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Aurélien BESNARD, Corinne NOUVEAU, Alex MONTAGNE, B. TLILI, S. NAAMANE, Khalil AOUADI - Effect of Bilayer Variation on the Properties of CrN/CrAlN Multilayer Coatings Produced by DC Magnetron Sputtering - In: 2nd International Conference on Innovative Materials, Manufacturing, and Advanced Technologies. IMMAT 2022, Tunisie, 2022-10-27 - Proceedings of the 2nd International Conference on Innovative Materials, Manufacturing, and Advanced Technologies. IMMAT 2022 - 2023

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Effect of Bilayer Variation on the Properties of CrN/CrAlN Multilayer Coatings Produced by DC Magnetron Sputtering

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Abstract. In this study, CrN/CrAlN multilayer coating with different periods ($\Lambda = 1, 2, 3, 4$) were deposited on stainless steel (90CrMoV8) and silicon Si (100) samples by DC magnetron sputtering. The results obtained exhibited that the increasing of the number of periods considerably improves the properties of multilayer coatings. All CrN/CrAlN multilayer coatings have a dense columnar microstructure, and the surface morphology showed a pyramidal shape with nanopores. The coating hardness and Young's modulus of the CrN/CrAlNmultilayer coating increases with the increase of bilayers number and reach 40 and 392 GPa respectively. Friction coefficient in seawater environment was calculated and it show that the increase in bilayer number decreases friction contact and reduce the friction coefficient. Also, wear resistance improves with increasing interfaces and increasing hardness.

Keywords: Multilayer CrN/CrAlN · Microstructure · Hardness · Wear · Friction

1 Introduction

Chromium Nitride coating (CrN) is widely used to enhance and protect cutting tools against wear. It's used to improve performance and lifetime of cutting tools in many industrial applications. This coating has a good wear resistance, high hardness, and good corrosion resistance. Indeed, CrN films exhibited a better resistance to high temperature oxidation, better corrosion resistance, better stability and better wear resistance than that of TiN (Yamamoto et al. 2021). CrN coatings have been deposited on stainless steel by various physical vapor deposition techniques (Wang et al. 2022, Liu et al. 2022).

During the last twenty years this reference layer (CrN) has enormously evolved and enriched by different addition elements such as Al, Mo, Ti, Si, …. The previous research demonstrates that the incorporation of an addition element in a binary coating will create new phases and it generally a good way to improve mechanical and tribological properties.

The addition of Al improves the mechanical properties and the oxidation resistance of CrN film coatings. In fact, Al atoms can replace the lattice position of Cr atoms in CrN lattice. Thereby, a solid solution strengthening will be created and enhance mechanical properties (Xia et al. 2021). Ding and Zeng, who deposited CrN and CrAlN films by magnetron sputtering, found that all the CrAlN films produced under different Al/Cr ratios exhibit harnesses greater than that of CrN. In addition, it has a better thermal stability and corrosion resistance than CrN. In addition, CrAlN films have a higher resistance than that of TiN because the chromium and the aluminum will form protective oxides which eliminate the diffusion of oxygen. In addition, CrAlN may be a promoter candidate for high-speed machining of other high-temperature wear applications. Uchida et al. (Uchida et al. 2004) who prepared CrN and CrAlN film by cathodic arc ion plating confirm that CrAlN coating showed a better wear resistance and a higher hardness than CrN film. Also, Deng et al. (Jiaxian et al. 2012) who deposited CrN, TiN, CrAlN and TiAlN films using cathode arc evaporation reported that CrAlN and TiAlN coatings possess a better erosion resistance than that of CrN et TiN.

The increasing demand for improving the properties of thin films of nitrides has led to the development of new techniques and the use of various growth parameters. Comparing with the monolayer structure, multilayer coatings could have improved corrosion resistance, oxidation resistance, wear resistance and mechanical properties (Wang et al. 2016). Several nitride-based multilayer coatings such as.

In this study, multilayer coatings Cr/CrN/CrAlN were deposited successfully on 90CrMoV8 stainless steel using an industrial machine with the DC magnetron sputtering technique. Our aim is to investigate the effect of periods number on microstructure, mechanical properties and the tribological behaviour conserving the same thickness (2 μm). The periods number of CrN/CrAlN is varied from 1 to 4. A Cr layer of 100 nm is deposited in the interface between substrate and multilayer films as a bonding layer.

