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ARTICLE

Microstructure and Tribological Properties of CrN Films Deposited by Direct Current Magnetron Sputtering

Ren Xingrun[1], Zhang Qinying[1], Huang Zhu[1], Su Wei[2], Yang Jiangao[2,3], Chen Hao[1,2,3]

[1] Jiangxi University of Science and Technology, Ganzhou 341000, China; [2] Engineering Research Center of High-efficiency Development and Application Technology of Tungsten Resources, Ministry of Education, Ganzhou 341000, China; [3] Central South University, Changsha 410083, China

Abstract: CrN films were deposited on 304 stainless steel by DC reactive magnetron sputtering. The effects of nitrogen flow on the microstructure, mechanical and tribological properties were characterized by X-ray diffraction, scanning electron microscopy, atom force microscope, microhardness, wear tester and Nanomap 500LS profile. The results show that with the increase of nitrogen flow, the CrN films exhibit a preferential orientation in the (200) direction. The deposition rate of CrN films decreases with the increase of nitrogen flow. Besides, the surface roughness decreases first and then increases with further increase of nitrogen flow. As nitrogen flow increases from 15 cm^3/min to 30 cm^3/min, microhardness HV is improved from 5273 MPa to 10422 MPa, and then decreases to 9180 MPa when the nitrogen flow further increases to 35 cm^3/min. Wear test results show that the CrN films deposited at nitrogen flow of 30 cm^3/min achieve minimum friction coefficient value of 0.93 and wear rate 2.02×10^{-15} $m^3\cdot(N\cdot m)^{-1}$, which present best wear resistance performance.

Key words: magnetron sputtering; CrN films; microstructure; tribological property

Nowadays, CrN films are widely used in cutting tools and mechanical parts due to their high hardness, wear resistance and oxidation resistance[1-3]. These films are generally prepared by physical vapor deposition techniques, among which direct current magnetron sputtering has attracted considerable interest[4,5]. What is more, CrN films can significantly improve the drilling performance and extend the service life of the cutting tool[6,7]. However, the development of industry has came up with high performance for films to satisfy the more stern machining conditions. Therefore, the attention have been paid to improving the mechanical and tribological properties and developing new coatings by optimizing the growth morphology to obtain the needed microstructure at deposition process[8,9].

It is well known that the deposition parameters, such as the pressure, target power, nitrogen flow and so forth, have a considerable influence on the microstructure and properties[10-14]. Daniel et al. [15] reported a way to control the microstructure of CrN films deposited onto Si (100) substrates, which showed a preferred (111) growth orientation. Zhang et al.[16] reported that substrate bias and nitrogen flow have an effective influence on microstructure and mechanical properties. Kalsoom[17] reported that CrN films deposited on AISI-304 stainless steel by DC magnetron sputtering presented the maximum film thickness (755 nm) and hardness HV (11820 MPa) at 150 W input power and 5% nitrogen contents. The above results show that careful control of the deposition parameters is crucial for optimizing the properties of the CrN films.

We are interested in the differences on the behavior of films grown and tribological properties deposited on 304 stainless steels under different nitrogen flow. Although there are many reports on effects of nitrogen flow on CrN films[17-19], the relationship between the nitrogen flow and microstructure, surface roughness, mechanical properties and tribological behavior are worth systematic investigating. In the present

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Corresponding author: Chen Hao, Ph. D., Professor, School of Material Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China, E-mail: chenhao_168168@126.com

work, CrN films were deposited using direct current magnetron sputtering under various nitrogen flow. The microstructure, mechanical and tribological behavior were analyzed in detail.

1 Experiment

As the substrate, the 304 stainless steels (30 mm×30 mm×2 mm) were polished by the sandpapers and then ultrasonically cleaned in alcohol for 20 min. The CrN films were prepared by a magnetron sputtering system. In order to enhance the bonding force, the samples were deposited with Cr transitional layers before depositing the CrN films. Prior to deposition, the chamber was pumped down to a base pressure below 2×10^{-3} Pa. During films deposition, two chromium targets (purity>99.8%) were sputtered and then final deposition was conducted at a bias voltage of −300 V, target sputtering power of 150 W, substrate temperature of 200 °C, and the total pressure of sputtering gas was controlled at 3 Pa for Cr transitional layers and 0.5 Pa for CrN films. The flow rate of Ar (purity 99.99%) was 60 cm^3/min for the Cr transitional layer and 40 cm^3/min for CrN films.

