The influence of repetitively pulsed plasma immersion low energy ion implantation on TiN coating formation and properties

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Abstract. Application of high frequency short pulse plasma immersion low energy ion implantation for titanium nitride coating deposition using vacuum arc metal plasma and hot-cathode gas-discharge plasma on R6M5 alloy was investigated. Implementation of negative repetitively pulsed bias with bias amplitude 2 kV, pulse duration 5 μs and pulse frequency 10^5 Hz leads to 6.2-fold decrease of vacuum arc macroparticle surface density for macroparticles with diameter less than 0.5 μm. Ion sputtering due coating deposition reduces the production rate approximately by 30%. It was found that with bias amplitude range from 1.1 to 1.4 kV and pulse duration 5 μs yields to formation of coatings with local hardness up to 40 GPa. This paper presents the results of experimental studies of adhesion strength, tribological properties and surface morphology of deposited TiN coatings.

1. Introduction

Hard thin-film nitrides coatings formed by Physical Vapor Deposition (PVD) are widely used to improve wear-resistant, anticorrosive properties of cutting tools, machine parts and etc. Among these materials the most widely studied is titanium nitride (TiN). Typically, the standard method of TiN forming involves the use of plasma of vacuum arc discharge. Vacuum arc has undeniable advantages such as high degree of ionization, high coating growth rate, the ability to generate plasma of almost any conductive material [1–3]. The drawback of the vacuum arc is associated with the presence of debris metal particles, with sizes from nanometers up to hundreds of micrometers [3], often refer as macroparticles (MP). Deposition of the MPs on the treated surface significantly impair the functional characteristics of obtained coatings.

Several different approaches were proposed and used to reduce the MP density in the deposited coatings [4–7]. One of the methods based on the application of a negative DC bias to a substrate, immersed in vacuum arc plasma [4, 5]. The authors of these papers mentioned that the number of MPs on titanium nitride coating can be reduced by approximately 3–4 fold with the increasing of negative bias potential up to -1 kV. In other Refs [8, 9], the authors used high-frequency short-pulse negative biasing during the deposition of unfiltered vacuum-arc plasma. The application of pulsed negative bias (with pulse duration of microseconds) allowed increasing the amplitude of the negative bias up to 2–3 kV. The quantitative reduction of the surface density of aluminum or titanium MPs by several orders of magnitude was demonstrated.

This work studies the regularities of synthesis of TiN coatings with lower MP-content and improved physical-mechanical properties using vacuum-arc plasma deposition and negative high-frequency short-pulse biasing of the sample.

2. Experimental setup

The coating synthesis were carried out on an experimental setup presented in figure 1. The working pressure in vacuum arc chamber was 10^{-3} Pa. The unit is equipped with an industrial vacuum-arc source of metal plasma, and gas plasma source “PINK”. Titanium VT-1 was used as the cathode material. Arc current was equal to 100 A and the density of ionic current saturation of metal plasma near the surface of the substrate was approximately 4.4 mA/cm^2.

Experimental samples were made of R6M5 high speed steel and were mounted on a massive holder located in the center of the vacuum chamber. The distance from the sample to the cathode of vacuum-arc evaporator was 40 cm. The surfaces of the substrates were polished to roughness $R_a \sim 0.25$ μm.

The negative bias was formed by the high-frequency short-pulse negative bias generator with following parameters: pulse duration τ = 1–9 μs, pulse repetition rate f = 10^5 Hz, bias potential amplitude φ = 0.25–3 kV.

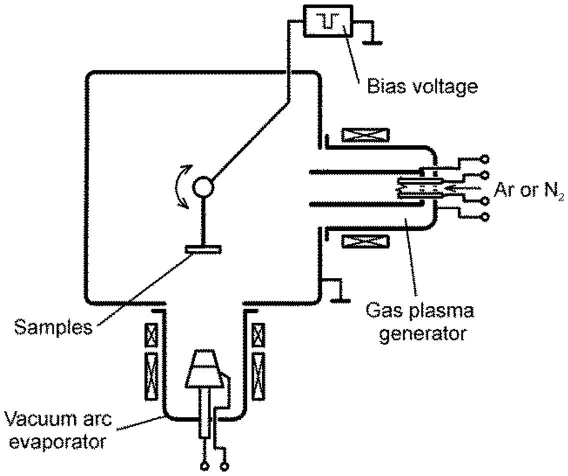

Figure 1. The experimental setup scheme.

