Product surface hardening in non-self-sustained glow discharge plasma before synthesis of superhard coatings

P S Krasnov, A S Metel and H A Nay
Moscow State University of Technology “STANKIN”, 1 Vadkovsky per., Moscow GSP-4, 127055, Russia
E-mail: a.metel@stankin.ru

Abstract. Before the synthesis of superhard coating, the product surface is hardened by means of plasma nitriding, which prevents the surface deformations and the coating brittle rupture. The product heating by ions accelerated from plasma by applied to the product bias voltage leads to overheating and blunting of the product sharp edges. To prevent the blunting, it is proposed to heat the products with a broad beam of fast nitrogen molecules. The beam injection into a working vacuum chamber results in filling of the chamber with quite homogeneous plasma suitable for nitriding. Immersion in the plasma of the electrode and heightening of its potential up to 50–100 V initiate a non-self-sustained glow discharge between the electrode and the chamber. It enhances the plasma density by an order of magnitude and reduces its spatial nonuniformity down to 5–10%. When a cutting tool is isolated from the chamber, it is bombarded by plasma ions with an energy corresponding to its floating potential, which is lower than the sputtering threshold. Hence, the sharp edges are sputtered only by fast nitrogen molecules with the same rate as other parts of the tool surface. This leads to sharpening of the cutting tools instead of blunting.

1. Introduction
Ion-plasma processing is widely used in industry for strengthening the surface layer of various products [1]. The useful life of any product can be substantially increased using hard wear-resistant coating. This is due to the coating hardness of about 25 GPa [2], which exceeds the bulk material hardness by many times. Necessary for synthesis of titanium nitride and other hard coatings metal vapor is produced by means of vacuum arc evaporation [3] and magnetron sputtering [4]. To prevent the formation of droplets in the coatings, the vacuum arc plasma can be filtered [5]. The density of magnetron discharge plasma near the product surface and the sputtering rate are substantially enhanced when a pulsed DC magnetron [6] is used. Metal vapor can be also produced due to sputtering a target at the bottom of a hollow cathode [7].

It was shown in [8] that under certain physical conditions, superhard coatings with hardness of 40–80 GPa and ultrahard coatings with hardness of 80–105 GPa can be synthesized. The survey of those conditions is given in [9]. Usually, the coating thickness amounts to a few microns. When its hardness is higher than the hardness of bulk material by an order of magnitude, the thin coating can be broken by external loads as an egg shell or a thin ice on the water surface. Performance and useful life of the coated product can be substantially improved when the thin coating is deposited on a strengthened surface layer of the product, the layer being by an order of magnitude thicker than the coating.
Strengthening of the surface can be carried out, for instance, by means of nitriding. Nitrided surface layer exhibits a high loadbearing capacity and fatigue strength, thus preventing elastic and plastic deformations of the product as well as brittle rupture of synthesized coating [10].

Combined processing of substrates made of high-speed steel in vacuum arc discharge plasma, which included nitriding and subsequent deposition of titanium nitride coatings, has been successfully carried out in [11]. Drawbacks of the arc method are soft metal droplets in the hard coatings, non-practical consumption of the target material and nonuniformity of the discharge plasma. To eliminate the droplets and the plasma nonuniformity, it was proposed in [12, 13] to produce the nitrogen plasma in hollow cathode glow discharge [14, 15] using the working vacuum chamber as the hollow cathode.

When a product immersed in any plasma is heated by ions accelerated from the plasma by negative voltage applied to the product, the ion current density on its surface depends on the product shape. It can be 10 to 100 times higher on its sharp edges than in the cavities. During 1-hour-long pre-nitriding of cutting tools, the thickness of the surface layer sputtered from the tool cutting edge by the ions can exceed the mean thickness of the sputtered tool material by 10 to 100 times and amount to 20–30 μm. When initial radius of the cutting edge is equal to 15 μm, nitriding can result in an increase of the edge radius up to 45 μm, thus making the tool dull.

