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Low-Friction and Wear-Resistant Carbon Nitride Coatings for Bearing Components Grown by Magnetron Sputtering

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To my family

"Fate leads the willing and drags along the reluctant".

— L.A. Seneca

Abstract

The scope of this thesis is the investigation of magnetron sputtered carbon nitride coatings suitable for roller bearing components. The research field of tribology of bearings focuses on minimizing friction between components by improving the lubricants. The development of lubricants is, however, expensive and involves environmentally deleterious chemical byproducts. A solution to avoid such harmful conditions, reduce the processing cost, and more importantly, minimize the friction, is to apply a low-friction and wear-resistant coating on the surface of the bearing. The deposition of such coatings on components can substantially increase their lifetime, reduce the maintenance costs, and eventually increase the reliability of the machinery.

Carbon nitride (CN_x) coatings have high resiliency and can withstand the demanding conditions of bearing operation. The morphology of CN_x coatings is highly affected by applying a negative substrate bias voltage. At high bias (100-120 V), the coatings become denser and more homogeneous with decreased porosity, resulting in more wear-resistant materials. I also found that the duty cycle of the applied bias affects the layer morphology. Less homogeneous films are produced using lower duty cycles (i.e., in high power impulse magnetron sputtering, HiPIMS) for a specific value of bias voltage. Thus, changing bias voltage, we can manipulate the structure of CN_x and design layers, depending on the requirements of the bearing application.

My results show that denser films yield higher hardness and wear-resistance, but also higher compressive stress, which is a disadvantage for the coating-substrate adhesion. In order to obtain improved adhesion on bearing steel, we developed an *in-situ* surface treatment, prior to the CN_x deposition, which also surpasses the limitations set by the properties of each material. The steel substrates are successfully pretreated using W or Cr ions originating from a HiPIMS source. Plasma ions are accelerated to the substrates with energies of 900 eV, due to the application of a synchronized high bias voltage, which clean effectively the substrate surface from residual contaminants and strengthen the interfacial bonding.

CN_x -coated rollers are tested in rolling operation and show the absence of run-in period in all lubrication regimes. This is a big advantage for applications which rotate under boundary lubrication (BL). The coated rollers yield friction coefficients in the range of 0.020 and 0.025 in elastohydrodynamic (EHDL) and hydrodynamic (HDL) lubrication regimes, being lower than the friction coefficients of 0.026-0.052, exhibited by the uncoated rollers. Here, friction decreases steadily with increasing number of cycles, due to the presence of CN_x in the contact. In BL, CN_x -coated rollers present an increased friction coefficient of 0.052, but the wear is much lower than in the case of uncoated rollers. All rollers are covered with CN_x in the wear tracks after the tests, avoiding failures and presenting low abrasive wear. The obtained tribological performance of the CN_x -coated rollers in rolling is overall improved compared to the established operation of uncoated rollers. Thus, CN_x layers can function as low-friction and wear-resistant coatings protecting the steel components in several roller bearing applications, such as in gearboxes and wheels in automotive, aerospace, marine, and turbine industry.

Populärvetenskaplig sammanfattning

Kullager har funnits sedan antiken, men det moderna kullagret utvecklades i samband med cyklismens genombrott först i slutet av 1800-talet. Kullager används i de mest skilda roterande tillämpningar, från mikromekanik för hårddisken i datorn till axellager för bilen eller vindturbiner och valsarna på ett pappersbruk. Lagret består av kuler eller rullar som roterar mellan två ringar, oftast av stål eller keramer. I båda fallen används material som är så starka som möjligt för att tåla stora och långvariga belastningar.

Kulorna är sällan i direkt kontakt med metallytorna till inner- och ytterringarna utan rullar mot en tunn oljefilm som smörjer de mikroskopiska ojämnheter som finns på ytorna av ringarna. Slitaget blir därmed mindre och beror främst på hur rent smörjfettet är.

I dagens verklighet, då produktivitet kommer ur högre varvtal, högre driftstemperaturer och minskat underhållsbehov, måste fagren överträffa allt vad som tidigare ansågs vara möjligt. Nya och allt mer avancerade tillämpningar ställer också högre krav, framför allt under extrema driftsförhållanden, där det finns risk för otillräcklig smörjning, ryckiga förändringar i belastningen eller överhettning. För att klara av dessa svåra driftsvillkor kan moderna lager levereras med en keramisk ytbeläggning med mycket låg friktion på kontaktytorna i lagret. Sådana lager klarar långa perioder av otillräcklig smörjning och även snabba varvtalsändringar och vibrationer. Diamant är det hårdaste material vi känner till och har många önskvärda egenskaper, men rena diamantlager fungerar inte. I stället använder man en beläggning av diamantlikt kol, eller "*DLC*" (för engelskans "diamond-like carbon") som kombinerar hårdhet med låg friktion och minskar förslitningen och ökar lagerens livslängd. *DLC* är det allmänna namnet för en blandning av de olika kolformerna grafit och diamant i en ordnad, amorf, struktur. Den kan beläggas i extremt tunna skikt, bara några tusendels millimeter på de flesta av dagens lagerkomponenter. *DLC*-beläggningen ger lagret unika egenskaper. Den gör det möjligt att kombinera slitstyrkan och segheten hos ett vanligt stål med den exceptionellt låga friktionen och den höga

hårdheten hos en *DLC*-beläggning. Resultatet är ett hårt lager som samtidigt har mycket låg friktion. Att anpassa de mekaniska egenskaperna hos beläggningen till dem hos det underliggande stålet är viktigt för prestandan hos den belagda komponenten.

Det finns en viktig skillnad mellan *DLC* och fasta smörjmedel och det är att *DLC* inte slits bort vid höga tryck. En annan unik egenskap hos *DLC* är inkörningsegenskaperna hos beläggningen. Även om ytan är mycket hård ombildas en liten del av den till en självsmörjande kontaktzon, vilket bidrar till skyddet av stålytorna, som annars skulle skadas av den hårdare beläggningen. Kombinerad med materialets hårdhet resulterar denna effekt i ideala smörjförhållanden. Denna egenskap utnyttjas idag för att dimensionera ner smörjsystem och skapa miljövänligare lösningar.

Jag föreslår här ett nytt material för ytbelagda lager: En förening av kol och kväve, som kallas kolnitrid. Kolnitrid har den ovanliga kombinationen av hårdhet och elasticitet, dvs styrka och seghet. Därför är det särskilt bra för de stora krafterna mellan kula och lagerring. Kolnitridbeläggningar har sitt ursprung på Linköpings universitet och tunnfilmgruppen. Mina studier visar att kolnitrid har mycket låg friktion och högt nötningsmotstånd, samtidigt är det ännu outforskat när det gäller smorda lagertillämpningar.

Jag har tillverkat kolnitridbeläggningar med olika moderna varianter av en beläggningsmetod som kallas magnetronsputtring med mer eller mindre intensivt bombardemang på komponentytorna av joner och atomer från ett plasma som ingår i själva ytbeläggningsprocessen, vilket ger god vidhäftning. Jag har också studerat nötningsegenskaperna och friktion hos kullager från SKF med avancerade analysinstrument och elektronmikroskopi i Linköping. Resultaten visar på oöverträffade egenskaper med ytterligare sänkt friktion och, som kan leda till kraftigt ökad livslängd för produkterna, besparingar för underhåll och framför all ökad tillförlitlighet i maskinerna.

Preface

This thesis is the outcome of my research made in the Thin Film Physics Division at the Department of Physics, Chemistry & Biology (IFM) of Linköping University (Linköping, Sweden) and the Tribology and Lubrication Department of SKF Engineering & Research Centre (Nieuwegein, The Netherlands), between October 2012 and October 2016.

Many results presented herein have been continuously published in international peer-review journals¹⁻³ and are also a continuation of my Licentiate thesis with the title "Low friction and wear resistant carbon nitride thin films for rolling components grown by magnetron sputtering", published in June 2015.⁴

The project was financially supported by *VINN Excellence Center Functional Nanoscale Materials (FunMat*, grant #2005 – 02666) and I was also awarded a travel grant from *Ångpanneföreningens Forskningsstiftelse (ÅForsk)* for attending the 43rd International Conference on Metallurgical Coatings and Thin Films 2016 (ICMCTF 2016) in San Diego, where I presented results of my research.

Note of the author

For me as a physicist and material scientist, the applied nature of the project was a big challenge *per se*. Not only because every scientific project includes difficulties and dangers, but also because science and engineering sometimes are very different and I had to find a common ground. This led me to the real beauty of my research, which was the scaling up and down. The changes that we can induce in the materials structure depend on the growth conditions and, lead to changes of the observed mechanical and tribological properties in real engineering applications. In order to understand the function of carbon nitride coatings in real bearings, I scaled down, studied their nanostructure, modified materials and/or methods, investigated the responsible tribological mechanisms, and tested the altered materials again at the macroscale, improving them. I believe that following this way, as many researchers did and do for many years now, the scientific research has an immense impact on everyday life.

Personally, the process was not untroubled, including moments of despair, anguish, high stress, and mistakes. At the time that I write these lines, I still try to balance the significance of my wins and losses, during my PhD studies. There are things that I would have done differently, if I had had the chance. However, I considered the entire process as a pathway to reinforce my patience, persistence, and tolerance, which led me to learn new things and meet good people. I hope that the final outcome is close to what my supervisors expected from me.

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Introduction

"The most merciful thing in the world, I think, is the inability of the human mind to correlate all its contents. We live on a placid island of ignorance in the midst of black seas of infinity, and it was not meant that we should voyage far. The sciences, each straining in its own direction, have hitherto harmed us little; but some day the piecing together of dissociated knowledge will open up such terrifying vistas of reality, and of our frightful position therein, that we shall either go mad from the revelation or flee from the deadly light into the peace and safety of a new dark age".

— Howard Phillips Lovecraft, *The Call of Cthulhu*
(1928)

The high significance of thin films in everyday life is evident by the vast variety of applications, in which they are used. Thin films are used in sectors such as semiconductor industry (electronics), green energy applications (i.e., photovoltaics, optical devices), printing technology, as well as cutting tools industry or bearings from automotive to wind turbine applications. In particular, ball and roller bearings are the heart of every rotating component. The range of applications which include bearings for their operation is huge, extending from nano- and microelectromechanical systems (MEMS), using the smallest bearings, to factory tools and wind turbines, using the biggest manufactured bearings. In bearing applications, the improved performance and high reliability of the components are extremely important in order to reduce cost and increase energy efficiency and safety. Thus, with respect to the demanding conditions of bearings operation, improvements are focused on their

tribological performance, failure prevention and therefore, the extension of their lifetime.

In the previous years, development was mainly performed in the field of lubricants and additives, by means of exploring the lubrication mechanisms in the contact of the counterparts. However, improvements on the overall operation of bearings can be achieved using thin films as protective coatings. Thin films effectively change the characteristics of the substrates surface (for instance their resistance, reflectivity, surface energy, friction etc), providing improved or even new properties. An emerging field in materials engineering is the low-friction and wear-resistant coatings, which are used in tribological applications. These coatings protect the component's surface from severe wear, granting the component with new enhanced tribological properties (surface adhesion, lubrication, friction etc). The use of thin films as protective low-friction and wear-resistant coatings for bearing components can lead to higher efficiency and improve the overall performance of the components, covering weaknesses of the lubricants. This may potentially lead to reduced need for lubricants and anti-wear additives, which are produced with environmentally harmful methods. Thus, functional low-friction coatings can be also proved more environmentally friendly, by reducing the use of anti-wear additives. Moreover, the high wear resistance of such coatings can reduce the frequency of equipment maintenance and, as a result, reduce the cost of machinery.

1.1 Aim and motivation

The aim of this work is to develop low-friction and wear-resistant carbon-based coatings, suitable for use in bearing applications, using relatively low-temperature, T , (below 150°C) physical vapor deposition (*PVD*) processes. The study involves the design, growth, and characterization of the coatings, as well as the tribological testing of coated components. The investigations focus particularly on amorphous carbon nitride ($a\text{-CN}_x$) coatings, which combine a set of structural, mechanical, and tribological properties, such as moderate hardness, very high elasticity, ultralow friction and very high resistance to wear. These properties render them suitable for use in bearing applications. The growth and characterization protocols are designed in line with the industry requirements, using state-of-the-art techniques.

The deposition procedures are conducted in an industrial deposition chamber in order to ensure that presented research delivers an effective, controlled, and fast

production process. The thesis includes also the characterization of the coatings prior and after the tribological tests of the coated components. The characterization before the tribological tests gives useful insights with regards to the influence of the deposition parameters on the structure and properties of the layers, which is the topic of Paper I. The connections between the process parameters used in the depositions, especially the substrate bias voltage, and the resulted properties are analyzed. Selection criteria for the most suitable coatings for roller bearings are also listed (cf. Paper I).

Another significant part of the thesis is the physics and chemistry at the substrate/coating interface, which constitutes the main field of investigation of Paper II. The substrate is the AISI 52100 bearing steel grade, a very tough and resilient material *per se*. It is well known that the adhesion of carbon-based coatings is generally poor on steel substrates^{5,6} (cf. Paper II and included references). For this reason, we developed a process, which effectively cleans and prepares the substrate surface prior to the coating deposition, resulting in much better coating/substrate adhesion. This is achieved by an *in-situ* bombardment of the steel substrates with ions, originating from a high power impulse magnetron sputtering (HiPIMS) source, that alter the chemistry of the substrate surface (cf. Paper II).

The tribological properties of the CN_x coatings in sliding and rolling tests are studied in Papers III, IV, V, and VI. The tribological properties of the coatings are measured using both macro- and microscale experiments and the results are compared (cf. Paper III). The characterization of the wear tracks after the tribological tests shed light in the way that the coating presence affects the overall rolling operation (cf. Papers IV, V, and VI). The performance of uncoated and coated rollers is compared under various tribological testing conditions (rolling speed and lubrication). In particular, the effects of the CN_x coatings in the rolling operation of bearings are emphasized in Papers IV, V, and VI. In spite of the fact that the science behind the operation of roller bearings is very well established,^{7,8} the theoretical and practical background with regards to the performance of coated roller bearings is still in embryonic stage.⁹⁻¹³ The latter is essential for the design and development of new and reinforced materials, since the use of protective coatings in tribological applications attracts increasing attention. Based on this, we use advanced microscopy and spectroscopy techniques, which reveal the friction mechanism(s) and wear modes of the coated rollers (cf. Paper VI). Furthermore, my experiments aim towards deeper understanding of the friction properties and wear performance of CN_x coatings.

1.2 Challenges

Roller bearings consist of four different steel parts: a) rollers, b) cage, c) inner ring, and d) outer ring (Fig. 1.1).¹⁴ Common materials for roller bearings are high carbon chromium steel grading AISI 52100, several high-speed steels (for use at high-temperature applications), stainless steel grading AISI 440C (for use at corrosive environments) and carburized hardened steels, whereas ceramic and silicon nitride bearings are also options for high performance applications.^{15,16}

Figure 1.1: Schematic of a roller bearing attached to a shaft; (a) cross-section, (b) top view. Adopted from.⁹

The contact between the rollers and the rings is characterized as "line" contact and it has a more or less rectangular shape (Fig. 1.2), with contact pressures ranging between 0.5 and 3 *GPa*, depending on the application. Specifically, the contact between the rollers and the inner ring is non-conformal, whereas the contact between the rollers and the outer ring is conformal.¹⁴ The type of contact is important as its specification determines the proper operation parameters for the formation of the lubricant film and its thickness.¹⁷ The general operation of bearings is very well known and has been extensively described.^{7,9,14,15} However, an important complexity of the rolling mechanism, arising from the above characteristics, is that some degree of sliding occurs during rolling, which can potentially cause failure such as fatigue, seizure or even corrosion.

According to the elastohydrodynamic (EHD) theory, a thin lubricant layer is formed during the operation of a roller bearing, separating effectively the counterparts. The surface separation prevents the direct steel-to-steel contact and consequently adhesive and abrasive wear are avoided.^{9,15} When the thickness of the lubricant film is not adequate for the lift-off of the counterparts and the separation of the surfaces, severe wear and fatigue take place, and as a result, the bearings are

led to failures, such as seizure, spalling or pitting. This may occur at very low or very high rolling speeds.

Figure 1.2: Schematic illustration of line contact between a roller and a part of a ring.

Pitting or micropitting (due to the size of the pits which can be in the μm range) is regarded as a serious type of fatigue for roller bearings, that reduces the performance and lifetime of the component. Due to these failures, rollers need regular maintenance, if not early replacement. Thus, the improvements in the performance and lifetime of the rollers result in several benefits. For instance, the reduced service frequency implies better cost-effective solution, directing the rolling operation towards a more environmental-friendly process. Moreover, an improved bearing results in a better overall performance of the component which makes use of the bearing.

