Researches on obtaining performant carbon based coatings with enhanced wear and corrosion resistance

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Diamond-like carbon (DLC) coatings feature excellent mechanical properties and chemical properties, such as high hardness, low friction coefficient, wear resistance and corrosion resistance. This paper discusses issues relating to the friction, corrosion resistance and mechanical behaviour, for different types of DLC coating systems deposited on heat treatable steel hardened and high-tempered (a multilayer of a-C:H:W; a-C:H:Cr, a single layer of a-C:H, a-C:H:Si. These films were synthesized using a single or a combined process consisting in either r. f. reactive magnetron sputtering or / followed by Plasma Assisted Chemical Vapour Deposition (PACVD). For corrosion characterization salt spray testing according to DIN 50 021-SS standard has been performed.

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1. Introduction

The diamond-like carbon (DLC) coatings have been developed for a wide range of technological and industrial applications. It is a tribological coating used mainly in the field of mechanical engineering in order to reduce friction and wear, such as drilling and cutting tools [1-3].

In recent years,diamond-like carbon (DLC) films have attracted widespread attention due to their extreme characteristics of high hardness, chemical inertness, low friction coefficient, good wear resistance, thermal conductivity,and high transparency across a large part of the electromagnetic wave spectrum [4-7].

In mechanical engineering, low friction signifies a lower loss of energy, higher reliability and a better wear resistance [8]. However, these films have a problem; they may easy peel off from the substrate in certain situations involving friction. The failure of the film is related to a bad adhesion to the substrates, and other characteristics of the film itself, for instance internal stresses, hardness, surface roughness, topography and elastic modulus. In order to overcome this problem and improve the mechanical and tribological behavior of the films according to various requirements, different interlayer systems have been proposed. The deposition of interlayers such as titanium, silicon, chromium, CrN or tungsten, have been developed to enhance the adhesion on metal substrates, compositionally graded coatings have been deposited to minimize the stress concentration and improve the coating adhesion , and also duplex process including diffusion treatments previous to the coating have been proposed. Plasma nitriding of a steel substrate is a good possibility because it improves the tribological behavior,increases the load capability of the coating and extends its lifetime. But the characteristics of the nitride interlayer are very important because they can influence not only the adhesion but also the mechanical behavior of the system, for example, the presence of a compound layer may deteriorate the load bearing capacity in low alloyed steels . Also in stainless steels, a top porous and brittle nitrided layer affects the adhesion and it is necessary to remove it prior to the DLC deposition [9].

DLC films may be produced by a great number of deposition techniques such as plasma-assisted chemical vapor deposition (PACVD) through a hydrocarbon discharge, sputtering of a graphite target, arc-discharge, pulsed laser deposition (PLD), and ion-beam assisted deposition (IBAD) [10,11].

Different types of DLC coatings have different mechanical and electrical properties, depending mainly on the type of deposition. The tribological properties of DLC coatings do not depend only on the type of coating, but also on the working conditions or contact parameters. For this reason the coefficient of friction depends on the coating's thermal stability, which is subject to the structure, as well as on the atmosphere in which the coating is operating. A very important factor in DLC coating performance is also the humidity and the type of gas in which a coating is operating. DLC coatings with hydrogen content show a very low friction in dry air of about 0.05. The increase of humidity results in the increase of the coefficient of friction and at humidity over 90%, friction shows values from 0.15 to 0.3 . On the other hand, for the amorphous carbon (a-C), the coefficient of friction decreases with the increase in the relative humidity [8]

However, the tribological properties of diamond-like carbon coatings change significantly with the change in environment as in vacuum, in room atmosphere [12], and in different relative humidity [13,14,15].

The doping of DLC coating with different metals (Ti, Nb, Ta,Cr, Mo, W, Ru, Fe, Co, Ni, Al, Cu in Ag) leads to the changes in their mechanical properties (lower internal stress and hardness, improved adhesion) as well as in their tribological properties [8].

