Characterization of CrAlN Films Synthesized by DC Reactive Magnetron Sputtering

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Abstract. CrAlN films were synthesized by DC reactive magnetron sputtering. The influence of the aluminium content on the microstructure, hardness and the friction coefficient of the CrAlN films have been investigated. Results indicate that all CrAlN coatings present a columnar and dense structure. Also, CrAlN coatings present a better hardness than CrN coating. The increase of Al rate from 3.5 to 11% is accompanied by a decrease of hardness from 28 to 24 GPa and then it increases for an Al rate of 24%. The addition of Al to the CrN system causes an increase of the friction coefficient and the wear resistance.

Keywords: CrAlN coatings · Hardness · Friction coefficient · Wear

1 Introduction

For the past few years, chromium nitride coatings are widely used in various applications and especially for the protection of cutting tools. This is due to their good wear resistance, high hardness, and good oxidation and corrosion resistance (Kong et al. 2011; Jianxin et al. 2012; Shan et al. 2014). However, the incorporation of Al in the cubic lattice of CrN system improves their properties and especially enhances its hardness. Indeed; Wang and Nie (Wang and Nie 2014) studied the effect of annealing temperature on CrAlN and CrN coatings properties. They confirm that CrAlN coating exhibits a better thermal stability than that of CrN. Indeed, at 900 °C, CrAlN film presents a strong XRD intensity and it exhibits a higher hardness than that of CrN. The increase of the Al content can lead to the change of the structure from cubic to hexagonal (Reiter et al. 2005). Also, Nouveau et al. (Nouveau et al. 2012) deposited CrN and CrAlN films by DC magnetron sputtering. They varied Al rate and revealed that CrAlN coating hardness reaches a value of 35 GPa however the CrN coating hardness is about 18 GPa. Likewise, CrAlN films are known by their good oxidation resistance above 1000 °C which is due to the formation of a dense oxide layer of (Al, $Cr)_2O_3$ (Lin et al. 2008). Additionally, the incorporation of Al in CrN system improves it corrosion resistance. Ding et al. (Ding et al. 2008) compared the corrosion resistance of CrAlN and TiAlN films. They confirm that both coatings exhibit a good corrosion resistance while the CrAlN showed a better one. To study CrAlN coatings and to improve their properties many parameters were investigated. Lv et al. (Lv et al. 2012) deposited CrAlN coating by mid-frequency unbalanced magnetron sputtering system. They studied the effect of the duty cycle on the properties of CrAlN films. They confirm that coatings present cubic crystalline structure.

In the present work, a series of CrAlN coatings were deposited on stainless steel and silicon substrate using a DC reactive magnetron sputtering technique. The Al content is investigated. The microstructure, hardness and tribological properties of the CrAlN coatings were studied.

2 Experimental Procedures

CrAlN films were synthesized on silicon wafer and stainless steel (90CrMoV8) samples (20×20 mm^2 and 5 mm thick) using a Dc reactive magnetron sputtering technique. The deposition time was fixed to 4 h. The pressure during deposition was 0.5 Pa and the substrate temperature was held at 300 °C. The substrate bias voltage was held at -500 V. The flow rates of Ar and N_2 were 68.8 and 33.3 sccm respectively. To deposit CrAlN coatings a chromium and aluminum targets with 99.95% was used. All this parameters are optimized in a previous work (Aouadi et al. 2019). To study the influence of Al content on the properties of CrAlN films, different power were applied to the Al target (from 500 to 2800 W). Table 1 summarizes the CrAlN deposition conditions.

Table 1. CrAlN deposition conditions

Deposition parameter	Nominal value
Substrate bias voltage (-V)	500
Temperature during deposition	300
Argon flow rate (sccm)	68.8
Nitrogen flow rate (sccm)	33.3
Power of the Cr target (w)	1500
Power of the Al target (W)	500, 1000, 1500, 2200, 2800
Holder rotation speed (rpm)	3
Time of deposition (H)	4

The cross-section and film thicknes of obtained films was characterized by SEM field emission (JEOL JSM 7610F). The rotative ball-on-disk test is used to determine the friction coefficient: The sliding speed was 3 cm/s, the sliding distance is about 100 m and the applied load was 5 N. An alumina ball (Al_2O_3) with a diameter of 6 mm is used as counterpart. After friction sliding, wear volume was calculated by profilometre profiles. The coating hardness and the Young's modulus were measured by nano-indentation test using MTS XP Nano indenter. To determine hardness and Young's modulus, Rahmoun's model is used (Rahmoun et al. 2009). The adhesion tests were realized by means of a micro-scratch tester (Scratch Tester Millennium 200). The indenter is a Rockwell spherical diamond and equipped with an acoustic emission detector. For each CrAlN film, three tests were carried out.

3 Results and Discussion

3.1 Microstructure and Morphology

Figure 1 shows the SEM cross section observation of CrAlN films deposited under different Al rates.

