Rare Metal Materials and Engineering
Volume 47, Issue 4, April 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(4): 1100-1106.

ARTICLE

Comparison of Microstructure and Tribological Behaviors of CrAlN and CrN Film Deposited by DC Magnetron Sputtering

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Abstract: CrAlN and CrN films were deposited on 304 stainless steel substrate by direct current magnetron sputtering. The effects of Al incorporation on the composition and microstructure for CrN film were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectrons spectroscopy (XPS), atom force microscope (AFM). The tribological behaviors of CrN and CrAlN films were characterized by wear tester against Si_3N_4 ball of 3 mm in diameter under different conditions and the wear profiles of film were characterized by Nanomap 500LS. The results show that the main phases of CrN film are CrN and Cr_2N phase and the main phases of CrAlN film are Cr_2N and CrAlN phases. The CrAlN film presents CrAlN (200) preferred orientation and CrN film presents CrN (200) preferred orientation. In terms of CrAlN film, parts of Cr atoms are taken place by Al atoms to form the CrAlN phase which is beneficial to refining grain and improving the comprehensive performance of CrAlN film. Therefore, CrAlN film exhibits a better wear-resistance performance and a lower wear rate than CrN film in all the conditions.

Key words: magnetron sputtering; CrAlN film; CrN film; microstructure; tribological behaviors

Film techniques not only improve manufacturing efficiency and service life of the cutting tool and mechanical parts, but also reduce the product cost[1-3]. Due to the high hardness, melting and chemical stability, nitride films were used to protect the cutting tool and mechanical parts for various applications[4,5]. CrN films have been widely used in industry due to their superior properties[6,7]. However, CrN films have not satisfied the needs of industry since the operating conditions of industrial machines are much adverse, such as higher speeding and higher temperature[8-10]. Therefore, it is necessary to develop the excellent protective film. A third element, such as Al, Si, C, Cr, and Ce, was added to the traditional binary nitride film to improve the mechanical and tribological properties[11,12]. CrAlN films have been explored and it was concluded that Al could significantly affect the gain size, high anti-oxidation temperature and mechanical properties, thus the CrAlN became the subject of ever-increasing interest as a protective film[13,14]. Kim reported[15] that CrAlN coated micro-tool obtained an enhancement tool life of 100% due to its higher hardness and oxidation stability, compared with the CrN coated tool for high speed machining tests.

Researches on CrAlN and CrN films have been reported by Refs [16,17]. However, the majority of the studies is focused on the deposition technology, Al content and so on. Even more, the studies about tribological properties of film is focused on dry condition which is not consistent with the practical environment of lubrication and corrosion.

In the present paper, CrN and CrAlN films were deposited on 304 stainless steel by direct current magnetron sputtering. The effects of Al incorporation on the microstructure and mechanical for CrN films were investigated. In addition, the

Received date: April 20, 2017
Foundation item: National Natural Science Foundation of China (51464013); Project of Education Department of Jiangxi Province (GJJ14414); Innovation Special Funds for Graduate Students (ZS201550); Program of Qingjiang Excellent Young Talents, Jiangxi University of Science and Technology
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tribological behaviors of CrN and CrAlN films under different conditions were investigated.

1 Experiment

The films deposition were carried out with a JGP-560B type direct current reactive magnetron sputtering system. The substrate of 304 stainless steel with the size of 30 mm×30 mm×2 mm was polished by the sandpapers and then ultrasonically cleaned in alcohol for 20 min. After putting samples into the vacuum chamber, the vacuum pumping system with a turbo-molecular pump was used to create a vacuum in the chamber with 2×10^{-3} Pa. In order to enhance the bonding strength, Cr and Cr/CrN transitional layers were deposited for the CrN film and CrAlN film, respectively. The deposition time of Cr and CrN transitional layers were 30 min and that of the CrN and CrAlN films was 120 min. The single target of Cr and Al (99.95%) was used to deposit CrN and CrAlN film. –300 V bias was applied to the substrate holder. The film deposition process was performed at 40 cm^3/min of Ar flow rate and 20 cm^3/min of N_2 flow rate with the targets power of 150 W.

