Helena Ronkainen

Tribological properties of hydrogenated and hydrogen-free diamond-like carbon coatings

Tribological properties of hydrogenated and hydrogen-free diamond-like carbon coatings

Helena Ronkainen

VTT Manufacturing Technology

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Mechanical Engineering for public examination and debate in Auditorium E at Helsinki University of Technology (Espoo, Finland) on the 15th of June, 2001, at 12 noon.

Abstract

The amorphous hydrogenated carbon coatings (a-C:H) deposited by plasma-assisted chemical vapour deposition (PACVD), and tetrahedral amorphous carbon coatings (ta-C) deposited by pulsed vacuum arc discharge were evaluated by scratch adhesion testing, load-carrying capacity testing and tribological testing in unlubricated and lubricated sliding conditions. The wear surfaces of the coatings and counterparts were analyzed by optical and scanning electron microscopy, secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), and micro-Raman spectroscopy.

The adhesion of the a-C:H coating was improved by titanium and titanium carbide intermediate layers. The most important parameters affecting the load-carrying capacity of the a-C:H and ta-C coated systems proved to be the hardness and Young´s modulus of the substrate, and the Young´s modulus and internal stresses of the coating.

In general, the ta-C coating was more wear-resistant compared to the a-C:H coating due to the higher hardness of the coating. The wear of the counterparts sliding against the ta-C coating was one order of magnitude higher compared to the a-C:H coating due to higher surface roughness combined with the high hardness of the ta-C coating.

For the a-C:H coating, the increase in normal load and sliding velocity reduced the coefficient of friction from 0.42 to 0.1 against steel, and from 0.13 to 0.02 against alumina. The formation of graphite in the tribocontact of the a-C:H coating was observed by micro-Raman analyses when high normal loads and sliding velocities were applied causing high contact pressures and increased contact temperatures. The coefficient of friction of the ta-C coating was low and

rather stable, in the range of 0.10 to 0.19 in humid air (50% relative humidity). Some graphitization on the wear surface of the ta-C coating was observed, but the amount of graphite detected was rather small due to the stable sp^3 structure of the ta-C coating. When the ta-C coating was tested in dry air (0% relative humidity) the coefficient of friction increased to the value of 0.71. However, by doping the ta-C coating with hydrogen or methane, the coefficient of friction reduced as the hydrogen content of the coating increased. These friction properties of a-C:H and ta-C coatings can be related to the friction properties of graphite, which verifies the importance of graphite formation and the availability of hydrogen for low friction properties of the a-C:H and ta-C coatings.

In water-lubricated tests, the ta-C coating showed excellent tribological performance with a dramatic drop in the coefficient of friction from 0.07 to 0.03, but the a-C:H coating was susceptible to sliding wear in water-lubricated conditions, which resulted in an early failure of the coating. The performance of the a-C:H coating in water could be improved by alloying the coating with titanium.

In oil-lubricated conditions, the a-C:H and particularly ta-C coatings showed further improved tribological performance compared to unlubricated sliding conditions. In oil-lubricated conditions the tribofilm formation typical for the a-C:H and ta-C coatings in dry sliding conditions was prevented and the oil chemistry governed the tribochemistry in the contact. The DLC coatings are not only suggested for use in dry sliding conditions, but also in boundary lubricated conditions to provide safe operation in demanding conditions.

Preface

This thesis was supervised by Professor Hannu Hänninen, to whom I would like to express my gratitude for his valuable advice, comments and support. I would also like to thank Professor (pro tem) Martti Vilpas for his kind help during the preparation of this doctoral thesis.

To the pre-examiners of this thesis, Professor Juha-Pekka Hirvonen and Dr.Sc. (Tech) Petri Vuoristo, I would like to express my sincere thanks for their kind comments.

I would like to express my sincere gratitude to Professor Kenneth Holmberg for his encouragement, valuable discussions and good advice throughout the course of the research work and during the finalization of the thesis. I am also indebted to him for providing me with the possibility of carrying out my post-graduate studies as part of the post-graduate school in the Research Field of Operational Reliability in VTT Manufacturing Technology.

My colleagues, Mr. Simo Varjus and Ph.D. Jari Koskinen, I want to thank sincerely for their most valuable co-operation and for the pleasant collaboration during the research work. I also want to thank the personnel of our research group for all the help and support they have given to me during the course of this work as well as the personnel working in Metallimiehenkuja 6 for the enjoyable atmosphere.

Most of all, I want to express my deepest and warmest gratitude to my family, my dear husband Veli and my dear children Aino and Eero. The love, patience, understanding and care they provided were most valuable and indispensable for me during this effort.

June 2001

Helena Ronkainen

Contents

Appendices

Publications I–VIII

Appendices of this publication are not included in the PDF version.
Please order the printed version to get the complete publication
(http://otatrip.hut.fi/vtt/jure/index.html)

Nomenclature

μ	(dynamic) coefficient of friction
a-C	amorphous carbon
a-C:H	amorphous hydrogenated carbon
DLC	diamond-like carbon
ta-C	tetrahedral amorphous carbon
Al_2O_3	aluminium oxide, alumina
TiN	titanium nitride
TiC	titanium carbide
CVD	chemical vapour deposition
PACVD	plasma-assisted chemical vapour deposition
PVD	physical vapour deposition
PLD	pulsed laser deposition
MSIB	mass selected ion beam
r.f.	radio frequency
UHV	ultra high vacuum
RH	relative humidity
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
AES	Auger electron spectroscopy
EP	extreme pressure
sp^3	the four valence electrons of carbon assigned to a tetrahedrally directed sp^3 hybrid orbital forming strong covalent bonds with adjacent atoms
sp^2	three of four valance electrons assigned to trigonally directed sp^2 hybrid orbital forming strong covalent bonds with adjacent atoms
sp^1	only two electrons form strong covalent bonds
eV	electron volt

Original features

This thesis describes the different factors affecting the tribological performance of two different diamond-like carbon (DLC) coatings, namely the amorphous hydrogenated carbon coating, a-C:H deposited by the r.f. plasma technique, and the tetrahedral amorphous carbon coating ta-C, deposited by the pulsed vacuum arc discharge technique. The following features and observations are believed to be original in this thesis:

1. The unlubricated sliding tests in humid air (50% relative humidity) demonstrated that the wear of the ta-C coating was lower compared to that of the a-C:H coating. On the other hand, the wear of the counterpart was one order of magnitude higher for the counterparts sliding against the ta-C coating compared to that of the a-C:H coating due to the higher hardness and higher surface roughness of the ta-C coating.

2. The wear surfaces of counterparts sliding against the a-C:H and ta-C coatings showed the formation of tribolayers containing mainly oxides of pin material with some carbon and hydrogen detected by SIMS and AES. The thick tribolayer formation on the steel pin sliding against a-C:H coating in high normal load and high sliding velocity conditions protected the steel pins from excessive wear. On the wear surfaces of the coatings, a transfer of pin material (Fe, Cr or Al) was observed by SIMS.

3. For the a-C:H coating two different regimes of friction were detected: the increase in normal load and sliding velocity in tribological tests carried out in humid air (50% relative humidity) decreased the coefficient of friction of the a-C:H coating from the high friction regime of 0.42 to a low friction regime of 0.10 against steel, and from the high friction regime of 0.13 to a low friction regime of 0.02 against alumina. The low friction was related to graphite formation in the tribocontact, which was detected by micro-Raman analyses. The graphitization was enhanced by the high contact temperature and high contact pressure.

4. The ta-C coating had a rather stable coefficient of friction in the range of 0.14 to 0.19 against steel, and in the range of 0.10 to 0.14 against alumina

when the normal load and sliding velocity were varied in humid air (50% relative humidity). Graphite was also formed in the tribocontact of the ta-C coating, but the amount detected was lower than that for the a-C:H coating due to the highly sp^3 bonded thermally stable hydrogen-free structure of the ta-C coating.

5. In dry air (0% relative humidity) the ta-C coating exhibited a high coefficient of friction ($\mu \approx 0.7$), but the friction decreased as the hydrogen content of the hydrogen- and methane-doped ta-C coatings was increased.

6. The structure and deposition method affected the stability of coatings in water-lubricated contacts. The ta-C coating had a highly stable nature and excellent tribological properties in water showing no wear and a dramatic drop in the coefficient of friction from 0.07 to 0.03 in water-lubricated conditions. The a-C:H coating was susceptible to wear in water and did not survive in water-lubricated conditions. The performance of the a-C:H coating in water-lubricated conditions could be improved by alloying the coating with titanium.

7. In oil-lubricated conditions, the tribofilm formation typical for a-C:H and ta-C coatings in unlubricated conditions was prevented, and the oil chemistry governed the tribocontact. The a-C:H and particularly ta-C coatings showed better tribological performance under oil lubrication compared to unlubricated sliding conditions. The coefficient of friction was reduced by 10–40% under boundary lubricated conditions. The DLC coatings can thus be suggested for the boundary lubricated conditions to provide safe operation in demanding conditions.

List of publications

This dissertation consists of a summary of main results and eight appended publications I–VIII.

Publication I   Ronkainen, H., Koskinen, J., Varjus, S. & Holmberg, K. 1999. Experimental design and modelling in the investigation of process parameter effects on the tribological and mechanical properties of r.f.-plasma deposited a-C:H films. Surface and Coatings Technology, Vol. 122, pp. 150–160.

Publication II   Ronkainen, H., Vihersalo, J., Varjus, S., Zilliacus, R., Ehrnstén, U. & Nenonen, P. 1997. Improvement of a-C:H film adhesion by intermediate layers and sputter cleaning procedures on stainless steel, alumina and cemented carbide. Surface and Coatings Technology, Vol. 90, pp. 190–196.

Publication III   Ronkainen, H., Koskinen, J., Varjus, S. & Holmberg, K. 1999. Load-carrying capacity evaluation of coating/substrate systems for hydrogen-free and hydrogenated diamond-like carbon films. Tribology Letters, Vol. 6, pp. 63–73.

Publication IV   Ronkainen, H., Koskinen, J., Likonen, J., Varjus, S. & Vihersalo, J. 1994. Characterization of wear surfaces in dry sliding of steel and alumina on hydrogenated and hydrogen-free carbon films. Diamond and Related Materials, Vol. 3, pp. 1329–1336.

Publication V   Ronkainen, H., Likonen, J., Koskinen, J. & Varjus, S. 1996. Effect of tribofilm formation on the tribological performance of hydrogenated carbon coatings. Surface and Coatings Technology, Vol. 79, pp. 87–94.

Publication VI   Ronkainen, H., Varjus, S., Koskinen, J. & Holmberg, K. 1999. Friction and wear performance of a-C:H films in a wide normal load and sliding velocity range. Tribologia, Finnish Journal of Tribology, Vol. 18, No. 1, pp. 3–12.

