Study of Gas-Mixture Composition Influence on Structure and Properties of Titanium Alloy VT6 at Low-Temperature Nitriding[1]

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Abstract—The influence of gas-mixture composition on structure and properties of titanium alloy VT6 (Ti–6Al–4V) at low-temperature nitriding in plasma of non-selfsustained low-pressure arc discharge is studied. The material was in two states: coarse-grained and submicrocrystalline. It is shown that mechanical properties and thickness of the modified layer depend on preliminary formed structure.

INTRODUCTION

At present time high-chromium steels of martensite type and stainless maraging steels are mostly used for manufacturing of cutting, piercing and peeling groups of medical instruments. Main disadvantages of the first group of steels are a low corrosion resistance (that appears both at presterilizing treatment and sterilization, and short-time contact with bio-environment), insufficient hardness, low stability to biological mediums of human body (blood, lymphatic fluid and others). Stainless maraging steels allow to completely excluding influence of technological factors on corrosion resistance. But low level of hardness doesn't allow obtaining functional properties of instruments. Also disadvantage of both groups of steels is magnetic properties that make difficult to use such instrument in many surgical procedures [1].

Thus it seems appropriate to search for new materials with optimal combination of physical-chemical properties for wide usage in manufacturing of cutting, piercing and peeling groups of medical instruments. Titanium and its alloys could be such materials due to their unique properties like low density, low modulus of elasticity, high corrosion resistance, non-magnetic property and biocompatibility. But low hardness and poor wear resistance do not allow producing high-quality cutting instrument of titanium alloys.

It is possible to increase technical characteristics of titanium alloys in coarse-grained (CG) state by different methods, e.g. using modification of surface and near-surface layers. The most common are the following methods—deposition of functional coatings, nitriding [2–5], microarc oxidation. In other hand, now severe plastic deformation (SPD) methods are effectively developed with which submicrocrystalline (SMC) or nanostructure (NS) state is created in entire volume of a material [6–8]. As a result of such treatment an increasing of strength occurs, and in some cases simultaneous enhancement of plasticity takes place. Combination of SPD method and nitriding can give significantly better results compared to traditional methods of improving the service characteristics of materials and products. However, the methods used for nitriding of titanium alloys, such as traditional gas nitriding and nitriding in plasma of glow or arc discharges, cannot be used for titanium alloys in SMC- or NS-state with saving pre-formed structure in a bulk of material. In such processes the nitriding is performed at temperature 550°C and higher [2, 3], that leads to growth of grains and deterioration of material properties.

The aim of the present work is to study the structure and properties of modified surface and near-surface layers of titanium alloy VT6 (Ti–6Al–4V) in CG- and SMC-states after low-temperature nitriding in nitrogen-argon plasma with different percentage of gases.

METHODS OF STUDY

Titanium alloy VT6 (chemical composition, weight %: 6.46 Al; 3.84 V; 0.020 Zr; 0.010 Si; 0.083 Fe; 0.005 C; 0.166 O_2; 0.003 N_2; 0.003 H_2; 0.043 admixtures) was chosen as a initial material for study. The material was in two states: CG with average size of grains ~7–9 μm (Fig. 1a) and SMC with average size of grains ~0.4 μm (Fig. 1b). The SMC-structure was done by method of multi-step isothermal forging [8].

Low-temperature nitriding has been performed in plasma of non-selfsustained low-pressure arc discharge with usage of vacuum ion-plasma installation NNV6.6-I1 [9]. The process was performed at temperature 420°C during 40 min in mixture of gases nitrogen–argon. The percentage of argon was varied from 5 to 25% in gaseous mixture. Microhardness tests