The a-C:H:W coating, which was a WC doped hydrogenated diamond-like carbon coating with a multilayer structure of WC and a-C:H, was deposited in a reactive sputtering process at a deposition temperature of ~230 °C. The undoped a-C:H coating was deposited by a commercial plasma-assisted chemical vapour deposition (PACVD) process with a deposition temperature of ~200 °C. A thin (≈0.1 μm) intermediate Cr layer was used for all coatings in order to improve the adhesion. The doped and undoped DLC coatings were about 2 μm thick and had a hardness of 1200 HV and 2000 HV respectively [8].

Nanoindentation and nanoscratch tests were performed for diamond-like carbon (DLC) coatings on the different steel substrates in order to investigate the deformation and failure behaviors of the coating/substrate systems and their tribological properties [1].

Staedler and Schiffmann have systematically investigated the correlation of nanomechanical and nanotribological behaviors of thin DLC coatings on different substrates (AlTiC, Si(100), fused silica, SU8 photoresist) using nanoindentation and nanoscratch techniques. The substrates cover the range of very soft (SU8 photoresist) up to very hard (AlTiC ceramic) materials showing a clear influence on the tribological response of the DLC/substrates. Therefore, the primary focus of the research is to investigate the mechanical and tribological properties of DLC coatings on different steel substrates in order to gain a better understanding of the predominant deformation mechanisms that occurred in response to nanoindentation and nanoscratch and further choosing the ideal steel substrate [1].

In this paper nanoindentation and nanoscratch tests were performed for diamond-like carbon (DLC) coatings on the single steel substrate in order to investigate their mechanical and tribological properties.

2. Experimental procedure

Physical vapour deposited (PVD) diamond-like carbon (DLC) coatings have been well known for their excellent tribological properties with low friction [16]. Recent reports showed that properties of DLC can be favourably influenced by doping with ceramic compounds. The a-C:H:W coating is a WC-doped hydrogenated a-C:H coating , which contains W in the diamond-like amorphous-hydrogenated-carbon matrix . The a-C:H:W coatings usually show low friction, high wear resistance and good adhesion, and thus are particularly suitable for friction reduction, structural and engineering applications. Moreover, the low deposition temperature (lower than 200 °C) makes it possible for a-C:H:W coatings to be deposited on lots of materials. Thus, the a-C:H:W coatings are gaining considerable scientific and industrial interest [17]. Most experimental studies and reports so far about a-C:H:W coatings have been on the deposition techniques and mechanical characterizations [18], but the general tribological properties of such coatings are beginning to get more attention.

The enhanced sputtering process is combined with PACVD in order to apply carbon-containing multifunctional coatings such as a-C:H:Cr. A hard, tough metal layer is deposited by sputtering, and PACVD is used to build up the tribologically effective carbon coating on top of it. In contrast to conventional combination coatings, multifunctional coatings are made in a single process that yields homogeneous, defect-free coatings of uniquely high quality and adhesion strength.

In the present study, the CSM Nano Indentation Tester (Nano Hardness Tester: NHT) has been used to evaluate Hardness and elastic modulus of the DLC films.

Film's hardness and Young's modulus were determined from the loading and unloading curves, carried out with an ultra low load-depth sensing Berkovich nanoindenter. The maximum load used was 30 mN, with a loading time of 30 s, holding of 30 s and unloading of 30 s, producing an average number of 10 indentations per sample[19].The hardness was measured continuously during the indentation, with the continuous stiffness measurement (CSM) technique employed.

