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ARTICLE

Influence of Microstructure and Stress State on Service Performance of TiN Coatings Deposited by Dual-Stage HIPIMS

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Abstract: TiN coatings were prepared by the novel dual-stage high power impulse magnetron sputtering (HIPIMS) technique under different deposition time conditions, and the effects of microstructure and stress state at different coating growth stages on the mechanical, tribological, and corrosion resistance performance of the coatings were analyzed. Results show that with the prolongation of deposition time from 30 min to 120 min, the surface structure of TiN coating exhibits a round cell structure with tightly doped small and large particles, maintaining the atomic stacking thickening mechanism of deposition-crystallization-growth. When the deposition time increases from 90 min to 120 min, the coating thickness increases from 3884 nm to 4456 nm, and the stress state of coating undergoes the compression-tension transition. When the deposition time is 90 min, TiN coating structure is dense and suffers relatively small compressive stress of −0.54 GPa. The coating has high hardness and elastic modulus, which are 27.5 and 340.2 GPa, respectively. Meanwhile, good tribological properties (average friction coefficient of 0.52, minimum wear rate of 1.68×10^{-4} g/s) and fine corrosion resistance properties (minimum corrosion current density of 1.0632×10^{-8} $A\cdot cm^{-2}$, minimum corrosion rate of 5.5226×10^{-5} $mm\cdot A^{-1}$) can also be obtained for the coatings.

Key words: dual-stage HIPIMS; TiN coatings; stress; service performance

Transition metal nitride hard coatings, such as TiN, are widely used in many industries due to their excellent performance[1], especially in the precise instruments and devices. As a substrate protective layer, intact structure must be maintained during the service in order to ensure the reliability of device, equipment, etc[2–3]. Coating failure may result in enormous damage, and the most common forms of failure include cracking, peeling, delamination, etc. It was reported that high residual stress was the main cause of coating bonding failure[4–5]. The residual stress is usually closely related to the microstructure, which is determined by the characteristics of preparation techniques. Therefore, the microstructure and residual stress state determine the service performance of coatings[6–8]. One of the common shortcomings of traditional magnetron sputtering and high power impulse magnetron sputtering (HIPIMS) techniques is that the residual stress of the prepared coating is high, which promotes the peeling and fracture of coatings during long-term service, seriously affecting the practical application in industrial engineering[9–10].

Through in-depth analysis of HIPIMS principles, it is known that high power pulsed glow discharge has the dual nature. The advantage is that high power pulsed glow discharge can be used to achieve high ionization deposition of the plating material, which improves the coating microstructure and enhances the mechanical properties[11]. The disadvantage is that the generation of high-density plasma inevitably requires extremely high voltage (nearly kilovolts) or extremely high power, according to the principle of high

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voltage induced atomic ionization. On the one hand, the ionized plating material in the cathode sheath area of the target surface is easily attracted by the negative high voltage and then returns to the target surface, causing serious loss of plating material. On the other hand, the discharge duty cycle is at a low efficiency level (below 5%), which seriously affects the deposition rate of the coatings[12].

Therefore, the concept of dual-stage high power pulsed electric field is proposed. The electric field is designed as a stepped dual-stage high power pulsed electric field with intensity variation from weak stage to strong stage[13] and the duty cycle from 10% to 100%. In the weak ionization stage, lower power causes Ar to undergo initial ionization, forming low-density plasma within the vacuum chamber. In the strong ionization stage, high power further ionizes the atoms, forming high-density plasma. The pre-ionization effect generated during the weak ionization stage can significantly reduce the voltage of the high-density plasma generated during the strong ionization stage, decrease the return probability of the coated particles to the target surface by electric field, and avoid the loss of coated material. In addition, pre-ionization has a certain reducing effect on residual stress in the coating. With the significant increase in target current, the intensity and frequency of Ar^+ bombardment on the target surface during the strong ionization stage are increased significantly, and the collision ionization rate of the plating material and the deposition rate of the coating are also greatly increased. High ionization rate during deposition of HIPIMS materials and high-speed deposition[14–15] are expected to be simultaneously achieved.

