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STRUCTURAL, MECHANICAL AND TRIBOLOGICAL PROPERTIES OF $Al_xCr_{1-x}N$ COATINGS

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Abstract - The aim of this study was to check the influence of Al content into CrN films on their properties. CrAlN films were deposited by reactive magnetron sputtering using chromium and aluminium pure targets. The atomic content of aluminium in CrAlN films was varied from 0 to 51 at. %. It was found that the addition of Al improved the stoichiometry and the structural properties of the films. Indeed, CrAlN morphology was changed from amorphous to columnar structure. The CrAlN films present compressive residual stresses from -1,1 to -3,58 GPa. The maximum value of stress was obtained at 30 at.% of aluminium content in the films. The coatings showed a high hardness and Young's modulus, which varied between 15-36 GPa and 331-520 GPa respectively. The friction coefficient of the CrAlN films varied from 0,55 to 0,7. All the CrAlN films showed a high friction coefficient and a high wear resistance as we observed parts of the pion-on-disk ball on their surface.

Résumé – Propriétés structurales, mécaniques et tribologiques des films $Al_xCr_{1-x}N$. L'objectif de cette étude est de vérifier l'influence du pourcentage d'aluminium sur les propriétés du système CrN. Des films de CrAlN ont été déposés par pulvérisation cathodique magnétron en utilisant deux cibles, une de chrome et l'autre d'aluminium. Le pourcentage atomique de l'aluminium dans les films CrAlN varie entre 0 à 51 %. Il a été constaté que l'ajout d'Al améliore la stœchiométrie et les propriétés structurales des films CrN. En effet, la morphologie des films CrAlN change d'une structure amorphe à une structure colonnaire. Les films CrAlN présentent des contraintes résiduelles en compression, variant entre -1,1 et -3,58 GPa. La valeur maximale des contraintes résiduelles a été obtenue pour un pourcentage d'Al de 30 %. Les revêtements CrAlN ont montré une dureté et un module d'Young élevés, ils varient entre 15 et 36 GPa et entre 331 et 520 GPa respectivement. Le coefficient de frottement des films CrAlN varie entre 0,55 et 0,7. Les films CrAlN montre une résistance à l'usure élevée, en effet, des traces de la balle utilisée pour les tests de pion-disque ont été observées sur la surface des films.

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1. INTRODUCTION

The application of binary coatings on tools for machining of materials has been intensively studied for many years. Recent works showed that the addition of a third element improves considerably the mechanical, structural and tribological properties of the binary systems. Various ternary coatings based on titanium and chromium nitride have been produced by PVD to improve the intrinsic properties of TiN and CrN systems [1,2]. It has been reported that addition of Al in TiN and CrN films improved their structural, mechanical and tribological properties [3-5]. In this study, deposition of CrAlN by magnetron sputtering was carried out in order to study the effect of aluminium content on the properties of the CrN system.

2. EXPERIMENTAL

CrAlN coatings were deposited using a RF dual magnetron sputtering system (NORDIKO 3500), as shown on *figure 1*. Two pure Cr and Al targets (4" of diameter) were used. The targets/substrates distance was 90 mm. Two series of CrAlN deposition films were made in order to control the Al atomic content in the CrAlN films: first, we fixed the applied tension of the Cr target at -900V and we varied the Al one from 0 to -900V. Secondly, we fixed the applied tension of the Al target at -900V and we varied the Cr one from 0 to -900V.

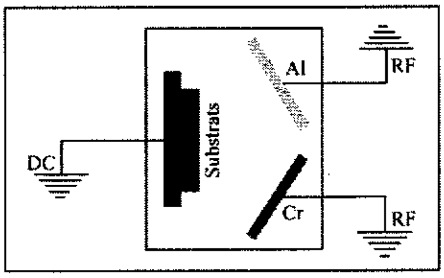

Figure 1. Schematic inside view of the deposition chamber of the RF dual magnetron sputtering.

To study the Al content effect on physicochemical, mechanical and tribological properties of CrAlN layers, different kinds of substrates were employed: silicon 10mm10mm×0,38mm, SiO2 10mm×10mm×2mm and 90CMV8 steel samples frequently used for tools in wood machining 20mm×20mm×4mm. The ex situ cleaned substrates were fixed on a vertical and rotative substrate holder which is also polarized in DC. Prior to deposition, the vacuum chamber was pumped down to 2×10-6 mbar and the substrates were in situ etched under argon ions bombardment during 5 min. The deposition gas mixture was Ar+N2. The working pressure was 4×10-3 mbar and the deposition time was fixed to 90 min. The *table I* illustrates the deposition conditions of CrAlN films.

