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Understanding of hybrid PVD–PECVD process with the aim of growing hard nc-TiC/a-C:H coatings using industrial devices with a rotating cylindrical magnetron

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ABSTRACT

Titanium–carbon hard coatings were deposited by sputtering using a rotating cylindrical titanium target in an argon/acetylene gas mixture on cemented tungsten-carbide substrates which were placed on a DC-biasable holder to perform a complex rotation around the central rotating cylindrical Ti cathode. While the optimal deposition process parameters to grow the coating of the highest possible hardness and low friction coefficient were sought, the plasma parameters were monitored and correlated with the properties of the deposited coatings. The Ti/Ar line intensity and the cathode voltage exhibited a sudden drop at the conditions for which the maximal hardness was reached. EDX analyses also showed a sudden drop in the atomic concentration of titanium and a sudden increase in that of carbon at the same moment. The maximal hardness of the coating was always achieved at the conditions that preceded these sudden changes, so this phenomenon was used to set the optimal deposition parameters to produce hard, well-adherent and sufficiently thick titanium–carbon coatings using the industrially attractive concept of a rotating cylindrical magnetron.

1. Introduction

nc-TiC/a-C:H coatings are nanocomposite coatings that consist of TiC crystallites that are embedded in an amorphous hydrogenated carbon matrix. Combining these two distinct phases can result in properties that are not found in the individual components. Depending on the chemical composition (ratio of Ti/C), the properties of these coatings can be tailored from hard coatings, with a hardness of greater than 40 GPa [1–3] (bulk TiC hardness is referred to be 32 GPa [4]) to tribological coatings, with coefficients of friction lower than 0.1 and wear lower than 2×10^{-7} mm^3/Nm [5–8] and the structure can range from columnar to glassy [9]. The most advantageous mechanical properties with the highest hardness are often reached for a Ti content of approximately 40% [2,9–11]. The magnitudes of the maximal obtained hardness reported in different papers spread over a very wide range, from 22 GPa, [9] to 41 GPa [11]. For industrial use, the combination of a low coefficient of friction, high hardness, high elastic modulus and good chemical stability is important.

nc-TiC/a-C:H coatings are usually deposited using a hybrid physical vapour deposition–plasma enhanced chemical vapour deposition (PVD–PECVD) process of sputtering with a Ti target in an atmosphere that contains hydrocarbon (mostly methane or acetylene) [3,6,8,12,13]. A key process parameter that determines the properties of nc-TiC/a-C:H coatings is the supply of gaseous hydrocarbon that is introduced into the chamber, which determines the composition of the coatings. The properties of nc-TiC/a-C:H coatings are well described [5–10] however, the correlation of the plasma parameters, such as the cathode voltage, pressure and optical emission, with the composition and mechanical properties of the prepared coatings is not usually discussed. Moreover, these coating are usually prepared using laboratory equipment and only few papers [8,14] have reported results obtained using industrial sputtering devices.

In our research, an industrial device equipped with a central titanium rotating cylindrical cathode was used to sputter titanium in a mixture of argon and acetylene, and we investigated the influence of the acetylene gas supply and the target erosion on the properties of the deposited coatings. The evolution of the plasma parameters, such as the cathode voltage, total pressure and optical emission spectra, was studied and correlated with the composition and mechanical properties of the coating. The evolution of the deposition process obtained using rotating cylindrical cathodes was compared to that obtained with a planar magnetron. This correlation enables us to propose a reliable deposition procedure suitable for industrial devices with rotating cylindrical magnetrons to grow titanium–carbon coatings to be used as protective coatings with good adhesion, thicknesses of several micrometres and the maximal possible

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hardness. The range of the applied acetylene supply that was used in our research was chosen to investigate the deposition process under the conditions in which those coatings are expected to grow.

2. Experimental details

The experiments were carried out using an industrial coating machine developed by the Pivot Company. The dimensions of the vacuum chamber were W580 × D566 × H580 mm. A single central rotating cylindrical titanium cathode (size Ø110 × H510 mm) was driven by a Solvix SA Magic 30 kW DC generator. The chamber was evacuated using a turbomolecular pump to a base pressure of 10^{-3} Pa. The pressure was monitored by a MKS 626A11TBD4 Baratron Profibus manometer. Argon (purity > 99.999%) and acetylene (purity 99.8%) gases were dosed via a mass flow controller. The gasses were mixed in pipes before being introduced into the chamber by showers located in front of the carousel substrate holder. The optical emission spectra of the discharge were measured using an Ocean Optics HR4000 high-resolution miniature fibre optic spectrometer, which provided an optical resolution of 0.025 nm (FWHM) and was responsive from 200 to 1100 nm.

The cemented tungsten-carbide samples were pre-cleaned in a chemical bath and ultrasonicated in a degreasing agent. The cleaned samples were inserted into the chamber and placed in substrate holders surrounding the central cathode. The samples performed a complex rotation around the central cathode and two other vertical axes. The chamber was heated to 450 °C and evacuated to base pressure. Oxides and other impurities on the target surface and on the substrates were removed by an argon-ion bombardment, while the substrates and the cathode were separated by the shutter. The target-cleaning process was performed until the cathode voltage stabilised indicating that the target was completely cleaned of any contaminants.

