Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2006) 1063 – 1068
www.elsevier.com/locate/tsf

Characterization of magnetron co-sputtered W-doped C-based films

C.W. Moura e Silva [a], J.R.T. Branco [a], A. Cavaleiro [b,*]

[a] *REDEMAT/CETEC - Laboratório de Engenharia e Modificações de Superfícies, CETEC, Av. José Cândido da Silveira, 2000, Horto, 31.170-000, Belo Horizonte, Minas Gerais, Brazil*

[b] *ICEMS - Grupo de Materiais e Engenharia de Superfícies, Faculdade de Ciências e Tecnologia da Universidade de Coimbra - Pólo II - Pinhal de Marrocos, 3030-788 Coimbra, Portugal*

Available online 20 September 2006

Abstract

In this paper, W-doped C-based coatings were deposited on steel and silicon substrates by RF magnetron sputtering, using W and C targets, varying the cathode power applied to the W target and the substrate bias. The chemical composition was varied by placing the substrates in a row facing the C and W targets. W content in the films increased from 1 to 2 at.% over the C target to ∼73 at.% over the W target. The coatings with W content lower than ∼12 at.% and ∼23 at.%, for biased and unbiased conditions, respectively, showed X-ray amorphous structures, although carbide nanocrystals must exist as shown by the detection of the WC_{1-x} phase in films with higher W content. C-rich films were very dense and developed a columnar morphology with increasing W content. An improvement in the hardness (from 10 GPa, up to 25 GPa) of the films was achieved either when negative substrate bias was used in the deposition, or when the WC_{1-x} phase was detected by X-ray diffraction. The adhesion of the coatings is very low with spontaneous spallation of those deposited with negative substrate bias higher than 45 V. Varieties in cathode power (90 W or 120 W) applied to the W target showed no observable influence on the characteristics of the films.

Keywords: DLC; W-doped DLC; C-based coatings; Co-sputtering; Mechanical properties

1. Introduction

In the last few years, there has been a huge amount of research work on the development of C-based coatings. Among them, Diamond-like Carbon (DLC) coatings have high hardness and a low friction coefficient which make them suitable for many different fields of industrial activities. However, due to the high level of residual stress, their use has sometimes been restricted, particularly when mechanical components are exposed to high loading. Doping DLC with elements, such as Ti, W, Cr, Si and N, has been proposed as an alternative way to reduce the residual stress while maintaining fairly constant hardness values. Furthermore, this solution permits improved adhesion to different substrates and contributes to the inhibition of the graphitization of the films [1–9]. Finally, the incorporation of chemical elements in C-based coatings which can lead to carbide formation has been recently used for the deposition of nanocomposite coatings consisting of nanocrystals of the carbide phase immersed in a C-based amorphous matrix [3–7].

This study is a part of a research effort with a primary objective to evaluate the influence of the hydrogen content on the tribological properties of metal-doped carbon films, particularly with W as the dopant. In the first part of the study, the concern is to optimize the W content in H-free carbon films in order to reach the best compromise between good mechanical properties and low residual stresses. The optimized W value will then be maintained while the H content in the films is varied. Hence, in this paper, the influence of substrate bias and W-content on the chemical, physical and mechanical properties of sputtered C-based films are studied.

2. Experimental details

The W-doped C-based coatings were deposited by magnetron sputtering from W and C targets in an Ar atmosphere. An ESM 100 Edwards apparatus working with balanced cathodes powered by r.f. current was used. The discharge pressure was kept constant during the entire deposition procedure at 0.8 Pa. The cathode power was kept constant at P_C=600 W on the C target (100 mm diameter) whereas, in the W target, values of P_W=90 or 120 W were used. The use of two P_W values resulted in W distributions

* Corresponding author. Tel.: +351 239 790 745; fax: +351 239 790 701.
E-mail address: albano.cavaleiro@dem.uc.pt (A. Cavaleiro).

0040-6090/$ - see front matter
doi:10.1016/j.tsf.2006.07.084

along the samples placed over the two targets with shallower or steeper W content variation curves. With the higher P_W value, a steeper slope in the increase of W content with increasing distance from the center of the C target was expected. The total deposition time was 180 minutes. Before deposition, a discharge was established close to the substrates for 20 min for surface cleaning purposes. The influence of a negative bias (Vs) on the films' properties was studied by r.f. biasing the substrate in the range from −90 V to 0 V. Polished high speed steel (M2 heat treated to reach a final hardness of 9 GPa) and Si pieces were used as substrates.