The bearing lifetime can be extended by the deposition of a thin film coating on the roller or the rings surfaces. Coatings can contribute to lower friction at the contact between the rollers and the rings.^{9,18–20} There are different types of films that are, or can be used, as protective and low friction coatings on bearings. Examples include *Au*, *Pb*, *Cu*, *Cr*, *MoS₂*, *TiN*, *TiC*, and diamond-like carbon (*DLC*). Among them, there are mechanically soft coatings, which regarded as solid lubricants, i.e. *MoS₂*, due to their capability to operate without oil or grease lubrication.²¹ These coatings are successfully used in space applications.²¹ Another group includes hard compound coatings, such as *TiC*, *TiN* or *DLC*, grown by chemical vapour deposition techniques (*CVD*) at elevated temperatures ($> 1000^\circ C$).^{22–26} On the other hand, using *PVD*, *TiN* coatings have been produced at a temperature as high as $600^\circ C$.²⁷ However, a limitation for the coatings depositions is the substrate tempering temperature¹, which in the case of AISI 52100 steel is below

¹Tempering temperature is the temperature at which carbon precipitates are assumed to be

200°C.¹⁵ This restricts depositions using temperature higher than 170°C. Such process temperatures confine also the range of available techniques for coatings depositions. For example, *CVD* techniques are excluded for coating depositions on roller bearings, turning the interest towards *PVD*. Here, the growth temperature can be dramatically reduced below 200°C in *PVD* processes.^{28,29}

The hard and elastic fullerene-like microstructure of CN_x appears at substrate temperature above 300°C.^{30–32} At lower T , the a - CN_x compound structure prevails, yielding, considerably lower elasticity than the fullerene-like CN_x .^{31,32} To overcome this problem, different *PVD* magnetron sputtering techniques are used, at $T \leq 150^\circ\text{C}$. Hence, the challenge is to develop a - CN_x coatings, which combine properties such as increased elasticity, high hardness and low friction. Among parameters that influence the microstructure and consequently the properties of CN_x is the applied bias voltage, V_b . By applying a negative bias at the substrate table, ions are attracted with increased energy towards the substrates. The higher energy and flux of ions, incident at the grown film, result in different growth energetics, affecting the film properties to a great extent. Since the temperature variation is limited, I synthesize CN_x coatings using different V_b , at a substrate temperature of $\sim 150^\circ\text{C}$.

One problem, limiting the practical application of CN_x films, is the poor adhesion to the steel substrates (cf. Paper II).⁵ Adhesion is influenced by the high residual stress of the coating, the low electron affinity of C to Fe , and complex 3-dimensional shapes, such as the cylindrical, when rollers are used as substrates (cf. Paper I and Paper II).³³ Several techniques have been used in the past for the improvement of adhesion of the C -based coatings on steel.^{33–36} However, the conditions of the rolling operation in bearing applications are very demanding, including high contact pressures and lubrication, thus the coating-substrate adhesion is also a very essential research area. This issue is addressed herein by employing the treatment of the substrate surface prior to coating deposition. For this pretreatment, a metal ion bombardment process with HiPIMS is utilized, applying a high synchronized pulsed V_b (cf. Paper II).

diffused in the steel matrix, causing changes of the microstructure and hence, softening of the steel.

Carbon-based coatings

"All truly great thoughts are conceived by walking".

— Friedrich Nietzsche

Considering the function of coatings in bearing applications, the goal is the reduction of friction and the enhancement of bearing wear resistance. A suitable material for this purpose is *DLC* and its derivatives. The use of *C*, as the base material for the films, has several advantages, such as its abundance and high availability, its low cost and many abilities for customization of such films. *C*-based thin films have been proven very attractive, due to their mechanical and tribological properties, as well as robust, due to the variety of their structural characteristics.^{25,29,37–40} They exhibit low to ultralow friction coefficients, μ , and high wear resistance,^{39,41,42} high hardness (in tetrahedral amorphous carbon, *ta-C* films), and for some compounds high elasticity (for instance, fullerene-like carbon nitride, *FL-CN_x* films)⁴¹. Such films are already used as protective low friction coatings in hard disk drives technology^{37,40,43} and biomedicine⁴⁴. However, their use can be expanded to application which employ higher loads and contact pressures such as bearings, gears, and shafts in automotive industry. This requires investigations of the structural, mechanical, and tribological properties of existing and new carbon-based materials. Furthermore, exploration of new or improved methods to fabricate carbon-based coatings for specific applications are needed, in order to implement them into applications of everyday life and in accordance to the demands of each application.

2.1 Diamond-like carbon

Carbon (from Latin: *carbo*, "coal") is a remarkable element. It exists in the $\sim 90\%$ of all known chemical substances and has the largest number of allotropes compared

to any other element. It is nonmetallic, offering four electrons for the formation of covalent bonds with electronic configuration $[He]2s^22p^2$. In nature, carbon appears in the forms of diamond and graphite. Diamond (from the ancient Hellenic: *ἀδάμας*, "unbreakable") is most commonly met in gemstones, having exclusively two interpenetrating face-centered cubic Bravais lattices. Diamond exhibits the highest hardness (~ 100 GPa) and bulk modulus (~ 433 GPa) of all known natural and synthesized materials up to date, with a density of 3.52 g/cm³ and remarkably high thermal conductivity (20 W/cm°C). On the other side, graphite (German *Graphit* from Hellenic: *γραφειν*, "to write") is the most common form of natural carbon and its structure differs from that of diamond. The structure of graphite is hexagonal with carbon rings coordinated in a plane. Nevertheless, graphite ore can also be found in nature as amorphous. Graphite is much softer than diamond and its loose interplanar bonding between the graphene sheets provides very good lubricating properties. *C* allotropes have been technically synthesized, with amorphous or tetrahedral amorphous forms (*a-C* or *ta-C*). Solid *C* materials exhibit also allotropic properties, depending on their microstructure. Apart from the solid bulk materials, *C* is also used as building block for *C*-based allotropes, including nanotubes, fullerenes, glassy carbons, carbon nanofibers, and numerous other compounds.

The chemical bonding in *C*-based compounds is often discussed using the concept of hybridization, proposed by Linus Pauling in 1931. Within this nomenclature, the four valence electrons of *C* can form three hybridization states, the sp^3 (with four hybridized σ orbitals), sp^2 (with three hybridized σ orbitals and two π orbitals) and sp (with two σ orbitals and four π orbitals). sp^3 hybridized orbitals with tetrahedral coordination appear in diamond, sp^2 hybridized orbitals are mainly met in graphitic configurations, while sp orbitals form configurations similar with alkalines (Fig. 2.1). In an sp^3 hybridized carbon, the four valence electrons form σ orbitals, which point towards the corners of a tetrahedron and a network of sp^3 bonds has a 3-dimensional configuration (Fig 2.1(a)). The link between the *C* atoms in this configuration is achieved via covalent bonds and the tetrahedral atomic bonding forms an extremely strong molecule. Thus, the high bulk modulus of diamond is a direct consequence of the sp^3 -bonding. The sp^3 *C-C* bonds exhibit a bond energy of 3.9 eV with a bond length of 154 pm.

Carbons with an sp^2 -rich network, have three electrons participating in three planar σ bonds with an angle of 120° , while the fourth electron has a π orbital

Figure 2.1: C atoms in (a) sp^3 hybridization, like in diamond structure, (b) sp^2 hybridization, like in graphite, and (c) sp hybridization, like in alkynes.

perpendicular to the σ orbitals (Fig 2.1(b)). These hybridization states occur in graphite and graphene, with enhanced in-plane strength, due to a shorter $C-C$ bond length of 133 pm and energy of ~ 7.5 eV . In sp -hybridized bonding states carbon forms two orthogonal π orbitals and two linear σ orbitals, comprising a bond length of 120 pm and energy of 9.9 eV (Fig 2.1(c)).

The production of *DLC* films was realized in the early 1950's by Schmellenmeir⁴⁵, although *DLC* coatings attracted attention almost two decades later, with the work of Aisenberg and Chabot⁴⁶. *DLC* films consist of a mixture of sp^2 and sp^3 carbon structures, usually with sp^2 bonds embedded in an sp^3 matrix.

A phase diagram proposed by Robertson summarizes the microstructures of *a-C* materials (Fig. 2.2)²⁵. They are mainly amorphous materials that can be divided into *H*-containing and *H*-free carbons. Both films occur in different amorphous types; tetrahedral amorphous (*ta-C*) and hydrogenated tetrahedral amorphous carbon (*ta-C:H*), amorphous carbon (*a-C*) and hydrogenated amorphous carbon (*a-C:H*), sputtered amorphous carbon and hydrogenated sputtered amorphous carbon, as well as glassy or graphitic carbon (*g-C*).

This classification depends on the *H* content and the amount of sp^3 and sp^2 hybridization states in the material.^{25,47} As the amount of sp^3 hybridized states increases, *ta-C* structure prevails, with a corresponding influence on the mechanical properties of the films, where very hard materials are formed. If the sp^2 bonding dominates, the *DLC* films exhibit more graphitic structures (due to the configuration of sp^2 -hybridization, as described above), forming *a-C* and *a-C:H* films. Carbon nitride (CN_x) films are another category of *C*-based materials, which contain a high sp^2 fraction, mainly induced by *N* incorporation in the *C* matrix.⁴⁸ The introduc-

Figure 2.2: Ternary phase diagram of a -C and a -C(:H) materials. Figure adopted from.²⁵

tion of N in a carbon matrix can change the microstructure, promoting a degree of cross-linking and bending of basal planes and providing enhanced elasticity to the films, like in case of fullerene-like films.⁴⁹ Finally, an emerging category is also the metal/amorphous (a -C: M) composite films, where a metal is embedded in the a -C matrix.^{50–52}

2.2 Carbon nitride

The introduction of a small amount (~ 10 -25%) of foreign element in the C matrix, like N , F , P , S , Si or metals like Ti , Cr , Ta , W , can alter the structure and properties of the initial film.^{53–60} Nitrogen is an element with similar hybridization states as C . It can also form covalent bonds, having an electronic configuration $[He]2s^22p^3$. It also forms sp^3 - and sp^2 -hybridized states, but the extra electron introduces some changes regarding the bond angles in sp^3 configuration and also, results in two configurations when it bonds with sp^2 states (Fig. 2.3). The sp^3 formation is similar to that of ammonia, leaving an unbonded pair of electrons, while the sp^2 states are similar to that of (i) pyridine or to (ii) a 3-fold coordination substituting a C atom in a graphitic site.³¹

Figure 2.3: N atoms including (a) sp^3 -hybridized bonds, like in ammonia, (b) sp^2 -hybridized bonds, like in pyridine and (c) sp -hybridized bonds with 3-fold coordination with C atoms.

Carbon nitride is a carbon allotrope material, which attracted a lot of attention when Liu and Cohen^{61,62} predicted the metastable β phase of C_3N_4 in 1990, which in theory exhibited a bulk modulus (427 GPa) very close to that of diamond (433 GPa⁶³). The synthesis of β - C_3N_4 was not successful up to date, although other interesting materials were synthesized, such as elastic and resilient sp^2 -rich α - CN_x and FL - CN_x compounds.^{39,48,64–67} The synthesis of α - CN_x is dated earlier than FL - CN_x compounds, because all tries for the deposition of β - C_3N_4 resulted in the growth of amorphous phases. In 1995, the first fullerene-like CN_x compound was synthesized by Sjöström *et al.*⁵³ at Linköping University, a material that was further investigated experimentally by Hellgren *et al.*,^{68,69} Neidhardt *et al.*,^{30,67} and Schmidt *et al.*^{32,70} Simultaneously, theoretical studies performed by Gueorguiev *et al.*,^{49,71} showed the possible structural evolution of CN_x compounds, described by cross-linkage of individual graphene sheets and bending basal planes extended in a 3-dimensional network.

Both carbon allotropes were synthesized by several PVD deposition techniques, such as radio frequency magnetron sputtering (RFMS),^{72,73} direct current magnetron sputtering (DCMS)^{32,68,74,75} (cf. Paper I), high power impulse magnetron sputtering (HiPIMS)^{32,70} (cf. Paper I), pulsed laser deposition (PLD),^{39,76} filtered pulsed cathodic arc deposition,^{39,77} and ion beam assisted deposition (IBAD).⁷⁸ The structure of magnetron sputtered CN_x films shows a clear dependency on the deposition temperature. For CN_x films deposited with DCMS at a low substrate temperature of $< 200^\circ\text{C}$, amorphous and dense films are grown, while increasing the substrate T , FL microstructure prevails.³¹ The N content in the films and the degree of N incorporation also depend on the substrate temperature.⁴¹ For films grown at $T < 200^\circ\text{C}$, N_2 fraction does not influence the film growth, while at $T > 200^\circ\text{C}$,

chemical sputtering interactions take place at the substrates.^{31,69} For CN_x films deposited by HiPIMS, similar temperature dependency is found, where at elevated substrate temperature, the FL structure becomes dominant.³² $a-CN_x$ thin films have been deposited by several research groups with the use of different magnetron sputtering techniques, mainly RFMS and DCMS. Kleinsorge *et al.*²⁸, Hellgren *et al.*⁶⁸ and Ferrari *et al.*⁶⁴ have thoroughly studied the bonding of N within C matrix in $a-CN_x$, concluding that N incorporation promotes sp^2 hybridization states.⁷⁹ This has immense effects on the mechanical response of the films, especially their elasticity. It is believed that the cross-linking and bending of the basal planes are responsible for the increased resiliency of the $FL-CN_x$ films. $a-CN_x$ films exhibit also enhanced resiliency and elasticity, but not to the same degree as the $FL-CN_x$ compound, which can potentially reach 100% of elastic recovery after indentation.³⁰

Synthesis of carbon nitride coatings

"A man will be imprisoned in a room with a door that's unlocked and opens inwards; as long as it does not occur to him to pull rather than push".

— Ludwig Wittgenstein

3.1 Sputter deposition

The process of thin film growth is conducted under high or ultra high vacuum conditions to avoid contamination of the films. A noble gas (*Ar*, *Kr*, *Ne* or *Xe*) - the working gas - is let into the vacuum chamber as the sputtering agent. A negative potential is applied to the cathodes. A small amount of background electrons and ions, present in the chamber, are accelerated in the cathode field. Electrons cause ionization of the working gas, once they gain sufficient energy, and a glow discharge is initiated. The positively charged gas ions (i.e., *Ar* for convenience) are then attracted towards the cathode, which has a highly negative potential in the range of 400 to 800 V. Then they collide with the target, which is the plate containing the desired growth material mounted on the cathode. Due to the energy and momentum transfer, particles are ejected from the target, in the process called *sputtering*, discussed in more detail below. A number of other particles are also emitted from the target namely, secondary electrons, reflected ions and neutrals, and photons, creating a plasma; an ionized phase of the sputtered gas, with glow colors characteristic of each gas. The secondary electrons increase ionization of working gas atoms, producing an avalanche effect and the discharge is sustained.

The term *sputtering* can describe several ion-surface interactions. Sputtering is the process in which atoms are ejected from the surface of a solid material (target),

due to collisions between projectile/recoil atoms and atoms of the surface of the target. Impinging ions create a collision cascade at the area of incidence and surface atoms are removed from the target, when they have sufficient energy (Fig. 3.1).

Figure 3.1: Schematic illustration of the sputtering process on a theoretically pure target containing only one material element. The cathode and the configuration of an unbalanced magnetron are shown below the target. The dimensions of the target and ions/atoms are exaggerated and do not correspond to the cathode and magnetron sizes.

The sputter yield of a target is formulated as:

$$S = \frac{\text{Number of sputtered atoms}}{\text{Incident ion}}, \quad (3.1)$$

and is a measure of the efficiency of the sputtering process or an estimation of the average amount of particles removed from the target per incoming ion. The sputter yield depends on the type and energy of the impinging particle, the incident angle, as well as, the target material.

Very important components, incorporated in sputtering techniques, are magnets which are placed behind the cathodes. Their magnetic field lines confine the motion

of electrons in the region close to the cathode surface. In this way, the time that electrons spend in the vicinity of the target is increased and the collision probability between the confined electrons and the plasma species increases. Hence, the plasma is easier maintained and higher plasma densities are achieved. There are two different magnetron configurations, namely the balanced and the unbalanced magnetron. In a balanced magnetron, all magnets have the same strength, while in an unbalanced magnetron configuration, different magnets are used. The unbalanced magnetron configuration is a very effective way to enhance the ionization and ion bombardment. In an unbalanced magnetron, a selective strengthening of the magnetic field at the target ends can be chosen, so that more of the secondary electrons escape from the confinement, increasing the plasma ionization.