The adhesion/cohesion of the coatings was evaluated by scratch-testing technique. In the scratch testing, a diamond tip was pulled over the coated surface with continuously increasing normal load from 1 N to 30 N. The diamond tip was a Rockwell 100C6 diamond with a 120^0 cone and a 100 μm radius spherical tip. The loading rate was 43 N/min and the loading speed was 6 mm/min and the scratch length was 4 mm. The critical loads Lc values corresponding to the adhesive failure mechanisms were measured by analysing the failures events in the scratch track by optical microscopy. Regarding to the critical loads Lc, it has been taken into consideration all the three parameters Lc1, Lc2 and Lc3, which represent the load corresponding to apparition of the first cracking (Lc1), the load for first delamination (Lc2) and the load for full delamination (Lc3) [19].

The scratch test procedure is described in more detail in the European Standard prEN 1071-3. An optical microscopy examination was carried out for the coatings after scratch testing and the typical crack behavior was recorded [20].

The dynamic friction coefficient and wear rate values (abrasion wear) were estimated using a ball-on-disc tribosystem (CSM Instruments). The tribological tests were performed in dry air. A 6 mm diameter steel ball (AISI 100Cr6) was used as the mating material. The 10 N loads were used, respectively, on the ball for measurements. The sliding speed was kept in 7.85 [cm/s] for a fixed sliding contact cycle of 1500.0 [lap]. Ambient temperature in the chamber was controlled between 23 and 24 ^{0}C. The friction coefficient of the films was continuously recorded during the test.

The equipment used for the corrosion test is Vötsch VSC 450 Salt Spray Chamber (450 refers to the capacity expressed in l). According to the standard DIN 50021-SS the minimum capacity for this salt spray test is 400 l.

For the purposes of this standard, spray tests are tests in which the corrosive agent is an aqueous sodium chloride solution with a concentration by mass of 5g/100 ml that is sprayed continuously by means of compressed air.

The samples were set up on edge, inclined at 60° to the horizontal position; temperature: 35⁰C; pH value 6.5 to 7.2; test duration: 12, 24, 48, 72, 96, 120 h; salt spray test solution: 50 g/l NaCl; according to the conditions specified for the salt-spray test DIN 50021-SS. For mass evaluation before and after the test was used an analytical balance (max 220 g, e=1 mg, min 10 mg, d=0.1 mg)

3. Results and discussion

Ten indentations were made on each sample at the same condition and the results are presented in the fig. 1. The hardness was measured continuously during the indentation.

The ratio of hardness to modulus is related to wear resistance, the higher the ratio is, the better the wear resistance is. It is found that element Cr improves the hardness, the modulus and the roughness, but reduces the wear resistance [21].

As shown in fig.1 a-C:H:Cr has good hardness end modulus values.

For the a-C:H:Si, **t**he lower coefficients of the elastic modulus are found for the films that had highest Si (at.%) incorporation. An increase in Si content in DLC could reduce the coefficient of elastic modulus but grows the ratio of hardness.

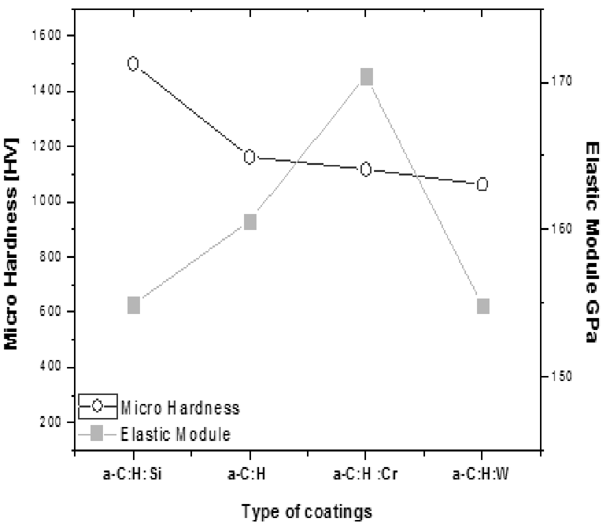

Fig. 1 The nanoindentation results with ten separate indents for the four samples

Although it has good properties of hardness and modulus of elasticity fig. 2 shows that a-C:H:Cr has a high coefficient of friction.