In this research, the novel dual-stage HIPIMS technique was used to prepare TiN coatings under different deposition time conditions. The influence and mechanism of microstructure and stress state at different coating growth stages on the mechanical properties, tribological properties, and corrosion resistance of the coatings were analyzed. This research is of great significance to evaluate the quality, service life, and practical application of the coatings in the industrial fields.

1 Experiment

The experiment adopted a self-developed dual-stage high power impulse supply system (peak power of 12 kW, duty cycle of 10%–100%) coupled with MSIP-019 unbalanced closed field magnetron sputtering host equipment (vacuum chamber size of Φ450 mm×400 mm) for coating preparation. By changing the deposition time, TiN coatings were deposited on the surfaces of M2 high-speed steel sheets and monocrystalline silicon sheets with the target substrate distance of 130 mm and workpiece frame speed of 5 r/min. The detailed experiment parameters are shown in Table 1. The microstructures of the coating surface and cross-section were observed by SM-6700F scanning electron microscope (SEM) and JEM-3010 transmission electron microscope (TEM). The three-dimensional morphology and roughness of the coating surface were characterized by SPI3800-SPA-400 atomic force microscope (AFM). X-ray diffractometer (XRD)-$\sin^2\varphi$ fit method was used to calculate the residual stress of coatings. The hardness and Young's modulus of the coating samples were tested by the G200 nano-indentation instrument. The friction and wear performance of the coatings was tested by the friction and wear testing machine. The Correst-CS350 electrochemical test system was used to characterize the corrosion resistance of the coatings. The polarization curve characteristics of the samples in 3.5wt% NaCl corrosive medium were measured by potentiodynamic scanning method, and the obtained polarization curves were fitted using C-view software.

2 Results and Discussion

2.1 Microstructure

Fig. 1 shows the surface microstructures of TiN coatings prepared by dual-stage HIPIMS under different deposition time conditions. With the prolongation of deposition time, the particle morphology on the coating surface presents a densely doped circular cell structure with tight bonding between particles and no obvious defects can be observed. When the deposition time increases to 120 min, the coating still maintains the circular cell growth characteristics, and these particles are tightly arranged together, showing a certain protrusion. Besides, it is found that these protrusions are formed by the aggregation of several smaller clusters. The presence of these protrusions inevitably cause gaps, which

Table 1 Dual-stage HIPIMS deposition parameters for TiN coating preparation

Parameter	Value
Deposition time/min	30, 60, 90, 120
Target peak current, I_p/A	2.2, 20.0
Pulse conduction width in weak ionization stage, T_{on}'/ms	2
Pulse conduction width in strong ionization stage, T_{on}''/ms	4
Pulse turn-off width, T_{off}/ms	8
Target voltage, U_t/V	220, 525
Bias voltage, U_s/V	−60
N_2 flow/mL·min^{-1}	20
Ar flow/mL·min^{-1}	60
Chamber temperature, T_s/°C	50, 55, 62, 70