A common magnetron sputtering method is DCMS, where DC power supplies are utilized to deliver a continuous current, yielding also a continuous production of ions during the deposition. DCMS is a widely used technique, both in research and industry, due to its fairly acceptable deposition rates. It is a well-understood process nowadays, especially for C and CN_x films.

In mid-frequency magnetron sputtering (MFMS), pulsed power supplies (AC) are used for the generation of the plasma. Commonly, MF is used to deposit insulating materials, which were subjected to unstable discharges with arcing.⁸⁰ Arc generation causes defects in the films, such as macroparticles. In an effective MF configuration, two operating targets are necessary, where one target works as a cathode and the other as an anode and their polarity is altered every half cycle. The operating frequency can vary, depending on the deposition system. In MF conditions, frequencies are in the range of few hundreds of kHz (50 - 250 kHz).

MF produces tetragonal pulses with the pulse-on times of the cathode equal to the pulse-off times of the anode. Duty cycles are usually in the region of 50% - 50% and are given from:

$$D = \frac{t_{pulse}^{ON}}{T} = f \cdot t_{pulse}^{ON}, \quad (3.2)$$

where t_{pulse}^{ON} is the pulse-on time, T is the pulse length (period), and f is the operating frequency.

High power impulse magnetron sputtering (HiPIMS) is also a pulsed process. High pulsed power supplies are used to generate high amplitude voltage pulses and

deliver high amounts of energy to the plasma, in short time intervals (tens to hundreds of μs). These high peak currents are two orders of magnitude higher than the average target currents in a DCMS process, resulting in high plasma densities (of the order of $10^{18} m^{-3}$,⁸¹ while for DCMS respective values are $\sim 10^{16} m^{-3}$). The high plasma densities increase the possibility for ionization of the sputtered material. Kouznetsov *et al.*,⁸² investigated *Cu* targets in HiPIMS conditions and found that the ion fluxes in HiPIMS were two orders of magnitude higher than in a DCMS process. The pulses in HiPIMS processes exhibit usually low duty cycles of $< 10\%$ and frequencies $< 1 kHz$. It has been demonstrated that HiPIMS often leads to deposition of dense and homogeneous thin films, while avoiding droplets due to arcing. However, a reduction of the deposition rate, has been observed compared to DCMS mode.⁸³

3.2 Carbon nitride coatings deposited by magnetron sputtering

If a reactive gas (for instance N_2 , O_2 , methane) is added to the working gas, the process becomes reactive magnetron sputtering. In reactive sputtering, chemical reactions take place at the substrate and compound materials, such as oxides (Al_2O_3 , SiO_2), nitrides (TiN , AlN , SiN_x , CN_x), carbides (TiC , SiC), sulphides, oxycarbides and oxynitrides, can be formed. CN_x films are typically deposited in a mixture of N_2/Ar gas or entirely in N_2 atmosphere. When N_2 is present during the sputtering process, N^+ and N^{2+} ions can be formed. These ions are involved in physical and chemical sputtering of C , creating dangling bonds at the target surface. In the case of chemical sputtering, dangling bonds are passivated with atomic N species or C_xN_y ($x, y \leq 2$), if no recombination with C or H occurs. Then, volatile CN -species can desorb, with incident ion energies lower than the threshold energies for physical sputtering, from the target surface and travel through the plasma to the substrates.⁶⁹

The interactions, during chemical sputtering in CN_x depositions, have been previously studied by Hellgren *et al.*,⁶⁹ Hammer *et al.*,⁸⁴ Kaltoven *et al.*,⁸⁵ when DCMS was used for the synthesis of CN_x films and by Schmidt *et al.*,⁷⁰ when HiPIMS was used. For films grown by DCMS, the chemical sputtering on the film is pronounced at elevated gas flow ratios ($N_2/Ar > 0.5$) and for process temperatures above $200^\circ C$, leading to a N content in the films lower than $25 at.\%$ and lower growth rates.

Hecimovic and Ehasarian⁸⁶ demonstrated that, the plasma characteristics and the sputtering of C targets in HiPIMS mode differ significantly from sputtering of metal targets, using the same method. Here, the amount and energy of C ions were found lower than heavier metal elements, moreover, no doubly charged C ions were detected, in contrast to metals. CN_x thin films have been deposited in N_2/Ar by reactive HiPIMS later in 2012 by Schmidt *et al.*, where amorphous films were shown to prevail at low growth temperatures and fullerene-like structures were produced at high temperatures,³² following the general course mentioned above for DCMS. Lower deposition rates were also reported for CN_x film synthesis using HiPIMS compared to DCMS.³² An extensive and thorough comparison regarding the plasma characterization and film growth, between DCMS and HiPIMS depositions of CN_x can be found in references.^{32,70,87} While reactive DCMS of CN_x films is well understood, the HiPIMS and MFMS processing of graphite targets, operating in metallic or reactive mode, for pure C and CN_x film synthesis, need to be further explored.

In this thesis, an industrial deposition chamber is used for the growth of CN_x thin films, employing MFMS, HiPIMS or DCMS under similar growth conditions. The chamber configuration is illustrated in Fig. 3.2, where the mode that the cathode can operate is indicated next to each cathode/target. For my MFMS depositions, cathodes indicated as MF are working together, while during HiPIMS processes, one of the two HiPIMS cathodes is employed. The table carry separate holders, where each holder carry separate steel rods for the mounting of the substrates. Thus, a 3-fold rotation with 1 *rpm* of the substrates is used during the depositions, which guarantee the uniformity of the coating.

For the synthesis of the CN_x films in this thesis, pure graphite targets are sputtered in a gas mixture of Ar and N_2 , using a N_2/Ar flow ratio of 0.16 at a total pressure of 400 *mPa*. The power of the targets is set at 1200 W in all processes. This results in a N content of $\sim 15 - 19\%$ in the films, when a deposition temperature of 150°C is used (more details about the growth procedures in Paper I).

In HiPIMS mode, the operation of the cathode-target assembly can usually lead to severe arcing, since it is governed by very high currents through the cathode-target. It is expressed as a drop in the cathode voltage, following an explosive event, normally a release of a highly concentrated discharge from a region of the target's surface. The high ionization potential of C , which requires higher electron energies could play a role, since higher currents need to be accumulated in order to ionize C atoms. During arcing, carbon macroparticles are ejected from the target,

Figure 3.2: Illustration of the top view of the deposition chamber. The components of the chamber are also shown, such as cathodes, table and holders with 3-fold rotation, gas inlets, and heaters.

during HiPIMS depositions, and may land on the substrates. The diameter of these macroparticles can be as large as the film thickness, often of the order of several μm . An example of a macroparticle, incorporating during the reactive-HiPIMS deposition of CN_x , is shown in Fig. 3.3(a). This macroparticle extends almost from the middle throughout the film, meaning that it was generated and implemented into the film approximately in the middle of the process. Fig. 3.3(b) shows a defect in the same film, which does not constitute a macroparticle, but it could be generated by the deposition of a macroparticle of a smaller size, during the initial stage of the process. In this case, the macroparticle was deposited on the film and the deposition at that point continued with different route, resulting in defect creation. Macroparticles may be generated during DCMS processes as well, although the problem is not so pronounced, resulting in much smoother and defect-free surfaces. In contrast, MFMS mode allows essentially for arc-free processes. Since depositions of CN_x coatings in HiPIMS mode lead to surfaces that include defects (i.e., various types of macroparticles), the friction and wear properties of the coatings can be affected. Thus, processes that produce less or no macroparticles, i.e., DCMS and MFMS, are preferred instead, for defect-free CN_x surfaces.

Ion bombardment of the substrates during film growth is an influential factor and crucial for the structural properties of the films. Moreover, the limitation for exclusive use of low temperatures during the depositions, confines the customization of the film morphologies through temperature variations. The application of a negative bias voltage (DC or pulsed) at the substrate is a method to increase the

Figure 3.3: (a) Cross-sectional SEM micrograph, visualising a macroparticle that was incorporated in the film during deposition and (b) nodular growth of a defect, grown after a smaller macroparticle was initially deposited on the substrate.

flux and energy of ions incident at the growing film surface, such that films with different morphology can be produced.⁸⁸ At higher ion energies (> 100 eV), more homogeneous films result, although increased defect density and impurity incorporation, such as inert gas species, appear. For CN_x , Laskarakis *et al.*⁸⁹ investigated the structural changes that low and high energy ions induce in the C matrix, with N incorporated in a different manner. Neidhardt *et al.*³⁰ showed that small variation of the ion energies from 25 to 40 eV can alter the mechanical properties of $FL-CN_x$ films, producing harder and more elastic materials. However, to our best knowledge, there are no studies, addressing the effect of ions with energies higher than 40 eV on the morphology of low-temperature CN_x films, either amorphous or fullerene-like in a specific deposition system. Ion bombardment including energies higher than 40 eV is expected to have a high impact on the microstructure and morphology of CN_x coatings. This is important since morphology is detrimental for layers intended for use in tribological applications.

High film density and homogeneity are pre-requisites for the formation of hard and wear-resistant thin films. Both are a function of the ionization conditions that can be altered using different deposition technique, along with different type of bias voltage (V_b). MF, HiPIMS, and DC plasmas are characterized by various degree of ionization, which combined with different duty cycle at the substrate bias, has a decisive influence on the way that the ion fluxes affect the evolution of the film microstructure.

These effects are illustrated in Fig. 3.4, which shows fracture cross-section scanning electron microscopy (SEM) micrographs of CN_x films deposited by MFMS, HiPIMS, and DCMS as a function of bias voltage. At $V_b < 20$ V, columnar structures with intercolumnar voids are observed for all methods, which then disappear and, more homogeneous films are obtained with increasing V_b . The increased homogeneity is ascribed to higher ion energies at higher V_b , which increase the extend of forward sputtering and renucleation sites at the growing films (cf. Paper I). The differences between CN_x films, deposited with different methods at the same bias, are due to the different amount of ions present in each case, and the different duty cycles used (cf. Paper I). The low duty cycles of HiPIMS processes hinder the formation of homogeneous films at $V_b < 120$ V. During DCMS, the continuous operation of V_b contributes to the formation of homogeneous films with $V_b \geq 100$ V, while in MFMS processes the high ion densities together with the high duty cycle (44%) contribute to the formation of homogeneous films with V_b as low as 60 V. The different CN_x coating morphology is related to their obtained mechanical properties and wear performance. Here, the harder CN_x coatings (i.e. coatings grown using higher bias voltages) have a column-free, highly homogeneous morphology, which lead to higher wear resistance in tribological tests (cf. Paper I). Hence, bias voltage, indirectly affects the tribological performance of the CN_x coatings and is an essential parameter for the customization of their mechanical and tribological properties.

Figure 3.4: Fracture cross-sections of CN_x thin films deposited by (a)-(c) MFMS, (d)-(f) HiPIMS, and (g)-(i) DCMS at different values of substrate bias. Duty cycle is 6% and 44% for the HiPIMS and MFMS process, respectively, at a growth temperature of $150^\circ C$.

Tribology

"Our life is frittered away by detail... simplify, simplify".

— Henry David Thoreau

Tribology (from the Hellenic word $\tauριβω$, "to rub") is the science of contacted surfaces in relative motion. Tribology science and technology covers the aspects of friction, wear, and lubrication. The first attempts to scientifically describe the laws of friction were made by Leonardo da Vinci, between the 15th and 16th century, who introduced the concept of friction coefficient, however, his works remained unpublished for years.⁹⁰ Hundred years later, in 1699, Amontons expressed the laws of friction, which were verified by Coulomb, in the late 1700's.⁹¹ The fundamentals of tribological laws were the basis for advances in numerous engineering applications such as wheels, gears, cams, tappets, nuts, bolts, bearings, and other components that include sliding and/or rolling surfaces in contact.

4.1 Tribology of diamond-like carbon and carbon nitride coatings

DLC coatings are considered to be excellent solid lubricants due to their ultralow friction and high wear resistance, stemming from their unique properties, such as chemical inertness, high hardness, and surface adhesion.^{25,50,51,92,93} *DLC* coatings do not have predominantly crystalline structure like diamond, but they include a mixture of sp^2 and sp^3 bonding configurations.^{25,28,47} They are used as hard protective coatings in industrial applications, due to their low friction and high hardness, yielding also high wear resistance.^{37,43} A variety of industrial tribological applications make use of *DLC* coatings nowadays. They are extensively used in hard

disk drives technology with success, as overcoats on thick multilayered structures.³⁷ They are biocompatible allowing their use also in medical implants.^{44,94} In more demanding high-cycle applications, employing also high contact pressures and harsh environments (lubrication), such as in automotive industry,⁹⁵ *DLC* coatings can be used, but their fatigue and adhesion are still problematic.^{96,97} Nowadays, in racing cars and motorcycles, especially in Formula 1 and MotoGP, *DLC* protective coatings on cam shafts and gears in engines are widely applied, drawing the attention¹. Nevertheless, most of the engine failures in races occur due to unsatisfactory lubrication of a contact, followed by severe coating wear or delamination and eventually engine failure. However, both Formula 1 and MotoGP are testing environments, which employ the most demanding conditions (high loads, high temperatures, and extreme speeds) for the coating operation. Therefore, any development in the coatings technology from racing can potentially lead to utilization of these coatings in conventional car components, increasing reliability and performance. It is noteworthy that *DLC* coatings are not extensively used in conventional car engines. Up to date, only one car company, i.e., Renault advertises the use of a non-hydrogenated *DLC* coating in parts of one of their car engines, providing the same coated parts also to Nissan.

Both hydrogenated (*a-C:H*) and non-hydrogenated (*a-C*) *DLC* coatings are important for tribological applications. However non-hydrogenated *DLC* are more relevant to CN_x coatings, due to the different surface termination of CN_x films, provided by the incorporation of *N*. Moreover, CN_x shows similar friction properties to those exhibited by non-hydrogenated *DLC*.⁴¹ In CN_x , *N* occupies the surface dangling bonds and much less *H* is incorporated.²⁹ CN_x coatings can also exhibit low friction and high wear resistance.^{30,39,41,98–100} Most of the studies based on the tribology of CN_x were triggered when the CN_x started to be regarded as a suitable material for the use in the hard disk drives technology.^{37,101–103}

In 1996, Khurshudov *et al.* compared the tribological performance of commercial carbon and CN_x overcoats for hard disk drives, sliding also against Si_3N_4 , in a relative humidity (RH) of 40% - 60% without the use of lubricants.^{102,103} The authors showed that CN_x coatings have 10 times lower wear rate than the *N*-free *C* coatings.¹⁰² Furthermore, CN_x shows 3 - 30 times longer lifetime and a friction coefficient between 0.12 - 0.14, demonstrating the capabilities of CN_x as protective low friction material. In the case of the *N*-free *C* coating, a friction coefficient

¹http://www.grandprixengines.co.uk/Note_103.pdf

of ~ 0.3 is recorded. Later in 1999, Scharf *et al.* demonstrated that hard disks coated with CN_x thin films show higher wear resistance and resistance to plastic deformation than disks coated with N -free C layers, due to a strengthening of the coating-substrate interface.³⁷ A higher amount of N , bonded in sp^3 configurations, was found to contribute to better adhesion at the interface, compared to the sp^2 -rich interface in the case of N -free C films.

4.2 Friction

As mentioned in Sec. 4.1, CN_x coatings exhibit low friction and their tribological properties have been studied in the past.^{39,104} However, the mechanisms and causes of friction in CN_x is still a mystery. In this thesis, I investigate the friction characteristics of CN_x layers at different scales and using different tribological tests. Rolling contact fatigue (RCF), reciprocal macroscratch, and nanoscratch tests are conducted in order to study the friction properties of the coatings. CN_x is a material with very high elasticity and this changes the characteristics of the contact between coated counterparts and thus, the theory of friction needs more investigation for the understanding of the prevailing friction mechanisms. Guillaume Amontons and Charles-Augustin Coulomb first described the mechanisms of friction. They showed that friction between two metallic, non-flat, surfaces can be attributed to the mechanical interaction of the surface hills, which are local maxima with varying amplitudes, referred to as *asperities*. However, a more complete description of the friction mechanisms was given by Bowden and Tabor in 1964,¹⁰⁵ who stated that when two rough metallic surfaces are brought into dry contact under a normal load, the real area of contact is restricted only to peaks of the asperities, whereas the bodies weld together upon the applied load (body I and body II in Fig. 4.1). Figure 4.1 shows areas of contact between the asperities of body I and the flat surface of body II, where the shaded areas indicate the contact zones.

