Al Content Effects on Mechanical and Tribological Properties of Cr/CrN/CrAlN Multilayer Nanocomposite Coatings

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Abstract. In this study, four Cr/CrN/CrAlN multilayer nanocomposite coatings with various Al content controlled by Al target power were successfully prepared on 316L stainless steels by plasma enhanced magnetron sputtering (PEMS). The surface morphology, chemical composition, phase structure and surface roughness of the coatings were characterized by SEM, EDS, XRD and AFM, respectively. The micro-hardness, Young's modulus and adhesion of the coatings were measured by nano-indentation and nano-scratch, respectively. The friction and wear behavior of the coatings was investigated by a friction and wear tester. The effects of Al content on the microstructure, mechanical properties and wear resistance of the coatings were studied in detail. Results show that Al content in coatings increased with the increase of Al target power. The coatings exhibited the NaCl crystal structure. As the Al content increased, the hardness, Young's modulus, bonding force and wear resistance of the coatings increased first and then decreased. The Cr/CrN/CrAlN coating with Al content of 37.8% has the optimal comprehensive properties.

1. Introduction

With the improvement of industrial materials, machine tool performance and environmental protection requirements, a growing number of industrial machines are used under harsh working conditions such as high speed, high temperature and strong corrosion, which seriously shorten the lifetime of traditional tools [1]. Among them, wear is one of the main damage forms of mechanical parts. More than 70% of equipment failures are caused by wear and tear, resulting in a large amount of material and energy losses [2]. To this end, the coating technology has been developed to deposit a metal compound film with excellent properties by using chemical or physical methods on the tool surface. As a result, the coated cutting tools are given new properties such as high hardness, high toughness, low friction coefficient and good resistance to corrosion and high temperature oxidation. Among various coating materials and preparation methods, transition metal nitride films such as TiN and CrN fabricated by physical vapor deposition (PVD) have been widely applied in cutting tools since 1980s, due to their outstanding chemical stability and mechanical properties [3–5].

In recent years, CrN coating has received intense interest because of its better corrosion resistance and abrasion resistance than TiN coating [6, 7]. However, with the process of science and technology and the development of industry, binary CrN coatings are difficult to meet the current more demanding service environment. Previous reports proved that the preparation of multicomponent multilayer nanocomposite coatings and the combination of different advanced coating preparation technology are the future research trends [8–10]. It was found that the further improvement
incomprehensive properties of binary coatings can be achieved by adding a third metal or non-metal element such as Al [11], Mo [12], Zr [13], Ni [14], Si [15, 16], V [17]. For example, the properties of CrN coatings, especially the microhardness and high temperature oxidation resistance, were significantly improved after Al addition. This is because Al entered CrN lattice with a consequent formation of CrAlN solid solution and thus the solid solution strengthening effect improves the mechanical properties to some extent[18]; on the other hand, dense Al₂O₃ and Cr₂O₃ films were formed on the surface of CrAlN coating at high temperature [19], resulting in the great enhancement in the thermal stability and high temperature oxidation resistance. Therefore, CrAlN coatings have been attracting increasing attention as a good alternative to conventional coatings [20, 21].

The common PVD methods for coating preparation mainly include arc ion plating, evaporation plating and magnetron sputtering. Among them, the plasma enhanced magnetron sputtering (PEMS) can realize high metal ionization rate and coating deposition rate at the same time, which is hopeful to further improve the comprehensive properties of existing coatings. Moreover, no systematic study on tribological properties of CrAlN coatings can be obtained in the literature. Consequently, the Cr/CrN/CrAlN multilayer composite coatings with different Al doping were produced by PEMS in this work, and the influence of Al content on mechanical and tribological properties of the coatings was investigated in detail. The multilayer design of Cr/CrN/CrAlN coating can reduce the stress between coating and substrate and strengthen the bonding force between them, thus restricting the crack propagation in the coating [22].

2. Experiment

2.1. Coating deposition

The PEMS system (MS650B, SKY Technology Development Co. Ltd, Shenyang, China) with an independent electron-emitting device was employed to prepare Cr/CrN/CrAlN coatings on 316L stainless steels (25 mm×25 mm×3 mm). All substrates were ground and polished with waterproof abrasive paper and diamond abrasion paste followed by ultrasonic degreased in acetone and ethanol. Subsequently, the cleaned substrates were dried and then attached on the sample holder in the vacuum chamber. The coatings were prepared from two Cr targets (99.99%) and one Al target (99.99%) and these targets were connected with DC magnetron power supplies. The chamber was pumped down to a pressure of approximately 3×10⁻³ Pa and deposition temperature was 300°C. The substrates were cleaned by Ar⁺ bombardment for 30 min with negative bias voltages of 800 V (impulse voltage 600 V, DC voltage 200 V) to remove any oxides and contaminants on the surface. Prior to the CrAlN deposition (300 min), the Cr bonding layer and CrN transition layer were prepared for 30 min to weaken the stress between different kinds of materials. The Al target power ranged from 350 W to 800 W was adopted to evaluate the Al content influence on the mechanical and tribological properties of Cr/CrN/CrAlN multilayer nanocomposite coatings. The detailed parameters were displayed in Table 1.

