

TRIBOLOGICAL BEHAVIOUR OF REACTIVE AND CO-SPUTTERED W-S-C COATINGS

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ABSTRACT: W-C-S films were deposited either by a reactive process in an Ar + CH₄ atmosphere or by co-sputtering WS₂ and C targets. The films were characterized concerning their chemical composition and mechanical properties. The results showed that the films, in both systems, have similar properties. Co-sputtered films are amorphous, whereas in the reactive process a gradual loss of crystallinity is observed with the increase of C content in the films. The hardness and the adhesion are similar for both systems. The increase of C alloying to the films led to the improvement of both their hardness and adhesion.

The tribological performance of the coatings was tested by ball-on-disk. The films deposited by co-sputtering present better results than the reactive deposited ones. With the increase of C content in these coatings an increase of the wear resistance is observed, reaching in the best case a wear coefficient of $3.1 \times 10^{-16} \text{ m}^3/\text{N}\cdot\text{m}$. In the films deposited by reactive process, low wear coefficients can also be reached but no regular trend with increasing C contents can be observed.

Keywords: Tungsten disulfide; WS₂; Friction coefficient; Wear coefficient; Self-lubricant

1. INTRODUCTION

Layered metal dichalcogenides such as WS₂ and MoS₂ are extensively used as tribological coatings, but their endurance in tribological applications is affected by the ambient conditions. The films present better tribological behaviour in dry Ar or vacuum than in room atmosphere [1]. These films present porous morphologies which have a deleterious effect on their mechanical and tribological behaviour. On the other and, the presence of oxygen also undertake their tribological performance, particularly concerning their friction coefficient.

To improve the toughness and the loading bearing capacity of W-S films it is necessary alloying them with other chemical elements or compounds [2-5]. The pioneering research works carried out with C-alloyed films [4] and previous works developed by the authors proved that the C element could improve significantly the hardness [6, 7] and be useful, together with a Ti interlayer deposition between the films and the substrate [8], for improving the adhesion of these films and, consequently, their tribological behaviour. Furthermore, it is well known that the use of different sputtering techniques and deposition parameters influences the structural, morphological and chemical characteristics of W-S films [9-11].

The aim of this work is to evaluate the influence of the deposition method on the mechanical properties, particularly the hardness and the adhesion, and tribological performance of W-S-C films. The films were deposited with increasing C

contents by either a reactive process in an Ar + CH₄ atmosphere or co-sputtering WS₂ and C targets.

2. EXPERIMENTAL DETAILS

W-S-C coatings were deposited by radio-frequency magnetron sputtering, in a basic Edwards ESM 100 unit, with two cathodes ($\varnothing = 100 \text{ mm}$), by two different methods: a reactive process in an Ar + CH₄ atmosphere and co-sputtering WS₂ and C targets. The depositions, in the reactive process, were carried out with a power density of $\approx 5.1 \text{ W/cm}^2$ for the WS₂ target, whereas the mass flow ratio of the reactive gas was varied from 0.0 to 10.0 % in order to change the C content in the coatings. In the co-sputtering mode the power in the WS₂ target was kept constant at 2.0 W/cm^2 and the increase in the C content in the films was reached by varying the power in the C target in the range $[1.9 - 7.0 \text{ W/cm}^2]$. Quenched and tempered L1 and M2 (AISI) steels with hardness close to 5 and 9 GPa respectively, were used as substrates, which were polished with diamond paste of particle size down to $3 \mu\text{m}$. Before the deposition, the substrates were sputter cleaned during 20 min by establishing the plasma close to the substrates electrode. As the deposition chamber has two cathodes, only in the films deposited in a reactive process was possible to deposit a Ti interlayer to improve the adhesion to the substrate. The transition to the deposition was made gradually. The depositions were performed with rotation of the substrates. The deposition time was kept constant at 150 min (15 min for Ti interlayer, 15 min for the transition and 120 min for the W-S-C film deposition); in the reactive

process, in co-sputtering mode the deposition time was kept constant at 215 min.