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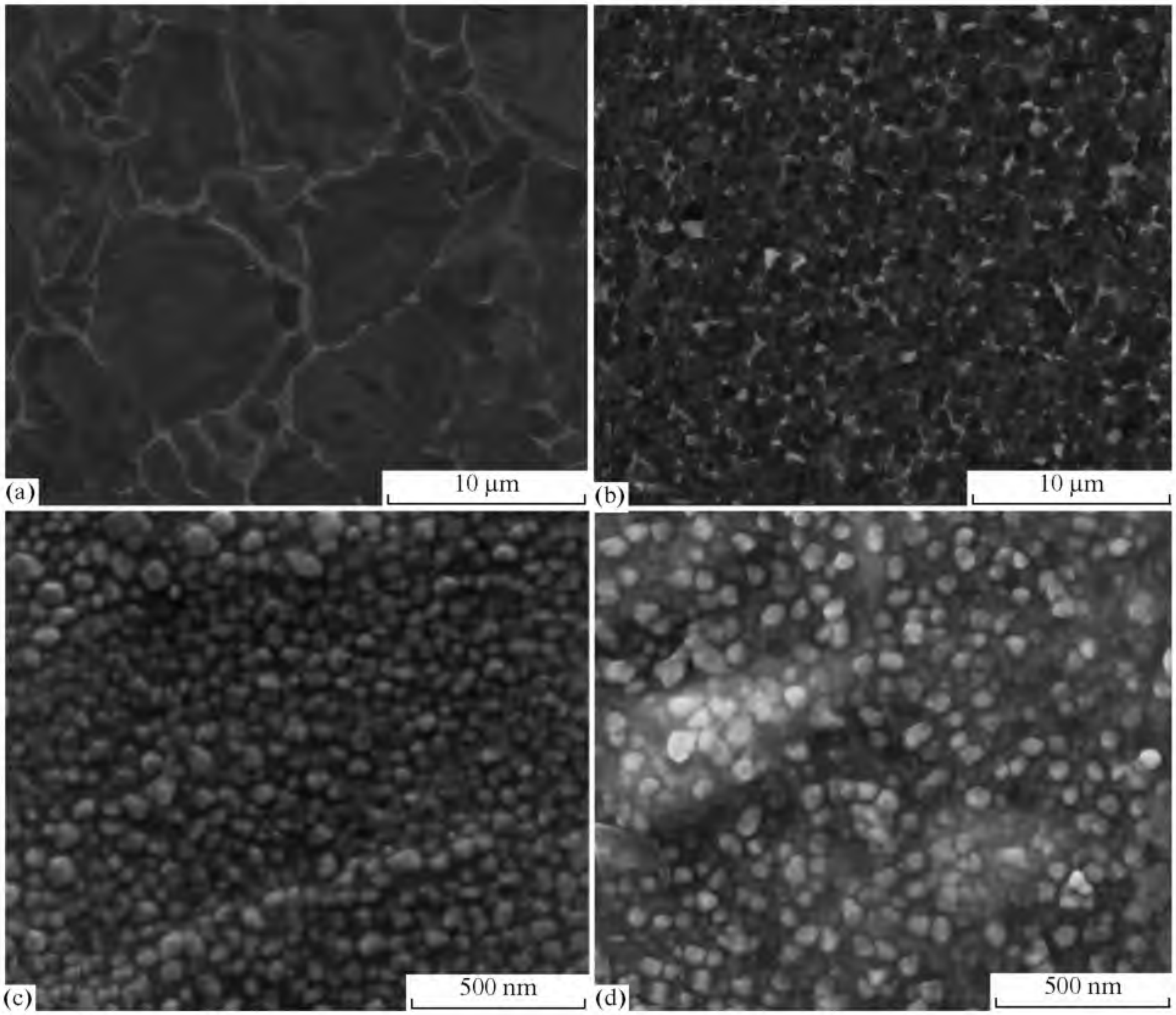

Fig. 1. SEM images of surface morphology of titanium alloy VT6 with different state of structure before and after nitriding in plasma of non-selfsustained low-pressure arc discharge: CG-state without treatment (a); SMC-state without treatment (b); CG-state after nitriding in gaseous mixture 5% Ar + 95% N_2 (c); SMC-state after nitriding in gaseous mixture 5% Ar + 95% N_2 (d).

