Self-adaptive and self-healing nanocomposite tribocoatings
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SUMMARY AND OUTLOOK

7.1 SUMMARY

In this Thesis the design and exploration of environmental self-adaptive and damage self-healing tribocoating with both an ultralow coefficient of friction and a low wear are studied. The work concentrates on nanocomposite WS₂/a-C(H) coating. WS₂ is well known for their solid lubricating behavior. However, its wide application is limited by the poor tribological properties in oxygen or moist environments and the low load bearing capacity. These backsets make WS₂ base coatings less attractive for practical operations in harsh environments and under high contact load. Our objective is aimed at producing WS₂ in which the porous structure with micocracks are healed and the tribo-system becomes self-repairing and even self-curing. Within the framework of the proposed project we prepared WS₂ with an amorphous carbon matrix using sophisticated magnetron sputtering methods. We also abandoned the standard idea to deposit “ideal” defect free coating; instead, we focus on the development of self-adaptive and self-healing systems.

In Chapter 3, WS₂/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 WS₂ targets under different Ar flow rates. It is found that increasing the argon flow rate (higher deposition pressure) increases the chemical stoichiometric S/W ratio but at the expense of the coating density. The coating gradually becomes porous and shows columnar-like morphologies. Correspondingly, preferential re-sputtering of sulfur reinforced by impingement at low Ar pressure accounts for a low stoichiometric ratio in the coatings. The hardness of the coatings increases with increasing carbon content or a decreasing Ar flow rate. In particular, the hardness peaks at 10.6 GPa in the coating with around 40 at. % C when prepared at an argon flow rate of 10 sccm. Tribotests show that, together with a ultralow wear rate of 10⁻⁷ mm² m⁻¹N⁻¹, the coefficient of friction retains as low as ~ 0.02 in dry air (5% RH) and around 0.15 in moisture (55% RH) and it is rather stable within a sliding distance of 1000 m. It is also found that contrary to the literatures, pure WS₂ coating, when deposited at a relatively low pressure leading to a hardness up to about 3 GPa, could also survive over a long sliding distance of 1000 m corresponding to a reliable wear life.

In line with Chapter 3, Chapter 4 further explored the effect of the target-substrate distance and the negative bias voltage on the S/W ratio in both the cosputtered WS₂/a-C and reactive sputtered WS₂/a-C:H coatings. It was found that upon
increasing the target-substrate distance from 70 mm to 290 mm, the stoichiometric S/W ratio increases from 0.51 to 1.89. Besides, sulfur preferential resputtering is greatly aggravated if a negative bias voltage is applied. A physical understanding from the energy momentum transfer theory is thus proposed to understand the sulfur preferential resputtering issue. Moreover, experimental results revealed that to achieve an ultralow friction it is not necessary to reach the stoichiometric WS$_2$ in the WS$_x$C(H) coatings, for instance, a S/W ratio above 0.95 is sufficient for a low CoF of 0.05 (in dry air) and 0.10 (in ambient air). Instead, the total content of sulfur in the coatings may be more relevant. This study also indicates that carbon may at least play the role of lubricating properties in a humid environment. The nonreactive WS$_2$/a-C coating is superior to the WS$_2$/a-C:H one for the future development of self-adaptive coatings in varied humidity conditions.

Chapter 5 reported the reversible self-adaptive tribological behavior of WS$_2$/a-C coating by switching the sliding conditions forth and back, namely alternating from dry air (5% relative humidity) to humid air (55% relative humidity) several times. It is found that the tribological behavior can be reversible as the testing atmosphere cycles between dry air and humid air. Advanced focused ion beam technique (FIB) was then employed to slice TEM lamella at both the wear track and the worn ball scar. HR-TEM observations reveal an instant WS$_2$ platelets rearranged parallel to the sliding direction. This corresponds to a short tribological running-period and thus self-adaptive “frictionless” response.

The direct HR-TEM confirmation of the reorientation of WS$_2$ platelets in the tribofilm stimulates us in Chapter 6 to further explore the potential self-healing capabilities in tribocoatings from nano- to micro-scale by following the idea: by sliding contact, segmented TMD nanoplatelets are reoriented and bridged to form a closed continuous tribofilm that may consequently repair damages in an adaptive way.