Phases of films were characterized using X-ray diffractometer. The surface chemical bonding states of the films were characterized by X-ray photoelectron spectroscopy. The morphologies of films were observed by atomic force microscope with a 10 μm×10 μm measurement area and scanning electron microscope. The tribological properties of the film were evaluated by wear tester against a Si_3N_4 ball of 3 mm in diameter under three different conditions of ambient air, distilled water and 5 wt% salt solut ion. The experimental parameters were as follows: loads of 3 N; reciprocating length of 4 mm; reciprocating frequency of 300 times·min^{-1}. The wear scar profile and wear rate were measured by scanning electron microscope and Nanomap 500Ls profile as well.

2 Results and Discussion

2.1 Surface interface morphologies

Fig.1 shows the morphologies of CrN and CrAlN films at different magnification. It can be seen from Fig.1 that the surface of CrAlN and CrN films are both relatively dense. However, the CrAlN crystalline grains are more uniform than CrN grains. Some atoms clusters are found on the surface of both the film which demonstrates their film growth is a typical island mode[18]. Barshilia et al.[19] reported that the Al atoms play a significant role in refining grains and compacting film which reduce the surface roughness and increase the microhardness of CrN film. Similar results were reported by Refs [20,21]. Therefore, the surface roughness of the films were measured by AFM and the results are shown in Fig.2. The average surface roughness of CrAlN film is 8.09 nm which is lower than 11.7 nm of the CrN film.

Fig.3 shows the interface morphologies of CrAlN and CrN film. The thickness of CrAlN film is lower than that of CrN

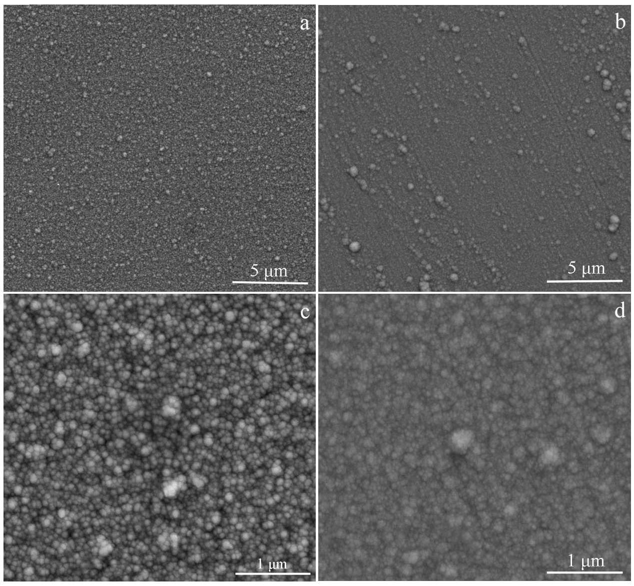

Fig.1 Surface morphologies of CrAlN (a, c) and CrN (b, d) films

film due to the incorporation of Al atoms into the CrN film which contribute to the higher ionization rate of Cr atom[22]. It can be seen from Fig.3 that both of the CrAlN and CrN films show a single transition layer and CrAlN film doesn't exhibit two transition layers of Cr/CrN layers as deposition which results in the shorter deposition time for the transition Cr/CrN layers and the diffusion phenomenon occurs between Cr and CrN layers.

2.2 XRD and XPS analysis

Fig.4 shows the results of XRD patterns of CrAlN and CrN films. According to the XRD results, the (111) reflections of the Cr_2N phase exist in both of the CrN and CrAlN films. What is more, the (111), (200) and (220) reflections of the