The chemical composition, the morphology and the structure of the films were evaluated by a Cameca electron probe micro-analysis (EPMA) apparatus, a Jeol scanning electron microscope (SEM) and a Phillips X-ray diffractometer (XRD) with Co-Kα radiation, respectively. The thickness of the films was evaluated with a Mahr profilometer and was confirmed by cross section SEM analysis. The hardness measurements were determined by depth-sensing indentation using a Fischerscope H100. A 10 mN applied load was used for the measurements by following the experimental procedure presented by Fernandes et al. [10]. The experimental results were corrected for the geometrical imperfections of the indenter (Vickers), for the thermal drift of the equipment, and for uncertainty in the zero position, following the method proposed by Antunes et al. [11]. The hardness value was obtained by averaging at least the results of 10 different indentations.

The adhesion/cohesion of the coatings was studied by scratch testing with a commercially available equipment (CSEM Revetest), under standard conditions [12]. The critical load (Lc) was determined by the first adhesive failure detected in the scratch channel. At least three scratch-tests were performed for each sample.

3. Results and discussion

3.1. Coatings deposited without substrate bias (Vs = 0 V and P_W = 120 W)

3.1.1. Chemical composition and deposition rate

In order to deposit films with a large range of chemical compositions in a single batch, a particular geometrical configuration was used for the substrate/target as sketched in Fig. 1. Several substrates were placed in a row over the two targets between the points corresponding to the projections of their centers. By performing the deposition with the substrate holder in a stationary position it was possible to study the influence of a given set of deposition parameters on the properties of C-based films doped with different W-contents. Fig. 2 shows the generic trend in chemical composition variation, for unbiased conditions, by normalizing to 100% the W and C contents. As expected, there is a progressive increase in W content from 1–2 at.% over the C target up to ∼73 at.% over the W target. Thus, in similar positions over the centre of both targets, the W content over the C target is much lower than the C content over the W target, a fact that can be attributed to two main factors as follows:

1. The power applied to the W target (120 W) is much lower than the one to the C target (600 W). Such a difference gives rise to a lower deposition rate on the sample over the W target (6 nm min^{-1} against 11 nm min^{-1} on the C target) enhancing the role of the atoms coming from the opposite target.
2. The lower atomic weight of C in relation to W ensures that collisions in the interelectrode space interfere much more efficiently with the trajectories of C compared to W sputtered atoms. For the values of the discharge pressure and the target/substrate distance used in this work (0.8 Pa and 65 mm, respectively), the loss of energy of sputtered C atoms during collisions in the interelectrode space is expected to be higher than for W sputtered atoms (see e.g. [13]). As a consequence, C atoms will arrive at the substrate with altered trajectories compared to W atoms which will maintain approximately the original ejection paths from the target. Thus, C atoms can reach zones further from the emission points in the C target than W atoms in relation to W target, which explains the differences in content of both elements in relation to the opposite target (1–2 at.% for W over C cathode against ∼27 at.% for C over W cathode).

The deposition rate is maximum over the C target (∼11 nm min^{-1}) decreasing progressively between both targets down to a

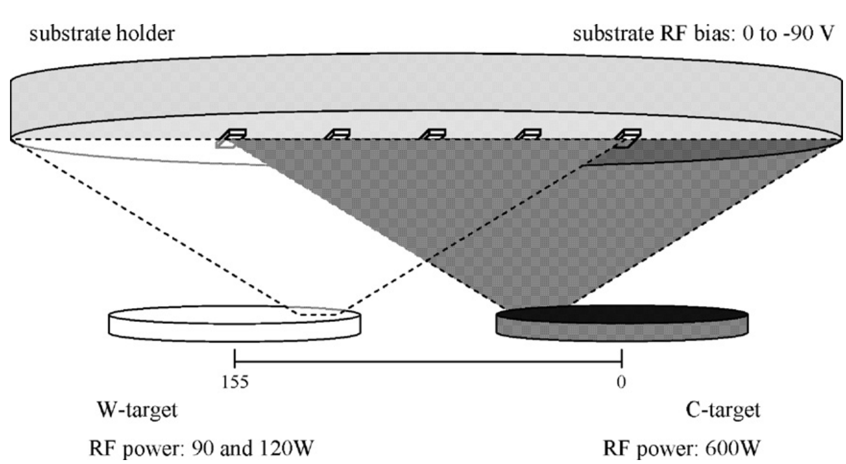

Fig. 1. Schematic drawing of the setup for the deposition of W-doped C-based coatings.