The crystallographic structure of the films was characterized by X-ray Diffraction. The surface morphologies of films were analyzed by Scanning Electron Microscopy. The thickness of the films was measured by interface morphologies which was used to calculate deposition rate via the corresponding deposition time. The surface roughness was measured by AFM with a 10 μm×10 μm measurement area. The microhardness was measured by Digital microhardness tester: load of 10 g, dwell time 10 s. The microhardness test were conducted three times under the same condition to enhance the reliability and reproducibility of the experimental results. Furthermore, the tribological property of CrN films were measured by wear tester against with a diameter of 3 mm Si_3N_4 ball and Nanomap-500Ls contact surface profiler, and the parameters were as follows: load of 300 g; reciprocating length of 4 mm; reciprocating frequency 300 per minute.

2 Results and Discussion

2.1 surface morphologies and deposition rate

Fig. 1 shows the surface morphologies of CrN films as a function of nitrogen flow. It is clear that the nitrogen flow has a significant effect on the surface morphology. As can be observed, the films surface distributes the round particles of abnormal grain clusters. With the increase of nitrogen flow from 15 cm^3/min to 30 cm^3/min, the films become more uniform and compact with fewer and smaller particles. The defects on the surface decrease as well. However, further increasing of the nitrogen flow causes an increase of particles of abnormal grain clusters. In case of 35 cm^3/min, the film surface is relatively compact. However, it presents more particles than it when nitrogen flow is 30 cm^3/min. It is consistent with the result of AFM as shown in Fig. 2. The surface roughness first decreases from 11.7 nm to 4.77 nm, and then increases to 10.4 nm when further increase the nitrogen flow. The phenomenon can be explained by the following reasons. On the one hand, increasing the nitrogen flow will increase the N content in chamber room which react with Cr ions in proper condition resulting in uniform and compact films in surface. On the other hand, increasing the nitrogen flow also increases the number of plasma which will increase the plasma collision frequency and decrease the mean

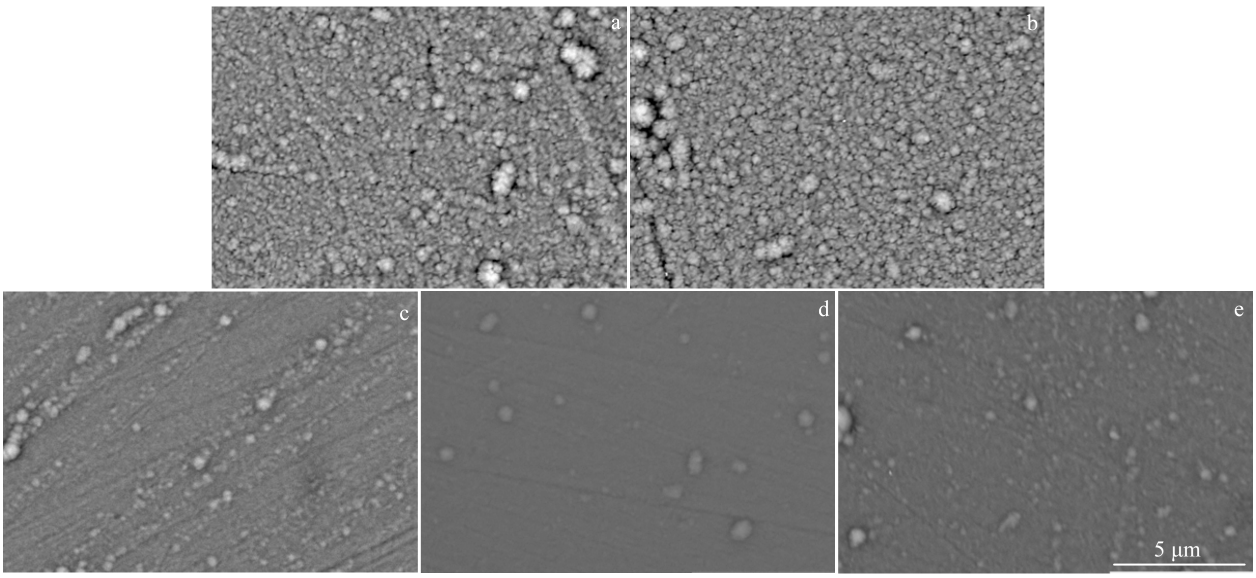

Fig. 1 Surface morphologies of CrN films at different nitrogen flow: (a) 15 cm^3/min, (b) 20 cm^3/min, (c) 25 cm^3/min, (d) 30 cm^3/min, and (e) 35 cm^3/min