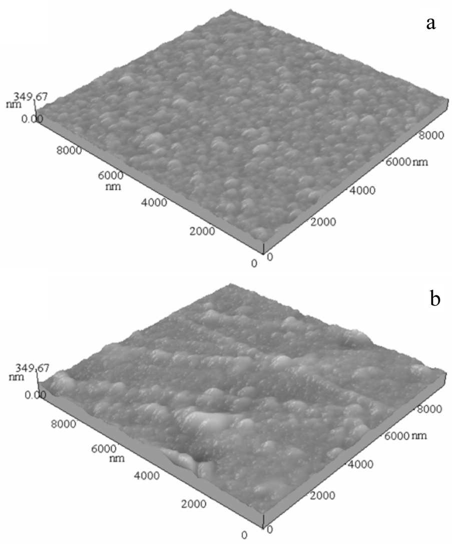

Fig.2 AFM images of CrAlN (a) and CrN (b) films

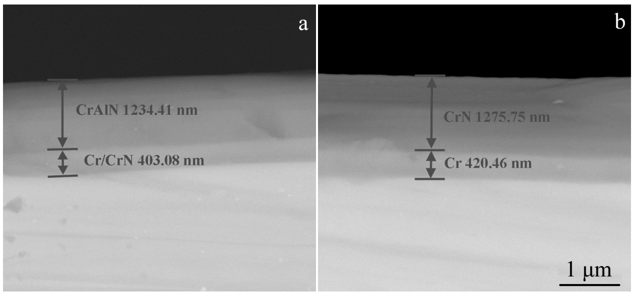

Fig.3 Interface morphologies of CrAlN (a) and CrN (b) films

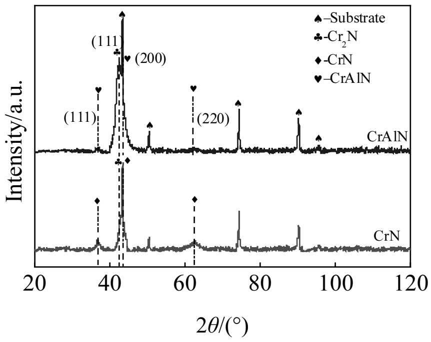

Fig.4 XRD patterns of CrAlN and CrN films

CrN phase can be seen in the CrN film. For Al doped CrAlN film, parts of Cr atoms are replaced by Al atoms at CrN lattice to form a crystal structure of CrAlN, still keeping face-centered cubic structure of CrN film which is beneficial to improving the hardness of CrAlN phase[23]. Lin[24] found when the Al contents is between 22 at% and 64 at%, the crystal grows in a preferred orientation of CrAlN (200) plane. In the present work, the composition of CrAlN film was determined by XPS, and the Al:(Cr+Al) ratio is 63.4 at%.

Fig.5 and Fig.6 show the results of fitting spectra by XPS of CrAlN and CrN films, respectively. As shown in Fig.5a and Fig.6a, both of the CrAlN and CrN films show strong peaks of O 1s and C 1s due to the film exposed to the air and chromium oxide and aluminum oxide[18]. The Al 2p spectra of CrAlN film show the characteristic peaks at a bonding energy of 73.5 and 74.6 eV, which correspond to (Cr, Al)N and Al_2O_3, respectively[18]. The Cr $2p_{3/2}$ peaks of CrAlN film represent three phases Cr_2N (574.3 eV), CrAlN (575.3 eV) and Cr_2O_3 (576.7 eV). It is similar to the Cr $2p_{3/2}$ peaks of CrN film which represent three phases Cr_2N (574.1 eV), CrN (575.0 eV) and Cr_2O_3 (576.3 eV)[25,26]. The N 1s spectra of CrAlN film is described by three peaks with different intensities centered at 396.2, 397.1 eV corresponding to the CrAlN, Cr_2N phase and peak centered at 399.9 eV which can be assigned as Cr-O-N bonding states and the presence of Cr-O-N bonds might be ascribed to surface oxidation[24]. The N 1s spectra of CrN film also exhibit three peaks of CrN (396.4 eV), Cr_2N (397.3 eV) and Cr-O-N (399.1 eV)[26,27]. As shown in Fig.5d and Fig.6c, the intensity of Cr_2N peak increases with the incorporation of Al which is consistent with the XRD results.