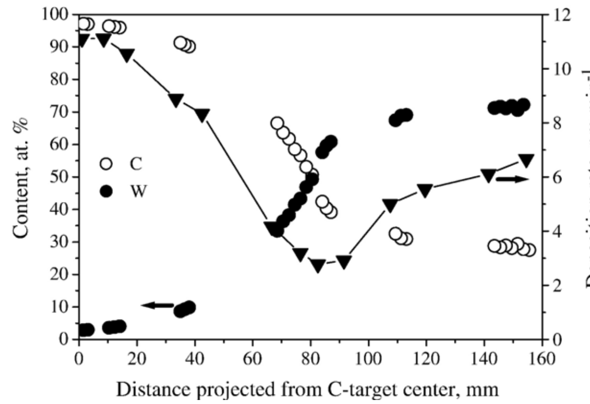

Fig. 2. Evolution of the deposition rate and the chemical composition of W-doped C-films (at.%W+at.%C=100%) as a function of the distance projected from the center of the C target (Vs=0 V, P_W=120 W).

minimum of 3 nm min^{-1} and increasing again over the W target (~7 nm min^{-1}), as shown in Fig. 2.

3.1.2. Structure and morphology

Generally, the films having low W content are X-ray amorphous (Fig. 3). However, as referred to in other research, it is expected that, even for low metal content, carbide nanocrystals will exist immersed in the C-rich matrix [6,7]. In similar coatings with Ti as the doping metal, deposited using the same equipment, high resolution transmission electron microscopy detected the existence of these carbide nanocrystals act low Ti doping levels [3]. The small size of the crystals in conjunction with their low number makes it difficult to obtain well defined diffraction peaks. The evolution of structure, with increasing W content confirms the poorly crystallized status of these films. In fact, the broad peak characterizing this structure starts to decompose into two broad ones whose positions are coincident with the standard ones of a W-carbide phase (β-WC_{1-x}). With a further increase in W content, the films present a well defined XRD pattern with clear evidence of the β-WC_{1-x} phase.

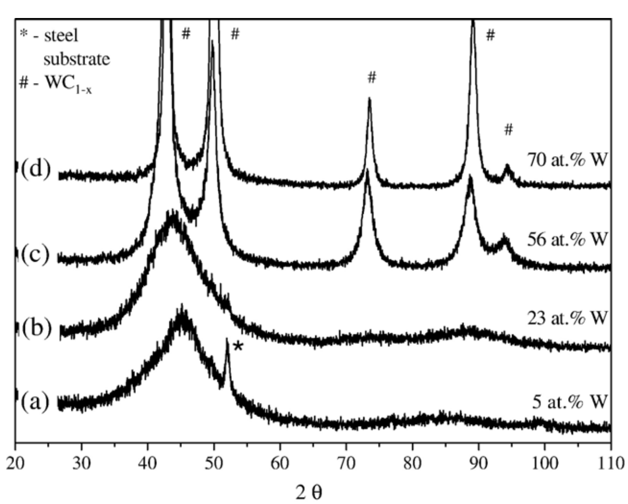

Fig. 3. Typical XRD patterns for increasing contents of W incorporated in C sputtered films (Vs=0 V, P_W=120 W): (a) and (b) C-based amorphous matrix with nanocrystals of β-WC_{1-x} phase, (c) and (d) β-WC_{1-x} phase.

Fig. 4 presents micrographs of the cross section morphologies of W-doped C films. Films with low W content show a very dense morphology which becomes progressively more columnar with increasing tungsten content. In all cases, it was possible to detect a thin layer (300–400 nm), close to the interface with the substrate. This is very dense but becomes progressively less compact, with visible nanopores, towards the film's surface. Preliminary analysis by EDS in cross section did not show any significant change in the chemical composition from the substrate surface to the film's surface. No plausible explanation was yet suggested for this change in morphology, which is now under more detailed study using high resolution electron microscopy techniques. The trend in morphology evolution is very similar to the one found previously for Ti-doped DLC coatings deposited using the same equipment [3].

