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Směrem k povrchům s nulovým třením
Towards frictionless surface

Summary

Here we review the results on the tribological behavior of nanocomposite coatings composed of nanoplatelets of transition metal dichalcogenides (TMD) immersed in a C-rich amorphous matrix. It is shown that such a microstructure produces low friction coefficients under different operating conditions such as air humidity, contact pressure or temperature. Special attention is paid to the analysis of the worn surfaces after the tests. Nanoscale analysis of the wear track has revealed the formation of a thin tribolayer exclusively consisting of TMD platelets oriented to exhibit the lowest friction. In some cases, the depth reorientation of the originally randomly oriented TMD platelets as a reaction to the sliding process has been observed. This self-adaptation explains the low friction coefficient together with a high load-bearing capacity and a limited sensitivity to air humidity. Future perspectives for self-lubricant nanocomposite coatings based on the TMD-C concept are presented as well. Ultra-low friction W-S-N coating is briefly described; it shows identical tribolayer formation as TMD-C films. Finally, simulations of frictional behaviour of MoS_2 bilayer are shown.

Souhrn

V tomto pojednání shrneme tribologické chování nanokompozitních vrstev složených z molekulárních vrstev dichalkogenidů přechodových kovů (TMD) zabudovaných do uhlíkové matrice. Díky této specifické mikrostruktuře vrstvy dosahují nízkého součinitele tření v různých podmínkách jako je různá vlhkost vzduch, kontaktního tlaku či teploty. Zvláštní pozornost je věnována analýze povrchů po třecích testech, která odhalila tenký tribofilm výhradně složený z TMD fáze orientované tak, aby bylo dosaženo nejnižšího tření. V některých případech došlo k reorientaci původně náhodně orientovaných molekulárních vrstev TMD i hlouběji pod povrchem. Tato adaptace vysvětluje kombinaci nízkého třecího součinitele společně s vysokou nosností a minimální reakcí se vzdušnou vlhkostí. Průmyslový potenciál TMD-C nanokompozitních vrstev je rovněž stručně zmíněn. Poté jsou zmíněny amorfní W-S-N vrstvy, které dosahují ultra-nízkého třecího součinitele; tyto vrstvy vykázaly stejný mechanismus otěru a formování tribofilmu jako TMD-C vrstvy. Závěrem se věnujeme simulaci tření dvojvrstvy MoS_2.

Keywords: transition metal dichalcogenide; solid lubricant; thin film; magnetron sputtering; friction; tribology

Klíčová slova: dichalkogenidy přechodových kovů; pevný lubricant; tenká vrstva; magnetronové naprašování; tření; tribologie

Content

1 Solid lubricants

Friction is part of our everyday lives. We can use our fingers to estimate it. Everyone knows that friction should be high to avoid a slippery fall, or low to enjoy skiing, and we know that lubrication can significantly reduce friction. Friction and wear also have a significant impact on society. It is estimated that the energy required to overcome friction and its associated maintenance costs totals 5% of the GDP of an industrialised country. The majority of this energy comes from non-renewable sources. Friction is directly related to the dissipated energy, which is mostly transformed into heat, causing local structural surface changes, such as oxidation, and changing the mechanical properties of materials in contact. Moreover, high friction is typically related to extensive wear, meaning most materials cannot be used in dry sliding conditions. As such, all problems associated with friction and wear are surface-related phenomena. There are only two ways to reduce the friction of bulk materials – surface treatment or use of lubricants, the latter being the widely used, traditional solution. However, lubricants are mostly produced from fossil fuels, and oil additives often contain dangerous and toxic chemicals that have significant impact on the environment.

Furthermore, the wear of materials decreases their lifespan, which is associated with high production costs, extensive use of limited materials, and issues related to disposal and recycling. It is estimated that 16% of global fuel energy is wasted due to friction and wear – any improvement in this area immediately saves millions of tonnes of fuel and reduces the corresponding amount of CO2 released into atmosphere. Reducing friction and wear is therefore not just a way to save money, but also makes an important contribution towards a sustainable society. The friction coefficient of traditional engineering materials such as steels, alloys, or ceramics is typically much greater than 0.5 for dry sliding, but lower than 0.1 for lubricated sliding. Over the last few years, this has posed a continual technical challenge to R&D teams worldwide, to find surface treatment that reduces dry friction to, or even below, the level typical for lubricated contact while also improving wear resistance.

We will present here our recent results in the area of self-adaptive low and ultra-low friction solid lubricant coatings.

1.1 Fundamental properties of transition metal dichalcogenides

The lamellar crystal structure is found in many chemical substances, and several of these have lubricating properties, such as naturally occurring micas, talc and graphite or synthetically prepared compounds. However, many of them were found to be unsatisfactory for friction applications and many of those found satisfactory cannot be applied directly as solid lubricants.