To evaluate the chemical composition of the films, 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 the film. The standard deviation is in the range ± 0.02 to ± 0.3 . The hardness was determined by depth-sensing indentation technique using a Fisherscope H100. The load was increased in steps (60) until a nominal load of 20 mN was reached. The hardness value was obtained by averaging eight different indentation results. The adhesion of the coatings was evaluated in 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 the films was analysed by XRD in glancing mode using a Phillips diffractometer (Co K_{α} radiation). The tribological tests were performed in a ball-on-disk equipment at room temperature, the relative humidity of the laboratory was in the range 40-60 %. Steel balls, 100Cr6 (L1 AISI), (diameter $\varnothing = 10$ mm) were used as counterbody material. The sliding speed was 0.1 m/s and the normal load applied was 10 N. The wear coefficient for both the coated disk (k_f) and the ball (k_b) 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 determined by integrating the mean area of 6 profiles, taken across the sliding track, over its entire perimeter. For the ball, the diameter of the crater was measured and a spherical calotte was considered. The measure of the tangential force allowed the calculation of the friction coefficient.

3. RESULTS AND DISCUSSION

Table 1 presents the total thickness of the coatings as well as their chemical composition, normalized to $\text{at.\% W} + \text{at.\% S} + \text{at.\% C} = 100 \text{ at.\%}$. Besides these elements the presence of oxygen was also detected. With the increase of the C content in the films a small decrease of the oxygen could be observed. The films deposited by co-sputtering present higher levels of oxygen than the reactive deposited ones. The decrease of O in these films can be associated with the chemical reactions occurring in the chamber during the deposition. The presence of active C species in the discharge atmosphere makes possible the combination with O atoms, forming CO or CO₂ molecules, which are pumped out from the deposition chamber. Moreover, in the reactive process similar reaction can take place between H and O atoms, also contributing to a lower incorporation rate of O in the growing film. This synergetic action of C and H atoms in the discharge justifies the lower O content in W-S-C coatings deposited by the reactive process. Also, the improvement in the coatings density with C alloying reduces significantly the specific area exposed to the environment and, consequently, the absorption of O in the films leading to a lower measured content [12].

The S/W ratio remains practically constant for the co-sputtering films while in the films deposited by the reactive process it decreases progressively with C content increase. In the films deposited by the reactive process, due to the presence of CH₄ in the deposition chamber, the combination of H with sputtered S atoms in either their trajectories from the target to the substrate or at the surface of the growing film is allowed. The H₂S gas formed may be pumped out leading to a decrease of the final S/W ratio in the films with increasing CH₄ content in the chamber [12].

Table 1. Chemical composition and thickness of W-S-C coatings.

Sample	Power in C Target [W/cm ²]	Chemical composition			S/W	Thickness [μm]
		at.% C	at.% S	at.% W		
1	1.9	34.6	40.9	24.5	1.7	1.3
2	3.2	39.1	38.3	22.7	1.7	1.2
3	4.5	39.8	38.3	21.9	1.8	1.0
4	5.8	51.7	29.7	18.6	1.6	1.6
5	7.0	63.2	22.8	14.0	1.6	1.7
	Relative flux of CH ₄ [%]					
6	0.0	---	62.5	37.5	1.7	2.1
7	2.0	15.3	51.4	33.3	1.5	2.3
8	3.0	22.5	44.8	32.8	1.4	1.5
9	4.0	29.3	37.0	33.7	1.1	1.3
10	6.0	43.8	26.6	29.7	0.9	0.8
11	8.0	56.2	21.8	22.1	1.0	0.9
12	10.0	72.0	13.9	14.1	1.0	0.9

Fig. 1 presents the X-ray diffractograms for two sets of W-S-C films. In the co-sputtered films, only one very broad peak is observed at the same positions of the (10L) line of the WS₂ phase, indicating that their structure is amorphous. In the reactive deposited films a gradual loss of crystallinity with the increase of C content is observed. However, for the highest C-alloyed films, although not undoubtedly defined, new phases such as W-C carbides and graphite can be formed in agreement with previously obtained results for the highest C-alloyed W-S-C films deposited with the substrate negatively biased [13].

