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Improvement of the magnetron sputtered coating adhesion through pulsed bombardment by high-energy ions

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Abstract. Comparative study of titanium nitride deposition has been carried out, the growing coating being uninterruptedly bombarded by 100-eV ions or ions accelerated by high-voltage pulses applied to the substrate. The study revealed that microhardness of coatings synthesized using 25-kV pulses rises from 21 GPa to 29 GPa when percentage of nitrogen in the mixture with argon increases from 15% to 20%. With a further increase of nitrogen percentage to 30%, the microhardness slightly diminishes to 27 GPa. In contrast to golden coatings synthesized at low-voltage substrate biasing, the color of titanium nitride coating produced using high-voltage pulses is brown. The most striking difference of coating deposited using high-voltage pulses applied to the substrate is its perfect adhesion despite the interface formation at the room temperature without any preheating and activation. The adhesion characterization using a scratch-tester has revealed that critical loads of coatings synthesized using 25-kV pulses are several times higher than those of conventional nitride coatings synthesized at uninterrupted substrate biasing of 100 V. When the pulse amplitude diminishes to 5 kV, the critical loads and microhardness of the coating decrease to conventional values.

1. Introduction

For production of various functional coatings on the surface of machine parts and tools, plasma- and beam-assisted deposition methods are widely used [1]. The growing coating properties depend on the energy transferred to the atoms condensing on the product surface. When this energy is supplied by accelerated ions bombarding of the product, the equilibrium heating of the coating and product is replaced by a non-equilibrium atomic scale heating [2], the coating properties depend on the ion energy and are independent of the substrate temperature. This enables the coating deposition on heat sensitive materials and a wide-range regulation of the coating properties.

For instance, the density of Mg films deposited using a Mg^+ ion beam grows with the ion energy from 83% of the bulk material density at the energy of 24 eV to its maximal value (about 100% of the bulk material density) at the ion energy of 48 eV and then falls down to 50% and 15% with the energy increasing to, respectively, 120 eV and 300 eV [3]. At the same time, the Mg-film adhesion rises with the ion energy monotonically due to deeper penetration of accelerated particles into the substrate.

When slow atoms are condensing on the substrate and the growing film is bombarded by accelerated ions, the film properties depend not only on the energy of ions, but also on the ratio of their flow density on the substrate surface to that of condensing atoms. At the ion energy rising up to hundreds and thousands of volts, their sputtering efficiency monotonically rises, and the ions are able to sputter all deposited atoms. For this reason the film modification with high-energy particles is

usually carried out in pulsed regimes [4, 5]. This work is dedicated to the investigation of the coating adhesion dependence on pulsed ion bombardment.

2. Experimental setup

Figure 1 presents schematic of the experimental setup used for the deposition of coatings with pulsed bombardment by high-energy ions. On vacuum chamber *1* is mounted a planar magnetron with water-cooled 150-mm-wide and 370-mm-long titanium target *2*. Magnetron power supply *3* is connected between target *2* and grounded flange *4*, which serves as the magnetron discharge anode. The power supply ensures stabilized current in the target circuit ranging from 1 to 8 A at the discharge voltage up to 650 V between the anode and the target.