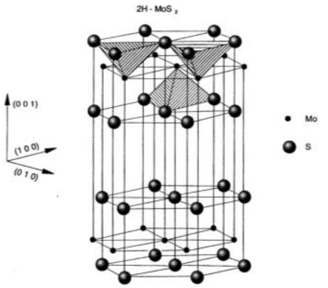

Fig. 1 Structure of MoS$_2$

Transition metal dichalcogenides (TMD) are, in many ways, a gift of the Nature to the mechanical engineers looking for friction reduction. TMDs exist in two crystal forms, hexagonal and rhombohedral. We will only deal here with the hexagonal structure, which is the most common and important for low-friction applications. The hexagonal crystal structure with six-fold symmetry, two molecules per unit cell, exhibits a laminar, or layer-lattice structure. Each chalcogenide atom is equidistant from three metal atoms, end each metal atom is equidistant from six dichalcogenide atoms. The attraction between the metal and dichalcogenide atoms is due to powerful covalent bonding; however, there is only weak Van der Waals attraction between the lattice layers (Fig. 1). TMD family (i.e. low-friction structures) consists of molybdenum, tungsten and niobium disulphides and diselenides.

To reduce friction, TMD is often used either as an oil additive or as a coating. The latter could be prepared as a thick film (e.g. burnished, films prepared by electrochemical processes, etc.) or a thin film deposited mainly by Physical Vapour Deposition (PVD) [1]. TMD could be formed as well during the sliding process on the surfaces in the contact by tribochemical reactions [2].

Recently, attention has been paid to fullerene-like TMD [3] and TMD nanotubes [4], both as additives and films. However, despite several successful laboratory tests, their industrial applicability is still very limited.

Thanks to its unique highly anisotropic crystal structure, TMD could behave as an excellent solid lubricant, i.e. a material with friction lower than 0.01. Martin et al [5] reported MoS_2 film deposited and tested in UHV conditions with friction coefficient as low as 0.001. In fact, they observed "loss" of friction in several cases confirming the theoretical prediction [6] of the frictional anisotropy of the friction-oriented sulphur basal planes of MoS_2 grains [5]. To achieve such low friction, the adhesive forces between MoS_2 and the solid substrates must be higher than the weak attractive forces between lamellae; consequently, the slip occurs preferentially between the lamellae and the friction coefficient is very low.

1.2 Drawbacks of TMD solid lubricant films

Friction lower than 0.001 is not necessary for mechanical applications; even a two orders of magnitude higher friction would be sufficient in many applications. Why is it so difficult to use pure TMD films deposited by conventional magnetron sputtering in terrestrial atmosphere?

I. Deposition of TMD by magnetron sputtering leads inevitably to a disordered structure. The low-friction prominent orientation, (0002), cannot be achieved except for a very thin film not exceeding tens of nanometers.

II. TMD films are extremely sensitive to environmental attacks. When sliding in air, a very likely reaction is their oxidation producing metal oxides. The presence of WO_{3-x} and MO_{3-x} oxides increases the friction, although there is still controversy in the estimation of how detrimental such oxides are. Nevertheless, the reactive prismatic edges on the (1120) face are more prone to chemical attack than the inert (0002) van der Waals basal plane [7]. Therefore, well oriented TMD with basal planes parallel to the surface resists oxidation better. Another issue related to environment is the storage of the films. It has been documented that TMD deteriorates when stored in the presence of oxygen and, particularly, water vapor. Diselenides are less sensitive to water than disulfides [8].

III. The hardness of TMD is very low compared to other competitive low-friction coatings, such as diamond-like carbon (DLC). It is typically in the range of 0.3 to 2 GPa depending on the stoichiometry, morphology, and deposition conditions. The adhesion to steel substrates could be improved by a thin metallic interlayer, typically Ti or Cr; however, it is still limited. Consequently, the load-bearing capacity is very low and TMD coatings peel off the substrate under high contact pressures.

Various countermeasures have been applied to remedy the above referred limitations. The reduction of water in the residual chamber atmosphere to diminish the oxygen content in the film, the variation of the deposition temperature or the gas pressure and other approaches slightly improved the TMD tribological behavior. However, the main issues remained and pure sputtered TMDs are restricted to vacuum applications.

1.3 Doping and alloying of TMD with metals and non-metallic elements

The first attempts to modify TMD films by alloying were aimed to increase density and consequently reduce porosity, improve adhesion and significantly increase of the hardness. In general, the aims have been achieved. Among many metals for alloying (Ti, Al, Au, Pb, Ni, Cr), titanium was probably the most successful from the commercial point of view (MOST® by Teer, Ltd., i.e. MoS_2 alloyed with Ti [9]). The improvement of the mechanical properties was evident; however, Ti addition could explain the increase in the wear resistance and the load-bearing capacity but not the fact that low friction was observed. It has been speculated that Ti reduced the oxidation of TMD films by i) a getter effect during the deposition and ii) preferential oxidation of the film compared to the TMD [9]. However, new results do not support such hypothesis, and the alloying with "inert" metals, such as Au, resulted in similar sliding properties.

All films referred to above show two general features: prevalence of the TMD phase (maximum content of alloying is about 20 at.%) and limited interaction between the TMD phase and the alloying element. TMD coatings alloyed with non-metallic elements usually show a higher non-TMD content; moreover, alloying elements might react either with the transition metals or the dichalcogenides. A typical example is nitrogen forming tungsten nitride, niobium forming NbS_2, or carbon producing tungsten carbides [10,11]. We will focus here mainly on the most analyzed TMD film alloyed with carbon.

