

NANOCOMPOSITE COATINGS OF CARBON-BASED AND TRANSITION METAL DICHALCOGENIDES PHASES: A REVIEW

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Received: January 22, 2007

Abstract. The results obtained at Instituto de Ciências e Engenharia de Materiais e Superfícies-ICEMS on the development of W-S-C coatings are reviewed and compared with literature data on the same system. The coatings have been deposited by r.f. magnetron sputtering using several approaches including reactive and co-sputtering processes. The chemical composition, structure and morphology of the coatings were analyzed and correlated with the mechanical properties. A complete detailed tribological characterization was performed by pin-on-disk tests varying the applied load, the humidity ratio and the temperature.

The most important result achieved was the significant increase in the hardness with C addition that allows expecting a higher loading bearing capacity. From the tribological point of view, the coatings with C content close to 40 at.% showed a remarkable thermal stability up to 400 °C, with friction coefficients lower than 0.05 and 0.1 in dry and room environments, respectively.

1. INTRODUCTION

The great advantage of solid lubricants is the possibility to be used in environments where oil lubrication is prohibited as the vacuum applications or the sliding contacts where the presence of contaminants must be avoided, such as in food industry. Furthermore in last years European Union has emanated restrict directives for the use of environment harmful products which is the case of most of the liquid lubricants. Thus, the development of self lubricating materials has increased exponentially in last decades with the main scope of reducing or even eliminating the use of synthetic oil lubrication.

As wear and friction are surface phenomena, it is not surprising that a great part of the research

work on self lubricating materials was dedicated to thin coatings. Among the different alternatives which have been suggested, transition metal dichalcogenides (TMD) have been adopted by several research groups for studying. Therefore, several TMDs were analysed although the main focus had been pointed on MoS₂. However, it was shown that for some particular applications WS₂ could be advantageous since its thermal resistance in oxidant atmospheres outstands that of MoS₂ in more 100 °C and its oxide, WO₃, has lower friction coefficient and is more protective than MoO₃ [1,2]. In comparison to their competitors, such as C-based coatings, particularly those known as diamond like carbon (DLC), TMDs have the advantages of presenting extremely low friction coefficients in vacuum or dry environments and a better tribological per-

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formance at high temperatures (<400 °C). The main drawbacks of TMDs, which has been the most important reason for their limited application in many situations where low friction is required, is their low tribological performance in H₂O containing atmospheres as well as their low hardness values [3-6]. Thus, their use is prohibited in most of terrestrial applications requiring high loading bearing capacity. Besides the existence of weak Van der Waals forces between basal planes, the very low mechanical strength is also been attributed to typical columnar morphology with high levels of porosity when they are deposited in the form of thin coatings [6-9].

In order to overcome the drawbacks of TMDs, many different approaches have been tried almost always involving an improvement of the density with the double aim of impeding the coating oxidation and increasing the mechanical strength. The alloying of the coatings with metals or compounds are good examples of these solutions [10-13].

Still in the 90's, at Air Force Research Laboratory in the USA, a research work was started concerning the deposition of coatings integrating simultaneously carbon and TMDs. The objective of the study was the use of the well known concept of composite materials, i.e. trying to deposit coatings which could take advantage of the good properties of both materials and avoid their drawbacks. This study was prolonged during several years [14-17] and, already in this century, ICEMS, Portugal, enlarged the range of chemical compositions studied by those authors from 0 to 100% of TMDs [18-24]. Finally, very recently another group in Japan presented their first results of the deposition of C-TMDs by co-sputtering [25].

The aim of this paper is to present a review of the results obtained up to now at ICEMS on the alloying of TMDs coatings with C. Whenever important, the results of the other authors on W-S-C system will be presented and discussed for comparison means.

2. EXPERIMENTAL DETAILS

All W-S-C coatings have been deposited on 100Cr6 and M2 polished steel samples, with hardness close to 5 GPa and 9 GPa, respectively, and mirror-like polished Si wafers. Three different approaches were tried for co-deposition of coatings using a radio-frequency magnetron sputtering Edwards ESM 100 unit, equipped with two cathodes or targets ($\varnothing=100$ mm): (1) reactive sputtering, with one Ti target for an adhesion interlayer,

one WS₂ target and deposition in a CH₄-containing atmosphere; (2) co-sputtering from individual C and WS₂ targets, and (3) co-sputtering from a C target embedded with WS₂ pellets (composite target) and one Ti target. Prior to deposition the substrates were sputter cleaned during 20 min by establishing the plasma close to the substrates electrode. Immediately after, in the cases where it was possible, a Ti interlayer was deposited with an approximate thickness of 300 nm for improving the coating adhesion. The chemical composition of coatings was varied by playing in each approach with the flow rate of the reactive gas, the power applied to the C target (the power of the WS₂ target was kept constant at 160 W) and the number of WS₂ pellets on the C target, respectively.