| Table 1. Deposition parameters of Cr/CrN/CrAlN coatings. |
|-------------|-----------------|
| Parameter   | Value           |
| Based pressure (Pa) | 3×10⁻³         |
| Working pressure (Pa) | 0.5            |
| Substrate temperature (°C) | 300            |
| Bias voltage (V)     | -50            |
| N₂/Ar flow ratio (mL·min⁻¹) | 60:20         |
| Target power (W)     | Pₜₐr: 500(Cr bonding layer) |
|                      | Pₜₐr: 400(CrN transition layer) |
|                      | Pₜₐr: 300; Pₐl: 350, 500, 650, 800(CrAlN coating) |

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2.2. Coating characterization

The crystal structure was analyzed by an X-ray diffraction (XRD, XRD-6100, Shimadzu, Japan) with a Cu-\(\text{K}\alpha\) 40 kV/30 mA X-ray source. The scanning range from 20° to 80° and scanning speed was 5°/min with step size of 0.02°. The microstructure and chemical composition were examined by a field emission scanning electron microscopy (FE-SEM, Sigma, Zeiss, Germany) and energy dispersive spectroscopy (EDS, Inca, Oxford, UK) with gun energy of 20 kV. The surface roughness and three-dimensional morphologies was characterized by atomic force microscopy (AFM, CSPM5500, Guangzhou Being, China) in tapping mode. The mechanical properties including hardness, Young's modulus and bonding strength were measured by nano-indentation and nano-scratch (PB1000, Nanovea, USA), respectively. In the indentation test, the indenter penetration depth was adjusted by changing the loading. The pressure depth was controlled at about one-tenth of the total coating thickness in order to reduce the effects of substrate and surface roughness. To obtain a reliable mean value and standard deviation, at least 9 points were tested for each sample. The reliable data was obtained by the average values after eliminating the maximum and minimum ones. Moreover, the bonding strength between coating and substrate was investigated by the scratch experiment in which each sample had three scratches in different areas with a load range from 0 N to 40 N and the scratch length of 3 mm in different areas.

2.3. Tribological property

Tribological tests of Cr/CrN/CrAlN coatings were conducted by a friction and wear tester (MS-T3000, Lanzhou Huahui, China) in rotary friction mode without lubricant. Al\(_2\)O\(_3\) ceramic balls with a diameter of 5 mm were used as a counterpart material for the planar test. The measurement parameters were as follows: the load, test time, measuring radius, and rotate speed were 5 N, 30 min, 3 mm and 800 r/min, respectively. In addition, the microstructure and composition of the particles after wear test were also observed by SEM and EDS, respectively.

3. Results and discussion

3.1. Microstructure evaluation

The main chemical composition, grain sizes and surface roughness of the four CrAlN coatings were listed in Table 2. In this paper, the ratio of Al atomic percentage to the sum of Al and Cr atomic percentage was used to represent the Al content in the coating. It can be seen from the table that with the increase of Al target power, the Al content in the coating becomes higher and higher (31.7% → 51.5%); both the grain size and surface roughness decreased first and then increased, and they have the smallest with the Al content of 37.8%.

Table 2. Chemistry compositions, grain sizes and Ra of the coatings with various Al contents.

| Al Target power (W) | Cr (at.%) | Al (at.%) | N (at.%) | Al/(Cr+Al) | Grain Size (nm) | Ra (nm) |
|--------------------|-----------|-----------|----------|------------|----------------|--------|
| 350                | 40.14     | 18.69     | 41.18    | 31.7       | 435.48         | 28.9   |
| 500                | 39.39     | 23.87     | 36.75    | 37.8       | 347.29         | 10.6   |
| 650                | 34.90     | 26.40     | 38.70    | 43.1       | 392.90         | 15.9   |
| 800                | 31.03     | 32.93     | 36.04    | 51.5       | 592.17         | 32.7   |