The morphology and the thickness of the layers were verified by SEM (Jeol JSM-5900LV microscope) equipped with an Energy Dispersive Spectroscopy (EDS) microanalysis to determine their composition. The structure of the coatings was analysed by XRD (SIEMENS D500 diffractometer, $\theta/2\theta$ configuration, CoK_{α} radiation). The stresses were determined using Stoney's equation [6] after measuring the radius of samples by the Newton's rings method. The hardness and Young's modulus of CrAlN coatings were obtained by nanoindentation tests (NHT from CSM Instruments with a Berkovich indenter, in sinus mode (1 Hz of frequency and 1mN of amplitude), max load 10 mN, load and unload rate 5 mN/min). The friction coefficient of the coatings was measured using scratch-test process with increasing load (Rockwell C indenter with an angle of 120° and a radius of 200 µm, linear load and constant displacement speed of the sample).

Table I. Deposition conditions of CrAlN films.

Films	Working pressure (µbar)	Nitrogen content (%)	Applied tension Cr target (-V)	Applied tension Al target (-V)	Deposition time (mn)
CrN	4	20	900	0	90
CrAlN				300	
				500	
				700	
			500	900	
			700		

3. <u>RESULTS AND DISCUSSION</u>

The *figure 2* shows the chromium, aluminium and nitrogen contents determined by EDS in the CrAlN films as a function of the applied tension of the Al and Cr targets. We can note that there is neither carbon nor oxygen in the CrAlN layers. EDS analysis of CrN film (0V) gives an N/Cr atomic ratio of 0.4, indicating that the layer is not stoichiometric. Before starting the series we have chosen the conditions of deposition film in order to have stoichiometric CrN layers. These conditions were obtained during previous work done within our laboratory [7]. However, because of the modifications made inside the deposition chamber, these conditions are no more the same, which explains the atomic ratio obtained. For CrAlN films, the Al content increases with the Al target tension. This result can be explained by the increase of the sputtering rate of Al target. However, between -700 and -900V, we observed a weak increase in the aluminium content from 28 to 30%. According to Ding and al. [8], for the same applied tension to the same targets, chromium has a greater sputtering rate than aluminium, which can explain the increase of chromium content compared to the aluminium one. We can also note the low increasing of nitrogen content, which indicates that the Al incorporation is benefit for the improvement of the stoichiometry of the coatings. For these CrAlN deposition conditions, the maximum value of Al content is 30 at.% which corresponds to the maximum tension (-900V) achieved by our RF generator.

To complete the experiments, we have decided to maintain the applied tension of the aluminium target at -900V and to vary the chromium one. Two depositions were made (-500 and -700V). The *figure 2* shows that we can obtain a CrAlN with Al content higher than chromium one. Indeed, it has reached a value of 51 at.% at -500V, when it reaches just 30 at.% at -900V for both applied tension of chromium and aluminium targets. It is also important to note that the nitrogen content in the films is similar to that in films deposited by varying the applied tension on the aluminium target.

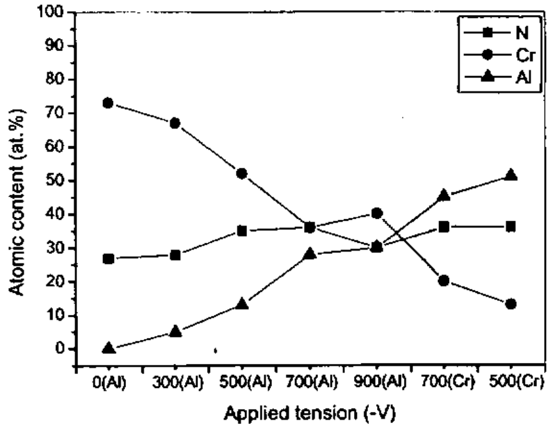

Figure 2. Atomic % of elements vs the applied tension of the Al and Cr targets.

At the beginning of our study, first we vary the applied tension of the aluminium target thinking that it would be more influent on Al content in CrAlN layers, but the results obtained shows that the variation of the applied tension of the chromium target is the major parameter, this can be explained by the fact that the sputtering rate of chromium is higher than that of aluminium.