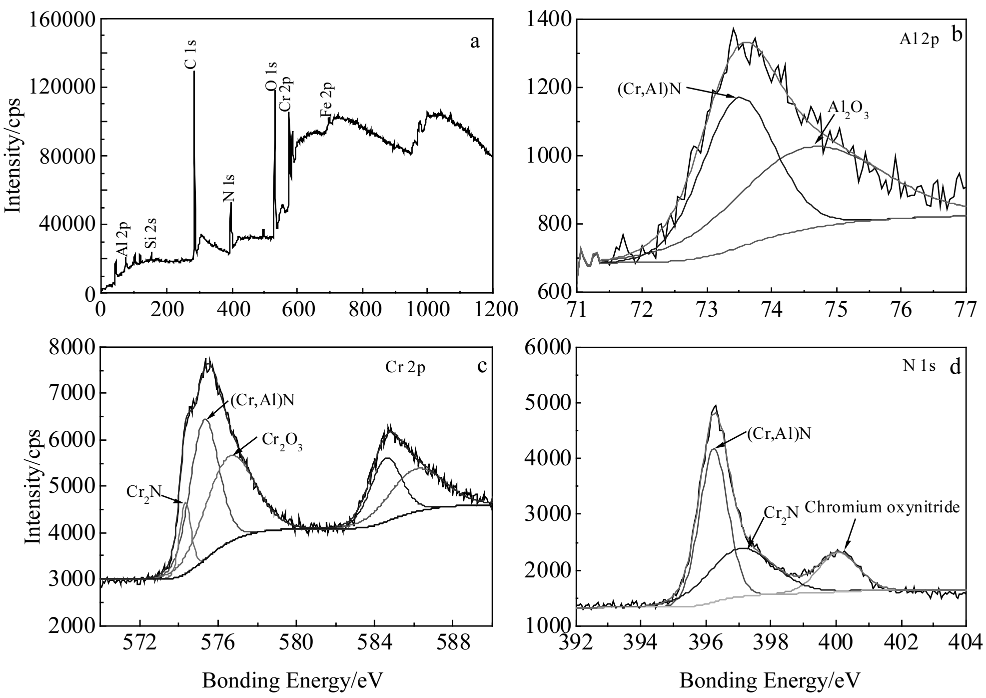

Fig.5 XPS spectra of CrAlN film: (a) full spectra, (b) Al 2p, (c) Cr 2p, and (d) N 1s

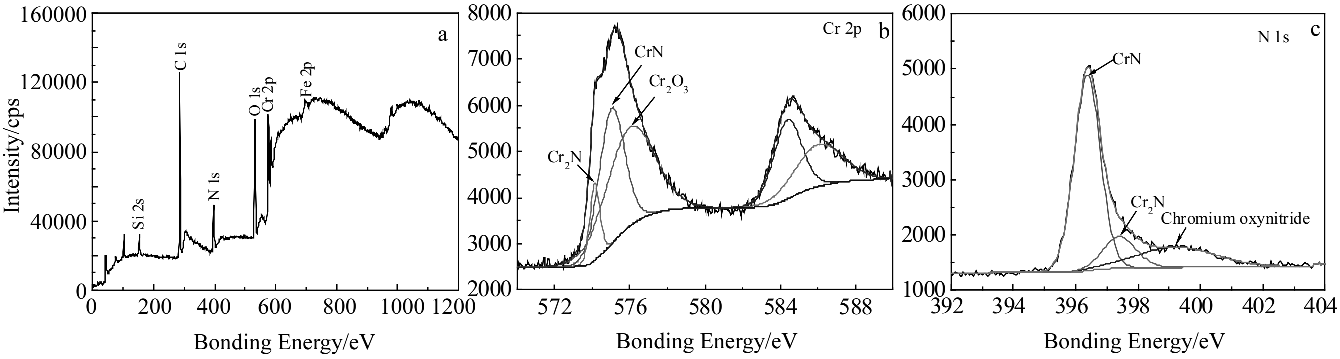

Fig.6 XPS spectra of CrN film: (a) full spectra, (b) Cr 2p, and (c) N 1s

2.3 Friction and wear properties

Fig.7 shows the friction coefficients of CrAlN and CrN films and both of them exhibit a similar curve tendency under the different conditions. From the evolution processes of friction, the friction coefficient of CrAlN film is lower than that of CrN film in ambient air and is higher than that of CrN film in the stable stage in distilled water.

As shown in Fig.7a, after an initial stage of about 5 min of sliding time, the friction coefficients of CrAlN and CrN films reach their stable values of approximately 0.99 and 1.36, respectively. Compared to the conditions of ambient air and distilled water, the friction coefficients of CrAlN and CrN films all exhibit lager fluctuation and do not reach stable stage all the time in 5 wt% salt solution. The friction coefficients of CrAlN and CrN films exhibit different tendencies and fluctuation due to the different debris behaviors and tribochemical reaction. All the average friction coefficients of the films in the distilled water and 5 wt% salt solution are lower than that in ambient air, which is attributed to the lubricating effect of discontinuous water film between the partial solid -solid contact faces[28].

Fig.8 shows the wear morphologies of film under different conditions. As shown in Fig.8a and 8d, CrAlN and CrN films suffer different damage in ambient air. Local film failure can be observed in the middle of wear track where the highest contact stress causes a partial detachment of the film[16]. In addition to the local film failure, wear track presents a smooth wear surface. The smooth wear track, like a polished surface, is formed possibly owing to the easy removing of debris particulates from the contact surface under the contact stress[29]. CrN film presents lager extensive microcracks and holes in the wear tracks. The concave and convex peaks are detached from the film, forming the fatigue microcracks under the regular contact stress.

In distilled water, lager micro pores are observed on the wear track both of CrAlN and CrN films. CrN film suffers more damage than CrAlN film. The studies have reported that water molecules play dual action to the film. The kinematics viscosity of water is 0.7 $m^2 \cdot s^{-1}$ at 40 °C[30]. Therefore, under the water-lubricated condition, the low viscosity can increase the difficulty of developing the continuous thin fluid water film between the contact face. It can efficiently decrease the solid-solid direct contact region and play an important role in lubricating effect to decrease the friction and wear. Furthermore, the temperature of contact region will increase because of reciprocating friction which will contribute to the

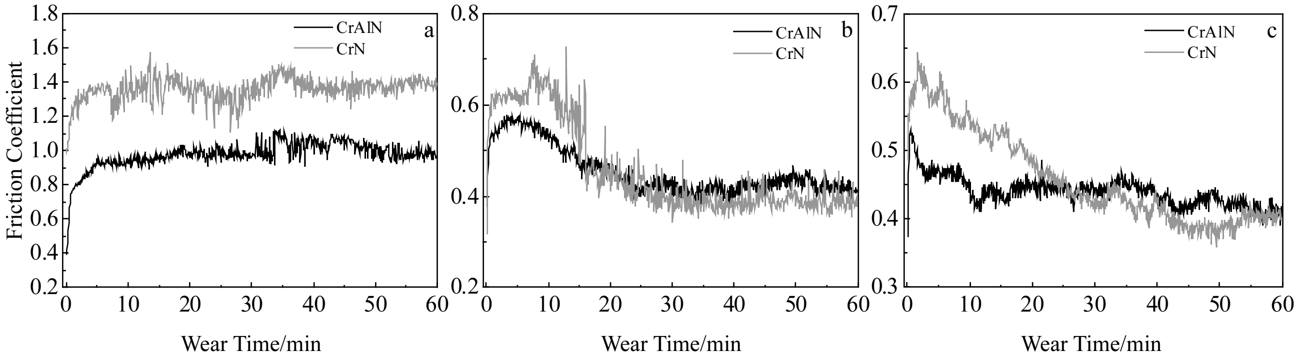

Fig.7 Friction coefficient of CrAlN and CrN films versus wear time under different conditions: (a) ambient air, (b) distilled water, and (c) 5 wt% salt solution

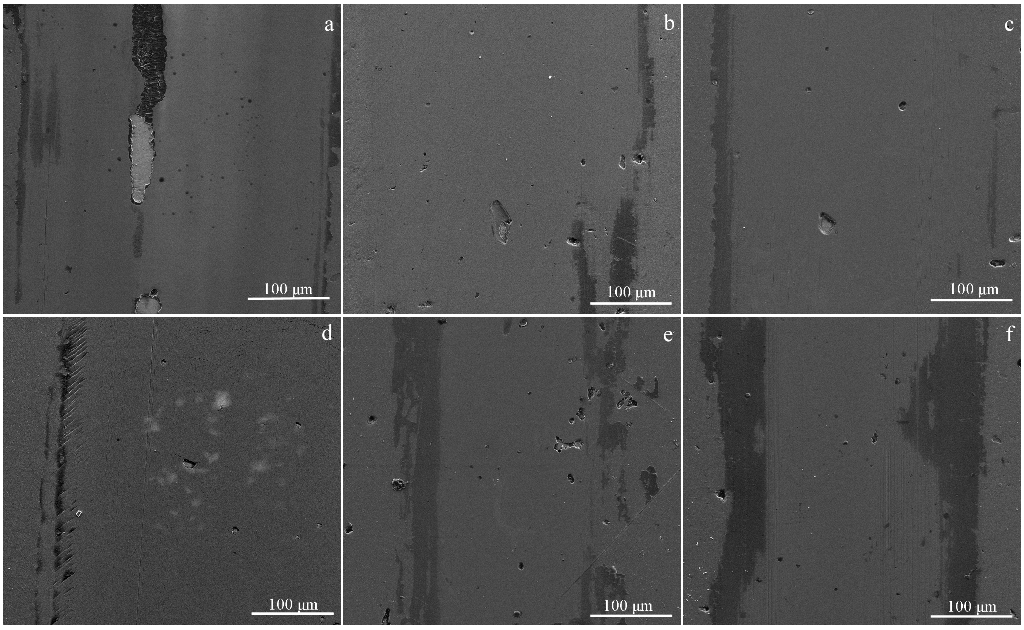

Fig.8 Wear morphologies of CrAlN (a~c) and CrN (d~f) films under different conditions: (a, d) ambient air, (b, e) distilled water, and (c, f) 5 wt% salt solution