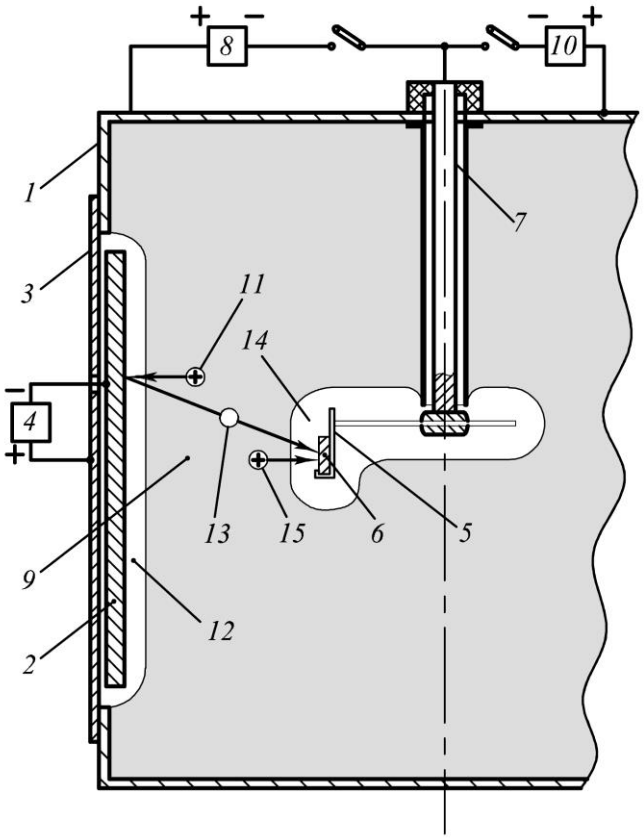

Figure 1. Schematic of experimental setup. *1* – vacuum chamber, *2* – target, *3* – anode, *4* – magnetron power supply, *5*– holder, *6* – substrate, *7* – feed-through, *8* – high-voltage pulse generator, *9* – plasma, *10* – DC power supply, *11*, *15* – ions, *12*, *14* – positive space charge sheaths, *13* – sputtered atom.

Holder *5* of substrates *6* is mounted on a horizontal rod passing through a guide bush, which rotates on high-voltage feed-through *7*. It is possible to connect high-voltage pulse generator *8* to feed-through *7* and to apply the pulses directly to substrate *6*. The generator allows regulation of the pulse amplitude from 3 to 30 kV, the pulse width from 5 to 50 μs, and the repetition rate from 5 to 50 Hz. To reduce the current of ions from plasma *9* filling, the chamber in the circuit of the feed-through its surface is covered with a grounded cylindrical screen. The holder design allows variation of the distance between substrate *6* and target *2* from zero to 300 mm. A negative voltage ranging from 100 to 1200 V can be applied to substrate *6* from DC power supply *10*.

After power supply *4* is switched on and the magnetron discharge is ignited, the chamber is filled with glow of discharge plasma *9*, which is most intensive near the target surface. Ions *11* accelerated

in sheath *12* of positive space charge bombard target *2*, and sputtered atoms *13* of the target material deposit on substrate *6*. When a high-voltage pulse is supplied to substrate *6*, sheath *14* of positive space charge is formed around holder *5* and accelerated in the sheath high-energy ions *15* bombard the coating growing on the substrate.

3. Experimental results

To appreciate the plasma density distribution a 120-mm-high and 160-mm-wide flat electrode was installed in parallel to the target surface. The electrode was attached to feed-through *7* instead of substrates holder *5* and negatively biased to 50 V. Currents in its circuit at argon pressure of 0.3 Pa, distance to the target h = 40 mm and currents in the target circuit of 3 A, 5 A and 8 A amounted to 0.6 A, 1.15 A and 1.65 A, respectively (solid curves in Figure 2). When the distance h rises to 100 mm, these currents nearly linearly decrease to 0.06 A, 0.14 A and 0.24 A. When the distance runs up to 150 mm, the currents amount to 0.02 A, 0.04 A and 0.08 A, respectively, and are only slightly reduced with the further increase of the distance.

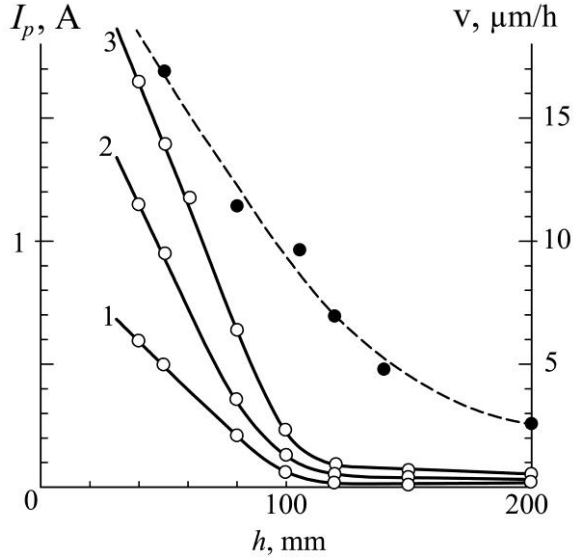

Figure 2. Dependence on the distance h from the target of titanium coating deposition rate v at current of 8 A in the target circuit (dashed line) and current in the probe circuit I_p (solid lines) at the current in the target circuit of 3 (1) 5 (2) and 8 A (3).