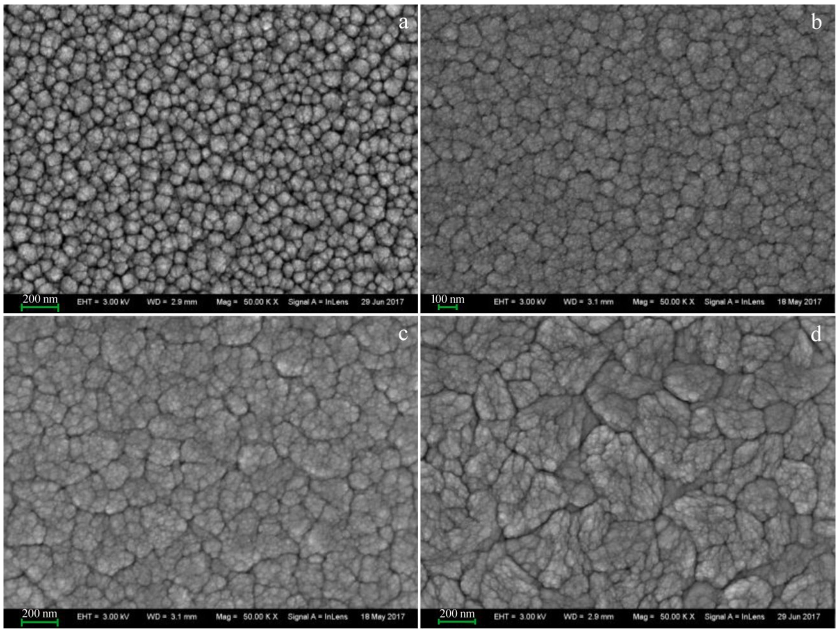

Fig.1 SEM surface microstructures of TiN coatings under different deposition time conditions: (a) 30 min, (b) 60 min, (c) 90 min, and (d) 120 min

slightly reduces the coating density, but the overall quality of coating is good.

The three-dimensional morphologies and roughness R_a of TiN coating surfaces are detected by AFM , as shown in Fig.2. Significant differences can be observed in the three-dimensional morphologies and through the roughness analysis of TiN coating surfaces under different deposition time conditions. When the deposition time is 30 min, the three-dimensional morphology of the coating surface presents sharp and small mountain peaks with many grooves between the peaks. The surface roughness of the coating is 16 nm. When the deposition time is 60 and 90 min, the three-dimensional morphologies of the coating surfaces still show the mountain peak shape, but the mountain peak structure gradually widens, indicating the increase in the average particle size of the coating surface. There are still obvious grooves between the peaks, and the roughness slightly increases: R_a becomes 22 and 27 nm when the deposition time is 60 and 90 min, respectively. Therefore, it can be concluded that during the relatively short deposition, the coating is mainly deposited as island-like manner with significant voids. With the further prolongation of deposition time to 120 min, the coating surface exhibits a slightly larger sand dune-like structure with dense clusters and reduced gullies between the sand dune-like structures. The surface roughness slightly increases (R_a=35 nm). Under the dual pulse electric field, with the prolongation of deposition time, the growth mode of the coatings gradually changes from island-like growth to island-layered growth, and the surface of the deposited coating is relatively flat with the maximum roughness of 35 nm.

The crystal structures of the TiN coatings after deposition for 30 and 120 min are analyzed by high-resolution TEM and selected area electron diffraction (SAED) analysis, as shown in Fig. 3. When the deposition time is 30 min, the crystallization degree of the coating is low, and discontinuous multi-round bright spots can be observed in the corresponding SAED pattern. When the deposition time is 120 min, a large number of complete lattice stripes with clear arrangement can be observed along different lattice directions. The corresponding SAED pattern shows the center-symmetric multi-circular bright ring. DM software was used to perform fast Fourier transform on the selected area I and area II in Fig. 3b. The calculated interplanar spacing d_{I} and d_{II} is 0.245 and 0.147 nm, respectively. Corresponding to the lattice constants of TiN (111) and TiN (220) crystal planes, the crystal during the coating growth exhibits a typical polycrystalline structure. The growth process of the coating is closely related to the characteristics of the dual-stage pulse electric field and the deposition time. The strong ionization stage has the instantaneous strong current characteristic, and the strongly ionized particles have intense activity on the substrate surface, promoting the polycrystalline growth of the coating and thereby leading to the coating preferential orientation along the polycrystalline plane direction. When the deposition time is short (30 min), the deposited particles do not have enough time to grow and diffuse, resulting in a lower degree of crystallization. With the prolongation of deposition time, the influence of electric field on the growth process of the coating is enhanced. The coating material has three characteristics to promote the optimal growth of polycry-stalline planes in the coating.