2 Experimental Procedures

The substrates employed were of 90CrMoV8 stainless steel used on wood cutting tools with a dimension of 20×20 mm^2 and a thick of 5 mm with a surface roughness Ra $= 0.5$ μm. Also, polished silicon (100) substrates with dimensions of 10x10 μm2 to dispose with a thickness of 380 μm were used for. Prior to deposition, all substrates were ultrasonically cleaned in acetone and ethanol for 5 min, then dried under compressed air.

The CrN/CrAlN multilayer coatings were deposited by DC reactive magnetron sputtering (KENOSISTEC-KS40V). Before deposition, all the substrates were cleaned in-situ under argon plasma at −700 V for 10 min to ensure better coatings adhesion.

Prior to deposition, the chamber pressure was first evacuated to 3.10^{-5} Pa. Also, substrates were preheated to 300 C for 7 h. During deposition, the working pressure was set at 0.5 Pa. The Ar and N_2 flow rates were 68.8 and 33.3 sccm, respectively. Chromium and aluminum targets with a purity of 99.95% and dimensions (406.4 × 127) mm^2 were used for the deposition process. The power applied to the Cr and Al targets had been set to 1500 W. and 1000 W respectively. In this work, we studie the effect of the number of CrN/CrAlN bilayer on the coating properties. The coating thickness is constant, and we change the interfaces number. Four bilayers number are chosen as shown. Table 1 summarizes the CrN/CrAlN multilayer coatings deposition conditions.

Table 1. Deposition conditions of CrN/CrAlN multilayer Coatings.

Parameters	Value
Argon flow rate (sccm)	68.8
Nitrogen flow rate (sccm)	33.3
Temperature (°C)	300
Working pressure (Pa)	0.5
Substrate bias voltage (V)	–500
Power of Cr target (W)	1500
Power of Al target (W)	1000
Rotation speed (rpm)	3

The surface morphology and the microstructure of the coatings were observed by scanning electron microscope SEM-FEG (JEOL JSM7610F). In order to determine multilayer films hardness, an MTS-XP type nanoindenter equipped with a vicker indenter was used. The hardness is calculated using the Rahmoun model (Rahmoun et al. 2009). To determine wear amount, a friction test must be performed. Thus, a test of friction by an alternative tribometer in a solution of 3,5%.at of NaCl is carried out. The ball used is an Al2O3 with a diameter of 6 mm, the normal load applied is 5 N and the distance is about 30 m. After the friction test, the wear volume is determined using an optical profilometer. The adhesion tests were carried out by means of a micro-scratch tester (Scratch Tester Millennium 200) equipped with Rockwell spherical diamond indenter and fitted with an acoustic emission detector. For each sample, an average adhesion value is calculated from three to five tests.

3 Results and Discussion

Figure 1 presents the cross section and the surface morphology of Cr/CrN/CrN multilayer films deposited by sputtering magnetron DC.

All coatings show a dense and columnar structure which is comparable to studies carried out by other researchers (Barshilia et al. 2007). The bonding layer of Cr is the