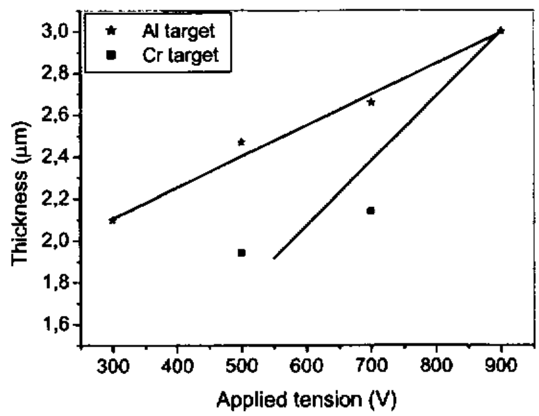

Figure 3. CrAlN thickness vs the applied tension of the Al and Cr targets.

The CrAlN film thickness variation as a function of the applied tension to Al and Cr targets is given in *figure 3*. The deposition rate of CrAlN films deposited when we increased the Al applied tension varied from 23.33 nm/min at -300V to 33.33 nm/min at -900V. We can explain this result by the sputtering speed increasing of Al target. For CrAlN films deposited when we change the Cr applied tension, the deposition rate varied from 21.55 nm/min at -500V to 33.33 nm/min at -900V. On the figure 3, we clearly see that the CrAlN film thickness where we change the Al applied tension exceed that where we change Cr applied tension. This confirms that the Cr sputtering rate is bigger than that of Al one. This result is correlated with that obtained by Ding et al. [8].

Figure 4 presents the XRD pattern of CrAlN films deposited with different Al content. A broad peak of Cr2N (111) was observed on the XRD spectrum of CrN film, which confirms the N/Cr atomic ratio obtained by EDS analysis. This broad peak shows that the deposited layer is almost amorphous. By adding the Al content to 13%, two peaks, CrN(200) and AlN(311) appeared showing that the aluminium addition improved the CrN films crystallization. This result is in correlation with other works [8,9]. At 30 at.% of Al content, a peak which reveals the presence of CrN (200) and AlN (200) appeared, showing that the layer is crystallized. This result was obtained by several researchers [5,8,9]. Moreover, there is a translation of this peak to wide angles showing that CrAlN films contain compressive stress, results also observed in other studies [5]. This peak disappeared completely at 45 at.% of Al content and only the AlN (311) peak exists, this one disappeared itself at 51 at.% of Al content and is replaced by a broad AlN (002) peak indicating that the deposited layers become amorphous.

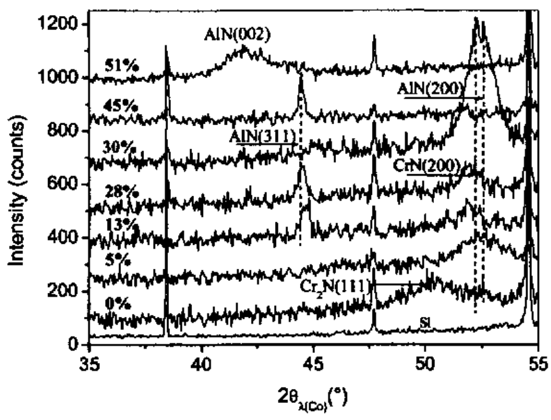

Figure 4. XRD patterns of CrAlN films obtained at different Al contents.

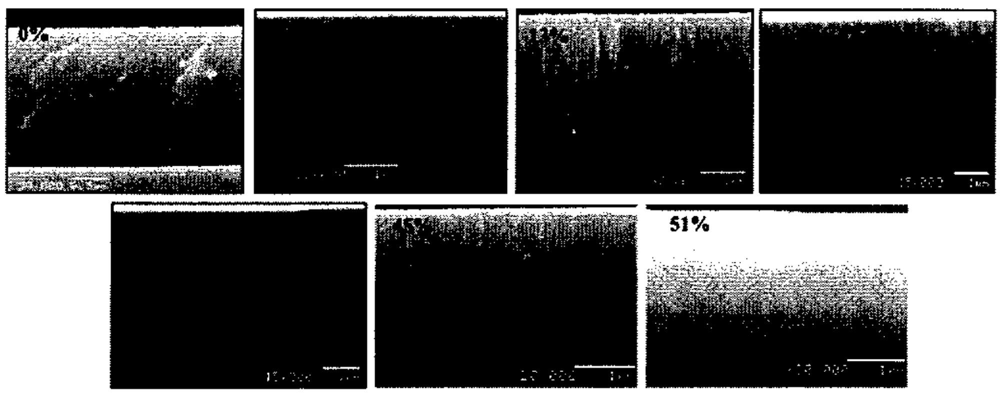

Figure 5. SEM cross-section observations of the CrAlN films.

