Formation of Wear-Resistant TiN and (Ti1-x, Alx)N Coatings Using DC Filtered Vacuum Arc Plasma[1]

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Abstract – The paper presents the results of investigation of structure, element composition and physico-mechanical properties of TiN and (TiAl)N coatings deposited under combined treatment of surface by vacuum arc discharge and gaseous microparticle-free metal plasma flows. Also, perspectives of industrial application of combined technologies are discussed.

1. Introduction

DC vacuum arc discharge (VAD) plasma has been used for industrial coating deposition for more than 25 years. Use of TiN as coating material allows decrease friction, wear, increase corrosion resistance of materials, protect substrate from overheating, and improve decorative properties of articles [1, 2].

Unfortunately, use of a dc VAD for such modern coatings as (TiAl)N, TiC, CrN, (TiC)N, (TiAl)N, ZrN, MoS_2, DLC, including multilayered ones, is bounded by parameters of existing technological equipment and methods of coating deposition. Coatings deposited using conventional technologies are characterized by low adhesion strength, high roughness, heterogeneous structure, and low wear resistance.

The paper presents the results of investigation of characteristics of TiN and (TiAl)N coatings deposited using industrial set-ups for ion and plasma coating deposition equipped with devices for cleaning plasma from microparticle fraction and PINK-type gaseous plasma generator.

2. Equipment and Experimental Methods

The investigations were carried out using the ННВ6,6-И1 industrial set-up for ion and plasma coating deposition. Fig. 1 shows the schematic of the experimental set-up.

Metal plasma was generated by three dc VAD-based vacuum arc evaporators (VAE). To clean vacuum arc plasma from microparticle fraction, the VAEs were equipped with plasma filters (PF) of the shutter type [3, 4].

Gaseous plasma flow was formed using the PINK plasma generator based on a non-sustainable arc discharge with a glow cathode [5]. The system of reactive gas input through a gaseous arc cathode was realized in the design of the plasma generator [6].

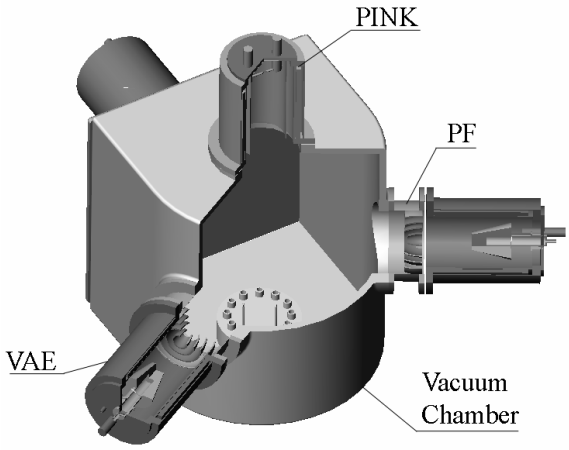

Fig. 1. Schematic of the experimental set-up

For the regime of ion and plasma coating deposition we applied negative potential onto samples. We used voltage source with the device of arc automatic extinction and device protecting from overvoltage resulting from arc current breakdown.

Pressure in the vacuum chamber was created using a diffusion oil and vapour pump H-250/25CO. The temperature of samples was controlled by a pyrometer “Smotrich”. Table 1 shows main technical characteristics of the set-up.

Element composition of coatings was defined by layered electron Auger spectrometry using the spectrometer “Shkhuna-2”. Sample surface microstructure and morphology were investigated by optical microscopy and 3D profiling with resolution up to 1 nm using MICRO MEASURE 3D Station (STIL). Coating hardness was measured using Nano Hardness Tester (CSEM) with the Vickers indenter at loadings of 100 mN. In investigate coating adhesion strength we used the scratch method with the help of Rockwell

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indenter with the diameter of 40 μm at time-dependent loading in the range of 0÷2 N using Micro Scratch Tester (CSEM) [7].