Fig. 2 shows the evolution of the hardness (a) and the adhesive critical load (b) of W-S-C films with the C content. The hardness values can be interpreted as a function of the morphology and the structure of the films [12]. In the reactive process, the highest value of hardness was reached in the coating with $\approx 40 \text{ at.\%}$ of C and (S/W = 0.9). The low value of S/W indicates that a great amount of C is available to establish bonds with W forming W-C compounds, then explaining the high value of the hardness [13]. A further increase of C in the films leads to a decrease of the hardness, a behaviour that can be justified with the formation of C-phases which are considerably softer than W-C carbides. For the highest C contents it seems that co-deposited films can be harder than reactive ones (see fig. 2 (a)). The sp^3/sp^2 ratio, in sputtered C-coatings is enhanced when H is present in the discharge atmosphere, as the case of the films deposited in the reactive process. In this case, the majority of the C-H bonds are sp^3 whereas C-C is sp^2 , which leads to a low hardness. In the co-sputtering process, the films have a higher number of C-C sp^3 bonds and, consequently, are harder [12].

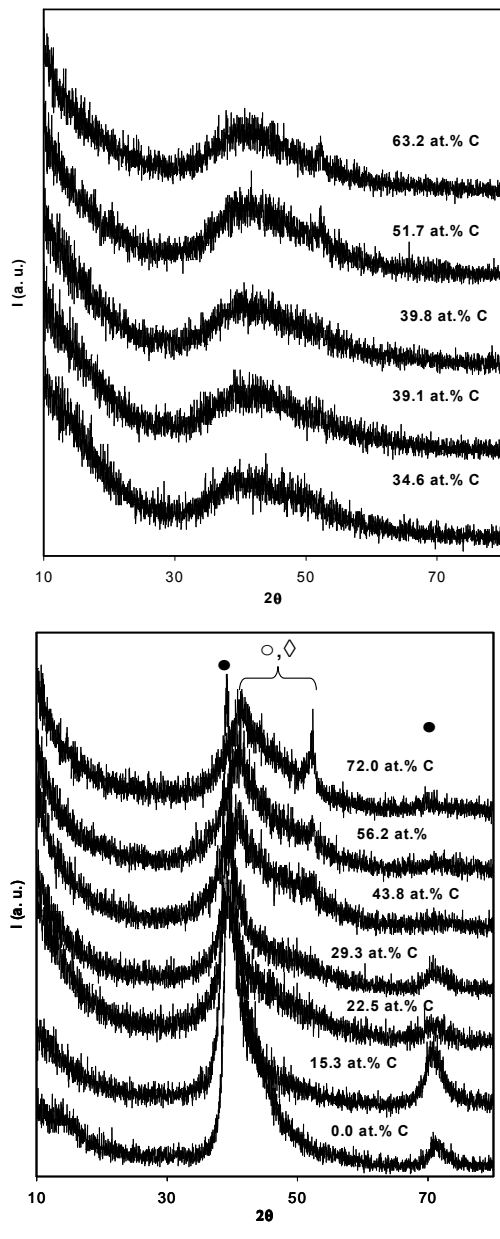


Fig. 1 XRD diffractograms of W-S-C as a functions of C content (a) co-sputtering (b) reactive process

In W-S-C films deposited by reactive process with a Ti interlayer, an increase of the adhesive critical load as a function of the C content was observed. This results is similar to that previously obtained [6] and was justified by the synergetic effect of both the Ti interlayer and the increase of C content in the films [8]. However, in the C-alloyed W-S films deposited by co-sputtering process, even without a Ti interlayer, the critical load values, L_c , are of the same order as those reached in the reactive process and much higher than those obtained previously in these films without a Ti interlayer [14].