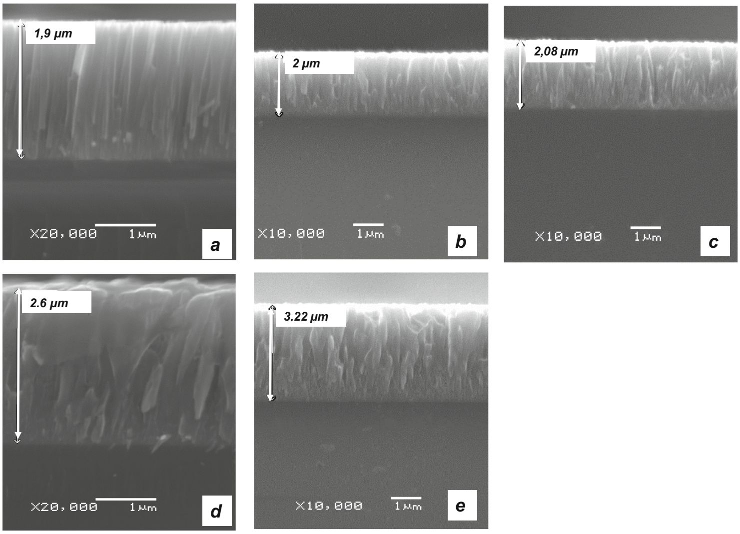

Fig. 1. SEM images of cross-section of coatings with different content of Al: (a) 3.5% (b) 7% (c) 11% (d) 19% (e) 24%

All CrAlN coatings exhibit a dense and a strong columnar structure. The columns are perpendicular to the substrate surface. The SEM images show that the size of the columns increases with the increase of the Al rate. This is ascribed to the increase of the grain size which increases with the increase of the Al rate. Likewise, it observed that the interface between the substrate and the coating doesn't represent any defects. This plays a crucial role to enhance the adhesion of films and consequently the improvement of their mechanical properties, resistance to wear and friction. Also, it's well seen that the film thickness increases by increasing Al content to 19 and 24% at. This is explained by the increase in the deposition rate for these two films.

3.2 Hardness

The hardness and Young's modulus of CrAlN films as a function of Al content are presented in Fig. 2.

From this figure, it can be seen that the addition of Al rate to the Cr-N binary system improves its hardness and Young modulus. Indeed, all CrAlN coatings exhibit a higher hardness and Young's modulus than that of CrN and it varies respectively between 22 and 30 GPa and 244 and 347 GPa. Similar values have been obtained in other works (Barshilia et al. 2006). The addition of 3.5% at. of Al permits to increase the hardness from 22 to 28 GPa. This improvement in hardness can be attributed to several factors such as the decrease of the grain size, the small inter-atomic distance of CrAlN films and the solution hardening (Barshilia et al. 2006). By increasing the Al rate up to 11 at.%, the hardness and the Young modulus slightly decrease and reach respectively 24 and 287 GPa. This can be explained by the relaxation of residual stresses. When the Al rates increase to 19 and 24 at.%, hardness and Young's modulus increase and are maximum, they reach respectively 30 and 347 GPa for 24% at. of Al. This is due to the formation of a solid solution that results from the substitution of Cr atoms by Al.

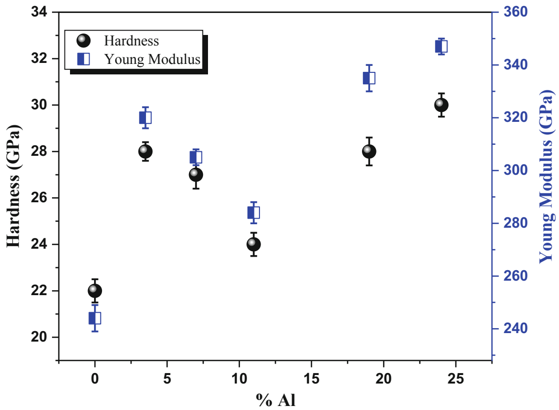

Fig. 2. Hardness and Young modulus of CrAlN films under different Al content

3.3 Friction Coefficient

The variation of the friction coefficient versus the sliding distance for the CrAlN films with different Al rates is shown in Fig. 3.

The addition of Al to the binary system (Cr-N) increases its friction coefficient. Indeed, the friction coefficient of CrN is about 0.68 and remains lower than that of CrAlN films. These results coincide with the work of Lin et al. (Lin et al. 2006). Ding and Zeng (Ding and Zeng 2005) explained this by the effect of the high roughness of CrAlN compared to that of CrN. Also, this increase in the friction coefficient is due to the AlN phase that exists in the CrAlN film. Indeed, the AlN phase has a coefficient of

