

# Tribomechanical Property and Structure of Gradient Nanocomposite Coatings Ti-Al-B-N Formed by the Combined Method of Magnetron Deposition and Bombardment by a Composite Ion Beam

V.P. Sergeev, M.V. Fedorischeva, A.V. Voronov, F.R. Sungatulin, O.V. Sergeev, E.V. Kozlov\*

*Institute of Strength Physics and Material Science SB RAS, Akademicheskoy Ave., 2/1, Tomsk, 634023, Russia*

*\*Tomsk State University of Architecture and Building, Solyanaya Sq.2, Tomsk, 634003, Russia*

*retc@ispms.tsc.ru, retc@ispms.tsc.ru*

**Abstract** – Combined method of producing of gradient nanocomposite coatings was developed. The coating on the basis of Ti-Al-B-N system was produced using vacuum magnetron deposition of TiN and bombardment by composite ions beam (Al+B) with high energy. It was established that the main regularity of tribological behavior and mechanical properties of this coatings as function of its structural – phase condition including following vacuum annealing in a temperature interval from room up to 1373 K.

## 1. Introduction

Now on the basis of TiN system a new class of nanocomposite coatings has been developed with an average grain size less than 100 nm including multiphase coatings on the basis of nitrides, borides, carbides of titanium, aluminium, chromium, zirconium etc. [1–3]. Owing to an increase in the volume fraction of grain boundaries such coatings have high hardness, wear and oxidative stability and, simultaneously, a high coefficient of elastic recovery and a low friction coefficient. The mechanism of formation of nanocomposite structure is related to segregation of one phase on the grain boundary of the other, as a result of the growth of grain stops. It can be achieved if alloying elements enter the composition of the main structure. Alloying elements can enter in several ways: usage of composite targets (1), the bombardment of the growing structure by an ion flux, which differs from the coating by the elemental composition (2). Ion beam treatment also allows to producing a coating with a structure varying in depth of the so-called gradient coatings. The base layer of these coatings has a good coupling to a substrate and a high load-carrying ability. The upper layer provides the functional characteristics of coatings such as hardness, wear resistance, fire resistance and so on. The intermediate layer is a transient binding and should have a high strength and sufficient ductility. It is known [4], that the multiphase coatings on the basis of Ti-Al-B-N system demonstrate the best properti-

es compare with simpler Ti-N and Ti-Al-N systems. The purpose of the present work is the attempt to obtain gradient nanocomposite coatings on the basis of the Ti-Al-B-N system using magnetron deposition of Ti-N coatings followed by treatment with a high-energy ion beam (Al+B) and vacuum-annealing interval from room temperature up to 1373 K.

## 2. Experimental

Deposition of coatings was carried out using a magnetron of direct current with a target diameter of 120 mm made from titanium BT-1-0. The power of the magnetron was equal to 1,6 kW. The vacuum chamber was evacuated up to the pressure of the residual gas  $5 \cdot 10^{-3}$  Pa. An argon and nitrogen mix was used as a working gas in the deposition of nitride coatings. The total pressure  $p_0$  of the working gas was equal to 0,15 Pa and the partial pressure of nitride – 0,025 Pa. A molybdenum heater was used for heating samples up to 573 K. For X-ray diffraction and mass-spectrometer investigation, the coatings were produced with a thickness of 0.4  $\mu\text{m}$ . For investigation of tribotechnical and mechanical properties the thickness of coatings was about 9  $\mu\text{m}$ . Austenitic steel 12X18H10T was used as a substrate. After deposition of the coating the was surface bombarded a ion beam using a vacuum – arc pulse ionic source "Diana-2", built-in the evacuated chamber of the deposition setup. The accelerating voltage was equal to 80 kV, the current amplitude of an ion beam was 600–900 mA, pulse frequency – 50Hz, pulse duration – 250 ms. Residual pressure in the evacuated chamber during implantation was  $5 \cdot 10^{-3}$  Pa. The irradiation dose was varied from 32 up to 64 mQ/cm<sup>2</sup>. The composite cathodes were used for obtaining two-element ion beams. They were made using powder metallurgical techniques. There were 98 % of the AlB<sub>12</sub> phase and 2–4 % AlB<sub>10</sub>. Further, part of the samples with ion-implanted coatings was annealed in a vacuum furnace within one hour from room temperature up to 1373 K.