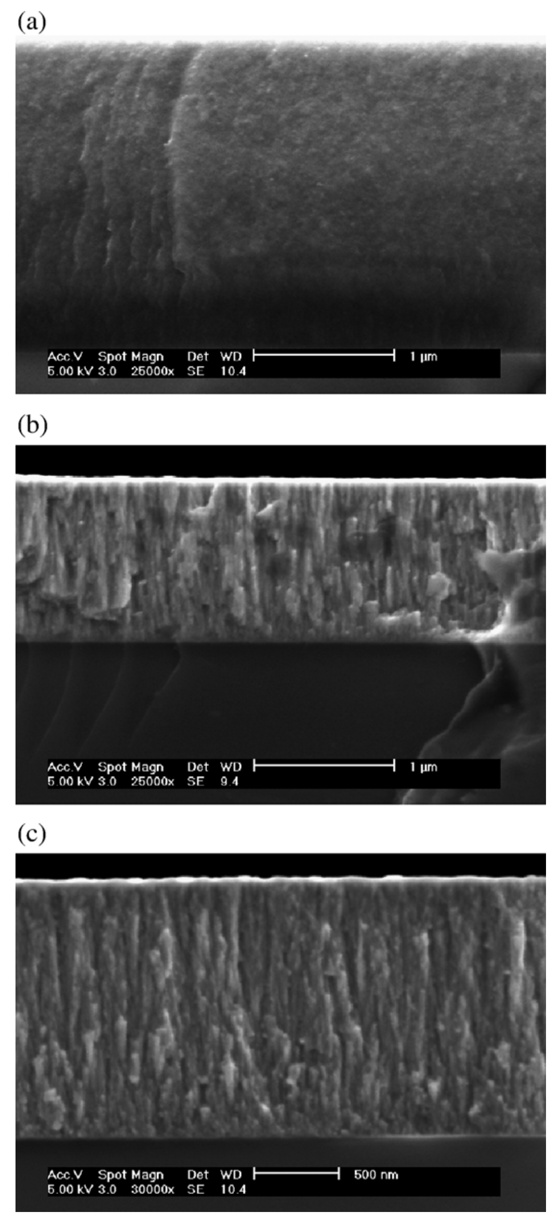

Fig. 4. SEM micrographs of the cross-sections of W-doped C-films deposited with increasing W content (Vs=0 V, P_W=120 W): (a) 4 at.%W, (b) 47 at.%W and (c) 71 at.%W.

3.1.3. Hardness

For the doping levels up to 23 at.% of W, no changes in the hardness of the films were observed. A value close to 10 GPa was found for these films which is slightly higher than the one measured for a pure C film deposited under similar conditions (H=8.2 GPa), showing that W-doping can have a beneficial role in the mechanical properties of C-based films. In the films with W content over 50 at. %, where the β-WC_{1-x} phase is clearly defined, the hardness increases significantly reaching values higher than 25 GPa. The H/E ratio was found to be close to 0.12 starting to decrease at 23 at.% W (0.10) and reaching only 0.07 for the hardest films. The H values are of the same order of magnitude as those measured in Ti-doped C-films deposited under similar processing conditions [3].

3.2. Influence of substrate bias and cathodes power

3.2.1. Chemical composition and deposition rate

As the objective of this research was to study the addition of W to C-based sputtered films, only chemical compositions up to 50 at.%W were evaluated.

No significant influence of substrate bias was observed in the distribution of W and C elements along the sample row as shown in Fig. 5 for the two values of P_W, 90 and 120 W. In fact, all the points concerning the W/C ratio can be plotted along the same trend line independently of the substrate bias used in the deposition. It should be noted that for negative Vs > 30 V, only a few values are shown due to the fact that extensive spalling occurred under these conditions. As expected, the W/C ratio increases more steeply with the distance from the centre of C target for P_W=120 W as a consequence of the higher number of W sputtered atoms under these conditions.