Tribotechnical characteristics of coatings were investigated using PC-Operated High Temperature Tribometer (CSEM). The friction coefficient was registered in situ. Sample wear was calculated by measuring material flow resulting from application of a fixed ball onto the rotating sample [7].

Table 1. Parameters of the experimental set-up

Metal plasma generator	
Discharge current, A	40–250
Plasma concentration, cm^{-3}	up to $4 \cdot 10^{10}$
Plasma flow diameter, mm	200
Decrease in microparticle fraction (Ti)	10^{-2}–10^{-3}
Gaseous plasma generator	
Working pressure area, Pa	10^{-2}–1
Plasma concentration, cm^{-3}	10^{9}–10^{11}
Discharge current, A	5–150
Homogeneity of plasma flow along the cross section, %	20
Gas	N_2

3. Formation of TiN and (TiAl)N Coatings

Coatings were deposited onto steel P6M5 samples with the diameter of 50 mm and 3 mm thickness, fixed in the center of the rotating table. Preparation of samples included surface mechanical polishing and burnishing with abrasive pastes ACH 40/28, 14/10 up to the roughness of $R_z \approx 0.7$ μm (TiN) and $R_z \approx 0.43$ (TialN) and chemical cleaning in ultrasonic bath.

Samples were cleaned and heated in the vacuum chamber using low temperature N_2 plasma at vacuum volume pressure of $1.5 \cdot 10^{-2}$–$2.4 \cdot 10^{-2}$ Pa with negative potential on samples equal to –1.2 kV. Temperature of samples was in the range of 450–500 °C.

For TiN coatings, sample surface was simultaneously treated by N_2 and microparticle-free Ti plasma. Bias voltage on samples increased up to –1.4 kV. Due to ion charge state, surface was processed mainly by sample heating and ion etching accompanied by formation of a large amount of active sorption centers. The temperature of samples was 580 °C.

With smooth decrease in bias voltage on samples (U_b), we observed formation of a transition layer and ion assisted coating deposition. The temperature was 450–500 °C, and pressure in the vacuum chamber was equal to $2 \cdot 10^{-2}$ Pa.

(TiAl)N coatings were deposited with the use of two VAEs with Al cathodes and one VAE with a Ti cathode. Coatings were deposited in the reaction gas (N_2) environment. Ratio of Ti and Al plasma flows depended on VAD current (I_d).

Figure 2 shows the results of investigation of element composition of TiN and (TiAl)N coatings. Stochiometric composition of deposited TiN (Ti ~ 45%; N ~ 45%) and (TiAl)N (Ti ~ 29.5%; Al ~ 27%; N ~ 39%) coatings corresponds to data on the diagram. Thick transition layers between the coating and substrate show that the regime of ion assistance was accompanied by intense diffusion processes near sample surface.

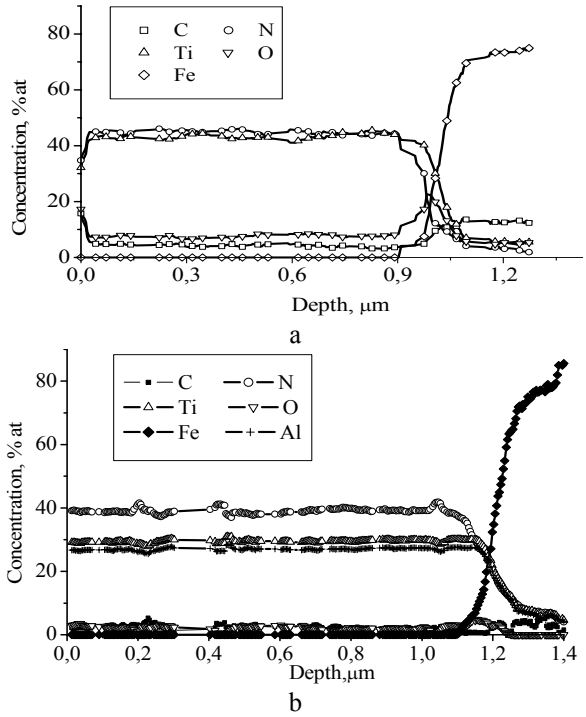

Fig. 2. Element distribution into the depth of the deposited coating: a – TiN, b – (TiAl)N