X-ray analysis was carried out using a diffractometer DRON-3 in the interval of angles  $\sim 20\text{--}140$  degrees at  $\text{FeK}_\alpha$  radiation. To determine the crystalline lattice parameter ( $a$ ), size of area of coherent scattering ( $d$ ), microstresses ( $\sigma$ ) and the texture of coatings, the main characteristic of diffraction peaks were used [5]. The concentration profiles of elements by depth of coating were investigated by a mass-spectrometer of secondary ions MC-7201M (MSSI) in a regime of etching by an argon ion beam.

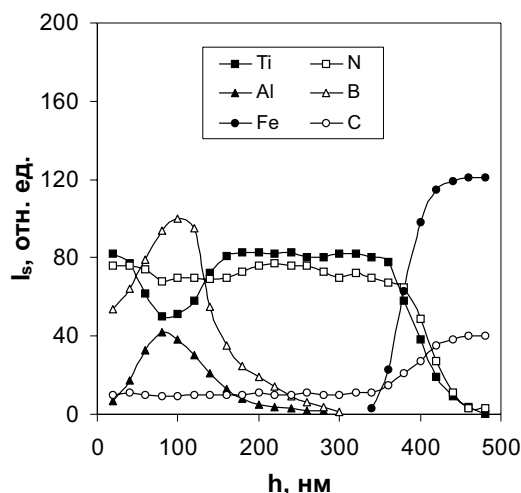


Fig. 1. Current change  $I_s$  of secondary ions as function of depth  $h$  of etching of surface layer of coating on the basis of Ti-N, treated by ions beam (Al+B) at accelerating voltage of 80 kV and radiation dose of  $48 \text{ mQ/cm}^2$

Friction and wearing tests were carried out using a machine under the scheme "a rotated disk – a fixed contact". Samples with the coating were used as a contact. The rider is a disc with a thickness of 10 mm and a diameter of 50 mm from steel ШХ-15 with hardness HRC=62 with a polished cylinder surface up to  $R_a=0,16 \mu\text{m}$ . Wear was carried out in the air in the conditions of dry slip friction rotated cylindrical rider with at a speed of 100 rpm relative to the fixed sample at a load of 49 N. Wear resistance of the coatings was determined as the relation of wear time to the loss of weight of the coating. The coating thickness was calculated using the weighing data before and after the deposition and it was also controlled using an optical microscope BMG-160.

The coating hardness was measured using nano-test NanoHardnessTester, CSM with an indenter load of 20 mN. Elasticity modulus were also determined using nanotester.

### 3. Results and discussion

Fig. 1 demonstrates the change of the current of secondary ions ( $I_s$ ) of a titanium, aluminium, iron, boron and nitride as a function of the depth ( $h$ ) of the TiN surface layer under deposition of argon ions in the mass-spectrometer chamber. It is known [6] that

the value  $I_s$  is proportional to atom concentration of these elements. The comparison of curves  $I_s$  versus of the ( $h$ ) implanted Al and B with the distribution curves of Ti, N and Fe from which, the coatings and substrate, accordingly, consists demonstrates that the Al and B ions penetrate to a depth of 200 nm at the accelerating voltage used. An average value of the depth of ion penetration is 102 nm, that is a little bit lower than the projective track length  $R_p=113 \text{ nm}$  [7] in titanium at a charge of these ions equal to 1. For aluminium ions an average depth of penetration is 91 nm that is higher and equal to 53 nm. The deviation of the experimental values from the estimated data can be related to the real structural – phase condition and the calculated elemental composition as compared with pure titanium, for which the calculation was made. At the same time, a larger value of  $R_p$  for ion penetration of aluminium can be related to the difference of the ion charge from 1. This takes place when vacuum – arc ionic sources operate, such as "Диана-2" as is shown in [8].