When sliding against pure titanium, the a-C:H:W coating exhibited mild wear and small tendency to pick up counter material in both the sliding conditions. The good anti-adhesion properties of the a-C:H:W coating in sliding contact with pure titanium can be attributed to the low chemical affinity of the a-C:H:W coating for titanium material and the graphitization of the a-C:H:W coating surface with formation of a protective graphite transfer film on the counterpart which had positive effect on the coefficient of friction and wear resistance of the friction pair. The a-C:H:W coating with good anti-adhesion properties is potential candidate in the fields of the tribological applications related to titanium material which usually has poor tribological characteristics because of the adhesion [16].

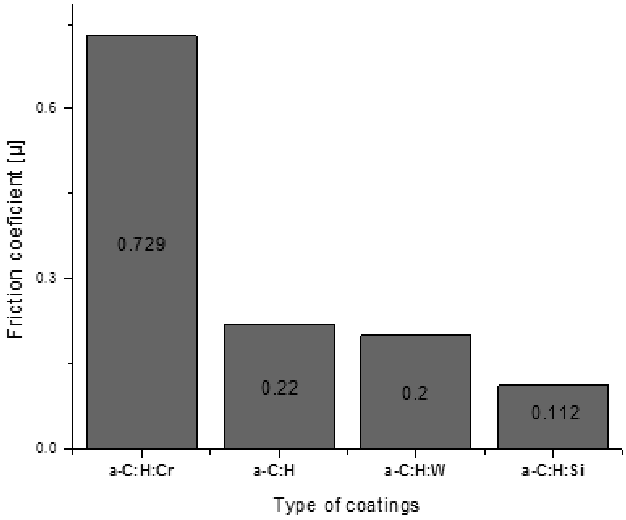

Fig. 2 Different frictions behaviour of DLC films at the same load.

The DLC film with a Si interlayer shows a low friction coefficient. This result reveals that the adhesion between the DLC film and the substrate is improved by the Si interlayer. Furthermore, a segment-structured DLC film shows a low friction coefficient until 12.000 revolutions, which is twice as many revolutions as the continuous film. This result led us to the conclusion that the fracture of the DLC film can be successfully avoided by applying segment structuring. Additionally, abrasive wear seems to be decreased because the debris were trapped in the spaces between segments, and the fracture of the film was stopped by the gaps between segments [22].

In the case of a-C:H:Si, **t**he lower coefficients of friction are found for the films that had highest Si (at.%) incorporation. An increase in Si content in DLC could reduce the coefficient of friction due to acceleration of tribo-chemical reactions [23].

Si incorporation has been widely studied and is reported as being effective in reducing friction coefficients in ambient humid air with only limited deterioration of the wear resistance [24].

The adhesion of the coatings was determined using the conventional scratch-test method [20], which showed that the L_{C2} (first delamination) value was comparable for all coatings, as can be seen in fig. 3.

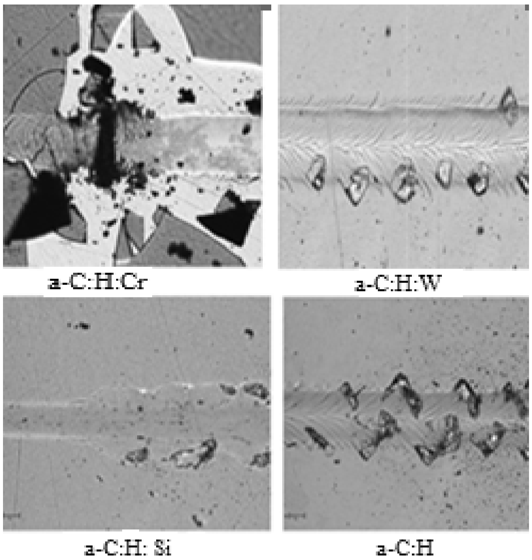

Fig. 3 The first delamination, the L_{C2} value, for different coating types.