Figure 1 showed the XRD patterns of Cr/CrN/CrAlN coating. It can be seen from figure 1 that CrAlN coatings with different Al contents presented diffraction peaks of (111), (200) and (220) plane of CrN crystals. When Al content was 31.7%, the coating showed an obvious CrN (111) preferred orientation. With the increase of Al content in the coating, the preferred growth trend of grains in the
coating changed from the CrN (111) plane to the CrN (200) plane, and the diffraction peak intensity of the CrN (111) plane decreased significantly. In addition, more and more Cr was replaced in CrN crystal, and the lattice constant decreases, so that the diffraction peak of CrN(111) plane has a small angle deviation when the Al content was 37.8%. There were mainly two reasons for the decrease of lattice constant, firstly, all atoms in the crystal were in a state of dynamic equilibrium and vibrate at their equilibrium positions. After replacing Cr in CrN crystal with Al, the difference in radius will cause lattice contraction and resulted in a decrease in the average distance of atomic vibration around Al. As a result, the lattice distortion made the lattice constant move towards a decreasing trend. Secondly, the effective radius of N atoms in the crystal structure of CrN decreases, so the crystal cell volume decreases and the lattice constant decreases after lattice collapse[23]. The optimal growth of grain mainly depends on the surface energy and strain energy in the crystal. With the increase of energy, the strain energy in the crystal plays a major role. Excessive energy will make the grain grow in the direction of lower energy to reduce the impact of excessive stress in the crystal. For face center cubic (fcc) structure, (200) plane was the one with the lowest surface energy and the highest density. Therefore, with the increase of Al target power, the growth of grains along the CrN (200) plane presents a preferential trend.

The surface morphologies of Cr/CrN/CrAlN coating are depicted in figure 2. When Al content was 31.7%, the grains presented an irregular multilateral cone shape, the accumulation was not dense and the surface was uneven. With the increase of Al content to 37.8%, the grain size (table 2) of the coating decreased obviously and compacted. Coating grain size increases with increasing Al content, the grain size was the largest and the gap between grains was wide when the content of Al was 51.5%. The possible reason was that the large target power leads to the appearance of large particle sputtering particles on the surface of target material in the process of sputtering. On the other hand, the large power makes the sputtering particles have high energy, and a large number of defects will occur when the sputtering particles were deposited on the substrate surface.

The three-dimensional morphologies of Cr/CrN/CrAlN coating are shown in figure 3. When Al content was 31.7%, the grain growth in the three-dimensional morphology of the coating presented an inclined columnar structure and the grain size was larger, which was not conducive to the improvement of mechanical properties of the coating. However, the grain of the coating was a columnar structure with dense growth and the height difference of grain was small when the Al content was 37.8%. With the further increase of Al content, the mechanical properties of the coating decreased due to the coarse grain size and loose grain accumulation. The grain growth of coating was
mainly affected by temperature and energy during deposition. The temperature of deposition increases with the increase of target power, and the grains rapidly grow into larger cells after nucleation. On the other hand, the energy of sputtering particles increases with the increase of power. A large number of defects were produced and the grains grow too fast in the deposition process, thus affecting the density of coating [24]. The surface roughness of four coatings with different Al content was shown in table 2. It can be concluded that the surface roughness of the coating first decreases and then increases with the increase of Al content, and the surface was smoothest when the Al content was 37.8%, which was consistent with the results of three-dimensional morphology of the coating.

**Figure 2.** Surface morphologies of Cr/CrN/CrAlN coatings with different Al contents: (a): Al=31.7%; (b): Al=37.8%; (c): Al=43.1%; (d): Al=51.5%.

**Figure 3.** 3d morphologies of Cr/CrN/CrAlN coatings with different Al contents: (a): Al=31.7%; (b): Al=37.8%; (c): Al=43.1%; (d): Al=51.5%.
3.2. Mechanical properties

The hardness and Young's modulus of Cr/CrN/CrAlN coatings with different Al contents are shown in figure 4. As can be seen from the figure, the hardness and Young's modulus of the coating increased first and then decreased with the Al content increased, the maximum value was achieved when the Al content was 37.8%. The coating hardness was mainly affected by many factors such as grain size, internal stress and crystal structure. Cr atom replacement in CrN crystal by partial Al atom to form CrAlN substitutional solid solution, and the coating hardness was improved due to the solid solution strengthening effect. In addition, the atomic radius of Al was smaller than that of Cr which will cause lattice shrinkage, while the increase in Al content will aggravate the degree of lattice distortion, so the coating hardness will be improved. With the further increase of Al content, it can be seen from the microscopic morphology and surface roughness of the coating that the increase of Al content makes the grain size increase and the deposition of the coating leads to the decrease of the density, leading to the decrease of the hardness of the coating when the Al content was 43.1% and 51.5%. On the other hand, uneven particles appear in the process of sputtering with the increase of target power, resulting in the increase of defects in the coating after deposition. Moreover, the energy of sputtering particles increases with the increase of power and the stress in the coating increases, which also reduces the hardness of the coating [25].