The observation of the layers morphology was carried out by SEM on silicon coated samples then cleaved with a diamond tip. The *figure 5* shows clearly that the CrN film structure is dense and amorphous. By adding Al, the films have a dense and columnar structure, this structure is clearly visible for 13, 28 and 45 at.% of Al content. According to the XRD analysis, we note the appearance of AlN (311) pick for these films; we can explain this morphology by the formation of AlN phase. It's important to note also the morphological change of CrAlN films deposited with 30 at.% of Al content. Indeed, at this value, we note the disappearance of AlN (311) peak and the presence of the broad peak composed of the CrN (200) and Al (200). The morphology of CrAlN films deposited with 51 at.% of Al shows an amorphous structure which is in correlation with the XRD analyses of these layers.

The *figure 6* shows the residual stress variation in CrAlN films as a function of Al content. CrAlN films shows low and compressive stresses which varied from -1.1 to -3.58 GPa, these results have already been obtained in previous studies [10]. The residual stress of CrN layer is about -2 GPa, after adding Al, this value decreased and then stabilized at a value of -1.43 GPa for 28 at.% of Al content. According to the SEM cross-section observations, we can explain this result by the formation of a columnar structure which is less dense and therefore less stressed than the amorphous one. The maximum value of the residual stress is about -3.58 GPa corresponding to 30 at.% of Al content. According to XRD analysis of CrAlN films, for this Al content, we can see the appearance of the broad peak composed of the CrN and AlN (200). We can say here that the coexistence of these two phases creates a significant distortion of the lattice parameter because of the difference between chromium and aluminium atomic radius. After this value, the residual stress decreased to a value of 1.13 GPa at 45 at.% of Al content. This can be explained by the columnar structure of the deposited layer. In fact, this morphology is confirmed by the presence of AlN (311) peak on the XRD pattern showing that the deposited film is crystallized. Depending of XRD analysis and SEM cross-section observation, CrAlN deposited films with 51 at.% of Al content is amorphous, which explains the slight increase of the residual stress to 1.62 GPa.

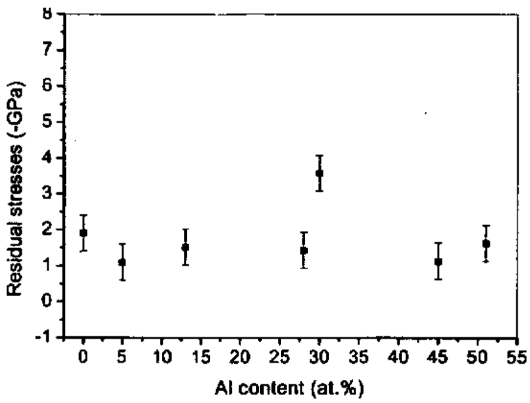

Figure 6. Residual stresses vs the Al content in the CrAlN films.

The *figure 7* shows the hardness and the Young's modulus variation of the CrAlN coatings as a function of the Al content. All CrAlN films showed a high hardness and Young's modulus, which varied between 15-36 GPa and 331-520 GPa respectively. Similar values were obtained previously [11]. We note also that the hardness and Young's modulus present a similar behaviour as the residual stresses which has already been observed in another study [10]. In fact, the maximum values of hardness and Young's modulus are observed at 30 and 51 at.% of aluminium content which are the same values that gave the maximum values of residual stresses. Both Al content values correspond to the formation of a CrN/AlN composite and an AlN amorphous phase respectively.