Publication VII   Ronkainen, H., Varjus, S., Koskinen, J. & Holmberg, K. 2001. Differentiating the tribological performance of hydrogenated and hydrogen-free DLC coatings. Wear, Vol. 249, pp. 260–266.

Publication VIII Ronkainen, H., Varjus, S. & Holmberg, K. 1998. Friction and wear properties in dry, water- and oil-lubricated DLC against alumina and DLC against steel contacts. Wear, Vol. 222, pp. 120–128.

1. Introduction

The interest in the constituent parts of tribology is older than recorded history, but it was not until 1966 that the word tribology was first introduced. The word tribology was derived from the Greek word *tribos* meaning rubbing according to Peter Jost [Dowson 1998]. Since the beginning of the twentieth century, the enormous industrial growth has led to the demand for better tribological solutions, which tremendously expanded the knowledge in all areas of tribology [Bowen & Tabor 1950, Halling 1978, Suh 1986, Bhushan 1999].

Tribology is defined as the science and technology of interacting surfaces in relative motion and of related subjects and practices. The nature and consequence of the interactions that take place at the interface control the friction, wear and lubrication behaviour. Friction is determined as the resistance to motion during sliding or rolling, which is experienced when one solid body moves tangentially over another with which it is in contact. Wear is the surface damage or removal of material from one or both of two solid surfaces in a sliding, rolling or impact motion relative to one another.

Nowadays, tribology is crucial to modern machinery that incorporates sliding and rolling surfaces. The importance of friction reduction and wear control must be emphasized for economic reasons and for long-term reliability. The savings achieved by better tribological practices are significant and therefore research in tribology is aimed at minimizing and eliminating the losses resulting from friction and wear. Tribology has turned out to be the art of applying solutions to problems of great economical significance, namely, the reliability, maintenance and wear of technical equipment, ranging from spacecraft to household appliances.

Surface engineering provides an excellent means of combining the low friction properties and high wear resistance of different materials and components by incorporating the technologies of surface treatments and coating deposition. Surface engineering can be defined as the design of a composite system, *i.e.* the coating and the substrate, which has a performance that cannot be achieved by either the coating or substrate alone. This possibility to provide bulk material with desired tribological surface properties has greatly increased the utilization of surface engineering during recent decades. Surface coatings can be produced

by several methods, but chemical vapour deposition (CVD) and physical vapour deposition (PVD) have been the most widely adopted techniques for tribological applications [Rickerby & Matthews 1991, Gissler & Jehn 1992, Mencík 1996]. The surface coatings have favourable tribological properties, which have been applied in many practical applications in the field of cutting and forming tools, bearings, gears and magnetic recording devices. Diamond and diamond-like carbon coatings have attracted much attention and been under intensive research since the middle of the 1980s [Holmberg & Matthews 1994].

Diamond is the hardest natural material known. It also has other unique properties, like a high elastic limit and yield stress, high thermal conductivity, chemical inertness, excellent electrical insulation characteristics, high dielectric constant, low coefficient of thermal expansion and the lowest compressibility of any material. Diamond can also be doped with other elements to make it a semiconductor. Diamond is highly transparent to light from the visible to the infrared parts of the spectrum [Ball 1997]. In addition to this, it exhibits good tribological properties when polished [Gardos 1998]. The properties and the high density of diamonds tell us that they crystallize at very high pressures. In nature, this means that diamonds are created by geological processes at great depths within earth, generally more than 150 kilometres deep. The first man-made diamonds were synthesized in the 1950s by using high pressure and high temperature techniques. Later in the 1980s, diamond could also be produced at lower pressures in the form of polycrystalline coating by using CVD deposition techniques [Ball 1997, Lee *et al.* 1999]. These polycrystalline diamond films possess many of the excellent properties of diamond, even though the surface roughness limits the use of diamond in many tribological applications. Diamond-like carbon is a name commonly accepted for hard carbon coatings that have similar mechanical, optical, electrical and chemical properties to diamond, but which do not have a dominant crystalline lattice structure. They are amorphous and consist of a mixture of sp^3 and sp^2 carbon structures. DLC coatings can be deposited by advanced CVD and PVD techniques, which provide a smoother surface quality compared to diamond films. Diamond-like carbon is a term used to describe a variety of carbon-based materials that have attractive properties, such as low coefficient of friction, high wear resistance, high hardness, chemical inertness, a relatively high optical gap and high electrical resistivity. For these properties, DLC coatings are used as protective coatings in several applications from razor blades to hard disc drives in personal computers.

The aim of this work was to study the tribological performance of two different types of DLC coatings, namely amorphous hydrogenated carbon, a-C:H, and tetrahedral amorphous carbon, ta-C, coatings. The fundamental phenomena affecting the tribological performance were investigated by tribological tests and by using different analysis techniques. The tribological performance was evaluated in unlubricated and lubricated sliding conditions. Additionally, the adhesion of the coating and the load-carrying capacity of the coating-substrate systems were studied in order to improve the functional performance of the coatings in tribological contacts.

1.1 Structure and deposition of diamond-like carbon coatings

Carbon has three different types of bonding configurations, namely sp^3, sp^2 and sp^1. In diamond, carbon has four sp^3 hybridized orbitals. These sp^3 orbitals contribute to the formation of four equal carbon-carbon bonds with adjacent atoms, which produces the tetrahedral structure of diamond. This covalently bonded tetrahedral structure is the origin of the superior properties of diamond, like high hardness and high thermal conductivity. Graphite has three trigonally directed sp^2 hybrid orbitals, which lie in plane. Each carbon atom in plane is bonded to three other carbon atoms with strong covalent bonds. The layers of carbon atoms are attracted to each other by weak van der Waals forces producing the layered structure of graphite. The layers can cleave easily, which accounts for the typical low friction property of graphite [Guy 1976, Bhushan 1999]. The diamond-like carbon films have a mixed sp^3/sp^2 structure with different proportions of sp^3 and sp^2 bonds depending on the deposition techniques and deposition parameters used. The structure is claimed to consist of sp^2 bonded clusters embedded in an amorphous sp^3 bonded carbon matrix [Dischler 1987, Robertson 1992].

One major group of diamond-like carbon coatings is the hydrogenated amorphous carbon, a-C:H, coatings. The hydrogen content of a-C:H films can differ considerably depending on the deposition method, hydrocarbon source gas and the deposition parameters used. For a-C:H films, hydrogen is important for obtaining a wide optical gap and high electrical resistivity and stabilizing the diamond structure by maintaining the sp^3 hybridization configuration [Donnet &

Grill 1997]. Another group of DLC coatings is the metastable form of amorphous carbon (a-C). For a-C films, hydrogen is generally treated as an impurity. The hydrogen-free form of amorphous carbon, which is highly sp^3 bonded, is known as tetrahedral amorphous carbon, ta-C. It is also referred to as amorphous diamond because the structure is locally tetrahedral, like diamond, even if the structure is disordered on a larger scale. The compositions of diamond-like carbons can be displayed on a ternary phase diagram of sp^3 ratio, sp^2 ratio and hydrogen content of the film, as shown in Figure 1. The sp^2 bonded graphitic carbon lies in the lower left-hand corner. Phases that have too high a content of hydrogen cannot form an interconnected molecular structure, but form gas or liquid molecules, and lie at the lower right-hand corner of the diagram. The typical a-C:H coatings are situated in the middle of the diagram showing a varying ratio of sp^3/sp^2 bonding and hydrogen content. The ta-C coatings are situated on the left side depending on the ratio of sp^3/sp^2 bonding [Robertson 1999].

DLC coatings are formed when ionized and decomposed hydrocarbon or carbon species hit the surface with energies ranging from several tens of eV to 200 eV [Angus 1987]. All methods for the deposition of DLC films are non-equilibrium processes characterized by the interaction of energetic ions with the surface of the growing films. The methods can be divided into chemical vapour deposition and physical vapour deposition techniques. The CVD techniques, such as d.c. plasma and radio frequency (r.f.) plasma assisted chemical vapour deposition, and PVD techniques, like sputter deposition, ion-plating techniques and ion beam techniques can be used for depositing the hydrogenated a-C:H coatings. The PVD techniques, such as magnetron sputtering, mass selected ion beam (MSIB), cathodic arc and laser plasma deposition can be used for hydrogen-free a-C and ta-C coatings [Weissmantel 1985, Neuville & Matthews 1997, Robertson 1999]. DLC coatings can be deposited at temperatures that are below 200 °C [Donnet 1995] to 325 °C [Donnet & Grill 1997]. This property makes it possible to deposit DLC coatings on most relevant engineering materials, including polymers.
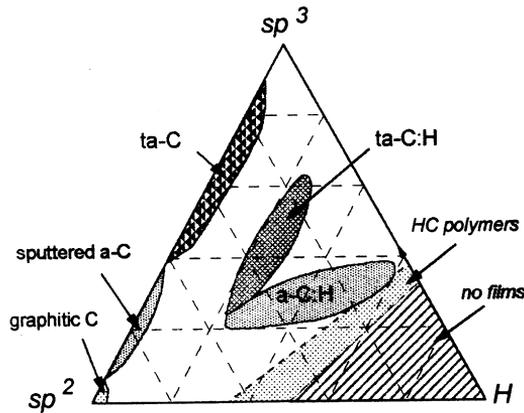
Figure 1. Ternary phase diagram of sp^3, sp^2 and hydrogen contents of various forms of diamond-like carbon [Robertson 1999].

1.2 Fundamental properties of diamond-like carbon coatings

The structure and properties of DLC coatings largely depend on the deposition technique and deposition parameters applied, but some common features characterizing DLC coatings can be mentioned. Firstly, the most important deposition parameter that influences the film properties is the ion energy. This is often expressed as the negative bias voltage in techniques based on hydrocarbon decomposition. The other significant parameters of influence, such as deposition pressure or flux density, depend on the deposition techniques used. Secondly, the films are typically formed on substrates at rather low temperatures, typically less than 100 ^{o}C, and heating of the substrate over a few hundred degrees Celsius usually has detrimental effects on the film properties. As a third feature, the substrate material seems to have only little influence on the film growth and the film properties [Weissmantel 1985].

Diamond has the highest Young´s modulus (1100 GPa) and hardness (~100 GPa) of any materials due to its high molecular density. The values of hardness for many types of present amorphous hydrogenated diamond-like carbon films reach only about 15% of the hardness of diamond itself, essentially

because they may contain 20–50% sp^2 carbon and 20–60 at.% hydrogen, as shown in Table 1 [Robertson 1992]. Young´s modulus and hardness of a-C:H may reach values of 200 GPa and about 25 GPa, respectively. The ta-C films are typically mainly sp^3 bonded and therefore the Young´s modulus and hardness can reach values of 700 GPa and 60 GPa, respectively [Robertson 1999].

Table 1. Properties of various forms of carbon [Robertson 1992].

