Tribological behaviour of C-alloyed transition metal dichalcogenides (TMD) coatings in different environments

Manuel Evaristo · Tomas Polcar · Albano Cavaleiro

Abstract W-S-C films were deposited by non-reactive sputtering from a carbon target incrusted with WS_2 pellets in the eroded zone. This process allows depositing coatings with a wide range of compositions, with a precise control of their carbon content. Before the deposition, a Ti interlayer was interposed between the film and the substrate to improve the final adhesion. The carbon content in W-S-C system was varied from 29 at.% to 70 at.%, which led to an hardness enhancement from 4 GPa up to 10 GPa where the maximum hardness was reached in films with a carbon content between 40 at.% and 50 at.%. The tribological behaviour of the coatings was evaluated by pin-on-disk testing, in environments with different humidity levels. Generally, the tribological performance of W-S-C coatings in environments with moderate to high humidity is better for coatings with high carbon content. Friction coefficients, as 0.05 or lower could be reached at low humidity ranges (<7%) to all compositions. However, for higher humidity values, friction coefficient increased up to 0.30 in the W-S-C film with low carbon content whereas it was kept approximately constant for the others compositions.

Keywords C-TMD · Low friction · Self-lubricant · Wear behaviour · WS_2

1 Introduction

Transition metal dichalcogenides (TMD) have excellent self-lubricant properties in dry air or vacuum; however, these films are easily rusted in the presence of moist environments and their reduced mechanical resistance makes them inappropriate for applications requiring high loading bearing capacity. On the other hand, hard coatings are often employed to protect from abrasive and erosive wear; however, they do not have low friction and they are frequently brittle. Therefore, there is a need to design coatings combining low friction with high load bearing capacity; moreover, a good adhesion to the substrates is required. Recently (Voevodin et al. 1999) made use of the concept of nanocomposite structured coatings to reach very low friction coefficients in a large range of environments. Based on their previous experience with diamond like carbon (DLC) coatings, they co-deposited DLC with WS_2 using pulsed laser deposition. DLC is a very hard material (hardness from 10 GPa to 60 GPa) presenting very low friction coefficient in humid air. However, inversely to WS_2

M. Evaristo · T. Polcar · A. Cavaleiro (✉)
ICEMS – Departamento Engenharia Mecânica, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Rua Luís Reis Santos, Coimbra, 3030-078, Portugal
e-mail: albano.cavaleiro@dem.uc.pt

T. Polcar
Faculty of Transportation Sciences, Department of Applied Mathematics, CTU in Prague, Na Florenci 25, Prague 1, Czech Republic

coatings, the friction coefficient increases significantly when tested in moisture free environments. Thus, with a nanostructure consisting of nanocrystals of WS_2 and WC enclosed in an amorphous carbon matrix, values lower than 0.1 could be envisaged whatever the testing environment was. Our recent works (Nossa and Cavaleiro 2001, 2003) showed that the synergetic effect of doping W-S films with carbon or nitrogen together with the deposition of a Ti interlayer could give rise to significant improvements of the mechanical properties and the tribological behaviour, particularly in the case of films alloyed with carbon.

There are several ways to produce multi-element thin films by a non-reactive process; one of the most common is by co-sputtering form individual targets (Fox et al. 1999). However, among the drawbacks of this process is either the non-homogeneity in the coatings composition when stationary large substrates are used, or the formation of a multilayer structure if the substrates are rotated (Noshiro et al. 2006). Thus, it was decided to deposit W-S-C coatings by non-reactive magnetron sputtering from carbon target with pellets of WS_2 placed in the target erosion zone, in order to assure the homogeneity in the coatings composition. Furthermore, the chemical composition can also be easily controlled by changing the number of WS_2 pellets.

The objective of this work was the development of coatings capable of being used in a wide rage of applications, with different applied loads, temperatures and environments. In this study, the structural and mechanical properties of W-S-C coatings are presented, as well as their tribological behaviour is evaluated when sliding in a pin-on-disc tribometer in different environments.