2.2 Residual stress

Fig. 4 shows the average thickness and residual stress of TiN coatings under different deposition time conditions. The coating thickness is 1220, 2535, 3884, and 4456 nm when the deposition time is 30, 60, 90, and 120 min, respectively. When the deposition time increases from 30 min to 90 min, the coating thickness is increased linearly. When the deposition

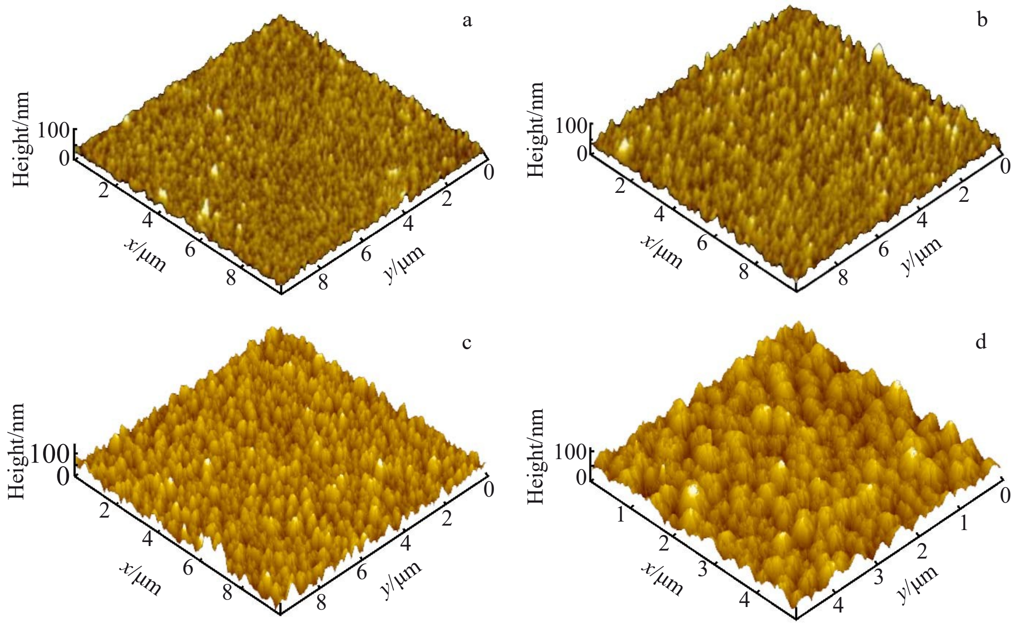

Fig.2 AFM three-dimensional morphologies of TiN coatings under different deposition time conditions: (a) 30 min, (b) 60 min, (c) 90 min, and (d) 120 min

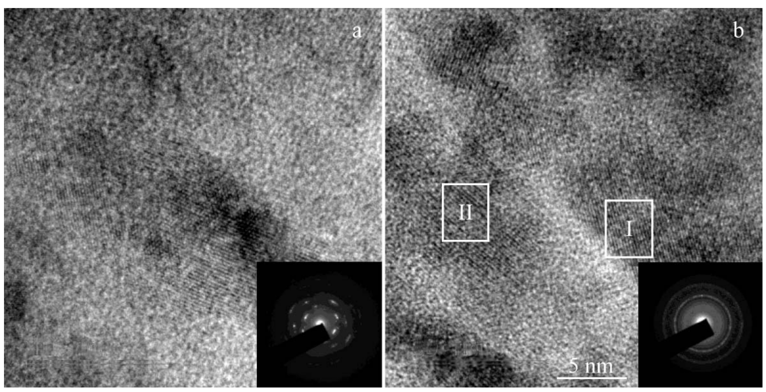

Fig.3 High-resolution TEM images with corresponding SAED patterns of TiN coatings after deposition for 30 min (a) and 120 min (b)