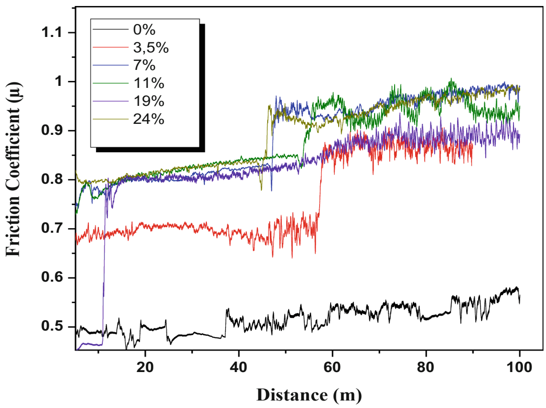

Fig. 3. Friction coefficient of CrAlN coatings

friction higher than that of CrN (Bobzin et al. 2007). According to Lin et al. (Lin et al. 2006), the increase of the friction coefficient of CrAlN films compared to that of CrN is ascribed to the increase of the oxidation resistance. They consider that the oxide layer formed in the surface of CrN coating acts as a lubricant because of its low shear strength, resulting in a low coefficient of friction. The friction coefficient of CrAlN films varied between 0.7 and 0.8. Similar values were obtained in other works (Wang et al. 2010) (Aihua et al. 2012). The addition of a small amount of Al of 3.5% at. to the binary system Cr-N causes a slight increase in the friction coefficient up to 0.7. This can be explained by the low presence of the AlN phase in this film. By adding a quantity of Al between 7 and 24% at., the friction coefficient is almost stable (about 0.8) and the increase in the Al content hasn't any effect. Similar results were found by Wang et al. (Wang et al. 2010). At the end of the test, all coatings exhibit an increase of friction coefficient and it reaches that of the substrate. Thus, the CrAlN layer is delaminated. It can be observed that CrAlN coating with 3.5% at. of Al has the best wear resistance and that with 24% at. possesses the worst one.

3.4 Wear Volume and Critical Load

The adhesion of thin films to cutting tools is an important parameter that affects their lifetime. Thus, it's imperative to perform a scratch-test to determine the adhesion of CrAlN films.

Figure 4 shows the evolution of Lc_2 as a function of Al rate in the layer. Here, the adhesion is represented by the resistance to spallation (Lc_2). The critical load (Lc_2) of CrAlN films varies between 49 and 64 N. Indeed, by adding 3.5% at. Al, Lc_2 increases up to 64 N. By increasing Al rate to 7% at., Lc_2 decreases to 54 N and then stabilizes for higher Al contents. The reduction in the resistance to spallation with the increase in Al content is attributed to its microstructure (Hua et al. 2006). Indeed, the CrAlN film with an 3.5% of Al exhibits the densest structure (Fig. 1). This dense structure has strong inter-columnar bonds, thus a strong resistance to the formation of inter-columnar cracks. Also, Li et al. (Li et al. 2007) explained this trend of adhesion by the evolution of the grain size. They observed that the increase of grain size leads to the decrease of Lc_2.

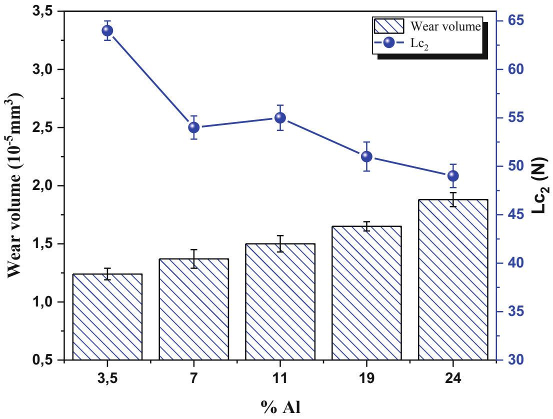

Fig. 4. Critical load and wear volume of CrAlN coatings under different Al content

After the ball-on-disk tests, the wear volume is calculated and it presents in Fig. 4. The increase of the Al %, is accompanied by a slight increase in the wear volume. Indeed, it varies from 1.2 10^{-5} mm^3 for an Al rate of 3.5% at. to 1.9 10^{-5} mm^3 when the Al rate is about 24%. This increase in wear volume is related to the decrease in hardness, adhesion and microstructure density. Nevertheless, from Fig. 3 the hardness decreases by increasing the percentage of Al from 3.5 up to 11 at.%. Then, it increases for 19 and 24% at. However, the critical load Lc_2 decreases with increasing Al content in the layer (Fig. 4). So, the increase in wear volume is due to the decrease in adhesion. Shew and Huang (Shew and Huang 1995) reported that mechanical properties and chemical stability have a great influence on the wear resistance of films. As the oxidation temperature of CrAlN films is high (≈ 1000 °C), it is always higher than the ball/deposit contact temperature. Thus, the wear behavior of CrAlN films is controlled by the mechanical properties and not by the chemical stability.

4 Conclusion

The aim of this work was to investigate the effect of Al content on the properties of CrAlN films obtained by DC reactive magnetron sputtering. The above results show that the addition of Al rate affects the CrN properties. CrAlN coating hardness was increased with the increase of Al rate. The maximum hardness is about 30 GPa obtained in the coating with 24% of Al content. The friction coefficient of CrAlN films was superior than that of CrN and is about 0.8. CrAlN coatings present a good behavior of adhesion which reaches 64 N. However the increase of Al rate in the layer of CrAlN films is accompanied by a decrease of Lc_2. CrAlN film with 3.5% rate of Al exhibits the best wear resistance. The increase of Al% rate leads to the decrease of the wear resistance.

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