2 Experimental details

All W-S-C coatings were deposited on 100Cr6 discs with a diameter of 36 mm and M2 polished steel samples with hardness close to 5 GPa and 9 GPa, respectively.

The depositions were carried out in a radio-frequency magnetron sputtering Edwards ESM 100 unit, equipped with two cathodes ($\varnothing = 100$ mm). Prior to the depositions the substrates were sputter cleaned during 20 min by establishing the plasma close to the substrates electrode. Immediately after, a Ti interlayer was deposited with an approximate thickness of 300 nm. The main sputtering target was pure carbon, partly covered by WS_2 pellets placed in the preferentially eroded zone. The dimensions of the pellets were $4.1 \times 3.5 \times 1.5$ mm. The degree of target coverage determined the overall chemical composition of the sputtered film. The depositions were carried out with constant power density of 7.6 W/cm^2 in the carbon target.

To evaluate the chemical composition of the films, a Cameca SX 50 electron probe microanalysis (EPMA, Cameca, France) apparatus was used. The hardness was determined by depth-sensing indentation technique using a Fisherscope H100; the coatings deposited on M2 steel were used for these measurements. The load was increased in steps (60) until a nominal load of 20 mN was reached, following the procedure indicated somewhere (Antunes et al. 2002).

The tribological tests were carried out with a pin-on-disk tribometer (CSM Instrument) on 100Cr6 samples. The linear speed was kept constant (20 mm s^{-1}), while the diameter varied from 12 mm to 16 mm. The 100Cr6 steel balls were used as sliding partners. The diameter of the ball was 6 mm, which together with the applied 5 N load gives the maximum Hertz contact pressure of ~ 0.7 GPa. The coatings tribological behaviour was evaluated in air with different humidity rate (5–70%). The friction coefficient reported in this study is the average value of the whole sliding test, unless stated otherwise. Each test was repeated three times; standard deviation of the average friction coefficient and the wear rate was lower than 10%. Standard number of laps during pin-on-disc measurement was 1500.

3 Results

Different carbon contents were achieved in the coatings by varying the number of WS_2 pellets in the C target. As it was expected, the carbon content of the films decreases with the increase of the total area of pellets, see Fig. 1; the decrease is almost linear. A closer analysis of the arrangement of the experimental points allows estimating the reproducibility of chemical composition. We deposited coatings with the area of pellets 260 and 1070 mm^2 (corresponding
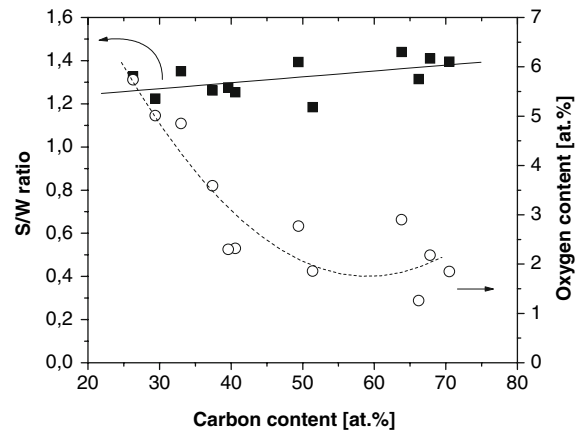
to composition of low and high carbon content) three times (always with new re-distribution of pellets), which allows estimating the reproducibility of the coating chemical composition. Considering the variation in the pellet distribution over the target erosion zone and the errors of measurements, it can be concluded that the used deposition process is quite reproducible.

The deposition rate rises up with increasing number of pellets, as may be expected due to the higher deposition rate of WS_2 compared to carbon (Fig. 1). However, after reaching a maximum for an area of pellets of 400–600 mm^2, the deposition rate started to decrease. This behaviour is difficult to explain, since the difference of the sputtering yield for the target and the pellets is usually considered as the main factor contributing to the increase/decrease of the deposition rate as a function of the pellets area (Yokomichi et al. 2002). Moreover, the densification of the coatings with increasing carbon content, as it will be shown later on, is as well in favour to the increase of the deposition rate with the pellets area. This matter requires further study, particularly with respect to the possible mutual interference of the pellets during the deposition process.

