

# Modification of the structure and properties of commercially pure titanium through nitriding and subsequent TiN coating deposition in a single vacuum cycle

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**Abstract.** The modification of titanium by ion plasma methods consisting of hard coatings deposition on a specimen surface subjected to nitriding is carried out. It is shown that complex modification of the titanium in a single vacuum cycle is followed by formation of multilayered multiphase structure which tribological properties multiply exceed the corresponding properties of the material treated on two vacuum separated setups.

## 1. Introduction

It is shown that the formation of hard and superhard coatings on the surfaces of material allows to increase significantly the strength and tribological properties of the material [1–10]. The main problem of such method consists in insufficiently high level of adhesion forces between coating and substrate. For the increase of the adhesion forces the different transitional layers, which form the multilayered coatings, etc., are deposited. That raises significantly the price of technology and not always results in desirable results [11, 12].

The purpose of the present work is the comparative analysis of the revealed regularities of transformation of structure and properties of commercially pure titanium surface layers which are implemented as a result of ion plasma treatment at the use of two vacuum separated setups and complex setup for electron-ion plasma finishing modification of metals and alloys in a single vacuum cycle.

## 2. Material and research technique

The research material was commercially pure VT1-0 titanium (0.25 Fe, 0.07 C, 0.1 Si, 0.04 N, 0.2 O, 0.01 H wt. %, the rest is Ti) [13]. The specimens had a form of plates (15×15×4.5 mm). Nitriding (650 °C, 3 h) was realized in plasma of low pressure gas discharge on the TRIO setup equipped with PINK plasma generator based on non-self-sustained arc discharge with a filament cathode. The plasma source allows to increase the plasma concentration at rather low discharge voltage, to regulate discharge current irrespective of its burning voltage and gas pressure in the working camera [14–16]. The synthesis of hard TiN coating of 0.5 μm thick on the nitrided specimen surface of commercially pure VT1-0 titanium was carried out on ion plasma QUINTA setup [17]. The complex modification of commercially pure VT1-0 titanium (nitriding and subsequent coating deposition) in a single vacuum cycle was realized on the laboratory COMPLEX setup for electron-ion plasma finishing treatment of metals and alloys which was developed and created in IHCE SB RAS (Tomsk, Russia) as a result of



execution of RSF grant (project No. 14-29-00091). The treatment modes in a single vacuum cycle were identical to that used above for two vacuum separated setups.

The researches of modified material structure and properties were carried out by methods of scanning (SEM-515 Philips) and transmission diffraction (JEM-2100F) electron microscopies; X-ray diffraction analysis (XRD-7000s Shimadzu diffractometer). The microhardness was measured by Vikers method (PMT-3 microhardness tester, loads: 0.2 N and 0.5 N); wear resistance and friction coefficient were revealed by "Tribotechnic" tribometer (dry friction at the room temperature according to the "ball-on-disk" scheme (WC-8% Co, 6 mm; load of 5 N).

### 3. Results and discussion

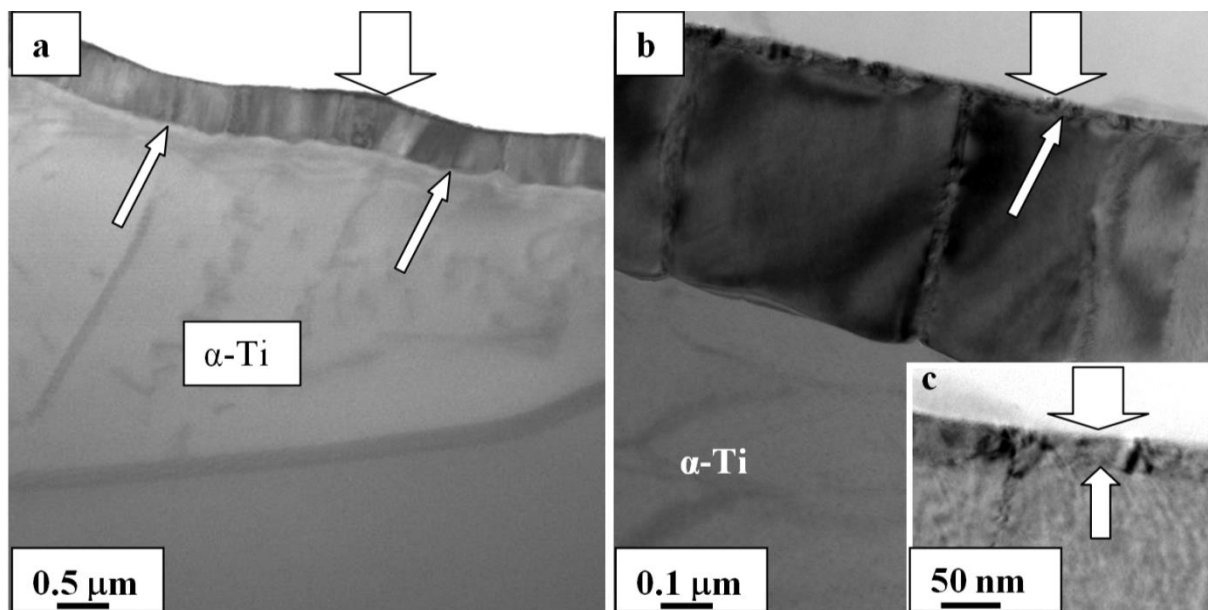
The combined treatment on the above cycle, carried out on the laboratory COMPLEX setup, leads to the formation of a modified layer. The wear resistance of the last one exceeds that of the initial material more than 30 times, the friction coefficient decreases by 1.3 times at the same time. Modification of titanium on two vacuum separated setups leads to decrease of the material wear resistance in  $\approx 0.7$  times with a constant friction coefficient. The microhardness values of the surface layer of the modified commercially pure VT1-0 titanium are close and vary in the range of 5500–6000 MPa in the both cases.