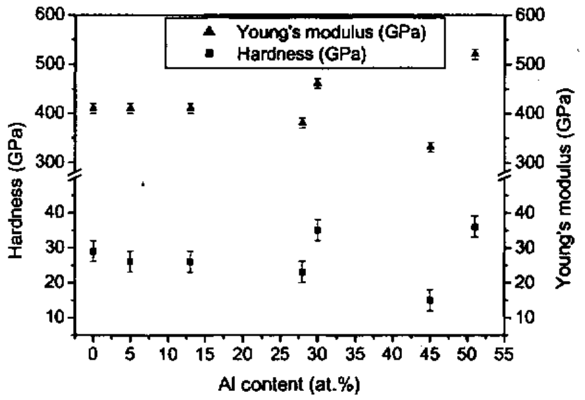

Figure 7. Hardness and Young's modulus vs. the Al content in the CrAlN films.

The *figure 8* shows the friction coefficient of the CrAlN films as a function of the Al content. It varied from 0,55 to 0,7 as observed in an other study [8]. It increased with the Al content in the CrAlN films from 0,55 to 0,7 until 28 at.% of Al content, then it decreased to 0,65 at 30 at.% of Al content. It's worthy of note that AlN films have a higher friction coefficient than CrN and CrAlN films [12], so we can say that increasing Al content in CrAlN films promotes the AlN formation which caused the increase of the friction coefficient. At 30 at.% of Al content, chromium content increased slightly which explains the decrease of friction coefficient of CrAlN films.

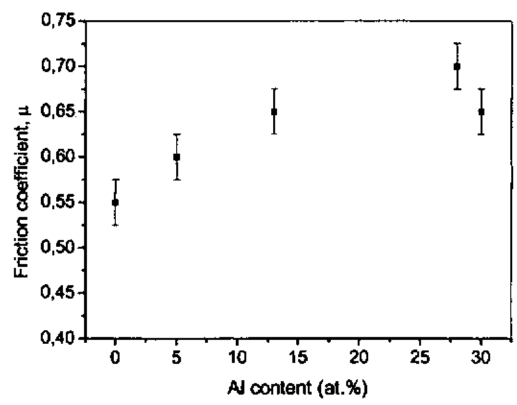

Figure 8. Friction coefficient vs. the Al content in the CrAlN films.

The surface morphology of the CrAlN films after pin-on-disc tests (*figure 9*) showed that whatever the Al content, the steel ball was scratched against the CrAlN coatings which means that they have a high wear resistance. The surface morphology of the CrAlN coating which contains 30 at.% of Al is different from the others, which could explains its lower friction coefficient.

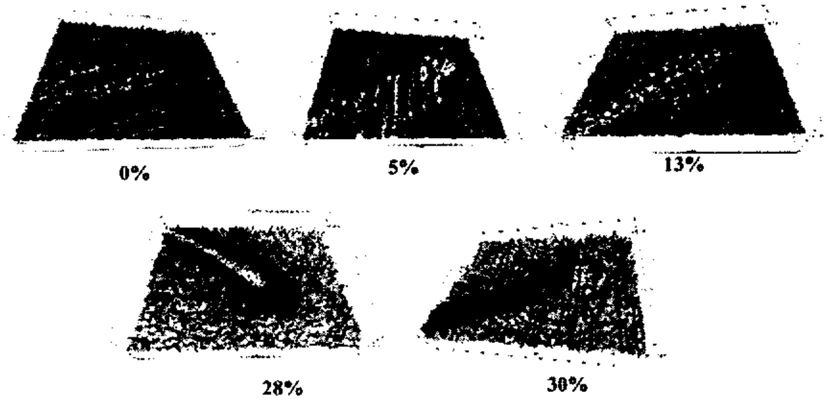

Figure 9. Surface morphology after pin-on-disc tests.

Based on the results presented above, we can see that the CrAlN coatings with 30 and 51 at.% of Al give the maximum values of hardness and Young modulus. However, coatings wish give the smallest values of friction coefficient are more efficacies in wood machining. Indeed, this is verified in MDF cutting, wile we fond that the CrAlN coating with 5 at.% of Al protect better the carbide insert. This result it will be present in our next articles.

4. CONCLUSION

In this study, CrAlN films were optimized in order to be applied on cutting tools in woodmachining. The effect of addition of aluminium on the stoechiometric, structural, mechanical and tribological properties of the Cr-N system was studied. The addition of aluminium improved the stochiometry and the morphology of the CrN as-deposited films. Indeed, a transition from amorphous to columnar structure was observed by SEM. All CrAlN films showed low compressive residual stresses which means that thick films could be applied in different application of machining. The hardness and Young's modulus of the CrAlN films varied between 15-36 GPa and 331-520 GPa respectively. The friction coefficient increased with the increase of Al content.

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