To evaluate the chemical composition of coatings, a Cameca SX 50 electron probe microanalysis (EPMA, Cameca, France) apparatus was used. The chemical composition is an arithmetic average of four values measured in different parts of samples. The standard deviation was in the range ± 0.02 to ± 0.3 . The hardness was determined by depth-sensing indentation technique using a Fisherscope H100 with a nominal load of 20 mN, following the procedure indicated elsewhere [26]. The hardness value was obtained by averaging eight different indentation results. The adhesion of coatings was evaluated with a commercially available scratch testing equipment (CSEM Revetest), under standard conditions. The critical load, for each coating, was obtained by averaging four different scratch results. The structure of coatings was analysed by X-ray diffraction (XRD) in glancing mode using a Phillips diffractometer (Co K _{α} radiation).

Most of tribological tests were carried out in a pin-on-disk tribometer (CSM Instrument). 100Cr6 steel balls were used as sliding partners. The diameter of balls was 6 mm and the load was varied in the range (5-48) N. Different testing environments were used by varying either the humidity degree (from 5 to 90%) or the testing temperature (from room to 400 °C). The sliding speed was 0.05 m·s⁻¹. The friction coefficient reported is the average value of the whole sliding test, unless stated otherwise.

The wear coefficient for the coated disk (K) was calculated using the equation:

$$K = v / (s \cdot l), \quad (1)$$

where v is the worn volume, s the total distance of sliding of the ball over the disk and l the normal load. The worn volume of the coated disk was de-

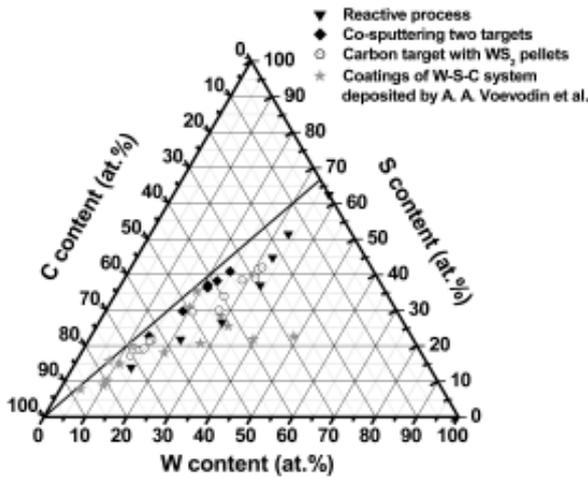


Fig. 1. Chemical composition of the W-S-C coatings. Literature data on the same system are also shown for comparison [14].

terminated by integrating the mean area of 6 profiles, taken across the sliding track, over its entire perimeter. The measure of the tangential force allowed the calculation of the friction coefficient.

The microstructure and the changes in the bonding structure were investigated using a Renishaw micro-Raman spectroscopy system 1000 at a wavelength of 514.5 nm. Raman spectroscopy was carried out in different places in the wear tracks and outside. Two groups of peaks could be observed, one corresponding to carbon (i.e. D and G peaks) and another consisting of two peaks (325 and 416 cm^{-1}) identified as WS_2 . The ratio I_c/I_{WS_2} was calculated as the sum of the carbon peaks areas divided by the sum of the WS_2 peaks areas.