The scratching values shown in Fig. 4 were used to study the behavior of DLC coatings during the loading process.

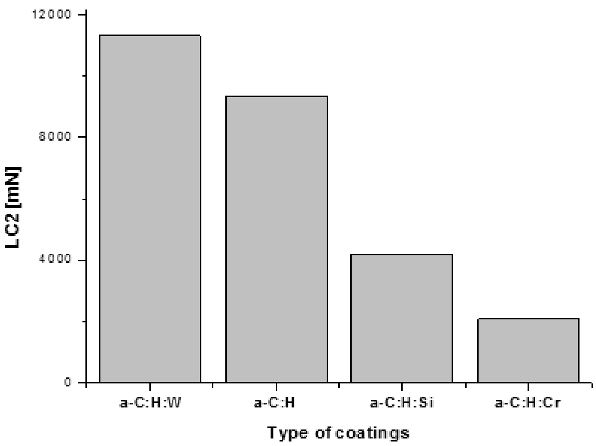

Fig. 4 Scratch penetration depth as a function of progressively applied normal load.

There are many papers reporting the friction and wear performance, certain DLC films are very soft and easily scratchable, while others show pretty hard and resistant to wear. On another hand, if the coating only cracked in a roughly semicircular arc along the scratch without peeling off, the adherence was considered good [25].

An optical microscopy examination was carried out for the coatings after scratch testing and the typical crack behaviour was recorded. The first cracks appeared for the different types of DLC coating as angular cracks on the edges of the scratch grooves and are followed by the first delamination , similarly to what is shown in Fig. 3.

According to data represented in fig. 4 a-C:H:W have the best adherence of all samples analyzed.

Dense coating materials, having good scratch resistance combined with other chemical, optical and tribological properties, are sought for many applications. Obviously, these properties can only be achieved when the quality of the adhesion is adequate[26].

The anti-corrosion properties are often required to be combined with antiscratch properties (i.e., the corrosion-resistant coating should generally not be destroyed by mechanical contacts). Their possible use at low thickness (below 1 μm) can contribute to the lower intrinsic stress and to the vital adhesion qualities[26].

The corrosion resistance is often considered to be dependent on the chemical stability of the coating and its diffusion barrier properties which are linked to atomic density and interconnecting bond strength and can prevent corrosive fluids from reaching the substrate. However, coating detachment or pin-hole defects may allow corrosive fluids to contact the substrate, with accelerated localised corrosion, and this shows the importance of coating adhesion on corrosion resistance, especially in the case of stressed coatings[26].

In Figs. 5 and 6 we can see the behavior of samples under the salt spray test.