After the cleaning phase, the deposition was carried out at the following parameters: 20 kW of magnetron power, a −100 V bias on the substrates, 25 sccm of Ar (~0.42 Pa) and a substrate temperature of 450 °C. The acetylene flow was either held constant or changed gradually during the deposition.

The analyses of the deposited coatings were performed on metallographic cut (inclined planes that were obtained by abrasive cutting through the thickness of the coatings). A Fischerscope H100 depth-sensing indentation (DSI) tester equipped with a Berkovich indenter was used to study the indentation response of the deposited titanium–carbon thin films and to evaluate the hardness and elastic modulus of the coatings. During the DSI tests, the load and the corresponding indentation depth were recorded simultaneously for both the loading and unloading processes. From the loading and unloading curves, it was possible to determine the hardness using the standard Oliver–Pharr method [15]. Typically, 70 indents were performed across the depth profile of a metallographic cut to reveal the depth evolution of the mechanical properties of the prepared coatings. The first indent was located at the interface between the coating surface and the plane of the metallographic cut; the last one was located at the interface between the metallographic cut and the substrate. The location of each indent was logged. The load was set to 40 mN. To determine the chemical composition, EDX analyses of the metallographic cuts were performed using a Tescan MIRA FEG equipped with an Oxford Instruments EDX detector at an electron energy of 7.5 keV. For the evaluation of the composition, the internal library of standards included in programme Aztec by Oxford Instruments was used. Both the chemical composition and the mechanical properties were determined as a function of the coating thickness; for details see reference [16]. The composition of monolayers was provided by EDX analyses. The XPS measurements were done on the ESCALAB 250Xi (Thermo Fisher Scientific). XPS system is equipped with a 500 mm Rowland circle monochromator with a microfocused Al Kα X-ray source. An X-ray beam with 200 W power (650 micron spot size) was used. The survey spectra were acquired with a pass energy of 50 eV and a resolution of 1 eV. High-resolution scans of C, O and Ti peaks were acquired with a pass energy of 20 eV and a resolution of 0.05 eV. The measurements were done under an ultrahigh vacuum of 10^{-6} Pa, at room temperature. All spectra were recorded at a 90° take-off angle. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using the Avantage software. 10 etching cycles were used. The ion energy was set to 500 eV and the etching time was set to 600 s at each cycle.

The frictional properties of the coatings were evaluated using a high-temperature tribometer (CSM Instruments) via the ball-on-disc method. For all tribological tests, a 100Cr6 steel ball was used as counterpart. The following parameters were selected for the tribological tests: radial wear traces were investigated from 2.7 mm to 6.6 mm in steps of 1.3 mm, the normal force ranged from 5 to 10 N and the temperature was 20 °C.

A thin lamella for transmission electron microscopy (TEM) study was prepared using a focused ion beam in a scanning electron microscope (SEM) LYRA 3 XMU FEG/SEM × FIB by Tescan. A JEOL JEM-2100F transmission electron microscope was used to study the microstructure.

3. Results

3.1. Plasma characterisation

Fig. 1 depicts the evolution of the cathode voltage and the total pressure for the sputtering of the titanium target while the acetylene supply was slowly, linearly increased from 0 to 70 sccm at a rate of 0.15 sccm/min. The rate of the acetylene supply increase was selected to allow the acquisition of the steady-state values of the measured quantities. Increasing the acetylene supply from 0 to 25 sccm caused the total pressure and the cathode voltage to increase. The further increase in the acetylene supply led to a more pronounced pressure increase, while the cathode voltage decreased. At an acetylene supply of approximately 55 sccm, a sudden drop in the cathode voltage was observed and the further increase in the acetylene supply led to another gradual decrease of the cathode voltage. At the same moment, the increasing trend of the pressure with the increasing acetylene supply terminated, and after the drop of the cathode voltage, the pressure decreased as the acetylene supply increased. This unexpected sudden change in the measured quantities will be investigated in detail, motivated by the fact that the coatings with the desired maximal hardness grow at conditions close to those of the sudden change.

Fig. 2 provides a detailed view of the process evolution close to the drop of the cathode voltage. The acetylene supply was slowly, linearly increased from 50 to 65 sccm at a rate of 0.3 sccm/min, and in addition

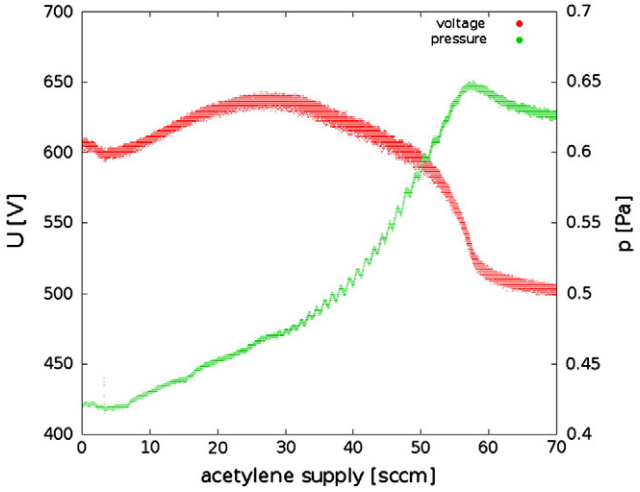

Fig. 1. Evolution of discharge voltage and pressure for sputtering of titanium target while acetylene supply was slowly linearly increased from 0 to 70 sccm at a rate of 0.15 sccm/min.