3. RESULTS

3.1. Chemical composition and structure of coatings

Coatings with various C contents have been deposited as summarized in the ternary diagram shown in Fig. 1. From now coatings with C contents higher than 50 at.% will be considered as high C-content coatings. In relation to the samples studied by Zabinski *et al.* [14], there is an extension of the domain of analysis for lower C contents. It should be noted that almost all the coatings are shifted in relation to the tie line representative of the stoichiometry $S/W=2$, meaning that the coatings are sulphur deficient compared to WS_2 pel-

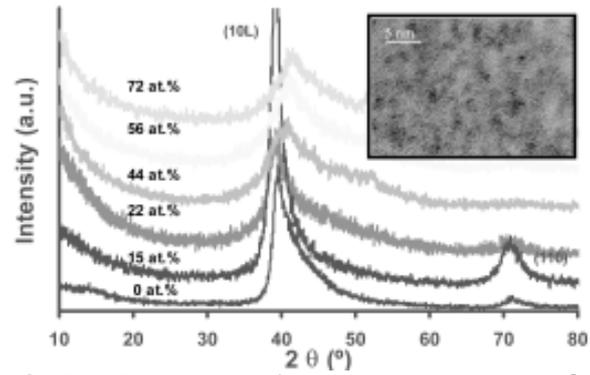


Fig. 2. XRD patterns of reactively deposited W-S-C coatings with increasing C content. A TEM micrograph of the cross section of a high C content coating is shown inset [22].

lets. The shift reaches high values particularly for coatings with low C contents studied in [14]. The coating procedure which seems more favourable for keeping the stoichiometry close to $S/W=2$ is co-sputtering, particularly when performed from individual targets (see \blacklozenge and \circ in Fig. 1). The deposition with reactive gas (\blacktriangledown) is very detrimental for S/W ratio. This trend can be attributed to the presence of energetic H species in the discharge due to the decomposition of CH_4 . These species combine with sputtered S atoms forming H_2S which is evacuated from the deposition chamber leading to a lower S incorporation in the growing coating.

Coatings of the W-S-C system deposited by co-sputtering from individual targets (WS_2 and carbon) were also deposited by other authors [25]. They showed that, depending on the power applied to the WS_2 target, the coatings could have different arrangements (nanocomposite or nanolaminate) depending on the possibility of forming a continuous TMD layer during the short time as the substrate is passing over each target. With ICEMS conditions, the formation of a laminate structure does not seem to be possible since a period lower than 0.2 nm is expected, which does not permit the formation of a layered structure. Since Noshiro *et al.* [25] presented a power ratio between WS_2 and C targets, $P(\text{WS}_2)/P(\text{C})$, much lower than the ICEMS case (range [0.04-0.4] against [0.29-1.07], respectively) their coatings should exhibit higher C contents.

The coatings deposited by co-sputtering from the two individual targets (WS_2 and C) presented XRD patterns typical of an amorphous structure,

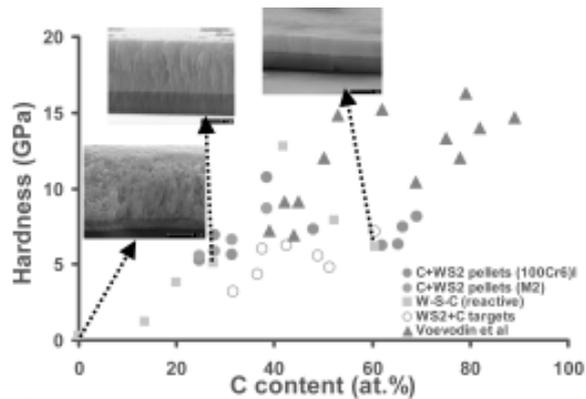


Fig. 3. Hardness of W-S-C sputtered coatings as a function of the C content. SEM micrographs of the cross section of selected coatings are shown inset. W-S-C system deposited by A. A. Voevodin *et al.* are also shown for comparison [14].

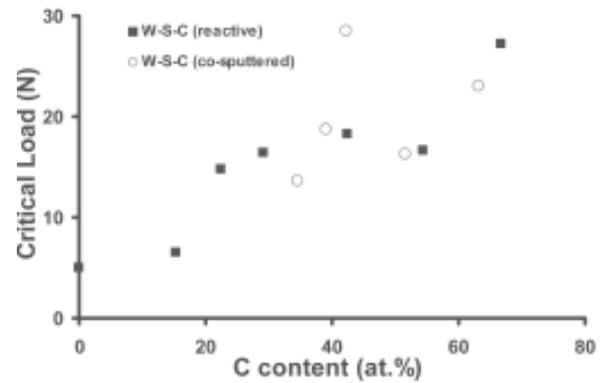


Fig. 4. Scratch test critical load of W-S-C sputtered coatings as a function of the C content.