Before the synthesis of nitride coatings in a single vacuum cycle ion cleaning, surface activation of the samples and their heating were carried out, using gas-discharge plasma of argon at the pressure of the working gas of 1 Pa and high-frequency short-pulse biasing with amplitude up to 1.2 kV. As a result of ion bombardment, the surface layer of the samples was activated to ensure the best adhesion between the coating and the substrate, and heated to a temperature of 300–400 °C. In addition, the formation of the nitride coating was preceded by 5 min deposition of the transition titanium layer. The deposition of the nitride coating was performed for 40 min. The pressure of the working gas (nitrogen) was chosen in the range 0.1–2.4 Pa. The parameters of the pulsed bias potential were varied in the following ranges: pulse amplitude, 0.9–2.0 kV; pulse duration, 3–5 μs.

The surface morphology and the macroparticle surface density were studied using electron scanning microscope “Hitachi TM-3400S” and three-dimensional profilometer “STEL MicroMeasure 3D Station”. To obtain statistically reliable results, for each experimental point, the total area for macroparticles quantification was 270×210 μm.

The element composition of the formed coating analyzed by Auger electron spectroscopy (AES). The hardness was measured using “CSM Nano-Hardness Tester”. The Vickers indenter load was 100 mN. The adhesion properties examined using “CSM Micro-Scratch Tester”. In the scratch test, a Rockwell diamond indenter with the diameter of 20 μm was used. The tribological properties were investigated by ”CSM HighTemperature Tribometer”. Wear studies were carried out by the “ball-on-disc” method using a ball with the diameter of 3 mm at the normal load of 2 N.

3. Results and discussion

Prior to the TiN coating deposition with high-frequency short-pulse negative bias, a series of experiments with a DC negative bias of 0.3 kV was performed to determine the optimal pressure of the working gas (nitrogen) for the formation of the coating with the best properties. Figure 2 presents the results on the hardness and critical load studies of the obtained coatings versus nitrogen pressure in the vacuum chamber. The coatings with the best properties were synthesized at the pressure of 0.6 Pa. Therefore, all subsequent experiments on the coating formation were carried out at the same pressure.

The experiments on the formation of TiN coatings with different parameters of negative high-frequency short-pulse bias were done. Table 1 presents the modes of the TiN coating synthesis and main physical and mechanical characteristics.

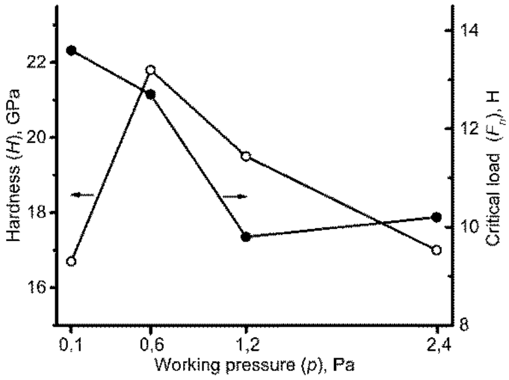

Figure 2. The influence of nitrogen pressure on hardness and adhesion of TiN coatings formed with DC negative bias of 0.3 kV.

Table 1. The modes of synthesis and physical properties of the TiN coatings.

N	Coating synthesis parameters				Characteristics of the deposited coatings				
	-φ [V]	τ [μs]	f [Hz]	P(N_2) [P]a	Thickness (s) [μm]	Hardness (H) [GPa]	Critical load (F_n) [N]	Mean friction coeff. (μ)	Wear [relative unit]
1	0.3	D.C.		0.6	5.2	21.8	12.5	–	–
2	0.9	3	10^5	0.6	5.3	18.7	11.8	–	–
3	0.9	4			5.0	20.5	9.5	0.22	0.69
4	0.9	5			5.0	23.2	10.2	0.22	0.69
5	1.1	5			4.9	28.1	16.0	0.27	0.66
6	1.4	5			4.4	27.5	13.0	0.22	0.57
7	2.0	5			3.6	19.5	8.4	0.25	0.62
8	Initial sample HSS (R6M5)				–	16.0	–	0.42	1.0