Paper [8] shows the results of diffraction electron-microscopic phase analysis of TiN coatings, which show that when U_b was in the range of 250–750 V, multi-phase structures composed of δ-titanium nitride (TiN) with grain size of 110–150 nm, respectively, were formed. When U_b was equal to 100 V, ε-titanium nitride (Ti_xN_y) and δ-titanium nitride phases are observed in the coatings, however, size of grains of the former phase is half size of grains of the TiN phase.

Figure 3 shows the results of morphological investigation of the deposited coatings as profiles and images of TiN and (TiAl)N film surfaces. The presented data confirm that use of PF results in decrease in surface roughness by several times.

For (TiAl)N coatings formed without PF, surface roughness equals to tens of microns. The phenomenon is attributed to presence of a large amount of microparticle fraction in Al plasma flow (up to several tens of percents). For this case droplet size can be equal to more than 100 μm. Use of PF for cleaning Al plasma allows decrease content of microparticle fraction in the flow by several orders of magnitude, which permits deposit coatings with the roughness not more than 0.64 μm.

Comparative analysis of curves 1 and 2 (Fig. 2) shows that decrease in I_d and increase in U_b allow significantly decrease surface roughness of TiN coatings. This effect can be explained by increase in plasma ion component transportation efficiency in PF electrodes

and decrease in microparticle fraction in the arc plasma flow at the expense of decrease in I_d, as well as due to reflection of droplets from negative potential near the sample surface [9] and sputtering of microedges on coating surface.