We use a CSM scratch tester to purposely induce two types of notched cracks to mimic the potential damages afflicted to coatings in real services: one is ~2 µm wide, and the other up to 45 µm wide. The interrupted in-situ observations of the wear evolution in the damaged areas indicate both the two types of damages could be successfully healed autonomously, namely the so-called healing agent directly originates from the bulk coating. In fact, the notched damages are acting as microreservoirs restoring debris which become transformed at a later stage into tribofilm consisting of well aligned WS$_2$ lubricants. In this sense, the damage at the surface may be healed with beneficial effects in lubrication in the WS$_2$/a-C coating. The study sheds new light on the release of the requirement of producing flawless coatings for tribo-applications. Consequently it facilitates the coating production efficiency and reduce costs in industrial applications substantially. HR-TEM also
elucidates the conformal rearrangement of WS$_2$ platelets at the curved notch interface, implying that the reorientation goes with local sliding along the curving interface of the notch during tribofilm filling rather than always parallel with the counterpart ball sliding direction.

### 7.2 Outlook

The outcome of the WS$_2$/a-C(H) nanocomposite coatings for environmental self-adaptation and damage self-healing is both positive and exciting. We have successfully figured out and resolved the long-standing sulfur deficiency problems and after that developed an excellent lubricating tribocoating with both a low coefficient of friction and low wear rate. More importantly, we extensively used advanced site-specific FIB lamina-slicing approach for HR-TEM observation at nanoscale, which offered an in-depth understanding and also some new insights into the scientific phenomena that occur at the wear interface, either on the wear track or the counterpart ball scar. However, the research is still needed to continue along some potential lines as follows.

**(a) Lubricating mechanisms in wet sliding conditions and carbon effect**

WS$_2$-based coatings, let it be pure WS$_2$ film, WS$_2$/a-C, and WS$_2$/a-C(H), all tribologically perform better in vacuum or dry air sliding than that performed in humid condition, normally with a CoF of the first being one order of magnitude lower than that obtained in the later (e.g. 0.02 vs. 0.15). HR-TEM observations can easily trace the well aligned WS$_2$ nanoplatelets along with the local wear interface after dry air sliding. According to the light microscope images of the wear track of WS$_2$/a-C coating, there are clear dark adhesive tribofilms formed in the wear track after dry air sliding in contrast to the shining clean surface of that slid in humid air. This may lead to a different mechanism of the formation of tribofilms in the two cases that need to be elucidated by the FIB-TEM direct analysis. Comparative studies between WS$_2$/a-C and WS$_2$/a-C(H) coatings with similar hardness show that the former outperforms the latter in humid air tribop erformance, implying the role of carbon in affecting the frictional behavior rather than only increasing the mechanical properties.. The real effect of carbon in WS$_2$/a-C coatings still need further clarifications.

**(b) The platelet reorientation mechanism**

From Chapter 6, it can be concluded that the formation of a tribolayer for TMD coatings may partially be the result of the detachment of worn coating particles and their agglomeration in the contact area. The worn particles (third body), after the
release of carbon, become softened and thus are easily flattened between the surfaces in the contact. Such worn particles consequently form an adhered layer covering over the counterpart or the wear track.

According to the HR-TEM results as shown in Figure 7.1, it seems that along the well aligned TMD at the local interface between the tribofilms and the either originally randomly orientated or even amorphous TMDs in the bulk coatings below, there are no indications of traces of rotation or bending of TMDs. In reality, the new TMD platelets can be almost perpendicular to the original ones (see Figure 7.1a and b). Figure 7.1c evidently shows that short TMD platelets are jointed or bridged after defect movement, thereby long continuous aligned (002) basal planes are achieved.

![Figure 7.1 WS₂ platelets alignment in WS₂/a-C coating: the rearrangement of new WS₂ units rather than the rotation or bending of the previous platelets.](image)

This may lead to the conclusion that the reoriented TMD layer may be a newly formed material made of worn particles rather than the result of subsurface reorientation of bulk coatings; alternatively, at the subsurface the sliding induced shear force firstly pulls down the previous orientation of nanoplatelets at atomic scale and then shorter WS₂ units joint together via defect and again form a new orientation with a “reoriented appearance”. Note that the reorientation by rotation cannot explain how TMD platelets are aligned from a fully amorphous state, see Figure 7.2; in this sense, the rearrangement of WS₂ units at atomic scale is more reasonable to describe the platelet reorientation mechanism than the rotation. However, this hypothesis still awaits further careful analysis.

