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How can H content influence the tribological behaviour of W-containing DLC coatings

Carlos W. Moura e Silva^{a,b,1}, José R.T. Branco^{a,1}, Albano Cavaleiro^{b,*}

^a REDEMAT/CETEC – Surface Engineering and Modification Laboratory, José Cândido da Silveira Avenue 2000, 31170-000 Belo Horizonte, Minas Gerais, Brazil

^b ICEMS – Mechanical Engineering Department, University of Coimbra, Luis Reis Santos Street, 3030-788 Coimbra, Portugal

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ABSTRACT

In this paper, the influence of the addition of W and H to pure DLC coatings on the structural, mechanical and tribological properties will be presented. The coatings were deposited by r.f. magnetron sputtering from a C target embedded with different numbers of W pellets. Working in non-reactive or reactive atmosphere allowed to deposit H-free or H-containing coatings, respectively, on steel and Si substrates. A Cr adhesion interlayer was interposed between the films and the substrate. Films with W content from 0 to 12 at.% and H incorporated up to a maximum value close to 40 at.% were deposited. All coatings had an amorphous structure, although vestiges of crystallinity could be detected in W-containing films. The addition of W led to a significant hardening of the DLC coating (from ~10 to 18 GPa); inversely, with H incorporation the hardness drop down to values even lower than that of pure DLC films. It was possible to establish a good correlation between the hardness and the residual stresses. In spite of decreasing friction and wear coefficients when alloying DLC with W, almost no difference was found among the W–DLC films whatever the W content was. A similar trend was achieved with the H addition. However, in this case a decrease in the friction coefficient was registered whereas the wear rate increased. The best performance concerning the friction was obtained for an H-containing coating (0.05) whereas, for the wear resistance, H-free W–DLC films were better performing ($0.3 \times 10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$).

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1. Introduction

The coating of tools and moulds has gained increasing importance for improving their tribological performance in industrial service. DLC (Diamond-Like Carbon) coatings have high hardness and low friction coefficient against metals which make them appropriate for being used as self-lubricating materials. On the other hand, they allow a reduction in the use of liquid lubricants with the consequent benefits for the environment [1]. However, due to the peculiar structure of DLC, with C atoms aggregated in an amorphous phase with different hybridization states, the films can reach very high compressive residual stress that limit their extensive application [1–3]. In order to overcome this problem, DLC films have been doped with metallic elements [4–6].

This paper is a part of a systematic study of the influence of the hydrogen content on the tribological properties of W-doped carbon films. In a first study [7], the optimization of the W content in the films was performed in order to achieve the best compromise

between the tribological and mechanical behaviors and the residual stresses. In this paper the scope is to compare the tribological behaviour of W-alloyed DLC films deposited with increasing H contents.

2. Experimental methods

H-containing and H-free W–DLC coatings were deposited by r.f. magnetron sputtering from a graphite target embedded with W pellets in reactive ($\text{Ar} + \text{CH}_4$) and non-reactive atmospheres, respectively. The ESM 100 Edwards equipment had two cathodes, one for the C–W target and another for a Cr target used for depositing an interlayer (~300 nm thickness) to improve the adhesion [8,9]. The deposition pressure was kept constant at 0.8 Pa and the C + W target, 100 mm diameter, was powered with 600 W. During reactive deposition, the CH_4 flux was controlled in order to keep constant the total deposition pressure and giving $p_{\text{CHA}}/p_{\text{total}}$ of 7, 12 and 25%. A negative bias of 30 V was applied to the substrate in all the depositions. M2 (AISI) HSS steel (structure, mechanical and tribological properties) and silicon (thickness and chemical composition) were used as substrate materials for the coatings deposition.

* Corresponding author. Tel.: +351 239 790745; fax: +351 239 790701.

E-mail addresses: carlos.moura@cetec.br (C.W. Moura e Silva), jose.branco@cetec.br (J.R.T. Branco), albano.cavaleiro@dem.uc.pt (A. Cavaleiro).

¹ Tel.: +5531 3489 2366; fax: +5531 3489 2200.

The chemical composition, morphology and structure were evaluated by means of electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The characterization of the molecular structure was completed by Raman spectroscopy with a laser wavelength of 514.5 nm. ERDA (Elastic Recoil Detection Analysis) was used for determining the H content in the coatings. The thickness, t , of the films was accessed by profilometry.