on samples surface were done with usage of automatic microhardness tester DM-8B (Affri) by diamond indenter under a load $P = 0.098$ N on the indenter (GOST 9450-76). Changes of surface morphology after nitriding and structure of nitrided layer were studied by means of scanning electron microscopy (SEM) Quanta 600 FEG in zoom range from ×1000 to ×160000. Study of phase-structure composition of surface and near-surface layers was performed with help of transmission electron microscopy (TEM) Tecnai G2 20F S-TWIN with field emission. Wear resistance tests were done on automatic Tribometer (High-Temperature Tribometer, CSM Instruments, Switzerland) by scheme "ball-on-disc". The tests meet international standards ASTM G99-959, DIN 50324 [10]. As a rider a 100Cr6 steel ball with 6 mm diameter was chosen. Tests were done in air at load on indenter $P =$ 2 N and rotation speed 10 cm/s. Control the surface roughness of samples before and after nitriding was carried out by the arithmetical mean deviation of the profile. Measurements were performed with a precision contact profilometer SURTRONIC (GOST 2789–73).

RESULTS AND DISCUSSION

Investigations of surface morphology, performed with help of SEM, have shown that layer of highly dispersed particles with globular shape and sizes from 20 to 100 nm forms on samples surface after nitriding in gaseous mixture with minimum addition of argon. Moreover the layer of particles is less dense on a surface of titanium alloy VT6 in SMC-state (Fig. 1c, 1d). The formation of this layer may be caused by the fact that simultaneously with the etching the deposition of removed material occurs on a sample surface. With further increasing of argon concentration the formation of highly dispersed particles on the surface is not observed, that may be due to the predominance of etching process of samples surface over the process of deposition of removed material [2].

Measurements of surface microhardness have shown that increasing of argon concentration in gaseous mixture leads to increasing of modified layer microhardness (Table 1). Performing the process in gaseous mixture (25% Ar + 75% N_2) leads to maximum increase in microhardness, and for samples in SMC-state the percentage increasing of microhardness is higher and makes 40%.

Analysis of SEM images of modified layers structure has shown that nitrided layer consists of pronounced thin brittle layer. Diffusion zone has not been revealed on images. Aiming to define phase-structure composition of surface and near-surface layers TEM investigations have been done. As the result of performed investigations it was found that thin brittle layer consists of titanium nitrides Ti_2N (Fig. 2) and TiN. The diffusion zone settles under the nitrided layer, smoothly going into bulk of material. It should be noted that preliminary formed structure for the material in SMC-state does not change after nitriding.

Changing the composition of the plasma-forming gaseous mixture leads to a change in thickness of the nitride layer. Maximum thickness of titanium nitride layer is observed at minimum concentration of argon in gaseous mixture (FigS. 3a, 3b). The increasing of argon concentration up to 15% is resulted in decreasing of nitrided layer thickness (Figs. 3c, 3d). The following growth of the argon percentage in gaseous mixture does not lead to significant change of the titanium nitride layer. Such variation of nitrided layer thickness may be explained by the fact that high concentration of nitrogen on the surface leads to fast formation of surface nitrided layer, which prevents further diffusion of nitrogen in to the bulk of material. The increase of argon concentration is results in a decrease of nitrogen part on the surface, and, consequently, to reducing of the thickness of the nitrided layer and increasing of the depth of diffusion zone [2]. At the same time the structure of material also causes essential influence on thickness of nitrided layer. It may be seen from Fig. 3 that for the material in SMC-state the thickness of the nitrided layer is less than for the material in CG-state. It is possible that this phenomenon caused by the fact that effective diffusion coefficients are higher for the SMC-state than for the CG-state [11]. Thus, when other things being equal (temperature, concentration of atomic nitrogen on the sample surface), the nitrided layer begins to form faster in the CG-material and prevents further diffusion of nitrogen into the bulk of material [2].