Table I. Tribomechanical properties of coatings ( $H$  – nanohardness,  $\Delta t/\Delta m$  – wear resistance,  $E$  – elastic modulus)

Regime of treatment coatings	$H$ , GPa	$E$ , GPa	$\Delta t/\Delta m$ , $\times 10^6 \text{ s/g}$
Initial state	$25,7 \pm 2,3$	$433 \pm 25$	$0,7 \pm 0,1$
Annealing at $T=1373\text{K}$	$26,8 \pm 1,9$	$462 \pm 29$	$1,5 \pm 0,2$
Radiation dose is $32 \text{ mQ/cm}^2$	$29,5 \pm 2,4$	$438 \pm 27$	$1,6 \pm 0,2$
Radiation dose is $64 \text{ mQ/cm}^2$	$31,8 \pm 2,6$	$456 \pm 31$	$2,0 \pm 0,2$
Radiation dose is $32 \text{ mQ/cm}^2$ , annealing at $T=773\text{K}$	$36,0 \pm 2,0$	$555 \pm 23$	$3,1 \pm 0,3$
Radiation dose is $32 \text{ mQ/cm}^2$ , annealing at $T=1373\text{K}$	$27,1 \pm 2,0$	$562 \pm 21$	$2,2 \pm 0,2$

Using X-ray analysis is shown that the TiN is the main phase of the coating with a cubic lattice B1 (NaCl type) with the preferred orientation of grains of (200) Fig. 2. Vacuum annealing of coatings results in the change of the texture of coatings. A relative intensity of X-ray reflection with orientation (200) decreases, and, on the contrary, it increases with orientation (111). And at temperature of 1373K the coatings have only texture (111) (Fig. 2, f). The implantation of ions of aluminium and boron in the TiN coating, at first, also results in a decrease of the relative intensity reflection with (200) orientation and an increase with (111) orientation. When a radiation dose increases this effect increases too (Fig. 2, b, c). Secondly, the phase composition of the surface layer changes. The volume fraction of the TiN phase decreases down to 86 and 57 %, accordingly, at radiation doses of 32 and  $64 \text{ mQ/cm}^2$  (Fig. 2, b, c). New phases of titanium-aluminium diboride with a hexagonal lattice P6/mmm appear. The volume fraction of the  $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$  was 12 % and 37 % at radiation doses of 32 and  $64 \text{ mQ/cm}^2$ , accordingly. In addition, there is titanium boride TiB with an orthorhombic lattice and titanium nitride of aluminium  $\text{Ti}_3\text{AlN}$  with a cubic lattice in a small am-