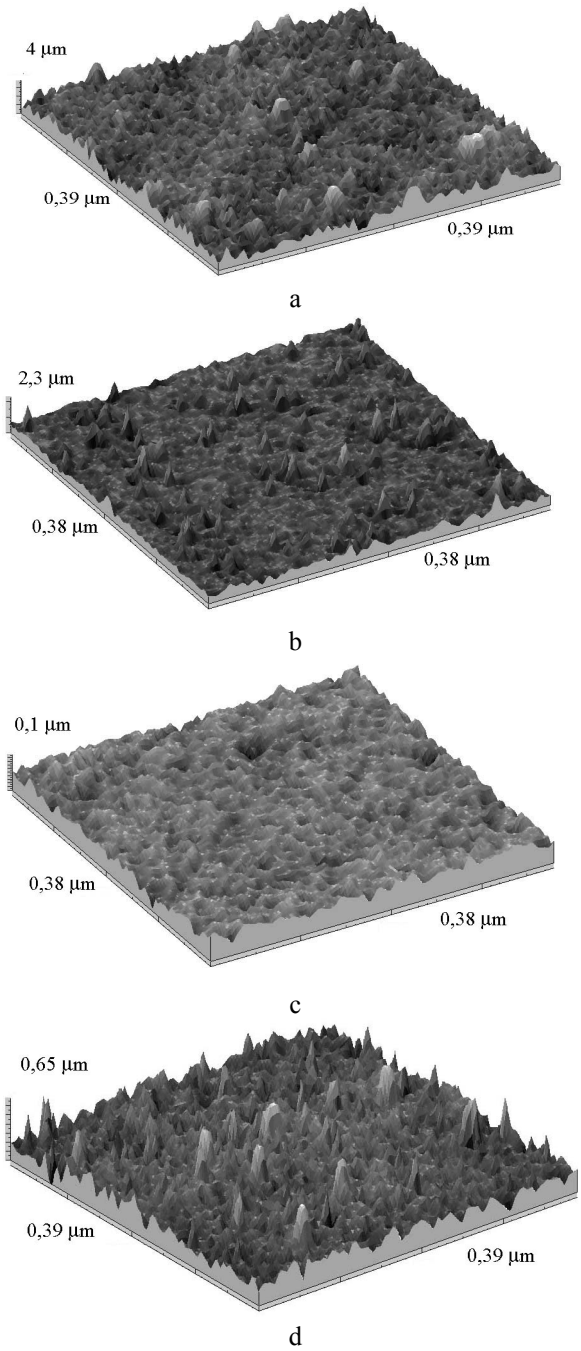

Fig. 3. Profile of TiN and TiAlN coating surfaces: a – without PF, b – with PF (I_d = 125 A, U_b = 500 V), c – with PF (I_d = 100 A, U_b = 800 V), d – (TiAl)N

Figure 4 presents the results of investigation of (TiAl)N coating hardness depending on ratio of Ti and Al plasma flow concentration. According to the data, coating with the hardness HV = 3670 kg/mm^2 was obtained at I_d = 80 A. Data of the element analysis show that the measured hardness corresponds to optimal stochiometric composition of the coating.

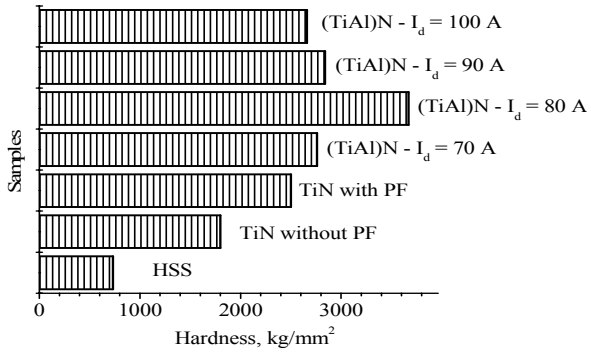

Fig. 4. Change in hardness values depending on regimes of coating deposition

The data presented at Fig. 4 confirm that use of PF allows increase TiN coating hardness by 40%. It was also found out that increase in U_b in the range of 100–750 V results in decrease in coating hardness by 15–20%. The phenomenon can be explained by the fact that in case of application of gaseous plasma generator, the ratio of metal and nitrogen atoms required for formation of the coating with optimal stochiometric composition is ensured at decreased pressure of N_2; with increase in U_b we observe metal growth in the coating, which negatively influences coating hardness.

At the same time increase in U_b results in insignificant decrease in inner tensions in samples, which we demonstrated by comparing loading and unloading curves of the Nano Hardness Tester indenter (Fig. 5). The phenomenon can also be explained by change in conditions of phase formation, in particular, by formation of structures with grains of larger sizes with the increase in U_b – contrary to conventional notion on increase in compressing voltages with increase in intensity of heating [8].

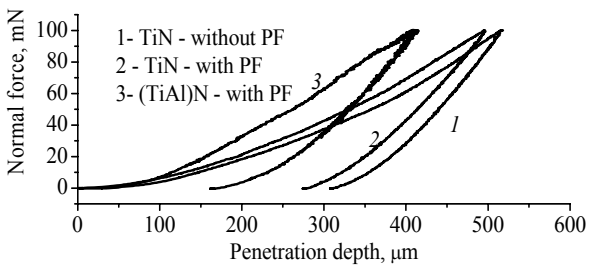

Fig. 5. Curves of indenter loading and unloading

Figure 6 shows the results of investigation of adhesion strength of the deposited coatings in the form of acoustic emission signal depending on loading and indenter penetration depth. The presented data confirm that delamination of the TiN coating deposited by conventional technology begins at loading equal to ~ 0.81 N. Surface image near the indenter track (Fig. 6a) shows that the structure is porous, which reveals high inner tensions in the material.