**c) High temperature service performance**

High temperature tribology is an important research area. It was taken for granted that TMD coatings could offer adequate triboperformance at a relatively high temperature. However they normally fail at 300-350 °C in literature due to the degradation as a result of severe oxidations at elevated temperature. It is recognized
that TMDs are better lubricants than their trioxides (CoF: 0.02 vs. 0.2)\[1\]. However, there are also some arguments suggesting that, at least to some extent, the formation of MO$_3$ ($M = W, Mo$) may not necessarily have a strong detrimental effect on the friction and wear of TMD \[2,3\]. Some studies even aim at making use of MO$_3$ as high temperature lubricants due to the so-called Magnéli phases formed from some layered MAX phases materials such as W$_2$BC or Mo$_2$BC in tribo-sliding \[4\]. From a material design point of view, our thermogravimetric analysis (TGA) results show a degrading temperature at around 560 °C for the pure WS$_2$ powder, which implies that the high-temperature tribological potential for WS$_2$ is far from being fully exploited.

**Figure 7.2** WS$_2$ platelets alignment originates from a fully amorphous high-carbon WS$_2$/a-C bulk coating.

**Figure 7.3** High-temperature tribological performance of WS$_2$/a-C coating from 100 °C to 500 °C: ultralow CoF obtainable up to a temperature of 500 °C in air.
Because WS$_2$ is a rather outstanding solid lubricant in vacuum or dry air environment, and at a temperature over 100 °C there is a release of water molecules. Thus, for the development of high-temperature solid lubricant servicing at least within the temperature range of 100-500 °C, WS$_2$ dominated coating would still be expected as a rather appropriate choice provided with suitable material design and process control. This method may be of advantages as compared with the MAX phases materials because MO$_3$ are only byproduct of TMD, where in TMD based coating the original TMD and later formed MO$_3$ phases may jointly achieve a more satisfactory high temperature triboperformance. In fact, we have already observed such expected tribological behavior as shown in Figure 7.1. It is further confirmed that at a temperature of 457 °C the WS$_2$ induced superlubricity may still play the predominated role (constant CoF around 0.02 comparable as that performed in dry air at room temperature).

(d) Self-healing of coatings at damaged spots and LFM nano-tribology

In Chapter 6, although we have achieved the self-healing functionality in the WS$_2$/a-C tribological coating, there are still some issues to be resolved, e.g. we still do not have a clue what is the limit of the damage size (width) that can be healed. It would be more intriguing in industrial applications if damages with mesoscale size (e.g. hundreds of micrometer to even several millimeters) could be healed. Cracks or scratches may often be formed parallel to the sliding direction rather than the pre-notch vertical to the sliding direction as in this study, which poses another challenge. Still, sliding flattens the asperity of the cauliflower-like coating into debris which later may transfer into tribofilm, obviously therefore the factors such as the coating surface roughness and loading pressure will definitely affect the healing process, which need to be clarified. In addition, it is also interesting to build up the relationship between the starting of healing process (damages being filled) with the friction and coefficient of friction. This is achievable via nano-tribology method where usually the Lateral force microscopy (LFM) tip slides over a pre-notch or crack at nano-scale to trace the on-going frictional signal against the in-situ healing process.

(e) Development of a really versatile chameleon coating

To meet the increasing demands of high-performance protective coating in highly severe services, the development of a new-generation versatile chameleon coating for a wide range of service applications such as in nano-micro tribology from room to elevated temperature, from vacuum to humid air and even corrosive conditions simultaneously should be placed on the research agenda. The current self-adaptive behavior is mainly limited in the humidity variations, namely the triboperformance is only reported reversible as humidity switches, but coating may lose their
functionality after high-temperature treatment. To achieve the reversible functionality in various conditions, a nanocomposite structure consisting of at least WS$_2$ part in association with many other elements such as a more potent matrix and some use of doping elements (e.g. Cr, Ti, Si, Pb) may provide some constructive avenues. Lastly, since the most ambitious result of the project is the real use of the coatings in industry, upscaling for industrial applications should also be considered.

References:


