(Ti, Al)N and (Ti, Al)N/TiN Multilayer Coating Deposition Using Filtered Vacuum Arc Plasma

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Abstract – The paper presents the research results on deposition of monolayer (Ti, Al)N and multilayer (Ti, Al)N/TiN coatings. The deposition technology presents a synthesis of principles of arc deposition with separation of microparticle fraction and plasma-immersion ion implantation. An opportunity of obtaining thick nanostructure multilayer (Ti, Al)N/TiN coatings, which have better mechanical and exploitation properties than the monolayer coatings has been shown. The experimental results of the elemental composition investigation, various mechanical and exploitation properties (Ti, Al)N and multilayer (Ti, Al)N/TiN coatings have been presented.

1. Introduction

Currently, the technologies of monolayer coatings deposition with the thicknesses of 3 to 10 μm with an application of a DC vacuum-arc discharge are widely used to improve the exploitation characteristics of materials and items. However, the monolayer coatings are characterized by a number of disadvantages, among which the following ones can be distinguished: high level of inner tensions, destruction mechanism from the surface to the depth of material identical to construction items, heterogeneous phase composition, and dispersion of the phases being formed, which are connected in many aspects with microparticle fraction presence in plasma.

Besides, multilayer coatings which basis is constituted by thousands of alternating by properties nanosize (2 to 100 nm) and nanostructure layers of various composition [1], now take a priority place in the sphere of protective coatings investigation. The advantage of such coatings is connected with the fact that alternation of nanosize layers prevents from the growth of phases and their size is limited by the thickness of the layer being formed. The reduction of the phase size considerably decreases inner tensions in the coatings and on the border with the substrate, which increases their exploitation properties.

The paper presents the research results of formation conditions and regularities of change in the coatings properties of multicomponent (Ti, Al)N and nanostructure, functionally-gradient, multilayer (Ti, Al)N/TiN.

2. Equipment and investigation methods

The scheme of the experimental installation is presented in Fig. 1.

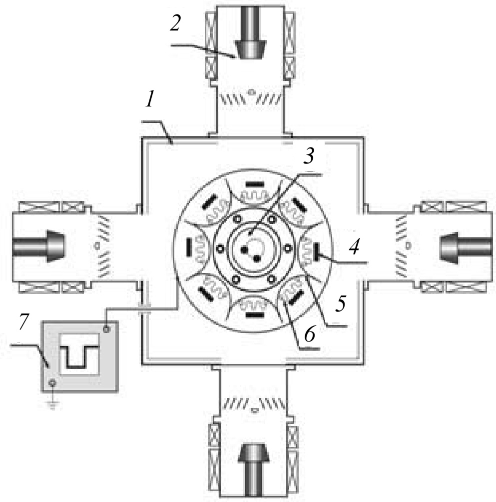


Fig. 1. Scheme of the technological installation for multilayer (nanoscale thickness of the layer) (Ti, Al)N/TiN coating deposition: *1* – vacuum chamber; *2* – vacuum arc evaporator; *3* – gaseous plasma generator; *4* – samples; *5* – shield; *6* – heating devices; *7* – high voltage generator

The installation is equipped with four plasma generators of conductive materials based on DC VAD. To clean vacuum arc plasma from microparticle fraction, the VAEs were equipped with plasma filters (PF) of the shutter type [2]. The installation was equipped with high frequency bias potential generator to realize the regimes of preliminary ion clearing and plasma-immersion ion implantation [3]. The reactionary gas was supplied through a leak valve, installed on the vacuum chamber.

The elemental composition of the ion-alloyed surface layer was analyzed by Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS).

Depth dependence changes of the hardness due to the implantation were studied by measuring the dynamic nanohardness with the Nano Hardness Tester "NHT-S-AX-000X" (CSM). A Vickers nanoindentor was used for the investigation of the microhardness. The indenter load was in the range of 15–280 mN. The tribological properties were investigated by High Temperature Tribometer "THT-S-AX000" (CSM). Wear studies were carried out by means of a method "ball-on-disc". Measuring of the surface morphology was realized on 3D profilometer "Micromesure 3D Station" (Stil).