The hardness, H , was evaluated by depth sensing indentation using a Fischerscope H100 ultra-microindenter, with a maximum load of 10 mN. With this load only the hardness of the film was measured as confirmed by the analysis applied to the experimental data as suggested by Fernandes et al. [10]. The experimental data were corrected for the geometrical defects of the Vickers indenter as well as the thermal drift and the initial contact point of the equipment, following the methodology proposed by Antunes et al. [11]. The hardness was obtained by averaging at least 10 valid measurements for each sample.

The cohesion/adhesion of the coated sample was accessed by scratch-testing under standard conditions [12]. The critical load, L_c , was determined by the first adhesive failure detected in the scratch channel. The residual stress, σ , was calculated using the Stoney's equation applied to the deflection data of a plate measured before and after deposition [13]. Pin-on-disk tests were carried out to characterize the tribological behaviour of the coatings. The friction coefficient, COF, and the wear rate were evaluated in room conditions (25 °C, 55% RH), with a normal applied load of 5 N and a 100Cr6 steel ball as counterbody (6 mm diameter). The sliding was done with 0.1 m s⁻¹ speed during 26,500 cycles to which corresponds a total distance of 1000 m. The wear rate was calculated by dividing the worn volume (determined by integrating the cross-profile of the track to the entire worn circle) by the applied load and the total distance [14].

3. Results and discussion

3.1. Chemical composition, morphology and structure

The use of different numbers of W pellets in the C target allowed to deposit films with increasing W contents from 0 to 12 at.%. Due to the higher sputtering rate of W in relation to C an increase of about 30% in the deposition rate (V_{dep}) of W-containing coatings was achieved (Table 1). When the films were deposited in reactive mode, the C species were originated from two sources, the C target and the reactive gas. Thus, when the same power is applied to the C + W target, a significant increase in the deposition rate occurred (Table 1). When studying the influence of the H content, it was necessary to adapt the number of W pellets in the C target to achieve the same final W content in the coatings close to 10 at.%. As it would be expected, the increase in the partial pressure ratio, p_{CH4}/p_{total} , led to higher H contents in the films. However, a linear growing trend was not observed: for low p_{CH4}/p_{total} values, a steep

incorporation occurred which tends to stabilize for higher values, result probably related to the saturation of the available places (or bonds) for hydrogen incorporation. As observed in previous studies [7], all the films are XRD amorphous (Fig. 1). The asymmetry in the main broad peak visible in the film containing W indicates vestiges of crystallinity. The presence of the β -WC_{1-x} phase [15] was already suggested previously [7,16,17], giving rise to a structural arrangement characteristic of a nanocomposite material with carbide nanocrystals immersed in a C-rich amorphous matrix. The addition of H did not change the aspect of the XRD profiles. Slight asymmetry is still observed in the main broad peak, not changing with the H content.

The molecular structure of the coatings was studied by Raman spectroscopy and the spectra were analysed as a function of the two characteristic peaks of the graphite, the G peak, close to 1580 cm⁻¹ (related to sp²) and the D peak, close to 1350 cm⁻¹, representing the disorder in the sp² rings configuration under the form of graphite-like clusters [2]. The spectra shown in Fig. 2 allow concluding:

- when the spectra of pure DLC film (Fig. 2a) and W-containing films (Fig. 2b,c,d) are compared, strong changes can be detected;
- no significant differences were found in either the position or the broadening of the peaks among spectra of W-containing films;
- the incorporation of H in W-DLC films promotes an inverse trend of that detected for W-alloying, i.e. a progressive return back of the Raman spectra to the one of pure DLC film.

The first two conclusions suggest that the modification of the molecular structure is achieved with the addition of a low W content. The incorporation of W atoms during C deposition will interfere in the graphitic clustering leading to lower cluster sizes and distorting the graphitic rings [2]. For higher W contents, the excess of W atoms will precipitate in the form of W-carbide nanocrystals. The disordering effect gives rise to either the shift of the G peak position for lower frequencies or its broadening [18,19]. Similar behaviour was found for DLC films alloyed with Ti and Si [4–6].

The main effect of the addition of H is to saturate the C=C bonds mainly converting sp² C sites into sp³ =CH₂ and ≡CH sites [2]. If H promotes the formation of chains a soft polymeric material can be formed. However, depending on the energetic conditions during film formation, the sp² sites can stay predominantly organized in aromatic rings giving rising to important D band intensity [20]. In the present case, the addition of H promotes the formation of aromatic rings allowing an enhanced ordering of the graphitic clusters as demonstrated by the strong decrease in the linewidth and giving rise to the increase of the D peak intensity. The ordering trend comes in countercurrent in relation to the effect of the W addition to the C matrix, having as final result a return back of the Raman spectrum to the shape shown by the unalloyed H-free DLC film.