whatever the C content. For the others process (reactive sputtering and co-sputtering form a C target with WS_2 pellets) crystallinity could be observed, which was progressively lost with increasing C content (see e.g. the evolution of XRD patterns in Fig. 2 for reactively sputtered coatings). Very similar results were also achieved by Voevodin *et al.* [14]. Pure W-S, (or with a low C content) coatings present a dark surface which, if wiped with a soft cotton, changed to a metallic aspect, fact accompanied with the appearing of a peak that corresponds to the (002) plans of the 2H- WS_2 phase due to the re-orientation of the basal planes parallel to the coating surface. The main XRD peak placed at $2\theta \sim 40^\circ$ with a long tail corresponds to the turbostratic stacking of (10L) planes ($L=1, 2, 3, \dots$) which can be interpreted as a 2D organization of the basal planes [27]. With increasing C content, the lateral dimension of the basal planes decreases leading to broader and less intense peaks until only one typical peak of an amorphous structure is observed. For C contents higher than 40 at.% small features in the XRD pattern suggest the presence of other phases such as tungsten carbides. Such a fact was confirmed by X-ray photon-electron spectroscopy (XPS) [21] which clearly showed the presence of different types of bonds such as, W-S, W-C and C-C suggesting the formation of a nanocomposite structure where nanocrystals of WS_2 and W-C phases were dispersed in a C-rich amorphous matrix. The differently contrasted zones in the TEM micrograph of

one of these coatings (inset in Fig. 2) and the direct observation of crystalline planes in darker areas support this assessment.

3.2. Mechanical properties and morphology of coatings

Fig. 3 presents the evolution of the hardness (H) of coatings with increasing carbon content for all the approaches adopted for deposition. The general trend was: the hardness rises with increasing C content, up to ~ 45 at.%, and decreases thereafter. The first increase should be closely correlated to either the great improvement in the density of coatings (see typical cross section morphologies inset Fig. 3) or the formation of other harder phases such as W-C or C-based. With the addition of carbon in the coating, there is no more W available to establish W-C bonds and the domination of carbon phases takes place. As the deposition conditions used in this work leads to only 7 GPa for the hardness of pure C coatings, the growing influence of C in the W-S-C coatings justify the observed decrease in hardness values.

The hardness values reported by other authors [14,25] were found to be overlapped with those presented above but only up to C contents close to 50 at.%. For higher contents, those authors stated the continuation of the monotonous growing of hardness with increasing C content. This difference can be attributed to the much higher hardness value of their single C coating (close to 18 GPa) which,

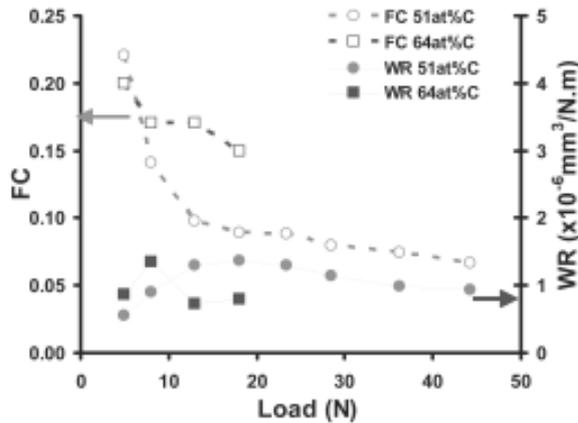


Fig. 5. Friction and wear coefficients of W-S-C coatings as functions of the testing applied load.

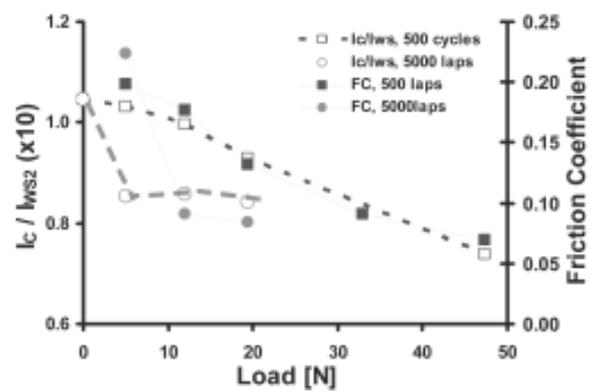


Fig. 6. Friction coefficient and I_C/I_{WS2} ratio, determined by Raman spectroscopy, of a W-S-C coating, containing approximately 41 at.% of C, as functions of the testing applied load.

again, determines the hardness of W-S-C coatings when its importance progressively grows. Also Noshiro *et al.* [25] found a higher value for single C content (17 GPa) and the consequent monotonous decrease down to 10 GPa with increasing TMD content. It should be remarked, as referred to above, that these authors only deposited C-rich coatings which can explain that the hardness did not decrease under 10 GPa. Both these research groups worked with lower deposition pressures (in the range from 0.2 to 0.3 Pa) than in ICEMS work (~0.8 Pa) which can explain the higher hardness values reached for pure C coatings.