Figure 3 shows SEM images of the coating surfaces depending on the deposition conditions. The microphotographs demonstrate a slight decrease in the number of small MPs on the surface of the substrates with increase in the bias amplitude. Figure 4 demonstrates the size distribution of MP for some typical modes of deposition. The application of high frequency negative bias with a frequency of 10^5 Hz, amplitude of 2 kV and duration of 5 μs enables the 6.2-fold reduction of the number of MPs with diameter less than 0.5 μm. The total number of MPs is decreased 2.8-fold. In addition, the SEM images in Figures 3c and 3d show a significant erosion of the coating surface, which may be associated with intensive ion sputtering at the high bias amplitudes.

Figure 5 presents the thickness of coatings formed under various conditions. According to the data, the increase in the amplitude of the bias up to 2 kV leads to a decrease in the coating growth rate by approximately 30%.

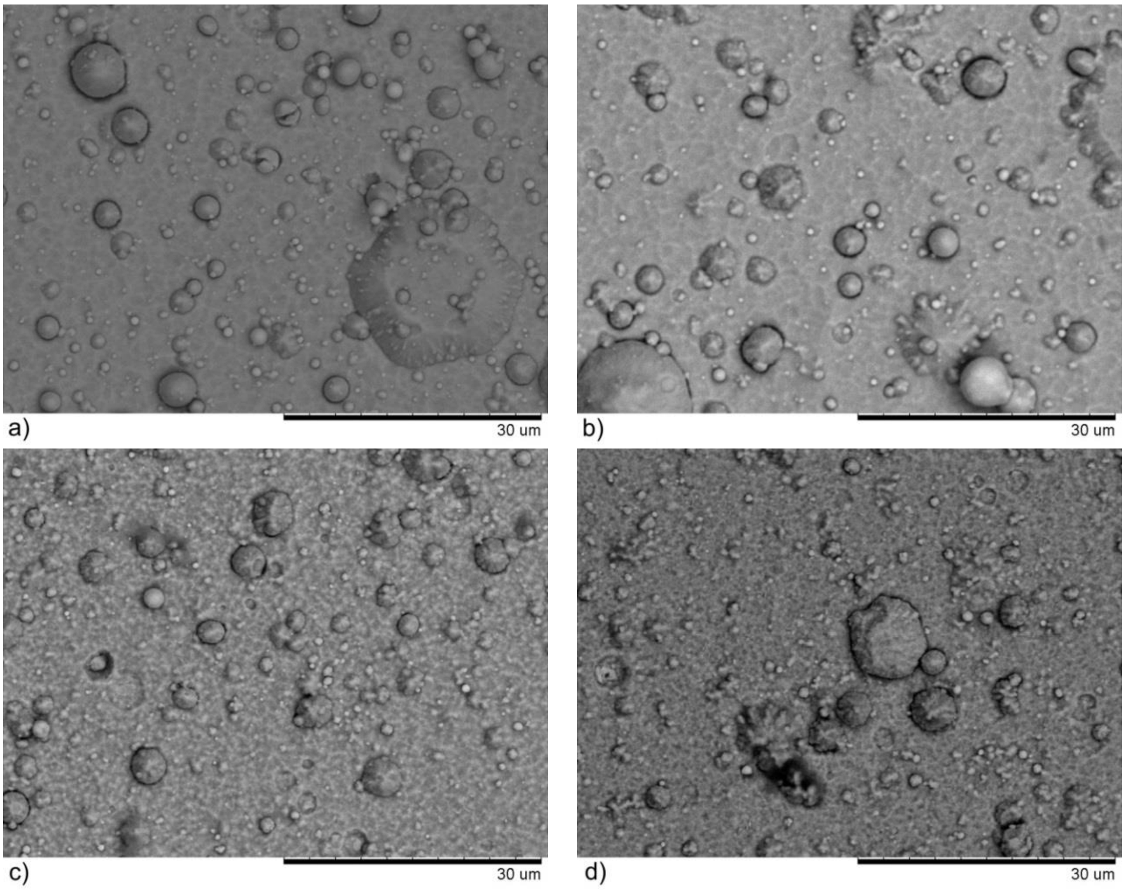

Figure 3. Microphotographs of the TiN coating surface with the deposited MPs in different modes of deposition: a) at anode potential of 0 V; b) at negative DC bias of 0.3 kV and negative pulsed bias (f = 105 Hz, τ = 5 µs) with an amplitude c) φ = –1.1 kV; d) φ = –2.0 kV.