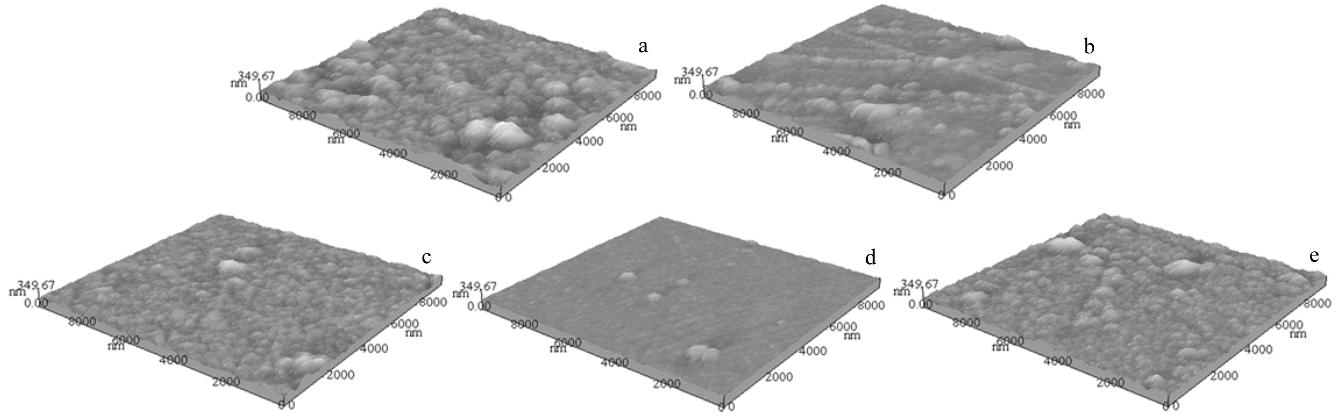

Fig.2 AFM images and roughness of CrN films at different nitrogen flow: (a) 15 cm^3/min, R_a=11.7 nm; (b) 20 cm^3/min, R_a=10.7 nm; (c) 25 cm^3/min, R_a=6.53 nm; (d) 30 cm^3/min, R_a=4.77 nm; (e) 35 cm^3/min, R_a=10.4 nm

free paths of gas particle. It has been reported that the decrease of mean free paths also means less energy and momentum delivery on the substrate leading to less extent of surface damage[18]. Besides, further increasing the nitrogen flow will lead to serious target poisoning which is not beneficial to forming uniform and compact films[20].

Fig.3 shows the deposition rate of CrN films as a function of nitrogen flow. The deposition rate decreases markedly with the increase of the nitrogen flow in this work. As shown in Fig.3, the deposition rate of CrN films decreases from 15.11 nm/min to 9.33 nm/min when the nitrogen flow increases from 15 cm^3/min to 30 cm^3/min. In the deposition process, increasing the nitrogen flow will increase the nitrogen partial pressure which increases the probability of atomic collision and then decreases the deposition rate. However, the main reason of it is target poisoning level. Previous literature reported[21,22] that the relationships between nitrogen partial pressure and deposition rate deposited by magnetron sputtering. When some nitrogen is introduced into the vacuum chamber, CrN will be formed on the target surface. Hence, with the increase of nitrogen flow, the state of target surface can be assumed from metal surface to "mixed" metal-nitride surface, and then be fully covered by CrN which indicates the target is fully poisoned[10]. What is more, CrN has a lower sputtering rate than pure metals. Therefore, based on the above results, the deposition rate will decrease and become a constant with the increase of nitrogen flow, as shown in Fig.3.

