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Self-adaptive and self-healing nanocomposite tribocoatings

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CHAPTER 1

Introduction

This chapter highlights the motivation and objectives of the thesis work on the self-adaptive and self-healing tribocoatings and provides an overview of the structure of the dissertation. It briefly reviews how transition metal dichalcogenides (TMD), WS_2 in particular, based coatings can be used in triboapplications and the reasons why they can be beneficial when embedded in an amorphous carbon matrix. It is shown that the nanocomposite characteristics of TMD in an amorphous carbon matrix provides capabilities of self-adaptation and of self-healing in different tribo-environments.

1.1 TRIBOLOGY

The surface of a component is usually the most important engineering component. In practice it is often the surface of a work-piece that is subjected to wear and corrosion, which causes losses or failures in functionality. The complexity of the tribological properties of materials and the economic aspects of friction and wear justify an increasing research effort. In industrialized countries around 30 % of all energy generated is ultimately wasted through wear and friction. In highly industrialized countries losses due to friction and wear are estimated between 1% and 2% of Gross Domestic Product (GDP) [1].

Wear from sliding surfaces is typically the result of one or more of the following main mechanisms [2,3]: (i) abrasive wear, whereby a hard counterface slides across a softer surface, which includes two-body abrasive wear (e.g. hard particles are generated and adhered to the surface) and third-body abrasive wear (e.g. hard particles are free to roll and slide); (ii) adhesive wear, whereby material is removed (material transfer) due to the adhesive forces; (iii) fatigue wear, whereby wear particles are detached due to crack nucleation and crack propagation in the subsurface area; and (iv) tribo-chemical wear, whereby wear particles are generated in a corrosive environment by a chemical reaction (e.g. corrosive wear) or a chemical reaction owing to friction or mechanical energy (e.g. tribo-chemistry). One should realize that wear is a rather complex process with many influential factors such as kinematics, mechanical stress, the formation of a lubricating tribofilm, chemical environment, temperature, humidity, and materials properties. In the evaluation of the tribological properties of a materials, the extrinsic conditions should be emphasized.

To an increasing degree continuous search is on the surface modification techniques and advanced coatings or films that can largely decrease friction and increase the wear resistance of the protected materials. There have been significant progress in surface modification and engineering fields providing very thick, hard, slippery and polished surfaces for severe tribological applications. Advancing wear resistance is typically accomplished by the introduction of a shear-accommodating layer between contacting surfaces. For instance, the field of plasma vacuum surface engineering utilizes a family of plasma based surface modification technologies, such as plasma-assisted chemical vapor deposition, ion beam implantation & deposition, magnetron sputtering, cathodic vacuum arc and plasma-enhanced electron beam evaporation. The layers produced with these techniques are called “thin films”, limiting to several μm thick, in comparison to “thick coatings” that can be built-up in a large scale up to several mm thick such as by laser surface modification (e.g. cladding, hardening, alloying) or thermal-mechanical processes including plasma arc spraying and tungsten inert gas

(TIG) wire deposition. For industrial production efficiency, in many cases if a thin protective layer is sufficient to do the job, it is not necessary to produce a thick layer on the top of a substrate. This thesis highlights the novel thin functional protective thin coating ($< \sim 2 \mu\text{m}$) prepared by magnetron sputtering for advances in sliding wear and low friction.

1.2 SOLID LUBRICANTS: DLC AND TMD

Liquid lubricants (e.g. oils) are used to suppress contact pressure, to reduce friction and to facilitate the sliding between solid bodies. However, in many industrial applications where the operating conditions are beyond the liquid realm: the presence of a liquid is inappropriate or even fully impossible to be introduced (e.g. the vacuum environments and high-temperature applications, or situations with incompatibility problems). Thus, for these reasons liquid lubricants should be avoided. Consequently, the design and development of solid self-lubricating coatings becomes an attractive subject of fundamental and applied research. The solid lubricating behavior of materials such as graphite and mica are well developed. Recent modern coating technologies (e.g. PVD) has greatly expanded the application of solid lubricant materials including diamond-like carbons (DLC) and transition metal dichalcogenides (TMD).

Amorphous carbon consist of a disordered network of carbon atoms with a mixture of both sp^3 - and sp^2 -coordinated bonds. The family of amorphous carbon is called diamond-like carbon (DLC) [4,5]. In DLC, the carbon sp^3 bond hybridization results in a diamond-like structure, which provides properties such as extremely high hardness, chemical inertness and low wear rate. The carbon sp^2 bond hybridization represents a typical component of graphite which is internally coupled through weak Van der Waals force fields. DLC films can be in divided into two categories based on their hydrogen content, hydrogenated (a-C:H, 10-60 at.% H) and hydrogen-free (a-C, < 1 at.% H). Amorphous carbon films with a high fraction (> 50 -90%) of tetrahedral sp^3 bond called ta-C [5]. Compared with conventional DLC, ta-C coating is favorably used in applications requiring ultrahigh strength and hardness such as tooling due to its super-high hardness. Also, it should be pointed out that the test environment has a profound influence on the friction and tribological performance of hydrogenated and hydrogen-free DLC films, respectively, e.g., in inert dry gases the coefficient of friction (CoF) of highly hydrogenated DLC is very low (< 0.02) in comparison to an increased value to 0.1-0.2 in humid air. On the contrary, such ultralow CoF values are typically measured for the hydrogen-free DLCs in humid environment, whereas they perform unsatisfactorily in dry conditions (CoF 0.4-0.7) [6]. The lubricating mechanisms for DLC have attributed to the hydrogen-terminated bonds with Van der Waals forces