In the late nineties, a new concept of coatings based on the alloying of transition metal dichalcogenides (TMDs) with carbon started to attract the attention of several scientific groups. The original idea was to combine the excellent frictional behavior of TMDs in vacuum and dry air with the tribological properties of DLC coatings. Moreover, an increase in the coating compactness in relation to TMD and an improvement in the mechanical properties, particularly the hardness, was expected (Fig. 2). Zabinski et al [10] prepared W-S-C coatings either by magnetron-assisted pulsed laser deposition (MSPLD – target WS_2) or by laser ablation of a composite target made of graphite and WS_2 sectors.

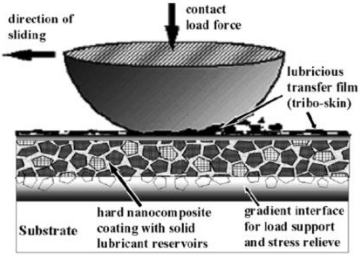

Fig. 2 Structural design of nanocomposite solid lubricant coatings proposed in Ref. [10]

The friction coefficient in dry air was lower than the one measured in humid air (0.02 and 0.15, respectively) and the so-called “chameleon behaviour” observed during environmental cycling was considered as the most interesting feature. The low friction in dry air increased in the presence of humid air and was reduced when the atmosphere was dried again.

W-S-C coatings prepared by magnetron sputtering have been intensively studied by Cavaleiro et al. In a first set of studies, W-S-C films were deposited by sputtering from a WS_2 target in a CH_4-containing reactive atmosphere. The flow of CH_4 and the target power were varied to prepare a large range of chemical compositions from pure WS_2 to W-S-C with carbon contents up to 70 at.%; the S/W ratio was about 1.2. The main disadvantage of TMD films, the detrimental effect of the humid air, was not overcome and the friction in these conditions was relatively high whatever the carbon content was [12]. However, the rapid film failure typical of pure tungsten disulphide was not observed and the coating wear rate was quite low, result attributed to the significant increase of the hardness, from 0.5 GPa (WS_2) up to ~10 GPa, achieved by incorporating carbon.

The analysis of the microstructure of the reactive deposited W-S-C coatings allowed us conclude that, for high carbon content, they were formed of a mixture of nanocrystals of WS_2 phase side by side with nanocrystals of W-C phases and small C-based amorphous zones or just by WS_2 nanograins dispersed in an amorphous carbon matrix (low carbon content). A similar behavior was observed elsewhere for WS_2/DLC/WC coatings showing a huge friction coefficient difference when sliding in humid or dry air [10,11]; the friction behavior was attributed to the alternative formation of a WS_2-rich or a C-rich layer during the cyclic change of the environment from dry to humid, respectively. Another concept presented in the literature for the TMD+C composite coatings deals with nanolayered structured coatings with tungsten disulphide and carbon layers (the thickness of layers is in the nanometer scale). The performance of these films was only moderate.

All these three different coating microstructures schematically shown in Fig. 3 proved to be unsatisfactory for reducing the friction coefficient in humid air sliding conditions. The multilayer films are vulnerable to cohesion damage, since the interlayer sliding could occur in the interior of the film where the shear stresses are larger than at the surface. This problem could be partially solved by thinning layers down to nanometer thicknesses; however, such a nanolayered structure is difficult to achieve in typical industrial substrates with standard surface roughness.

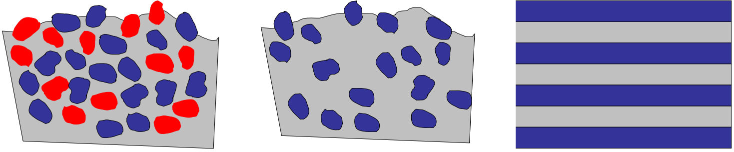

Fig. 3 Schematic view of previous W-S-C films designs: left - Nanocomposite coatings with hard WC nanoparticles (red) embedded together with WS_2 nanograins (blue) in an amorphous carbon matrix (grey); center - nanograins of WS_2 in an a-C matrix (center); right - nanolayered WS_2+C layers film

On the other hand, the other two microstructures could not simultaneously guarantee that either the TMD nanocrystals could be re-oriented with the basal planes parallel to the sliding distance or the oxidation of the dangling bonds would not occur. In fact, during the re-orientation process the extremities of the grains will be directly in contact with the atmosphere and therefore be immediately oxidized.

It has been obvious that a new concept is required for a modern low-friction universal coating exhibiting high wear resistance, load-bearing capacity and, particularly, low friction in various sliding environments (vacuum/dry air or nitrogen/humid air; elevated temperature, etc.). This paper summarizes recent research in the area of nanocomposite TMD-C coatings, their deposition, structural and mechanical characterization, and tribological properties.

2 New concept of coating microstructure based on TMD-C system

2.1 Approach

The basis for producing a low friction coating in a great variety of environments could be envisaged as a micro(nano)structure where TMD nanocrystals could be deposited completely enclosed within a protective C-rich matrix. If possible, these nanocrystals should have shapes that allow an easy reorientation of the basal planes parallel to the sliding direction. The carbon matrix will contribute to improving the hardness and the compactness of the coatings as well as protecting the TMD crystals from oxidation until the moment that they are completely aligned and risen the contact surface. For its part, TMD should assure the low friction coefficients, due to the easy sliding of the basal planes, and only a few strong bonds, promoted by the oxygen, should exist. In parallel with this approach, the use of other types of TMDs with less sensibility to oxidation than tungsten and molybdenum disulphides, such as $MoSe_2$ [8], should also be envisaged, since the carbon matrix could improve their very low hardness and mechanical properties.