Figure 2 shows the decreasing content of oxygen in the coatings with their carbon content. It is not surprising, since WS_2 pellets exhibit a high porosity and affect the residual atmosphere in the deposition chamber. The variation of S/W ratio is negligible in the range 1.2–1.45; however, a slight increase can be observed, as demonstrated in Fig. 2. The sulphur
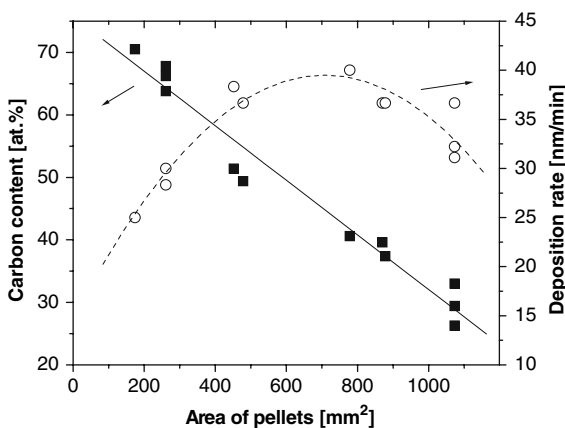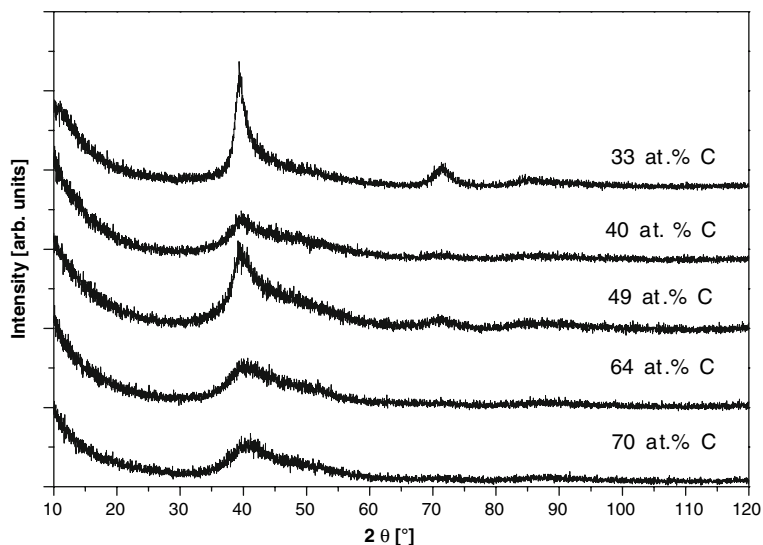

Fig. 2 S/W ratio and oxygen content as a function of carbon content in the coatings. The lines are guides to the eye

deficiency is probably caused by the re-sputtering of the sulphur atoms from the substrate and by the chemical reactions of sulphur with the residual atmosphere. It should be pointed out that the S/W ratio is lower than that of co-sputtering from two targets under similar conditions (~ 1.7) (Evaristo et al. 2005).

Figure 3 presents the X-ray diffraction patterns of W-S-C films with different chemical composition. With the increase of carbon in the coatings, a gradual loss of crystallinity is observed. The films with low carbon content presents the typical XRD patterns of Me–S (Me–transition metal) sputtered films with prominent peaks at $2\theta \approx 40°$ with an extended shoulder corresponding to a turbostrating stacking of (10L) planes (L = 0, 1, 2, 3), and $2\theta \approx 70°$ indexed as (110) plans. Weise et al. (1997) demonstrated that these XRD pattern could be explained by a 2D organization of the basal plans which could have several tenths of unit cells dimension. With the progressive decrease of the lateral dimensions of the basal plans, either broadening or drop in the intensity of the (10L) plan occurred until a unique low intensity and broad peak typical of an amorphous structure was detected. This situation would arise when the lateral order of the basal plans did not exceed a couple of lattice parameters. In previous work (Nossa et al. 2005), it was shown by HRTEM that W-S-C films with high C contents were formed by a nanocomposite structure with WS_2 grains with only some nanometers size, in agreement with Weise et al. interpretation.

Fig. 1 Carbon content and deposition rate as a function of the total area of WS_2 pellets. The lines are guides to the eye

Fig. 3 XRD patterns of W-S-C as a function of carbon content

Typical cross section morphology of the films deposited on Si wafers obtained by Scanning Electron Microscopy (SEM) can be observed in Fig. 4. As it would be expected, based on previous results with W-S-C films deposited by other procedures (Evaristo et al. 2005), more compact morphologies are reached with increasing C contents.

The hardness of W-S-C films increases with increasing carbon content, reaching a maximum at ∼40 at.% of carbon. This trend can be related to the increase of the compactness of the films associated with the possible formation of nano-sized carbide phases, intrinsically harder than tungsten disulphide. With the addition of more carbon to the films, there is no more W available to establish W-C bonds and the formation of carbon phases leads to a decrease of the hardness (see Fig. 5). However, the hardness of W-S-C coatings is generally about one order of magnitude higher than that of pure tungsten disulphide (Watanabe et al. 2004).

The evolution of the friction coefficient is almost identical for all coatings up to humidity level of 30%. The average friction coefficient in dry air (RH < 5%) is very low reaching values in the range 0.03–0.06. The tests in humid air exhibited similar increase of the friction value up to about 0.2 for a humidity rate of 40%. Above this value, difference in the coefficient can then be observed (Fig. 6). In general, the coatings with higher carbon content are much less sensitive to high level of humidity, showing even benefits from these conditions as it is demonstrated

by the small decrease in the friction. On the other hand, the coatings with high content of WS_2 behave similarly to pure transition metal dichalcogenide, showing the typical monotonous increase of the friction coefficient with increasing humidity rates.

In contrast to the friction coefficient, the wear rate of the coating with the highest carbon content (66 at.% C) significantly differs from the others when sliding in dry air (see Fig. 7). Moreover, the coatings with 33 and 37 at.% C exhibited the best wear resistance, even in humid air, with wear rates slightly increasing with humidity. The hardest coating (41 at.% C) showed the highest wear in humid air.

To explain the friction and wear behaviour, detailed analysis of either the friction curves or the wear tracks was performed. As documented in Fig. 8, the initial friction coefficient of the coating with 66 at.% C is very high during the first 25 turns and falls down abruptly to a steady-state regime at the lowest stabilised value. The coating with low carbon content reaches the steady-state more slowly, only after approximately 250 laps; nevertheless, its maximum initial friction coefficient is only 0.15 compared to the 0.65 obtained for 66 at.% C coating. The comparison of the wear tracks of both coatings shows fundamental differences. In the case of the coating with high carbon content it is full of large cracks and delaminations (Fig. 9b), while that of low carbon shows only shallow scratches parallel to the relative movement of the ball over the coating surface.
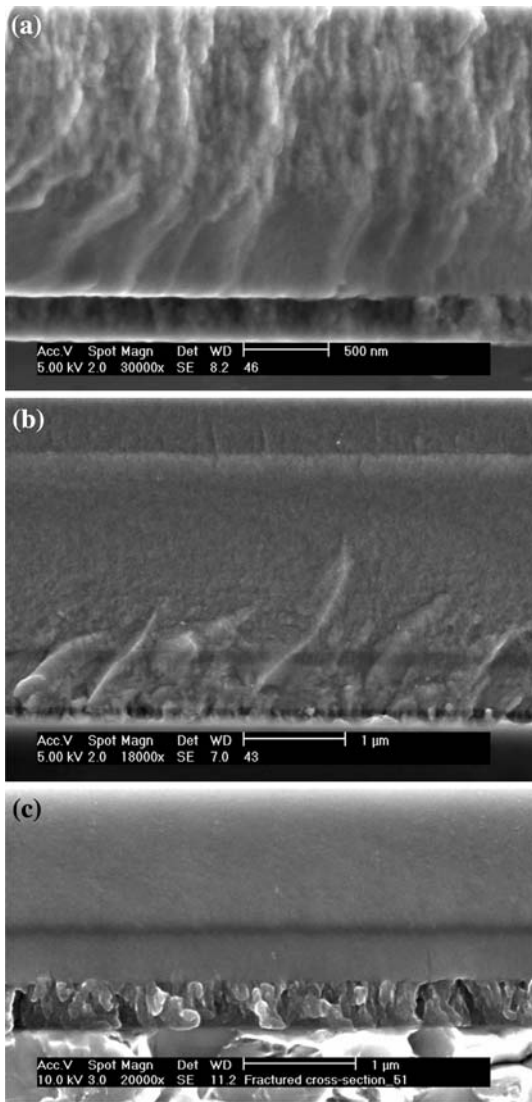
Fig. 4 SEM images of the cross-section of W-S-C films with different carbon contents. (**a**) 33 at.%; (**b**) 41 at.%; (**c**) 66 at.%