Fig. 3 presents the wear coefficients for the balls and the W-S-C films as a function of C content. In W-S films alloyed with C, the wear resistance was improved. This effect is very probably associated with the increase of both

the hardness and the adhesion of the films to the substrate. Generally, the films deposited by co-sputtering present better tribological behaviour than the reactive deposited ones. In co-sputtered films, with the increase of C content, the wear rate drops. However, for the films with the highest C contents (51.7 and 63.2 at. % C), lateral delamination occurred in some zones of the wear track (fig. 4, 4th row). In many other zones, the film remains adherent to the substrate. If the wear is measured in these zones (e.g. depth profile of the wear track in fig. 4, 4th row)) very low wear coefficient ($< 2,0 \times 10^{-16} \text{ m}^3/\text{N}\cdot\text{m}$) are measured, in spite of the higher values of the friction coefficient which is rather irregular (fig. 4, 4th row)). For the other films μ values are also low in the range of ≈ 0.1 -0.2. Fig. 4, 3rd row, shows the aspect of the wear track and worn ball for the best film where μ is even lower than 0.1. This was the film for which the highest adhesion critical load was measured (see fig. 2). The friction coefficient values are somewhat lower than those typical for W-S films tested in room conditions [15, 16].

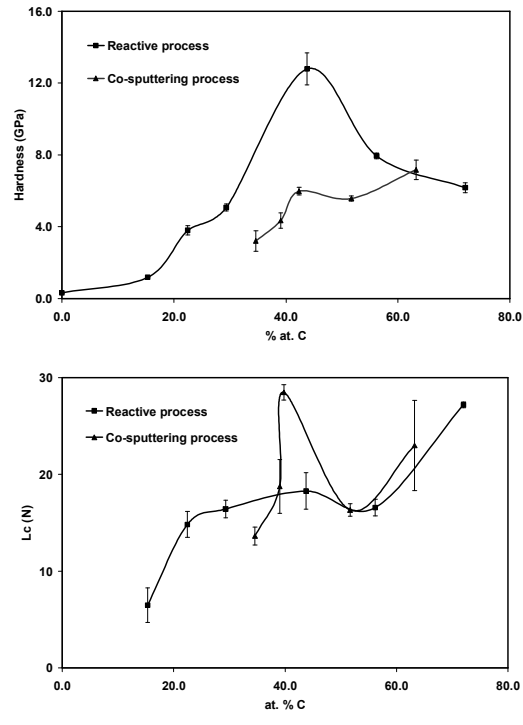


Fig. 2 Mechanical properties of W-S-C films as a function of C content: (a) hardness and (b) adhesive critical load.

In the films deposited by the reactive process no linear trend of the wear behaviour with the C content increase was found. The films without or low C-alloyed got a precarious wear resistance. These films are very soft and their lack of adhesion to the substrate give rise to the spalling of the films on the wear track during the test. With further addition of carbon a structural alteration occurred which influenced their tribological behaviour. Typically, when the formation of W-C phases can take place, the coatings become harder and, in the beginning, there is a beneficial effect in the tribological behaviour with a low friction coefficient and a significant decrease of the wear rate in relation to unalloyed film (see fig. 3 and 5). However, with further increase in the

hardness the friction coefficient increased and a drop in the wear resistance was observed (fig. 3). Finally and in agreement to previous research work [6], a further increase in C led to the lowest wear coefficient of the reactive deposited films, even if μ is higher than 0.2. However, this fact did not occur as before [6] for the highest C content since in this work the complete destruction of the film in the wear track was observed as can be confirmed in fig. 5, 4th row. The best wear resistance of this coating, in spite of presenting a low S/W ratio and a higher friction coefficient, should be related with its high hardness combined with a reasonable friction coefficient. The S content in the films has an important role due to the fact that W-S phases are responsible for the low friction properties. Therefore, as the carbon content in the films increases and the S decreases an increase of the friction is observed (see fig. 5). On the other hand, the higher is the film hardness the higher is the mechanical strength and the lower should be the wear coefficient. Thus, the wear resistance in this type of coatings is a compromise between low friction coefficient and high hardness. This can explain the fact that neither the coating with the highest hardness value (43.8 at.%C) nor the one with the highest S/W ratio, and the lowest friction coefficient, have lower wear rate than 58.2at.%C coating.

Comparing the two sets of coatings, the better tribological behaviour of co-sputtering deposited films can be associated with the fact that the S/W rate is kept constant at ≈ 1.7 . Then, these films have enough S content to the formation/reorientation of the W-S phase in the contact area, during the tribological tests and guaranteeing the lubrication. It should be noted that for these coatings the hardness is kept at reasonable high values, close to 4-6GPa, which in addition to the low friction coefficient allows a good compromise concerning the wear behaviour. This situation is much more difficult to occur in the reactive deposited films due to the absence of S and the excess of C.

The wear coefficient of the balls depends mainly on the formation of a protective 3rd body. Every time this phenomenon took place the ball wear is low. When no 3rd body formation occurs the wear is as high as harder is the coating.

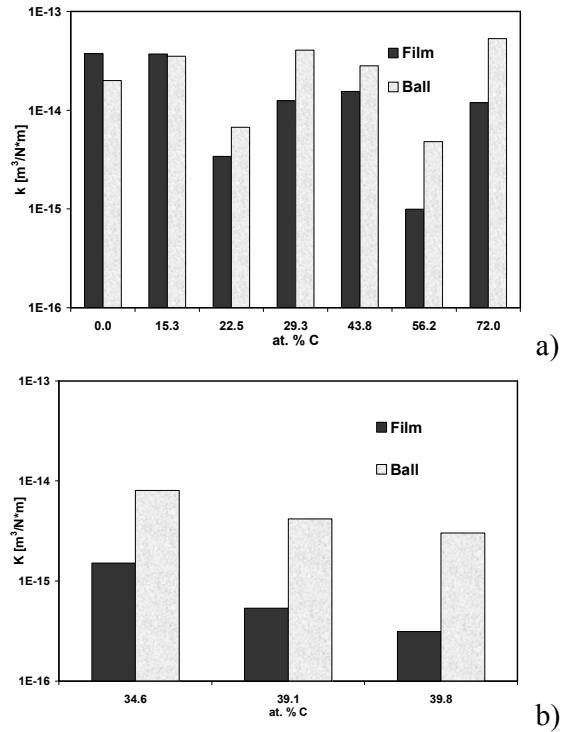


Fig. 3 Wear coefficients for the ball and film as a function of C content (a) reactive process (b) co-sputtering