	Density (g cm^{-3})	Hardness (GPa)	% sp^3	at.% H	Band gap (eV)
Diamond	3.515	100	100		5.5
Graphite	2.267		0		-0.04
C$_{60}$			0	0	3
Glassy C	1.3–1.55	2–3	~0		0.01
a-C, evap.	1.9–2.0	2–5	1		0.4–0.7
a-C, sputt.	1.9–2.4	11–15	2–5		0.4–0.7
a-C, MSIB	3.0	30–130	90±5	< 9	5.5–1.5
a-C:H, hard	1.6–2.2	10–25 [1]	30–60	10–40	0.8–1.7
a-C:H, soft	0.9–1.6	< 5	50–80	40–65	1.6–4
Polyethylene	0.92	0.01	100	67	6
ta-C [2]	3.0	55–65	mainly	< 1	

[1] Data from Robertson [1999]

[2] Data from Voevodin *et al.* [1996b].

The evolution of high compressive internal stresses in DLC films depends on the deposition method and deposition conditions used and can result in severe problems. The internal stresses of several GPa, up to 4–6 GPa, have been measured from a-C:H films [Weissmantel 1985] and in ta-C films even higher stresses, up to 10–12 GPa, have been observed [Robertson 1999].

Diamond-like carbon is a thermodynamically metastable form of carbon, compared to graphite. When the temperature is increased, thermal decomposition/graphitization of a-C:H films will occur accompanied with the out-diffusion of hydrocarbons and/or hydrogen. The threshold temperature for

gas out-diffusion increases from 300 °C to 600 °C with increasing ion energy used in the deposition process [Dischler *et al.* 1983]. Additionally, the mass of the desorbed molecules decreases with increasing bias voltage and only hydrogen out-diffusion is observed in films deposited with high ion energy [Wild & Koidl 1987]. When the threshold temperature is exceeded, the film transforms to graphite crystallites due to the dehydrogenation of the a-C:H film. The hardness remains approximately constant up to a temperature of 700 °C, which may be attributed to incomplete crystallization of the graphite grains at high temperatures [Liu *et al.* 1993]. Since the ta-C films contain no hydrogen and they are predominantly bonded with strong sp^3 bonds, their thermal stability is good even up to 1000 °C. The thermal stability decreases with the decreasing sp^3 component and, for instance, a 40% sp^3 bonded ta-C film starts to graphitize at 430 °C [Kalish *et al.* 1999].

In order to fulfil the requirements of the application, the coatings need to have sufficiently good adhesion to the substrate. The adhesion depends on the substrate material and can be affected by the surface pre-treatment, deposition method and deposition parameters used. Good adhesion of DLC films has been found with carbide- and silicide-forming substrates. The adhesion properties of DLC films can be improved by applying intermediate layers, graded and multilayered structures, such as TiC, SiC, Ti, or TiN/TiC [Donnet & Grill 1997, Voevodin *et al.* 1996a].

1.3   Tribological properties of diamond-like carbon coatings

The friction and wear properties of diamond-like carbon coatings are affected by the properties of the coatings, and the environmental as well as tribological parameters applied [Holmberg & Matthews 1994, Gangopadhyay 1998]. Generally speaking, DLC coatings can be considered as low-friction coatings compared to most bulk materials and, for example, to ceramic coatings, such as TiN. While TiN typically has a coefficient of friction of about 0.5 against a steel counterpart [Ronkainen *et al.* 1992], DLC films typically have a coefficient of friction of $\mu \leq 0.2$ in normal atmospheres.

The tribological performance of diamond and graphite is influenced by environmental parameters, such as atmosphere and temperature. In humid air, diamond and graphite show comparable values of coefficients of friction, namely 0.2 for graphite and 0.1 for diamond against diamond. In vacuum they both exhibit a high coefficient of friction, for graphite 0.5 and for diamond 0.9 [Buckley 1981].

From the pioneering tribological experiments of Enke *et al.* [1980], a-C:H films are known to be sensitive to environmental parameters. The coefficients of friction of DLC films range from less than 0.01 to more than 0.5, depending on the nature of the DLC film and the tribotesting conditions. The coefficient of friction of hydrogenated a-C:H films in vacuum typically ranges from 0.007 to 0.02, and in ambient air (20% < RH < 60%) from 0.1 to 0.4 [Donnet 1998]. The coefficient of friction of a-C:H is low also in humid nitrogen or oxygen and extremely low in dry nitrogen. The loss of hydrogen in annealing at high temperatures causes a marked increase in the coefficient of friction in ultra-high vacuum (UHV), but not in humid environments [Grill 1997].

Different mechanisms have been proposed for the tribological performance of DLC films. The ultra-low friction in inert environments is attributed by Gardos to a high surface finish and the presence of an ultra-thin polymer-like layer on top of the coating with weak van der Waals forces acting in the layer. In the humid oxygen-containing environment, the coefficient of friction increases. A ten-fold increase in friction corresponds to an increase in bond strength from about 0.08 eV per bond, typical for van der Waals bonding of hydrocarbons, to about 0.21 eV per bond, typical for hydrogen bonding of water molecules at C=O sites [Gardos 1994].

Other mechanisms that have been proposed are micrographitization and the formation of a transfer layer. In micrographitization, mechanical interactions between sliding interfaces are claimed to lead to graphitization of microcontact regions. As a result, DLC films tend to behave more or less like graphite and graphite-like carbon with sp^2 type bonding [Jahanmir *et al.* 1989].

Formations of a transfer layer have been reported by, *e.g.* Memming *et al.* [1986], Hirvonen *et al.* [1990], Sugimoto & Miyake [1990] and Kim *et al.* [1991] among the first authors. Memming *et al.* found material transfer during

sliding, which affected friction in dry nitrogen and dry oxygen. Hirvonen *et al.* observed an essentially different transfer layer from the initial coating structure when studying ta-C films deposited by an arc discharge technique. Kim *et al.* discovered material transfer that affected both the friction and wear properties of a-C:H films, whereas Sugimoto *et al.* observed the transfer of hydrocarbons with a specific orientation to the ball surface, which reduced friction. Miyoshi [1990] observed the generation of a layer with evidence of a build-up of reaction products that caused a drastic decrease in friction behaviour.

Erdemir *et al.* [1993] discovered a carbon-rich transfer layer formation on the pin wear surface after a long sliding distance against a-C:H coating produced by ion beam deposition. The carbon-rich transfer layer was found to reduce friction [Meletis *et al.* 1995] and later evidence of graphitization was detected in the transfer layer [Erdemir *et al.* 1995]. The mechanisms governing the friction behaviour were studied and the wear-induced graphitization of a-C:H films was presented by Liu *et al.* [Liu *et al.* 1996a, Liu & Meletis 1997]. Thus, wear-induced graphitization was expected to result in microcrystalline graphite when the accumulation of sliding-induced heat caused the gradual destabilization of carbon-hydrogen bonds in the tetrahedral structure [Erdemir *et al.* 1996, Liu *et al.* 1997]. The removal of hydrogen can, thus, trigger the transformation of an sp^3 structure into a graphite-like sp^2 structure [Liu *et al.* 1996b].

Donnet *et al.* studied the friction and wear performance of a-C:H films in UHV and ambient air. They claim that the friction of a-C:H films is strongly influenced by the presence of water vapour at partial pressures higher than 0.05 kPa (RH=2%). The coefficient of friction increases from 0.01 to 0.1, within the water vapour pressure range of 0.01–0.05 kPa. Oxygen has no effect on the ultra-low friction performance up to a gas pressure of 6 kPa. They found no evidence of friction-induced tribo-oxidation of DLC and the friction level was found to be governed by the thickness of the transfer film on the counter surface of steel [Donnet *et al.* 1998b]. Kim *et al.* [1991], however, reported that, in dry and humid air, the oxidation affects DLC by the tribochemical formation of C=O bonds. This was verified with *in-situ* analysis at high loads (1.07 GPa). For modest loads (7.8 kPa), the creation of carbon-oxygen single bonds was reported [Olsen *et al.* 1996].

Donnet *et al.* also reviewed the influence of coating properties on the friction properties of a-C:H films in ultra-high vacuum. Ultra-low friction ($\mu<0.01$) is reached, when the hydrogen content is high enough (about 40 at.%), the carbon network is sufficiently cross-linked and the structure has a noticeable fraction of hydrogen unbonded to carbon. High friction in UHV ($\mu>0.5$) was found for a-C:H films of lower hydrogen content, a lower fraction of hydrogen bonded to carbon, a lower sp^3 fraction and a more cross-linked carbon network, which is observed for coatings deposited with high impact energy [Donnet & Grill 1997, Donnet *et al.* 1998a].

The pulsed laser deposited (PLD) hydrogen-free films have a coefficient of friction of less than 0.1 in vacuum and 0.03 in dry nitrogen [Grill 1997]. Voevodin *et al.* [1996b] studied hydrogen-free DLC coatings prepared by a PLD technique. They showed the formation of a graphite-like transfer layer during sliding friction. The sp^3 to sp^2 phase transformation was observed after several thousands of sliding cycles. The surface graphitization was found to be responsible for low friction in humid air, and for high friction in vacuum. The hydrogen-free carbon films deposited by cathodic vacuum arc, are found to give coefficient of friction values in the range of 0.04 to 0.18 in ambient atmospheres [Donnet 1995].

The properties of DLC films can be changed or tailored by different techniques. Alloying the DLC structure can be used to inhibit the trioactivity of the hydrogenated a-C:H coatings. Different alloying techniques may also be used to reduce the internal stresses of the DLC coatings. Silicon incorporation in a-C:H structure affects most coating properties, including a decrease in surface energy and internal stresses, and the tribological behaviour. The coefficient of friction appears to be significantly reduced, below $\mu=0.1$, compared to an undoped a-C:H film in ambient air. Fluorine incorporation in the a-C:H structure affects the surface properties and reduces the internal stresses. Nitrogen-containing DLC films show a reduction in internal stresses, but no significant differences in the tribological performance are shown compared to undoped DLC. Alloying a-C:H films with different metals, such as Ti, Nb, Ta, Cr, Mo, W, Ru, Fe, Co, Ni, Al, Cu, Ag, generally reduces the compressive stresses to values below 1 GPa. The metal-alloyed a-C:H structures exhibit steady-state friction values in the range of 0.10 to 0.20 with slight dependence on the humidity. The tribological behaviour of these metal-alloyed a-C:H films has been explained by

a combination of ceramic-like properties (high hardness) and polymer-like properties (high elasticity, low surface energy) [Donnet 1998]. The internal stresses can also be reduced by applying complicated composite structures to DLC coatings. Different types of graded and multilayer coatings, functionally gradient coatings or nano-composite coatings have been used to reduce internal stresses in both a-C:H and ta-C coatings [Voevodin *et al.* 1997, Venkatram *et al.* 1999].