The question now is: does the wear rate of the high carbon coating arise from the very high initial friction? To shed some light on this subject, a short sliding test (number of laps was set to 50) in dry air was carried out with this coating. The worn volume of the coating after this short test was almost identical to that of the 1,500 laps test with the wear track exhibiting similar features. It seems that the tribological behaviour in dry air is particularly driven by the formation of a third-body between the surfaces in the contact by the transfer of the self-lubricant
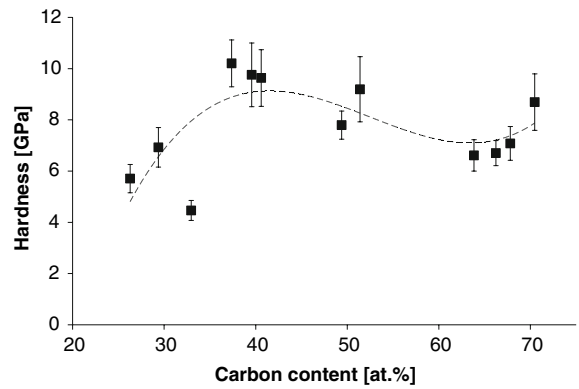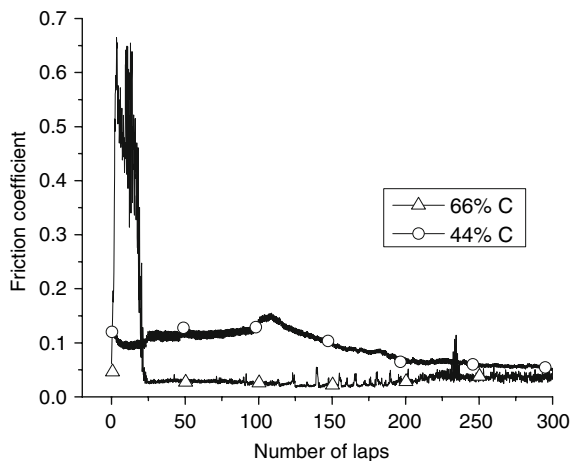