The real contact area, A_r , in this case can be described by

$$A_r = \frac{L}{H}, \quad (4.1)$$

where L is the normal load and H is the hardness of the material. If body I moves relatively to body II in a tangential direction, a resistance appears, originating from the welded asperities. This motion breaks the asperity junctions and leads to the

Figure 4.1: Profile of a contact between a rough and a flat body under normal load. The mean line is a reference line, such that the area between the profile and the mean line, above this line, is equal to that below the mean line. Figure adopted from.¹⁰⁶

formation of new junctions, causing also a resistance, considered as the friction force, F ,

$$F = s_m A_r, \quad (4.2)$$

where s_m is the shear strength² of the material. For a lubricated contact, the friction force is expressed by:

$$F = A_r [\alpha s_m + (1 - \alpha) s_l], \quad (4.3)$$

where s_l is the shear strength of the lubricant film and α is a fraction of the unlubricated area. Thus, the coefficient of friction, μ , can be derived as:

$$\mu = \frac{F}{L} = \frac{s_m}{H}, \quad (4.4)$$

for a dry contact and

$$\mu = \frac{F}{L} = \frac{\alpha s_m + (1 - \alpha) s_l}{H}, \quad (4.5)$$

for a lubricated contact.

When the two counter bodies are not identical in terms of mechanical properties, then the s_m and H of the softer material are taken into account. From the analysis above, it is inferred that the coefficient of friction depends on L and does not depend on A_r . However, friction is not an inherent property of the materials and can

²Shear strength is the magnitude of shear stress that a material can sustain before it catastrophically breaks or fails.

be influenced by possible surface contamination (reactive oxide layers), the environmental conditions (humidity and temperature), and sliding or rolling speed.^{105,107} These parameters may affect adhesion and plastic deformation between the counter bodies and consequently the friction. Another factor, that was originally neglected in the friction model, is ploughing, which is the deformation of the softer material by plastic flow, and was added to the friction equation later by Tabor in 1959,¹⁰⁸ such that

$$F = s_m A_r + F_p, \quad (4.6)$$

where F_p is the friction force due to ploughing phenomena. Thus, friction can be reduced by decreasing any component in the equation above. In the coatings technology, hard materials reduce the real contact area and possibly the ploughing effects, due to their high resistance to plastic deformation. On the other hand, softer coatings can decrease the shear strength.¹⁰⁵

CN_x coatings have high elasticity and the real contact area is altered, thus the approach from Greenwood and Williamson for the determination of the friction mechanism is employed.¹⁰⁹ The problem of the real contact area was addressed by Greenwood and Williamson in 1966,¹⁰⁹ where the mechanical properties of the materials in contact were taken into account. For ductile materials, one very important parameter affecting friction is the surface asperities and their deformation upon the contact of the surfaces under normal load. The effect of the asperities can be visualized by two surfaces that are brought into contact. Let us consider that one surface is rough (body I in Fig. 4.1), including high asperities and the other is flat (body II in Fig. 4.1). Upon the applied load, the rough surface compresses the smooth flat surface, with the highest asperities initially in contact. Asperities with lower heights come in contact as the load increases. For CN_x coatings deposited on flat *Si* substrates and steel disks the roughness is $< 2 \text{ nm}$, while CN_x -coated roller exhibit a roughness of $\sim 60 \text{ nm}$ resembling the topography of the polished rollers before the film growth. The real contact area depends on the applied load, the roughness of the surfaces, and the elasticity of the bodies. In this case, the effective elastic modulus of the mating surfaces is considered and given by:

$$E^* = \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{-1}, \quad (4.7)$$

where ν_1 and ν_2 are the Poisson ratios, and E_1 and E_2 are the elastic moduli of the two bodies. Also, the composite roughness of the two bodies is used:

$$\sigma^* = \sqrt{\sigma_1^2 + \sigma_2^2}, \quad (4.8)$$

where σ_1 and σ_2 are the roughnesses of the two bodies. Finally, the composite of the sum of asperity radii, is calculated by:

$$\beta^* = \frac{\beta_1 \beta_2}{\beta_1 + \beta_2}, \quad (4.9)$$

where β_1 and β_2 denote the asperity radii of the two surfaces.

Hence, the contact can be either elastic or plastic depending on the surface roughness and the elasticity of the counterparts. For an elastic contact, which applies also to CN_x -coated surfaces, the coefficient of friction, μ_α , as stated by Bhushan in reference¹⁰⁷ becomes:

$$\mu_\alpha \propto \frac{s_m}{E^* \gamma}, \quad (4.10)$$

where γ is a function which contains the roughness information of the mating surfaces as obtained from eq.(4.8) and (4.9).

Thus, for elastic contacts, surface roughness plays a predominant role. Moreover, adhesion between the counterparts, as well as elastic hysteresis (mainly in polymers and especially elastomers)³, should not be neglected. For plastic contacts, such as between two bearing steel surfaces, the friction coefficient depends mainly on the shear strength, as shown by eq.(4.4). For such contacts, an increase of the contact area occurs, under tangential and normal stresses, yielding ploughing effects, which influence friction greatly,¹⁰⁷ as follows from eq.(4.6).

An implication of the above considerations is that, a contact between two bodies is elastic, until a critical deformation depth is reached, above which the contact becomes plastic. This is described by Greenwood and Williamson¹⁰⁹ as the plasticity index,

³Elastic hysteresis is a deformation component in friction for elastic contacts. During sliding, the material is stressed and thereafter recovers, releasing the induced stress. During the stress of the material, elastic energy is dissipated. Most of this energy is released, but a small amount is lost as heat, as a result of elastic hysteresis losses.

$$\psi = \frac{E}{H} \sqrt{\frac{\sigma^*}{\beta^*}}. \quad (4.11)$$

It has been proposed that, for $\psi < 0.6$ the contact is essentially elastic and for $\psi > 1$, the contact is mainly plastic.

Similar expression as eq.(4.6) is valid for the friction forces at the surface of the coatings. However, the origin of friction is still under debate, since the experimental results obtained for different materials, do not always agree with the theory. Factors, such as the environment, the experimental equipment, sample surface oxidation or contamination, lubrication, the mechanical properties, as well as the surface termination of the materials, influence the extracted values of friction coefficient significantly. Furthermore, in the case of coatings, the properties of the interface and the coating material play also important role in tribological tests.⁹

According to the above analysis, the presence of an elastic CN_x coating in the contact between two rolling components can affect the friction forces. This can be seen in Fig. 4.2, where the friction coefficient of an uncoated and a coated roller is shown, as a function of the number of cycles, recorded during a rolling contact fatigue test, using a rolling speed of 1 *m/s* and a slide-to-roll ratio (SRR) of 2%. The uncoated roller shows a clear and fast run-in during the first 20 *kcycles* of the test, accompanied by an increase in friction coefficient to ~ 0.062 and a decrease to a constant value of ~ 0.045 thereafter. In the case of the coated roller, the run-in period appears to start after the first 15 *kcycles*. In this region, the friction coefficient shows a relatively low value of ~ 0.025 and an increase to ~ 0.050 is observed after 15 *kcycles*.

This indicates that severe run-in phenomena are avoided in the beginning of the test, and only after 15 *kcycles*, the CN_x coating starts to partially wear or delaminate and debris is created. It should be mentioned that, the friction coefficient of the uncoated roller reaches a steady-state after the first 50 *kcycles*, while the friction coefficient of the coated roller continuous to decrease until the end of the test. This implies that the surface of the uncoated roller was chemically stabilized after run-in, stabilizing also the friction coefficient, since all the structural changes occurred during the run-in. The continuous reduction of the friction coefficient of the coated roller suggests that chemical or structural changes on the coated surface take place during the entire test. However, Raman analysis of the rollers after the tests suggests that the remaining coating is essentially stable in terms of sp^2 and sp^3 bonding (cf. Paper V). Moreover, the roughness of the surface after the test

Figure 4.2: Friction coefficient for an uncoated (black) and a coated roller (red), tested in a rolling contact fatigue test, using a rolling speed of 1 m/s and a slide-to-roll ratio of 2%, as a function of the number of cycles.

is much higher (~ 180 nm) than the lubricant film thickness (less than 50 nm) in the elastohydrodynamic lubrication regime (cf. Paper V). Here, the dynamically induced roughness does not facilitate the formation of a lubricant film with an effective thickness for the counterparts lift-off during the test, promoting a CN_x -to-steel contact. Thus, the friction coefficient evolution is determined by the CN_x -to-steel contact and, as a result, by the different mechanical characteristics of the coating and the uncoated steel surface (cf. Paper V).

4.3 Wear

Abrasion has been identified as a responsible mechanism for the wear of CN_x in the past.³⁹ However, in other studies, the wear mechanism of CN_x was not determined.¹¹⁰ In all cases though, no delamination of the CN_x coatings was observed, however, the contact pressures used in those studies are much lower than the ones used in our studies.

Wear is defined as the removal of a material from a contact between two bodies, after sliding, rolling or machining. According to Archard,¹¹¹ the wear of a material can be quantified as

$$V = K' \frac{Ls}{H}, \quad (4.12)$$

where K' is the coefficient of wear, L is the normal load, and s is the sliding distance or the distance moved. In most cases, instead of wear, *wear rate* is used to describe the material removal from the contact and is symbolized with the letter K . It is usually given with the dimensions mm^3/Nm , which is the worn volume per unit of the mechanical energy input at the contact,⁹ expressed as

$$K = \frac{V}{Ls}. \quad (4.13)$$

In reality, the calculation of the wear rate is not always an easy task, because counter bodies with complex shapes and sizes, may be involved in the tribological tests, as in the case of this study where roller bearings are used. Hence, the exact calculation of the worn volume of the material, as well as the wear rate are difficult, since they strongly depend on the geometry of the bodies and the wear tracks.

Material wear can be due to different mechanisms, depending on the properties of the materials and the conditions of the testing (environment and experimental parameters). The basic wear mechanisms are schematically shown in Fig. 4.3 and can be classified as (a) adhesive, (b) abrasive, (c) fatigue, and (d) chemical wear.

Adhesive wear can occur when the asperities of the two counter bodies come in contact and the asperities of one body adhere strongly to the asperities of the other body. The relative tangential movement of the two bodies causes the detachment of the asperity from the softer body and thus, material is removed, as shown in Fig. 4.3(a). No adhesive wear was observed for CN_x coatings fabricated in my studies, after tribological tests.

Abrasive wear is characterized by ploughing phenomena in the contact.¹¹² Abrasion takes place when a harder material moves in tangential direction over a softer material or when hard particles are trapped in the contact between asperities (Fig. 4.3(b)). The hard asperities (or particles) press the asperities of the softer material under the applied load, causing plastic flow of the soft material around the hard one. When the tangential motion starts, ploughing of the soft material takes place, resulting in the creation of scratches and grinding marks on the soft surface. When the abrasive wear is caused by entrapped hard particles in the contact, then the mechanism is referred to as *third-body abrasion*.^{113,114} Both asperity deformation and third-body interactions can create mechanical intermixing, which can potentially change the chemical composition of the surface.¹¹⁵

Fatigue wear is the cyclic process of loading-unloading the surface at a high stress level that the material can withstand once, but not if the process is repeated

Figure 4.3: (a) Adhesive, (b) abrasive, (c) fatigue, and (d) chemical wear. Adopted from⁹

several times. This kind of wear is responsible for crack initiation and propagation at any stage of the cyclic test (Fig. 4.3(c)), especially in roller bearings, possibly due to dislocation pile-ups or material voids.⁹ The repeated fatigue test creates stress volumes at the surface and subsurface of the roller, leading to premature fatigue and failures, such as pitting, fretting and/or spalling. If the fatigue is too severe, the pits can exceed 1 mm in diameter and 50 to 100 μm in depth. The initiation of cracks at the subsurface can also lead to delamination of material, due to crack propagation in parallel to the surface.¹¹⁶

In the case of CN_x -coated rollers, fatigue and abrasive wear contribute to the wear mode of the coatings, during rolling contact fatigue tests, as shown in Fig. 4.4. Here, the CN_x -coated roller was tested at a rolling speed of 1 m/s in poly-alpha-olefin (PAO) oil, which lies in the elastohydrodynamic lubrication regime.¹¹⁷

The white circles indicate areas where the coating/interlayer system was detached during the test, removing possibly material from the steel substrate. Here, the hardness difference between interlayer and substrate promotes crack initiation and propagation in the substrate and eventually, fatigue of the substrate (cf. Paper V). The red circle and the red arrow show areas where substrate or coating debris are observed, implying abrasive wear. Finally, the white arrows show adherent coating fragments on the substrate after the test. It can be inferred that the uncovered areas consist only of the substrate material and that the coating delaminated due to failure in the coating-substrate adhesion.

Figure 4.4: Plan view SEM image obtained over the wear track of a roller coated with CN_x , tested in a rolling contact fatigue test, using a speed of 1 m/s with a slide-to-roll ratio of 2% in PAO.

Chemical wear is characterized by chemical reactions in the contact, influenced mainly by the environmental conditions but also the mechanical contact mechanisms present during testing (Fig. 4.3(d)). The combination of mechanical wear and chemical interactions results in removal of material and debris creation. The most common chemical type of wear is oxidative wear, during which, a thin layer of oxides is formed on the top of metal surfaces. This thin oxidized layer protects the metallic surface from direct metal-to-metal contact with the counterpart, thus, reducing the friction. During testing though, the oxide layers are removed and renewed, resulting in oxidative wear, which includes debris formation and chemical changes at the subsurface (Fig. 4.3(d)).¹¹⁸ Corrosive wear can also be classified as a type of chemical wear. Corrosion can expand from the surface to the subsurface of metallic bodies. It can be caused by humid environments, water, lubricants and anti-wear additives used in bearings, gears, and camshafts. Despite that corrosion

is a common wear mode in metallic contacts, there is no indication that corrosion occurs in CN_x coatings or CN_x -coated components.

The deposition of a coating on top of the substrate introduces an abrupt layer with different properties in the contact. The coating can protect the substrate from wear and improve the frictional properties of the surface, however, it also complicates the identification of the wear mechanisms and failure modes. In coatings, all the above wear mechanisms can possibly occur, depending on the conditions of the experiment. Moreover, other wear modes can be presented during a tribological test, since the stress levels can affect the coating-substrate interface. For instance, delamination of the coating may take place, if the coating-substrate adhesion is poor. This can lead to more severe conditions for wear of the substrate, since wear debris of different sizes is introduced in the contact, an effect that is also observed in the CN_x coatings of this study (cf. Paper II and Paper IV). Here, in rolling contact fatigue tests of CN_x -coated rollers including an adhesion interlayer consisting of W , wear debris from the interlayer are moving into the contact between the counterparts, after the wear of CN_x . This hard W -containing debris causes severe fatigue wear, resulting in micropitting after the tests. Abrasive wear or even corrosion can be caused, if coating debris interacts with the constituents of the substrate.¹¹⁹ Furthermore, if the coating toughness is not adequate or if the substrate is soft enough and a hard coating is deposited on the top of it, coating fracture may occur. This can also be seen in Fig. 4.4, where the coating is delaminated in areas that the coating-substrate adhesion fails. A reason can be that the substrate cannot withstand the load and is deformed under the coating, which exceeds a stress limit and as a result, crack nucleation and propagation takes place.¹²⁰

4.4 Tribology under lubrication

The seamless operation of roller bearings is ensured by the proper lubrication of the contacts between the rollers and the rings. The lubrication can be achieved mainly by natural oils, such as PAO with or without additives, commonly Zinc dialkyldithiophosphate (*ZDDP*), depending on the application and the contact pressures. For roller bearings used in our study, and for a contact pressure of 1.5 *GPa*, both PAO and *ZDDP* were used in rolling contact fatigue tests. In machine components i.e., roller bearings, the adequate lubrication at the contact is determined by the thickness of the formed lubricant film.¹⁷ According to the fluid film lubrication theory,

the lubricant film should be thick enough in order to satisfactorily separate the two surfaces being in contact. The thickness of the lubricant film depends on the lubrication regime, in which the component runs in. The lubrication regimes are described by the Stribeck curve for fluid lubrication. Figure 4.5 shows the Stribeck curve obtained from a rolling contact fatigue test of an uncoated (black squares) and a coated (red triangles) roller against three, also uncoated, inner rings (cf. Paper V). The Stribeck curve of the uncoated roller is identical to a theoretical Stribeck curve for any tribological test under fluid lubrication.^{7,117}

Figure 4.5: Stribeck curve obtained from an uncoated steel roller bearing, rolling against three uncoated steel inner rings, in a micropitting rig tribometer for a range of rolling speeds from 0.2 to 2 m/s.

