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Tribological and electrochemical performances of Cr/CrN and Cr/CrN/CrAlN multilayer coatings deposited by RF magnetron sputtering

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ABSTRACT

CrN/CrAlN and Cr/CrN/CrAlN multilayers were grown with dual RF magnetron sputtering. The application of these multilayers will be wood machining of green wood. That is why ball-on-disc and electrochemical tests in NaCl aqueous solution were realized to elucidate the tribological and corrosion behavior of these coatings as they will be exposed to wear and corrosion during wood machining process. The samples/alumina and samples/WC coupling showed different wear mechanisms. The 300 nm thick Cr/CrN/CrAlN multilayer demonstrated the best tribological behavior and corrosion resistance. The influence of growth defects on corrosion resistance has been shown.

1. Introduction

The physical vapor deposition (PVD) technique is well established as an environmentally friendly method to protect materials surfaces. Thus a variety of binary carbides and nitrides have been developed in the last three decades. Ternary compounds were obtained by adding a third element (transition metal) to traditional binary nitride films (CrN, TiN, AlN etc.) in order to increase mechanical and tribological properties. Further improvement in high-temperature properties of multicomponent (quaternary and higher systems) coatings can be achieved by the proper choice of additional alloying elements, such as Al, Si, Ti or Cr. Accordingly, for our part, we are interested in the addition of Al into the CrN system. This results in the formation of a metastable CrAlN ternary solution. Under operating conditions, this leads to the formation of complex aluminum and chromium oxides, which exhibit improved mechanical and tribological properties.

It is well known that Al and Cr additions can have a positive effect on the thermal stability and oxidation resistance of CrN and TiN based coatings, respectively [1–3]. The CrAlN films are probably the most promising coatings for high-temperature applications. Compared with TiAlN and AlTiN coatings, CrAlN presents better anti-spalling and anti-adhesion properties [4]. And, a high hardness (~30 GPa) and a high oxidation resistance temperature (900 °C) were reported for CrAlN coatings [5]. The effect of Al concentration in the Cr–Al–N system on its mechanical properties (hardness, elastic modulus, adhesion, oxidation…) as well as different wear behaviors has already been reported [6–8]. Sanchéz et al. [9] showed that high hardness (30 GPa), reduced elastic modulus (303 GPa), medium friction coefficient (0.45), high critical load (59 N), and good electrochemical behavior of Cr_{1-x} Al_xN coatings can be achieved at $x=0.54$. Wang et al. [10] reported that the simultaneous improvement of hardness and toughness is achievable when the negative bias voltage applied to the substrate is properly controlled. On the other hand, the incorporation of Al into the cubic CrN lattice can lead to increased roughness and porosity, as reported by Lee et al. [11]. As a consequence, the corrosion resistance of the CrAlN coating may be diminished, as shown by Sanchéz et al. [9]. To our knowledge, the exact Al concentration that must be incorporated into the Cr–N system to obtain optimal values of hardness and elastic modulus, simultaneously with high oxidation resistance has never been indicated in the literature [12,13].

To overcome some of these shortfalls, the surface engineering community has looked to the development of multilayered coatings. In terms of tribology, adhesion, and electrochemical properties, these coatings show better performance than their single-layer counterparts. CrAlN-based multilayered films with reasonable

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properties, such as CrAlN/AlON [14],CrN/CrAlN [15], CrAlN/BN [16] and TiAlN/CrAlN [17], have been developed. In addition to improving the tribological, adhesive, and electrochemical properties of the coatings, the mechanical properties can also be improved. For example, the hardness can be increased with a decrease in the CrAlN layer thickness. A maximum hardness of 34.7 GPa was obtained for a 3 nm thick CrAlN layer in a study on CrAlN/AlON multilayer coatings [14]. Nanoindentation tests reveal a hardness ranging from 37 to 46 GPa in case of CrN/CrAlN multilayer thin films [15].

Another opportunity for improvement is the mechanical response at high temperatures. CrAlN/BN coatings show superior oxidation resistance compared to CrAlN coatings. After annealing at 800 °C in air for 1 h, the hardness of CrAlN coatings decreased to 50% of the as-deposited ones; in contrast, the hardness of CrAlN/BN nanocomposite coatings stayed the same, or in some cases increased to about 46 GPa, as revealed by Nose et al. [16]. Recently, Li et al. [18] developed a ZrO_2/CrAlN multilayer and obtained excellent mechanical properties at elevated temperatures. After annealing at 1000 °C for 30 min, the hardness and elastic modulus were as high as 36.8 and 465.7 GPa, respectively. Another study [17] reported that TiAlN/CrAlN multilayer coatings have high hardness (~38 GPa) and adhesive strength (~98 N) with the thermal stability of TiAlN and the oxidation resistance of CrAlN.