Fig. 5 Evolution of the hardness with the carbon content in the films. The line is a guide to the eye
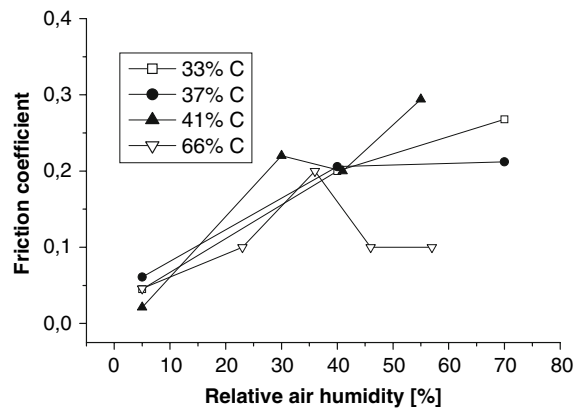
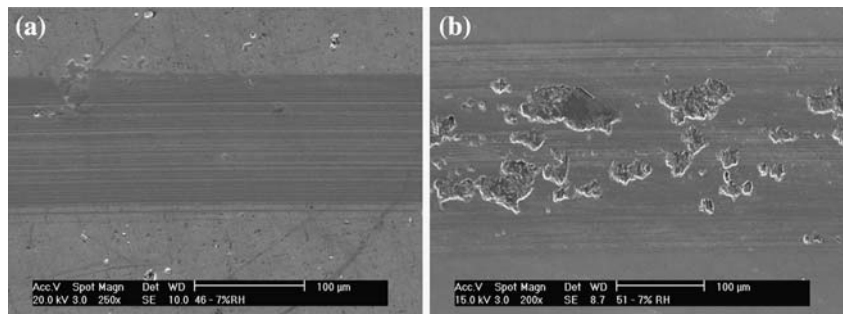**Fig. 6** Evolution of average friction coefficient with humidity
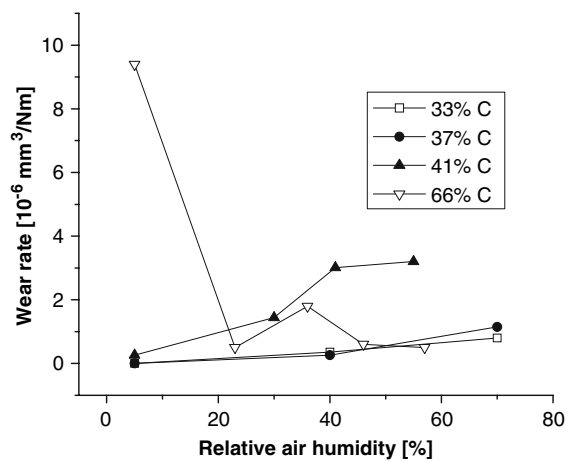
Fig. 7 Wear rate of coatings with different carbon content as a function of relative humidity of air
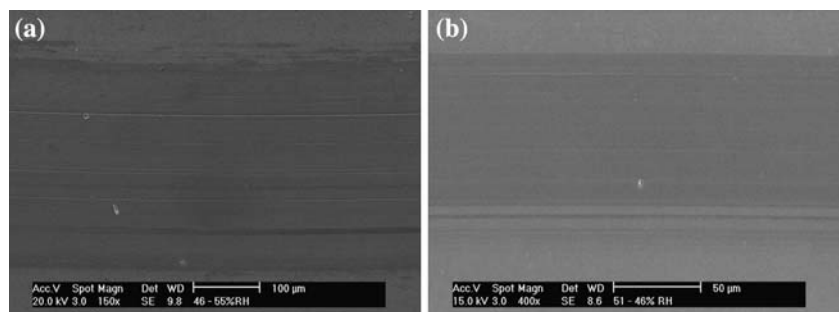
Fig. 8 Friction curves of W-S-C coatings sliding in dry air, first 300 cycles

surface. During this period a rapid release of a large quantity of material between the ball and the coating occurs, which facilitates the quick forming of the transfer layer of self-lubricant material on the ball surface. From that moment on, the friction rapidly falls down from the highest to the lowest value.

In the coating with low carbon content the high initial wear is much less. Since the worn volume is very limited, it takes more time to reach the steady-state regime. Immediately from the first contact moment, the WS_2 phase starts to influence the friction behaviour with a progressive and moderate decrease of the friction coefficient. We assume that the wear rate of low-carbon coating is as well higher during initial part of sliding tests, though the difference should be much lower compared to high-carbon coating. However, it is difficult to prove this hypothesis, since the wear rate of low-carbon content coating is very low for precise wear track profile measurements.

