRAPHY, HARDNESS, ELASTIC MODULUS AND WEAR RESISTANCE OF NITRIDE COATINGS ON TITANIUM

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The roughness, hardness and elastic modulus of the surface layers of c.p. titanium after thermodiffusion saturation with nitrogen at temperatures of α and β phase regions were investigated. It was established that the increasing temperature of gas nitriding provided a higher level of surface hardening (hardness, elastic modulus, depth of hardened layer) of the material but worsened the roughness of its surface. The tribological tests of hardened by nitriding c.p. titanium in pairs with 304L stainless steel showed lower friction coefficients in the period of rubbing, where the surface of the titanium was nitrided below the temperature of the transus temperature.

Keywords: c.p. titanium, nitriding, nanoindentation, wear resistance

1. INTRODUCTION

The light metal materials that work under the high temperatures and intensive wear, including aggressive environments, are widely used in modern high-tech industries. Titanium and its alloys are promising and widespread representative materials of this class [1]. Due to unique properties of titanium such as high specific strength, corrosion resistance, low elastic modulus, cold-brittleness temperature and biocompatibility, it is used in aviation, space, engineering, shipbuilding, chemical industries and medicine [2, 3]. However, titanium has a low wear resistance. This results to micro cold welding and adhesive junctions with other metals during friction. Therefore, the use of titanium in the friction units of mechanisms and machines without special surface treatment is impossible [4, 5].

The antifriction properties of titanium alloys can be increased by thermochemical treatment (TCT), in particular nitriding. After such treatment a hardened nitride layer with increased hardness, wear resistance, heat resistance, corrosion resistance and fatigue strength is formed on the surface of the titanium. The nitride coatings have also a high density, good adhesion to the base material and form a smooth gradient of properties along the depth of the surface modified layer. This method allows to process parts of arbitrary shape, control the composition, structure and depth of the hardened layer [6–8].

The purpose of this work was to evaluate the effect of nitriding temperature on the properties of the surface hardened layer of commercially pure (c.p.) titanium (Grade 2), since the surface properties of the treated titanium influence the operational properties: wear resistance, corrosion resistance, fatigue strength, heat resistance etc.

2. EXPERIMENTAL

The research was carried out on samples (30×10×3 mm) of c.p. titanium Grade 2. The specimens were ground using 15 μm Al_2O_3 (corundum) abrasive bands. Further polishing was carried out by abrasive

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bands with 9 µm corundum grains. The treatment duration was 30 min for every process with a 0.1 MPa contact loading.

The nitriding regime was as follows: heating in a vacuum (p=10^5 Pa) to a temperature of 750 °C (α–region) or 900 °C (β–region), exposure for 5 h in nitrogen atmosphere (1 atm N_2), cooling in a vacuum (p=10^5 Pa) with a furnace. We used commercially pure gaseous nitrogen deoxygenated and dehydrated as a result of passage through a capsule with a silica gel and titanium chips heated at the temperature ~50 °C above the saturation temperature.

The phase composition of the surface layers was performed by using a DRON–3.0 X-ray diffractometer with CuK_α–radiation. The tube was focused according to Bragg–Brentano scheme. The microstructure analysis was determined by Carl Zeiss EVO 40XVP scanning electron microscope with energy dispersive X-ray spectrometer INCA Energy 350. The surface roughness was analyzed with the help of two-step Phase-Shifting interferometry with arbitrary phase shifts [9]. The level of surface hardening after each technological operation was determined by PMT–3M device at the loads on the Vickers indenter of 0.49 and 0.98 N. The nanoindentation was carried out on a Micro Combi Tester device using a diamond Vickers indenter. The maximum load during nanoindentation was 200 mN, loading and unloading speed was 400 mN/min. The tribological tests were performed on a friction machine realizing reciprocating motion according to a pin – plate scheme. The specific load was 2 MPa; length of the friction track was 2 mm; test time was 1800 s. The plate was made of c.p. titanium Grade 2 and the pin (counterbody) – 304L stainless steel.

3. RESULTS AND DISCUSSION

The dense and well adhered to the matrix nitride film was formed on the surface of c.p. titanium Grade 2 as a result of nitriding. A color and reflective ability of the nitride surface are different depending on treatment temperature. At low temperatures of thermodiffusion saturation (750 °C) a shiny film of a light gray color with a golden hue was formed on the surface. With increasing treatment temperature to 900 °C matt film with a dark golden hue was received.

The specimen surface color after thermochemical treatment depends generally on a stehiometry of the titanium nitride formed on the surface and on its thickness, stechiometry, density and other characteristics. According to X-ray diffraction analysis of the specimens after nitriding under temperature of 750 °C, a film based on titanium nitride Ti_2N (ε–phase) was formed (Fig. 1 b). The reflections [111] and [022] dominate in the diffraction spectrum of Ti_2N nitride. The texture of the Ti_2N phase was, in general, arranged in the direction [111]. This is typical for materials with a cubic structure. With a temperature increase during thermodiffusion saturation to 900 °C formed nitride film contains TiN (δ–phase) mononitride and Ti_2N (ε–phase) nitride. At the same time, the intensities of Ti_2N and α–titanium reflections decreased that indirectly indicate the nitride film growth due to formation of the titanium mononitride layer (Fig. 1 c). The increasing nitriding temperature, degree of the ε–phase texture in the direction [111] was weakened and there was a tendency towards the appearance of a dominant orientation in the direction [002]. It should be noted that the relative intensity of the reflections of the ε–phase of titanium was higher than the intensity of the reflections of the δ–phase of titanium, indicating a greater number of the ε–phase in the surface layer. With the increasing temperature of the TCT the intensity of the α–Ti lines decreased. This indicates qualitatively the growth and thickening of the nitride film.

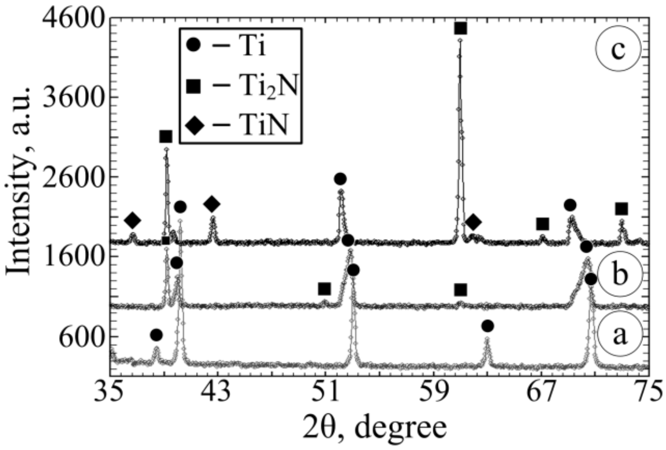

Figure 1. Diffraction patterns taken from titanium Grade 2 surface in initial state (a) and after nitriding at temperatures of 750 °C (b) and 900 °C (c).

The surface nitride film, which was formed on the surface of titanium after gas nitriding, has a characteristic relief. With increasing the temperature of the TCT from 750 ºC to 900 ºC the relief of the hardened surface intensified (fig. 2). This is explained by the fact that during thermodiffusion saturation the nitrogen atoms primarily diffused along grain boundaries, since they are the favorable ways for intensification of their diffusion. At higher temperatures of the TCT the nitride films are grown by the grain boundaries, join, grow one on another and fill gradually all treated surface. As a result, the topography of the surface repeats the grains boundaries and the more clearly the higher nitriding temperature. According to the results of energy dispersive X-ray analysis of the samples after nitriding, increased nitrogen concentration at the grain boundaries of titanium was fixed. This allows us to confirm that the grain boundaries are the new centers for the formation of nitride films. That is, the diffusion of nitrogen atoms in titanium occurs according to the grain boundary mechanism (fig. 2 and Table 1).