chemical reaction including reaction (1), (2), and (3)[31-33]. It is obvious that Cr_2O_3 and Al_2O_3 are beneficial to improving the wear resistance of film. What's more, the Al_2O_3 can play a self-lubricating role in decreasing the wear loss[34,35]. In addition, it has been found that chemical product such as SiO_2 would be formed on the friction contact surface which will promote the further tribochemical products of colloidal silica with a function of good lubrication between the contact surfaces, as reaction (4) and (5)[36-38].

Contrary to the positive side, the water molecules also play an erosive role to the coatings under the synergistic action of the mechanical and chemical functions. Tribochemical products of NH_4^+ and OH^- will increase the ions concentration which can form the micro primary battery with water molecules and accelerate the wear in where defects[35]. In addition to the above function, the high Cl^- ion concentration has a strong corrosive effect on promoting film delamination and inducing more defects in 5 wt% salt solution[32,35].

$$2CrN+3H_2O=Cr_2O_3+2NH_3 \quad (1)$$

$$2AlN+3H_2O=Al_2O_3+2NH_3 \quad (2)$$

$$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^- \quad (3)$$

$$Ni_3N_4+6H_2O=3SiO_2+2NH_3 \quad (4)$$

$$SiO_2+2H_2O=Si(OH)_4 \quad (5)$$

2D single wear track profiles cross the sliding directions was obtained on the wear tracks of CrAlN and CrN films under different conditions, as shown in Fig.9. The CrAlN and CrN films all exhibit the maximum wear depth and width in ambient air which do not exceed the thickness of films. The wear rate of films were also calculated with 3D morphologies corresponding to wear tracks, as shown in Fig.10. The films

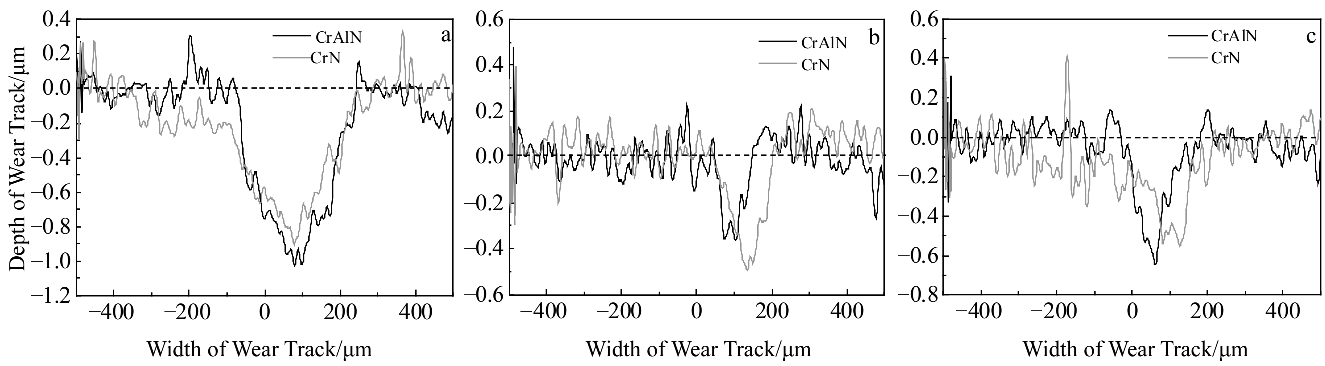

Fig.9 Wear track profiles of CrAlN and CrN films under different conditions: (a) ambient air, (b) distilled water, and (c) 5 wt% salt solution