The formation of titanium nitride with TiN structure and a face-centered cubic crystal lattice (space B1 group) and titanium nitride of  $\text{Ti}_2\text{N}$  composition with tetragonal crystal lattice (space  $\text{P4}_2/\text{mm}$  group) after nitriding on a TRIO setup at a temperature of  $650^\circ\text{C}$  for 3 h was found using X-ray phase analysis. The subsequent deposition of the nitride coating is accompanied by the formation of a multiphase state. The main phases formed after modification on the vacuum separated setups are  $\alpha\text{-Ti}$  ( $\approx 35$  vol. %) and TiN ( $\approx 65$  vol. %). The main phases after nitriding and subsequent nitride coating deposition obtained on the laboratory COMPLEX setup are  $\alpha\text{-Ti}$  ( $\approx 27$  vol. %),  $\beta\text{-Ti}$  ( $\approx 20$  vol. %), TiN ( $\approx 39$  vol. %) and  $\text{Ti}_2\text{N}$  ( $\approx 14$  vol. %). As a result of the researches carried out by X-ray diffraction analysis it was shown that microdistortions of the  $\alpha\text{-Ti}$  crystal lattice of the "coating/substrate" system formed on the COMPLEX setup are  $\approx 1.8$  times lower compared with that formed on the two vacuum separated setups. In addition, the value of the microdistortions of TiN coating crystal lattice is practically independent on the number of setups used for titanium modification.

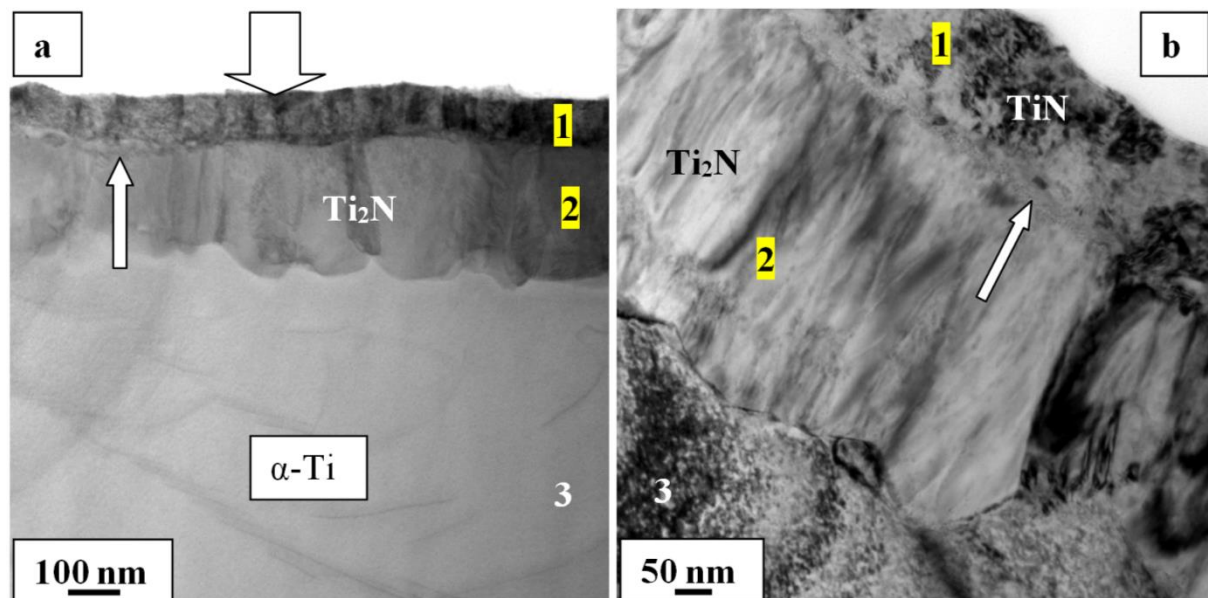
The defective substructure and phase composition of the modified titanium layer were analyzed by transmission electron diffraction microscopy. It is established that a multilayer structure is formed as a result of nitriding. The typical image of that is shown in figure 1. There are the thin (40–50 nm) surface layer (figure 1(b), (c), the layer is indicated by an arrow), the transition layer (figure 1(a), the layer is indicated by arrows) with thickness of 450–500 nm, and the bulk of the material. The surface layer has a nanocrystalline structure (figure 1(c)). The dimensions of the crystallites forming the surface layer vary in the range of 5–10 nm. The transition layer has a columnar structure (figure (1)); the cross dimensions of the columns vary from 150 to 500 nm.