Preventing the tool blunting requires homogeneity of the tool surface sputtering. This paper is dedicated to the production of a uniform nitrogen plasma and heating of the tools immersed in the plasma by a broad beam of fast nitrogen molecules [16, 17].

2. Experimental setup

Figure 1 presents the scheme of 500-mm-diameter vacuum chamber 1 equipped with a beam source of fast neutral molecules, which comprises 400-mm-diameter and 120-mm-deep titanium hollow cathode 2, 40-mm-diameter disc anode 3 and 300-mm-diameter emissive grid 4 made of 2-mm-thick titanium sheet.

![Figure 1. Scheme of experimental setup.](image)
Ions 9 are accelerated between plasma emitter 10, filling cathode 2 and plasma 6, potential of the latter being by 2–3 V higher than the ground potential of chamber 1. For this reason, the energy of accelerated ions corresponds to measured voltage between anode 3 and chamber 1 with kilovoltmeter 11. At the gas pressure \( p = 0.2 \text{–}1 \) Pa and the distance of 0.1 m from grid 4 most of accelerated ions 9 turn into fast neutral molecules 12 due to charge exchange collisions \( [18] \) with gas molecules 13. The current of slow ions 14 in the circuit of chamber 1 through feedback resistor 15 with 3-kΩ resistance induces negative bias voltage of 100–200 V of the grid, thus preventing penetration of electrons from plasma 6 through grid 4 into positive space charge sheath 16 between grid 4 and plasma emitter 10.

Neglecting the secondary electron emission from grid 4 we may assume that beam current is equal to the measured with ammeter 17 sum of currents in chamber 1 and grid 4 circuits multiplied by the grid transparency \( \eta = 0.8 \). The energy of ions 9 is regulated using high-voltage power supply 18, the beam current is regulated using power supply 19 between anode 3 and cathode 2. Ion current in the circuit of cathode 2 is measured with ammeter 20, and cathode potential drop is controlled with voltmeter 21. Using feedthrough 22, a 2-mm-thick flat electrode 23 is immersed in plasma 6, its surface area amounting to 0.03 m². The electrode is connected to positive pole of power supply 24; its bias voltage can be regulated from zero up to 500 V and measured with voltmeter 25, the current in its circuit being measured with ammeter 26.

3. Experimental results

Figure 2 presents the dependence of ion current density \( j_i \) on the probe surface at the beam axis at the probe distance \( x \) from grid 4 at nitrogen pressure \( p = 0.2 \) Pa, equivalent beam current \( I_b = 0.8 \) A and energy of molecules \( E_b \) ranging from 1 to 4 keV. The dashed curve presents \( j_i(x) \) at \( I_b = 0.8 \) A, \( E_b = 4 \) keV and gas pressures \( p = 0.5 \) Pa. As the plasma density \( n \) is proportional to the ion current density, the presented in Figure 2 distributions show that \( n \) reaches its maximum at distance \( x = 0.05–0.1 \) m from the grid surface and monotonically diminishes with a further increase of the distance.

![Figure 2](image)

**Figure 2.** Dependence of ion current density \( j_i \) at the beam axis at distance \( x \) between the probe and the grid at nitrogen pressure \( p = 0.2 \) Pa, beam equivalent current \( I_b = 0.8 \) A and energy of molecules \( E_b \) ranging from 1 to 4 keV, as well as at \( I_b = 0.8 \) A, \( E_b = 4 \) keV and \( p = 0.5 \) (dashed curve 5).

At the molecule energy of 1 keV, the axial distribution of plasma density \( n \) is highly nonuniform and exhibits a fourfold decrease in \( n \) when \( x \) is increasing from zero to 0.5 m. After the molecule
energy rises to 4 keV, the plasma nonuniformity does not exceed ±30%. At the same energy of fast molecules, the plasma density increases, when the nitrogen pressure $p$ rises from 0.2 Pa to 0.5 Pa.

The plasma density can be substantially increased and its homogeneity improved using a non-self-sustained glow discharge with electrostatic confinement of electrons [19] between chamber 1 and electrode 23 immersed in plasma 6 filling the chamber. Figure 3 presents dependences of current $I$ in the circuit of electrode 23 on its bias voltage $U$ at $p = 0.5$ Pa, beam current $I_b = 0.1$ A (solid curves), $I_b = 0.2$ A (dashed curves) and energy of molecules $E_b = 1$ (1), 2 (2) and 4 keV (3). When the voltage $U$ exceeds 20 V, current $I$ of non-self-sustained discharge and velocity $dI/dU$ both grow due to the gas ionization by electrons emitted by the chamber 1 and accelerated in the sheath 27 up to energy $eU$ exceeding the ionization threshold $E_i = 15.6$ eV of nitrogen [21]. At one and the same $U$ value velocity $dI/dU$ is rising when the beam equivalent current $I_b$ and/or its energy $E_b$ are growing (Figure 3). At $U > 150$ V electrons produce in the chamber more ions than fast neutral molecules of the beam.

![Figure 3. Current-voltage characteristics (CVC) of non-self-sustained discharge at $p = 0.5$ Pa, beam current $I_b = 0.1$ A (solid curves), $I_b = 0.2$ A (dashed curves) and energy of molecules $E_b = 1$ (1), 2 (2), 4 keV (3) and CVC of the self-sustained discharge (dash-dot curve) at $p = 0.5$ Pa.](image)

Dash-dot curve in Figure 3 presents current-voltage characteristic of self-sustained glow discharge between its anode 23 and chamber 1 playing the role of hollow cathode, when the beam source is switched off. It shows that only at the voltage $U$ exceeding 300 V the discharge supported by the beam does not expire after the beam source is switched off.

Radial distributions of ion current density $j_i$ in the discharge plasma demonstrate an increase of plasma density by an order of magnitude with increasing voltage $U$ of the non-self-sustained discharge and a decrease of plasma nonuniformity down to ±5%, which is quite suitable for the products nitriding.

Ten cutting plates 8 (Figure 1) made of high-speed steel were positioned in the center of chamber 1 on rotating table 7. They were heated by the beam of fast neutral nitrogen molecules with 4-keV energy and 0.4-A equivalent current up to 500 °C and soaked in plasma 6 of non-self-sustained discharge at voltage $U = 100$ V and nitrogen pressure $p = 0.5$ Pa. After the one-hour-long processing, the initial microhardness 860 HV of the plates increased up to 1350 HV. Usual for plasma immersion ion nitriding increase of the mean radius of cutting edges was not observed. On the contrary, the radius even decreased from 20±3 μm down to 17±3 μm.

4. Discussion

The data presented above prove that injection of a broad beam of fast neutral nitrogen molecules into a vacuum chamber results in production of quite nonuniform plasma. The plasma density grows with the
beam equivalent current, energy and nitrogen pressure. This fact reveals the leading role of fast neutral molecules in gas ionization. At an adequate pressure, the current of ions produced by fast molecules [20] may exceed two times and more equivalent current of the beam.

Nonuniformity of the beam-produced plasma can be readily improved using non-self-sustained glow discharge with electrostatic confinement of electrons [19]. At the discharge voltage $U$ exceeding 150 V fast electrons many times return back to the cathode sheath 27 and produce therein new electrons capable of ionizing the gas. Multiplication of fast electrons in the cathode sheath [14] is the basic process of electrostatic trap effect in glow discharge. It results in ionization intensity growth, plasma density increase by an order of magnitude and its nonuniformity decrease to ±5%.

Figure 4. Scheme of the knife sputtering in homogeneous plasma.

1 and 6 – knifes; 2 – plasma; 3 – ions; 4 – positive space charge sheath; 5 – sputtered by ions knife surface in three equal time intervals; 7 – fast molecules; 8 – the knife surface sputtered by fast molecule beam in three equal time intervals.