Yet, for all this research into multilayer coatings, only a few studies report simultaneously on the wear and electrochemical behavior of multilayer coatings based on Cr–X–N (X = transition metal). In previous work [19], the physical and mechanical properties of multilayer CrAlN-based coatings were reported. In this work, we conduct a comparative study of the wear and electrochemical behavior with respect to the hardness, total coating thickness, and the role of a Cr underlayer. Indeed, overriding goal of our research is the development of a new protective multilayer coating system to improve the service life of cutting tools in wood machining. They would be submitted to wear (abrasion, shocks etc) but also to corrosion (machining of green/wet wood) that is why our study focused on the tribological (pin-on-disc tests) and corrosion behavior (using potentiodynamic polarization and electrochemical impedance spectroscopy measurements) of the coatings.

2. Experimental details

2.1. Materials

Multilayer coatings of CrN/CrAlN and Cr/CrN/CrAlN (Fig. 1) were deposited on mechanically polished steel substrates (AISI 4140; H = 4.1 GPa) at 200 °C, using a radio frequency (RF) dual magnetron sputtering system (NORDIKO type 3500), operating at 13.56 MHz and equipped with two confocal sputtering guns. The Cr and Al targets had purity levels of 99.95% and 99.999%, respectively. The distance from target to substrate was fixed at 100 mm and the applied bias voltage was −300 V and −900 V for Al and Cr respectively. The deposition conditions of the studied multilayers are described in detail elsewhere [19,20]. Besides, the physico-chemical (composition, thickness), structural (XRD patterns), mechanical (stress, hardness, Young's Modulus) and thermal properties of these multilayers systems were also determined in these previous works [19,20]. The chemical compositions (Scanning Electron Microscopy (Jeol JSM 5900 LV) equipped with Energy Dispersive Spectroscopy (EDS))and some characteristics of coatings are given in Table 1. The average value of surface roughness, estimated by optical profilometry(VEECO, Wylo NT-1100), was 0.056 ± 0.004 μm.

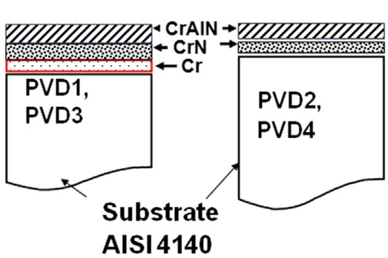

Fig. 1. Scheme of the multilayer systems on steel substrate.

2.2. Tribological tests

Dry wear tests were carried out using a ball-on-disc tribometer (CSM Instruments), which continuously records the coefficient of friction (COF) as a function of time/sliding distance. The tribological tests parameters are summarized in Table 2. The counterparts were alumina (H = 16.14 GPa) and WC- 6%Co ball (H = 15 GPa), 6 mm in diameter (supplied by CSM Instruments). Alumina and WC are widely used as standard counterparts for tribological tests. These materials have a higher hardness than steel and as we expect abrasion and shocks during wood machining process they are more suitable to test the wear resistance of our coatings. Besides, we could compare the COF of our coatings in contact with materials that have different roughness (Table 2) (many wood species of different surface state are machined and then the range of wood/coating COF is large).

A proprietary software package was used to control the experimental set-up and provide data handling. The velocity and applied load have been chosen according to the tribometer limits and to previous studies [20] (Table 2). The wear track diameter depends on the balls diameter, the velocity and the applied load. A sliding distance of 200 m permits to observe the wear of the entire coatings (until their disappearance from the substrate). Tests were conducted at room temperature (20 °C) with a relative humidity below 40% to almost reproduce wood manufacture conditions (in air or moderate room temperature, wet wood machining).

An optical profilometer (VEECO-Wyko NT1100) was used to measure the cross-section of the wear track at several locations. Based on

Table 1
Coatings properties obtained by RF dual magnetron sputtering.

PVDi	Multilayer thickness (nm)	Hardness (GPa)	Adhesion L_{C1} (N)	Chemical composition (at%)		
				N	Al	Cr
PVD1	(Cr/CrN/CrAlN) (~132/~368/~1000)	26	78	51.8	4.2	42.9
PVD2	CrN/CrAlN (~150/~150)	22	40	50.8	4	43.1
PVD3	Cr/CrN/CrAlN (~45/~106/~150)	32	56	50.5	4.7	42.5
PVD4	CrN/CrAlN (~500/~1000)	17	40	52	5	41.3

Table 2
Tribological tests parameters.

Applied load (N)		1
Velocity (m/s)		0.01
Total sliding distance (m)		200
Wear track diameter (mm)		4
Ball diameter (mm)		6
Roughness of balls (R_a, μm)	Alumina	1.52
	WC	0.388
Environment		Air
Temperature (°C)		20 ± 3
Humidity (%)		40 ± 5