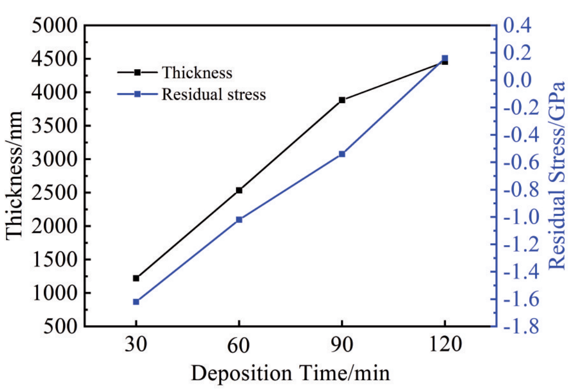

Fig.4 Thickness and residual stress of TiN coatings under different deposition time conditions

time continues to increase to 120 min, the increment of coating thickness significantly decreases. When the deposition time increases from 30 min to 90 min, the residual stress exhibits the compressive stress. When the deposition time is 30 min, the highest compressive stress of the coating is about −1.62 GPa. When the deposition time increases to 90 min, the minimum compressive stress of the coating is about −0.54 GPa. When the deposition time continues to increase to 120 min, it is evident that the residual stress is transformed into tensile stress of about 0.16 GPa. With the prolongation of deposition time, the residual stress of the coating changes from compressive stress to tensile stress, resulting in the compression-tension transition phenomenon of the coating stress state, namely the coating thickening effect[16].

The residual stress changes during the coating growth process. The initial atomic shot peening effect during the coating growth under the dual-stage pulse electric field is the main control mechanism for stress. The energetic particle flow composed of rebounding working gas atoms and sputtering atoms will generate significant compressive stress on the growth interface of the coating. With the prolongation of deposition time, the atomic shot peening effect is not sufficient to continuously generate significant compressive stress during the coating growth process. When the coating grows to a certain extent, the recovery effect surpasses the atomic shot peening effect and becomes the dominant mechanism. The deposition process of the coating is non-equilibrium, and the stress state is closely related to the coating microstructure. During the deposition process of coatings, the surface diffusion time obtained by the deposited atoms may not be long enough to keep the atoms at lattice positions with the lowest energy, resulting in the formation of a metastable structure with lower degree of order. During the recovery process, the elimination of point defects, surface defects, and atoms with ordered arrangement usually accompanies the elimination of void defects, thereby promoting the volume shrinkage and densification. This process also generates tensile stress, and thicker coatings often have more voids and defects. Therefore, when the coating thickness exceeds a certain critical value, the recovery effect dominates.

2.3 Mechanical properties

The mechanical properties of TiN coatings are important factors to evaluate the service life of coatings[19]. The nano-indentation was used to characterize the hardness and elastic modulus of the coatings with an indentation depth of 1/10 of the coating thickness, and the multi-point averaging method was used for calculation. The hardness and Young's modulus results are shown in Fig.5. With the prolongation of deposition time, the hardness and elastic modulus (Young's modulus) of TiN coatings are firstly increased and then decreased. When the deposition time is 90 min, the hardness and elastic modulus of the coating are the highest as 27.5 and 340.2 GPa, respectively. When the deposition time is 120 min, although the coating thickness is relatively large, there are still some obvious defects, such as protrusions and voids, in the coating, which reduce the hardness and elastic modulus of the coating.

2.4 Tribological properties

Fig.6 shows the friction coefficient curves of TiN coatings under different deposition time conditions. It can be seen that the friction coefficient of TiN coatings gradually enters a gentle stage after a rapid rise during the friction and wear process, and eventually reaches a stable stage. The average friction coefficient in the stable stage represents the friction coefficient[20] for analysis. With the prolongation of deposition time, the average friction coefficients of TiN coatings are 0.60, 0.56, 0.52, and 0.53 when the deposition time is 30, 60, 90, and 120 min, respectively, showing the variation trend of first decreasing and then slightly increasing. The friction coefficient is mainly related to the characteristics of the coating material and surface roughness. There is no significant difference in surface roughness of the coatings under different deposition time conditions in this research: R_a of all samples are below 50 nm. Therefore, the characteristics of the coating material play an important role in the sliding friction coefficient, such as surface defects and crystal structure. The less the surface defects, the more uniform the crystal structure, and the smaller the friction coefficient.