During sliding in pin-on-disk testing, strong shear stresses arise which could contribute to the re-orientation of the TMD crystals in the C-based amorphous matrix. However, during the alignment of the TMD nanocrystals parallel to the sliding direction, the dangling bonds of the end planes are exposed to the atmosphere and oxidized, leading to a consequent increase in friction. In pure TMD coatings, the porous structure and very low hardness give rise to a very high wear rate. Therefore, as generally accepted in the wear models, it is expected that the worn out TMD material adheres to both surfaces in the contact and is also subjected to the high stresses developed there. This tribolayer is very thin (nanometer scale) with the TMD phase highly oriented, mainly with the basal planes parallel to film surface [13].

The problems referred to above could be avoided if the crystals were already aligned in the material, since in this case almost no dangling bonds would be available for the reaction [7]. Thus, it was decided to prepare TMD-C films with very small nanograins of the TMD phase (reduced, if possible, to one cell of TMD), since small grain size could more easily promote the re-orientation of the TMD phase inside the carbon matrix.

2.2 TMD-C coating deposition

Deposition by co-sputtering from TMD and C sources, either from separate targets or by a combined target with both materials was chosen in order to produce coatings containing simultaneously C and the TMD phase with a new microstructure different from that achieved in reactive deposited coatings. The TMD-C coatings were deposited with a carbon content in the range 25-70 at.%. Since the best tribological properties were achieved for a carbon content of approximately 50 at.%, we selected films with this composition to be presented in this paper. The deposition conditions, chemical composition and hardness of the films are shown in Table 1. It is clear that alloying with carbon significantly improves the hardness, since that of pure sputtered TMD films was lower than 0.5 GPa. X-ray diffraction and Raman spectroscopy undoubtedly confirmed the presence of the TMD and the C phases [14,15,16]. The XRD peaks representing the TMD phases were very broad indicating very small dimensions of the TMD phase exhibiting mixture of (002), (10L; L = 1,2,3...), and (110) orientations. TMD peaks observed in Raman spectra were very broad compared to bulk TMD, which was related to a high degree of

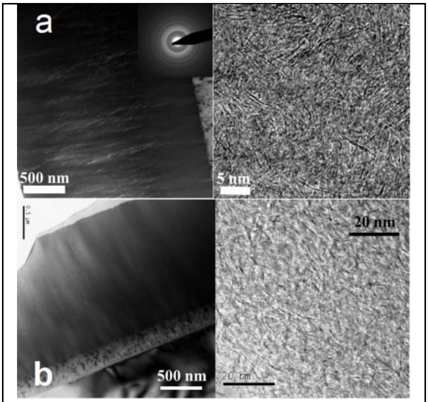

Fig. 4 TEM images of W-S-C (a) and Mo-Se-C (b) co-sputtered films deposited with ~ 50 at.% C. Note separated TMD platelets (right).

structural disorder. Finally, the Mo-Se-C and W-S-C films with ~50 at.% C were analyzed by HR-TEM technique. The nanostructure was quite different from the reactive deposited C+TMD films particularly regarding the TMD crystals, i.e. randomly oriented TMD platelets with only a couple of stacked basal planes can be observed (Fig. 4). The platelets are completely enclosed within the C-matrix [17,18].

2.3 Friction and wear performance

TMD-C coatings were intensively tested under different conditions, such as relative air humidity (RH from dry air to 90%) [19,20], load (pin-on-disc: 5 to 48 N; reciprocating ball-on-disc: 20 to 1000 N) [15,21,23], sliding speed (from 10 to 1000 $mm.s^{-1}$) [15,23], temperature (from room temperature to 500 ^{o}C; only W-S-C and Mo-Se-C were tested) [14,20], and test duration (from several cycles to one million) [18]. In all tests, the wear of the counterbody was very low; the ball wear scars were typically covered by transfer layer of coating material as referred to above.

The detrimental effect of air humidity on the friction coefficient was decreased compared to pure TMDs; however, the coatings are still sensitive to air humidity. The friction coefficient in dry nitrogen is in the range 0.01-0.08, whereas values from 0.10 up to 0.25 were measured in humid air (RH ~ 50%). In general, the friction coefficient of Mo-based films was lower than that of W-based. However, the increase in the friction coefficient was not followed by rapid coating destruction, since the wear rate was relatively low. The coatings based on diselenides exhibited lower friction in humid air.

When the test temperature was increased, the friction dropped to a very low level, typically about 0.02 lower than the friction measured in dry air. In our previous study, we suggested that the higher temperature facilitated the slipping of the weakly bonded TMD basal planes [14]. However, it might be possible that residual air humidity during tests in dry air was high enough to affect the friction, since complete absence of humidity is expected when the test temperature exceeds 100 ºC. W-S-C coatings survived the tests at 400 °C, whereas Mo-Se-C films were worn out at 300 °C. Nevertheless, the functional temperature limit for TMD-C is low, since the wear increased considerably with the temperature.