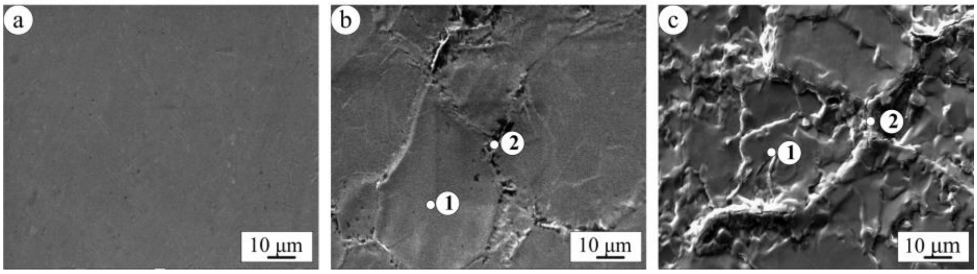

Figure 2. Surface of titanium Grade 2 in initial state (a) and after thermodiffusion saturation by nitrogen at temperatures of 750 °C (b) and 900 °C (c).

Table 1. Energy dispersive X-ray analysis of titanium surface after nitriding (see fig. 2).

Element	Nitriding at 750 °C				Nitriding at 900 °C			
	Spectrum №1		Spectrum №2		Spectrum №1		Spectrum №2	
	wt., %	at., %	wt., %	at., %	wt., %	at., %	wt., %	at., %
Ti	99.57	89.55	96.29	89.57	91.33	87.13	84.05	80.65
N	0.43	1.45	3.29	10.43	8.07	12.87	15.95	19.35

The surface hardening of titanium after thermodiffusion saturation with nitrogen is confirmed by the results of microindentation. After nitriding at a temperature of 750 °C the surface microhardness of titanium increased by 2.5 times. At higher temperature of the TCT the microhardness of the treated samples increased because of the activation of the phase formation processes on the surface. This is due to the fact that the TiN mononitride hardness is higher than Ti_2N nitride (20...22 GPa vs. 12...14 GPa). Therefore, the formation of a two-phase nitride film provided higher surface microhardness, which is almost 8 times higher than the microhardness of the untreated samples (Table 2).

Table 2. The results of micro and nanoindentation of titanium surface after nitriding (according to ISO 14577–1:2002).

Treatment	Microindentation		Nanoindentation					
	$HV_{0.98}$, GPa	$HV_{0.49}$, GPa	H_{IT}, GPa	E_{IT}, GPa	C_{IT}, %	R_{IT}, %	H_{VIT}	η_{IT}
Initial state	1.3	1.2	2.7	134.7	2.48	–0.09	251.4	12.8
Nitriding at 750 °C	3.2	3.0	11,5	191.3	1.25	–0.16	1082.8	38.2
Nitriding at 900 °C	10.3	9.9	16.3	238.9	0.48	–0.17	1537.8	50.2

As a result of nanoindentation, it was established that with increasing temperature of TCT, nanohardness and Young's modulus of hardened material increased. A step was observed on the diagram of the initial (without TCT) sample. This indicates the destruction of the natural titanium oxide film for a load of ≈170 mN (Fig. 3). Load-unloading curves narrowed with increasing nitriding temperature, indicating an increase of the elastic deformation during nanoindentation. In this case, the creep during nanoindentation decreased. This indicates qualitatively the packing density of nitrogen atoms in the nitride coating. It should be noted that the microhardness values correlated with the nanohardness values, but the nanohardness values was about 2 times higher than microhardness ones. This is due to the fact that surface microhardness is an integral characteristic. It depends on the number of phases and their ratios in the hardened modified layer, and, consequently, on the penetration depth of the indenter. The observed nature of the change of surface hardness, depending on the load on the indenter, indicates a gradient near-surface hardening characteristic of diffusion processes. With greater penetration depth of the indenter (that is, an increasing of the load on the indenter), the hardness decreases, as the content of the diffusing element (in particular, nitrogen) decreases and, consequently, the level of hardening. This is caused by the formation of a thin surface layer of titanium nitride (Table 2).

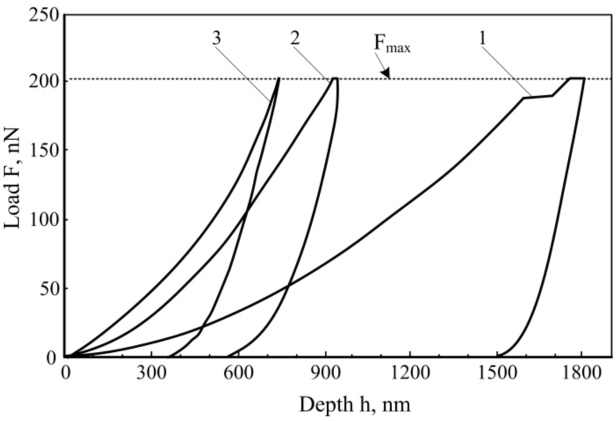

Figure 3. The loading and unloading curves of titanium during nanoindentation in the initial state (1) and after nitriding at temperatures of 750 ºC (2) and 900 ºC (3).

The deterioration of the surface relief of the titanium with increasing the nitriding temperature as a result of the intensification of nitriding processes, formation and growth of the nitride film affected the roughness of the treated surface. The surface topography before and after TCT was analyzed according to the 3D interferograms (fig. 4).

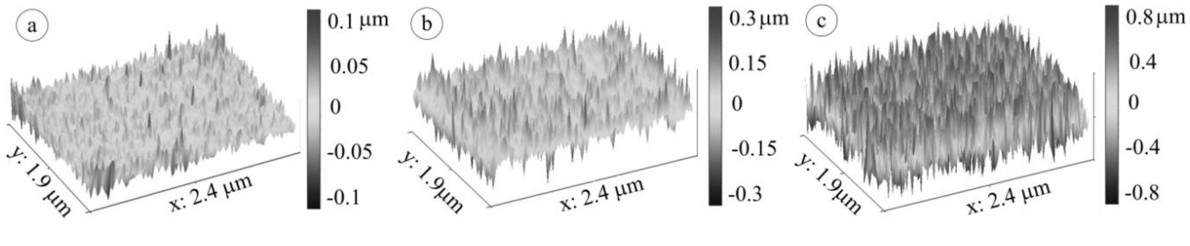

Figure 4. Surface relief of titanium alloy Grade 2 recovered by the interferometric method in initial state (a) and after nitriding at temperatures of 750 °C (b) and 900 °C (c)

After polishing the studied specimen had mirror surface with presented separate microscratches (fig. 4 a). The surface roughness was submicroscopic, which corresponds to the ISO grade scale number 2 (Table 3). During further nitriding under the temperature of 750 °C the nitrogen interstitial atoms, primarily, diffused along the grain boundaries, increasing surface relief (Fig. 4 b). The relief height parameters increased approximately 2.5…2.7 times and step parameters decreased slightly (Table 3). It is connected with the fact that after thermodiffusion saturation a new microrelief, where new peaks are formed by nitride phases, which were created on the grain boundaries, is formed on the surface. With the increase of the temperature of thermodiffusion saturation to 900 °C the height parameters increased in 8.5 ... 10.0 times, and steps parameters decreased by half compared to the initial parameters (Table 3).This is caused by the formation of additional peaks of the surface profile due to the formation of the TiN nitride phase. Finally, the surface topography with mirror relief transformed into the relief, which reflect grain boundaries the more the larger process temperature (Fig. 4 c).
The standard height and step characteristics of the surface roughness are not always the key factor during operation. That is why we used in these paper the additional surface roughness characteristics, namely, a material ratio curve of the profile (Abbott-Firestone curve), skewness and kurtosis. Such parameters are very important for the description of composite surface topography and analysis of their service conditions [10].