Table 1. The surface microhardness after nitriding depending of gaseous mixture composition: 1—initial; 2—5% Ar + 95% N_2; 3—15% Ar + 85% N_2; 4—25% Ar + 75% N_2. The percentage increase of surface microhardness indicates in parentheses compared with initial one

Sample	Microhardness, GPa			
	1	2	3	4
VT6-CG	2.95	3.12 (5%)	3.75 (27%)	4 (35%)
VT6-SMC	5.8	7.1 (22%)	7.8 (34%)	8.1 (40%)

Tribological tests have shown that the nitriding of titanium alloy VT6 in SMC-state in a gaseous mixture with minimum part of argon leads to an increasing of value of wear factor on the order of magnitude com-

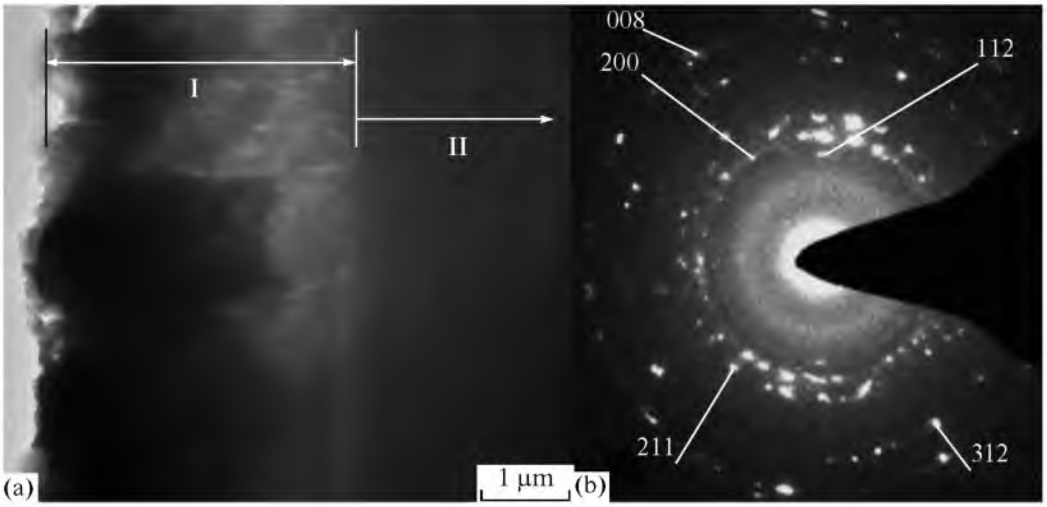

Fig. 2. Microstructure of the nitrided layer of titanium alloy VT6 with SMC-structure obtained by TEM (a): I—nitrided layer; II—diffusion zone, (b): diffraction pattern of the nitrided layer Ti_2N.

