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Preparation and comparison of a-C:H coatings using reactive sputter techniques

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ABSTRACT

Amorphous hydrogenated carbon (a-C:H) coatings are widely used in several industrial applications. These coatings commonly will be prepared by plasma activated chemical vapor deposition (PACVD). The main method used to prepare a-C:H coating in industrial scale is based on a glow discharge in a hydrocarbon gas like acetylene or methane using a substrate electrode powered with medium frequency (m.f. — some 10 to 300 kHz). Some aims of further development are adhesion improvement, increase of hardness and high coating quality on complex geometries. A relatively new and promising technique to fulfil these requirements is the deposition of a-C:H coatings by a reactive d.c. magnetron sputter deposition from a graphite target with acetylene as reactive gas. An advancement of this technique is the deposition in a pulsed magnetron sputter process. Using these three mentioned techniques a-C:H coatings were prepared in the same deposition machine. For adhesion improvement different interlayer systems were applied. The effect of different substrate bias voltages (d.c. and d.c. pulse) was investigated. By applying the magnetron sputter technique in the d.c. pulse mode, plastic hardness values up to 40 GPa could be reached. Besides hardness other mechanical properties like resistance against abrasive wear were measured and compared. Cross sectional SEM images showed the growth structure of the coatings.

1. Introduction

Amorphous hydrogenated diamond-like carbon coatings (a-C:H or simply DLC) have several excellent properties like high hardness, high wear resistance and low friction coefficients. These outstanding combinations of different properties make this material a high potential tribological coating. Today diamond-like carbon (DLC) coatings are already established for a lot of technical applications and in several industrial branches, for example in the automotive industry [1–3] and for machine elements or cutting and forming tools [4,5]. Besides the coating properties, it is an important feature that DLC coatings can be deposited at relative low coating process temperatures (<200 °C). This means that a DLC coating deposition is possible on most temperature sensitive steel components without reaching their annealing temperature and without leading to a steel hardness decrease.

DLC coatings consist of a cross linked network of carbon (with sp^2 and sp^3 bonding states) and hydrogen atoms. Commonly these films exhibit intrinsic compressive stress up to a few GPa [6]. Such high stress values can lead to a lack of adhesion to the substrate and could limit the technical application.

The most commonly applied method to deposit hard DLC films is carried out in a PACVD (plasma activated chemical vapor deposition) process, more precisely in a radio frequency (r.f.) glow discharge of hydrocarbon gases with negatively self-biased substrates [7]. Unfortunately, there exist several problems in up-scaling of this r.f. technique to industrially relevant dimensions. Therefore, coating processes with mid frequency discharges (m.f., some 10–100 kHz) were developed and applied successfully [8].

To improve the adhesion of DLC coatings, due to the compressive stress to the substrate, interlayer systems, e.g. the metallic interlayer like Ti or Cr were developed [9]. Such interlayer coatings commonly were deposited with the PVD (physical vapor deposition) technique e.g. d.c. magnetron sputtering [10]. This means a technically relevant DLC coating process, including an interlayer, combines a PVD process step with a following PACVD step. This combination could lead to some drawbacks, e.g. resulting from different process pressures and therefore the difficulty to establish a gradient change from one layer to the other. Another drawback of PACVD techniques compared to PVD sputter techniques concern the coating of different components with complex geometries. In PACVD processes the gas distribution as well as the cathode surface and the distances between biased parts have to be carefully adjusted to get a homogeneous coating quality [9]. In contrast to this, PVD sputtering processes are reasonably independent from the substrate geometry [11]. To overcome these drawbacks a PVD process for a-C:H (DLC) coatings was developed. DLC coatings were prepared by reactive d.c. magnetron sputter deposition using graphite targets. For this material, the name C-DLC was introduced. C-DLC coatings have a nearly identical composition and structure and also rather similar mechanical and tribological properties like DLC deposited by r.f. or m.f. processes [12].

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In this present paper we report on DLC coatings prepared by the well established PACVD technique as well as by the reactive sputter deposition technique with graphite targets in the same coating equipment. Additionally the pulsed sputter deposition of DLC coatings is introduced as an enhancement. The mechanical and tribological properties of these sputtered C-DLC coatings deposited with different techniques will be reported. For comparison, the corresponding features and data of PACVD DLC coatings prepared by m.f. glow discharge processes are added.

2. Experimental details

2.1. Coating deposition

Both PVD C-DLC and PACVD DLC coatings were prepared using a CemeCon CC800/9 sputtering system (CemeCon AG, Würselen, Germany). The process chamber has a volume of about 0.8 m^3 and is equipped with 4 magnetron sources (target dimensions 500 mm × 88 mm). The residual pressure before starting the process was $<10^{-3}$ Pa.

As reference metal free PACVD DLC (a-C:H) coatings (2–3 µm thick) were prepared by m.f. glow discharge processes with acetylene as precursor gas. As adhesion layer an approximately 0.5 µm thick sputtered titanium layer was applied. The process pressure was around 1.5 Pa with pure acetylene gas.