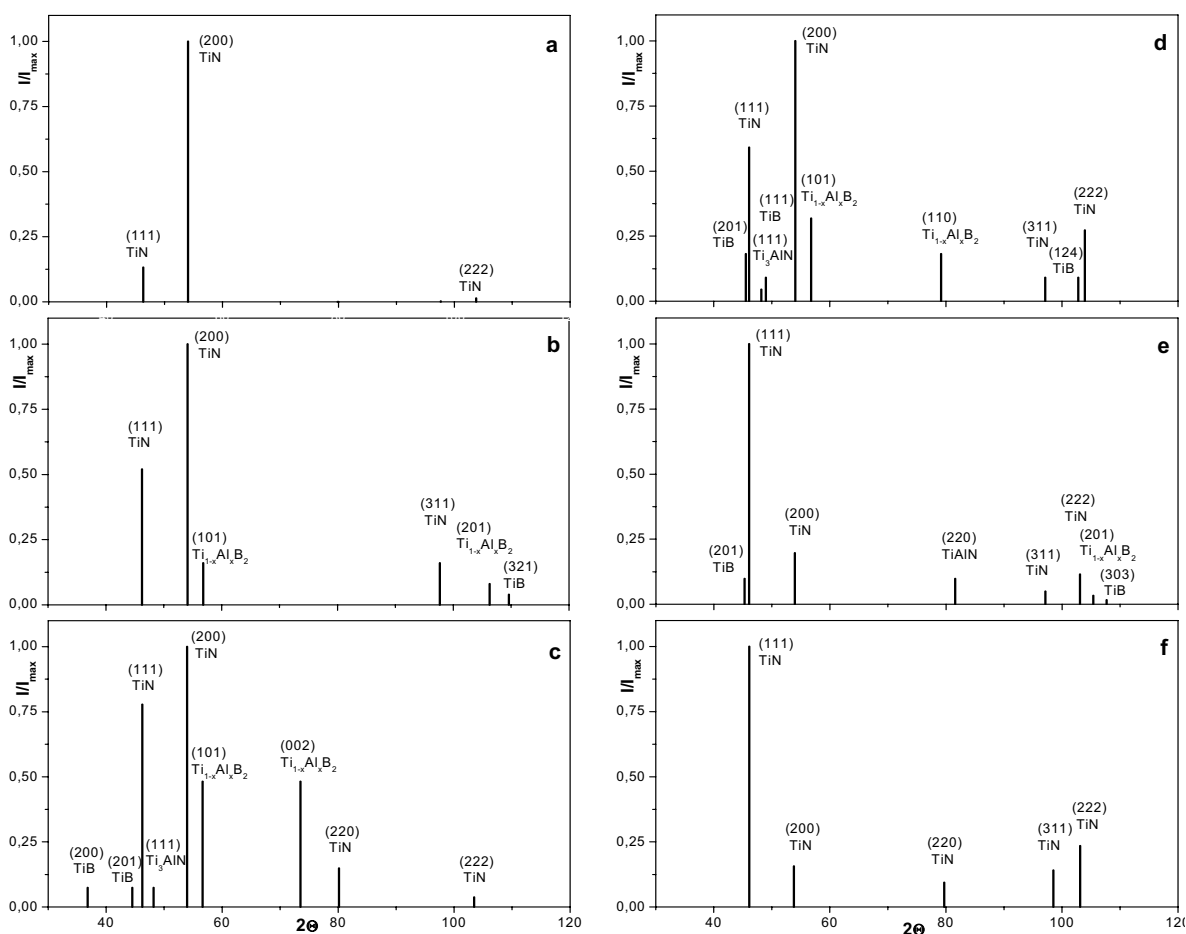


Fig. 2. X-ray pattern of coatings on the basis of TiN: initial state (a), Al+B ion beam treatment at dose of 32 mQ/cm<sup>2</sup> (b), Al+B ion beam treatment at dose of 64 mQ/cm<sup>2</sup> (c), Al+B ion beam treatment at dose of 32 mQ/cm<sup>2</sup> with annealing at 773K (d), Al+B ion beam treatment at dose of 32 mQ/cm<sup>2</sup> with annealing at 1373K (e), an annealing at 1373K (f)

ount (2–6 %). Vacuum annealing of coatings at a temperature of 773 K with a dose of 32 mQ/cm<sup>2</sup> results in further decreasing of the volume fraction of the main TiN phase down to 67 % and an essential increase in the boride phases – Ti<sub>1-x</sub>Al<sub>x</sub>B<sub>2</sub> up to 18 % and TiB up to 13 % (Fig. 2, d). At annealing of the irradiated coatings at 1373 K (Fig. 2, e) the boride phases and double nitride Ti<sub>3</sub>AlN dissolves so that the volume fraction of Ti<sub>1-x</sub>Al<sub>x</sub>B<sub>2</sub> Al<sub>x</sub>B<sub>2</sub> and TiB decrease down to 2 % and 7 %, accordingly, and aluminium enters a solid solution of the Ti<sub>1-x</sub>Al<sub>x</sub>N. With an increase in the annealing temperature for the irradiated coatings the same regularity in the texture change is observed as for unirradiated samples. The difference consists in a higher grain fraction with orientation (111), which they obtained at ion-beam treatment before annealing. The average grain size of the main TiN is equal to 45–50 nm in the initial coatings, and decreases down to 14–16 nm at bombardment of the surface layer with an ion beam. After annealing of the irradiate coatings the grain size increases up to 25–50 nm.

The bombardment by an ion beam (Al+B) of coatings on the basis of Ti-N system leads to an increase in nanohardness and wear resistance of the surface layer (Table). With an increase in the radiation dose the effect increases. At a dose of 64 mQ/cm<sup>2</sup> the wear resistance increases ~3 times, nanohardness ~15 %. Vacuum annealing of the irradiated coatings results in increasing wear resistance and nanohardness up to 4 and 1,4 time accordingly. At a further rise in temperature of annealing up to 1373 K the decrease in nanohardness is observed up to the initial value, while the wear resistance decreases, but remains a sufficient high level ~3 times exceeding the initial value. The annealing of unirradiated coatings increases their wear resistance ~2 times at invariable nanohardness which is within the limits of experimental error.

It can be related one of the mechanism of the observed increase in tribological and mechanical properties of coatings at annealing and ion beam bombardment. The other causes can be grain-boundary strengthening due to a decrease in the grain size, which according to the ratio of Hall-Petch [10] leads

to strength improvement of polycrystalline materials. Besides, when the highly disperse boride phase precipitates, maximum concentration is achieved at a temperature of 773 K. The decreasing value of tribomechanical properties at further heating can be related to the growth of grains due to recrystallization, the dissolution hardening of the boride phase and transition of alloying elements in to solid solution. The high value of wear resistance of coatings irradiated by an ion beam is remains up to 1373 K. It can be due to the high contents of aluminium in the coating. In conditions under study, the oxidative wearing takes place. During friction the temperature of the surface layer of the coating increases. Thus, as is shown in [11], aluminium diffuses to the surface and, combining with oxygen, it forms a protective layer of  $Al_2O_3$ , which make difficult further oxidation of the coating. A higher concentration of aluminium creates a high-strength protective layer of  $Al_2O_3$ .

Thus, the combined treatment of coatings on the basis of Ti-N by bombardment with a composite ion beam (Al+B) and vacuum annealing result in a 4-times increase of wear resistance and a 1.4 times nanohardness of coatings. On the basis of X-ray analysis it is shown that the observed change of tribomechanical behavior can be related to the precipitation and dissolution of highly disperse boride phases, change of an average grain size and a preferred orientation of grains of the main phase.

*The work was supported by the Russian Foundation for Basic Research, grant № 05-08-33412-a.*

## References

- [1] D.V. Shtanskii, E.A. Levashov, Rus. Izvestiya Vuzov, Fizika, Non-ferrous metallurgy 3, 52 (2001).
- [2] S. PalDey., S.C. Deevi, Material Science and Engineering. A342, 58 (2003).
- [3] V.P. Sergeev, *Deformation, localization, destruction*, Tomsk, NTL, 2005, pp. 112–126.
- [4] C. Reibold, A. Leyland, J.M. Schneider, A.A. Voevodin, A. Matthews, Surf. Coat. Technol., 120–121, 412 (1999).
- [5] S.S. Gorelic, Yu.A. Skakov, L.N. Rastorguev, *X-Ray and electronoptical analysis*, Moscow, MISIS, 1994, pp. 1–328.
- [6] V.I. Nefedov, V.T. Cherepin, *Physical method of investigation of surface of solid*. Moscow, Nauka, 1983, 296 p.
- [7] *Table of Parameter of space distribution of ion implanted dopant*. Editing by A.F. Burenkov, F.F. Komarov, M.A. Kumachov, M.M. Temkin, Minsk, BGU, 1980, 352 p.
- [8] I.G. Brown, B. Feinberg and J.E. Galvin, J. Appl. Phys. 63/10, 4889 (1988).
- [9] J. Pelleg, L.Z. Zevin, S. Lungo, N. Croitoru, Thin Solid Films 197, 117 (1991).
- [10] R.A. Andrievski, J. Mater. Sci. 32, 4463 (1997).
- [11] O. Knotek, M. Bohmer, T. Leyendecker, F. Jungblut, Mater. Sci. Eng. A105–106, 481 (1988).