1.4   Applications of diamond-like carbon coatings

The physical and mechanical properties of DLC films make them suitable for a variety of applications, many of them exploiting the attractive tribological characteristics of DLC.

The DLC coatings used in industrial applications can be divided into two major categories, namely undoped single-layer DLC films and DLC films with the addition of other elements. The former are used when contact pressures are relatively low, shear stresses are low and/or heat generation is minor. Some examples of such applications are found in knives used in the textile industry to cut through many layers of synthetic fibre, and dies used in the extrusion of polystyrene in the packing industry. For high shear stress applications, DLC coatings with interfacial bonding layers and alloyed or layered coating structures are typically used. Such applications range from gears for aircraft landing-flap controls, ball bearing races or cages, journal bearings, compressor screws, and extrusion dies in cutting tools for aluminium [Matthews & Eskildsen 1994]. In addition, a number of moving parts inside automobile engines and, for example, diesel engine injection systems, have been coated and wear rates have been successfully reduced [Bloyse 2000]. DLC coatings have also been used as anti-reflection coatings on germanium and silicon optics and solar cells or for the protective coating on zinc sulphide IR windows. The scratching resistance of metal objects has been improved by DLC coatings. DLC has been proposed for biomedical applications, such as orthopaedic pins and screws and for bearing surfaces of artificial joints [Lettington 1998]. One widely used application for DLC coatings is the protection of the hard disc drives and other magnetic recording media [Talke, 2000]. The softer DLC films are mostly used for components, whereas hard DLC films are widely used as tool coatings [Grischke *et al.* 2000].

2. Materials and test methods

2.1 Deposition methods

This thesis describes the research work carried out on two different types of DLC coatings, namely an amorphous hydrogenated a-C:H coating and a hydrogen-free ta-C coating, which is also known as tetrahedral amorphous carbon coating. The name a-C, which is used in publications IV and VIII, refers to the ta-C coating. Two different deposition techniques were used for the coating deposition. The hydrogen-free ta-C coatings were deposited by a pulsed vacuum arc discharge method and the hydrogenated a-C:H coatings by the plasma assisted CVD method.

The deposition of the a-C:H coatings was carried out with a capacitively coupled r.f. (13.56 MHz) plasma-assisted CVD method. The substrates were placed directly on the powered cathode and methane (CH_4) was used as the source gas. Prior to deposition, the substrates to be coated were sputter cleaned in argon plasma and a thin titanium (Ti) or titanium carbide (TiC) intermediate layer was deposited on the substrate surface by evaporating titanium into argon or methane atmosphere. The pressure and the bias voltage were controlled during the deposition and the typical values for the coatings produced were 5.5 Pa and -550 V, respectively. For the deposition, a water-cooled cathode was mostly used and the deposition temperature was about 100 ^{o}C after the deposition (Publications I & IV & V & VI & VII & VIII). For some studies, no cooling of the cathode was applied and the deposition temperature in these cases varied in the range of 200–250 ^{o}C (Publications II & III). The deposition rate was about 0.5 μmh^{-1} and the film thickness was typically about 1 μm.

The study of the effect of the deposition parameters on the coating properties was carried out for the a-C:H coating. The deposition pressure was varied in the range of 0.7 to 10.7 Pa and the bias voltage in the range of -100 to -1000 V. The central composite design method was used for experimental design and a statistical analysis and three-dimensional response surface modelling was used for the analysis of the results (Publication I).

The ta-C coatings were deposited by a pulsed vacuum arc discharge method in which the arc discharging on a cylindrical graphite cathode provided the carbon species for the plasma. The capacitor arrangement was used to provide a current pulse, which accelerated the carbon species to the substrate surface, situated at about 300 mm distance from the cathode. Two different deposition apparatus were used for ta-C deposition, namely the equipment with curved magnetic field to deflect the plasma (Publication IV) and the equipment with a direct carbon arc (Publications III & VII & VIII). In order to improve the adhesion of the coating, a thin titanium layer was deposited as an intermediate layer on the substrate by using a continuous current arc device with curved magnetic field to deflect the plasma (Publications III & VII & VIII). The substrates were sputter cleaned by using argon ion beam sputtering prior to the deposition. The pressure of different deposition runs varied in the range of $3 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$ Pa and the deposition temperature was typically below 80 ^{o}C. The nominal deposition rate was in the range of 0.5 to 0.7 μmh^{-1} and the film thickness commonly used was 0.5 μm (Publications III & IV & VII & VIII).

2.2 Properties of a-C:H and ta-C coatings

The fundamental characteristics of the amorphous hydrogenated a-C:H coatings and hydrogen-free ta-C coatings deposited for the research work (Publications I–VIII) are represented in Table 2.

Table 2. The fundamental characteristics of a-C:H and ta-C films.

Coating	Deposition parameters			Coating properties			
	U_B	p	Temp.	H-content	sp^3 bonding	Hardness	Young´s modulus
	V	Pa	^{o}C	at %	%	GPa	GPa
a-C:H	-550	5.5	100	26–33	70	14±1	129±5
ta-C	-	$3x10^{-4}$	60	< 1	66 [1]	54±18	445±57

[1] Data from Koskinen *et al.* [1998].

Besides the single-layer coatings, also doped a-C:H and ta-C coatings were deposited. The a-C:H(Ti) coating was produced by depositing a titanium-doped a-C:H surface layer by evaporating titanium into an argon-methane glow discharge (Publication VIII). For the ta-C coating, hydrogen-doped surface layers were produced by depositing the films in hydrogen or methane atmospheres in order to produce coatings (ta-C)+(H_2:ta-C) and (ta-C)+(CH_4:ta-C) (Publication VII).

The ta-C coating was hydrogen-free, hard, and mostly an sp^3 bonded carbon coating. The a-C:H coating was hydrogenated and softer compared to ta-C. The studies by SEM showed that the surface of the a-C:H film was smooth and dense in appearance and the surface roughness of the a-C:H deposited substrate remained the same after the deposition. The ta-C film had a greater number of particles embedded in the film, which increased the surface roughness of the ta-C coated samples to about R_a 0.05 µm from the original surface roughness of R_a 0.03 µm typically used in this research (Publications I–VIII).

2.3   Test methods

The coating properties were evaluated using different techniques. For adhesion evaluation scratch testing was used, and for the load-carrying capacity evaluation of the coating-substrate systems the ball-on-disc test set-up was utilized. The tribological testing was carried out by using a pin-on-disc tester and a reciprocating ball-on-disc wear tester. Different characterization techniques were applied for the analyses of the coatings and wear surfaces.

2.3.1   Adhesion and load-carrying capacity tests

The practical adhesion, which is a function of fundamental adhesion and method-dependent factors, signifies the force required to detach the coating from the substrate [Mittal 1995]. The practical adhesion of the a-C:H coatings was measured by using the scratch adhesion testing method [Valli *et al.* 1985, prEN1071-3 1999]. The diamond stylus, with a tip radius of 200 µm, was loaded against the coated substrate with a loading rate of 100 Nmin^{-1} and a horizontal displacement rate of 10 mmmin^{-1}. By optical microscopy, the critical load value (L_{C2}) describing the onset of adhesive failure of the coating was determined. The

substrate materials used for the adhesion studies were stainless steel, alumina and cemented carbide (Publication II).

The load-carrying capacity was determined in this case as the ability of the coating-substrate system to withstand the normal and tangential forces created by the system in a way that the functional properties of the coated system remained unchanged. The reciprocating ball-on-disc test set-up produced the most comprehensive information on the load-carrying capacity of the coated systems. In this test, alumina (Al_2O_3) balls with two different diameters, 4.8 mm and 10 mm, slid against the coated substrate with a normal load of 100 N, which created initial Herzian maximum contact pressures of 2.5 and 4.1 GPa, respectively. The sliding velocity applied was 1 mms^{-1} and the stroke length was 10 mm. Two (for ta-C) to five (for a-C:H) reciprocating passes were performed on the coated samples. The substrate materials used for load-carrying capacity evaluation were annealed stainless steel (340 HV), hardened stainless steel (700 HV), alumina (2470 HV) and cemented carbide (2670 HV) (Publication III).

2.3.2 Tribological tests

The unlubricated tribological tests were carried out in ambient air with controlled 50±5% relative humidity (RH) and 22±2 ^{o}C temperature. The tribological performance of a-C:H coating was evaluated by unlubricated pin-on-disc tests against steel (100 Cr 6, AISI 52100) and alumina (α-Al_2O_3). When the effect of the deposition parameters on the tribological performance of the a-C:H coatings was evaluated, the sliding velocity of 0.6 ms^{-1} and normal loads of 10 N and 5 N were applied to the steel and alumina pins, respectively (Publication I). When the tribological performance of the a-C:H coatings was assessed by pin-on-disc tests, the normal force and sliding velocity were varied in the range of 5 to 40 N and 0.02 to 3.0 ms^{-1}, respectively. The initial Herzian contact pressure increased from 0.78 GPa to 1.56 GPa for the steel pin, and from 0.92 to 1.84 GPa for the alumina pin as the normal force increased. The sliding distance was 2000 m (Publications IV & V & VI & VII). The tribological performance of the ta-C coatings was evaluated by pin-on-disc tests by increasing the sliding velocity from 0.1 to 3 ms^{-1} and the normal force from 5 to 35 N. The sliding distance was 2000 m (Publications IV & VII). For the micro-Raman analyses, longer sliding distances were used. Steel and alumina balls slid against the a-C:H

coating (2.6 ms^{-1}, 35 N) with 5000 m and 3120 to 9360 m distances, respectively. For the ta-C coating (0.5 ms^{-1}, 10 N), a 5400 m sliding distance was used.

The ta-C coatings were tested in dry synthetic air (80% N_2/20% O_2) with the pin-on-disc tester. The tests were carried out after rinsing the test set-up covered with a plastic cover for 7 hours before the test. The humidity was measured during rinsing and testing. The steel balls (100 Cr 6, AISI 52100) were used with a normal load of 5 N, which created the initial Herzian contact pressure of 0.78 GPa. The sliding velocity was 0.02 ms^{-1} and the sliding distance was 24 m (Publication VII).

The a-C:H and ta-C coatings were evaluated in unlubricated and oil-lubricated tests against steel (100 Cr 6, AISI 52100) counterparts by using the reciprocating ball-on-disc tester. The normal force applied was 10 N, which created an initial Herzian contact pressure of 0.98 GPa. The sliding velocity was 0.004 ms^{-1} in order to provide boundary lubricated conditions in lubricated tests. The stroke length was 10 mm and the sliding distance was 300 m. For lubrication, two different oils were used. One oil was a mineral base oil with a low viscosity (7.5 cSt/40 ^{o}C) and with no additives. The other oil was a more viscous (21.6 cSt/40 ^{o}C) mineral base oil with a small amount of extreme pressure (EP) additives (Publication VIII).