acting in the contact between surfaces and the graphitization at micro-contrast regions leading to transfer films [6]. In all, DLC has many significant features that contribute to excellent tribological characteristics, such as high hardness, anti-wear property with low friction coefficient and low wear rate as well as chemical inertness. DLC is probably the only material that can provide both high hardness and low friction under dry sliding conditions [7]. DLCs, however, face several drawbacks: for instance, it is only possible as a thin film material, not as a bulk glassy solid; besides its thin films tend to have a large residual stresses. In addition, it is not mechanically tough and it is usually alloyed with metals or other elements (a-C: Me) to solve these problems. Still, the thermal stability of DLC is relatively low ($< 400\text{ }^{\circ}\text{C}$), potentially limiting its application in high temperature.

Alternatively, appealing lubrication properties are also found in other compounds with a layered crystal structure, like transition-metal dichalcogenides (LTMD), i.e., compounds of transition-metal atoms (group Xe: IVb, Vb, VIb) and chalcogens (group X: S, Se, Te). The chemical bonds between the atoms within the sandwich are relatively powerfully covalent, whereas the bonding between adjacent sandwiches is weaker Van der Waals interactions [8], as illustrated by the structure of WS_2 in **Figure 1.1**. Consequently, glide occurs preferentially between the lamellae leading to the ultralow friction coefficient. Given the weak interactions between the sandwiched layers, they can be stacked into several ways (e.g. 1T, 2H, 3R) of which the most common form has a stacked sequence of two sandwiched layers (the stacking sequence is X-Me-X-X-Me-X and is denoted 2H-MeX₂), giving a trigonal symmetry and exhibiting a marked two-dimensional behavior despite its three-dimensional atomic structure. In this anisotropic structure, a close-packed layer of transition-metal atoms is sandwiched in between two layers of chalcogen atoms. Each chalcogenide atom is equidistant from three metal atoms, and each metal atom is surrounded by six equidistant dichalcogenide atoms at the corners of a small trigonal prism.

Crystalline TMD coatings are often categorized into two categories depending on the orientation of the (002) basal planes. As illustrated in **Figure 1.2**, for type I orientation the basal planes are perpendicular to the surface (namely with the c axis is parallel to the surface), while the type II orientation has basal planes parallel to the surface (and the c axis vertical to it). Unless there are defects, the basal plane surface is unreactive while dangling bonds are found on the plane edges such as (110), which are active sites for environmental attacks such as oxidations. Therefore, the type II orientation with horizontal basal planes is favorable for tribological properties and efforts have been made to grow such coatings [9–12], otherwise the resulting products are often type I orientation with standing platelets, making it highly porous with poor adhesion, as

shown in **Figure 1.3**. On visual inspection, such type has a rather matt and dark appearance due to less reflection of visible light.

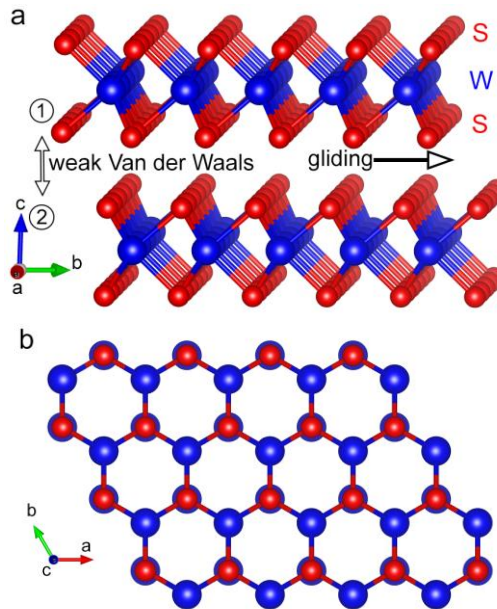


Figure 1.1 Crystal structure of 2H-WS₂: (a) side view; (b) top view (Red: sulfur atoms; Blue: tungsten atoms).