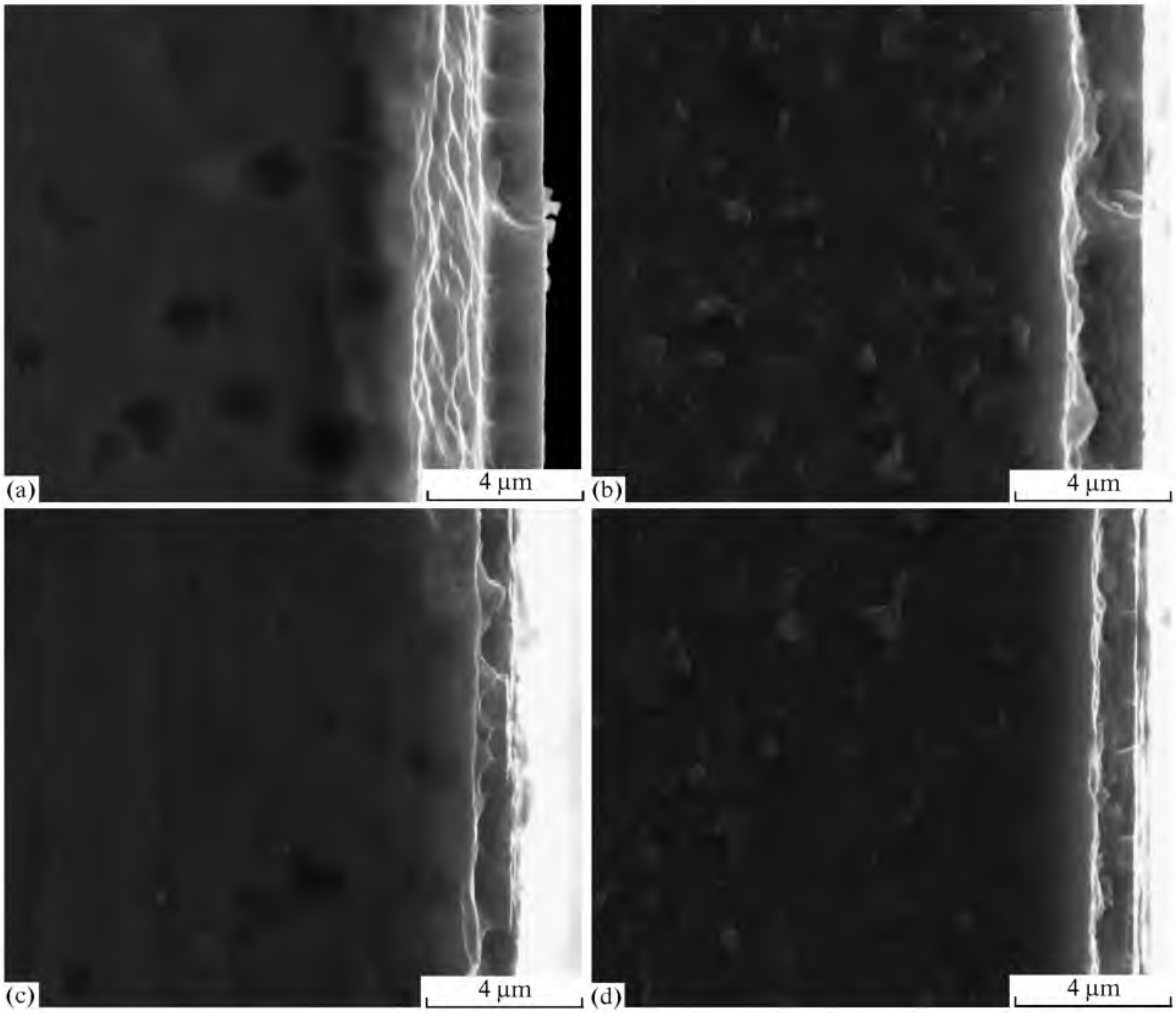

Fig. 3. SEM images of the modified layer structure of titanium alloy VT6 after nitriding: CG-state, 5% Ar + 95% N_2 (a); SMC-state, 5% Ar + 95% N_2 (b); CG-state, 15% Ar + 85% N_2 (c); SMC-state, 15% Ar + 85% N_2 (d).

paring with initial one (Table 2). This indicates a sharp decreasing in wear resistance. Performing the process at higher percentage of argon does not allow changing drastically the wear resistance of titanium alloy VT6 in SMC-state. Nitriding of titanium alloy VT6 in CG-state leads to decreasing of wear factor and, consequently, to increasing of wear resistance.

Decreasing wear resistance of the titanium alloy in SMC-state may be caused by short-time increasing of local temperature at a border of contact and in contacts of surface irregularities due to short-time "flashes" [12]. The rapid increase of temperature up to 550–600°C may lead to local softening of the SMC-material. Such "flashes" are responsible for fast oxida-

Table 2. The wear factor after nitriding depending of gaseous mixture composition: 1—initial; 2—5% Ar + 95% N_2; 3—15% Ar + 85% N_2; 4—25% Ar + 75% N_2

Sample	Wear factor, $mm^3\ N^{-1}\ m^{-1}$			
	1	2	3	4
VT6-CG	5.13×10^{-4}	5.04×10^{-4}	3.26×10^{-4}	3.20×10^{-4}
VT6-SMC	6.68×10^{-4}	3.00×10^{-3}	5.58×10^{-4}	7.92×10^{-4}

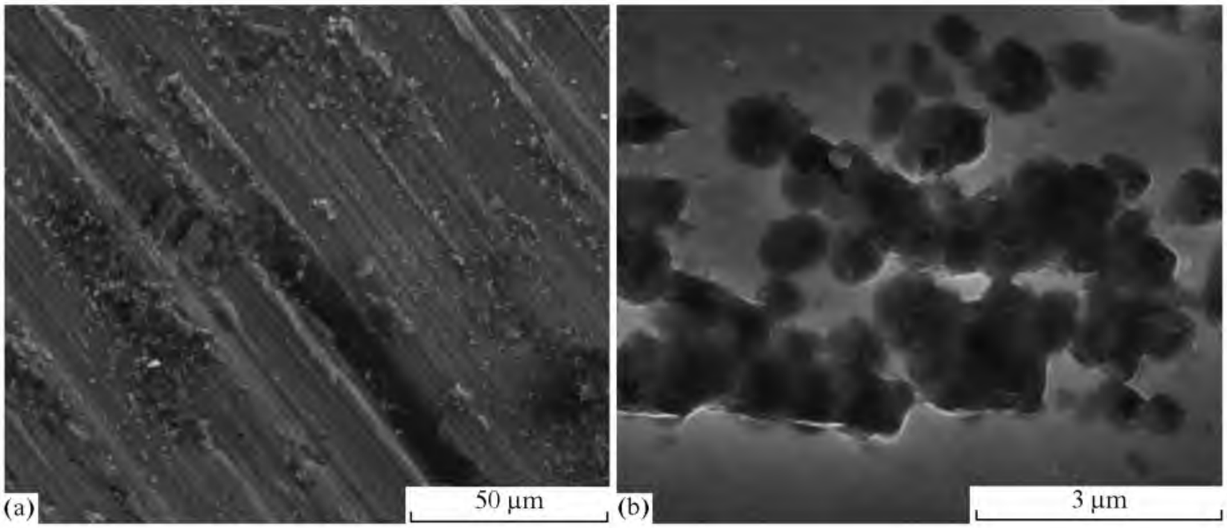

Fig. 4. SEM images of the friction surface of titanium alloy VT6 with CG-state after nitriding in gaseous mixture 15% Ar + 85% N_2: center of friction "groove" (a); edge of friction "groove" (b).

tion and other reactions between surface of alloy and ambient atmosphere. In the aggregate these factors result in the increase of wear factor of material in SMC-state comparing with one in CG-state. A decrease of thermal conductivity of titanium alloy in SMC-state up to ≈30% comparing with CG-state promotes this phenomenon too. Studies of wear tracks have shown that characteristic "grooves" have been formed on a wear surface. These "grooves" have been produced as the result of abrasive wear (Fig. 4a). Particles of the titanium nitride play role of abrasive, the nitrided layer is crumble out on particles with globular shape (Fig. 4b). The given type of wear is typical for material both in CG-state and in SMC-state.

In the traditional nitriding there is a significant increase in roughness, as well as changing the geometry of a product, that is limiting the field of usage of the nitriding process. Therefore, measurements of the surface roughness have been performed. The control the surface roughness of samples was carried out by the arithmetical mean deviation of the profile. It was found that the surface roughness of samples practically does not change during nitriding in plasma of non-selfsustained low-pressure arc discharge (Table 3). Moreover, a change in gaseous mixture composition does not significantly affect on the change of surface roughness.