Table 1
Summary of the properties of DLC-based coatings.

Coating	W (at.%)	H (at.%)	V_{dep} (nm/min)	t (nm)	H (GPa)	σ (GPa)	L_c (N)	COF	Wear rate $\times 10^{-16}$ (m ³ N ⁻¹ m ⁻¹)
a-C	0	~5	12.0	2200	10	-1.1	23	0.22	0.8
WC _{1-x} /a-C	6	-	14.9	1790	18	-3.2	45	0.09	0.5
	9	-	15.9	1910	18	-2.7	46	0.11	0.7
	12	-	14.8	1770	18	-3.0	68	0.12	0.3
WC _{1-x} /a-C:H	8	28	20.8	2500	10	-0.9	82	0.05	0.7
	8	33	24.2	2900	8	-0.7	78	0.05	0.6
	10	39	27.8	2500	8	-0.5	72	0.08	1.2

Deposition rate (V_{dep}), thickness (t), hardness (H), residual stress (σ), critical load (L_c), friction coefficients (COF).

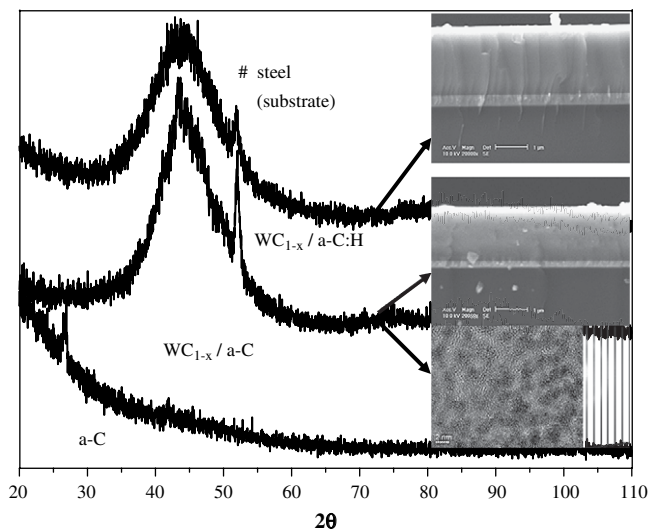


Fig. 1. XRD patterns of typical DLC-based thin coatings. In inset, cross-section SEM and TEM micrographs of H-free DLC-W (12 at.% W) and W-DLC:H (10 at.% W, 39 at.% H) are also shown.

H-free DLC films are compact showing featureless cross-section morphology (see e.g. Fig. 1). No influence of the W content on the films morphology was detected. However, with H addition a slight decrease of the compactness can be observed, the films showing a compact but columnar aspect (Fig. 1). Fig. 1 also shows that the Cr interlayer is less dense with a columnar morphology typical of metal coatings.

3.2. Mechanical properties

The main results for the hardness (H), residual stress (σ) and critical load (L_c) for adhesion are shown in Table 1. As for the structure, no influence of the W content was detected on the hardness and residual stress of the W-containing films, although all of them are significantly harder than the pure DLC. The hardness

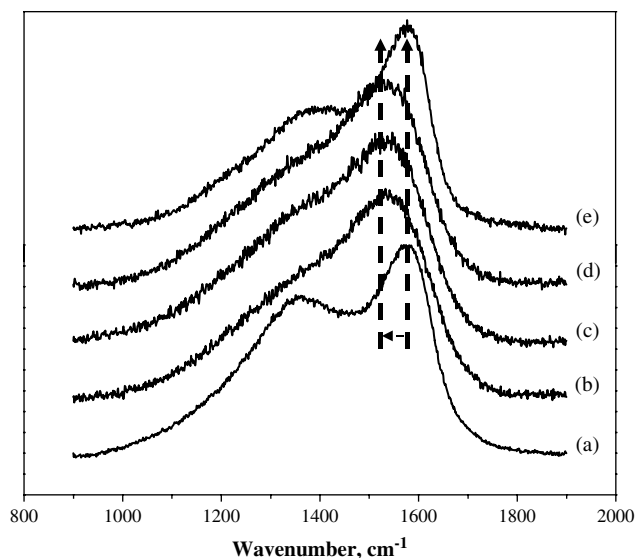


Fig. 2. Raman spectra of DLC-based coatings: (a) “pure” DLC, H-free DLC-W coatings alloyed with increasing W contents, (b) 6 at.% W, (c) 9 at.% W, (d) 12 at.% W and (e) W-DLC:H (10 at.% W) deposited with 39 at.% H content.

