Pulsed-DC sputtered TIC/DLC nanocomposite coatings
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Chapter 1
INTRODUCTION

1.1 Introduction

A large variety of structural and functional properties can be optimized separately for the bulk material and the surface by applying an appropriate coating. Therefore, coated parts usually show a superior performance compared to uncoated work pieces. In the second half of the 20th century, surface coatings have emerged as an important industrial branch. In the beginning, coatings have been mainly deposited electrochemically. However, coatings exceeding the hardness of hard chrome (HV about 1000) like transition metal nitrides and carbides cannot be deposited from solution.\footnote{In the late 1960s, TiC coatings deposited by CVD (chemical vapor deposition) on hard metal cutting tools have been introduced to the market. The beginning of the eighties saw the first PVD (physical vapor deposition) hard coatings appearing on the market.} The ever-expanding need for superior coatings to withstand various operating conditions, to have low friction, to last longer is the driving force for further development of new hard coatings. One of the areas of applications for new hard coatings is the use of coated tools for dry machining. Moreover, new coatings have to show improved wear resistance to extend their lifetime. Coatings with increased hardness are expected to fulfill this demand. High load bearing and rolling applications do not necessarily need extremely hard surfaces, but toughness and low friction are key requirements, which may be matched by nanocomposites or multilayers with lubricating solid phases. A composite coating usually consists of two or more phases combined either as different layers (multilayer) or as a homogeneous isotropic mixture of different phases (multiphase). The aim of a multicomponent coating is to combine desired properties from different components as well as the creation of new properties generated by the combination of suitable materials.

In many tribological applications adequate liquids are used as lubricants. However, in some applications, such as food processing, chemical pumps, biological applications, space technology, hard disks, etc. the use of liquid lubricants is not possible. In these cases self-lubricating coatings such as diamond-like-carbon (DLC) coatings are used. A tribological system is usually described by the external parameters such as contact load,
apparent macroscopic contact area, friction partners, surface textures, lubricant used and the environmental parameters. The coefficient of friction (CoF) and the wear are the main parameters used to describe the performance of a tribological system. Whereas from the CoF the energy consumption of the movement of the two counter bodies can be obtained, the wear describes the lifetime of the materials and the amount of wear products produced.

Amorphous DLC consists of strongly cross-linked carbon atoms with mainly sp² (graphitic-like) and sp³ (diamond-like) bonds. In the sp³ configurations, as in diamond, a carbon atom’s four valence electrons are each assigned to a tetrahedrally directed sp³ orbital, which makes a strong σ bond to an adjacent atom. In the three-fold coordinated sp² configuration as in graphite, three of the four valence electrons enter trigonally directed sp² orbitals, which form σ bonds in a plane. The fourth electron of the sp² atom lies in a π orbital, which lies normal to the σ bonding plane. This π orbital forms a weaker π bond with a π orbital on one or more neighboring atoms. The DLC can be roughly divided in amorphous carbon (a-C) and amorphous hydrocarbon (a-C:H). Basically, a-C:H is an amorphous network composed of carbon and hydrogen. The coating structure is metastable as all methods for deposition are non-equilibrium processes based on thermal quenching of energetic ions impinging on a cold surface. The properties of these coatings depend strongly on the sp³/ sp² ratio, which in turn, depend on the deposition process and its parameters. The most prominent advantages of DLC coatings are their high hardness, their low CoF and their low wear rates. Under tribological conditions, usually the softer of the two materials will be worn. In the case of DLC, a different behavior is often observed. Wear products from the DLC coatings, which have a graphitic nature, are transferred to the partner surface forming a so-called transfer film on the partner surface. The DLC then slides on this transfer film that protects the softer partner surface from wear and the harder DLC coated surface wears off at an extremely low rate. The transfer film is believed to be formed by a friction-induced phase transformation of surface layer of DLC, and is mainly composed of amorphous graphite-like carbon that isolates the counterface material. As a result, sliding occurs mainly between the transfer film and the DLC coating, yielding low friction. The transfer film formation is affected by the environment, contact pressure and sliding velocity. DLC has been studied extensively as a tribological coating as described in the review articles by Grill, Donnet, Gangopadhyay and Erdemir and Donnet.

Because of their increasing popularity and diverse potential applications, DLC coatings have gone through numerous modifications in their microstructure and chemistry during the past decade. Using advanced deposition techniques, researchers have developed nanocomposite or alloyed DLC coatings to provide much improved physical, mechanical and tribological properties. In particular, doping DLC with certain
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metals, metalloids and gaseous species (such as Ti, B, S, Si, Cr, F, W and N) has become popular for various applications. Introducing nanocrystalline ceramic particles into an amorphous matrix generate a high density of interphase interfaces that assist in crack deflection and termination of crack growth. DLC based nanocomposites incorporating nanosized particles, like carbides, nitrides or diamond reinforcements are expected to further improve the structural and functional properties of pure amorphous DLC materials. The addition of metallic elements such as Ti, W or non-metallic elements such as N and Si are observed to decrease the compressive stresses of the coatings, improving their adhesion to the substrate. The tribological behavior of DLC coating can additionally be influenced by alloying DLC with different elements.

Various deposition techniques such as chemical vapor deposition, DC reactive magnetron sputtering, cathodic arc deposition and pulsed laser deposition have been employed for the synthesis of TiC/a-C or TiC/a-C:H coatings. The deposition method to grow these coatings and their properties are described in the review articles by Robertson and Grill. Pulsed DC (p-DC) magnetron sputtering has become a major technique for deposition of advanced coatings during the last decade. It was originally developed for the reactive deposition of insulating coatings to suppress arc events at the target and to stabilize the process. In addition, it has been observed that pulsing magnetrons influences the plasma density and electron temperatures in the plasma, which often result in improved coating microstructure and properties. The crucial parameters determining the intensity of ion impingement are the energy distribution of the impinging ions and the flux ratio of impinging ions. It has been observed that pulsing magnetrons in the mid frequency regime (up to 350 kHz) leads to a much extended energy distribution of impinging ions and higher ion current density towards the substrate. As a result, dense and well-structured coatings can be grown in pulsed mode. A thorough understanding of the mechanism of plasma controlling and microstructure manipulation with pulsed DC magnetron sputtering is still under development and will definitely promote its strength in the production of advanced coatings.

Recently, it has been reported that the columnar boundaries (CBs) of DLC nanocomposite coatings are a potential source of failure under loading and contact sliding. The CBs are harmful as initiation site of cracks and preferential cracking path, attributed to the fact that the homogeneity of nanocomposite is interrupted by the CBs that are enriched in carbon and voids. The columnar boundaries originate at the deep groove networks formed on the growing interfaces. Also, self-assembling has been realized and utilized in the growth of thin coatings with nanoscale ordered structures, like superlattices or multilayers in metal-metal and metal-carbon systems. Despite the experimental accomplishments, understanding of the physical mechanism and the driving
force is still rather limited, partially due to the fact that a high spatial resolution examination of the structures were not performed. Also, despite the importance and extensive study on amorphous and nanocomposite carbon systems, several aspects regarding the deformation and fracture behavior at the nanoscale, and the underpinning physical mechanisms are not yet understood. Recently several molecular dynamics (MD) simulations have been reported on the deformation and fracture mechanism of DLC and DLC-based nanocomposite at atomic scale. However, direct experimental validations of the theoretical models are not available. High resolution transmission electron microscopy experiences a practical difficulty in the examination of DLC or DLC based nanocomposites due to the amorphous nature of DLC. In crystalline materials, HRTEM makes use of the fact that defects create local discontinuity in the otherwise perfect periodicity of the crystalline structure. Thus, it is the presence of a lattice, which acts as an intrinsic reference, that allows the detailed characterization of various defects like line defects (dislocations), and planar defects (homophase and heterophase interfaces), and to investigate their evolution during or after deformation. However, in pure DLC or a homogeneous DLC-based nanocomposite the amorphousness and homogenous state at various length scales make tracing of defects, and evolution of nanostructure, during and after deformation quite elusive. However, by controlling the distribution of nanocrystallites (NCs), so that they form nanoscale multilayers, the NCs can serve as perfect markers for distinguishing various deformation patterns.

![Figure 1.1 Schematic showing growth effects including diffusion, shadowing, reemission that may affect surface morphology during coating growth. The incident particle flux may arrive at the surface with a wide angular distribution depending on the deposition methods and parameters.](image)

The growth dynamics of the coatings determines the microstructure (columnar/column-free) of the coatings. Many growth effects are operating during the growth of a coating and contribute to the surface roughness evolution. A summary of common growth effects is illustrated in Figure 1.1. First, there is always random noise that exists naturally during the deposition process. The origin of randomness is the non-uniform nature of incoming flux i.e. atoms reach the surface at random positions, with random time intervals between them. This randomness is generally referred as noise. These random fluctuations, which are inherent in the deposition process, can create growth front roughness. Noise competes with surface smoothing processes, such as surface diffusion,
to form a rough morphology if the experiment is performed at either a sufficiently low temperature and/or at a high growth rate. In addition, growth front roughness can also be enhanced by growth processes such as geometrical shadowing. Shadowing is a result of deposition by a nonnormal incident flux. In many commonly employed deposition techniques such as sputter deposition, atoms do not always approach the surface in parallel; very often they arrive at the surface with a distribution of trajectories. The non-normal incident fluxes can lead to a shadowing effect during growth, as some of the incident atoms will be captured at high points on a corrugated surface at the expense of lower valleys on the surface, resulting in a dramatic enhancement of the growth front roughness. Another important effect to consider is the value of the sticking coefficient. The sticking coefficient is defined as the probability that a particle will stick to the surface when it strikes. In both sputter deposition and chemical vapor deposition, the sticking coefficient may not be equal to unity. A non-unity sticking coefficient would allow the particle to be reemitted from the surface upon impact. The particle may then deposit on the surface at a different location, or it may bounce around the surface more before it settles, which leads to a smoothing effect. Both shadowing and reemission effects are inherently nonlocal because an event that occurs at one place on the surface can affect the surface profile a far distance away.

As with most other materials and coatings, the factors that influence the frictional behavior of DLC coatings are many and may vary from one type of DLC to another. Intrinsically, the degree of sp$^2$ versus sp$^3$ bonding as well as the relative amounts of alloying elements in the structure or on the sliding surfaces of DLC coatings can have a strong effect on their friction and wear behaviors. Extrinsically, the frictional behavior of these coatings can be affected by the extent of chemical, physical and mechanical interactions between the rubbing surfaces of DLC coatings and their surroundings. The frictional behavior of DLC based coatings is known to be affected by the humidity, load and sliding velocity.$^{51,52}$ Rough surfaces can certainly cause high friction and severe wear losses in most sliding contacts. Specifically, if the sliding surfaces of DLC are very rough, a high level of mechanical interlocking can take place between surface asperities and lead to high frictional losses.$^{12}$ For metals, in most cases, initial surface textures are rapidly destroyed as soon as wear starts. However, under low loading conditions and/or for materials with a high hardness, wear rate is low and thus the initial surface roughness may play an important role in tribology. This is usually the case of hard protective coatings like DLC.$^{53}$ In general, it is believed that a high surface roughness yields major frictional and wear losses mainly during the running-in period.$^{12}$ However, the surface roughness may also influence the overall frictional behavior of these coatings. Moreover, the hardness of the mating materials also influences the tribological properties of DLC coatings.$^{54}$ As a consequence, it is important to understand the influence of roughness on
the formation of the transfer film and CoF of these coatings sliding against different counterface materials in order to underpin their tribological properties. Apart from the adverse effects of surface roughness on friction and wear, the extent of chemical and/or adhesive interactions between sliding DLC surfaces may also strongly influence their friction. In these coatings, the adhesive interactions can primarily result from several types of bonding. Among others, covalent bond interactions between unoccupied or dangling $\sigma$-bonds of sliding carbon coating interfaces can account for a significant source of adhesion. Covalent bonding is the strongest type in carbon-based materials, and if it is not taken care of then very strong adhesion and hence friction may result between such sliding surfaces. It is known that hydrogen has a strong chemical affinity towards carbon; it bonds strongly to some of the carbon atoms and thus effectively passivates their unoccupied or free $\sigma$-bonds. Once passivated, such carbon atoms become chemically inert and cause very little adhesive interactions during sliding and lead to low friction.12

1.2 Scope of the thesis

This research was carried out under the project number MC7.06246 in the framework of the research programme of the Materials innovation institute (M2i), Delft, the Netherlands. With the spirit of teamwork, I have worked in close cooperation with Changqiang Chen, Anatoly Turkin, Diego Martinez-Martinez, and my supervisors Yutao Pei and Jeff De Hosson to get the results presented in this thesis. In chapter 2, the deposition and characterization methodologies used for TiC/a-C and TiC/a-C:H nanocomposite coatings studied in this work are described. Chapter 3 is based on 55-61 and concentrates on understanding the growth dynamics of p-DC sputtered TiC/a-C nanocomposite coatings at various pulse frequencies. From detailed analyses of surface morphology and growth conditions, it is concluded that a transition in growth mechanisms occurs, i.e. a mechanism dominated by geometric shadowing at lower pulse frequency evolving to a surface diffusion mechanism driven by impact-induced atomistic downhill flow process by Ar$^+$ ions at higher pulse frequency which leads to transition from a strong columnar to a columnar-free microstructure. The models describing surface roughness evolution are briefly discussed and it was found that the model is in good agreement with atomic force microscopy measurements of roughness evolution. Chapter 4 is based on 62,63 and focuses on the microstructure and deformation behavior of TiC/a-C nanocomposite coatings deposited by pulse DC magnetron sputtering. The evolution in microstructure from homogeneous to multilayered structure with increasing pulse frequency was observed where the modulation of multilayer was controlled by the self-organization of nanocrystallites due to ion impingement. It is shown that by controlling the distribution of nanocrystallites forming nanoscale multilayers, the system can be used as a “microstructural ruler” that enables distinguishing various deformation patterns.
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which can be hardly detected otherwise in a homogenous structure. Chapter 5 is based on 64,65,66 and deals with the tribological performance of TiC/a-C and TiC/a-C:H nanocomposite coatings. The effect of roughness of TiC/a-C coatings on tribological behavior while sliding against different counterface materials having different hardness is described. Detailed analyses of the transfer film, sliding surfaces of the ball counterparts, and wear surfaces of the coatings are presented. Furthermore, in order to obtain ultra-low friction, mechanical, structural, chemical bonding (sp³/sp²) and tribological properties of TiC/a-C:H coatings are studied as a function of substrate bias voltage, Ti-target current, C₂H₂ flow rate and pulse frequency. Dense, column-free, smooth and ultra-low friction TiC/a-C:H coatings are discussed.

References

Chapter 1