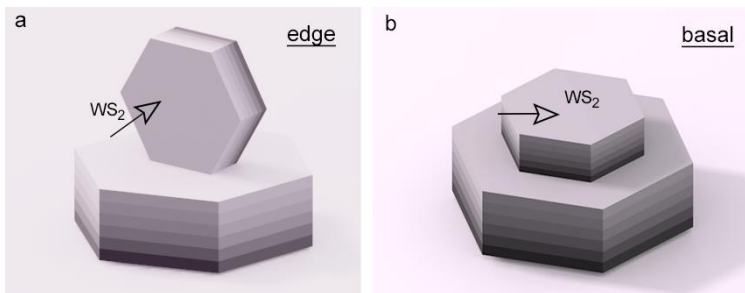


Figure 1.2 (a) edge orientation and (b) basal orientation.

Due to the weaker interlayer coupling, disordered stacking is also possible, for instance in the so-called turbostratic stacking, the sandwich layers are parallel but more or less randomly rotated around the c-axis [13,14]. Besides, other intercalants can also be inserted in between the layers [15]. In terms of lubrication, various mechanisms such as basal plane orientation, intra-granular shear and inter-crystallite glide were proposed for explaining the extraordinary lubrication [16]. For instance, Sokoloff [17] and Shinjo [18] pointed out that the intra-granular shear of MoS₂ is associated with the defects whereas the inter-crystallite slip requires a transfer film to be formed first on

the counterpart. In all, this anisotropic property lies the physical foundation for explorations of 2H-TMDs as superior solid lubricants.

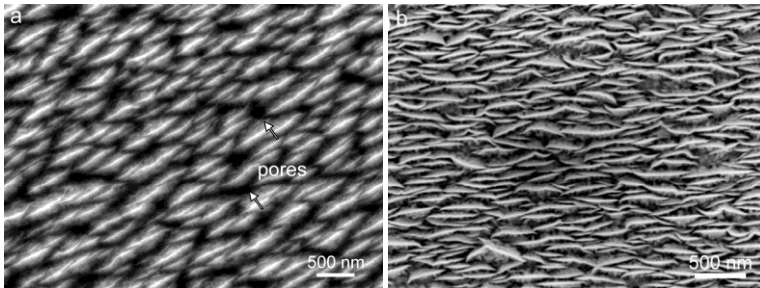


Figure 1.3 porous pure WS_2 film: (a) by pulsed-DC magnetron sputtering in this study; (b) by radio frequency magnetron sputtering in Ref. [23].

The LTMD family covers disulfides, diselenides and ditellurides of molybdenum, tungsten or niobium. The physical and tribological properties of LTMDs, particularly MoS_2 and WS_2 , have been intensively studied for the last decades in lubrications [8]. Nowadays, they are used mainly as oil additives playing a low-frictional role. They are also being prepared as a thick coatings or a thin film deposited mainly by physical vapor deposition (PVD) method. Other TMDs such as diselenides and ditellurides of molybdenum and tungsten, although with similar structure to WS_2 and MoS_2 , have not demonstrated as lubricious as the first two and are of less technological interests generally [19,20]. Compared with MoS_2 , WS_2 is even more advantageous due to the following reasons: (a) higher thermal stability (WS_2 was reported to be about ~ 400 °C while MoS_2 starts to oxidize above ~ 300 °C [21,22]; (b) potential lower friction (WO_3 is even superior to MoO_3 at high temperature) and (c) less volatile. Therefore, WS_2 is attracting more scientific and industrial attentions.

TMD lubricants are mostly finding their wide applications in aerospace industry or dry environments. The large-scale industrial applicability of TMD is still limited and the operational impact is constrained by environmental issues particularly of humidity and elevated temperature. The main problems to face are as follows [24,25]:

- LTMD films are porous with potential cracks mostly due to the columnar morphology, see **Figure 1.3**. In reality, it turned out to be very difficult to produce pure LTMD films without cracks and porosity defects using conventional magnetron sputtering.
- Only (002) basal plane orientation is functional for a superlubricity. However, deposition of LTMD by magnetron sputtering mostly leads inevitably to a disordered structure. The favorable low-friction orientation (002) cannot be

achieved except for a very thin film, i.e., not exceeding tens of nanometers, which may cause a lack of replenishment.

- LTMD films are extremely sensitive to environmental attacks. When sliding in humid air, very likely a reaction occurs between the unsaturated dangling bonds leading to metal oxides MO_3 , see **Figure 1.4**. Only well orientated LTMD with basal planes parallel to the surface may help resist oxidation.
- Extremely low hardness (0.3-2 GPa) with low load bearing capacity (corresponding to a large contact area). It is easily to peel off under high contact pressure and thus yield high wear rate particularly in high temperature applications.

As can be seen, all these above drawbacks make LTMD based coatings less attractive for operations in harsh environments and under high contact load. To achieve low friction and a low wear rate, other approaches for advancing TMDs are needed.

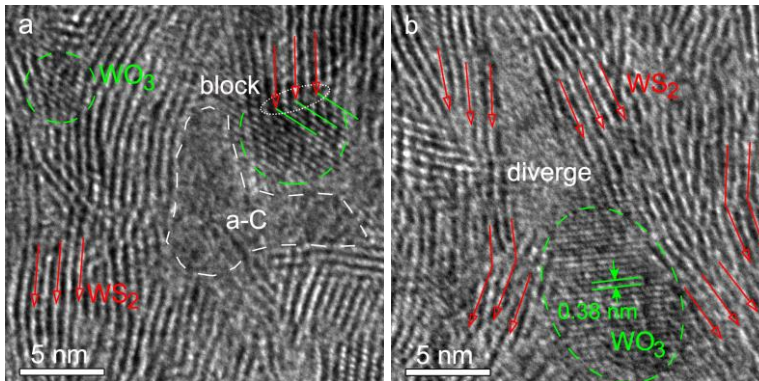


Figure 1.4 HR-TEM images indicating the formation of WO_3 formed in $\text{WS}_2/\text{a-C}$ coating, which may impede the sliding induced WS_2 (002) basal plane reordering process as a result of (a) blocking and (b) diverging [26].

1.3 SELF-ADAPTION AND SELF-HEALING FUNCTIONALITY

In the past decades, tribological coating and solid lubricant films developed towards from the (a) single component; (b) multicomponent; (c) multilayer; (d) nanostructured to the (e) smart adaptive coating. There is an increasing demand for environmentally robust solid lubricant coatings that can adapt themselves to different environments [27–29]. For instance, even if the targeted application is the friction and wear mitigation in space, usually the satellites and satellites launch vehicles requires some extended periods of time in humid coastal environments before launching [20]. This potentially expose the moving mechanical assemblies to humid environment,

which calls on development of multi-phase, nanocomposite materials known as adaptive lubricants since no single phase, either DLC or TMD, currently could provide solid lubrication by themselves under varying degrees of humidity. In an ideal case, chameleon wear protective coatings should be able to reversibly self-adapt their surface chemistry and structure to maintain low friction and wear while cycling over a broad range of ambient environments and temperatures. Self-adaptive coating selection is guided by several factors including operational environment, temperature, geometry, load, and speed considering that different materials perform optimally under a limited range of environmental and loading conditions. Chameleon tribological coatings are being designed to tackle the existing problem: single-constituent tribological materials cannot operate reliably over extended ranges of ambient humidity or temperatures. The key feature of chameleon tribocoating concept is to provide reversible self-adjustment of surface chemistry, structure, and mechanical behavior in the contact zone to obtain low friction and prevent wear at all anticipated operational conditions.

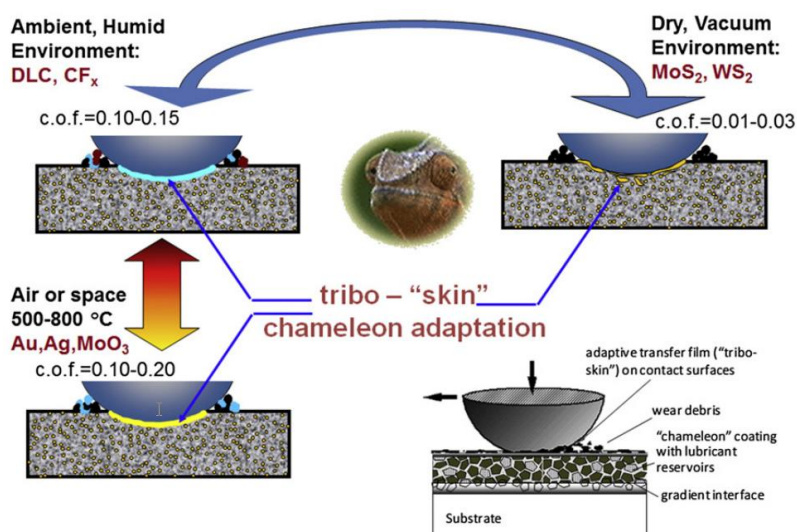


Figure 1.5 Schematic representation of a solid lubrication with a chameleon adaptive coating with environmental cycles [2,30].

The compliant amorphous characteristic of DLC in a nanocomposite coating render it to be dense and homogenous, generating a high density of interphase interfaces that assist in crack deflection and termination of crack growth and also increase in the load-bearing capacity as well as protection of TMD from oxidation [31,32]. All these features make DLC a promising matrix candidate for supporting the soft LTMD for self-adaptive functionality. In 1999, Voevodin and co-authors were the first to present a nanocomposite WC/DLC/ WS_2 coatings [33,34], deposited by laser ablation from a