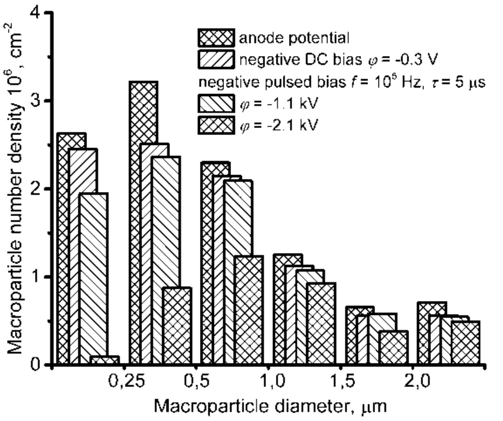

Figure 4. The number of counted MPs as a function of diameter for the case of anode potential, negative DC bias of 0.3 kV and negative pulsed bias (f = 105 Hz, τ = 5 µs) with amplitudes of 1.1 kV and 2.0 kV.

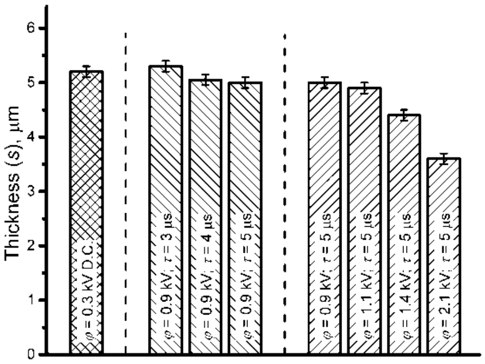

Figure 5. The TiN coating thickness obtained under various modes of deposition.

The results of the elemental composition studies of the coatings deposited in the experiments with a pulsed negative bias of the various amplitudes are presented in Table 2. The average concentration of nitrogen is 41 at.%, and concentration of titanium is 52 at.%. With an increasing amplitude, a slight decrease in the concentration of nitrogen is observed, probably due to the decomposition of titanium nitride at high temperatures (>700 °C).

Table 2. Element composition of TiN coatings.

N	Coating synthesis parameters				Element concentration [at.%]		
	$-\varphi$ [V]	τ [μs]	f [Hz]	$P(N_2)$ [Pa]	Ti	N	other
4	0.9	5	10^5	0.6	51.4	42.1	6.5
5	1.1	5			49.7	44.2	6.1
6	1.4	5			53.6	40.7	5.7
7	2.0	5			53.8	38.2	8.0

The obtained nitride coating has high hardness, exceeding the hardness of the default HSS sample. The average values for hardness of the formed films are presented in Table 1. The highest hardness of about 28 GPa is observed in TiN coatings synthesized with a negative pulsed bias with a pulse duration of 5 μs and amplitudes of 1.1 kV and 1.4 kV, the lowest hardness of 18.7 GPa in TiN coating with the following bias parameters: φ = 0.9 kV, τ = 3 μs. A large number of performed indentations (49 measurements for each sample) revealed the presence of superhard phases (≥40 GPa). Figure 6 shows the results of surface hardness measurements of different experimental samples in a form of histogram showing the relative frequency of the superhard coatings observation.

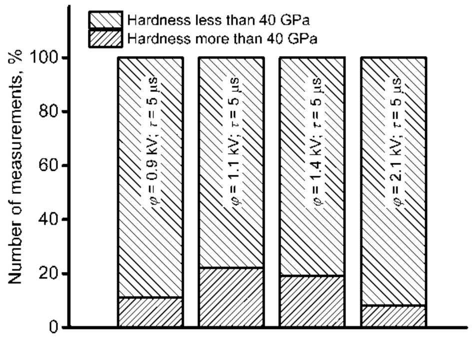

Figure 6. Histogram of the number of hardness measurements with values less or more than 40 GPa on coatings obtained with various negative bias parameters.