Whatever are the results considered, what is really remarkable is the huge increase in hardness resulting from C alloying, more than one order of magnitude, in relation to the single W-S coating (<0.5 GPa).

As for the hardness, a great improvement in the adhesion of W-S-C coatings could be found by scratch testing. Fig. 4 presents the evolution of the critical load with increasing C content. Although the highest values were not still high enough for guarantee a perfect success in real service applications, no problems were found for the tribological tests even when the highest testing loads were applied.

3.3. Friction and wear properties of coatings

The tribological characterization was accessed by studying the influence of different testing parameters during the pin-on-disk measurements as fol-

lows: applied load, temperature and humidity of the environment. Coatings with various C contents were studied and only the main trends are presented here.

3.4. Testing load

Fig. 5 shows the evolution of the friction (μ) and wear (K) coefficient as a function of testing load for two coatings, representative of coatings with high and low C contents. The same trend can be observed in both cases which is often found for self-lubricated coatings, particularly those based on TMDs coatings [28-30]. This is the first indication that the presence of TMD phases should determine the friction behaviour of these nanocomposite coatings. However, the coatings with C contents lower than ~50 at.%, have high μ values for low applied loads decreasing progressively with increasing load up to a steady state is achieved. On the other hand, in coatings with high C contents a small decrease in μ is detected being the values kept at a much higher level (>0.15) although it could be expected that, if the coatings were tested with a high number of cycles and higher loads, lower friction coefficient could be achieved as for the coatings with low C content.

The analysis of the wear track of the coatings allowed identifying some differences which can explain the different behaviour. SEM observations showed, on the one hand, that a transferred layer consisting of W, S, C, and O was formed on the pin, whatever the testing conditions protecting the

coating surface since no wear was there possible to be measured. On the other hand, a very smooth surface was found for coatings with low C contents whereas grooves were detected in the other coatings. Furthermore, Raman spectroscopy carried out on the worn tracks allowed to conclude that the low friction coefficients could be associated to an increase in the TMD concentration on its near surface by the action of the sliding process. Such enrichment was found neither with C-rich coatings nor under low loads [31].

Finally, as can be observed in Fig. 6, the changes in the surface layer of the wear track are also determined by the number of cycles. This figure presents the evolution of the I_C/I_{WS_2} ratio, i.e., the ratio between the area of carbon peaks (D and G band) and area of WS_2 peaks (325 and 416 cm^{-1}) calculated from Raman spectra, as well as the friction coefficient, as functions of the testing load for the same coating (~ 41 at.%C) tested with 500 or 5000 laps. Firstly, it confirms what was referred to above, i.e., for reaching a low friction coefficient it is necessary to apply a threshold load which is able to promote the enrichment of W-S phases in the surface of the sliding contact. Secondly, these changes can be achieved at lower applied loads but after much higher number of cycles. It seems that the surface transformation requires a threshold amount of work to occur, which can arise either from increasing load or number of cycles.

The decrease in friction coefficient with load of TMD coatings was explained by several authors as consequence of the frictional heating of the surfaces in the contact causing drying of the air humidity [32]. However, by applying the frictional heating analysis [33] for the tribological behaviour of TMD materials, it was possible to demonstrate that the low friction behaviour of nanocomposite W-S-C coatings cannot be interpreted by this way [31]. Thus, the decrease in friction coefficient with increasing load should not be attributed to the frictional heating, since the rate of the frictional heating per unit sliding area remained almost constant regardless on contact pressure. A different friction mechanism should exist for these materials in spite of the similar friction behaviour that they present in relation to pure TMDs.