The dashed curve in Figure 2 presents dependence on the distance to the target of the titanium coating deposition rate on flat substrates made of high speed steel. Substrate *6* was placed on holder *5*, and on its surface facing target *2*, a mask was fixed. After 5-minute-long etching of the substrate and the mask with argon ions, extracted from the magnetron plasma and accelerated by negative bias voltage of 1200 V applied from power supply *10*, titanium coatings were deposited on their surfaces.

During the deposition process, the bias voltage of the substrate amounted to 100 V. After the 30-minute-long coating deposition the mask was removed, and height of the step between the open surface of the substrate and its surface covered with the mask, was measured using the DektakXT profilometer (manufactured by Bruker Nano, Inc., USA). The titanium deposition rate was determined by dividing the height of the step by the deposition time. At the current in the target circuit of 8 A, it amounts to 2.5 μm/h at the distance from the target of 200 mm, rises to 9.5 μm/h at the distance of 100 mm and to 17 μm/h at the distance of 50 mm. Measurements have shown that at the distance of 120 mm from the target, the titanium deposition rate amounts to 7 μm/h and is independent of the argon pressure in the range from 0.2 to 2 Pa. When reducing the current in the target circuit, the deposition rate is decreasing proportionally to the current.

After addition of nitrogen to argon (15%), the blue glow of the discharge plasma changes its color to pink (Figure 3), and the coating deposition rate is reduced by 2 times. Increasing the nitrogen content in the gas mixture up to 20% reduces the deposition rate by 2.5 times, and addition of 30% nitrogen reduces the rate by 3 times. In all cases, a golden hard coating of titanium nitride is synthesized on the substrates. With the reduction of the nitrogen content in the gas mixture to 10%, synthesis of titanium nitride stops, and on the substrate is deposited titanium coating. In this case, the color of the discharge plasma is again light blue, and the deposition rate increases to the values measured during the discharge in argon without nitrogen addition (dashed curve in Figure 2). When the current in the target circuit amounts to 8 A and the pressure of argon mixed with nitrogen (15%) is equal to 0.4 Pa on the substrate made of high speed steel and distanced from the target at 90 mm is deposited within 1 hour a 5.6-μm-thick titanium nitride coating with microhardness of 2200 HV25.

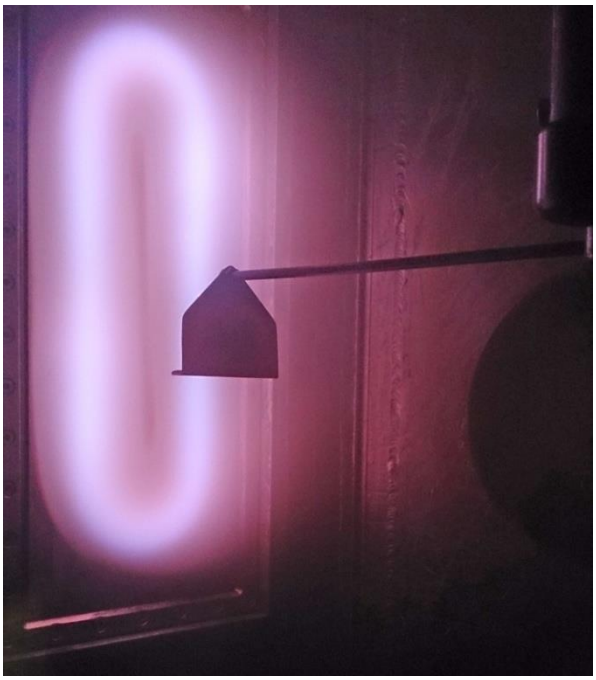

Figure 3. Photograph of the substrate holder and the magnetron discharge plasma glow.