combined WS₂/graphite target. The motivation was to combine the low friction and high wear resistance of amorphous DLC with the wear resistance of WC and the lubricating property of WS₂. The assumption is that TMD phase is attributed to be responsible for the lubrication and low-friction properties in dry environment, whereas DLC plays a role in lubrication in high humidity. Also it offers high strength and resistance to wear, and the coating becomes versatile in switching environments and present “chameleon behavior”, as illustrated in **Figure 1.5**. These smart coatings, at least consisting of one TMD component (WS₂ or MoS₂), were largely developed later in combination with a-C(N)[35,36], yttrium-stabilized zirconia (YSZ)/Au [37], Mo₂N/Ag [38], Ti [15], Cr [39], Sb₂O₃/Au [27], Pb [40]. The basic lubricating mechanism underlying the self-adaptation was proposed that in vacuum or dry gas conditions, friction induces TMDs to be crystallized and reorientated with their basal planes parallel with the sliding direction although sputtering nanocomposite of DLC and TMD may produce type I orientation TMD or even an amorphous state, as illustrated in **Figure 1.6**. While in humid air, graphite-like transfer film is formed by friction induced sp³ → sp² phase transition leading to low friction; however, the role of carbon is still controversial [37,39,41,42]. Besides, the YSZ, Au, Ag, MO₃ were reported as beneficial in high temperature triboapplications.

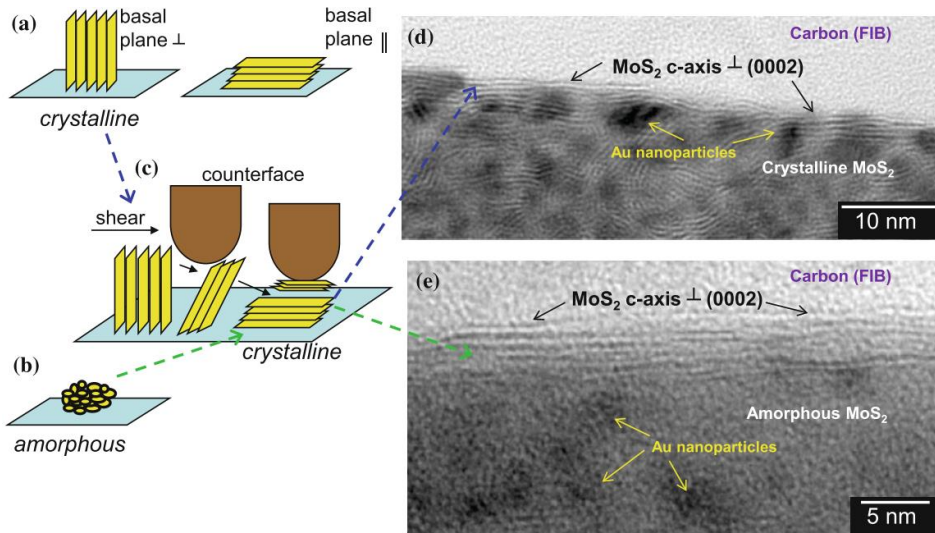


Figure 1.6 Schematic representations of (a) two crystallographic growth textures with basal planes perpendicular or parallel (preferred) to the substrate, and (b) amorphous structure. The process of sliding induced (a → c → d) orientation of perpendicular (or randomly oriented) basal planes parallel to the sliding direction to allow ultralow friction, or (b → c → e) amorphous to crystalline transformation to achieve low friction. Corresponding cross-

section TEM images from the wear track of (d) crystalline MoS_2/Au coating and (e) amorphous $\text{MoS}_2/\text{Sb}_2\text{O}_3/\text{Au}$ coating [20].

Self-healing materials possess the inherent capability to repair damage by themselves, or alternatively with some external stimulation such as temperature, light, chemical change, pressure change or some mechanical actions to adaptively reproduce or restore their original functionality [43]. It is known that coating prepared by PVD are mostly columnar-like, such columns are potential weak links for crack propagations (see **Figure 1.7**), which may consequently lead to catastrophic failures such as branch or delamination. In real severe wear conditions, accumulating fatigue or some sudden impact or damage further aggravate the degradation of coatings. It took numerous efforts for surface scientists and engineers to counteract the growth of columnar structures [31,44]. Therefore, the damage self-healing ability is a particularly intriguing property for tribocoatings to protect the material of a construction against wear.