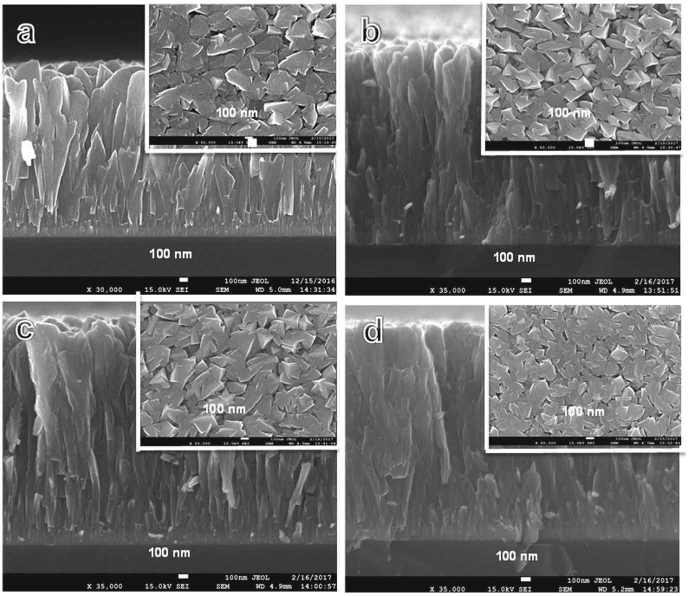

Fig. 1. Surface and cross section morphology of CrN/CrAlN multilayer coatings

first layer in connection with the substrate and its thickness is about 150 nm. Therefore, its presence improves adhesion and facilitates the nucleation of the CrN layer. Moreover, at the interface between coating and substrate, Cr grain size is very small. This zone is formed at the beginning of the PVD process when the temperature and the mobility of the adatoms are low. Thus, a large number of small grains are formed. During the deposition and due to the growth of CrN and CrAlN monolayers, grains of larger size and with a preferential orientation are formed. This can explain the difference of the column's width between the interface Cr/substrate and columns in the end of process (Wiecinski et al. 2017). Multilayer with one bilayer (Fig. 1a) has the widest columns while coating with 4 bilayers (Fig. 1d) has the lower columns and the densest one. For all films, the interfaces between the silicon substrate and multilayer films are clear and without defects. This can indicate that all coatings have a good adhesion.

Figure 1 show also the surface morphology of CrN/CrAlN multilayer films. All multilayer coatings present a pyramidal shape. It's seen that between columns, there is a presence of nanopores generated by the shading effect during the deposition process. The increase of bilayers number led to the decrease of the nanopores size. The increase of bilayers number to 4, causes the disappearance of nanopores and the shape of column becomes flattened.

Figure 2 presents hardness and Young Modulus of CrN/CrAlN multilayer coatings.

Results show that increase of bilayers number increase hardness. Hardness varies between 35 and 42 GPa and Young modulus varies between 361 and 390 GPa. Similar results were obtained by Kim et al. (Kim et al. 09). For a single bilayer, hardness and Young's modulus are about 35 and 361 GPa respectively. As the number of bilayers increases to 3, hardness and Young's modulus reach 40 and 390 GPa. This can be

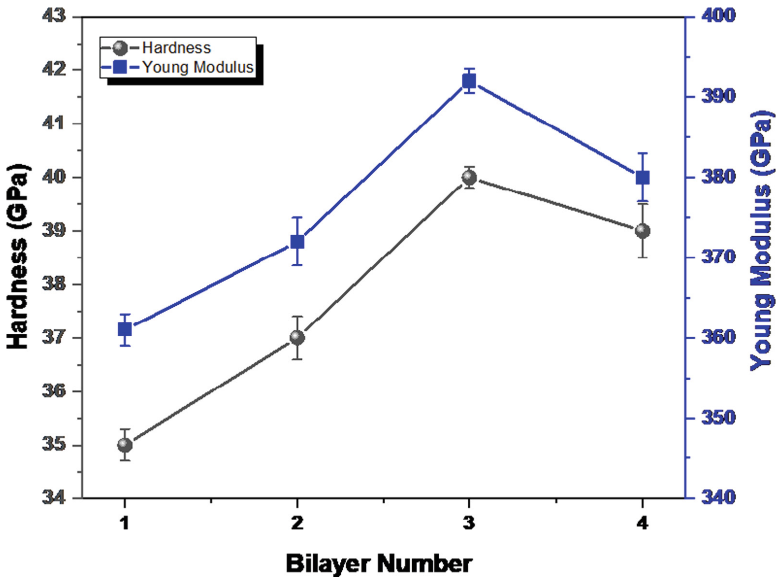

Fig. 2. Hardness and Young modulus of CrN/CrAlN multilayer coatings

explained by the increase in the number of interfaces. Indeed, interfaces prohibit the dislocation sliding and growth of columnar grains through the layers. The blocking of dislocations due to the growth discontinuity of columns contributes to the hardness improvement (Gua et al. 2017). The increase of bilayers number of CrN/CrAlN multilayer coatings to 4 is accompanied by a decrease in hardness and Young's modulus despite the increase in number of interfaces. The inter-diffusion and the interface state must be taken into account to explain the evolution of the hardness, the Young's modulus and their dependence on the process parameters. Therefore, the diffusion at the interfaces can be a reason for the reduction of multilayer hardness with 4 bilayers.