The main drawback of pure sputtered TMD coating is the low load-bearing capacity. On the other hand, their friction decreases with increasing contact pressure and working in high-load conditions would further reduce the loss of energy due to friction. Fig. 5 shows that the friction of TMD-C coatings decreases with the applied load and, thus, deviates from Amonton's law. For pure TMD films, it has been shown that the friction could be calculated using the formula for shear stress of solids at high pressures, where the contact pressure is calculated from the ideal Hertz contact model; however, such formula is not applicable to TMD-C.

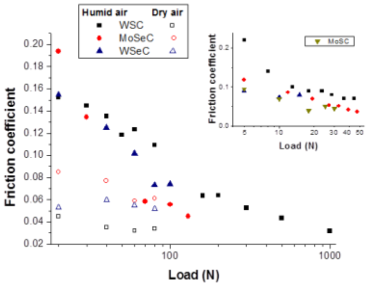

Fig. 5 Friction coefficient of TMD-C coatings as a function of the applied load in dry and humid air (relative humidity 50%).

The evolution of the friction could be approximated to a power law fit. The progressive decrease in the friction coefficient with increasing applied load suggests that the sliding process is driven by the TMD phases in the contact (such decrease is typical of TMD [22]), since pure carbon films, identical to the amorphous carbon matrix of these coatings, exhibit a slight increase in the friction with load [17]. It is also important to remark that a similar behavior is found under dry sliding conditions, although with a much lower starting value (~0.08 against ~0.20 for a 20 N load).

The evolution of the friction coefficient during the sliding process largely depends on the contact conditions. Typically, the initial friction is relatively high and drops to a low level after a short running-in process. When the contact pressure is higher, the running-in is shorter. However, we observed that the low friction level reached after several tens of laps was not a typical steady state sliding. There is a steep decrease in the friction coefficient in the first thousands of cycles and it is possible to reach a steady state value (~ 0.05), close to 100,000 cycles, which is not far from the lowest value for these coatings when tested with much higher loads. Such an observation is supported by the evolution of the friction coefficient as a function of the number of cycles for a W-S-C coating tested by changing the humidity in the atmosphere every 10,000 cycles [23]. Besides the progressive approach between the friction values in both dry and humid environments with increasing test duration, in both cases a decreasing trend in each step can also be observed.

In conclusion, low friction coefficients can be achieved in any environment providing that sufficient contact pressure or long test duration is used.

2.4 Evidence of the sliding mechanism

The progressive way in which the formation of the TMD tribolayer occurs can be demonstrated experimentally by the analysis of the top surface of the sliding track after wear testing. Fig. 6 shows the Raman spectra of TMD-C films obtained after tribological tests carried out with either the same number of cycles but different loads or the same load but a different number of cycles. It is clear that the increase in the load, and/or the number of cycles, gives rise to a more intense signal in the bands assigned to the TMD phase in comparison to those of the C-based material (G and D bands). This result confirms an increasing agglomeration of TMD material close to the contact zone.

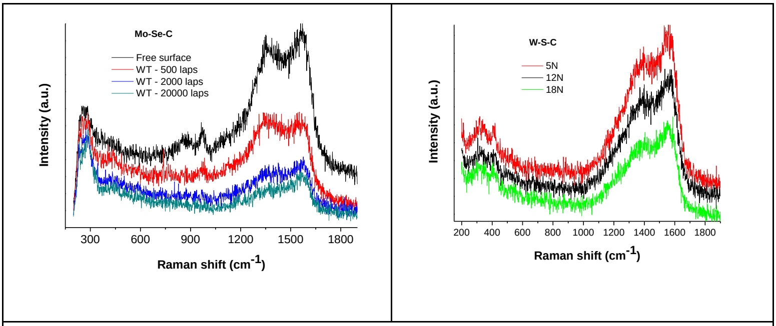

Fig. 6 Raman spectra taken from the center of the wear track as a function of the test duration (left) and applied load (right).

Auger spectroscopy (AES) chemical depth profiles show the thickening of the surface TMD tribolayer when the contact pressure and/or number of laps (i.e. test duration) is increased [17,18]. The absence of the C-signal on the top layer suggests that this is formed almost exclusively from the TMD phase. However, the agglomeration of the TMD material in the contact zone should only lead to the reduction of the friction coefficient providing that its basal planes are aligned parallel to the surface and no abundant oxidation occurs that can lead to strong bonding between them. It is, therefore, also important to note the absence of O in this top layer (compared to the residual signal of the material underneath) stating that the formation of the tribolayer is achieved in a protective way, without the oxidation of the dangling bonds of the original short TMD platelets.

The microstructural observation of the cross section of the top layer of the wear track by HR-TEM (high-resolution transmission electron microscopy) reveals platelets of TMD aligned parallel to the surface covering most of the zones which were analyzed, see Fig. 7.

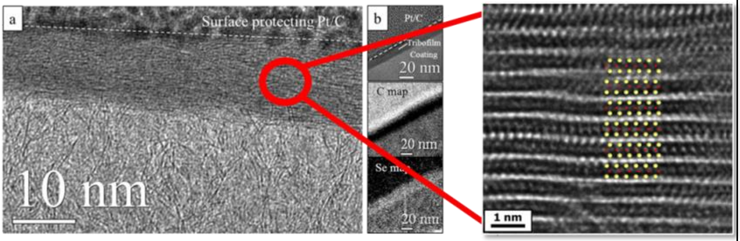

Fig. 7 Tribofilm formed on the surface of the wear track, MoSeC coating. High magnification image shows well ordered $MoSe_2$.