Fig. 7 shows the wear rate of TiN coatings under different deposition time conditions. When the deposition time is 90 min, the minimum wear rate of the coating is obtained as 1.68×10^{-4} g/s. When two objects in relative motion come into contact, friction occurs and inevitably causes wear and tear. The wear resistance of the coatings in this research is mainly related to the hardness, coating thickness, and residual stress. In a certain range, the thicker the coating, the higher the

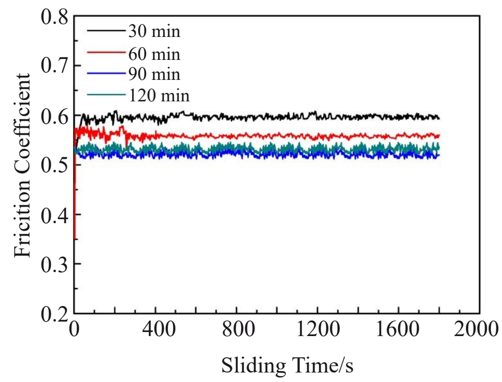

Fig.6 Friction coefficient curves of TiN coatings under different deposition time conditions

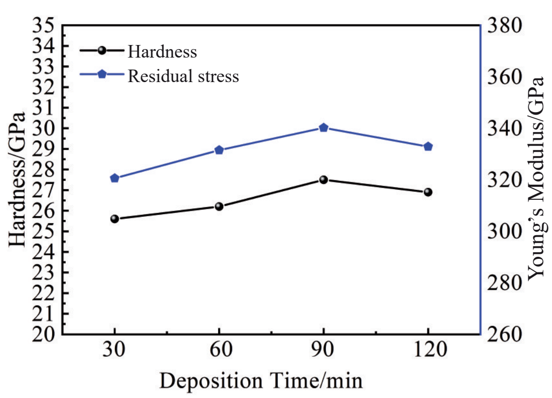

Fig.5 Hardness and Young's modulus of TiN coatings under different deposition time conditions

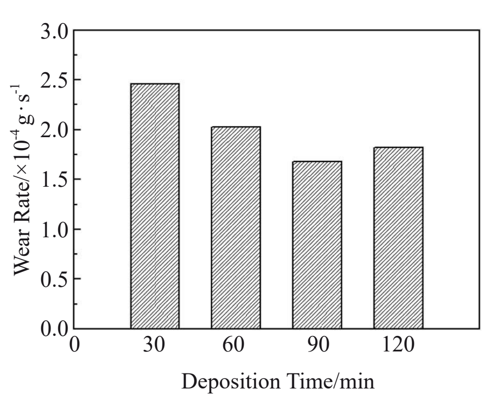

Fig.7 Wear rates of TiN coatings under different deposition time conditions

hardness, and the better the wear resistance.

2.5 Corrosion resistance

The electrochemical polarization curves of TiN coatings under different deposition time conditions are shown in Fig.8. The electrochemical parameters of the polarization curves are fitted by C-View software to obtain the corrosion potential (E_{corr}), corrosion current density (i_{corr}), and corrosion rate (v_{corr}), as shown in Table 2.

With the prolongation of deposition time, the corrosion current density and corrosion rate of TiN coatings are firstly decreased and then slightly increased. When the deposition time is 90 min, the corrosion current density and corrosion rate are the smallest as 1.0632×10^{-8} A·cm^{-2} and 5.5226×10^{-5} mm·A^{-1}, respectively, indicating the optimal corrosion resistance. According to the corrosion mechanism of the coating, the defects, such as micropores and voids, in the coating structure may lead to penetration of corrosion solution components into the substrate by capillary force, forming a corrosion channel and causing the initial corrosion at the interface between coating and substrate[21–22]. During the corrosion process, hydrogen gas is continuously released due to hydrogen evolution reaction and it accumulates at the interface between coating and substrate, generating high pressure and thereby promoting the pore formation as well as the coating peeling phenomenon. The schematic diagram of corrosion process of TiN coating is shown in Fig.9. It can be seen that the corrosion resistance of the coating is closely related to the density and thickness[23]. A coating with denser microstructure, less defects, and larger thickness can effectively hinder the contact, diffusion, and reactions between the corrosion solution and coating, which improves the corrosion resistance of the coating[24–25]. Therefore, when the deposition time is 90 min, the corrosion resistance of the coating is optimal.