Three lubrication regimes can be clearly identified; (a) the boundary lubrication (BL) regime, at low rolling speeds, (b) the mixed or elastohydrodynamic lubrication (EHDL) regime as the rolling speed increases, and (c) the hydrodynamic lubrication (HDL) regime at higher rolling speeds. Under BL conditions, μ presents its highest values, however, as the speed increases μ decreases and the rolling (or sliding) enters in the mixed or EHDL regime. In the BL regime, the lubricant film is not thick enough to separate the two surfaces, and in this regime, most failures occur. Moreover, this regime characterizes the run-in of the components, i.e., the deformation phenomena and possible debris creation in the first stages of the tribological test. In EHDL, there are areas in the contact where the thickness of the film is enough to lift-off the surfaces, but also other areas where the thickness of the lubricant film decreases dramatically and the steel-to-steel contact can not be avoided. This

regime is also responsible for severe wear or premature fatigue and failures of the components, such as micropitting, spalling or scuffing. With further increase of the speed, the rolling enters the HDL regime. Here, the thickness of the lubricant film is always large enough to lift-off the surfaces in contact and a full lubrication is achieved, yielding also the lowest μ values for specific pair of counterpart materials. In BL regime, where direct steel-to-steel contact takes place, the presence of a CN_x coating can result in better friction and wear performance, substituting the function of the inadequate, in this case, lubricant film.

According to our best knowledge, there is no published work with regards to CN_x -coated components, used in rolling applications. Commercial *DLC* coatings were synthesized for rolling applications by several coating manufacturers, providing low friction and high resistance to wear. When *DLC* coatings from different manufacturers were tested in rolling under similar conditions, it was found that the most common causes of failures were the lack of adhesion and the presence of defects in the lubricant.^{121–123} *DLC* coatings that performed best were dopant-free, hydrogenated amorphous carbon (*a-C:H*).¹²¹ It was also shown that the reproducibility of *DLC* film properties is an issue, since the quality of coatings produced even in the same batch differs.¹²¹ Moreover, the counterpart roughness affects the rolling operation of coated components with the same coating.¹²¹ The counterparts that have the lowest roughness yield better performance than the "as-grinded" counterparts.

The benefits of *DLC* coating in the boundary or elastohydrodynamic lubrication regimes were demonstrated by Bobzin *et al.*¹³ *DLC*-coated gear wheels, round blanks, and ball bearings outperformed other *CrN* coatings, providing the lowest μ in boundary, mixed or EHD lubrication.^{13,124} The authors attributed the better performance of the *DLC*-coated components to the thermal conductivity and specific heat capacity of *DLC* layers compared to steel, which act as thermal barrier, increasing the contact temperature and changing the shear resistance of the lubricant.

The properties of CN_x coatings differ from those of *DLC* coatings, since CN_x poses lower hardness than *DLC*, but a much higher elasticity as well as resistance to plastic deformation. This yields higher overall resiliency for CN_x , which leads to better wear performance of the material. In Paper V, it is demonstrated that the mechanical properties, and more specifically the elasticity of the coating, affects the evolution of friction coefficient and therefore, the entire rolling performance of the components.

It is concluded that the tribology of two mating surfaces with similar hardness, is affected by the elastic modulus of the materials, when a coating-to-steel contact occurs, i.e., in BL and EHDL. This has a high impact on the friction coefficient, where the run-in period is totally eliminated, as shown in Fig. 4.5 (red triangles), producing conditions of hydrodynamic lubrication, even at very low rolling speeds. Here, a CN_x -coated roller, tested in rolling contact fatigue test under similar condition with an uncoated roller, shows the absence of run-in period. This results in a scheme where BL, EHDL, and HL regimes are not separated, as in the case of uncoated rollers. This is in contrast to the prediction for *DLC*-coated components, where the Stribeck curve is just shifted towards lower friction coefficients in BL and EHDL, but with the run-in period still present at lower rolling speeds.¹²⁵ For the CN_x -coated components of our study, the real contact area changes and according to eq.(4.10), the composite elastic modulus of the mating materials highly influences the friction evolution (cf. Paper V). A less elastic contact is produced, due to the high hardness of the *W*-based interlayer, which increases the composite elastic modulus of the entire coating layer. This reduces the hysteresis losses of friction and increases the shear strength of the coated surface, yielding a lower friction coefficient (cf. Paper V).

4.5 Influential parameters for the tribology of carbon nitride coatings

4.5.1 Influence of environment

The tribological properties of CN_x (friction and wear) are strongly influenced by the environment, e.g. humidity and temperature. There is a large number of investigations focused on the tribology of *DLC* coatings under different environmental conditions.^{29,39,126–132} It was shown that environment probably plays the most dominant role in the tribological performance of *DLC* coatings. In the case of *a-C*, water vapors highly affect the friction of the coatings.¹²⁶ In vacuum environments, μ of *a-C* coatings are higher than μ obtained in ambient air, due to the lack of water vapors or hydrocarbon chains which facilitate the friction reduction.^{127–129} Similarly, in ambient air, but at very low relative humidities ($RH < 5\%$), *a-C* coatings show increased μ , due to the presence of non-passivated dangling bonds.^{29,130,133} In the presence of *H*, *a-C* coatings show a μ in the range of 0.01 - 0.05, while in *Ar* atmosphere, μ of

0.4 to 0.7 are recorded. This behavior was attributed to tribochemical interactions of hydrogen with the surface atoms of the coatings, creating hydrocarbons, which lower the adhesion between the counterparts.²⁹ The tribological properties of CN_x (friction and wear) are strongly influenced by the environment, e.g. humidity and temperature. In tribological tests performed with CN_x -coated parts against Si_3N_4 balls at a Hertzian contact pressure of 200 MPa, the test atmosphere and humidity played a detrimental role for the friction and wear performance of the coatings. Specifically, CN_x yields the lowest μ of ~ 0.01 , when tested in a N_2 atmosphere and a humidity of $\sim 35\%$.¹³⁴ Moreover, with increasing humidity to $\sim 70\%$ during the supply of the contact with N_2 gas, μ increases rapidly to a value of 0.39. An increasing trend of μ with a steadily increment of humidity is also observed. The water absorption in CN_x coatings was also investigated by Broitman *et al.* in reference,⁷⁴ concluding that $a-CN_x$ coatings can absorb an accountable amount of water molecules, which could affect their tribological properties. In tribological tests performed against SiC balls in water lubrication, CN_x coatings show a decreased μ of ~ 0.05 and generally low wear rates of 10^{-8} - 10^{-9} mm³/Nm.¹³⁵ Additionally, mechanical and tribochemical wear are identified as the main wear modes in water lubrication, which depend on the sliding velocity and normal load.¹³⁵ The highest values of 0.2 - 0.4 are recorded when the samples were tested in air, Ar or O₂ environment. In CO₂ and vacuum environments, the CN_x coatings perform satisfyingly, exhibiting μ of 0.05 - 0.14. Kato *et al.* concluded that the wear rate of the coatings depends on the environment and the wear mode is mainly abrasion due to low-cycle fatigue of the coatings, which generates wear particles with sizes in the nanometer range.¹³⁴

The coatings synthesized in this study are tested in ambient (cf. Paper III and VI) and in oil lubrication conditions (cf. Paper IV and V), with or without additives. In dry conditions, CN_x coatings, tested under reciprocal sliding against a diamond pin (cf. Paper III), showed mainly abrasive wear and the surface of the coating appeared polished after the test, as shown in Fig. 4.6(a). No delamination events of the coating were observed along the wear track. Moreover, in order to evaluate the friction properties of the coating, μ is measured at three different contact pressures, as shown in Fig. 4.6(b).

The evolution of the friction coefficient suggests that, the CN_x coatings show run-in periods in the first 50 m of sliding distance, however, only the coatings tested at the higher contact pressures of 3.3 and 3.9 GPa reach a steady-state after run-in.

Figure 4.6: (a) Plan view SEM micrograph obtained over the wear track of the CN_x coating, tested at a contact pressure of 3.9 GPa and (b) friction coefficient of the CN_x coating, recorded at three different contact pressures of 2.5, 3.3, and 3.9 GPa , as a function of the sliding distance.

The coating tested at 2.5 GPa may not have completed the run-in, since it does not reach a steady-state, implying that chemical changes at the surface occur during the entire test and recorded through the evolution of μ . The increasing friction coefficient of the coating tested at a contact pressure of 2.5 GPa indicates that continuous tribochemically induced changes (i.e., debris through bond breaking and new bond creation) take place on the surface during the entire test. In this case, it can be inferred that the applied load is too low to cause severe tribochemical changes at the coating surface, which is not chemically stabilized during the experiment. Hence, a constant friction behavior and a stable tribological operation are not reached using 2.5 GPa contact pressure. In contrast, at the higher contact pressures of 3.3 and 3.9 GPa , any tribochemical changes at the surfaces have been completed during the run-in periods, stabilizing the friction coefficients at constant values.

$a-C$ and $a-CN_x$ coatings are also tested in oil lubrication with and without additives in rolling contact fatigue tests (Fig. 4.7). Their friction coefficients show notable differences. When tested in PAO oil, $a-CN_x$ coating exhibits lower friction coefficient ($\mu \sim 0.025$) than $a-C$ ($\mu \sim 0.034$), while in the presence of ZDDP, $a-C$ performs better, showing $\mu = 0.023$, in contrast to CN_x , which yields μ of ~ 0.040 . The above behavior is an advantage for the CN_x over the $a-C$ coating. Here, better rolling performance is achieved by CN_x , without the need for the use of ZDDP additive in the lubricant. The difference can be attributed to the different surface termination of the coatings, which is assumed to yield different surface energy.^{136,137}

Figure 4.7: Friction coefficient of CN_x and $a-C$ coated-roller bearings tested in a rolling contact fatigue test, using a rolling speed of 2 m/s and a slide-to-roll ratio of 2% in (a) PAO oil and (b) PAO oil with 1 at% of anti-wear additive ZDDP.

4.5.2 Influence of contact pressure and load

An influence of the normal load on μ has also been reported for CN_x coatings by several studies.^{104, 135, 138} However, the results are not consistent. He *et al.* reported that μ increases with increasing normal load from 2 - 20 N,¹³⁸ while Charitidis *et al.* showed that it remains almost constant at ~ 0.15 with increasing load from 0.02 to 5 mN.¹⁰⁴ These trends were confirmed by Zhou *et al.* and Wang *et al.*, who showed that wear rate and μ of CN_x do not exhibit a specific dependency on normal load.^{135, 139} It is worth mentioning the fact that, the range of normal loads used in the studies above is different, resulting possibly in a different Hertzian contact pressure of the counterparts, which could lead to differences in the friction performance of the coatings. In order to investigate the dependency of the CN_x coatings on the normal load and contact pressure, I conduct tribological experiments keeping the contact pressure constant at the macro- and microscale. Figure 4.8(a) and (b) shows the friction coefficient and the wear rate of a CN_x coating, deposited using HiPIMS, as a function of contact pressure, at the macro- and microscale, respectively.

Thus, normal loads of 1, 3, and 5 N are used in the macroscale tests, corresponding to contact pressures of 2.5, 3.3, and 3.9 GPa, respectively. For the experiments conducted at the microscale, normal loads of 40, 120, and 200 μ N are used, corresponding also to a contact pressure of 2.5, 3.3, and 3.9 GPa. As shown in Fig. 4.8, the contact pressure affects the friction and wear of CN_x coatings. Here, a CN_x

Figure 4.8: Friction coefficient (squares, left axis) and wear rate (circles, right axis) as a function of the contact pressure for a CN_x coating, tested in a reciprocal sliding scratch test in ambient at the (a) microscale against a diamond tip and (b) macroscale against a diamond pin.

coating, deposited in HiPIMS mode, using $V_b = 200\text{ V}$, yields a hardness of 10.5 GPa and a reduced elastic modulus of 120 GPa . The friction coefficient shows a decreasing trend with increasing contact pressure at both macro- and microscale. In the microscale experiments, the coating exhibits a $\mu \sim 0.07$ at a contact pressure of 2.5 GPa , which decreases to ~ 0.063 at the contact pressures of 3.3 and 3.9 GPa . In the macroscale tests, the coating exhibits $\mu = 0.11$ at a contact pressure of 2.5 GPa , which decreases to $\mu < 0.06$ at 3.3 and 3.9 GPa . This decreasing trend of μ can be correlated to the more harsh conditions of the experiment at higher contact pressures, which create higher amount of debris, acting as third-body lubrication. On the other hand, wear rate shows an increasing trend with increasing contact pressure, at both micro- and macroscale, which is also a consequence of the more severe conditions at higher loads. At the microscale, the wear rate increases from $\sim 10 \times 10^{-9}\text{ mm}^3/\text{m}$ at a contact pressure of 2.5 GPa up to $\sim 210 \times 10^{-9}\text{ mm}^3/\text{m}$ at a contact pressure of 3.9 GPa . In the experiments conducted at the macroscale, the wear rate increases from $\sim 100 \times 10^{-9}\text{ mm}^3/\text{m}$ at 2.5 GPa to $\sim 500 \times 10^{-9}\text{ mm}^3/\text{m}$ at 3.9 GPa . The above trends show that the contact pressure is an influential factor for the tribological properties of CN_x coatings. Despite the increased wear rates with increasing contact pressures, the CN_x layer shows reduced friction at high contact pressures, which can be beneficial for applications employing high loads and contact pressures. Moreover, the tribological properties of CN_x show a dependency on the normal load, which is consistent at both micro- and macroscale. This allows us to identify and correlate the friction and wear mechanisms of the coating present at both scales.

4.5.3 Tribolayers and transfer tribofilms

In this study, CN_x coated rollers, tested in rolling contact fatigue tests in PAO and in all lubrication regimes, show that the transfer of graphitic-like tribolayers at the counter bodies is not necessary to obtain low friction coefficient and high wear resistance. This is confirmed by EDX measurements obtained at the surface of the ring counterparts after the tests, which show essentially similar C content in the wear track of the ring as the C content outside the tracks (cf. Paper V). Moreover, the CN_x coating at the surface of the rollers presents a stable chemical state, as Raman spectra confirm, which are shown in Fig. 4.9 (cf. Paper V).

Figure 4.9: Raman spectra obtained inside and outside the wear track of a CN_x -coated roller, after a rolling contact fatigue test in PAO, using a rolling speed of 1 m/s. The inset shows the friction coefficient recorded during the test as a function of the number of cycles.

The Raman spectra, obtained inside and outside the wear tracks of the CN_x -coated rollers, suggest that no graphitic-like structures are formed on the surface of the rollers. Moreover, the peak present at a wavenumber of $\sim 2200\text{ cm}^{-1}$, which is related to $C-N$ bonds, remains essential unaltered. Thus, the spectra indicate that the CN_x coating remains essentially stable, in terms of chemistry and bonding, during the entire test. Comparing the peak area ratio, I_D/I_G , inside and outside the wear track, a slight change is observed where, the ratio increases inside the track. This implies that any change in the chemical state of the coating, induced during

the rolling contact fatigue test, takes place slowly. This is also supported by the continuous decrease of μ , as shown in the inset of Fig. 4.9, which implies that the surface of the roller is not stabilized and continuous changes occur during the entire test. Nevertheless, these chemical changes cannot be associated with the formation of more graphitic-like structures, since the linewidths and intensities of both D and G bands remain essentially unaltered.

4.5.4 Influence of coating thickness

A dependency for $a\text{-CN}_x$ coatings with a thickness up to $1\text{ }\mu\text{m}$ is observed. $a\text{-CN}_x$ layers deposited with a thickness of $\sim 400\text{ nm}$ show the lowest μ of ~ 0.025 with high repeatability (Fig. 4.10). A relatively low μ of ~ 0.036 is also obtained for CN_x coatings grown with thicknesses $\geq 800\text{ nm}$. The wear rate of the CN_x also show lower values, when the coating thickness is $200 < t < 600\text{ nm}$. The later trend follows the results obtained by Klaffke *et al.* for N -free DLC .⁵⁰ According to the authors, the wear rate of the DLC coatings decreases for thinner layers, while thicker coatings fail earlier during the tribological tests.

Figure 4.10: Friction coefficient (green circles) and wear rate (red circles) as a function of the CN_x coating thickness after 720 *kcycles* of rolling contact fatigue tests in a micropitting rig tribometer.

Thus, a beneficial combination of low μ (0.025) and low wear rate ($1.1 \times 10^{-9} \text{ mm}^3/\text{Nm}$) is obtained for the CN_x coatings synthesized with a thickness of $\sim 400\text{ nm}$. Since, CN_x coatings with a thickness of $\sim 400\text{ nm}$ yield the lowest friction and wear, posing as the best candidates for use in roller bearings, I extensively used them for the tribological tests in my studies.

4.6 Tribological tests

4.6.1 Reciprocal scratch testing

In order to study the friction and wear mechanisms of CN_x , micro- or nanoscratch tests are conducted using a Hysitron Triboindenter TI 950. Using micro- and nanoscratch tests in combination with a tip of conical shape and high apex radius ($5\text{ }\mu\text{m}$), the surface layers of the CN_x are isolated for tribological testing and substrate influences are eliminated. In this way, the friction and wear mechanisms stemming only from the CN_x surface can be identified. During a micro- or nanoscratch test, the probe is moved laterally on the surface of a sample and the normal force, $\vec{F}_N$, on the Z-axis of the transducer can be controlled independently. The configuration of the experiment, with the applied forces and displacements can be seen in Fig. 4.11. The normal displacement (i.e., the penetration depth of the probe) and the lateral force are recorded simultaneously. The signals of lateral force and normal displacement are quantified in order to obtain information about the coefficient of friction, the critical loads for failures of thin films or the resistance to scratch.

Figure 4.11: Schematic illustration of a scratch test, conducted at the nano- or microscale, showing the tip moving in a lateral direction over the sample surface.

The experiments are conducted at $T = 25\text{ }^{\circ}\text{C}$ and a RH of $\sim 30 - 40\%$ to accord with the conditions of the RCF tests performed at the macroscale (cf. Sec. 4.6.2).

4.6.2 Rolling contact fatigue (RCF) testing

The CN_x coatings are intended for use in bearing components and thus an appropriate rig configuration is employed for best simulating the real conditions in terms of lubrication (poly-alpha-olefin, PAO), temperature ($T = 90^\circ$), and humidity ($< 10\%$) of a roller bearing operation. For the RCF tests included in this study, a micro-pitting rig tribometer (MPR, PCS Instruments) is used. The configuration of the mounting system of the equipment is shown in Fig. 4.12. The environmental conditions, as well as the applied loads and speeds of the tests, simulate application with generally harsh conditions.

Figure 4.12: The roller and rings mounting configuration in a micropitting rig tribometer.

The rolling performance and RCF tests of coated and uncoated rollers are conducted under lubricated conditions, using a poly-alpha-olefin (PAO), with or without anti-wear additive, with a kinematic viscosity of $4.6 \times 10^{-5} \text{ m}^2/\text{s}$ (46 cSt). The roller is mounted in the middle of three bearing inner rings (steel also graded AISI52100), each with a diameter of 54.45 mm and a width of 19 mm. A load pressure of 243 N, corresponding to a Hertzian pressure of 1.5 GPa, is applied during the rolling test at a normal direction, at the middle of the upper ring. This contact pressure is common for automotive applications. The rolling speed can vary between 0.2 and 3.5 m/s and the friction coefficient is recorded during the RCF tests. This allows for testing of the rollers in different lubrication regimes, starting from boundary to hydrodynamic lubrication.

Coating characterization methods

’Οὐδὲν τοῖς θαρροῦσιν ἀνάλωτον’.

— Μέγας Ἀλέξανδρος (356-323 π.Χ.)

”Nothing is impossible for him who tries”.

— Alexander the Great (356-323 B.C.)

5.1 Structural characterization

5.1.1 Scanning Electron Microscopy (SEM)

The relatively inexpensive as well as convenient operation of SEM, makes it a useful tool for fast structural evaluation. Typically, electrons are thermionically emitted from a tungsten, LaB_6 -cathode filament or in many modern microscopes from Schottky field-emission source and transferred to the microscope column through an anode, where they are focused by a sequence of condenser lenses into a beam.¹⁴⁰ Energies for the electron beams are between 1 - 50 keV . For the imaging of the samples of this thesis, electron beams with energies of 5, 10, and 20 keV are used.

The electron beam impinges the sample surface and the electrons interact with the sample at a probing depth of $\sim 1 \mu m$. As a result of this interaction, several particles are produced, such as secondary electrons, backscattered electrons and Auger electrons, as illustrated in Fig. 5.1. A common imaging mode relies on the detection of the secondary electrons, which increases the topographical resolution of the micrographs. In this study, the SEM imaging was performed using backscattered or secondary electrons depending on the surface characteristics of the sample. A

Figure 5.1: Illustration of the interactions on a sample surface after the e^- beam impinges on the surface.¹⁴⁰

combination of both modes was also used, in order to increase the topographical resolution as well as the detection of spatial distribution of elements.

The preparation of the samples for SEM includes fracture cross-sections of the film if the substrate material allows it. Cross-sectional SEM is a fast way to visualize the changes in the morphology and microstructure of the CN_x films on Si substrates. Moreover, the technique offers a practical method to measure the thickness of the coatings and determine their deposition rates.

Figure 3.4 shows SEM cross-sections of CN_x films deposited on $Si(001)$ substrates by different magnetron sputtering techniques and at different bias voltage. From the cross-sections in Fig. 3.4 differences in the morphology are observed through a contrast difference between denser and underdense areas (different porosity of the films).

SEM is proven also useful for the observation of the coating-substrate interface. Figure 5.2(a) shows a SEM cross-section from the interface between a CN_x coating and a W -based adhesion interlayer, obtained using the detection of backscattered electrons. The W -based adhesion interlayer consists of three areas; (a) a W layer with a thickness of $\sim 15\text{ nm}$ on top of the Si substrate, (b) a W_xN_y layer of a thickness of $\sim 70\text{ nm}$, and (c) a multilayer W_xN_y/C_zN_y . The latter is grown as a stack of two different layers; W_xN_y and C_zN_y , due to the rotation of the substrate table, which passes consecutively in front of the W and C targets during the process. Despite that the sequence of the stacked layers is easily discriminated, other morphological characteristics, such as intermixing or diffusion zones between the layers are not easily observable with SEM, limiting its potential. Figures 5.2(b)-(c) show SEM images obtained over a Rockwell C indent, performed on a CN_x -

coated flat steel disk, with the above adhesion interlayer, deposited prior to the CN_x deposition. Overall, the coating is still adherent on the substrate in the vicinity of the area of the indent, showing good adhesion. Only limited delamination events of the CN_x coating are presented at the periphery of the indent.

Figure 5.2: (a) SEM micrograph of the adhesion interlayer, deposited on top of a *Si* substrate, (b) SEM micrograph of a Rockwell C indent, and (c) a part of the indent, performed on a steel disk, coated with CN_x , for the investigation of the CN_x coating adhesion on the substrate.

SEM can also be utilized to investigate the surface morphology before the tribological tests and the wear modes after the tests, as can be seen in Fig. 5.3(a)-(b). Here, detection of both backscattered and secondary electrons was used. Figure 5.3(a)-(b) show plan views of areas inside the wear tracks of an uncoated and a coated roller, respectively, after a rolling contact fatigue test (cf. Paper V). The surface of the uncoated roller appears smoother than that of the coated roller, including grinding marks as shown in Fig. 5.3(a) (green arrows). These can be observed darker in contrast than the surface.

In the case of the coated roller, no grinding marks are observed (Fig. 5.3(b)). Here, the differences in the contrast, indicate the presence of uncovered substrate areas. The darker areas show the steel substrate, where CN_x coating detachment took place during the tribological test. The brighter areas imply coating presence (white arrows), thus in these places, the coating is still adherent on the substrate. In some areas, deeper holes are observed, as shown in Fig. 5.3(b) (blue circle), which look like scuffing marks.¹⁰⁶ Figures 5.3(c) and (d) show plan views of the wear tracks

Figure 5.3: Plan views of areas in the wear tracks of an (a) uncoated and (b) a CN_x -coated roller, after a rolling MPR tribological test. Plan views of areas in the wear tracks of uncoated ring counterparts tested against the above (c) uncoated and (d) CN_x -coated roller. Green arrows indicate grinding marks, white arrows show CN_x coating fragments, while the red arrows indicate pits or holes. The blue circle shows an event of scuffing.

of ring counterparts when tested against the above uncoated and coated rollers, respectively. In both cases, contrast differences reveal the presence of grinding marks (green arrows in Figures 5.3(c) and 5.3(d)).

5.1.2 Transmission Electron Microscopy (TEM)

TEM is a highly sophisticated and expensive, but important and powerful instrument for visualization of atomic arrangements in materials. The evolution of the transmission electron microscope, along with Louis de Broglie's theory for the wave characteristics of electron¹⁴¹ contributed decisively to the development of the electron microscopy. The robustness of the TEM technique relies on the fact that it offers direct information regarding the nanostructure of the materials, thus it is widely used in thin film technology. TEM can be operated in different modes, such as high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) or selected area electron diffraction (SAED), each providing complimentary information for better understanding of the structure of a

material.

TEM instrumentation and operation from the material science perspective are thoroughly treated in references.^{142, 143} In a very simplified way, TEM consists of three main parts: a) an electron gun, b) the column including magnetic lenses and apertures, and c) a CCD camera. Nowadays, in more sophisticated TEM instruments, electrons are emitted by field emission guns (FEGs), operating in the range of 60 - 300 *keV*, depending on the operation mode, but also on the instrument's limitations. The electrons are transmitted through the illumination system of the microscope, which consists of a sequence of magnetic condenser lenses and apertures. A focused electron beam exits this sequence of lenses and illuminates the sample, which is steadily placed in the sample holder (Fig. 5.4). The electron beam is transmitted through the sample, whereas some electrons are elastically or inelastically scattered upon their interaction with the sample atomic potentials. Thus, electrons with different wave functions exit the sample.

Figure 5.4: Illustration of imaging and diffraction mode of a TEM.

A sequence of an objective and a projector lens is placed under the sample holder responsible for the convergence of the appropriate scattered electron beams. A pattern of the electron densities is formed and projected at the back focal plane of the objective lens. The electron beam is magnified before it strikes the CCD camera. In the latter part of the electron beam route, imaging or diffraction mode can be

selected. For the observation of a certain specimen area of interest, the selected area diffraction (SAD) aperture is inserted at the image plane (Fig. 5.5), and a selected area electron diffraction (SAED) pattern is acquired. In the case of CN_x materials, SAED is useful technique to identify short-range-order phases in the coatings, such as fullerene-like features or SRO graphitic-like planes. Crystalline materials exhibit generally dots in a distinguishable pattern, while polycrystalline materials present rings often with spots. Amorphous materials, such as CN_x , present also rings, although broader, and without the spots observed in polycrystalline materials. For the imaging of crystalline materials, a proper alignment of the sample is required in the microscope, which is achieved by tilting and shifting the TEM specimen, in order to find the orientation of interest. In order to obtain high-resolution for the TEM imaging of the α - CN_x coatings of our study, a proper alignment cannot be achieved using the amorphous areas of the CN_x , since the identification of phases is not possible using diffraction mode. In this case, a first alignment is achieved by projecting the $\langle 001 \rangle$ orientation of the Si substrate, followed by an alignment of the Fourier transformation obtained from the amorphous areas of the CN_x coating.

Figure 5.5: Illustration of the SAED configuration in the imaging system of a TEM.

CN_x thin films were extensively examined using HRTEM and SAED modes in the past and three main structural configurations were identified; amorphous

carbon nitride ($a\text{-CN}_x$), fullerene-like carbon nitride ($FL\text{-CN}_x$), and graphitic-like carbon nitride ($g\text{-CN}_x$).^{144–147} The observations of CN_x films with TEM should be performed with caution. Cross-sectional TEM is a useful imaging mode and allows for observations of SRO in the coatings, although in some cases, SRO may be present, but not visible in the image. For CN_x films, such configurations like $FL\text{-CN}_x$ nanostructures, required skilled microscopist to be detected and correctly interpreted. Typically, the discrimination between $a\text{-CN}_x$ and $FL\text{-CN}_x$ is made by both imaging mode and SAED patterns. While $a\text{-CN}_x$ exhibits two distinct diffraction rings at $\sim 1.2 \text{ \AA}$ and $\sim 2 \text{ \AA}$ correlated to amorphous microstructure, the $FL\text{-CN}_x$ allotrope presents an additional diffraction ring at $\sim 3.5 \text{ \AA}$, which closely corresponds to the one observed in graphitic diffraction patterns at $\sim 3 \text{ \AA}$, indicating short-range order (SRO).¹⁴⁵ Fig. 5.6 shows a TEM micrograph with the corresponding SAED pattern of the CN_x film deposited with MFMS at $V_b = 120 \text{ V}$. Both the image and the SAED pattern reveal the amorphous character of the film (cf. Paper I).

Figure 5.6: HRTEM micrograph and SAED pattern (inset) of the CN_x film deposited at $V_b = 120 \text{ V}$ with MFMS. Reproduced with permission from Paper I.¹

For CN_x coatings grown by MFMS at a $V_b \geq 100 \text{ V}$, a third ring at a distance of $\sim 3.5 \text{ \AA}$ may be present, but difficult to observe, since it may be located within the limits of the central disk of the incident beam in the diffraction pattern. The microstructure of the CN_x layer demonstrated in Fig. 5.6 may show characteristics of SRO, where fragments of two or three bended planes form arrays smaller than 1.5 nm . Thus, despite that HRTEM and SAED are very powerful tools for the determination of SRO in CN_x coatings, a complete assessment of the film microstructure

should also include complementary techniques like x-ray photoelectron spectroscopy, since the spectra obtained from bonding configurations of C and N show prominent features and trends (cf. Paper I).

Scanning transmission electron microscopy (STEM) is another technique, which uses a convergent electron beam, rastered across the sample, instead of a nearly parallel electron beam in the case of TEM. In the case of STEM, the incident electron beam is focused at a much larger convergence angle, into a focal point on the sample. The beam then is rastered across the sample and the signal is collected as a function of the beam position.

Several detectors can be employed in STEM mode, depending on the electrons that need to be collected. Except for electrons in the incident electron beam, electrons are scattered while exiting the sample, over angles of $\theta > 10 - 50 \text{ mrad}$, and by using an angular detector, dark-field STEM images can be acquired. However, the Coulomb interactions of the electrons with the positive potential of the atom nucleus can be strong and electrons can also be scattered to larger angles, with $\theta > 50 \text{ mrad}$. These electrons are detected by a high-angle annular dark field (HAADF) detector (Fig. 5.7).

Figure 5.7: Illustration of the convergent beam operating in scanning transmission electron microscopy mode, passing through the sample, together with an array of bright-field and, annular and high-angle annular dark-field detectors, employed for the detection of elastic and inelastic scattered electron beams, respectively.

HAADF detector collects almost exclusively the inelastically scattered electrons,

hence the produced image contrast depends strongly on the atomic number of the sample constituents, and it is commonly referred to as *Z-contrast*. Heavier atoms scatter electrons with larger probability and sample areas with higher concentration of heavier elements appear brighter in images. The presence of *C* and *N* in our coatings required the use of HAADF detector. This STEM detection setup was used in combination with energy dispersive x-ray spectroscopy and electron-energy loss spectroscopy for accurate chemical and bonding characterization. Another factor that affects *Z-contrast* is the thickness of the TEM specimen, thus a direct correlation between contrast and both local mass and thickness is obtained. This makes STEM technique useful in quantitative chemical composition analysis of samples. If a field emission gun with probe sizes $< 0.3 \text{ nm}$ is used as a TEM source, an atomic resolution *Z-contrast* can be achieved.

5.1.3 Focused Ion Beam (FIB)

Focused ion beam has been used recently for the preparation of transmission electron microscopy (TEM) samples, especially when there is need for selection of a special area of the sample or when asymmetrical substrate shapes are analyzed. Sample pieces (of the order of a few μm) of material can be cut with FIB and the analysis of specific features is then possible. In thin film technology, FIB is used for the preparation of electron transparent plan views and cross-sections with thicknesses of less than 50 nm . FIB instruments resemble SEM, but instead of electrons, *Ga* ions are used for the imaging and milling of the sample. Two FIB configurations are available; a) the single-beam FIB where one source is used to produce the *Ga* ions for imaging and milling and b) the dual-beam FIB in which there are two guns, usually placed with an angle of $52^\circ - 54^\circ$, where one is an electron gun (usually FEG) and the other a *Ga* ion gun. A dual FIB configuration is presented in Fig. 5.8.

The CN_x thin films are sensitive to ion irradiation¹⁴⁸ and are treated carefully at the stage of TEM sample preparation in my investigations. Small angle cleavage technique (SACT) and conventional sample polishing followed by ion beam milling have been used to prepare TEM specimens. For the scope of this study however, the most appropriate technique was the focused ion beam (FIB). This is because steel substrates, used in applications such as ball bearings, cannot be cleaved, moreover the thickness and shape of the steel substrates may vary, prohibiting essentially the use of SACT and conventional polishing. The controlled milling process of FIB during TEM lamella preparation allows for precise selection of the area of interest.

Figure 5.8: Illustration of a dual FIB configuration, with a FIB and an SEM gun.

For instance, parts of wear tracks of specific interest can be milled and analyzed. A thin *Pt* layer is commonly deposited prior to the milling in order to protect the film from the *Ga* beam. The lift-out technique is used for the TEM cross-section preparation of thin films.¹⁴⁹ Ion energies of 30 *kV* and currents from 5 *nA* to 500 *pA* are used for the milling of the sample, although the case of CN_x films is an exception. Apart from *Ga* implantation, which poses problems for all kind of materials, it was reported that CN_x microstructure, in film form, is sensitive to high energy ion milling and features, exhibiting short-range order, may become amorphized. Thus, the identification of possible SRO graphitic or fullerene-like phases, in CN_x films deposited on steel substrates, becomes complicated, if not impossible. However, the thickness of the amorphized layers due to *Ga* milling can be reduced with decreasing *Ga* ion energy. The energy of the electron beam in TEM in the order of 300 *kV*, not only improves the image contrast, but also helps to enhance the imaging of the unaffected film areas. The selection of this electron beam energy enhances further the thickness ratio of the original unaffected area of the sample to the amorphized external layer due to FIB preparation.¹⁴⁸ In order to improve this thickness ratio, specific steps are followed in the preparation of the TEM lamella, described in the next paragraph.

The TEM cross-section of samples are prepared using the lift-out technique and initial milling ion energy of 30 *keV*, although for the final polishing of the TEM lamella, the *Ga* ion energy is reduced to 5 *keV*. Thus, the amorphized layer thickness is reduced to ~ 5 *nm* and the amount of *Ga* implantation decreases significantly.

The *Ga* implantation is further reduced using lower ion currents at the final stages of the polishing. During the milling with 30 *keV* ion energy, currents of 2 *nA*, 1 *nA*, 500 *pA*, 200 *pA*, 100 *pA* and 20 *pA* are sequentially used for the preparation of the lamella, in order to decrease the possibility for *Ga* implantation. At the final stage of the TEM lamella polishing, a current of 100 *pA* is used, which is the lowest possible value.

Figure 5.9: TEM cross-sections of a CN_x thin film, prepared using a *Ga* ion energy of (a) 30 *keV* and (b) 5 *keV*. The ellipses indicate areas of the specimen, where *Ga* implantation took place.

Fig. 5.9 shows a comparison between a CN_x film prepared by FIB using 30 *keV* and a CN_x film prepared using 5 *keV* *Ga* ion energy. In the case where 30 *keV* is chosen, the density of implanted *Ga* areas is higher compared to the case of 5 *keV*

Ga ions. In the latter case, the implanted *Ga* appears to affect areas with a diameter less than 2 nm, while such areas are much larger in the case of 30 keV. Especially, at thin parts of the film, such as the edges, higher amount of Ga implantation is observed and an interpretation of film structure is not possible.

FIB is also utilized for the preparation of TEM lamellae, taken from the wear tracks of the rollers and rings (coated and uncoated), following the rolling contact fatigue tests. The mounting of the roller or the ring piece in the FIB chamber requires careful positioning of the component on the sample holder.

Figure 5.10: Cross-section TEM lamella of a CN_x coating deposited on a steel substrate pretreated with Al ions. The lamella is prepared using the FIB lift-out technique and a *Ga* ion energy of 30 keV. A protective *Pt* layer and a CN_x coating are deposited on top of the steel substrate.

Special attention is paid to the sample height, since such components are larger than conventional samples used for milling. The cylindrical shape of both rollers and rings complicates also the procedure. In order to properly align the electron and *Ga* guns, a milling area at the apex of the component is always chosen. After the milling of the desired area, the lamella is transferred and glued on a *Cu* grid, as shown in Fig. 5.10, using the lift-out technique.¹⁴⁹ In Fig. 5.10, the TEM lamella comprises the steel substrate, which is initially pretreated using Al^+ that form an interlayer with a thickness of ~ 10 nm, and a CN_x layer with a thickness of ~ 1 μm , deposited on top of the pretreated steel (cf. Paper II). Pretreatments using ions are useful for the cleaning of steel substrates from residual contaminants and for adhesion improvements. The use of metal ions for substrate pretreatments relies on the fact that singly or doubly ionized species can effectively remove surface oxides and contaminants providing activated surface for enhanced CN_x -steel adhesion.¹⁵⁰ In the case Al^+ ions are used, large intermixing zones and interlayer formation are observed (Fig. 5.12). However, these cannot be observed using SEM techniques, due

to their small sizes (ranging between 5 and 10 nm), which led to the preparation of specimens using FIB for TEM imaging (cf. Paper II).

FIB is also used to construct TEM lamellae from wear tracks with sizes much smaller than those obtained from macroscale experiments. Following a nano- or microscratch on a CN_x coatings, the dimensions of the wear track are only 5 μm in length and 1 μm in width, but more importantly the depth of the track is not more than few nm . This makes identification of the scratch difficult in SEM or FIB mode. At these scales, more detailed FIB milling in the wear tracks is performed, as in the procedure described in Paper VI.

5.1.4 Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive x-ray spectroscopy is used in order to obtain information about the chemical composition of the solid. EDX relies on the ionization of an atom by an impinging electron, if an incident electron possesses higher energy than the energy required to eject an electron from the atom. As a result, an electron can be emitted, leaving a vacant state, which is then filled by an electron transition from a higher energy-state, accompanied by the emission of a photon. If an electron is ejected from one of the inner atom shells (K, L, or M), then the energy of the emitted photon is in the x-ray range of the electromagnetic spectrum and is characteristic of each element, allowing for quantitative analysis of elemental composition.

Drawbacks of the technique is the high depth of information acquisition, which can extend 1 μm below surface and the low reliability regarding the detection of light elements ($Z < 11$). This is due to absorption of x-rays in the sample, resulting in x-ray fluorescence, and overlapping characteristic peaks, at the low energy range for lighter elements. Hence, the detection of the constituents of our samples, C ($Z = 6$) and N ($Z = 7$), with EDX is not highly reliable, especially for the quantitative analysis of very small areas of the order or 10 - 20 nm in STEM mode (cf. Fig. 5(b) in Paper III). However, it can be utilized in order to detect heavier elements, for instance metals used for depositions in our investigations, such as W , Zr , Cr , Ti , and Al (cf. Paper II). For the detection of C and N , we use other analytical techniques, like electron-energy loss spectroscopy, which is discussed in detail in Sec. 5.1.5.

EDX mapping is another useful technique, in which the electron beam is rastered across a selected sample area. The photons are collected in one or more energy windows that are characteristic of the elements of interest and a colored coded

image is recorded.

For example, EDX mapping in SEM was used to identify the surface changes in Rockwell C indents on CN_x -coated steel substrates, pretreated with different metal ions, and to evaluate the coating-substrate adhesion in each case (cf. Paper II), as shown in Fig. 5.11(a).

Figure 5.11: SEM micrographs and maps of Fe , C , and Al (purple) or W (red), performed on the Rockwell C indent of CN_x -coated steel substrate, pretreated with (a) Al^+ and (b) W^+ . The insets at the right top corner of (a) and (b) show the combined EDX maps.

The combined maps of Al - and W -pretreated samples are shown in the insets at the upper right corners of Fig. 5.11(a) and (b), respectively. The insets show also elemental maps of Fe , C , and W (red).

EDX in STEM mode is used to acquire maps of the interface between CN_x coatings and metal ion pretreated steel substrates, and evaluate the degree of intermixing between different layers (cf. Paper II). Figure 5.12 shows a cross-section STEM/EDX map of a CN_x -coated steel substrate pretreated with Al^+ . Figures 5.12(a) and (b) show STEM micrographs of the CN_x/Al /steel interface region and Fig. 5.12(c)-(e) show magnified elemental EDX maps of the interface region.

EDX contributed to identify intermixing zones between CN_x and Al layer and Al

Figure 5.12: (a) STEM and (b) colored STEM cross-sections of the CN_x /Al/steel interface region of the Al pretreated sample. Figures 5.12(c)-(e) are EDX maps of (c) C (red), (d) Al (green), and (e) Fe (blue).

layer and steel substrate. The CN_x /Al and Al/steel interfaces exhibit intermixing zones with a thickness of ~ 20 nm and ~ 25 nm, respectively.

5.1.5 Electron-Energy Loss Spectroscopy (EELS)

With the use of electron-energy loss spectroscopy technique, the energy loss of the inelastically scattered electrons, transmitting the solid sample, is measured. The detection of the electrons is managed by a spectrometer, usually mounted underneath the projection plane. The spectrometer includes a magnetic prism, which spreads the electrons, depending on the energy that they lose during the scattering in the sample. The electrons that lose higher amount of energy are deflected to high angles. The electrons are collected at a CCD camera, which records their energy ranges in an EELS spectrum. The spectrometer allows to collect EELS spectra for different energy ranges.

The recorded EELS spectrum contains information about the chemical composition and the structure of the sample. EELS spectra are divided into three regions; (a) the zero-loss, (b) low-loss, and (c) core-loss region. Each region contains different information regarding the sample structure and properties. Zero-loss (ZL) peak arises due to electrons that do not interact or interact only elastically with the sam-

ple and do not lose energy. It appears at 0 eV and is the most intense signal in the EELS spectrum. The low-loss region includes losses in the range of energies between the zero-loss peak and ~ 100 eV energy. Plasmon peaks appear in this region and their intensity can give information about the thickness of the sample. Finally, the core-loss peaks are well-defined peaks present in the high-loss region of the EELS spectrum above the background. A core-loss peak corresponds to the energy lost by an electron after leaving the sample. The core-loss peaks are located at energy losses that are characteristic for each element and are useful for quantitative analysis of the material. The ionization process is described in section 5.1.4.

EELS is usually used with STEM, where the beam is rastered over the sample and EELS maps of certain sample areas can be recorded. Among the advantages of EELS technique, is its suitability for the detection of low atomic number elements, ($Z < 11$), since maximum sensitivity can be achieved for low energy losses in the spectrometer. Thus, EELS can be used for the detection of *C* and *N* in CN_x films. Figure 5.13(a) shows normalized EELS spectra acquired from the W/steel interface, at positions A, B, and C for the investigation of *C* and *N* presence at the interface and Fig. 5.13(b) shows a cross-section STEM micrograph, consisting of a *Pt* and a *W* layer on top of the steel roller, after a rolling contact fatigue test, where the CN_x coating was worn off and (cf. Paper IV).

Figure 5.13: (a) EELS spectra acquired from the *W*/steel interface at positions A, B, and C of the interface and (b) HRSTEM micrograph of the *W*/steel substrate interface of an initially CN_x -coated roller, pretreated with W^+ , after MPR test.

The sample originates from a CN_x -coated roller, tested in a RCF test, including a *W* pretreated steel substrate. All spectra show a doublet with two distinct features

in the energy loss range of 280 and 310 eV . The peak located at ~ 289 eV energy loss is attributed to a C K-edge and the peak located at ~ 302 eV , corresponds possibly to losses due to the presence of $C = N$ bonds (cf. Paper IV).¹⁵¹ The C K-edge of spectrum A is more prominent than that of spectra B and C, indicating that the amount of C at the W /steel interface is higher than at the Pt / W interface or in the W layer.

EELS technique is also utilized for the investigation of nanoscratches (cf. Paper VI). The nanoscratches have a width of ~ 1 μm and a length of ~ 4 μm . The difficulty, however, lies in the fact that the normal displacement (the penetration depth of the probe in the coating), monitored by the tribointenter after the test, is in the range of few nm . This means that the nanoscratch induces changes at the surface (cf. Paper VI), although their extent is too small to be detected by other spectroscopy techniques. Raman and x-ray photoelectron spectroscopy fail to measure any differences between C - C and C - N bonding configurations, inside and outside the worn areas, due to the large spot size in each technique. On the other hand, using high-resolution EELS, accurate information about the bonding configurations and composition can be extracted from a very small portion of the surface, using EELS mapping.

5.1.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface analytical characterization technique, extensively used in the past for the determination of the bonding type in a - C and a - CN_x films.^{70, 75, 76, 79, 144, 152–155} The technique is based on the photoelectric effect, i.e., emission of electrons from a solid surface upon irradiation with photons of sufficiently high energy. The probing depth of XPS is 3 - 10 nm and the technique provides useful information regarding the N bonding in the C matrix, extracted from $C1s$ and $N1s$ core level spectra.

For XPS measurements, the samples are placed in an ultra-high vacuum chamber and irradiated with photons with energies in the X-rays range. Commonly, Mg $K_\alpha = 1253.6$ eV or Al $K_\alpha = 1486.7$ eV sources are used. Due to the photoelectric effect, electrons are emitted and, if they are generated near the surface, they can escape into the vacuum chamber.

The binding energy, E_B , of the electron is then deduced using the Einstein's formula:

$$E_B = h\nu - \phi_{spectr} - KE, \quad (5.1)$$

where $h\nu$ is the photon energy, E_B is the binding energy of the core electron, ϕ_{spectr} is the work function of the spectrometer, and KE is the measured kinetic energy.

XPS is particularly useful to obtain information about concentration of C , N , and O in CN_x films, as well as give insights into the bonding configuration. For the deconvolution of peak components in XPS spectra of CN_x , there is a large number of publications, where authors assign all peaks to sp^2 or sp^3 bonding states, ignoring that N incorporation can induce either sp^2 , sp^3 or sp bonds, altering significantly the bonding configuration of the C matrix. Different components can contribute to the $C1s$ core level spectra, due to the presence of $C-N$ bonds. The peak model of $C1s$ and $N1s$ core level spectra of CN_x thin films, used extensively in this work, is presented in Fig. 5.14. $C1s$ core level spectra of CN_x films can be satisfactorily fitted with 5 components: $C1$ at ~ 284.7 eV and $C2$ at ~ 286 eV, also observed in N -free DLC films, are assigned to sp^2 - and sp^3 -hybridized states of C . The component at the binding energy of ~ 287.3 eV is due to $C-N$ bonds ($C3$), although no discrimination between sp^2 or sp^3 bonding states of N can be done. A resolution into sp^2 or sp^3 configuration cannot be carried out, since $C3$ component can arise due to an intermixing of sp^2 and sp^3 $C-N$ bonds. $C1$ and $C2$ components may also be influenced by N presence, since N can also form sp^2 and sp^3 bonding configurations with C .

Figure 5.14: XPS peak model for the deconvolution of $C1s$ and $N1s$ core level spectra of the film deposited by MFMS at $V_b = 120$ V.

$N1s$ core level spectra show three contributions; $N1$ at $\sim 398.6 \pm 0.2$ eV, attributed to N bonded in 2-fold coordination at the periphery of graphene sheets in the C network (the pyridine-like structure), $N2$ at $\sim 400.6 \pm 0.1$ eV, attributed

to sp^2 -hybridized N bonded to three C atoms in a graphitic network and $N3$ at $\sim 402.7 \pm 0.1$ eV attributed to N - O bond. The differences between the $N1s$ core level spectra and the $N1$ and $N2$ peak components are small. $N1s$ core level spectra reveal small differences between films deposited with different V_b . N presents a preference in bonding involving three C atoms, rather than in pyridine-like configuration, while $N2/N1$ peak area ratios do not show significant dependency on bias voltage. Thus, the low growth temperatures used in the present case, is the main factor that promotes the formation of amorphous CN_x films (cf. Paper I).

5.2 Mechanical characterization

5.2.1 Profilometry

CN_x coatings can develop high residual stress during the depositions, compromising coating adhesion on steel substrates. This can lead to a negative impact on the tribological performance of coated components. Moreover, the use of high bias voltages during depositions induce differences in the structural characteristics of the CN_x coatings, as shown in Fig. 3.4 (cf. Paper I). Thus, it is important to measure the residual stress of the coatings in order to correlate them to the induced stresses. The residual stresses of a - CN_x coatings can be measured easily and fast, using profilometry, which is a scanning technique, utilized for thickness or roughness measurements of thin films. During a profile acquisition, a stylus traces the topography of a film-substrate step, recording the thickness of the film. The roughness of the films can also be measured by the stylus as surface variations, recorded electromechanically.