The polishing of titanium with abrasive bands allowed to obtaine the surfaces with small negative skewness values, which is typical for the most of traditional technological surfaces. The kurtosis values of the polished surface were smaller than for Gaussian surface (Table 3). It can be explained by the fact that polishing was carried out for the grinded surfaces, where sharp peaks were cut out during polishing. That is why the polished surface is characterized by the relatively deep and narrow valleys and lower wider peaks.

Nitriding under the temperature of 750 °C had a slight effect on the skewness surface and reduced the kurtosis values by 2.9 times. This characterizes the surface with low peaks and narrow valleys (Table 3). At the higher temperature of gas nitriding the skewness values slightly decreased compared to the initial state. The kurtosis values increased and approached to the once of polished surface (without TCT) (Table 3). Such an increase of the kurtosis values occurred as a result of the formation of a new microrelief along the entire surface and the significant increase of the height characteristics of the surface roughness. Nitriding and increasing the temperature of this process reduced the values of material ratio curve of the profile Rmr and increased the values of the height of the individual peaks and the depth of the valleys (Table 3). For higher process temperature Rmr value decreased. This testifies the creation of new high peaks due to formation of TiN mononitride.

Table 3. The results of 3D profilometry analysis of titanium surface after nitriding (according to ISO 4287–2014 and ISO 13565–1996).

Treatment	3D surface roughness parameters							Bearing area curves parameters					
	Ra, μm	Rt, μm	Rp, μm	Rv, μm	S, μm	Rsk	Rku	Rmr, %	Rpk, μm	Rk, μm	Rvk μm	Mr1, %	Mr2, %
Initial state	0.054	0.241	0.124	0.117	2.21	–0.06	2.88	0.58	0.047	0.19	0.05	5	92
Nitriding at 750 °C	0.134	0.587	0.284	0.303	2.04	–0.17	2.89	0.56	0.116	0.43	0.22	5.5	86
Nitriding at 900 °C	0.465	1.704	0.741	0.963	1.01	–0.04	2.80	0.54	1.005	1.07	0.79	13	93

The tribological tests show that after polishing c.p. titanium (without nitriding) had a high friction coefficient. The subsequent nitriding reduces the friction coefficient. It was established that decreasing the nitriding temperature provided lower friction coefficients and shorter period of rubbing (fig. 5). This can be explained by the fact that during the friction the adhesive-abrasive mechanism of wear of the material is realized. It depends on the roughness and hardness of the wearing surfaces.

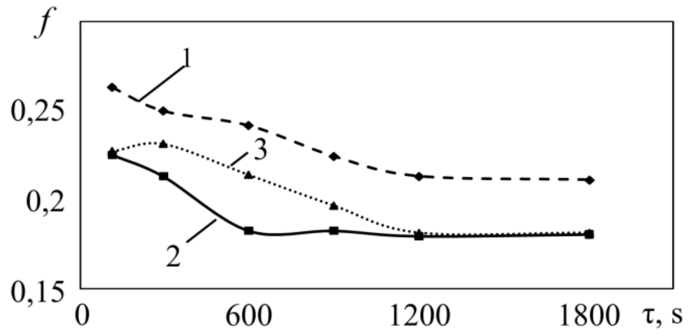

Figure 5. The kinetics change of friction coefficient for c.p. titanium in initial state (1) and after nitriding at temperatures of 750 °C (2) and 900 °C (3).

4. CONCLUSIONS

1. During saturation the specimen by nitrogen at the temperature of 750 °C a single-phase nitride (Ti_2N) film was formed on the surface. With an increase of the saturation temperature to 900 °C the single-phase surface film was changed to a two-phase (Ti_2N+TiN) one.

2. The microstructural analysis of the specimen surface indicated that activation of the surface nitride films and formation (growth) was occurred in the energy efficient locations (grain boundaries).

3. It was established that nitriding increased the micro- and nano-hardness, elastic modulus of titanium but decreased the quality of its surface. With increasing nitriding temperature this effect increased This affected negatively the tribological behaviour of the surface hardened material.

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