3. Ti(Al)N coatings deposition

The samples underwent mechanical polishing, involving abrasive paste and chemical cleaning in an ultrasonic bath. Sample surface pretreatment in the vacuum chamber was executed under the regime of microdroplet-filtered Ti plasma generation combined with high-frequency short pulse metal plasma immersion ion implantation (HFSPPI[3]). This regime allows us to decrease on-surface arcing which is typical of dc bias potential formation and, thus, get rid of the mechanism of microcrater formation on sample surfaces. The bias voltage amplitude (U_b) of up to 4 kV together with the pulse repetition rate of up to 440 kHz and pulse duty factor of 0.66 allow us to effectively pretreat, activate and heat the surface, including effective sputtering of thin films formed between voltage pulses.

In the case of decrease in pulse repetition rate and bias voltage pulse amplitude, plasma flow onto the target exceeds the flux of atoms sputtered from the target surface. This fact provides conditions for ion mixing of the substrate–coating boundary with formation of a transition layer. The sample temperature was in the range of 450–550 °C. TiN coating formation was executed at bias potential amplitude of (from −300 to −2500 V, with reactive gas pressure (N_2) of $2 \cdot 10^{-2}$ Pa. In contrast to widely used methods of coating deposition using magnetron sputtering systems [4] or vacuum arc evaporators with composite or compound cathodes [5, 6], in our experiments the coating formation regime using two VDEs with Al cathode and one VAE with Ti cathode was realized [7, 8]. Coatings were deposited in the reaction gas (N_2) environment. The ratio of Ti and Al plasma flows depended on VAD current (I_{arc}).

Figure 2 shows the results of investigation of element composition of TiN and (Ti, Al)N coatings. The stoichiometric composition of deposited TiN (Ti ~ 45%; N ~ 45%) and (Ti, Al)N (Ti ~ 29.5%; Al ~ 27%; N ~ 39%) coatings corresponds to the 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 the sample surface.

The investigation of the surface morphology of the obtained coatings show that for (Ti, Al)N coatings formed without PF, surface roughness equals tens of microns. This phenomenon is attributed to the presence of a large amount of microdroplets in the Al plasma flow (up to several tens of percents). For this case, the droplet size can be equal to more than 100 µm. The use of PF for Al plasma filtering allows us to decrease the content of microparticle fraction in the stream by several orders of magnitude, which permits us to deposit coatings with a roughness not more than 0.64 µm. Comparative analysis of TiN coating morphology shows that decrease in I_{arc} and increase in U_b allows us to significantly decrease the surface roughness of TiN coatings. This effect can be explained by an increase in plasma ion component transmission efficiency in PF electrodes and a decrease in microparticle fraction in the arc plasma flow at the expense of decrease in I_{arc}, as well as due to reflection of droplets from the negative potential near the sample surface.

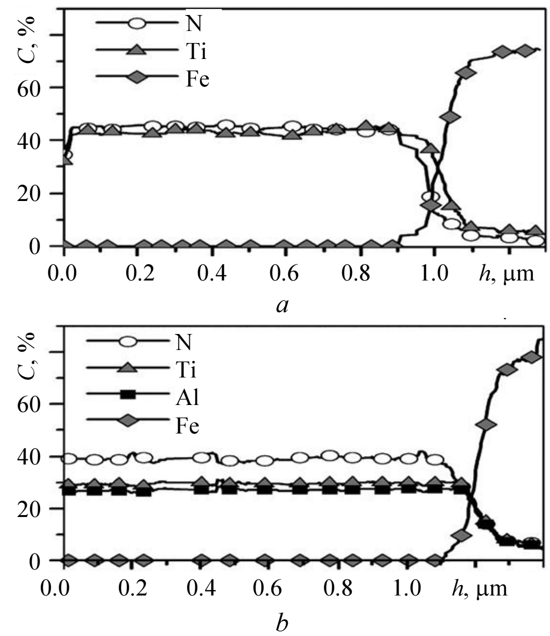


Fig. 2. Element distribution into the depth of the deposited coating: *a* – TiN, b–(Ti, Al)N; *b* – (Ti, Al)N/TiN

Figure 3 presents the results of investigation of (Ti, Al)N coating hardness as a function of the ratio of Ti and Al plasma concentrations. According to the data, coating with the hardness $H_V = 3670$ kg/mm^2 was obtained at $I_{arc} = 80$ A. Data from the elemental analysis show that the measured hardness corresponds to optimal stoichiometric composition of the coating.