In contrast to the above coating deposition at the negative voltage of 100 V after the substrate pretreatment by argon ions with energy of 1200 eV, no pretreatment has been carried out before the deposition with pulsed bombardment of the substrate by high-energy ions. At the pressure of argon and nitrogen mixture ranging from 0.2 to 0.8 Pa, first high-voltage pulses with specified amplitude, width and repetition rate are applied to the substrate, and only after that the magnetron discharge with specified current of 2 to 8 A is activated. The substrate with initial temperature equal to the room temperature immediately becomes immersed in the gas discharge plasma. Titanium atoms arrive to its surface and synthesis of the nitride coating starts, the growing coating being bombarded by argon and nitrogen ions accelerated by high-voltage pulses. Only a few minutes later the substrate temperature measured by IP 140 IMPAC pyrometers (manufactured by LumaSense Technologies, Inc., USA) grows up to 200-400 °C due to the substrate bombardment by high-energy ions and heating by the discharge radiation.

When high-voltage pulses are applied to the substrate, the coating deposition rate is a little lower as compared to the deposition at the bias voltage of 100 V. At the argon pressure of 0.4 Pa, current in the target circuit of 8 A, pulses amplitude of 25 kV, their width of 40 μs and their repetition rate of 50 Hz, the titanium coating deposition rate at a distance h = 90 mm from the target amounted to 10 μm/h. At

the same pressure and current, addition to argon of nitrogen reduced the coating deposition rate down to 5 μm/h.

In contrast to the golden coatings synthesized on the substrate at a constant voltage of 100 V, titanium nitride coatings produced using high-voltage pulses are brown. Measurements with the use of POLYVAR-MET durometer (manufactured by Reichert-Jung, Austria) showed that microhardness of 5-μm-thick coatings on hard alloy substrates, synthesized using 25-kV pulses grows from 2100 HV25 to 2900 HV25 with increase in the nitrogen content from 15% to 20%. With a further increase in the nitrogen content to 30%, it slightly diminishes to 2700 HV25. However, the increase in microhardness of coatings with increasing the nitrogen content occurs not regularly. Analysis of the gas medium and plasma composition in the vacuum chamber by means of the EQP energy-mass analyzer (manufactured by HidenAnalitical Ltd., England) revealed that increase of the microhardness requires a sufficiently low content of water vapor and, accordingly, of hydrogen and oxygen ions.

Evaluation of adhesion using a scratch tester, showed that critical loads for the coatings synthesized using 25-kV pulses are several times higher than for conventional nitride coatings synthesized at a constant bias voltage. When, however, the pulse amplitude diminishes from 25 to 5 kV, the critical loads and microhardness decrease to conventional values.

4. Discussions

The experimental results showed that usually titanium coatings delaminate if deposited without pre-heating and activation of the substrate by argon ions with energy up to 1200 eV. To ensure an admissible adhesion of titanium nitride coating, it is also necessary to deposit an adhesive titanium sublayer before the coating synthesis. The most striking difference of coatings deposited using high-voltage pulses applied to the substrate is their perfect adhesion despite the formation of the transitional layer (interface) at room temperature without any preheating and activation. The adhesion was improved due to bombardment of the metal substrate by ions with an energy ranging from 5 to 25 keV, which penetrate the substrate surface in the form of neutral atoms. In the surface layer with a thickness, respectively, from 20 to 100 nm, each of these ions triggers dislodgement of 100 to 500 atoms, respectively, from the crystal lattices of the substrate and the growing coating. As a result, atoms of the substrate and atoms of the coating mix together. This is the reason of the interface width increase and the adhesion improvement.

5. Conclusion

Pulsed bombardment of growing coating by high-energy ions results in the coating adhesion improvement due to increase in the interface width, caused by mixing by the ions of the substrate and coating atoms in the very beginning of the coating deposition.

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