The a-C:H and ta-C coatings were evaluated in unlubricated and water-lubricated tests against alumina (α-Al_2O_3) counterparts by using the reciprocating ball-on-disc tester. The normal force applied was 5 N, which created an initial Herzian contact pressure of 0.92 GPa. The sliding velocity was 0.004 ms^{-1}, the stroke length 10 mm and the sliding distance was 300 m. For lubrication, distilled water (0.63 cSt/40 ^{o}C) was used (Publication VIII).

During the tests, the coefficient of friction was recorded and the wear of the coated samples and the counterparts were assessed after the tests by profilometry and optical microscopy.

The stainless steel AISI 440B (X 90 CrMoV 18) with a hardness of 620 HV was mostly used as substrate material for tribological evaluation. The surface was polished prior to deposition to a surface roughness of R_a 0.03 μm for the

unlubricated pin-on-disc tests (Publications IV & V & VI & VII). For the lubricated ball-on-disc tests, the substrate surface was ground to a surface roughness of R_a 0.09 μm and the tests were performed against the machining mark orientation of the discs (Publication VIII). For evaluating the effect of the process parameters on the a-C:H coating properties, silicon wafers were used as substrate materials (Publication I).

2.3.3 Characterization of coatings and wear surfaces

The coating compositions were examined by Rutherford backscattering spectroscopy (RBS) (Publications IV & V & VII & VIII), forward recoil spectroscopy (FRES) (Publications I & II & IV & V & VI & VII & VIII), and secondary ion mass spectroscopy (SIMS) (Publication II). The film morphology was investigated by scanning electron microscopy (SEM) (Publications II & IV & V & VI & VII & VIII). Fourier transform infrared (FTIR) spectroscopy (Publications IV & V & VIII) and radial distribution function (RDF) (Publications IV & VIII) were used to characterize the bonding structure of the films.

The wear surfaces were investigated by optical microscopy and SEM (Publications I–VIII). The SIMS characterization of the wear surfaces was carried out using double focusing magnetic sector SIMS apparatus (Publications IV & V). The Auger measurements were performed using a scanning Auger spectrometer (Publication V). The micro-laser Raman spectroscope was used for Raman-analysis with an HeNe laser with a spot size of 2 μm. Raman analyses were done for locations inside the wear tracks and wear scars, and for the wear debris (Publications VI & VII).

3. Summary of main results

3.1 Effect of deposition parameters on a-C:H coating properties

The high hardness of the film was found to correlate with the decreased wear of the a-C:H film, which is in accordance with the classical Archard´s law of adhesive wear [Halling 1978]. By using response surface modelling, direct trends for the effects of the process parameters on the tribological properties were found. The best wear resistance was found for the coatings deposited with low pressures (0.7–2.5 Pa) and intermediate bias voltage values (-550 V). The films deposited with these parameters also showed the lowest wear of the steel ball sliding against the a-C:H film. For the friction properties of a-C:H coatings against steel, the results showed a minimum coefficient of friction for the coatings deposited with the intermediate pressure (5.5 Pa) and intermediate bias voltage (–550 V), even though the differences were not dramatic (Publication I).

3.2 Adhesion of a-C:H coatings

The adhesion of single-layer a-C:H coatings was not sufficient on stainless steel, alumina and cemented carbide, since self-delamination occurred after deposition. By using intermediate layers, the poor adhesion could be improved, and reasonably high critical load values were measured with scratch adhesion testing. For the stainless steel and cemented carbide substrates, the TiC interlayer provided the best adhesion, whereas for alumina, a Ti interlayer was the best. The adhesion was also improved by sputter cleaning of the substrates prior to deposition. Sputter cleaning improved adhesion most when medium to high power levels, *e.g.* 40 W corresponding to a self-bias of -300 V, and medium sputtering times (*e.g.* 10 min) were used (Publication II).

3.3 Load-carrying capacity of a-C:H and ta-C coated systems

A good load-carrying capacity of coated systems is important for the functional properties of the coating. When studying different factors affecting the load-carrying capacity of the coated systems, the importance of the support provided by the substrate was verified. The substrate must provide sufficient support for the coating, and, thus, Young´s modulus and the hardness of the substrate must be sufficiently high compared to the contact pressures acting in a particular application. Considering the coatings, Young´s modulus and the internal stresses of the coatings are the most important factors for the load-carrying capacity. Films with low internal stresses and sufficient adhesion can deform elastically or plastically with the substrate without a loss of cohesion. The hard coatings that have high internal stresses will fail if the substrate is deformed plastically, unless the substrate provides the capability of stress relaxation. Therefore, the combination of substrate properties and coating properties determines the load-carrying capacity of the coated system. It is also a matter of application-related demands, since some applications can allow plastic strain to occur, whereas for most applications only elastic strain is allowed. However, as a general rule, it can be concluded, that the substrate must provide sufficient support against plastic deformation for the thin coatings. The coating providing sufficient adhesion to the substrate should have such internal stresses that they can compensate or withstand the external stresses caused by loading in the intended application (Publication III).

3.4 Tribological properties in dry sliding conditions

The hydrogenated a-C:H and hydrogen-free ta-C coatings showed some variation in tribological performance in the different tests carried out. In general, the wear of the ta-C coating was lower compared to the a-C:H coating, which was due to the high hardness and high stability of the ta-C film. On the other hand, wear of the counterpart material against the ta-C coating was about one order of magnitude higher compared to that of the a-C:H coating (Publications IV & VI & VIII).

3.4.1 Friction and wear properties of a-C:H coating

The a-C:H coating proved to be sensitive to changes in the test conditions and two different regimes of coefficient of friction were detected. The coefficient of friction showed a dramatic decrease from the high friction regime of 0.42 to low friction regime of 0.10 against steel, and from the region of 0.13 to a low friction region of 0.02 against alumina when the sliding velocity and/or normal load were increased (Publications IV & VI).

On the wear surface of the pin, a tribolayer formation was observed, which increased in thickness as the sliding velocity and normal load increased. On the steel pins, the tribolayer was coloured or dark in appearance, whereas on the alumina pins the tribolayer was transparent (Publication VI).

The changes in the test parameters influenced the wear of the a-C:H coating and the counterparts. As a general trend, the wear rates of the a-C:H coating reduced as the normal load increased. The increase in sliding velocity had a reducing effect on the wear rates of the counterparts and the a-C:H coating when steel was used as the counter-material. The wear of the steel pins exhibited an interesting trend, since the lowest wear rates occurred with high sliding velocity and high normal load. This performance was associated with the tribofilm formation on the wear surface of the pin, which seemed to protect the pin from more pronounced wear. When alumina pins were used as counterparts, a different trend was observed, since the wear rates of the alumina pins increased with sliding velocity and an increase in the normal load had only a slight decreasing trend (Publication VI).

The results showed that the tribological performance of the a-C:H coating is sensitive not only to environmental changes, but also to factors related to the operating parameters, such as sliding velocity and normal load. The increase in normal load increased the contact pressure in the tribocontact. The increase in sliding velocity increased the contact temperature and, thus, influenced the tribochemistry in the tribocontact.

3.4.2 Friction and wear properties of ta-C coating

The ta-C coating showed a stable friction performance as the coefficient of friction varied against the steel pins in the range of 0.14 to 0.19 and against alumina in the range of 0.10 to 0.14 as the normal load increased from 5 to 22 N and the sliding velocity from 0.1 to 1.5 ms^{-1}. When the performance of the ta-C coating against steel was studied with a higher load and sliding velocity, namely 35 N and 2.6 ms^{-1}, the coefficient of friction slightly increased (μ=0.23). This could be attributed to a heating effect in the tribocontact caused by a combined high load and high sliding velocity. The heating effect was verified by the interference fringes on the wear surfaces of the steel pins sliding against the ta-C coating. The temperature rise was estimated by T-MAPS software to be approximately 700 ^{o}C, which suggests that the fringe colours may have arisen from the oxidation of the wear surface of the steel pins (Publication IV).

In terms of wear volume, the wear of the ta-C coating increased to some extent against steel when the sliding velocity was increased. Against alumina, the wear was similar with all test parameters, except the highest load (22 N) caused higher wear of the ta-C coating. In terms of the wear rates the ta-C coating showed a decreasing trend when normal load was increased.

The wear of the pins sliding against the ta-C coating typically presented more than one order of magnitude higher wear compared to the pins sliding against the a-C:H coating (Publications IV & VI & VII). This could be explained by the higher hardness combined with the higher surface roughness of the ta-C coating compared to the a-C:H coating (Publications IV & VIII). The wear volumes of the steel and alumina pins sliding against the ta-C coating increased as the normal load was increased. On the wear surfaces of the steel and alumina pins, visible tribolayers were formed. The layers showed similar appearance with different test parameters used, only the thickness of the layers varied slightly. The tribolayer could not protect the pins from wear in a similar way as was found for the steel pins sliding against the a-C:H coating (Publication IV).

The coefficient of friction of the ta-C coating in dry air (0% RH) reached high values, such as μ=0.71. When the surface layer of the ta-C coating was doped with hydrogen originating from hydrogen (H_2) or methane (CH_4) atmospheres in the deposition chamber during deposition, the coefficient of friction decreased.

When the hydrogen content was increased from 0 to 16 at.%, the coefficient of friction decreased from 0.71 to 0.28 (Publication VII).

3.4.3   Characterization of tribolayers and wear surfaces

When the wear surfaces of the pins and the coatings were investigated by optical microscopy and SEM, no visible layer formations were observed on the wear surfaces of the coatings, but on the wear surfaces of the pins clearly visible tribolayer formations were detected.

The SIMS elemental imaging revealed that the pin material was transferred onto the wear surfaces of the coated discs. In the case of the steel pin, iron and chromium signals were detected on the wear surfaces of the a-C:H coated discs as well as the ta-C coated discs. The thickness of this layer was typically 10 nm or less and the thickness did not change, even though the test parameters were changed. In a similar way, an aluminium signal was detected on the wear surface of the coating, when the alumina pin slid against the coated disc (Publication IV).

The SIMS depth profiles showed that the tribofilm formed on the wear surface of the steel pin sliding against the a-C:H coating contained iron, chromium, oxygen and hydrogen. Therefore, the tribofilm mainly consisted of iron oxides. The same composition was detected on the wear surface of the pin in the case where the surface was covered with a dark layer and also in the case when the surface had a metallic appearance; only the film thickness varied. Rather small amounts of carbon were detected by SIMS in the tribolayers formed on the wear surface of the pins. Only in the dark thick tribolayers and in the sliding deposit in front of the pins was some carbon observed. The sliding deposit in front of the wear surface of the pin usually had a higher concentration of hydrogen than the tribofilms formed on the wear surfaces of the pins. In addition, the concentrations of hydrogen and oxygen in the sliding deposits seemed to be higher in the case of low normal load than with high load and sliding velocity (Publication IV).

The tribofilm formed on the wear surface of the steel pin sliding against the ta-C coating also consisted of iron, chromium, oxygen and hydrogen, according to the SIMS analyses. Some carbon was detected and the amount of carbon was slightly higher in the dark areas of the tribolayer than in the areas with bright,

metallic appearance. Hydrogen was found in the tribolayer formed in tests with low normal load, but on the tribolayer formed in the tests with high normal load and sliding velocity, no hydrogen was detected (Publication IV).

When the alumina pins sliding against the a-C:H coatings were analyzed by SIMS, the tribofilm was found to consist mainly of aluminium oxide with some hydrogen and silicon. The concentration of carbon in the tribofilm on the wear surface of the pin was low in the case of low normal load and sliding velocity, and correspondingly slightly higher in the case of high normal load and sliding velocity. In the tribofilm formed on the wear surfaces of the pins sliding against the ta-C coating, some evidence of carbon was detected besides the pin materials (Publication IV).

Auger depth profiles from the tribolayers formed on the wear surfaces of the pins, when sliding against the a-C:H coating, revealed the formation of iron oxides. The Auger analyses performed on the outermost surface layer exhibited a carbon peak. However, a similar carbon peak was also observed on an unworn surface due to surface contamination. Therefore, it was not possible to distinguish the origin of carbon by AES. By Auger elemental imaging, an enrichment of carbon was detected in the sliding deposits formed in front of the wear surface of the pins when a high load and sliding velocity were used. In the tribolayer formed on the wear surface of the pin, striped formations containing carbon were also detected in some cases (Publication V).

In order to verify the presence of different carbon species on the wear surfaces, the micro-Raman analyses were carried out for the a-C:H and ta-C coatings and the steel and alumina counterparts. The analyses for a-C:H indicated that the structure of the wear debris on the disc wear track resembled the structure of the coating itself. However, the tribolayer formation on the wear surface of the ball and wear debris accumulated or transferred to the ball sides appeared to have some graphitic character. Especially the analyses of the wear surfaces of the steel balls showed a close resemblance to that of pyrolytic graphite. This showed that graphitization occurred in the tribocontact during sliding with high normal load and sliding velocity for the a-C:H coating. For the ta-C coating indications of graphitization were observed in the signal taken from the disc wear track. The signal showed a resemblance to pyrolytic graphite, but the intensity of the signal

was rather low. This suggests that the amount of graphite detected was smaller than that for the a-C:H coating (Publications VI & VII).

3.4.4 Role of tribolayers, graphitization and hydrogen in friction properties of a-C:H and ta-C coatings

On the wear surfaces of the a-C:H and ta-C coatings, a transfer layer consisting of pin materials was observed, although the layer was not visible. On the wear surfaces of the pins, visible tribolayers containing the oxides of the pin material were formed against both coatings. When high load and sliding velocities were applied the tribolayer against the a-C:H coating grew to a high layer thickness protecting the steel pin from excessive wear against the a-C:H coating. Carbon was detected by AES and SIMS analyses in the tribolayers and in the sliding deposits formed in front of the tribocontact. By micro-Raman spectroscopy, clear evidence of graphite formation was found for the a-C:H coating in high load and high sliding velocity conditions. Evidence of graphite formation was also detected for the ta-C coating by micro-Raman measurements, even though the amount of graphite detected was presumably smaller compared to the measurements carried out for the a-C:H coating.

The surface temperature at the sliding contact in the pin-on-disc test was estimated by using T-MAPS software. The flash temperatures (T_f) calculated were generally less than 100 $^{\circ}$C, but for the high loads and high velocities the flash temperature reached values of 350 $^{\circ}$C for the alumina pins against both types of coatings. The calculations showed similar temperatures for the steel pins sliding against the a-C:H coating but for the ta-C coating temperatures as high as 700 $^{\circ}$C were calculated. Since all the practical surfaces are formed of different distributions of asperities and valleys, the flash temperatures on the top of the asperities carrying the load in the tribocontact can easily reach values in the region of 350 $^{\circ}$C, as shown by the calculations. At this temperature, out-diffusion of hydrogen occurs in the a-C:H film. After hydrogen out-diffusion, the sp^3 structure of the a-C:H film transforms to an sp^2 structure and forms graphite, as verified by the Raman analyses. Graphite is formed locally on the top of the asperities, which are in tribocontact, and this graphite forms a layer with low shear strength providing low friction. The hydrogen of the a-C:H films and the hydrogen out-diffusing under the tribocontact, provide a reservoir of hydrogen, besides the surrounding humid air, for graphite resulting in low friction, as

shown by the tribological tests (μ=0.2 to 0.1 against steel pin and μ=0.1 to 0.02 against alumina pin). The graphitization process was thus enhanced by the high contact temperatures due to the increased sliding velocities. In addition, an increase in contact pressure (normal load) caused a reduction in the coefficient of friction, which suggests that graphitization can also be enhanced by increasing the contact stresses acting in the tribocontact.

During repeated sliding, some graphite is transferred into the tribofilm formed on the wear surface of the pin and also collected in the sliding deposit in front of the tribocontact, as detected by SIMS and AES. In the tribocontact an oxide-rich tribolayer formed on the wear surface of the pin slides against the thin graphite layer. The oxide-rich tribolayer may act as an inert and chemically stable counter-face for the graphite preventing direct contact between the graphite and iron.

In the case of low sliding velocities and low loads, the a-C:H films exhibited rather high coefficients of friction (μ=0.2 to 0.4), which suggests that the graphitization process did not occur effectively under these circumstances for the particular a-C:H coating. This was verified by the temperature estimations being around 100 $^{\circ}$C for the low loads and sliding velocities applied. In such conditions, the out-diffusion of hydrogen from a-C:H structure is not possible. However, in the presence of water vapour from the surrounding humid atmosphere, the hydrogen from the water can recombine with the hydrogen of the a-C:H structure because H-H bonding energy is higher (about 5 eV) than for C-H (4.3 eV) and for O-H (4.8 eV) bonding. The situation is similar at the surface as during out-diffusion, and the a-C:H surface material will be transformed into graphite even at low temperatures [Neuville & Matthews 1997]. This process is slow compared to the graphitization driven by the out-diffusion of hydrogen and thus the coefficient of friction remains in the high friction region.

For the ta-C coating, the coefficient of friction showed rather stable behaviour both in low load and low sliding velocity tests as well as in high load and high sliding velocity tests. Only the highest load/velocity combination against steel exhibited a slightly higher coefficient of friction (μ=0.23). The hydrogen content of the tribofilm was reduced in the tests carried out against the steel pins with high load and velocity, which correlated with the higher coefficient of friction

measured (μ=0.23). From the T-MAPS calculations it was estimated that the flash temperature against the steel pin would be as high as 700 $^{\circ}$C in the tests carried out with high load and velocity, which suggests that high temperatures reduced the amount of hydrogen in the tribocontact and caused an increase in the coefficient of friction. The structure of the ta-C coating consists of carbon atoms, which are predominantly sp^3 bonded and, thus, the film is thermally more stable compared to a-C:H. For the ta-C films with high sp^3 bonding (> 80%), the structure is thermally stable up to 1000 $^{\circ}$C. The thermal stability decreases with the decreasing sp^3 component of the film and for films with 60% sp^3 fraction, the thermal stability limit decreases to the range of 600 to 700 $^{\circ}$C. It has been suggested that the size of the sp^2 clusters formed by the thermal relaxation of the ta-C film increases with the initial sp^2 fraction, thus enabling the clustering of graphite nanoparticles. A sufficiently low sp^3 fraction would also enable a thermally induced sp^3 to sp^2 conversion. This will increase the sp^2 fraction and lead to further sp^2 clustering and eventually graphitization [Kalish *et al.* 1999]. The graphite formation was detected for the ta-C coating in this study, but the amount of graphite observed was relatively small compared to the a-C:H coating. This is in accordance with the graphitization process of the ta-C coating being related to the degeneration of the carbon sp^3 structure to an sp^2 structure, as described above, which occurs at higher temperatures compared to a-C:H. Thus, the ta-C coating requires higher contact temperatures and higher contact stresses to enhance the graphitization process. In the low load and low sliding velocity conditions when the graphitization is limited, water vapour can act as a lubricating medium on the ta-C coating surface in humid conditions.

Graphite requires humidity to provide low friction properties. Since graphite is formed in the tribocontact of the ta-C film and the coating itself contains no hydrogen, humidity from the environment is required for low friction of the coating. This performance was verified in the tests carried out in humid air when the typical coefficient of friction values of the ta-C coating were in the range of μ=0.1 to 0.2. When the ta-C coatings were tested in dry air (0% relative humidity), the coefficient of friction increased dramatically and reached values around μ=0.7. When the ta-C coating was modified by doping the surface layer with hydrogen or methane during deposition, the coefficient of friction decreased as the hydrogen content in the coating increased. This indicates that hydrogen plays an important role in the low friction behaviour of DLC coatings. The hydrogen-doped ta-C coating actually imitates the structure of the a-C:H coating,

which is known to provide low friction also in dry atmospheres (0% relative humidity) and even in vacuum due to the reservoir of hydrogen in the coating [Grill 1997].

3.5   Tribological properties in lubricated conditions

3.5.1   a-C:H and ta-C coatings in oil-lubricated conditions

The tribological performance of the ta-C coating could be further improved with oil lubrication. The coefficient of friction of the ta-C and a-C:H coatings decreased 10 to 40% under oil lubrication. The ta-C film had the lowest coefficient of friction in oil-lubricated conditions (μ=0.08). The titanium-alloyed a-C:H coating, a-C:H(Ti), however, showed the lowest friction in dry conditions (μ=0.1) (Publication VIII).

The wear performance of the counterparts and the visual appearance of the counterpart wear surfaces demonstrated the effect of oil in the tribocontact, since the oil changed the tribomechanism in the contact. When the mineral base oil without EP additives was used, the formation of tribolayers typical for the DLC coated contacts in dry sliding conditions was prevented, which caused increased wear in counterparts sliding against the ta-C and a-C:H coatings. When the mineral oil with EP additives was used, a boundary lubrication layer of EP additives was formed on the wear surface of the steel pins, and the wear of the counterparts decreased. This behaviour suggests that, when oil is introduced into the tribocontact, the oil chemistry governs the tribochemistry also in the case of the a-C:H and ta-C films, when the counterpart is made of steel (Publication VIII).

The wear of the a-C:H and ta-C coatings decreased when oil lubrication was applied, even though the additives used in the oils were designed for steel surfaces. This shows that the a-C:H and ta-C coatings have excellent performance in oil-lubricated conditions (Publication VIII). The a-C:H coating and particularly the ta-C coating can be suggested to be used not only in dry sliding conditions, but also in boundary lubricated conditions for providing safe operation in demanding operating conditions.

3.5.2   a-C:H and ta-C coatings in water-lubricated conditions

The hydrogen-free ta-C coating showed a dramatic drop in the coefficient of friction from $\mu=0.07$ to 0.03 in water-lubricated conditions. This verifies that water can be used as a lubricating medium for the ta-C coating. The ta-C coating showed an even smaller amount of wear in water-lubricated conditions compared to unlubricated conditions. In unlubricated tests, the smoothening wear of surface roughness peaks of the ta-C coated surface was observed, but for the water-lubricated conditions not even smoothening wear was visible. The wear of the counterparts was slightly increased in water-lubricated conditions (Publication VIII).

The a-C:H coating suffered from catastrophic wear in water soon after the beginning of the test and the coating could not survive under water lubrication. The composition and structure of the r.f. plasma deposited a-C:H coating is thus sensitive to water and cannot be proposed for aqueous environments. However, the performance of a-C:H film could be improved by alloying the coating with titanium. This titanium-alloyed carbon film, a-C:H(Ti), survived also in the water-lubricated conditions, even though water increased the wear of the coating. The wear of the counterpart was increased and the coefficient of friction was to some extent decreased in water-lubricated conditions (Publication VIII).

4. Conclusions

The a-C:H coatings deposited by r.f. plasma-assisted CVD technique and ta-C coatings deposited by the pulsed vacuum arc discharge technique were evaluated by scratch adhesion, load-carrying capacity and tribological testing. The following conclusions can be drawn based on the research conducted.

−   By using experimental design and modelling, the deposition parameters (bias voltage -550 V and pressure 0.7–2.5 Pa) for producing the most wear-resistant a-C:H coatings were defined with a limited number of coating depositions and tribological tests. For the low friction properties of a-C:H coatings, the optimum deposition parameters (bias voltage –550 V, pressure 5.5 Pa) were also determined for the deposition system used in the study.

−   The adhesion of the a-C:H coating was improved by applying a TiC interlayer on stainless steel and cemented carbide and by applying a Ti interlayer for alumina substrates. Optimum sputter cleaning values prior to deposition were around 40 W with a corresponding self-bias of -300 V, and sputtering time of around 10 minutes for the deposition system used in the study.

−   The most important parameters influencing the load-carrying capacity of the DLC coatings were the hardness and Young's modulus of the substrate as well as Young's modulus and the internal stresses of the coatings.

−   The unlubricated sliding tests in humid air (50% relative humidity) demonstrated that wear of the ta-C coating was lower compared to that of the a-C:H coating. On the other hand, the wear of the counterpart was one order of magnitude higher for the counterparts sliding against the ta-C coating compared to that of the a-C:H coating due to the higher hardness and higher surface roughness of the ta-C coating.

−   The wear surfaces of counterparts sliding against the a-C:H and ta-C coatings showed the formation of tribolayers containing mainly oxides of pin material with some carbon and hydrogen detected by SIMS and AES. The thick tribolayer formation on the steel pin sliding against the a-C:H coating in high normal load and high sliding velocity conditions protected the steel

pins from excessive wear. On the wear surfaces of the coatings, a transfer of pin material (Fe, Cr or Al) was observed by SIMS.

- For the a-C:H coating, two different regions of coefficient of friction were detected: the increase in normal load and sliding velocity in tribological tests carried out in humid air (50% relative humidity) decreased the coefficient of friction of the a-C:H coating from the high friction region of 0.42 to the low friction region of 0.10 against steel, and from the high friction region of 0.13 to the low friction region of 0.02 against alumina. The low friction was related to graphite formation in the tribocontact, which was detected by micro-Raman analyses. The graphitization was enhanced by the high contact temperature and high contact pressure.

- The ta-C coating had a rather stable coefficient of friction in the range of 0.14 to 0.19 against steel, and in the range of 0.10 to 0.14 against alumina, when the normal force and sliding velocity were varied in humid air (50% relative humidity). Graphite was also formed in the tribocontact of the ta-C coating, but the amount detected was lower than that for a-C:H due to the highly sp^3 bonded thermally stable hydrogen-free structure of the ta-C coating.

- In dry air (0% relative humidity), the ta-C coating exhibited a high coefficient of friction (μ=0.71), but friction was reduced as the hydrogen content of the hydrogen- and methane-doped ta-C coatings was increased.

- The structure and deposition method affected the stability of coatings in water-lubricated contacts. The ta-C coating had a highly stable nature and excellent tribological properties in water, and it exhibited no wear. The ta-C coating also had a dramatic drop in coefficient of friction from 0.07 to 0.03 in water-lubricated conditions. The a-C:H coating was susceptible to wear in water and did not survive in water-lubricated conditions. The performance of the a-C:H coating in water-lubricated conditions could be improved by alloying the coating with titanium.

- In oil-lubricated conditions the tribofilm formation typical for a-C:H and ta-C coatings in unlubricated conditions was prevented and the oil chemistry governed the tribocontact. The a-C:H and particularly ta-C coatings showed

better tribological performance under oil lubrication compared to unlubricated sliding conditions. The coefficient of friction was reduced 10 to 40% under boundary lubricated conditions. DLC coatings can thus be proposed for the boundary lubricated conditions for providing safe operation in demanding conditions.

References

Angus, J.C. 1987. Categorisation of dense hydrocarbon films. In: Koidl, P. & Oelhafen, P. (eds.). EMRS Symposia Proceedings, Volume XVII, Amorphous Hydrogenated Carbon Films. France. Les Éditions de Physique. Pp. 179–187.

Ball, B. 1997. Made to Measure: New Materials for the 21st Century. New Jersey, USA. Princeton University Press. 447 p.

Bhushan, B. 1999. Principles and Applications of Tribology. New York, USA. John Wiley & Sons, Inc. 1020 p.

Bloyse, A. 2000. Carbon PVD coatings wear it well. Materials World, March, pp. 13–15.

Bowen, F.D. & Tabor, D. 1950. The Friction and Lubrication of Solids. Oxford, UK. Oxford U.P. 321 p.

Buckley, D.H. 1981. Surface Effects in Adhesion, Friction, Wear and Lubrication. Tribology Series 5. Amsterdam, The Netherlands. Elsevier Scientific Publishing Company. 617 p.

Dischler, B., Budenzer, A. & Koidl, P. 1983. Bonding in hydrogenated hard carbon studied by optical spectroscopy. Solid State Communications, Vol. 48, No. 2, pp. 105–108.

Dischler, B. 1987. Bonding and hydrogen incorporation in a-C:H studied by infrared spectroscopy. In: Koidl, P. & Oelhafen P. (eds.). EMRS Symposia Proceedings, Volume XVII, Amorphous Hydrogenated Carbon Films. France. Les Éditions de Physique. Pp. 189–201.

Donnet, C. 1995. Tribology of solid lubricant coatings. Condenced Matter News, Vol. 4, No. 6, pp. 9–24.

Donnet, C. 1998. Recent progress on the tribology of doped diamond-like and carbon alloy coatings: a review. Surface and Coatings Technology, Vol. 100–101, pp. 180–186.

Donnet, C. & Grill, A. 1997. Friction control of diamond-like carbon coatings. Surface and Coatings Technology, Vol. 94–95, pp. 456–462.

Donnet, C., Grill, A., Fontaine, J., Le Mogne, T., Lefebvre, F., Patel, V. & Jahnes, C. 1998a. Fundamental on the friction mechanism of diamondlike carbon films. In: Proceedings of 25th Leeds-Lyon Symposium on Tribology, Lyon, France, 8–11 September 1998. 9 p.

Donnet, C., Le Mogne, T., Ponsonnet, L., Belin, M., Grill, A., Patel, V. & Jahnes, C. 1998b. The respective role of oxygen and water vapour on the tribology of hydrogenated diamond-like carbon coatings. Tribology Letters, Vol. 4, pp. 259–265.

Dowson D. 1998. History of Tribology. 2nd ed. London, UK. Professional Engineering Publishing Limited. 768 p.

Enke, K., Dimigen, H. & Hübsh, H. 1980. Frictional properties of diamond-like carbon layers. Appl. Phys. Lett., Vol. 36, No. 4, pp. 291–292.

Erdemir, A., Nichols, F.A., Pan, X.Z., Wei, R. & Wilbur, P. 1993. Friction and wear performance of ion-beam-deposited diamond-like carbon films on steel substrates. Diamond and Related Materials, Vol. 3, pp. 119–125.

Erdemir, A., Bindal, C., Pagan, J. & Wilbur, P. 1995. Characterization of transfer layers on steel surfaces sliding against diamond-like hydrocarbon films in dry nitrogen. Surface and Coatings Technology, Vol. 76–77, pp. 559–563.

Erdemir, A., Bindal, C., Fenske, G.R., Zuiker, C. & Wilbur, P. 1996. Characterization of transfer layers forming on surfaces sliding against diamond-like carbon. Surface and Coatings Technology, Vol. 86–87, pp. 692–697.

Gangopadhyay, A. 1998. Mechanical and tribological properties of amorphous carbon films. Tribology Letters, Vol. 5, pp. 25–39.

Gardos, M.N. 1994. Tribology and wear behaviour of diamond. In: Spear, K.E. & Dismuke, J. P. (eds.). Synthetic Diamond: Emerging CVD Science and Technology. New York, USA. John Wiley & Sons, Inc. Pp. 419–502.

Gardos M. N. 1998. Re(de)construction-induced friction signatures of polished polycrystalline diamond films in vacuum and hydrogen. Tribology Letters, Vol. 4, pp. 175–188.

Gissler, W. & Jehn, H.A. (eds.) 1992. Advanced Techniques for Surface Engineering. Dordrecht, The Netherlands. Kluwer Academic Publishers. 402 p.

Grill, A. 1997. Tribology of diamondlike carbon and related materials: an updated review. Surface and Coatings Technology, Vol. 94–95, pp. 507–513.

Grischke, M., Massler, O., Vaeckenstedt, A., Eberle, H., Berger, M., Michler, T., & Laakmann, M. 2000. Metal-carbon and DLC-films in industrial applications. Abstracts of the Seventh International Conference on Plasma Surface Engineering. Garmisch-Partenkirchen, Germany, September 17–21, 2000. Düsseldorf. Deutsche Gesellschaft für Galvano- und Oberflächentechnik e.V. P. 5.

Guy, A. G. 1976. Essentials of Materials Science. New York, USA. McGraw-Hill, Inc. 457 p.

Halling, J. (ed.) 1978. Principles of Tribology. Hong Kong. The Macmillan Press Ltd. 401 p.

Hirvonen, J.-P., Lappalainen, R., Koskinen, J., Anttila, A., Jervis, T.R. & Trkula, M. 1990. Tribological characteristics of diamond-like films deposited with an arc-discharge method. J. Mater. Res., Vol. 5, No. 11, pp. 2524–2530.