Table 3. The arithmetical mean deviation of the profile after nitriding depending of gaseous mixture composition: 1—initial; 2—5% Ar + 95% N_2; 3—15% Ar + 85% N_2; 4—25% Ar + 75% N_2

Sample	The arithmetical mean deviation of the profile, μm			
	1	2	3	4
VT6-CG	0.056	0.054	0.054	0.055
VT6-SMC	0.058	0.058	0.062	0.068

CONCLUSIONS

The fundamental possibility of diffusion saturation of titanium alloys by nitrogen at temperature 420°C with saving preliminary formed SMC-structure in a bulk of the material has been shown. The modified layer, consisting of diffusion and nitrided zones and the surface layer of highly dispersed particles with globular shape and sizes from 20 to 100 nm, is formed in the titanium alloy VT6 as the result of nitriding of in plasma of non-selfsustained low-pressure arc discharge. When the layer of highly dispersed particles is forming, the nitrided layer has maximum thickness (~3.5 mm) and is characterized by low wear resistance. It is shown that the phase composition of layers can be controlled by changing the composition of plasma-forming mixture: with increasing argon concentration the thickness of nitrided layer decreases, and the formation of highly dispersed particles on the surface of samples is not observed. The decreasing of nitrided layer thickness leads to increasing of wear resistance of titanium alloy in CG-state, for the alloy in SMC-state the change of wear resistance is not significantly. After the low-temperature nitriding it is possible to increase surface microhardness on 35% for titanium alloy VT6 in CG-state and on 40% for one in SMC-state, the surface roughness practically does not change. This fact allows using the low-temperature nitriding as a finishing treatment at a manufacturing of medical instruments.

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REFERENCES

1. V. Kh. Sabitov, *Medical Instruments* (Meditsina, Moscow, 1985) [in Russian].
2. B. N. Arzamasov, A. G. Bratukhin, Yu. S. Eliseev, and T. A. Panaioti, *Ion Chemical Thermal Processing of Alloys* (Mosc. Gos. Tekh. Univ. Baumana, Moscow, 1999) [in Russian].
3. A. A. Il'in, S. V. Skvortsova, E. A. Lukina, et al., Metally **2**, 38 (2005).
4. Yu. Kh. Akhmadeev, Yu. F. Ivanov, N. N. Koval', et al., J. Surf. Invest. **2**, 166 (2008).
5. N. V. Gavrilov and A. S. Mamaev, Tech. Phys. Lett. **35**, 713 (2009).
6. Yu. R. Kolobov, R. Z. Valiev, G. P. Grabovetskaya, et al., *Grain Boundary Diffusion and Properties of Nanostructured Materials* (Nauka, Novosibirsk, 2001) [in Russian].
7. Yu. R. Kolobov, Nanotechnol. Russia **4**, 758 (2009).
8. G. A. Salishchev, R. M. Galeev, S. V. Zherebtsov, A. M. Smyslov, E. V. Safin, and M. M. Myshlyaev, Metally, no. 6, 84–87 (1999).
9. D. S. Vershinin, T. N. Vershinina, Yu. R. Kolobov, M. Yu. Smolyakova, and O. A. Druchinina, in *Proceedings of the 8th International Conference on Interaction of Radiation with Solid VITT-2009, Minsk, 23–25 Sept. 2009*, pp. 160–162.
10. N. Randall, CSM Instrum. Appl. Bull., no. 18, 3 (2002); http://www.csm-instruments.com/en/tests-Standards.
11. Yu. R. Kolobov, A. G. Lipnitskii, M. B. Ivanov, and E. V. Golosov, Kompozity Nanostrukt., no. 2, 4–24 (2009).
12. N. K. Myshkin and M. I. Petrokovets, *Friction, Lubrication, and Wear. Physical Principles and Engineering Applications of Tribology* (Fizmatlit, Moscow, 2007) [in Russian].