Figure 4 can explain why the radius of cutting edge does not increase after nitriding in beam-produced plasma. When steel knife 1 is immersed in homogeneous plasma 2 and negatively biased, it is heated by ions 3 extracted from plasma 2 and accelerated in sheath 4 of positive space charge. At a bias voltage of 100–1000 V, the sheath width exceeds 1 mm. For this reason, the radius of cutting edge ~10 μm is hundred times lower than the radius of plasma surface surrounding the knife-edge and current density of ions sputtering the edge is hundred times higher than on the rest surface of the knife. Intensive sputtering results in a substantial increase of the edge radius. On the contrary homogeneous sputtering of the knife by fast molecules results in a decrease of the edge radius.

5. Conclusion

Nitrogen plasma can be produced inside a working vacuum chamber by the injection of a broad fast neutral molecule beam. In contrast to conventional plasma immersion ion nitriding, the above new method of tool strengthening in plasma produced by a broad beam of fast neutral molecules results in sharpening of the tools instead of blunting.

References
[1] Grigoriev S and Metel A 2004 Plasma- and beam-assisted deposition methods Nanostructured thin films and nanodispersion strengthened coatings ed A A Voevodin, A A Shantsky and E A Levashov (Boston, Dordrecht, London: Kluwer Academic Publishers) pp 147–154
[2] Zhitomirsky V N, Grimberg I, Rapoport L, Boxman R L, Travitzky N A, Goldsmith S and Weiss B Z 2000 Surf. Coat. Technol. 133-134 114
[3] Boxman R L and Zhitomirsky V N 2006 Rev. Sci. Instrum. 77 (2006) 021101/1
[4] Musil J, Rajsky A, Bell A J, Matous J, Cepera M and Zeman J 1996 J. Vac. Sci. Technol. A 14 2187
[5] Boxman R L, Zhitomirsky V N, Alterkop B, Gidalevich E, Beilis I, Keidar M and Goldsmith S 1996 Surf. Coat. Technol. 86-87 243
[6] Musil J, Lestina J, Vleck J and Tolg T 2001 J. Vac. Sci. Technol. A 19 420
[7] Grigoriev S N, Melnik Yu A, Metel A S, Panin V V and V.V. Prudnikov V V 2009 Instrum. Exp. Tech. 52 731
[8] Veprek S, Mannling H D, Karvankova P and Prochazka J 2006 Surf. Coat. Technol. 200 3876
[9] Veprek S 2013 J. Vac. Sci. Technol. A 31 050822/1
[10] Avelar-Batista J C, Spain E, Housden J, Matthews A and Fuentes G G 2005 Surf. Coat. Technol. 200 1954
[11] Grigoriev S N, Metel A S and Fedorov S V 2012 Met. Sci. Heat Treat. 54 8
[12] Metel A 2002 Surf. Coat. Technol. 156 38
[13] Metel A S, Grigoriev S N, Melnik Yu A and Prudnikov V V 2011 Plasma Phys. Rep. 37 628
[14] Metel A S 1985 Sov. Phys.–Tech. Phys. 30 1133
[15] Metel A S 1986 Sov. Phys.–Tech. Phys. 31 1395
[16] Metel A S, Grigoriev S N, Melnik Yu A and Bolbukov V P 2012 Instrum. Exp. Tech. 55 122
[17] Metel A S 2012 Plasma Phys. Rep. 38 254
[18] E.W. McDaniel E W 1964 Collision phenomena in ionized gases (New York, London, Sydney: John Wiley & Sons, Inc)
[19] Metel A S, Melnik Yu A and Panin V V 2011 Plasma Phys. Rep. 37 357
[20] A.V. Phelps A V 1991 J. Phys. Chem. Ref. Data 20 557
[21] Massey H S W, Burhop E H S 1952 Electronic and ionic impact phenomena (Oxford: Clarendon Press)
[22] Kaminsky M 1965 Atomic and ionic impact phenomena on metal surfaces (Berlin, Heidelberg, New York: Springer–Verlag)

Acknowledgements
This project was supported by Grant No. 14-29-00297 of the Russian Science Foundation.