Analysis of the data showed that with the application of pulsed negative bias with a pulse duration of 5 μs and amplitudes of 1.1 kV and 1.4 kV, approximately 20% of the total indentations expose the maximum value of hardness (≥40 GPa) distinctive for the superhard TiN phases. Further increase in the bias potential leads to a decrease of this parameter down to 8%. One of the possible explanations is the growth of the crystalline titanium nitride grain with the prolonged exposure of high temperatures. The Young's modulus of the obtained nitride coatings is in the range of 350-680 GPa.

Figure 7 shows the dependence of the dynamic friction coefficient versus the number of cycles of the tribological test for the R6M5 steel samples and for the samples with a TiN coating synthesized at different parameters of repetitively pulsed negative bias. During the test, the friction coefficient remains at the level of the average values of 0.22–0.27. Table 1 presents the average values of a friction coefficient and relative wear of the experimental samples. The mean coefficient of friction in the tribological tests for TiN coating is approximately 1.7-times less than that in the test with the default sample material. Figure 8 presents the data on the wear of the original sample material and some of the TiN coatings. The maximum wear resistance was observed on the samples modified with ion-plasma treatment at bias amplitude of 1.4 kV and a pulse length of 5 μs, which is 1.8-fold higher than that of the initial material. The minimum wear resistance of the coating deposited with the different bias parameters is also 1.5-fold higher than wear resistance of the default HSS sample.

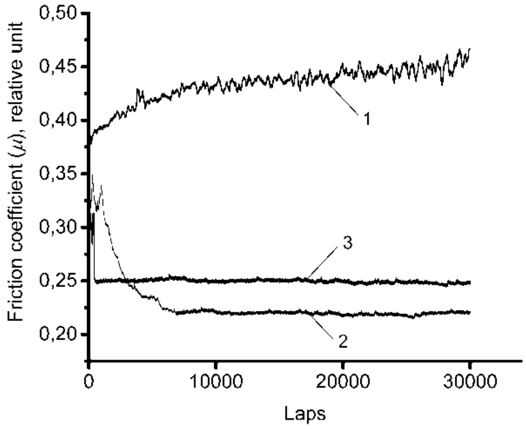

Figure 7. The dynamic friction coefficient: *1)* R6M5 alloy, TiN coating obtained with negative pulsed biasing (*f* = 105 Hz, τ = 5 μs) with an amplitudes of *2)* φ = –1.1 kV, *3)* φ = –2.0 kV.

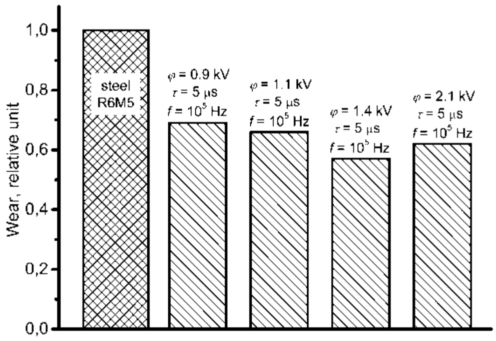

Figure 8. Wear of TiN coatings obtained at different bias parameters, with respect to the wear of the original sample of R6M5 steel.

The results of the scratch test of TiN coatings are presented in Table 1. Analysis of the dynamics on changes of friction forces and sensor data from the acoustic emission allowed determining the corresponding critical load of the coating separation from the substrate. The coating with high adhesion and a critical load of 16 N was obtained with a negative pulsed bias potential with the pulse duration of 5 μs and amplitude of 1.1 kV. The critical load of this sample is 1.9-fold greater than the critical load (8.4 N) of the sample with the smallest adhesion (sample N7 in Table 1).

4. Conclusion

In the process of synthesis of titanium nitride by vacuum-arc discharge, the application of negative high-frequency short-pulse negative bias with the frequency of 10^5 Hz with amplitude of 2 kV and duration of 5 μs provides the 6.2-fold reduction in the number of vacuum arc macroparticles (with the diameter less than 0.5 μm) on the surface of the coating. The use of pulsed bias with a pulse duration of 5 μs and amplitudes of 1.1 kV and 1.4 kV ensure the formation of TiN coatings with the hardness of 28 GPa with the best wear resistance and adhesion.

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Acknowledgements

This work was performed within the State Mission «Science» of the Ministry of Education and Science of the Russian Federation.