The values of wear rates of coatings with low and high carbon content sliding in humid air are almost equal. However, the wear tracks of low carbon content coatings exhibit scratches (Fig. 10), thus, the formation of hard large particles is possible.

material to the steel ball. When the third-body and transferred layer are formed, the steady-state wear regime takes place. With the high-carbon coating, in the beginning of the sliding test there is a limited self-lubricant WS_2 material available to form the third body. As a consequence, the initial friction force is very high causing severe damage to the coating

Fig. 9 SEM micrographs of the wear track, sliding in dry air, (**a**) coating with 33 and (**b**) coating with 66% of carbon content

Fig. 10 SEM micrographs of the wear tracks after sliding in humid air, (**a**) coating with 33 at.% of carbon (RH 40%), (**b**) coating with carbon content 66 at.% (RH 43%)

Moreover, the friction coefficient showed large variation during the test with low carbon content compared to very stable one of high carbon.

4 Conclusions

The W-S-C coatings were deposited by non-reactive magnetron sputtering from the carbon target with WS_2 pellets placed in the erosion zone. The carbon content linearly decreased with increasing area covered with the pellets, from 27 at.% to 70 at.%, while S/W ratio remained almost constant. The coatings exhibited hardness in the range 4–10 GPa; the maximum hardness was obtained in case of coating with 37 at.% of carbon content. The coatings with carbon content 37 and 41 at.% showed the best sliding properties in the dry and humid air.

References

Antunes, J. M., Cavaleiro, A., Menezes, L. F., Simões, M. I., Fernandes, J. V.: Ultra-microhardness testing procedure with Vickers indenter. Surf. Coat. Technol. **149**, 27–35 (2002)

Evaristo, M., Nossa, A., Cavaleiro, A.: W-S-C sputtered films: influence of the carbon alloying method on the mechanical properties. Surf. Coat. Technol. **200**, 1076–1079 (2005)

Fox, V. C., Renevier, N., Teer, D. G., Hampshire, J., Rigato, V.: The structure of tribologically improved MoS_2–metal composite coatings and their industrial applications. Surf. Coat. Technol. **116–119**, 492–497 (1999)

Noshiro, J., Watanabe, S., Sakurai, T., Miyake, S.: Friction properties of co-sputtered sulfide/DLC solid lubricant films. Surf. Coat. Technol. **200**, 5849–5854 (2006)

Nossa, A., Cavaleiro, A.: The influence of the addition of C and N on the wear behaviour of W-S-C/N coatings. Surf. Coat. Technol. **142–144**, 984–991 (2001)

Nossa, A., Cavaleiro A.: Mechanical behaviour of W–S–N and W–S–C sputtered coatings deposited with a Ti interlayer. Surf. Coat. Technol. **163–164**, 552–560 (2003)

Nossa, A., Cavaleiro, A., Carvalho, N. J.M., Kooi, B. J., De Hosson, J.Th.M.: On the microstructure of tungsten disulfide films alloyed with carbon and nitrogen. Thin Solid Films **484**, 389–395 (2005)

Voevodin, A.A., O'Neill, J.P., Zabinski, J.S.: Nanocomposite tribological coatings for aerospace applications. Surf. Coat. Technol. **116–119**, 36–45 (1999)

Watanabe, S., Noshiro, J., Miyake, S.: Tribological characteristics of WS_2/MoS_2 solid lubricating multilayer films. Surf. Coat. Technol. **183**, 347–351 (2004)

Weise, G., Mattern, N., Herman, H., Teresiak, A., Bascher, I., Bruckner, W., Bauer, H.-D., Vinzelberg, H., Reiss, G., Kreissig, U., Mader, M., Markschlager, P.: Preparation, structure and properties of MoS_x films. Thin Solid Films **298**, 98–106 (1997)

Yokomichi, H., Funakawa, T., Masuda, A.: Preparation of boron–carbon–nitrogen thin films by magnetron sputtering. Vacuum **66**, 245–249 (2002)