Surface & Coatings Technology 337 (2018) 396–403

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Investigation of Cr(N)/DLC multilayer coatings elaborated by PVD for high wear resistance and low friction applications

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ARTICLE INFO

Keywords:
PVD
Tribology
Wear resistance
Durability
Cr/DLC multilayers
Steel

ABSTRACT

Cr/CrN/(Cr,N)-DLC/DLC and Cr/Cr-DLC/DLC multilayer coatings have been synthesized using DC sputtering magnetron technique to protect steel substrates from wear. The microstructure was investigated by scanning electron microscopy and the chemical structure of the DLC layers was investigated by Raman spectroscopy. The mechanical and tribological properties were evaluated by nanoindenter, scratch tester and Rockwell 'C' indentation test, ball-on-disk tribometer and surface profiler. A new methodology for the selection of coating performance was proposed by using a performance index based on a mix of adhesion, mechanical and tribological properties.

1. Introduction

The increasing restrictions of sustainable manufacturing industries have generated new materials concepts to substitute harmful additives in lubricants. Previous tribological studies have confirmed that low-friction coatings such as diamond-like carbon (DLC) can considerably reduce the friction coefficients of dry and lubricated sliding contacts [1,2]. Although hydrogen-free DLC coatings are well-known for providing low friction, high wear resistance and high thermal conductivity [3–7], their high hardness and high residual stress often lead to a weak adherence on steel substrates [8], which is problematic for many fields of high-technology industries. These issues have been successfully addressed by adapting graded intermediate layers between the DLC and the substrate [9] and thus homogenising the stress distribution. Transition metal elements like Ti, Cr, W are typically used as intermediate layers and as dopants for DLC layers [10–14]. However, selection of the proper adhesion layer [15–17], optimized deposition parameters of coatings [18,19] substrate preparation [20,21] and multilayer structure [22] are primary for obtaining high interface adhesion and still need currently technical progress.

Up to now the literature has not described well enough the link between the mechanical and tribological properties with the adherence in order to select the best DLC coating and underlayer combination. An example of such relationship between materials and properties in a multilayer coating is summarized in Fig. 1. Our technical objective is to find an acceptable compromise between mechanical/tribological properties and interfacial adhesion between DLC and the steel substrate, knowing that interlayers play an important role for mechanical properties of the global multilayer system. The coating adhesion is critical at the interface with the substrate, but also at the various interfaces of the multilayers and influences the final product properties. The coating classification performance has to take into account this relationship between materials and properties and it is presented in this paper following a simple performance index criterion.

In the framework of this study, graded compositions based on Cr/CrN/(Cr,N)-DLC and Cr/Cr-DLC coatings were used to improve adhesion of the DLC multilayer and to progressively increase the coating hardness. The mechanical and tribological properties of these multilayer structures are presented and discussed in relation with the interlayers properties in order to generate a coating performance selection methodology, useful for industries.

2. Experimental details

2.1. Film deposition technique

All coatings were elaborated by magnetron sputtering technique using in-house equipment simulating a roll to roll deposition. Chromium and graphite targets ($300 * 125\ mm^2$) have been sputtered using conventional DC power supplies and conventional balanced magnetron cathodes. The graphite target operated at 600 V and 1.5 A, while the Cr target operated at 300 V and 1.5 A for Cr coatings and 320 V and 1.5 A for CrN coatings, respectively.

The deposition pressure was in the range of 0.3 to 0.5 Pa. N_2 was used as reactive gas for the deposition of CrN. The flow rate of the N_2 (150 sccm) was determined to obtain CrN with no presence of Cr_2N.

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https://doi.org/10.1016/j.surfcoat.2018.01.052
Received 29 August 2017; Received in revised form 22 December 2017; Accepted 15 January 2018
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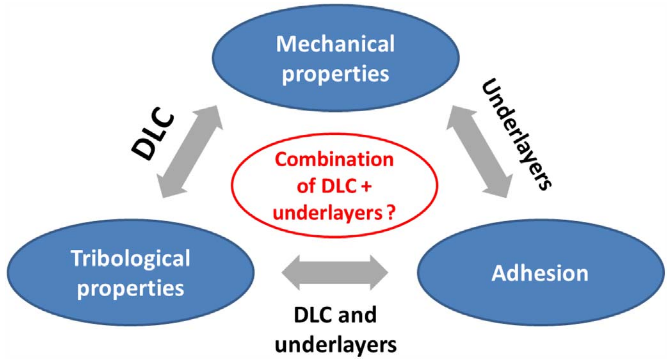

Fig. 1. Relationships between materials and properties in a multilayer sample.

The deposition is performed in dynamic back-and-forth mode with substrates (300 × 200 mm^2) facing the target mounted on a carrier holder moving with a linear speed of 50 cm/min. The distance between the target and the steel substrate is fixed at 5 cm. The substrate temperature, measured with an optical pyrometer pointing the back side of the substrate, does not exceed 100 °C for the deposition period. For this study the substrate was deliberately not biased as the coater simulates a roll to roll vacuum coater for metallic substrates. The substrate used for this study was mirror polished stainless steel MECA 8ND. An etching is performed prior to deposition by using an ion gun in order to remove the surface oxides of the substrate.