The analysis of microelectron pattern obtained from the modified layer revealed the presence of titanium nitrides reflexes of TiN composition. The surface layer with a nanocrystalline structure is formed by titanium nitride of TiN composition. The transition layer with a columnar structure is formed by titanium nitride of  $\text{TiN}_{0.3}$  composition.

The subsequent deposition of a nitride coating on the nitrated specimen which is carried out on the COMPLEX setup leads to formation of the "coating/substrate" system. This system keeps a multilayer structure and consists of the surface layer with thickness of 120–150 nm (figure 2, layer 1), thin intermediate layer with thickness of 15–25 nm (figure 2, the layer is specified by an arrow) and the transition layer  $\approx 400$  nm thick (figure 2, layer 2). The surface layer, as well as the intermediate, has nanocrystalline structure with the crystal grains average sizes of 8.8 nm. The transitional layer has the columnar structure. The analysis of the electron-microscopic diffraction patterns obtained from the modified specimen shows that the surface layer is titanium nitride of TiN structure, the transition layer is titanium nitride of  $\text{Ti}_2\text{N}$  structure.



**Figure 1.** The electron microscopic image of the structure of the surface layer of commercially pure titanium subjected to nitriding in a plasma of a low-pressure gas discharge. A large arrow indicates the nitriding surface, small arrows on (a) indicate a modified layer with a columnar structure; on (b) and (c) – a thin nanocrystalline layer.



**Figure 2.** The electron microscopic image of a cross-section of the «hard TiN coating/VT1-0 substrate after nitriding» system formed on the COMPLEX setup. The top arrow on (a) specifies the surface of modification; the lower arrow on (a) and (b) – the interlayer. Transmission electron diffraction microscopy.

Comparing the results of the electron-microscopic diffraction analysis of structure of the modified layer formed as a result of nitriding and the subsequent deposition of a nitride coating it is possible to conclude that the coating deposition is followed by saturation of a titanium with nitrogen. That led to transformation of titanium nitride of  $\text{TiN}_{0.3}$  structure to titanium nitride of  $\text{Ti}_2\text{N}$  structure.

The use of two vacuum separated setups at formation of the “coating/substrate” system leads to formation of a TiN structure coating with columnar structure and the cross sectional dimension of columns in the range of 100 nm. The columns have nanocrystalline structure with a crystal grains size of 50–80 nm. That significantly distinguishes them from the coating deposited on COMPLEX setup in a single vacuum cycle.

#### 4. Conclusions

It is established that modification of commercially pure VT1-0 titanium specimens on the COMPLEX setup is followed by formation of the multilayer multiphase nanocrystalline system. That has the tribological parameters which are multiply exceeding the corresponding parameters of material which was modified on two vacuum separated setups. It is possible to assume that the main external reasons causing higher values of tribological properties of commercially pure VT1-0 titanium, modified in a single vacuum cycle on the COMPLEX setup compared with the titanium treated on two vacuum separated setups is the following: (1) better vacuum conditions in the COMPLEX setup, which provides an ultimate vacuum of  $\approx 8 \cdot 10^{-4}$  Pa against  $\approx 5 \cdot 10^{-3}$  Pa in separate setups and suppresses the formation of undesired oxide and oxynitride films on the material surface; (2) possibility to avoid contamination and oxidation of nitrided surfaces in the COMPLEX setup, as opposed to separate setups in which the probability of these processes is high as specimens are to be transferred from one setup to the other.

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