The profiles of the wear tracks were very difficult to be evaluated with depths of only some hundreds of nanometers. As can be seen in Fig. 5, it does not seem there being significant influence of the applied load on the wear rate of coatings. The values are similar to those found by Voevodin *et*

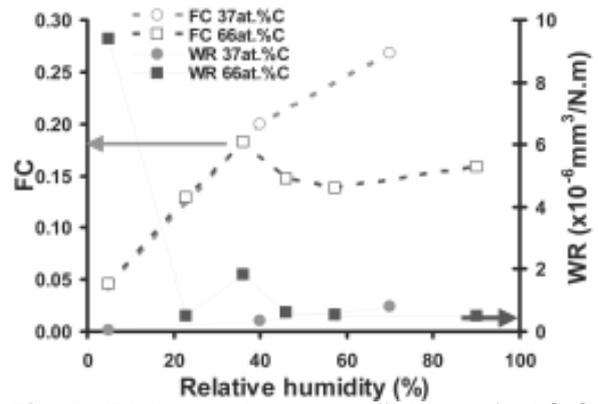


Fig. 7. Friction and wear coefficients of W-S-C coatings as functions of the humidity content in the testing environment.

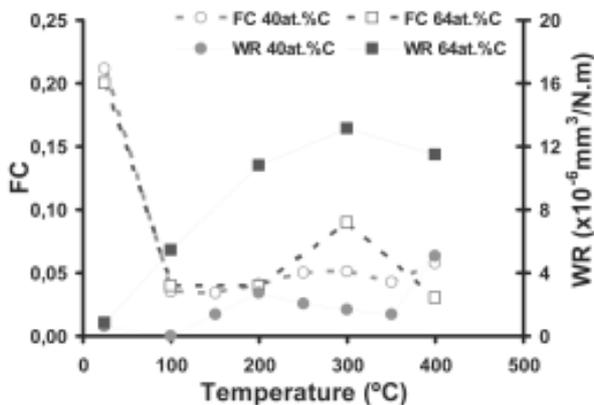
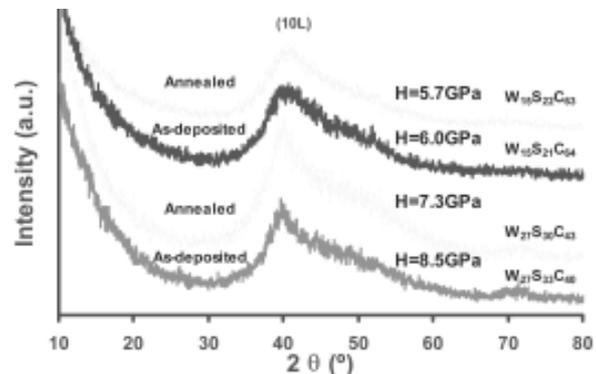
al. [14] for tests in dry environments and clearly inferior to those achieved in humid atmospheres.

3.5. Relative Humidity (RH)

One of the main objectives of the present research was to extend the application of TMD coatings to humidity containing environments. Thus, their tribological behaviour was studied as a function of the relative humidity. Fig. 7 shows the friction and wear coefficients achieved for two selected coatings exemplifying the tribological behaviour of the tested coatings, one with high and the other with low C contents, as a function of the relative humidity in the testing environment. As it would be expected, in dry nitrogen the coatings present very low friction coefficients (<0.05) including the one with high C content, in spite of the presence of C-based phases. Such behaviour suggests that the tribological behaviour should be exclusively determined by the presence of TMD phases in the sliding contact. With increasing relative humidity, a steadily degradation of the friction properties could be observed, with an increase in friction coefficient up to values close to 0.15 for 40 % of RH. However, for higher RH values an opposite trend is detected for both coatings: μ continue to increase for coatings with low C contents whereas a decrease has occurred for coatings with high C-contents. In this coating, the presence of C-based phases should permit improving the frictional properties as suggested by Wu *et al.* [15]. The μ values measured in these conditions are close to those found by these authors: (1) coatings with S con-

Table 1. Wear data for a high C containing W-S-C coating tested in dry nitrogen as a function of the duration of the test.