The deposition procedures included several steps: (*i*) Cr interlayer to promote adhesion, (*ii*) an optional intermediate CrN layer, (*iii*) a 3 µm thick buffer multilayer system composed of Cr(N) and DLC films deposited alternatively, (*iv*) a top DLC layer. Fig. 2 resumes the coating design for the various deposition conditions. Four coating systems have been investigated. For the coating designs called #coat 1 and #coat 2, thick CrN coatings were used as intermediate layers, while for #coat 3 and #coat 4 the Cr thickness was increased to 2500 nm in order to replace the CrN layer. Samples with only Cr, CrN or Cr/C multilayers have been also used in order to characterize the tribologic properties of each layer.

2.2. Characterization techniques

Morphology of the film and film thickness were analysed using a Field Emission Scanning Electron Microscope (FESEM, Sigma VP, Zeiss). Chemical nature of the DLC films were characterized by laser Raman Spectroscopy using micro-Raman spectrometer (in Via Renishaw) equipped with 532 nm wavelength laser source operating at 1 mW power.

Hardness of each layer and each system was evaluated by nanoindentation using the XP head of an Agilent G200 nanoindenter, which is equipped with a continuous stiffness measurement module, enabling accurate data acquisition, i.e. higher statistic for coating characterization. All tests were carried out with a diamond Berkovich tip and in displacement control mode for indenting at a maximal depth of 2 µm. Each test comprises series of 36 indents to get some statistic. Results are supplied as hardness vs. displacement (penetration depth) curves. The coating hardness value is taken at a displacement

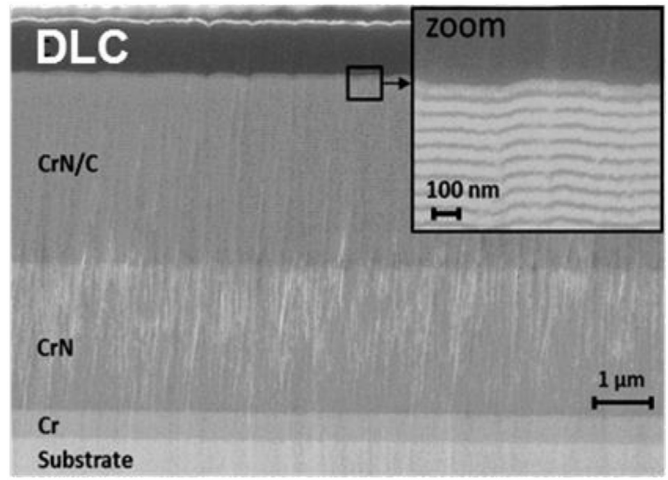

Fig. 3. SEM cross-section micrograph of the graded film #coat 1.

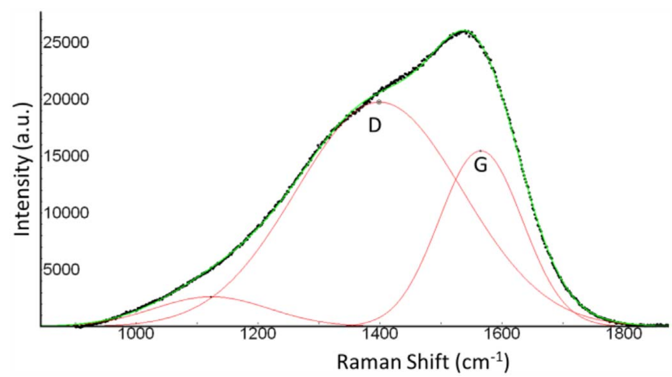

Fig. 4. Typical result of curve fitting for Raman spectrum of the DLC coating (#coat 1) using Gaussian function.

corresponding to 10% of the top layer thickness to avoid both substrate/sublayers influence and surface effect (roughness, tip calibration, contamination layer …), according to the Buckle's rule-of-thumb [23].

Coating adherence was characterized by two different techniques. The first one is the scratch test performed by the Anton Paar Revetest Xpress Scratch tester (RSX) device. The stylus is a conical diamond indenter (Rockwell C) with a spherical tip of a 200 µm radius. Each sample has been scratch over 1 cm under a progressive load from 1 N to 101 N with a loading rate of 100 N/min, and then observed by optical microscopy. The second one is based on the observation of Rockwell 'C' indentation test, called impact test; a conical diamond indenter penetrates into the coated surface inducing massive plastic deformation to the substrate thereby fractures the coating [24]. The coated specimen was then evaluated using conventional optical microscopy.

Friction coefficient of each system has been recorded using the Anton Paar CSM Pin-on-disk Tribometer. All tests have been performed with a 6 mm diameter alumina ball under 5 N normal load for 2000 laps with a linear rate of 10 cm/s and a radius of the groove equal to 10 mm. For representative final coated samples wear assessment has been

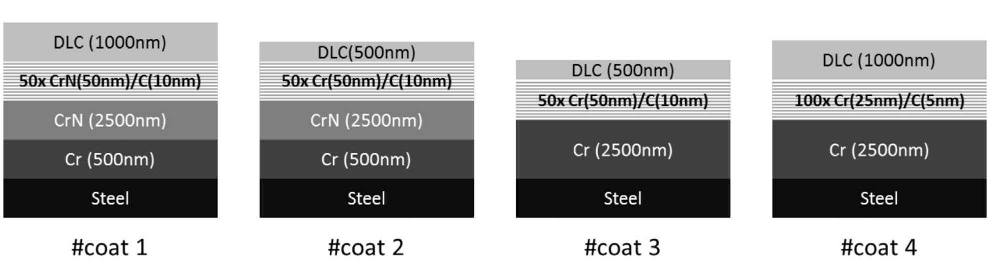

Fig. 2. Coating design for the various deposition conditions.