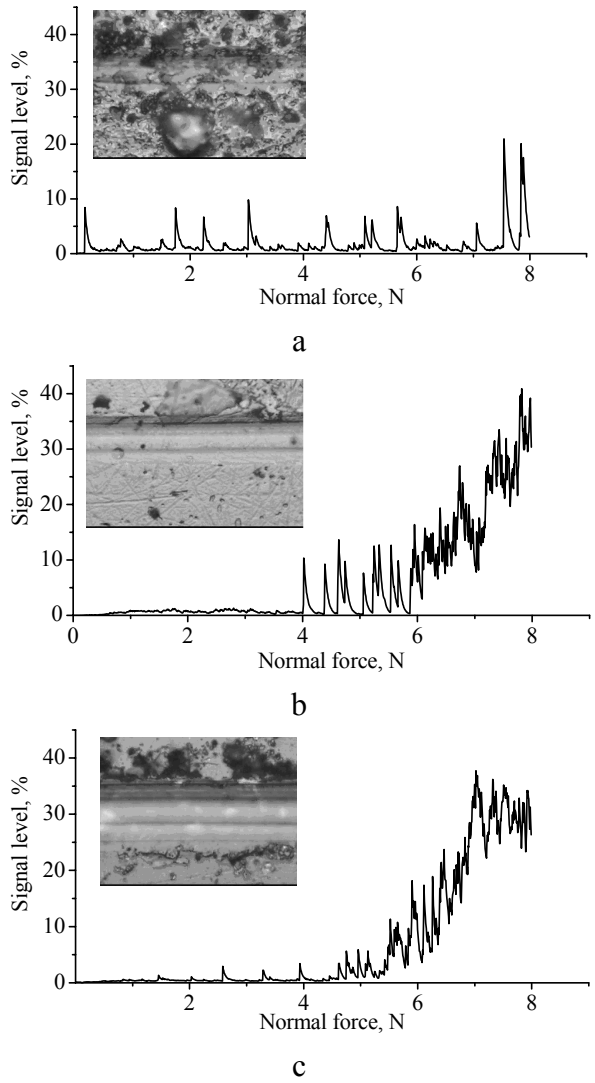

Fig. 6. Change in acoustic emission signal depending on penetration depth and indenter loading, and coating surface image near the indenter track: a – TiN without PF, b – TiN with PF, c – (TiAl)N

When we use combined method of TiN coating deposition, critical loading, at which coating delamination begins, increases up to 1.17 N, which confirms increase in coating adhesion strength by 70%. For this case we used high intensity combined ion cleaning, surface heating and activation, formation of a thick transition layer between the substrate and coating, and ion assisted coating deposition.

A complex of these factors allowed form a (TiAl)N coating from dc VAD plasma; coating delamination was observed at critical loading of ~ 1.13 N. For this case, cracking lines characteristic of materials with high level of tension are absent near the indenter track (Fig. 6,c).

In was experimentally found out that with the increase in U_b in the range of 100–750 V we observed increase in adhesion strength of TiN coatings by 20%. The highest values of adhesion strength were registered in the range of 100–250 V. The effect can be attributed to decrease in compressing residual tensions resulting from increase in temperature, radiation treatment of the surface, increase in formed phase sizes, etc.

Figure 7 shows the results of investigation of friction coefficient of TiN and (TiAl)N coatings. The data confirm that if we deposit TiN coating onto steel P6M5, surface friction coefficient decreases by 2.5 times – with and without PF. At the first stage of testing we observed sharp increase in friction coefficient, which can be explained by "rubbing" of samples because of surface roughness – the same was noticed for TiN coatings deposited with PF (curve 3). Due to low roughness, the effect of sample "rubbing" is absent at the initial stage, and more dense and homogeneous coating structure causes additional decrease in friction coefficient by 40 %.