Furthermore, in the same micrograph it is shown that as the analysis is being moved to the interior of the film, the alignment is less and less evident. The observation of a great number of micrographs of different zones of the wear track [18] indicated that the reorientation of the TMD platelets is done progressively from some tens of nanometers until the track surface. Almost all the platelets are orientated parallel to the surface in the first 5 nm top layer. Moreover, the platelets were re-oriented even in the deeper part of the coating; on the other hand, the number of well oriented platelets with basal planes parallel to the surface decreases with increasing distance from the surface.

3 Future perspectives of TDM-C coatings

The initial coating microstructure, the formation of a thin TMD tribolayer and the re-orientation of the TMD platelets inside the carbon matrix benefit the low friction behaviour of the TMD-C coatings. The TMD platelets inside the carbon matrix are protected against environmental attacks; the coating is much denser compared to pure sputtered TMD films. The tribolayer, i.e. the outermost surface of the wear track, exhibited a (002) orientation, which is optimal for low friction and oxidation resistance. Moreover, the tribolayer was very thin (several monolayers) limiting coating wear. The sub-surface re-orientation inside the carbon matrix keeps the friction low and stable. When the top TMD tribolayer is worn out, the carbon matrix is worn out quickly revealing well oriented TMD platelets. However, two fundamental questions emerge: the role of carbon in the sliding process and the platelet re-orientation mechanism inside the carbon matrix.

In WS_2/DLC/WC coating, Wu et al demonstrated using Raman spectroscopy the existence of a graphitic layer in the wear track when the tribotest was carried out in humid air, whereas the peaks of WS_2 were measured after tribotesting in dry nitrogen [24]. We also observed graphitic carbon using Raman spectroscopy; however, it was found in the free detached wear debris on the sides of the wear track. The graphitic carbon was mixed with well-ordered TMD (in this case, we tested three systems: Mo-Se-C, W-S-C, and Mo-S-C [20,23]). Very small spots of adhered layers were also found in the wear tracks with similar features (i.e. sharp peaks of TMD and graphitic carbon); nevertheless, the coverage of the wear tracks by these spots varied from zero (i.e. they were not found) to approx. 5% and thus they cannot play a dominant role in the sliding process. Based on the AES and TEM analyses, we suggest that the worn carbon is immediately released from the contact; the friction is predominantly driven by the properties of the TMD tribolayer. This behavior is supported by the decrease in friction with increasing contact pressure, typical for TMD; we showed that the carbon matrix (i.e. the carbon films deposited from the carbon target using identical deposition parameters) followed the Amonton law [17], confirming that the achieving of the low friction coefficient should be attributed to the TMD phase.

Before any discussion about the feasibility of subsurface re-orientation, we should confirm that such a process is genuine. The formation of a tribolayer for TMD or DLC coatings is typically described as the detachment of worn coating particles and their agglomeration in the contact. They could form an adhered layer on the counterpart or act as a third body between the surfaces in the contact [25]. Thus, we have to analyze whether the re-oriented TMD layer is newly formed material made of worn particles or the result of sub-surface reorientation. Raman spectroscopy provides the best evidence to support latter hypothesis. Raman results showed a huge difference between the free wear debris and the surface of the wear track. If the tribolayer were be formed from the worn particles graphitic carbon should be easily identified, but it was not observed. Moreover, the gradual decrease in the TMD ordering in the approximately hundred of nanometers and the absence of any interface in the coating separating the as-deposited film and the transformed surface layer further support the conjectured re-orientation of the TMD platelets inside the carbon matrix. Although there is a strong indication of sub-surface re-orientation, the exact mechanism is not known.

In general, the presented TMD-C coatings exhibit excellent load-bearing capacity and low friction in humid air. We believe that the self-adaptation of the coating microstructure as a reaction to the sliding process is vital to achieve desired tribological properties and should be considered when new self-lubricant TMD-based films are designed. In recent year we up-scaled the deposition process of W-S-C coatings from laboratory deposition device to an industrial-size machine. We collaborate with number of companies to prove validity of the concept in an engineering practice. Some examples of coated parts are shown in Fig. 8.

Fig. 8 Examples of coated parts for automotive industry

4 Ultra-low friction W-S-N amorphous films

Doping of the coatings with nitrogen was another promising route to adjust coating microstructure. Deposited W-S-N coatings were amorphous with a hardness of 7.7 GPa. Sliding tests exhibited extremely low friction coefficient in dry air and dry nitrogen; the friction was below 0.003, which is detection limit of the tribometer. The wear resistance was outstanding, since the coatings were not worn through even after 2 million laps. Analysis of the wear track surface and ball wear scars again indicated presence of well-ordered WS_2 tribolayer as shown in Fig. 9. The material below the thin aligned easy-shear layer transformed from amorphous to self-ordered WS_2 platelets. This layer was supported by the remaining underlying hard amorphous W-S-N matrix, which keeped the area of real contact low and provided the firm support that allowed the outermost basal planes to become ideally aligned during sliding.