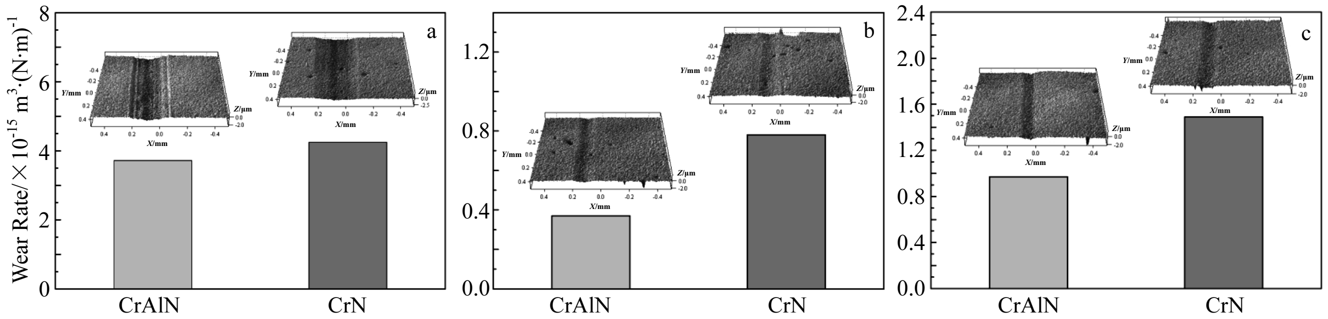

Fig.10 3D morphologies of wear tracks and wear rates of CrAlN and CrN films under different conditions: (a) ambient air, (b) distilled water, and (c) 5 wt% salt solution

all exhibit maximum wear rate in ambient air and minimum wear rate in distilled water. The results show that both of the CrAlN and CrN film exhibit maximum wear rates about 3.72×10^{-15} and 4.25×10^{-15} m^3/N·m under conditions of ambient air and minimum wear rate about 0.37×10^{-15} and 0.78×10^{-15} m^3/N·m in distilled water, respectively.

Based on the above results, the CrAlN film presents excellent tribological performance compared with CrN film under all conditions, demonstrating its more potential application than CrN film. On the one hand, as described above, CrAlN film shows small grain size due to the incorporation of Al atoms into the CrN film which is beneficial to improving the mechanical properties and wear resistance of the film. According to Hall patch theory, fine grain size will improve comprehensive performance of materials greatly. On the other hand, the tribochemical products of Al_2O_3 can play a self-lubricating role in decreasing the wear loss which leads to the lower wear rate and better wear resistance than CrN film.

3 Conclusions

1) The growth of CrAlN and CrN films is a typical island mode with atoms clusters. CrAlN film is relatively dense and uniform and presents a lower average roughness of 8.09 nm than 11.7 nm of CrN film.

2) CrN film mainly consists of CrN and Cr_2N hard phases. For CrAlN film, the Al element replaces part of Cr element to form the face-centered cubic structure CrAlN phase, which is conducive to improving the microhardness and wear resistance of CrAlN film.

3) Both of the CrAlN and CrN film exhibit maximum wear rates about 3.72×10^{-15} and 4.25×10^{-15} m^3/N·m under conditions of ambient air and minimum wear rate about 0.37×10^{-15} and 0.78×10^{-15} m^3/N·m in distilled water, respectively. CrAlN film with fine grain and lower surface roughness shows better wear resistance than CrN film no matter under what conditions.

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直流溅射沉积 CrAlN 和 CrN 薄膜微观结构与摩擦性能分析研究

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摘　要：采用直流反应溅射在 304 不锈钢表面沉积 CrAlN 和 CrN 薄膜。利用 X 射线衍射仪（XRD），扫描电子显微镜（SEM），X 射线光电子能谱仪（XPS），原子力显微镜（AFM）等表征 Al 元素的加入对 CrN 薄膜成分与组织结构的影响。采用摩擦磨损试验机和 3 mm 的 Si_3N_4 作为对偶球测试其在不同环境下的摩擦性能，并利用 Nanomap 500LS 三维轮廓仪表征磨痕轮廓。研究结果表明，CrN 薄膜主要物相是 CrN 和 Cr_2N 相，CrAlN 薄膜主要物相是 CrAlN 和 Cr_2N 相。CrN 薄膜的（200）晶面的 CrN 相呈择优取向，而 CrAlN 薄膜的（200）晶面的 CrAlN 相也呈择优取向。在 CrAlN 沉积的过程中，部分的 Cr 原子被 Al 原子替代形成有利于细化晶粒和提高薄膜的综合性能。因此，在所有的实验环境中，CrAlN 薄膜都比 CrN 薄膜具有更好的抗磨损性能和低的磨损率。

关键词：磁控溅射；CrAlN 薄膜；CrN 薄膜；显微结构；摩擦性能

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