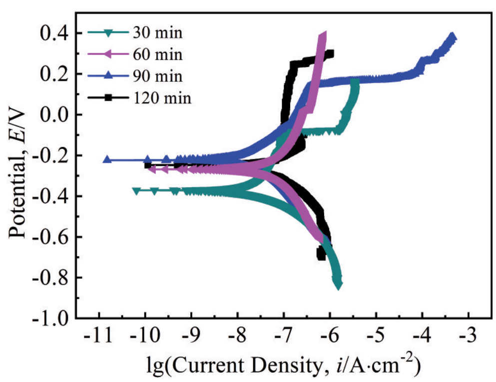

Fig.8 Electrochemical polarization curves of TiN coatings under different deposition time conditions

Table2 Electrochemical test results of TiN coatings under different deposition time conditions in 3.5wt% NaCl solution

Deposition time/min	E_{corr}/V	i_{corr}/ $\times10^{-8}$ A·cm^{-2}	v_{corr}/mm·A^{-1}
30	−0.375 82	2.068 9	$1.334\ 4\times10^{-4}$
60	−0.328 30	1.140 5	$1.083\ 1\times10^{-4}$
90	−0.224 35	1.063 2	$5.522\ 6\times10^{-5}$
120	−0.241 13	1.135 4	$5.921\ 7\times10^{-5}$

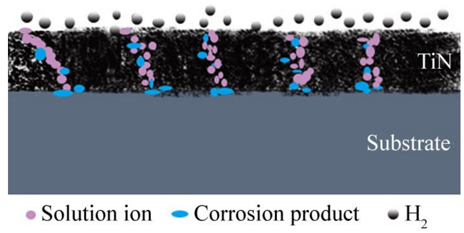

Fig.9 Schematic diagram of corrosion mechanism of TiN coating

3 Conclusions

1) TiN coatings are prepared by the novel dual-stage HIPIMS technique under different deposition time conditions. With the increase in coating thickness, the surface structure of TiN coating shows a round cell structure with tightly doped particles of different sizes, maintaining the atomic stacking thickening mechanism of deposition crystallization growth.

2) With the prolongation of deposition time from 30 min to 90 min, the residual stress of the coating is compressive stress, and the compressive stress is gradually decreased. When the deposition time further increases to 120 min, the residual stress is tensile stress, indicating that the coating undergoes the compression-tension transition, which is mainly caused by the change in the dominant mechanism during the deposition process of the coating.

3) When the deposition time is 90 min, the coating has the highest hardness value, good tribological resistance, and fine corrosion resistance, indicating that the dense structure and low compressive stress are beneficial to improve the service performance of TiN coatings.

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微观结构与应力状态对双级HIPIMS沉积TiN镀层服役性能的影响

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摘　要：利用新型双级高功率脉冲磁控溅射（HIPIMS）技术在不同沉积时间条件下制备TiN镀层，分析不同镀层生长阶段其微观结构与应力状态对镀层力学、摩擦、耐腐蚀等服役性能的影响。结果表明，随着沉积时间由30 min增加至120 min，TiN镀层表面结构均呈大小颗粒紧密掺杂的圆胞状结构，始终保持沉积-结晶-生长的原子堆积增厚机制；当沉积时间由90 min（镀层厚度3884 nm）增加至120 min（镀层厚度4456 nm）时，镀层应力状态出现压-拉转变。当沉积时间为90 min时，TiN镀层结构致密且受到较小的压应力（−0.54 GPa），镀层具有较高的硬度与弹性模量（27.5、340.2 GPa）、较好的摩擦学性能（平均摩擦系数0.52，最小磨损率1.68×10^{-4} g/s）及较好的耐腐蚀性能（最小腐蚀电流密度1.0632×10^{-8} $A\cdot cm^{-2}$、最小腐蚀速率5.5226×10^{-5} $mm\cdot A^{-1}$）。

关键词：双级HIPIMS；TiN镀层；应力；服役性能

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