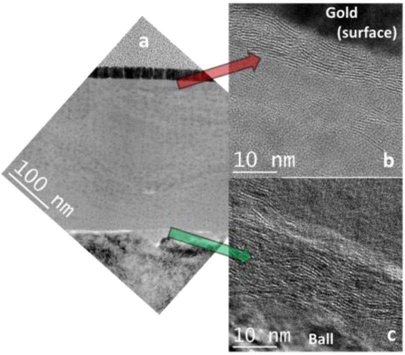

Fig. 9 Formation of a thin WS_2 tribolayer on ball surface tested against W-S-N coating.

The formation of a well-oriented self-lubricating phase further improves the low-friction behaviour, by being capable of immediately replenishing the worn contact layer. Moreover, the coating exhibits a remarkable damage recovery providing low friction despite coating delamination over large areas. This demonstrates that structures with self-adaptability, such as this amorphous W-S-N film, may offer friction levels almost one order magnitude lower than that of TMD-based sputtered films, TMD nanotubes or fullerene-like nanoparticles. Our results show that coatings with friction coefficients close to the intrinsic value for a WS_2 crystal could be prepared by a simple and robust process, which can be directly used in many engineering applications. Alloying tungsten disulphide with nitrogen is thus shown to be a promising way to achieve amorphous, extremely wear resistant coatings capable of providing ultralow friction.

5 Simulations of the frictional properties of TMD

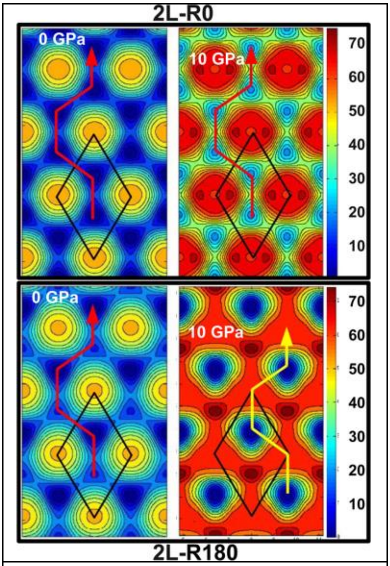

Fig. 10 PES for the sliding motion of MoS2 bilayers in the R0 (upper row) and R180 (lower row) configurations at zero load (left column) and at 10 GPa load (right column). Unit cells (black lines) and minimum energy paths (red/yellow lines) are reported for completeness. The color scale refers to the energy range of the PES corrugation (in meV) and is reported on the right.

Low friction of TMD-C and W-S-N coatings is due to a formation of a thin TMD tribolayer on surfaces in a contact. To understand behaviour of such thin layer, theoretical approach is required. Ab initio (density functional theory) and molecular dynamics have been selected as appropriate tools to answer following questions:

I. What is frictional behavior of TMD?

II. What is the role of oxidation?

II. What is the role of water molecules?

IV. What is the role of doping elements in the contact?

We started with simulation of frictional properties of MoS_2 bi- and trilayer. By means of ab initio modeling of the static potential energy surface and charge distribution analysis, we demonstrated how electrostatic interactions, negligible in comparison with van der Waals and Pauli contributions at zero load, progressively affected the sliding motion at increasing loads [26]. As such, they discriminated the relative stability and the frictional behavior of bilayers where the two monolayers defining the interface had a different relative orientation. In particular, for antiparallel sliding layers we observed a load-induced increase of both the depth of the minima and the height of the energy barriers compared to parallel ones. Potential energy surfaces (PES) were almost identical for different configurations at zero load; however, they were dissimilar at contact pressure 10 GPa, see Fig. 10.

Fabrication and characterization of TMD-C coatings

The W-S-C and Mo-Se-C coatings were deposited on steel substrates (chromium steel, quenched and tempered with a final hardness of 62 HRC) polished to a final roughness, Ra ≤ 30 nm. A two planar cathodes Edwards E306 machine with a 20 dm^3 chamber was used for the depositions. A rotating substrate holder placed 60 mm from the cathodes allowed the substrates to be placed over one or another cathode for depositing the titanium interlayer or the W-S-C or Mo-Se-C films, respectively. The Ti thin interlayer (~ 300nm) was deposited in order to improve the adhesion of the coatings to the substrate. The coatings were deposited by r.f. magnetron sputtering in an argon atmosphere from a graphite (99.999% purity) target with pellets of WS_2 or $MoSe_2$. The pellets (99.8% pure) were positioned in the erosion zone of the 100 mm diameter graphite target (hereinafter denominated “composite target”). The dimensions of the pellets were 1.5 x 3 x 4 mm and their number varied between 16 and 72. The discharge pressure and the power density were 0.75 Pa and 8 $W.cm^{-2}$, respectively. Mo-S-C and W-Se-C films were deposited using two targets, WSe_2 or MoS_2 and graphite (i.e. the films were deposited directly on the substrate without Ti interlayer). The carbon content in the films was controlled through the number of the pellets or power applied to the C and TMD targets. W-S-N coatings were deposited by reactive magnetron sputtering of WS_2 target in Ar/N_2 atmosphere. No bias was applied to the substrate holder during the deposition (floating bias); the substrate temperature was about 200 °C. The deposition time was one hour.