Holmberg, K. & Matthews, A. 1994. Coatings Tribology - Properties, Techniques and Applications in Surface Engineering. Tribology Series, 28. Amsterdam, The Netherlands. Elsevier Science B.V. 442 p.

Jahanmir, S., Deckman, D.E., Ives, L.K., Feldman, A. & Farabaugh, E. 1989. Tribological characteristics of synthesized diamond films on silicon carbide. Wear, Vol. 133, pp. 73–81.

Kalish, R., Lifshitz, Y., Nugent, K. & Prawer, S. 1999. Thermal stability and relaxation in diamond-like carbon. A Raman study of films with different sp^3 fractions (ta-C to a-C). Applied Physics Letters, Vol. 74, No. 20, pp. 2936–2938.

Kim, D.S., Fisher, T.E. & Gallois, B. 1991. The effects of oxygen and humidity on friction and wear of diamond-like carbon films. Surface and Coatings Technology, Vol. 49, pp. 537–542.

Koskinen, J., Hirvonen, J.-P. & Keränen, J. 1998. Relaxation of sp^3 bonds in hydrogen-free carbon films during growth. In: Silva, S.R.P., Robertson, J., Milne, W. & Amaratunga, G. A. J. (eds.). Amorphous Carbon: State of the Art. Singapore. Cambridge, UK. World Scientific Publishing Co. Ltd. Pp. 46–56. (ISBN 981-02-3449-X)

Lee, S.-T., Lin, Z. & Jiang, X. 1999. CVD diamond films: nucleation and growth. Materials Science and Engineering, Vol. R25, No. 4, pp. 123–154.

Lettington, A.H. 1998. Applications of diamond-like carbon thin films. Carbon, Vol. 36, No. 5–6, pp. 555–560.

Liu, Z.T., Xu, N.K., Geng, D.S. & Zheng, X.L. 1993. Thermostability of diamond-like carbon films. Surface Engineering, Vol. 9, No. 2, pp.148–150.

Liu, Y., Erdemir, A. & Meletis, E.I. 1996a. An investigation of the relationship between graphitization and frictional behaviour of DLC coatings. Surface and Coatings Technology, Vol. 86–87, pp. 564–568.

Liu, Y., Erdemir, A. & Meletis, E.I. 1996b. A study of the wear mechanism of diamond-like carbon films. Surface and Coatings Technology, Vol. 82, pp. 48–56.

Liu, Y., Erdemir, A. & Meletis, E.I. 1997. Influence of environmental parameters on the frictional behaviour of DLC coatings. Surface and Coatings Technology, Vol. 94–95, pp. 463–468.

Liu, Y. & Meletis, E.I. 1997. Evidence of graphitization of diamond-like carbon films during sliding wear. Journal of Materials Science, Vol. 32, pp. 3491–3495.

Matthews, A. & Eskildsen, S.S. 1994. Engineering applications for diamond-like carbon. Diamond and Related Materials, Vol. 3, pp. 902–911.

Meletis, E.I., Erdemir, A. & Fenske, G.R. 1995. Tribological characteristics of DLC films and duplex plasma nitriding/DLC coating treatment. Surface and Coatings Technology, Vol. 73, pp. 39–45.

Memming, R., Tolle, H.J. & Wierenga, P.E. 1986. Properties of polymeric layers of hydrogenated amorphous carbon produced by a plasma-activated chemical vapour deposition process, II: Tribological and mechanical properties. Thin Solid Films, Vol. 143, pp. 31–41.

Mencík, J. 1996. Mechanics of Components with Treated of Coated Surfaces. Dordrecht, The Netherlands. Kluwer Academic Publishers. 360 p.

Mittal, K. 1995. Adhesion measurement of films and coatings: a commentary. In: Mittal, K. (ed.) Adhesion and Measurement of Films and Coatings. Utrecht, The Netherlands. Koninklijke Wöhrmann BV. Pp. 1–13.

Miyoshi, K. 1990. Studies of mechanochemical interactions in the tribological behaviour of materials. Surface and Coatings Technology, Vol. 43/44, pp. 799–812.

Neuville S. & Matthews, A. 1997. Hard carbon coatings: the way forward. MRS Bulletin, September, pp. 22–26.

Olsen, J.E., Fisher, T.E. & Gallois, B. 1996. In situ analysis of the tribochemical reactions of diamond-like carbon by internal reflection spectroscopy. Wear, Vol. 200, pp. 233–237.

prEN 1071-3. 1999. Advanced technical ceramics - Methods of test for ceramic coatings - Part 3: Determination of adhesion and other mechanical failure by a scratch test. 42 p.

Rickerby D.S. & Matthews, A. (eds.) 1991. Advanced Surface Coatings: a Handbook of Surface Engineering. Glasgow, UK. Blackie & Son Ltd. 368 p.

Robertson, J. 1992. Mechanical properties and structure of diamond-like carbon. Diamond and Related Materials, Vol. 1, pp. 397–406.

Robertson, J. 1999. Deposition and properties of diamond-like carbons. Material Research Society Symposium Proceedings. Vol. 555, 12 p.

Ronkainen, H., Varjus, S. & Koskinen, J. 1992. Tribological properties of diamond-like carbon films. Tribologia, Vol. 11, No. 4, pp. 133–141.

Sugimoto, I. & Miyake, S. 1990. Oriented hydrocarbons transferred from a high performance lubricative amorphous C:H:Si film during sliding in a vacuum. Appl. Phys. Lett., Vol. 56, No. 19, pp. 1868–1870.

Suh, N.P. 1986. Tribophysics. New Jersey, USA. Prentice-Hall Inc. 498 p.

Talke, F. E. 2000. Tribology in magnetic recording technology. In: Bartz W.J. (ed.). Proceedings of 12th International Colloquium. Tribology 2000-Plus. Esslingen, Germany, January 11–13, 2000. Ostfildern: Technische Akademie Esslingen. Pp. 55–61.

Valli, J., Mäkelä, U., Matthews, A. & Murawa, V. 1985. TiN coating adhesion studies using the scratch test method. J. Vac. Sci. Technol., Vol. A3, No. 6, pp. 2411–2414.

Venkatram, C., Brodbeck, C. & Lei, R. 1999. Tribological properties of diamond-like nanocomposite coatings at high temperatures. Surface and Coatings Technology, Vol. 115, pp. 215–221.

Voevodin, A.A., Schneider, J.M., Rebholz, C. & Matthews, A. 1996a. Multilayer composite ceramic-metal-DLC coatings for sliding wear applications. Tribology International, Vol. 29, No. 7, pp. 559–570.

Voevodin, A.A., Phelps, A.W., Zabinski, J.S. & Donley, M.S. 1996b. Friction induced phase transformation of pulsed laser deposited diamond-like carbon. Diamond and Related Materials, Vol. 5, pp. 1264–1269.

Voevodin, A.A., Donley, M.S. & Zabinski, J.S. 1997. Pulsed laser deposition of diamond-like carbon wear protective coatings: a review. Surface and Coatings Technology, Vol. 92, pp. 42–49.

Weissmantel C. 1985. Preparation, structure and properties of hard coatings on the basis of i-C and i-BN. In: Klabunde, K.J. (ed.). Thin Films from Free Atoms and Particles. Florida, USA. Academic Press Inc. Pp. 153–201.

Wild, C. & Koidl, P. 1987. Network structure and thermal decomposition of plasma deposited a-C:H films studied by gas effusion spectroscopy. In: Koidl, P. & Oelhafen, P. (eds.). EMRS Symposia Proceedings, Volume XVII, Amorphous Hydrogenated Carbon Films. France. Les Éditions de Physique. Pp. 207–211.

Appendices of this publication are not included in the PDF version.
Please order the printed version to get the complete publication
(http://otatrip.hut.fi/vtt/jure/index.html)

Author(s)
Ronkainen, Helena

Title

Tribological properties of hydrogenated and hydrogen-free diamond-like carbon coatings

Abstract

The amorphous hydrogenated carbon coatings (a-C:H) deposited by plasma-assisted chemical vapour deposition (PACVD), and tetrahedral amorphous carbon coatings (ta-C) deposited by pulsed vacuum arc discharge were evaluated by scratch adhesion testing, load-carrying capacity testing and tribological testing in unlubricated and lubricated sliding conditions. The wear surfaces of the coatings and counterparts were analyzed by optical and scanning electron microscopy, secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), and micro-Raman spectroscopy.

The adhesion of the a-C:H coating was improved by titanium and titanium nitride intermediate layers. The most important parameters affecting the load-carrying capacity of the a-C:H and ta-C coated systems proved to be the hardness and Young´s modulus of the substrate, and the Young´s modulus and internal stresses of the coating.

In general, the ta-C coating was more wear-resistant compared to the a-C:H coating due to the higher hardness of the coating. The wear of the counterparts sliding against the ta-C coating was one order of magnitude higher compared to the a-C:H coating due to higher surface roughness combined with the high hardness of the ta-C coating.

For the a-C:H coatings, the increase in normal load and sliding velocity reduced the coefficient of friction from 0.42 to 0.1 against steel, and from 0.13 to 0.02 against alumina. The formation of graphite in the tribocontact of the a-C:H coating was observed by micro-Raman analyses when high normal loads and sliding velocities were applied causing high contact pressures and increased contact temperatures. The coefficient of friction of the ta-C coating was low and rather stable, in the range of 0.10 to 0.19 in humid air (50% relative humidity). Some graphitization on the wear surface of the ta-C coating was observed, but the amount of graphite detected was rather small due to the stable sp^3 structure of the ta-C coating. When the ta-C coatings were tested in dry air (0% relative humidity) the coefficient of friction increased to the value of 0.71. However, by doping the ta-C coating with hydrogen or methane, the coefficient of friction reduced as the hydrogen content of the coating increased. These friction properties of a-C:H and ta-C coatings can be related to the friction properties of graphite, which verifies the importance of graphite formation and the availability of hydrogen for low friction properties of the a-C:H and ta-C coatings.

In water-lubricated tests, the ta-C coating showed excellent tribological performance with a dramatic drop in the coefficient of friction from 0.07 to 0.03, but the a-C:H coating was susceptible to sliding wear in water-lubricated conditions, which resulted in an early failure of the coating. The performance of the a-C:H coating in water could be improved by alloying the coating with titanium.

In oil-lubricated conditions, the a-C:H and particularly ta-C coatings showed further improved tribological performance compared to unlubricated sliding conditions. In oil-lubricated conditions the tribofilm formation typical for a-C:H and ta-C coatings in dry sliding conditions was prevented and the oil chemistry governs the tribocontact. The DLC coatings are not only suggested for use in dry sliding conditions, but also in boundary lubricated conditions to provide safe operation in demanding conditions.