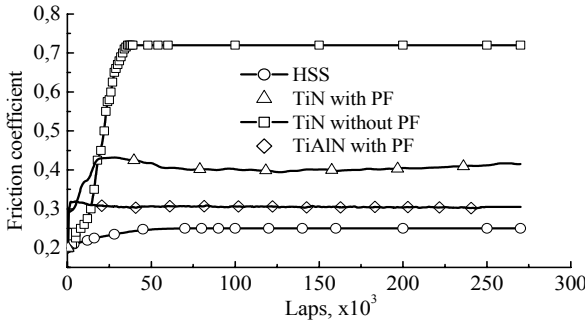

Fig. 7. Change in friction coefficient depending on a number of rotations

Figure 8 shows influence of surface morphology onto wear resistance of deposited coatings.

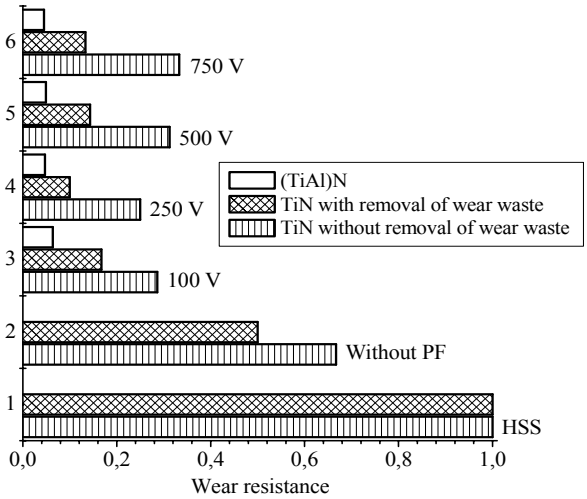

Fig. 8. Wear resistance of TiN and (TiAl)N coatings depending on deposition regimes

The diagram is normalized by unit with respect to wear intensity of steel P6M5 initial sample. The presented data show that TiN coatings deposited using the conventional technology are characterized by double increase in wear resistance. At the same time, use of PF allows additionally increase steel wear resistance by 5 times. The data obtained on wear intensity

without removal of wear waste show that presence of wear waste in the indenter track, later used as an abrasive, result in sharp increase in wear intensity. However, for this case wear-resistance decreases 4 times compared to initial state. Moreover, we didn't notice any dependence of coating wear resistance on sample bias potential.

4. Technological Applications of the Method and Its Future Perspectives

The presented combined regime of surface treatment with dc VAD gaseous and microparticle-free metal plasma under formation of a surface negative potential allows effectively clean and activate the surface, including use of metal plasma, form diffusion transition layers between the substrate and coating, plasticize coating materials, deposit homogeneous TiN and (TiAl)N coatings with good exploitation properties.

Experiments on combined use of the PINK plasma generator and VAE revealed that at the expense of effective ionization of the reactive gas one can decrease chamber pressure for deposition of composite coatings, increase coating deposition rate and increase coating adhesion strength at lower condensation temperatures compared to temperatures for the conventional method of coating deposition.

Practical application of the above-mentioned regimes of ion and plasma material treatment was carried out at a prominent RF tools plant "Tomsky Instrument". For this case TiN and (TiAl)N coatings were deposited onto metal-cutting tools.

Upgrade of technological equipment for ion and plasma coating deposition with gaseous plasma generators of PINK-type and PFs allowed improve quality of produced articles, expand nomenclature in the field of application of produced items, stimulate development and introduction of new types of coatings.

E.g., production of articles deposited with (TiAl)N coatings allowed both increase wear resistant characteristics and offered perspectives of coating application for aluminium alloy articles; heat resistant properties of (TiAl)N coatings permitted avoid tool cooling with liquids and significantly increase processing velocity.

Combined application of the PINK generator and PF allows generate high-quality coatings using dc VAD plasma on articles with the operating surface area equal to the size of microparticle fraction ~ 0.1–1 mm. Perspectives of application of dc VAD plasma for deposition of Al_2O_3, TiC, DLC, etc. coatings, which otherwise cannot be deposited using conventional VAE since the size of microparticle fraction for them is more than 100 μ, are revealed.

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