![Figure 4. Hardness and Young's modulus of the Cr/CrN/CrAlN coatings.](image)

Figure 5 shows the bonding force and Crack Propagation Resistance (CPRs) of Cr/CrN/CrAlN coating with different Al contents. According to the literature [26], during the scratch test, \( L_{C1} \) was defined as the critical load when initial crack appear and \( L_{C2} \) as the critical load when spalling occurs. CPRs refers to scratch crack growth resistance, which was derived from the product of \( L_{C1} \) and \( (L_{C2} - L_{C1}) \). The value of CPRs was proportional to the scratch resistance of coating. As can be seen from the figure 5(a), the bonding strength increases first and then decreases with the increase of Al content. When the Al content was 37.8%, the coating's bonding force reaches the optimal value (~30 N). The bonding strength of the coating was usually affected by factors such as grain size and internal stress. According to the above experimental results, the coating grain size first decreased and then increased with the increase of Al content. The grain size was the smallest when the content was 37.8%, and the bonding force of the coating was optimal under this condition. With the increase of Al content, the coating grain size increased obviously and the density decreased, which will reduce the bonding strength of the coating to a certain extent. On the other hand, with the increase of target power and vacuum chamber temperature, the grain growth rate was accelerated, the number and types of defects were increased, and thus the adhesion strength of the coating was greatly reduced [27]. It can be seen
from the figure 5(b) that the coating scratch resistance was the best when the Al content was 37.8%, and then indicated poor scratch resistance. The results were also consistent with the binding force data in the figure 5(a).

![Figure 5](image)

**Figure 5.** Bonding strength and CPRs of the Cr/CrN/CrAlN coatings.

![Figure 6](image)

**Figure 6** The friction coefficient curve and average friction coefficient of the Cr/CrN/CrAlN coatings.

3.3. **Tribological properties**

The friction coefficient curves and average friction coefficients of Cr/CrN/CrAlN coatings with different Al contents are shown in figure 6. As can be seen from the curve graph of the relationship between friction coefficient and friction time in the figure 6(a), the running-in period of the coating during friction was very short, no more than 2 minutes. When the Al content was 37.8% and 43.1%, the coating quickly reached the stable friction stage and the friction curve was stable. When the Al content was 37.8, the overall friction curve of the coating was lower than that of other coatings. When Al content was 31.7%, the friction coefficient will suddenly increase and then slowly decrease in the first 8 minutes, and then continue to rise slowly after 20 minutes. Cause the reason was that in a few minutes before the friction process belongs to the grinding ball and the larger point of friction between the particles, as the grain size of friction prolonged sharp was gradually smooth, entry point surface friction stage, so the friction coefficient rises abruptly. After the coating was worn out for about 8 minutes, the substrate bare leakage but the formation of adhesive layer of abrasive particles on the
surface can reduce the coating friction coefficient to a certain extent, while the shortening oxide layer formed by friction will be constantly worn and cause the increase of friction coefficient. The change of friction coefficient of the coating with an Al content of 51.5% was the same as that of 31.7%. However, due to the poor adhesion and scratch resistance of the coating, the friction coefficient curve of the coating was higher than that of other layers [28]. The figure 6(b) indicated the relation curve between Al content and the average friction coefficient of coating. The coating average friction coefficient curve first decreases and then increases with the increase of the Al content. The coating has the lowest friction coefficient when the content of Al was 37.8%.

Figure 7 shows the surface morphology of Cr/CrN/CrAlN coating after wear. When Al content was 31.7%, coating wear was more serious and the oxide adhesive layer partially joined together can be detected on the wear mark. However, when Al content was 51.5%, the width of coating wear mark was wider than when content was 31.7%, because the coating surface roughness with high Al content and the film base adhesion force were poor, resulting in lower wear resistance of the coating. However, the wear was relatively slight when the Al content was 37.8% and 43.1%, and the coating has the properties of high hardness, low roughness and strong film-base adhesion when the Al content was 37.8%, so the coating does not appear obvious crack or fall off after friction. With the increase of Al content to 43.1%, the wear marks of the coating become wider, and obvious peeling and deep indentation can be observed. The reason was that the hardness and adhesion force of the coating were reduced, but the coating has a low surface roughness, so the wear was relatively light and without causing a large area of peeling.

![Figure 7. Wear morphologies of Cr/CrN/CrAlN coatings with different Al contents: (a): 31.7%; (b): 37.8%; (c): 43.1%; (d): 51.5%.](image)

4. Conclusions
CrAlN coatings with different Al content were successfully prepared on the surface of 316 stainless steel by PEMS technology. The influence of Al content on the microstructure, mechanical properties and wear resistance of the coatings was studied. The main conclusions are as follows:

1) With the increase of Al content, the coating preferred orientation changed from the CrN (111) plane to the (200) plane; the grain size and surface roughness first decreased and then increased. When the Al content was 37.8%, the grain size of the coating was the smallest and the surface was the smoothest and densest.
2) The hardness, adhesion force and wear resistance of the coating increased first and then decreased with the increase of Al content. When the Al content was 37.8%, the coating had the optimal mechanical properties and wear resistance.

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