The coatings microstructure was studied by X-ray diffraction (XRD) in glancing mode (Co Kα radiation) and by high resolution transmission electron microscopy (HRTEM); the chemical composition was determined by electron probe micro-analysis (EPMA) whereas the chemical bonding was accessed by Raman (Ar^+ laser, 514.5 nm wavelength) and X-ray photoelectron spectroscopies (XPS - Mg Kα radiation). The hardness (H) and Young’s modulus (E) of the coatings were evaluated by depth-sensing indentation (maximum indentation load of 50mN).

Wear testing was performed using pin-on-disc and reciprocating (SRV) tribometers adapted to work in a controlled atmosphere; the sliding partners were 100Cr6 steel balls with a diameter of 6 and 10 mm, respectively. The air humidity (RH) was controlled by a precise hygrometer (error 1%). The number of laps (pin-on-disc) or cycles (SRV) is stated in the text. The morphology of the coating surface, the ball scars, the wear tracks and the wear debris were examined by scanning electron microscopy (SEM) and Raman spectroscopy; the chemical analysis of the wear tracks and the wear debris was obtained by energy-dispersive X-ray analysis (EDS). The chemical depth profiles in the wear track were obtained by Auger electron spectroscopy (AES). The profiles of the wear tracks were measured by a mechanical or 3D optical profilometer. The wear rate of the coating was calculated as the worn material volume per sliding distance and normal load. The average value of three profiles measured on the same wear track was used to calculate the coating wear rate.

References

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[1] H. Waghray, T.-S. Lee, B. Tatarchuk, Surf. Coat. Technol. 76-77 (1995) 415
[2] C. Grossiord, K. Varlot, J. -M. Martin, Th. Le Mogne, C. Esnouf, K. Inoue, Tribol. Int. 31 (1998) 737
[3] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, Nature 387 (1997) 791
[4] M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Ceh, J. Demsar, P. Stadelmann, F. Levy, D. Mihailovic, Science 292 (2001) 479
[5] J.M. Martin, C. Donnet, Th. Le Monge, Th. Epicier, Phys Rev 48 (1993) 10583
[6] M. Hirato, K. Shinjo, R. Kaneko, Y. Murato, Phys. Rev. Lett. 67 (1991, 2634
[7] G. Salitra, G. Hodes, E. Klein, R. Tenne, Thin Solid Films 245 (1994) 180
[8] T. Kubart, **T. Polcar**, L. Kopecký, R. Novák, D. Nováková, Surf. Coat. Technol. 193 (2005) 230
[9] D. G. Teer, Wear 251 (2001) 1068.
[10] A.A. Voevodin, J.S. Zabinski, Thin Solid Films 370 (2000) 223

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[11] A. A. Voevodin and J. S. Zabinski, Comp. Sci. and Technol. 65 (2005) 741.

[12] A. Nossa, A. Cavaleiro, Tribology Letters 28 (2007) 59

[13] J. Moser, F. Lèvy, Thin Solid Films 228 (1993) 257

[14] **T. Polcar**, M. Evaristo, A. Cavaleiro, Vacuum, 81 (2007) 1439

[15] **T. Polcar**, M. Evaristo and A. Cavaleiro, Plasma Processes & Polymers, 2007, 4, S541

[16] **T. Polcar**, M. Evaristo, M. Stueber, A. Cavaleiro, Surf. Coat. Technol. 202 (2008) 2418

[17] **T. Polcar**, M. Evaristo, A. Cavaleiro, Plasma Processes & Polymers, 2009, 6, 417-424

[18] **T. Polcar**, M. Evaristo, R. Colaço, C. S. Sandu, A. Cavaleiro, Acta Mater 56 (2008) 5101

[19] M. Evaristo, **T. Polcar**, A. Cavaleiro, Int. J. Mech. Mat. Design 4 (2008) 137

[20] **T. Polcar**, M. Evaristo, M. Stueber, A. Cavaleiro, Wear 266 (2009) 393-397

[21] J.V. Pimentel, **T. Polcar**, A. Cavaleiro, Surf. Coat. Technol. 205 (2011) 3274–3279

[22] I. L. Singer, R. N. Bolster, J. Wegand, S. Fayeulle, B. C. Stupp, Appl. Phys. Lett. 1990, 57, 995

[23] **T. Polcar**, M. Evaristo, A. Cavaleiro, Wear 266 (2009) 388

[24] J. -H. Wu, M. Sanghavi, J. H. Sanders, A. A. Voevodin, J. S. Zabinski and D. A. Rigney, Wear 255 (2003) 859

[25] T.W Scharf and I.L. Singer, Third bodies and Tribochemicstry of DLC coatings, in: A. Erdemir, Ch. Donnet, Editors, Tribology of Diamond-lika carbon films, Springer, 2008, p. 201-236

[26] G. Levita, A. Cavaleiro, E. Molinari, **T. Polcar**, M.C. Righi, Journal of Physical Chemistry C 118 (2014) 13809–13816

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6 PhD students defended thesis (4 University of Coimbra, Portugal; 1 Czech Technical University in Prague; 1 University of Southampton).
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H index 15 according to Web of Science; 420 citations
12 invited lectures; 3x prize of the rector