2.2 Microstructure and mechanical properties

Fig.4 shows the XRD patterns of CrN films as a function of nitrogen flow. Diffraction peaks corresponding to the (111), (200) and (220) planes for the cubic CrN structure are identified. These results are consistent with investigation performed by Ruden et al.[14,23] It is clear that the peaks tend to shift toward lower diffraction angles with the increase of nitrogen flow, which indicates the expansion of lattice constant by excess N atoms[24]. The diffraction patterns reveal a preferential orientation in the (200) direction. What is more, with the increase of nitrogen flow, the peak intensity of CrN (200) increases while the peak intensities of CrN (111) and

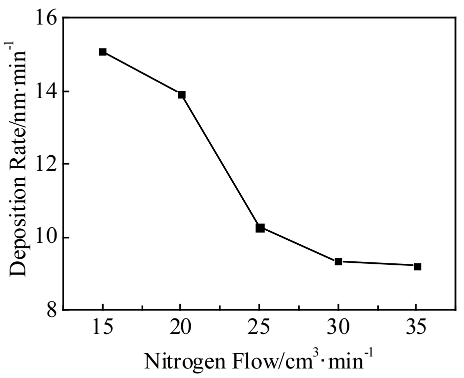

Fig.3 Deposition rate of CrN films as a function of nitrogen flow

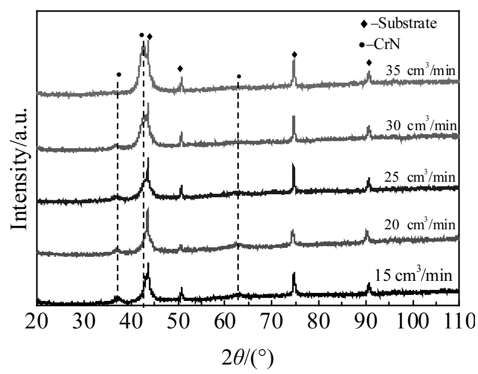

Fig.4 XRD patterns of CrAlN films at different nitrogen flow

(220) decrease. According to Ref. [25,26], the orientation of CrN (200) plane is the lowest surface energy of crystal plane in the films. Therefore, with the increase of nitrogen flow, the CrN (200) plane reveals a preferential orientation.

Fig.5 shows the microhardness versus nitrogen flow. It is clear that the microhardness first increases as the nitrogen flow varies from 15 cm^3/min to 30 cm^3/min, which is attributed to the increase of the ionized N atoms. However, microhardness decreases with further increase of nitrogen flow. The follow reason may contribute to this phenomenon. On the one hand, increasing the nitrogen flow will increase the nitrogen ion content in chamber room, which will provide the proper condition for forming the more uniform and compact CrN films. On the other hand, increasing the nitrogen flow results in the different levels of targets poisoning which will form a nitrided compound layer on the target surface and reduce the metal sputtering yield. References have reported the similar results[10,18]. Therefore, when the nitrogen flow increases to 35 cm^3/min, the microhardness presents a lower value than it when nitrogen flow is 30 cm^3/min.

2.3 Friction and wear properties

Fig.6 shows the friction coefficient versus wear time of the films sliding against Si_3N_4 ball in air. The evolution of friction coefficient is detected along the whole wear test. As shown in Fig.6, friction coefficient decreases from 1.3 to 0.93 as the nitrogen flow varies from 15 cm^3/min to 30 cm^3/min, then increases to 1.1 as further increase nitrogen flow to 35 cm^3/min. It is well known that the friction coefficient mainly depends on the surface roughness and mechanical properties of the films[27]. Due to the different surface roughness and mechanical properties, friction curves present different tendencies. As shown in Fig. 1, a large amount of particles are distributed on the surface which will hinder the friction pair of ceramic ball from sliding and it generates abrasive particles and debris which leads to the increase of friction fluctuation. Therefore, with the evolution of surface roughness and microhardness, the friction coefficient of films presents different values and tendencies, as shown in Fig.6. It can be seen from Fig.6 that the friction curve exhibits a minimum value and fluctuation when nitrogen flow is 30 cm^3/min with the lowest surface roughness and maximum microhardness.

Fig.7 shows the sectional profile of the wear tracks and wear rate of CrN films sliding against the Si_3N_4 ball. It can be seen from Fig.7 that the depth of tracks and wear rate decrease as nitrogen flow varies from 15 cm^3/min to 30 cm^3/min and then increase with further increasing nitrogen flow to 35 cm^3/min. Therefore, the depth of tracks and wear rate reach maximum values of 6.16 μm and 21.58×10^{-15} m^3/N·m, respectively when the nitrogen flow is 15 cm^3/min. Furthermore,

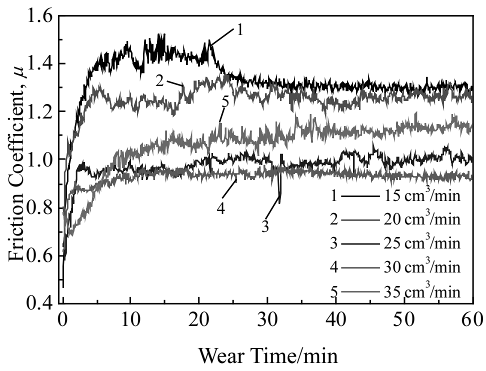

Fig.6 Friction and wear property of CrN films

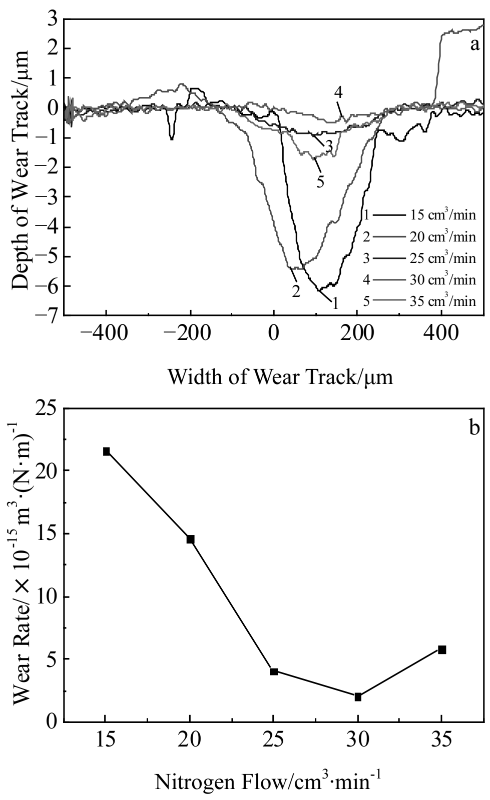

Fig.7 Sectional profile of the wear track (a) and wear rate (b) of CrN films

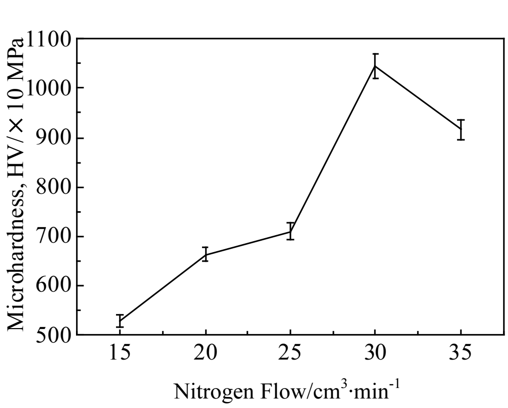

Fig.5 Impact of nitrogen flow on microhardness of CrN films

they reach minimum values of 0.49 μm and 2.02×10^{-15} m^3/N·m, respectively as the nitrogen flow is 30 cm^3/min. As shown in Fig. 7a, the maximum depth values of wear track exceed the thickness of films which indicates that the films couldn't play a protection role when the nitrogen flow is 15 and 20 cm^3/min. Therefore, when the nitrogen flow is 30 cm^3/min, the CrN films exhibit the best wear resistance due to the highest microhardness and lowest wear rate.

To further analyze the effects of nitrogen flow on the aar mechanism of CrN films, SEM images and 3D morphologies of wear track were presented in Fig. 8 and Fig. 9, respectively. It can be seen from Fig.8 that the films suffer serious damage when nitrogen flow is 15, 20, and 35 cm^3/min, especially at 15 and 20 cm^3/min, CrN films spall from the substrate, resulting in the films failure, as shown in Fig. 8a and Fig. 8b. Under the condition of contact stress for a long and regular time, the concave and convex peaks are detached from the films and crushed into fine abrasive. Abrasive wear along the sliding direction between the Si_3N_4 ball and films forms furrows under the contact stress which demonstrates that the abrasive wear dominates the main wear mechanism. However, as shown in Fig. 8e, the films suffer damage from the contact

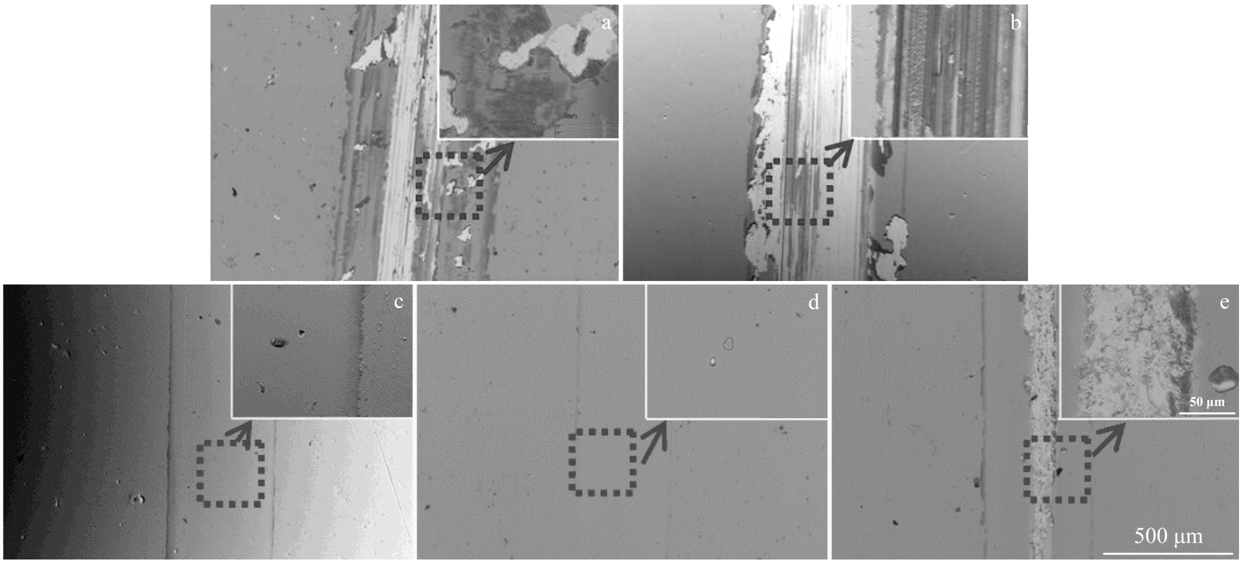

Fig. 8 Grinding crack of CrN films at different nitrogen flow: (a) 15 cm^3/min, (b) 20 cm^3/min, (c) 25 cm^3/min, (d) 30 cm^3/min, and (e) 35 cm^3/min

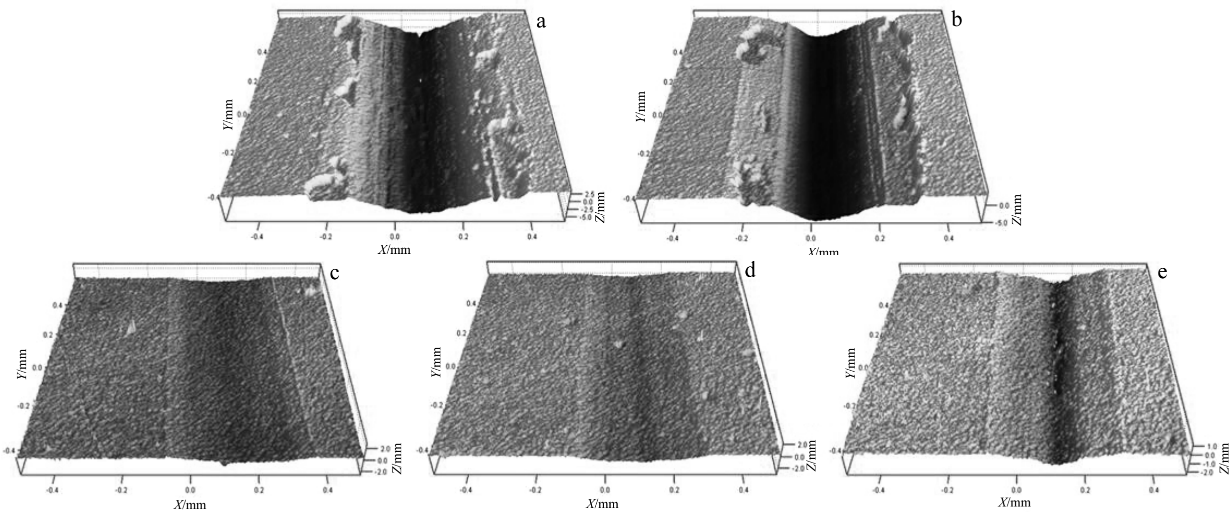

Fig. 9 3D morphologies of CrN films at different nitrogen flow: (a) 15 cm^3/min, (b) 20 cm^3/min, (c) 25 cm^3/min, (d) 30 cm^3/min, and (e) 35 cm^3/min surface under the contact stress which still play a protective role as the nitrogen flow is 35 cm^3/min. Due to the high contact stress and relatively lower surface roughness, the wear track present a distinct adhesion phenomenon in the central part of the wear track. Therefore, adhesive wear may dominate the wear mechanism when nitrogen flow is 35 cm^3/min. In case of 25 and 30 cm^3/min, the wear tracks exhibit smooth wear surface and no apparent damage occurs for both films which present better performance of wear resistance. With the higher microhardness and lower surface roughness, the particles distributed on the surface are easy to remove debris particulates from the contact surface under the contact stress which forms the more smooth surface[28]. In addition, Fig.9 shows the direct wear resistance of 3D morphologies of wear track corresponding to the CrN films as a function of nitrogen flow. The films deposited at 15 and 20 cm^3/min exhibit poor wear resistance. The track profiles are very wide and deep, which is attributed to the worn out film. However, the film deposited at 25 and 30 cm^3/min shows a relatively smooth worn surface. With the nitrogen further increasing, the wear track gets shallow. It is worth noticing that the film deposited at 15 cm^3/min has the roughest surface and lowest microhardness, which usually result in poor wear resistance. Based on the above analysis, the CrN films exhibit the best wear resistance when nitrogen flow is 30 cm^3/min.

3 Conclusions

1) The grain clusters are distribute on the CrN films prepared by direct current magnetron sputtering surface, which demonstrates that the growth is a typical island mode.

2) The surface roughness decreases with the increasing of nitrogen flow and then increases when further increasing nitrogen flow; the deposition rate decreases with the increasing of nitrogen flow.

3) The main phase is fcc-CrN and a preferential orientation in the (200) direction with the increasing of nitrogen flow. In contrary to the surface roughness, the microhardness of films increases first and then decrease with the increasing of nitrogen flow.

4) The films present minimum friction coefficient and wear rate values of 0.93 and 2.02×10^{-15} m^3/N·m, respectively when the nitrogen flow is 30 cm^3/min .

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直流溅射沉积 CrN 薄膜组织结构与摩擦性能分析

任兴润[1]，张钦英[1]，黄　柱[1]，苏　伟[2]，羊建高[2,3]，陈　颢[1,2,3]

(1. 江西理工大学，江西 赣州 341000)

(2. 钨资源高效开发及应用技术教育部工程研究中心，江西 赣州 341000)

(3. 中南大学，湖南 长沙 410083)

摘　要：采用直流反应溅射在 304 不锈钢表面沉积 CrN 薄膜。利用 X 射线衍射仪（XRD），扫描电子显微镜（SEM），原子力显微镜（AFM），显微硬度计，磨损试验机与三维轮廓仪等表征氮气流量对 CrN 薄膜组织结构与摩擦性能的影响。结果表明，随着氮气流量的增加，CrN (200)晶面呈择优取向，薄膜的沉积速率随着氮气流量的增加逐渐降低。另外，薄膜的表面粗糙度随着氮气流量的增加呈先降低后增加的趋势。随着氮气流量从 15 cm^3/min 增加至 30 cm^3/min 时，薄膜的显微硬度 HV 先从 5273 MPa 增加至 10422 MPa，当氮气流量再增加至 35 cm^3/min 时，薄膜的显微硬度却降低至 9180 MPa。磨损试验表明，当氮气流量为 30 cm^3/min 时薄膜具有最小的摩擦系数 0.93 和磨损率 2.02×10^{-15} $m^3\cdot(N\cdot m)^{-1}$，显示最佳的磨损性能。

关键词：磁控溅射；CrN 薄膜；显微结构；摩擦性能

作者简介：任兴润，男，1991 年生， 硕士，江西理工大学材料科学与工程学院，江西 赣州 341000，E-mail: sygtl2011@126.com