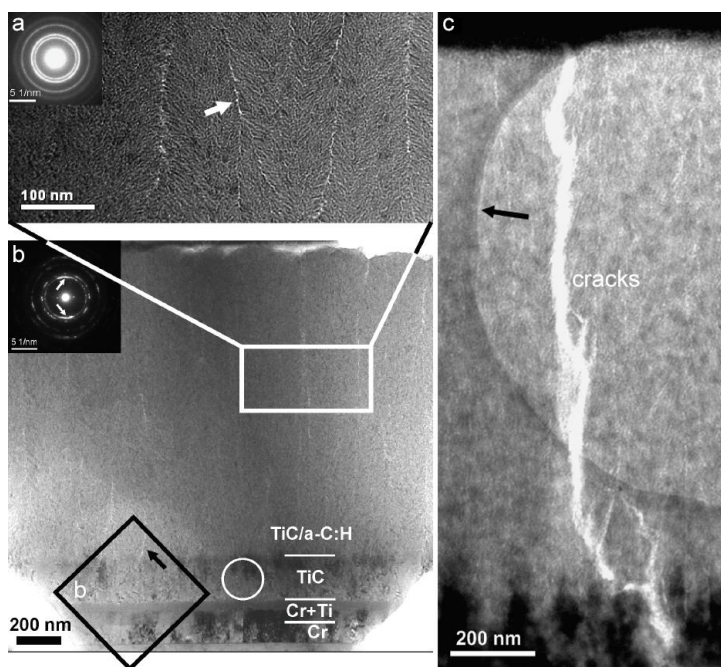


Figure 1.7 BF-TEM images of the sputtered TiC/a-C:H coating with columnar structure as indicated by an arrow in (a, b) and (c) shows a crack may propagate through a column boundary in the coating leading to potential failure. Note the circle in (c) is due to the presence of a sample-supporting holey carbon grid [45].

1.4 OUTLINE OF THE THESIS

The research goal of this thesis is to produce LMTD where the porous structure with microcracks are healed and the tribo-system becomes self-repairing and even self-curing. We intend to prepare WS_2 coating alloyed with amorphous carbon by using the sophisticated magnetron sputtering method. In particular, we have abandoned the standard idea to deposit “ideal” coating; instead, we focus on exploitation of the self-adaptive and self-healing capabilities of tribocoatings, as well as the high flexibility of the coating operating in different environments. The coating itself will consist of two different compounds: WS_2 in the form of nano-grains or nano-platelets as lubricants and amorphous carbon acting as the supporting matrix. The research follows the idea to allow the reorientation of the crystallized WS_2 phases to the “frictionless” direction inside the carbon matrix.

In **Chapter 2**, the techniques employed for the production of $WS_2/a-C(H)$ coatings, and the subsequent experimental methods applied for the sample characterization and data analysis are described in details. Closed-field unbalanced magnetron sputtering was employed to prepare the expected tribocoatings. Characterization tools including scanning electron microscope (SEM), high resolution/energy-filtering transmission electron microscope (HR-/EF-TEM), atomic force microscope (AFM), energy dispersive spectroscope (EDS), glazing incidence X-ray diffraction (GI-XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, nanoindentation and tribometry technologies were used to determine the coating morphology, chemical composition, phases, microstructure and their mechanical and tribological properties. Focused ion beam (FIB) was used to prepare site-specific TEM lamella at the wear track or the ball scar for HR-TEM to evaluate the self-adaptive mechanism in the coatings.

In **Chapter 3**, $WS_2/a-C$ coatings with various carbon contents (0-65 at.%) were deposited on single crystal silicon wafers by magnetron co-sputtering one graphite and two WS_2 targets under different Ar flow rates. Thus, a broad spectrum of coatings were prepared under varied sputtering parameters provided sufficient information for the determination of the microstructure, the phase, and the mechanical properties. The effects of the argon flow rate (deposition pressure) on the chemical stoichiometric S/W ratio and coating density were investigated. At the same time, the effect of carbon on the S/W ratio was also investigated on the nano-hardness and elastic modulus and tribological properties. The mechanical and tribological properties of pure WS_2 coating and nanocomposite $WS_2/a-C$ are also compared. The coating carbon concentration, deposition pressure and the testing atmospheres on the friction and wear were studied.

Chapter 4 further follows the **Chapter 3** to explore some other parameters influencing the S/W ratio in the coating: target-substrate distance and negative bias voltage applied to the substrates. The underlying physical understanding of sulfur preferential

resputtering was presented and the solutions to overcome the sulfur substoichiometry were provided. The real effect of S/W ratio on the tribological properties was discussed. Apart from the S/W ratio, the influence of total content of sulfur in the nanocomposite coating was discussed. In addition, the nonreactive sputtered WS₂/a-C and reactive sputtered WS₂/a-C:H coatings with similar composition and mechanical performance are scrutinized for the tribological tests in both humid and dry sliding conditions. This study also revealed the real role of carbon playing in the self-lubricating in the humid environment. Based on the triboperformance, a specific sputtering route to deposit WS₂ based coating is proposed for the favorable development of self-adaptive coatings versatile in harsh environments.

Chapter 5 reports on the self-adaptive behavior of WS₂/a-C coating by switching the sliding conditions, i.e., alternating the testing atmospheres from dry air (5% relative humidity) to humid air (55% relative humidity) several times. Reversible tribological behavior was exploited with the testing atmosphere cycling between dry air and humid air. Focused ion beam technique was then employed to slice TEM lamellae at both the wear track and the worn ball scar, and HR-TEM observations reveal the self-adaptive mechanism.

Based on the findings in Chapter 5, **Chapter 6** further explores the potential self-healing capabilities in tribocoatings from nano- to micro-scale, as illustrated by the nanocomposite WS₂/a-C coating. We first use a scratcher to induce two types of notched cracks to mimic the potential damages. After that, a sliding stimulus was exerted aiming to self-repair the damages autonomously. The FIB-TEM observations reveal the self-healing mechanism. The study sheds new light on the possibility to release the critical requirements of producing flawless coatings for triboapplications in industry.

Chapter 7 summarizes the outcome of the thesis work, and gives an outlook of possible future perspective involving the further optimization of the coatings in extreme service conditions. Possible new developments of advanced versatile self-healing and self-adaptive coatings are proposed.

References

- [1] K. Holmberg, A. Erdemir, Influence of tribology on global energy consumption, costs and emissions, *Friction* 5 (2017) 263–284.
- [2] Q.J. Wang, Y.W. Chung, Encyclopedia of tribology, Springer 2013.
- [3] B. Bhushan, Introduction to tribology, 2nd, Wiley 2013.
- [4] J. Vetter, 60 years of DLC coatings: Historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications, *Surf. Coat. Technol.* 257 (2014) 213–240.

- [5] K. Bewilogua, D. Hofmann, History of diamond-like carbon films-From first experiments to worldwide applications, *Surf. Coat. Technol.* 242 (2014) 214–225.
- [6] C. Donnet, A. Erdemir, Tribology of diamond-Like carbon films, Springer 2007.
- [7] C. Donnet, A. Erdemir, New horizon in the tribology of diamondlike carbon films, *Surf. Eng.* 24 (2008) 399–401.
- [8] N. Tak, R. October, Direct resolution of the layer lattice of molybdenum disulfide by transmission electron microscopy in relation to lubrication, *Wear* 124 (1988) 279–289.
- [9] C. Muratore, A.A. Voevodin, Control of molybdenum disulfide basal plane orientation during coating growth in pulsed magnetron sputtering discharges, *Thin Solid Films* 517 (2009) 5605–5610.
- [10] K. Ellmer, C. Stock, K. Diesner, I. Sieber, Deposition of c(perpendicular to)-oriented tungsten disulfide (WS_2) films by reactive DC magnetron sputtering from a W-target in Ar/ H_2S , *J. Cryst. Growth* 182 (1997) 389–393.
- [11] M. Regula, C. Ballif, M. Remškar, F. Lévy, F. Le, Crystallinity and texture promotion in crystallinity and texture promotion in WS_2 thin films, *J. Vac. Sci. Technol. A* 15 (2014) 2323–2328.
- [12] V. Weiß, S. Seeger, K. Ellmer, R. Mientus, Reactive magnetron sputtering of tungsten disulfide (WS_{2-x})films: Influence of deposition parameters on texture, microstructure and stoichiometry, *J. Appl. Phys.* 103502 (2013) 1–9.
- [13] D. Yang, R.F. Frindt, Powder X-ray diffraction of turbostratically stacked layer systems, *J. Mater. Res.* 11 (1996) 1733–1738.
- [14] J. Moser, F. Lévy, Random stacking of MoS_{2-x} sputtered thin films, *Thin Solid Films* 240 (1994) 56–59.
- [15] D.G. Teer, New solid lubricant coatings, *Wear* 251 (2001) 1068–1074.
- [16] J.M. Martin, H. Pascal, C. Donnet, T. Le Mogne, J.L. Loubet, T. Epicier, Superlubricity of MoS_2 : Crystal orientation mechanisms, *Surf. Coat. Technol.* 68 (1994) 427–432.
- [17] J.B. Sokoloff, Theory of energy dissipation in sliding crystal surfaces, *Phys. Rev. B* 42 (1990) 760–765.
- [18] K. Shinjo, M. Hirano, Dynamics of friction: superlubric state, *Surf. Sci.* 283 (1993) 473–478.
- [19] E. Bergmann, G. Melet, C. Müller, Friction properties of sputtered dichalcogenide layers, *Tribol. Int.* 14 (1981) 329–332.
- [20] T.W. Scharf, S. V. Prasad, Solid lubricants: A review, *J. Mater. Sci.* 48 (2013) 511–531.
- [21] W.A. Brainard, The thermal stability and friction of the disulfides, diselenides, and ditellurides of molybdenum and tungsten in vacuum (10^{-9} to 10^{-6} Torr), *NASA* (1969) 1-22.