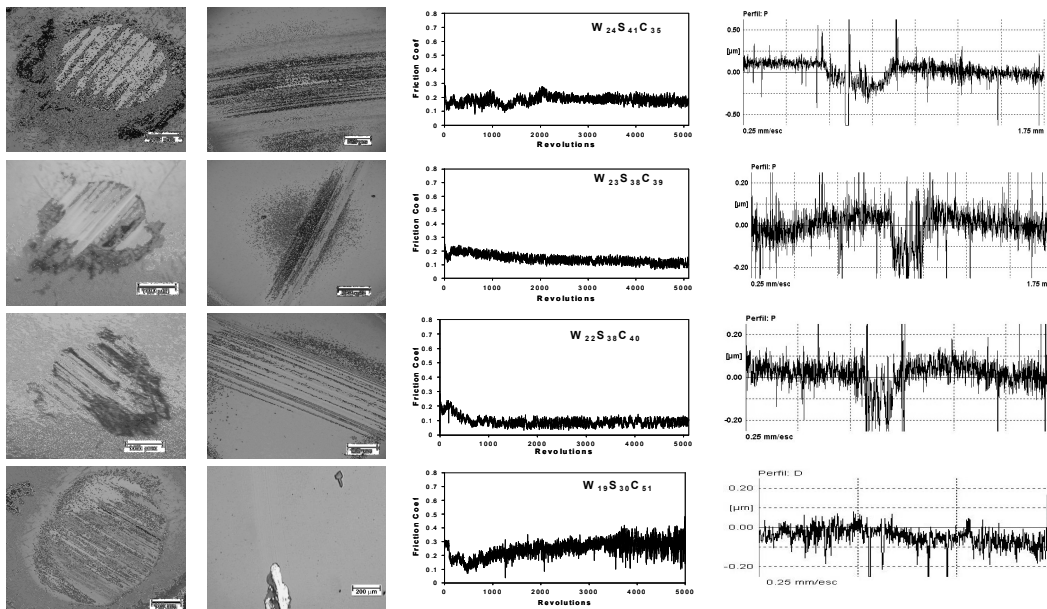


Fig. 4 Micrographs of the ball (1st column), micrographs of the sliding track (2nd column), friction coefficient of the films (3rd column), transversal section of the track (4th column), for the co-deposited films

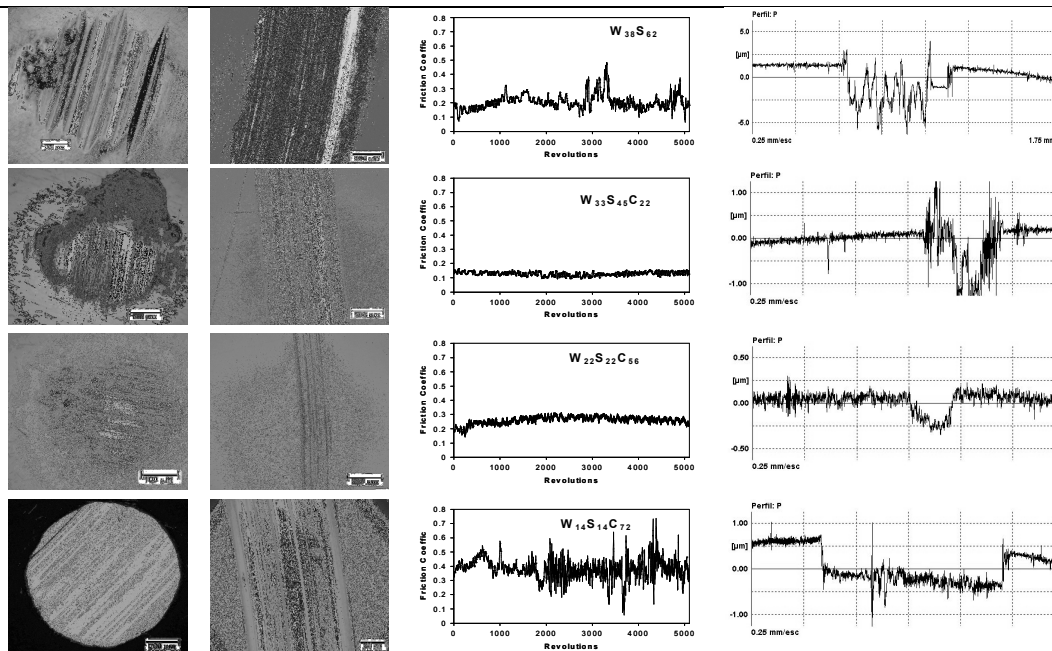


Fig. 5 Micrographs of the ball (1st column), micrographs of the sliding track (2nd column), friction coefficient of the films (3rd column), transversal section of the track (4th column), for the reactive process

4. Conclusions

Both reactive and co-sputtered W-S-C films were deposited with increasing C contents. S/W ratio in the co-sputtering was kept constant at ≈ 1.7 whereas in the reactive process it dropped down to ≈ 1 with the increase of C. All the co-sputtered films were amorphous while the reactive deposited ones lost progressively their crystallinity. Vestiges of W-C and C-based phases were detected for the highest C contents.

In both cases, the addition of carbon contributed for a significant improvement of the hardness and critical loads of the films. Similarly, also the tribological behaviour was improved with C alloying. Concerning this property the best results were reached in co-sputtered films for which lower wear and friction coefficients were obtained.

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