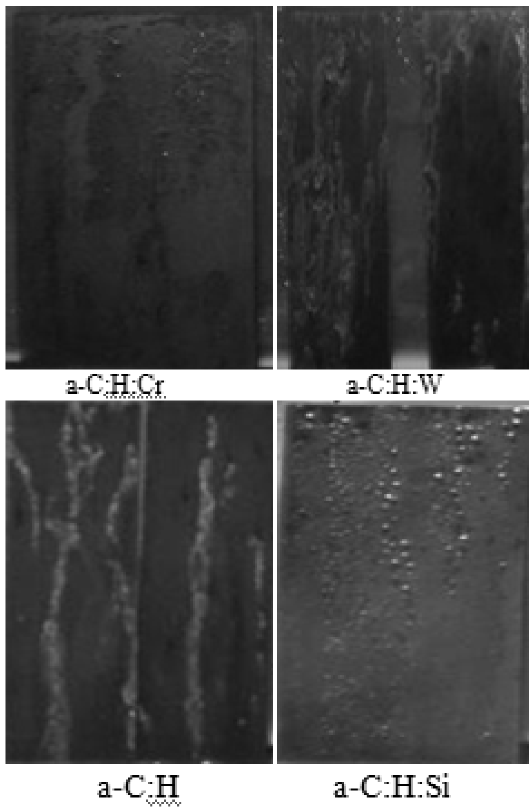

Fig. 5 Exposure time - 12h

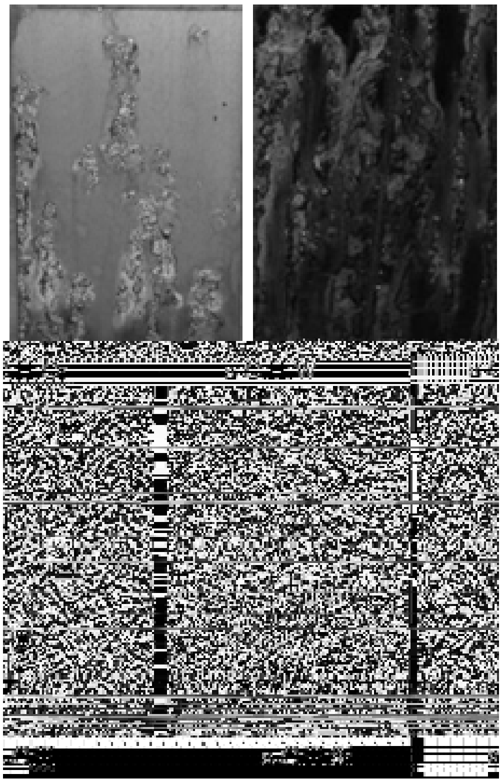

Fig. 6 Exposure time - 120h

The corrosion products are removed from the samples by pickling at ambient temperature using a solution of HCl. After the removal of corrosion products, the samples were thoroughly rinsed in water, dried and keep in a box.

The loss in mass is related to the surface area exposed to corrosion and is expressed in g/m^2.

As is mentioned in DIN 50021-SS the average mass loss shall be (140±20) g/m^2. All samples are in these parameters as is shown in figure 7.

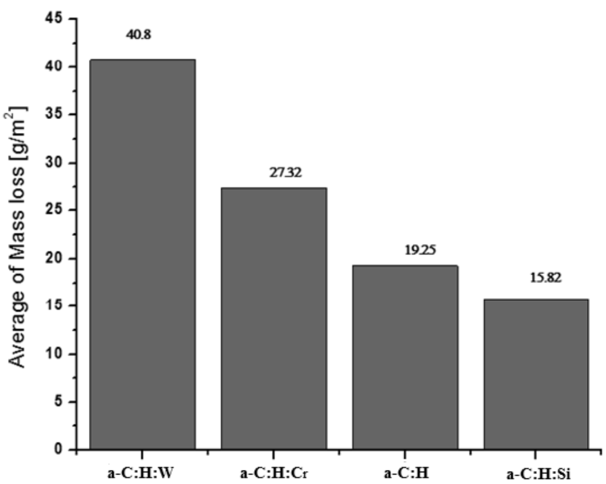

Fig. 7 Salt Test Spray- average of mass loss

The Si-incorporation in the DLC films improves the ability of corrosion protection of DLC film, and the performance of corrosion protection improved with increasing Si content in the DLC films. The insulating oxide layer on the a-C:H:Si film results in high anti-corrosion properties of the a-C:H:Si films, and very low internal stress in the a-C:H:Si films is also one of the reasons for high anti-corrosion properties of the a-C:H:Si films[27].

At room temperature, DLC films are chemically inert to practically any solvent and are not attacked by acid, alkalis or organic solvent. The films are found inert even to strong acid mixtures. So DLC is the best material for corrosion protection [28,29,30].

4. Conclusions

The nanoindentation /scratch technique can provide us very useful information about the elastic modulus, hardness, friction and wear properties.

It is found that element Cr improves the hardness, the modulus and the roughness, but reduces the wear resistance.

An increase in Si content in DLC could reduce the coefficient of elastic modulus and corrosion but grows the ratio of hardness.

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