The data presented in Fig. 3 confirm that use of PF allows us to increase the TiN coating hardness by 40%. It was also discovered that an increase in bias potential in the range from −300 to −2500 V results in a decrease in coating hardness by 15–20%. The observed effect can be explained by the increase in phase formation temperature and consequent increase in phase size. The results of nanohardness measurement show that for coatings formed with the use of micro-droplet-filtered plasma, high magnitudes of Young's modulus are typical. The data on coating adhesion strength were obtained on the basis of scratch test results. Research results show that delamination of the

TiN coating deposited without PF and at constant bias potential begins at loading equal to 0.81 N.

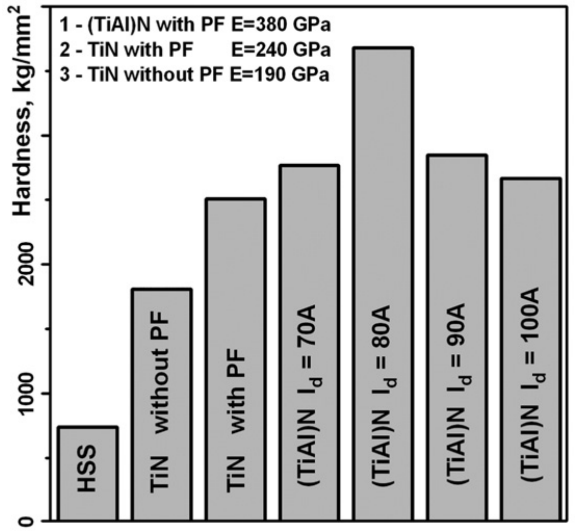


Fig. 3. Change in hardness depending on coating deposition regimes

A surface image made near the indenter track shows that the structure is porous, which reveals high inner tensions in the material. In the case of PF and pulsed negative bias potential application, the loading at which coating delamination begins increases up to 1.17 N, which confirms an increase in coating adhesion strength by 70%. For this case a high-intensity combined ion pretreatment, surface heating and activation, formation of a thick transition layer between the substrate and coating, and ion assisted coating deposition were used. A complex of these factors allowed us to form a (Ti, Al)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 internal tension are absent near the indenter track. In was experimentally found out that with the increase in U_b in the range from −300 to −2500 V, we observed an increase in adhesion strength of TiN coatings by 20%. The highest values of adhesion strength were registered in the range from −300 to −750 V. The effect can be attributed to decrease in compressing residual tensions resulting from increase in temperature, ion treatment of the surface, increase in formed phase sizes, etc.

Figure 4 shows the results of investigation of the friction coefficient of TiN and (Ti, Al)N coatings. The data confirm that if we deposit TiN coating onto HSS steel, the surface friction coefficient decreases by 2.5 times – with or without PF. At the first stage of testing we observed a 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. 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%.

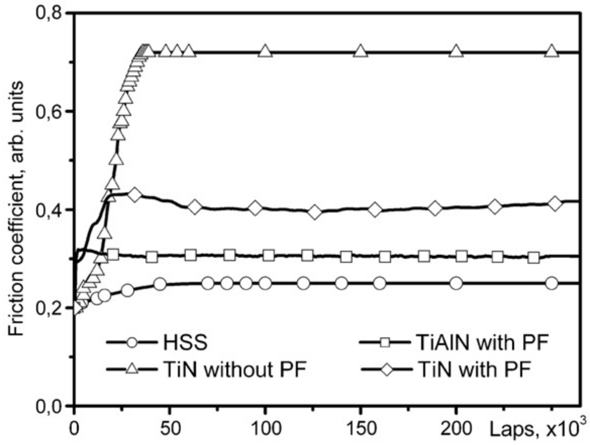


Fig. 4. Change in friction coefficient depending on the number of rotations

Influence of the proposed treatment regimes on surface morphology modification can be seen in the diagram of Fig. 5.