- [22] H.E. Sliney, Solid lubricant materials for high temperatures - A review, *Tribol. Int.* 15 (1982) 303–315.
- [23] D.S. Wang, M. Hu, D. Jiang, X.M. Gao, Y.L. Fu, Q.Q. Wang, J. Wang, Preparation and characterization of the CrN nanocone array textured WS₂ film, *Mater. Lett.* 188 (2017) 267–270.
- [24] F. Gustavsson, S. Jacobson, Diverse mechanisms of friction induced self-organisation into a low-friction material - An overview of WS₂ tribofilm formation, *Tribol. Int.* 101 (2016) 340–347.
- [25] T. Polcar, A. Cavaleiro, Review on self-lubricant transition metal dichalcogenide nanocomposite coatings alloyed with carbon, *Surf. Coat. Technol.* 206 (2011) 686–695.
- [26] H.T. Cao, J.T.M. De Hosson, Y.T. Pei, Self-healing of a pre-notched WS₂/a-C coating, *Mater. Res. Lett.* 07 (2019) 103–109.
- [27] T.W. Scharf, P.G. Kotula, S.V. Prasad, Friction and wear mechanisms in MoS₂/Sb₂O₃/Au nanocomposite coatings, *Acta Mater.* 58 (2010) 4100–4109.
- [28] J.J. Hu, R. Wheeler, J.S. Zabinski, P.A. Shade, A. Shiveley, A.A. Voevodin, Transmission electron microscopy analysis of Mo-W-S-Se film sliding contact obtained by using focused ion beam microscope and in situ microtribometer, *Tribol. Lett.* 32 (2008) 49–57.
- [29] C. Muratore, A.A. Voevodin, Chameleon coatings: adaptive surfaces to reduce friction and wear in extreme environments, *Ann. Rev. Mater. Res.* 39 (2009) 297–324.
- [30] A.A. Voevodin, C. Muratore, S.M. Aouadi, Hard coatings with high temperature adaptive lubrication and contact thermal management: Review, *Surf. Coat. Technol.* 257 (2014) 247–265.
- [31] Y.T. Pei, D. Galvan, J.T.M. De Hosson, Nanostructure and properties of TiC/a-C:H composite coatings, *Acta Mater.* 53 (2005) 4505–4521.
- [32] L. Gu, P.L. Ke, Y.S. Zou, X.W. Li, A.Y. Wang, Amorphous self-lubricant MoS₂-C sputtered coating with high hardness, *Appl. Surf. Sci.* 331 (2015) 66–71.
- [33] A.A. Voevodin, J.P. O'Neill, J.S. Zabinski, Nanocomposite tribological coatings for aerospace applications, *Surf. Coat. Technol.* 116–119 (1999) 36–45.
- [34] A.A. Voevodin, J.P. O'Neill, J.S. Zabinski, WC/DLC/WS₂ nanocomposite coatings for aerospace tribology, *Tribol. Lett.* 6 (1999) 75–78.
- [35] A. Nossa, A. Cavaleiro, The influence of the addition of C and N on the wear behaviour of W-S-C/N coatings, *Surf. Coat. Technol.* 142–144 (2001) 984–991.
- [36] A. Nossa, A. Cavaleiro, Mechanical behaviour of W-S-N and W-S-C sputtered coatings deposited with a Ti interlayer, *Surf. Coat. Technol.* 163–164 (2003) 552–560.

- [37] C.C. Baker, R.R. Chromik, K.J. Wahl, J.J. Hu, A.A. Voevodin, Preparation of chameleon coatings for space and ambient environments, *Thin Solid Films* 515 (2007) 6737–6743.
- [38] S.M. Aouadi, Y. Paudel, B. Luster, S. Stadler, P. Kohli, C. Muratore, C. Hager, A.A. Voevodin, Adaptive Mo₂N/MoS₂/Ag tribological nanocomposite coatings for aerospace applications, *Tribol. Lett.* 29 (2008) 95–103.
- [39] T. Polcar, F. Gustavsson, T. Thersleff, S. Jacobson, A. Cavaleiro, Complex frictional analysis of self-lubricant W-S-C/Cr coating, *Faraday Discuss.* 156 (2012) 383–401.
- [40] H. Li, G.G. Zhang, L.P. Wang, Low humidity sensitivity of MoS₂/Pb nanocomposite coatings, *Wear* 350–351 (2016) 1–9.
- [41] T. Polcar, M. Evaristo, A. Cavaleiro, Self-lubricating W-S-C nanocomposite coatings, *Plasma Process. Polym.* 6 (2009) 417–424.
- [42] T. Polcar, M. Evaristo, R. Colaço, C. Silviu Sandu, A. Cavaleiro, Nanoscale triboactivity: The response of Mo-Se-C coatings to sliding, *Acta Mater.* 56 (2008) 5101–5111.
- [43] B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, Self-healing polymers and composites, *Annu. Rev. Mater. Res.* 40 (2010) 179–211.
- [44] Y.T. Pei, C.Q. Chen, K.P. Shaha, J.T.M. De Hosson, J.W. Bradley, S. A. Voronin, M. Čada, Microstructural control of TiC/a-C nanocomposite coatings with pulsed magnetron sputtering, *Acta Mater.* 56 (2008) 696–709.
- [45] D. Galvan, Nanocomposite Coatings: Processing, structure and tribological performance, Thesis, University of Groningen, 2007.