Figure 3a shows the friction coefficient of CrN/CrAlN multilayer coatings against Al_2O_3 ball in seawater envirement. It seen that the increase in bilayers number reduce the friction coefficient. In fact, CrN/CrAlN with one bilayer has a friction coefficient about 0.47 and that of 4 bilayers is about 0,17. This lower average of friction coefficient should be due to the self-lubrication of the solid-liquid interface part of films in seawater environment. Also, absorbed water molecules cam prepare border lubrication. The friction coefficient for multilayer films is relatively high at first and then decreases. The first part of curve is attribute to the rough surface of multilayer coatings. The decrease of friction coefficient the run-in period. This is due to the rapid increase of the wear of films and Al_2O_3 ball which induces smooth sliding interfaces. The reduction of average of the fiction coefficient of the CrN/CrAlN multilayer films with the increase of the bilayer number, can be attribute to the interfaces. Indeed, multilayer structure prevents crack propagation and flake pits which making sliding smoother (Shan et al. 2015). Then, with the increase of the number of interfaces and the reduce of the interfaces distance sliding becomes smoother. Likewise, the remove of monolayers with sliding and abrasive

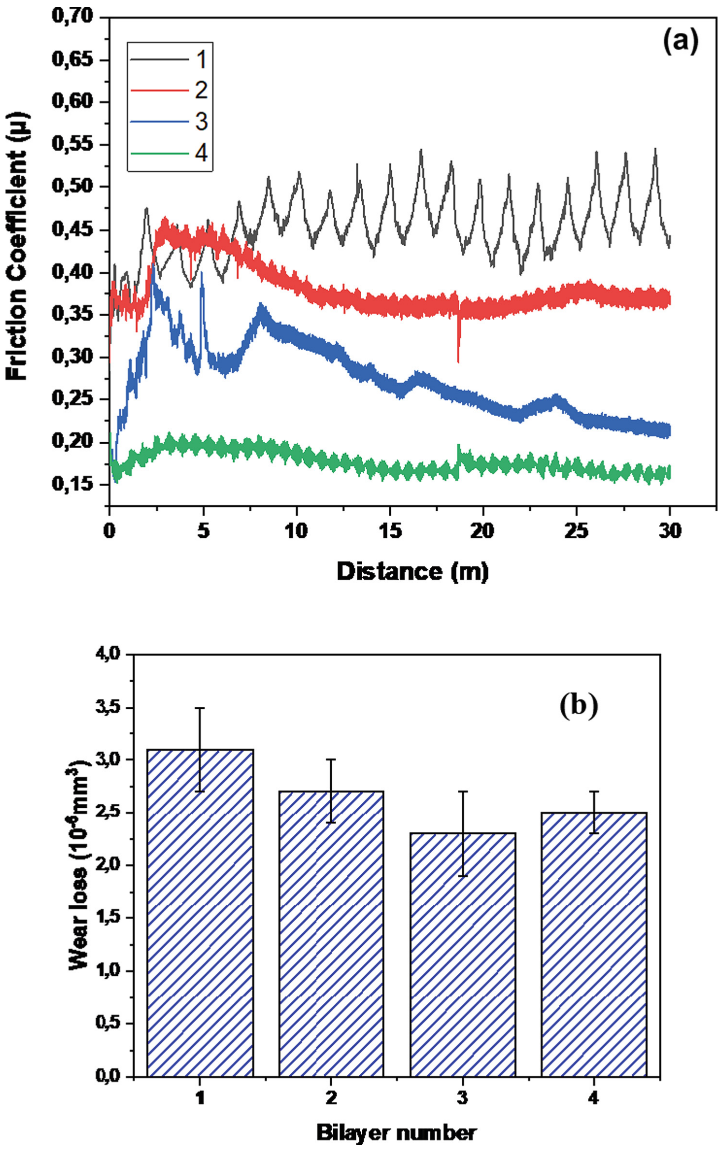

Fig. 3. Friction coefficient of CrN/CrAlN multilayer films in seawater environment, (b) volume loss of CrN/CrAlN multilayer coatings

remains produced oxide particles which can strength as a solid lubricant and decrease friction coefficient.