The deposition processes for C-DLC (PVD a-C:H) consisted of four main steps: (i) Ar ion etching for substrate cleaning; (ii) sputter deposition of an adhesion layer respectively layer system (Cr/CrN); (iii) increasing of the reactive gas flow and target power up to a maximum value; and (iv) deposition of the C-DLC layer under constant process conditions. In the deposition steps (iii) and (iv), two side by side targets (graphite) were used (see Fig. 1). The total coating thickness was commonly >2 µm. The main parameters are summarized below:

- Targets: C-DLC (PVD a-C:H): graphite; target power: 4 kW
- Reactive gas: acetylene (C_2H_2); gas flows: Ar: 300 sccm; C_2H_2 variable
- Total gas pressure: 0.3 Pa
- Substrate potential (supplied with a d.c. or m.f. generator): −50 to −500 V
- Planetary Ø 400 mm with 6 satellites (Ø 130 mm); height 650 mm
- Distance of target and planetary: 70 mm
- Substrate rotation: 1 rpm of planetary and 2.7 rpm of satellites (two-fold rotation, three-fold rotation possible)

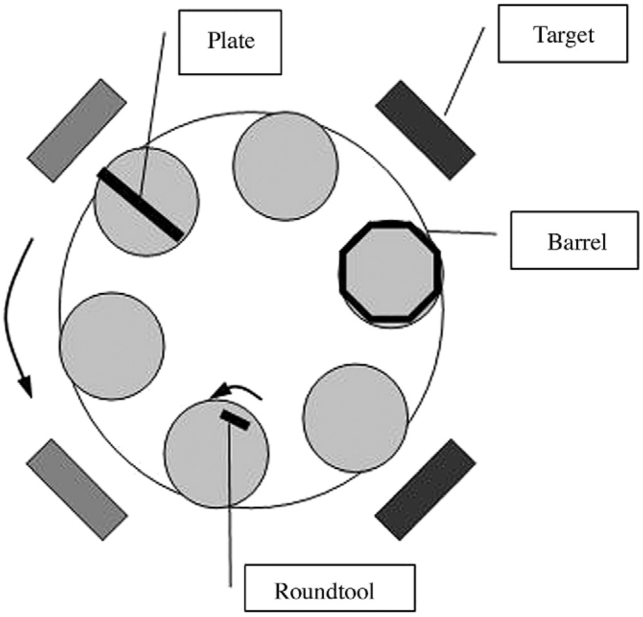

Fig. 1. Schematic illustration of the magnetron sputter machine CC800/9 from Cemecon, including different substrate positions.

The maximum substrate temperature in all processes (PACVD as well as PVD) was commonly lower than 200 °C. The temperature was derived from the well known relation of the hardness loss of hardened 100Cr6 steel in dependence of the temperature (tempering diagram). As substrate material polished steel substrates, e.g. ball bearing steel (100Cr6, hardened to 62 HRC) as well as Si wafers (one side polished, boron doped, single crystal, (100) orientation) were used. In order to get an impression of the effect of different substrate positions on the coating properties in every coating run the samples were arranged onto different substrate holders. Fig. 1 schematically shows a cross section of the process chamber and the different sample positions. Position "Plate" means the sample was clamped to a plate in the center of the satellite, "Barrel" means a position at the perimeter of the satellite and the "Roundtool" name is a free standing, exposed sample position in three-fold rotation.

2.2. Coating characterization

The morphology of the coatings was characterized by scanning electron microscopy (SEM). Furthermore the hardness (plastic hardness HU_{plast}) and Young's modulus of the coatings were measured by a Fischerscope H100 commercial instrument. The hardness and Young's modulus were derived from load vs. indentation depth curves. The indentation depth was more than 200 nm. Abrasive wear rates were determined with the ball cratering test operating with an alumina suspension (alumina glycerin suspension, 25% by weight Al_2O_3, particle size approximately 1 µm). To quantify the results, the volume of the crater ground into the coating was divided by the normal load and the track length of the rotating ball [5,13]. The unit used for abrasive wear of our coatings is 10^{-15} m^3/Nm. Further details of the abrasive wear test are published elsewhere [14].

3. Results and discussion

3.1. Comparison of PACVD and PVD processes

All coating processes were conducted in the CC800/9 coating machine. The PACVD a-C:H coatings (2–3 µm thick) were prepared by m.f. glow discharge processes with acetylene as precursor gas. The deposition rate was 1 µm/h. But at spikes and free standing samples the deposition rate in PACVD processes could be approximately two times as high as for samples clamped on plates.

The PVD a-C:H (C-DLC) films were deposited from two graphite targets powered in d.c. and also in pulsed mode with 50 kHz. For all PVD a-C:H samples reported here, the acetylene gas flow was fixed at 35 sccm. With increasing C_2H_2 content in the sputter gas, the targets will be more and more 'poisoned' with a weakly bonded hydrocarbon cover layer. This poisoning effect at higher C_2H_2 flows lead to arcing at the graphite targets in d.c. sputtering mode. For sputtering in pulsed mode stable processes are feasible even with higher C_2H_2 flows. An increase of the C_2H_2 flow leads to a higher deposition rate but mostly accompanied by a reduction of the coating hardness. The selected C_2H_2 flow is a compromise of coating properties and technical relevant deposition rates (between 0.6 and 0.7 µm/h). The process pressure was 0.3 Pa, which corresponds with a common process pressure in sputtering processes. The substrate rotation speed was kept constant also for the PVD coating processes but the applied negative substrate bias was variable. However, an additional direct hydrocarbon deposition from plasma must be taken into account for reactive sputter processes of a-C:H coatings. From former