The possibilities for residual stress measurements in amorphous films are limited, due to the lack of crystalline phase. This is also valid for fullerene-like films. Profilometry can be utilized for residual stress measurements of amorphous films. The radius of curvature of a coated substrate is measured and the residual stress is calculated by the modified Stoney's equation for thin films:

$$\sigma_{CN_x} = \frac{Y_{Si} d_{Si}^2}{6R(1 - \nu_{Si}) d_{CN_x}}, \quad (5.2)$$

where σ_{CN_x} is the residual stress of the CN_x coating, d_{Si} is the thickness of the substrate, ν_{Si} is the Poisson's ratio of the Si substrate, Y_{Si} is the Young's modulus of the Si substrate ($d_{Si} = 525 \mu m$, $\nu_{Si} = 0.36$ and $Y_{sub} = 169 GPa^{156}$), d_{CN_x} is the

thickness of the film and R is the radius of curvature of the sample as measured with the stylus profilometer. The radius of curvature of an uncoated substrate is used as reference and subtracted from the measured film stress. Fig. 5.15 shows the residual stress induced by CN_x coatings deposited on $Si(001)$ substrates by MFMS, HiPIMS, and DCMS, as a function of bias voltage.

Figure 5.15: Residual compressive stress of CN_x films deposited by MFMS (triangles), HiPIMS (circles), and DCMS (squares) as a function of bias voltage.

A strong dependency of residual stress on bias voltage is observed for CN_x coatings grown by all magnetron sputtering techniques. Moreover, stress at each technique is influenced to a different extent by V_b . The increasing compressive stresses with increasing bias are primarily due to the suppression of the columnar growth through reduction in the formation of voids (cf. Paper I). In the case of the CN_x coatings, the forward sputtering model accounts for the evolution of residual stress, which states that the main reason for increased stresses is the increased ion energies (cf. Paper I).

5.2.2 Nanoindentation

Hardness and Elastic Modulus

Nanoindentation is a method to measure the mechanical response of thin films and coatings. A tip of known geometry penetrates the surface of the film and the load versus the displacement in the material are recorded. In this way, the elastic and plastic response of the material is measured. In the case of coatings, the depth of penetration of the tip should be taken into consideration. If the tip penetrates deep

inside the film, the substrate may influence the measurement. Thus, Berkovich tips are chosen for shallow indents, due to their geometry, which gives higher contact areas with the film. The penetration depth is recommended to be $< 10\%$ of the film thickness in order to eliminate substrate effects. The very high elasticity of CN_x coatings may be a limiting factor, since the penetration depth can easily exceed the film thickness and influences from the substrate appear. Thus, the results are treated carefully.

Here, for nanoindentation measurements, a Triboindenter TI 950 from Hysitron is used, employing a three plate capacitive transducer, that is used both as the actuator and sensor of the instrument. The force is applied electrostatically, while the displacement is simultaneously measured by the change in capacitance. To apply a force, a large DC bias (up to 600 V) is applied to the bottom plate of the capacitor. This creates an electrostatic attraction between the centre and the bottom plate, which pulls the centre plate down. The force can be calculated from the magnitude of the applied voltage. The maximum normal force available from the standard transducer is approximately 10 mN. The load resolution of the Triboindenter and the force sensitivity of the transducer are both < 1 nN, resulting in a noise level of < 30 nN. Also, the displacement sensitivity is < 0.02 nm, with a noise level of < 0.2 nm.

An illustration of the cross-section of a hypothetical indent in a film is shown in Fig. 5.16(a). Here, a Berkovich indenter is used and a vertical load, P , is applied. The elastic and plastic deformation at the maximum load (h_t) and the part of the elastic deformation that recovers (h_e) are also shown. The radius of the circular impression, α , the displacement of the surface at the perimeter of the contact, h_s , the final depth of the residual hardness impression, h_f , and the residual depth after unloading, h_c , are also denoted.

Load versus displacement (L-D) curves are obtained from nanoindentation and can be seen in Fig. 5.16(b). According to the nanoindentation curves (shape and penetration depth), there are no substrate effects in the measurements, hence the hardness is calculated as:

$$H = \frac{P}{A}, \quad (5.3)$$

where P is the contact pressure and A the contact area of the tip with the surface of the film. The contact area should be calculated in order to determine the effective real contact of the tip with the surface. This calibration is done before

Figure 5.16: (a) Illustration of a cross-section of an indent geometry in a film before nanoindentation and the imprint of the contact area after the nanoindentation (adopted from reference¹⁵⁷). (b) Upper graph: an analysis of a load - displacement curve of the CN_x film deposited by MFMS at $V_b = 100$ V and (b) lower graph: load - displacement curves of CN_x film deposited by MFMS, HiPIMS, and DCMS deposited at $V_b = 120$ V, as obtained after nanoindentation.

the nanoindentation measurements and is called *tip area function calibration*. The approach of Oliver and Pharr¹⁵⁷ for nanoindentation with Berkovich tip on fused silica is used in order to determine the tip area function by fitting the relationship:

$$A(h_c) = 24.5h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \dots + C_8h_c^{1/128}, \quad (5.4)$$

where C_1 through C_8 are constants.

An example of an L-D curve of an $a-CN_x$ coating deposited by MFMS is shown in Fig. 5.16(b). It is also possible to extract the reduced elastic modulus of thin films, given the contact area, which is:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}, \quad (5.5)$$

where E_r is the reduced elastic modulus and S is the contact stiffness. The elastic recovery, ER, can be calculated as:

$$ER = \frac{h_t - h_c}{h_t} 100\%. \quad (5.6)$$

Adhesive force and work of adhesion

The high sensitivity of the Triboindenter TI 950 to load and penetration depth changes allows for very shallow indents (in the range of few nm) on the sample surface. This function of the instrument is useful in the situation that the adhesive force between a diamond tip and the sample surface is measured. The reason is that, in order to measure the adhesive forces, a meniscus (an adhesive neck between the tip and the steel surface) needs to be formed upon the tip-surface interaction, during the approach of the tip on the sample surface.^{158,159} At high penetration depths, the tip indents the sample surface and does not allow for adhesive force measurements.

Figure 5.17: Illustration of a normal force-normal displacement curve recorded after a nanoindent from an adhesive force experiment. Adopted from.¹⁶⁰

Here, a controlled penetration depth of 1 nm is used. Figure 5.17 shows a schematic illustration of an L-D curve, while performing a hypothetical experiment for extracting the adhesive force of the surface. The initial force sensed by the

transducer is zero until the tip reaches point #1, which corresponds to a point above the sample surface, although here the tip starts to interact with the surface. At point #2, the tip contacts the surface of the sample. Here, the tip senses the resistant and adhesive forces from the sample surface and the applied force from the transducer. As the tip penetrates the surface, point #3 is reached, where the sum of the forces (the stored elastic energy and the surface energy) is zero. From point #3 up to a maximum penetration at point #4, further viscoelastic deformation takes place. After maximum penetration, the tip starts to retract and at point #5 detaches from the surface, interrupting the contact. The pull-off force at point #5 is maximum and corresponds to the adhesive force of the surface.

There are several approaches for the determination of the work of adhesion, W_{adh} , of a surface. The two most widely used theories are the Derjaguin-Miller-Toporov (DMT) and the Johnson-Kendall-Roberts (JKR) model.¹⁶¹

Figure 5.18: Normal force versus normal displacement curves obtained from nanoindents performed on steel surfaces, pretreated using metal ions from a HiPIMS source.

The DMT model applies for material systems with low adhesion and small tip radii, while JKR model is applicable for systems with high adhesion and large tip radii. Considering that the apex radius of the tip used in this study is $5 \mu m$, the most suitable theory for the determination of W_{adh} of the low adhesive metallic surfaces is the DMT approach.¹⁶⁰ According to DMT definitions, W_{adh} is calculated using eq. (5.7):

$$F_{adh} = 2\pi W_{adh} R, \quad (5.7)$$

where F_{adh} is the adhesive force and R is the radius of the tip.¹⁶⁰

Figure 5.18 shows the unloading parts of such nanoindentation L-D curves, recorded for pretreated steel substrate surfaces, using different metal ions from HiPIMS source (cf. Paper II). During the nanoindent, the diamond tip approaches the sample surface, with a rate of $\sim 1 \text{ nm/s}$, starting from a distance of 50 nm above the sample surface. Then, it contacts the surface, indents the sample up to 1 nm depth, and retracts. The adhesive force is extracted graphically from the L-D curves, as the minimum normal force at negative values.^{160,161}

Papers

Ῥὰ ἀφανῆ τοῖς φανεροῖς τεκμαίρου’.

— Σόλων Ἀθηναῖος

“For the obscured, draw conclusions from the obvious”.

— Solon

Included papers

Paper I: **Bakoglidis K.D.**, Schmidt S., Garbrecht M., Ivanov G.I., Jensen J., Greczynski G., and Hultman L. Low-temperature growth of low friction wear-resistant amorphous carbon nitride thin films by mid-frequency, high power impulse, and direct current magnetron sputtering. Reproduced from *Journal of Vacuum Science and Technology A* **33**, 05E112 (2015); doi: 10.1116/1.4923275, with the permission of American Vacuum Society.

Paper II: **Bakoglidis K.D.**, Schmidt S., Greczynski G., and Hultman L. Improved adhesion of carbon nitride coatings on steel substrates using metal HiPIMS pretreatments. Reproduced from *Surface and Coatings Technology* 302 (2016) 454-462; doi: 10.1016/j.surfcoat.2016.06.048

Paper III: **Bakoglidis K.D.**, Glenat H., Greczynski G., Schmidt S., Grillo S., Hultman L., and Broitman E. Comparative study of macro- and microtribological properties of carbon nitride thin films deposited by HiPIMS. Submitted.

Paper IV: **Bakoglidis K.D.**, Nedelcu I., Schmidt S., Greczynski G., Ehret P., and Hultman L. Rolling contact fatigue of bearing components coated with carbon nitride thin films. Reproduced from *Tribology International* 98 (2016) 100-107; doi: 10.1016/j.triboint.2016.02.017

Paper V: **Bakoglidis K.D.**, Nedelcu I., Ivanov I.G., Meeuwenoord R., Schmidt S., Janzén E., Ehret P., Greczynski G., and Hultman L. Rolling performance of carbon nitride-coated bearing components in different lubrication regimes. Submitted.

Paper VI: **Bakoglidis K.D.**, Palisaitis J., dos Santos R.B., Rivelino R., Persson P., Gueorguiev G.K., and Hultman L. Self-healing in carbon nitride evidenced as negative wear rate and superlubric behavior. Submitted.

Papers

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Conclusions

"Do you not think that there are things which you cannot understand, and yet which are, that some people see things that others cannot? But there are things old and new which must not be contemplated by men's eyes, because they know, or think they know, some things which other men have told them. Ah, it is the fault of our science that it wants to explain all, and if it explain not, then it says there is nothing to explain".

— Bram Stoker, *Dracula* (1897)

The subject of the investigations included in this PhD thesis is the development of CN_x coatings suitable for use in roller bearings. Roller bearings are used in applications employing high loads and speeds, and lubrication. Thus, it is important to understand the operation of CN_x under such conditions. In order to apply the coatings to real bearings, two important requirements need to be met; (a) very good coating-substrate adhesion and (b) inherent low-friction and wear-resistance of the coatings.

The coating-substrate adhesion was achieved by developing a pretreatment technique for the specific bearing steel substrates. The CN_x -steel adhesion was improved by using metal targets in HiPIMS mode and a high-energy ion bombardment of the substrate surface. I found that a combination of factors affects the coating-substrate adhesion. For the CN_x -bearing steel system, the best result was achieved by forming a W -based interlayer, yielding the highest adhesion among several other tested metallic interlayers i.e., Cr , Al , Ti , and Zr . Here, a W interlayer of ~ 15 nm showed high affinity to Fe and C , which increased the interfacial bonding between CN_x and steel and was the material of choice for adhesion interlayers for all CN_x

depositions in this study.

The basic criteria for the choice of the most suitable CN_x coatings are as high hardness and elasticity as possible, low residual stress, as well as, high density and homogeneity. At a temperature of $150^\circ C$, which is lower than the bearing steel tempering temperature, CN_x coatings were deposited successfully, using physical vapor deposition methods, such as direct current (DCMS), mid-frequency (MFMS), and high power impulse magnetron sputtering (HiPIMS). Since the temperature constitutes a limiting factor, here the variation of the substrate bias voltage is proven to be an effective way to fabricate coatings with different properties. It plays a prominent role to the way that the ion flux and energy is delivered to the substrate and it is demonstrated that coatings with higher homogeneity and density can be produced at higher bias voltages. These CN_x coatings have higher hardness and improved wear performance, but they also develop high compressive stress.

CN_x coatings produced by HiPIMS show lower stress but also lower hardness, compared to layers grown by DCMS and MFMS. Lower compressive stress assists for achieving higher coating-substrate adhesion, however their lower hardness compromises their wear resistance. On the other hand, films grown by MFMS, are the hardest of my investigations, producing also one of the hardest $a-CN_x$ coating reported in the literature with a hardness of 26 GPa . However, the stress of these films essentially forbid their use in such applications, endanger early coating delamination in rolling contact fatigue tests. CN_x coatings synthesized by DCMS are more suitable for use in bearing applications requiring high wear resistance. Here, the problem of CN_x -steel adhesion is solved by introducing a W -based interlayer, following our previous investigations and by choosing a substrate bias voltage of 60 V . Using this value, I produced CN_x layers with a combination of adequate hardness ($11 \pm 1\text{ GPa}$) and tolerant compressive stress ($\sim 0.8\text{ GPa}$), showing a wear resistance of $\sim 12 \times 10^{-4}\text{ mm}^3/Nm$ in microscratching.

The CN_x film produced using DCMS at 60 V bias voltage was my choice for coating roller bearings and testing their rolling performance. The experiments, including different lubrication regimes, showed that CN_x -coated rollers perform better than uncoated steel rollers in all lubrication regimes, protecting effectively the steel surface from severe wear and fatigue. The presence of CN_x withstands run-in effects, whereas CN_x acts as solid lubricant, during inadequate or unsuccessful oil lubrication (under boundary lubrication conditions). Moreover, CN_x -coated components decreased the friction coefficient to ~ 0.025 under elastohydrodynamic and

hydrodynamic lubrication, compared to friction coefficients obtained from uncoated rollers. In this lubrication regimes, the coatings presented wear rates of $< 1 \times 10^{-9} \text{ mm}^3/\text{Nm}$. In this case, I found that the presence of both CN_x coating and W -based interlayer plays important role on the rolling performance of the bearings and influences the friction evolution and the presented wear modes. Here, the presence of the hard W -based interlayer prevents initiation and propagation of cracks due to high cycle fatigue processing and the composite elastic modulus of the coating (CN_x and W layers) determines the evolution and values of friction coefficient. According to my results, a high amount of CN_x coating fragments remain on the steel surface of the rollers after the tests, indicating that the coating-substrate adhesion at those areas is good. Here, a direct steel-to-steel contact is avoided and the surface of the roller is protected during the entire test. Thus, the proper combination of CN_x coating and W -based interlayer leads to improved tribological properties of the bearings.

Many applications using roller bearings, i.e., gearboxes and wheels, wear most when the rolling speeds are very low (in the beginning of the operation). Under this condition bearings roll within the boundary lubrication regime. The enhanced obtained performance of the coated rollers shows that they can be applied in bearings as solid lubricants, assisting the operation of components in the beginning of the rolling, when the rolling speeds are low or at full speeds. In both cases boundary lubrication can be avoided by the deposition of CN_x . These improved performance of CN_x -coated components is capable to increase the lifetime of the roller bearings, reducing maintenance cost and machinery.

As mentioned in the beginning of this section, one of the most important factors is the coating-substrate adhesion. There is much accumulated knowledge regarding the growth of CN_x and many methods for customization of these coatings, indicating that the proper ingredients (CN_x) for tribological applications exist. My results suggest that the adhesion interlayers, not only affect how well the CN_x coating is adherent on the substrate, but also the entire tribology of the contact between counterparts. I believe that future research on the field of protective coatings on bearings could focus on improving adhesion further. This can potentially lead to depositions of thicker CN_x coatings and fewer delamination events during rolling, exploiting their friction and wear performance even better.

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...Praise the Sun

Low-friction and wear-resistant carbon nitride coatings for bearing components grown by magnetron sputtering

By

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Errata

- Paper III is accepted for publication in *Wear* as of the 15th of November 2016.
- p.8, lines 4-5 (in Abstract): Delete the: "...and hydrodynamic (HDL)...".
- p.53: change figure 4.5 as below:

- p.55, line 8: change the word "hydrodynamic" to "elastohydrodynamic" and the abbreviation "HDL" to "EHDL".
- We have amended Paper V (Results and Discussion) such that all mentions of the "hydrodynamic lubrication regime" are replaced by the "elastohydrodynamic lubrication regime".