Figure 3b exbibits wear loss of CrN/CrAlN multilayer coatings after tribological tests. It can be seen that wear loss is affected by the increase of bilayers number. Also, all films own a good wear resistance. In fact, the wear loss varied between 3 10^{-6} and 2.4 3. 10^{-6} mm^3. In general, coating internal stress can accelerate crack propagation which can produce local fraction. Al elements improve bonds and has solution strengthening which can enhance coatings hardness. Also, multilayer structure could release internal stress that can explain the excellent wear resistance of CrN/CrAlN in seawater environment. This improvement of wear resistance can be ascribed to the hardness enhancement. Indeed, wear loss and hardness have the same trend (Fig. 2). This can explain the fact that multilayer coating with 3 bilayers has a better wear resistance then that with 4 bilayers. Moreover, increasing the number of interfaces improves the tribological behaviour of multilayers (Wiecinski et al. 2017). Indeed, interfaces interact with dislocations and crack propagation. The increase of interfaces number increases the number of barriers to crack propagation. Therefore, the wear resistance increases. Thus, the wear volume of multilayers decreases when the number of interfaces increases.

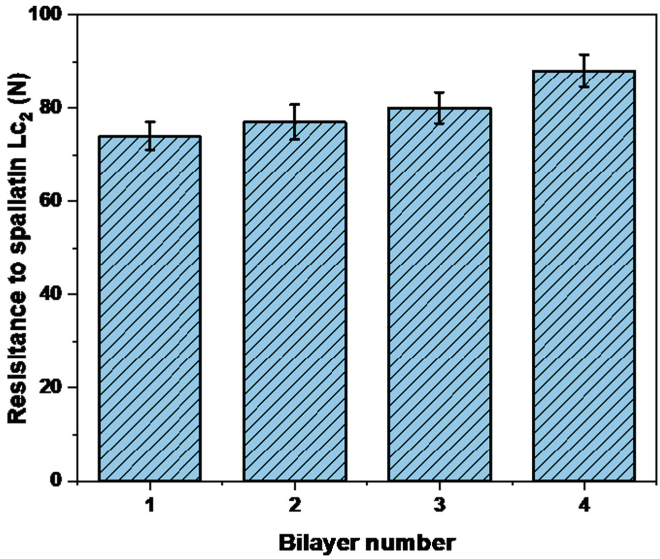

Fig. 4. Critical load Lc_2 versus bilayer number

Figure 4. Depicts critical load Lc_2 of CrN/CrAlN multilayer coatings which represents resistance to spallation. All coatings represent a good resistance to adhesion. In fact, Lc2 varied between 74 and 88 N. This good adhesion behaviour can be ascribed to the Cr bonding layer which strongly improve adhesion between substrate and coating. By increasing the number bilayers, adhesion improves considerably. For a single bilayer, the force necessary for the tearing layer (Lc_2) is about 74 N. With the increase of the bilayer number at 4, this force increases and reach 88 N. These values are higher than those determined by Tlili (Tlili 2010) who developed Cr/CrN/CrAlN layers by RF magnetron sputtering and for which Lc_2 did not exceed 78 N. This improvement may be due to the increase in the interfaces number which can delay the propagation of cracks towards the substrate. Thus, more interfaces number increases, more the coating is adherent.

4 Conclusion

The aim of this work was to investigate the effect of bilayer number t on the properties of CrN/CrAlN multilayer films obtained by DC reactive magnetron sputtering. The above results show that the variation of bilayer number (1, 2, 3 and 4) affects mechanical, tribological and microstructure properties. Multilayer coating hardness was increased with the increase the bilayer number and it reaches 43 GPa with four CrN/CrAlN bilayers. The friction coefficient under seawater environment decreases with the increase of bilayer number. Also, the increase of bilayer number enhances wear resistance. All multilayer coatings depict a good adhesion behavior which reaches 64 N and Lc_2 reach a value of 88 N.

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