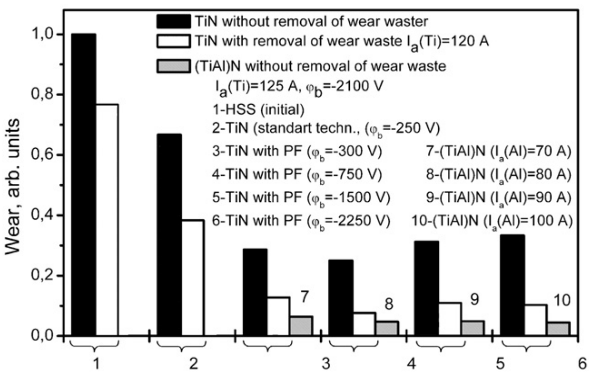


Fig. 5. Wear of TiN and (Ti, Al)N coatings depending on deposition regimes

The diagram is normalized by unit with respect to wear intensity of the HSS initial sample. The presented data show that TiN coatings deposited using the conventional technology are characterized by a double increase in wear resistance. At the same time, use of PF allows us to additionally increase steel wear resistance by 5 times. The data obtained on wear intensity without removal of wear debris show that the presence of wear debris in the indenter track, later used as an abrasive, results in a sharp increase in wear intensity. However, for this case wear resistance decreases 4 times compared to the initial state. Moreover, we did not notice any dependence of coating wear resistance on the sample bias potential.

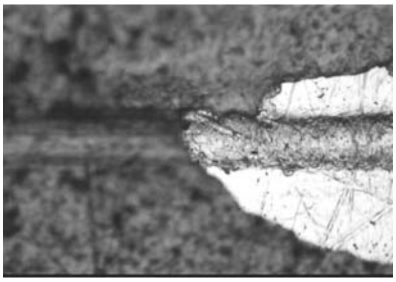
4. (Ti, Al)N/TiN coatings deposition

At the formation of a multilayer, nanostructure coating based on (Ti, Al)N/TiN system, complex installation comprised the gaseous plasma generator, four vacuum arc evaporator (VAE) with plasma filter (PF) with the cathodes of Ti and four VAE with PF with composite TiAl (50/50 at %) cathodes. The formation of a multilayer coating was carried out in the nitrogen plasma during the rotation of holders with the samples from one VAE to another one. Sharp boundary formation between separate nanolayers was provided by a protective shield, located behind the samples. The temperature regime of the coating formation (~ 450 °C) was supported by heating elements. Thickness of the separate layers was controlled by vacuum arc current and the rate of the samples rotation and changed from 2 to 10 nm. For example, with a total thickness of a coating 4.5 µm, more than 300 separate double (Ti, Al)N/TiN nanolayers were formed.

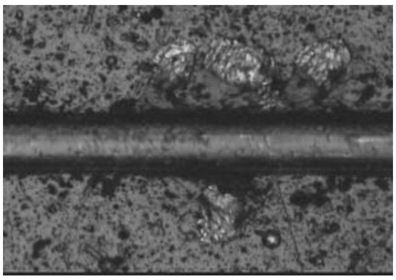
The measurements of the coating hardness of a multilayer (Ti, Al)N/TiN coating showed the value of H_V = 3850 kg/mm^2, which is only by 5% exceeds the hardness value of a monolayer (Ti, Al)N coating, obtained at an optimal regime.

But the advantages of a multilayer (Ti, Al)N/TiN coating become apparent during testing of an adhesion strength of thick enough coatings (4 to 10 µm).

Figure 6 presents the destruction of a monolayer (Ti, Al)N coating 4.5 µm thick, that begins at the load on indenter of 4.5 N.



a



b

Fig. 6. Indenter track after scratch-test: *a* – monolayer (Ti, Al)N coating (critical force 4.5 N); *b* – multilayer (Ti, Al)N coating (critical force 7 N)

Characteristic coating delamination near the indenter track is an evidence of high inner tensions in a coating. Destruction of a multilayer (Ti, Al)N/TiN coating began at a load on indenter of 7 N. At this, the character of destruction considerably changed. In particular, there were no cracks across the coating. This allows a conclusion of the formation of a structure with layers compensating inner tensions.

The results of comparative research of the wear intensity of a monolayer (Ti, Al)N coating and a multilayer nanostructure system (Ti, Al)N/TiN showed, that the wear intensity of a multilayer (TiAl)N/TiN coating (Ti, Al)N/TiN is 4 times less than that of (Ti, Al)N coating and 10 times less than that of TiN coating, formed with PF. This fact can be connected with the grain size of the coating material, which in the abrasion process appear as an abrasive, as well as with the occurrence of deep cross cracks in the coating, which are practically absent in a multilayer coating.

5. Conclusions

The analysis of research results of properties of monolayer TiN, (Ti, Al)N and nanostructure, functionally-gradient, multilayer (Ti, Al)N/TiN coatings, obtained by plasma treatment using DC VAD plasma filtered from microparticle fraction show that (Ti, Al)N/TiN coatings have the best mechanical and exploitation properties.

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