almost doubled. The critical load also increased appreciably. The constant hardness measured, whichever the W content was, permits to conclude that the effect of W atoms in the C-matrix should be the main factor determining the hardness of the coatings. In fact, at first sight it could be expected that the hardness increase in relation to the unalloyed film was due to the presence of W-carbide nanocrystals, taking into account their high hardness (>20 GPa). However, the constant hardness value measured in all the W-containing films, independently of the W-carbide content, associated with their similar molecular arrangement, as demonstrated by Raman spectroscopy, points to the disordered C-matrix as the main responsible for the hardness improvement. The presence of W atoms can establish stronger bonds between graphitic clusters having a consequence, by the one hand, impeding their growing and ordering and, on the other hand, contributing for the hardness increase.

The presence of W has also an indirect effect on the hardness by promoting an increase in the compressive residual stress. As shown in Table 1, W-containing films have a significant higher value of residual stress than unalloyed film (from 1.1 to ~3 GPa), factor which is currently indicated in the literature on hard coatings as one of the most important on determining the hardness of the material [21,22].

H incorporation has a complete inverse influence on the hardness of DLC films. In fact, the presence of H counterbalances the effect of W and the hardness drops to a value close to the one of pure DLC film. Similar arguments as those for W can be used for understanding this variation. The presence of H will close any dangling bonds in the graphitic structures forming sp^3 bonds [2]. The interconnection between the graphitic rings will be reduced and the hardness decreases. For the highest H contents, polymerization of the C networks’ starts to occur [23], i.e. chain like structures are formed instead of aromatic rings, with the consequent decrease in the hardness as it is shown in Table 1.

Again, and in close relation to the hardness variation, the addition of H led to an important decrease of the compressive residual stress [2], factor that indirectly can justify the hardness decrease as it was referred to above. If the hardness is plotted as a function of the residual stress values for all the DLC-based studied coatings, a fairly linear trend can be achieved (Fig. 3).

The decrease in the residual stresses could be in the origin of the higher L_c values shown by the H-containing DLC coatings after scratch-testing ($L_c \sim 75$ N). The adhesion failures are related to the shear stresses occurring in the interface induced by the normal

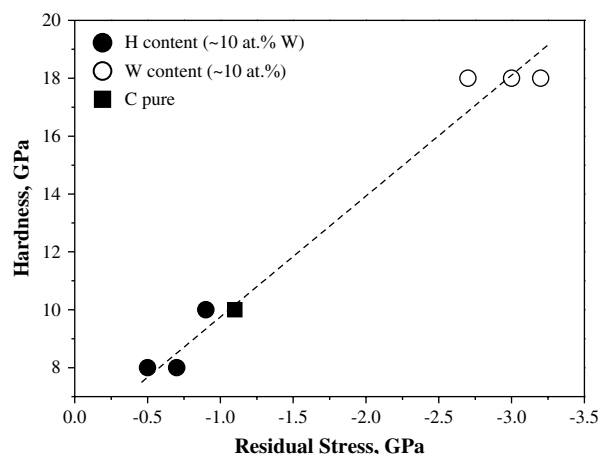


Fig. 3. Hardness values as a function of the residual stress of DLC-based coatings (the trend line is a guide for the reader).

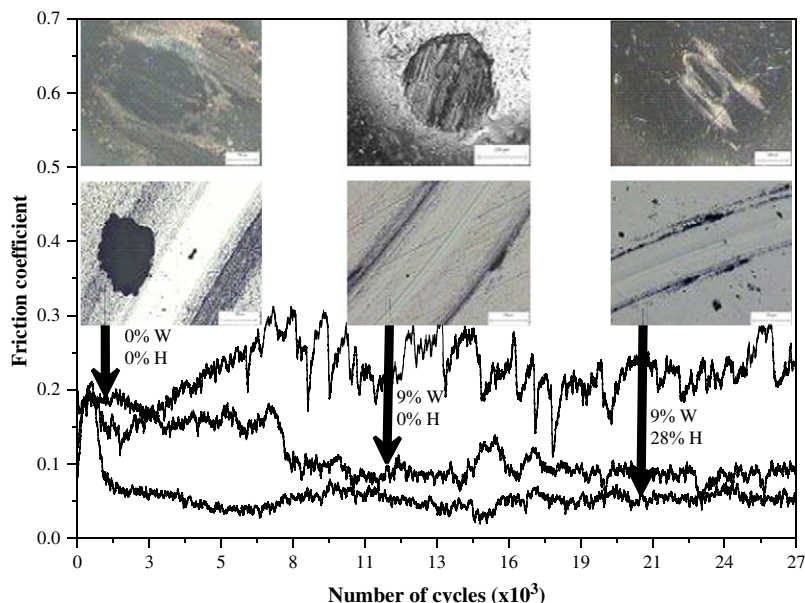


Fig. 4. Friction coefficients of DLC-based coatings deposited with and without W and H. Micrographs of the wear track and the transfer layer on the 100Cr6 ball after 26,500 sliding cycles are shown inset.

applied load and the tangential load generated during the indenter sliding. The observed spalling/chipping occurred in the front of the indenter suggest that the failure was due to compressive stress. Thus, the decrease of the residual compressive stress will retard the failure occurrence giving rise to higher critical loads [12].

3.3. Tribological behaviour

Unalloyed DLC film shows a rather high friction coefficient (>0.2) for a self-lubricating type material. The addition of W considerably reduced this value for the range [0.09–0.12]. The friction curves of these coatings are smoother than the one of pure DLC film as shown in Fig. 4. For this film, strong oscillations can be observed suggesting that stick-slip process is occurring during the sliding, giving rise to high friction. The presence of humidity in the testing atmosphere in conjunction with the dangling bonds existing in the C-matrix promotes the formation of strong bonds between the graphitic clusters impeding the easy sliding between their basal planes [24]. The addition of W will contribute for decreasing the number of dangling bonds and the presence of humidity can even improve the sliding process by forming a thin adsorbed layer in the contact, working as lubricant. This is one of the main justifications found in literature for the low friction of some C-based coatings sliding in room conditions [24]. When W content increases, a slight increase in the friction coefficient is detected related with the growing importance of W-carbide nanocrystals. The analysis of the ball after sliding permits to detect abrasion traces in the worn surface, showing the interaction of the hard tungsten carbide nanoparticles with the transfer layer giving rise to the increase of the friction coefficient.

The H incorporation led to a significant improvement of the sliding behaviour with a decrease in the friction coefficient for values lower than 0.1, trend also found in the literature by other authors [25]. As it was already referred to, the presence of H permits closing the dangling bonds avoiding establishing strong interactions between the graphitic clusters via the water vapour presents in the atmosphere. The values are even lower than for H-free W-DLC since the dimension of the graphitic clusters is higher facilitating the sliding between the plans of the material.

The presence of the humidity, as for W-containing coatings, works as a lubricant also contributing for the low friction coefficients.

In spite of the lower friction coefficients of H-containing coatings, their wear rates are generally higher than for H-free coatings. This result should be related with their lower hardness, which does not permit resisting so well to the abrasion process induced by the ball/transfer layer. On the other hand, the wear rates in the antagonist balls are, by a similar reason, lower than for H-free films. It should be remarked that the 100Cr6 steel ball, even though in heat treated conditions, has lower hardness than the films, being worn as much as the antagonist is harder. Fig. 4 shows typical micrographs of the wear tracks of the coated disks for pure DLC, W-DLC and W-DLC:H films. It is clear in all cases that a transfer layer is being formed on the antagonist ball, which should be related to the low friction coefficients presented in Table 1. It was also observed that there was a much higher wear of the ball in the case of H-free W-containing film with characteristic abrasive marks attributed to their higher hardness in comparison with pure DLC and H-containing coatings.

4. Conclusions

DLC films were deposited with increasing W contents up to 12 at.% and H contents up to 40 at.% by r.f. magnetron sputtering in non-reactive and reactive modes. The asymmetry of the broad XRD peaks allowed concluding that the structure of the coatings could be described as an amorphous C-matrix embedded with β -WC_{1-x} nanocrystals. H-free W-containing films were harder than both a-C and WC_{1-x}/a-C:H due to their higher compressive residual stress. WC_{1-x}/a-C:H films with high H content are softer, due to the increasing ordering of the graphitic clusters and the formation of polymeric like features as shown by Raman spectroscopy. All films showed good adhesion to the steel substrates, particularly those containing H for which critical loads close to 75 N were achieved.

The best tribological behaviour in relation to the friction coefficient was reached for the H-containing coatings for which values as low as 0.05 were obtained. The most wear resistant coatings were H-free ones when alloyed with W ($0.3\text{--}0.7 \times 10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$),

probably due to their higher hardness. On the other hand, they promote a much higher wear rate in the antagonist steel ball.

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