	Width of the wear track (μm)	Depth of the wear track (μm)	Friction coefficient
After 60 cycles	190	0.55	0.12
After 1500 cycles	250	0.52	0.05

**Fig. 8.** Friction and wear coefficients of W-S-C coatings as functions of the testing temperature.**Fig. 9.** XRD patterns of W-S-C coatings of various compositions, structures and hardness before and after annealing at 300 °C.

tents higher than 20 at.% (roughly C content lower than 70 at.%, which is typically the range of samples studied at ICEMS) exhibit friction coefficients in dry conditions lower than 0.05 whereas, in humid air, μ was in the range from 0.2 to 0.3; (2) for the coatings with lower S contents, down to 15 at.%, μ was in the range [0.18-0.3] and [0.25-0.4] when tested in dry or humid environment, respectively.

The wear rate of the coating with 37 at.% of C, representative of the W-S-C coatings with low C contents, is almost nil in dry tests. With increasing RH values the wear rate starts to increase which is characteristic of TMD materials in humid atmospheres. However, it should be remarked that it stays quite low and no destruction of the coating was detected. The C-rich coatings show a very high wear rate when tested in dry environment. However, such a high value should be attributed to an abnormal consumption of coating material in the initials cycles necessary to create the conditions for establishing lubricious surfaces. In fact, very short tests performed on these coatings in dry conditions (only 60 laps) showed that the dimensions of the wear track after the test are similar to those achieved in longer duration tests (Table 1). Thus, even with a low TMD content it is possible to cre-

ate conditions for a C-rich coating to reach low friction coefficients when tested in dry atmosphere. With increasing RH in the testing environment, there is an increased influence of the C-based phases leading to a significant decrease in wear rate which is kept approximately constant up to the highest RH studied.

3.6. Testing temperature

As it would be expected, when W-S-C coatings were tested at 100 °C, an abrupt decrease in friction coefficient was observed (Fig. 8). In fact, at this temperature the atmosphere will dry establishing the low friction conditions analysed above for the influence of RH. Excepting some punctual oscillation, the μ values are kept approximately constant up to 400 °C. For higher temperatures the destruction of the coating occurred.

The decrease in friction coefficient is not accompanied by a similar trend in the wear rate. For the coating with a C content of ~40 at.% the wear rate is kept approximately constant for all testing temperatures whereas an increase of almost one order of magnitude was observed for those with high C contents. Any changes observed in the tribological behaviour should not be attributed to

changes in the structural and mechanical properties, at least from what XRD and nanoindentation results make think. In fact, as it is shown in Fig. 9, no significant changes in the chemical composition, the XRD patterns and in the hardness values of the coatings could be detected, which could justify, for example, the increase in wear rate with testing temperature for the coatings with high C contents.

4. CONCLUSIONS

W-S-C films have been deposited by reactive and non-reactive magnetron sputtering with increasing C contents. The most suitable method for coating deposition was by co-sputtering from a C target embedded with pellets of WS₂. The C content was varied from 0 to 100 at.%. All coatings were sub-stoichiometric in relation to the ratio S/W=2. Significant improvements in the morphology of the coatings were achieved with increasing C content, whereas the crystallinity was progressively lost with a decrease in intensity and a broadening of the diffraction peaks. High resolution transmission electron microscopy allowed concluding that the coatings with high carbon contents were formed by a nanocomposite structure consisting of nanocrystals of W-S and W-C phases embedded in a C-rich amorphous matrix.

As a result of these variations a huge increase in hardness was reached with a difference of more than one order of magnitude between single W-S coating and those containing carbon (from 0.5 to more than 10 GPa). In the same way an increase in critical load determined by scratch testing was achieved from 5 N up to more than 30 N.

The coatings were tribologically tested in pin-on-disk equipment by varying the applied normal load, the humidity content and the testing temperature. The evolution of the mean friction coefficient as a function of the applied load was typical of TMD materials (i.e. decrease in friction coefficient with increasing load) which allowed suggesting that an enrichment of this phase in the sliding contact surfaces would be needed for achieving low friction coefficient. It should be noted that with loads higher than 40 N, μ values as low as 0.07 could be reached which is remarkable for a TMD rich material sliding in humid air. As it would be expected the coatings showed an excellent tribological behaviour in dry conditions which degraded when the RH value increased, again a typical behaviour for a TMD material. Finally, testing at temperatures higher than 100 °C led to very low friction coefficients due to

the drying of the atmosphere. The coatings with C content close to 40 at.% showed the best thermal stability keeping very low friction and wear coefficients when tested at temperatures up to 400 °C.

As a final remark, TMD-C coatings are very promising for industrial applications even when different environments could be present during the component lifetime. In-service testing is now required to test the validity of this assumption.

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