The substrate bias has a large influence on the O content of the films. Fig. 6 shows the variation of the O content, as well as of the deposition rate (Vdep), as a function of the distance from the centre of the C target for the case of P_W=120 W. Similar trends were found for P_W=90 W. Several conclusions can be drawn from the analysis of these results, as follows:

– First, the deposition rate decreases in the samples placed between both targets. This result is to be expected due to the cosine dependence of the ejected atoms [14] which makes the number of atoms ejected from a point for angles far from the normal decrease progressively. It should be remarked that due to the magnetron configuration, almost all the sputtered atoms come from the region between 15 and 35 mm in the scale of Fig. 6.
– Second, there is a strong influence of the substrate bias on the deposition rate. As a consequence of resputtering induced by the bombarding ions on the growing film, there is a decrease in the number of atoms attached to the film, with the consequent decrease in the apparent rate (Vdep). The magnitude of this effect is enhanced with increasing negative substrate bias values.
– Third, ion bombardment in negatively biased films explains their lower O content. In fact, the incoming Ar ions will promote the ejection of the loosely bonded physically adsorbed O atoms, impeding their incorporation into the growing film. However, this effect seems to have a threshold above which no further influence of ion bombardment occurs as demonstrated by the same O contents reached in the films biased with −30 or −45 V.

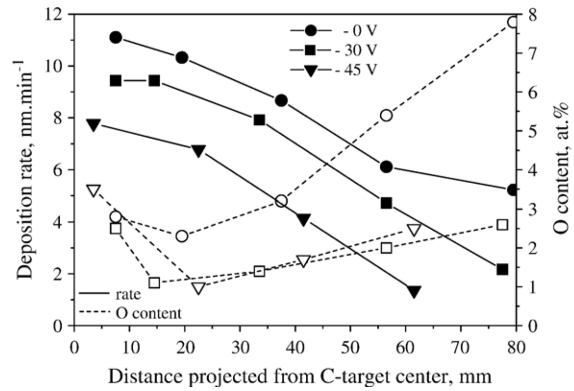

Fig. 6. Evolution of the deposition rate and O content of W-doped C-films as a function of (1) the distance projected from the center of the C target (P_W=120 W) and (2) the substrate bias.

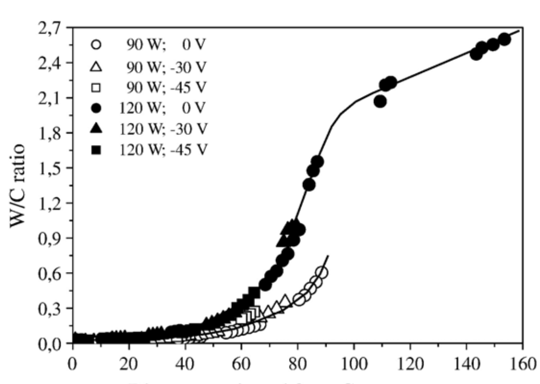

Fig. 5. Evolution of the chemical composition (at.%W/at.%C) of W-doped C-films as a function of (1) the distance projected from the center of the C target; (2) the substrate bias and (3) the W-cathode power applied.

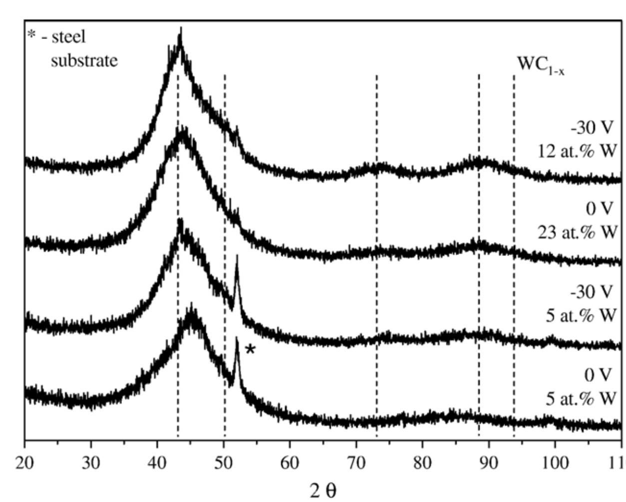

Fig. 7. Typical XRD patterns for increasing contents of W incorporated in C sputtered films as a function of the substrate bias.

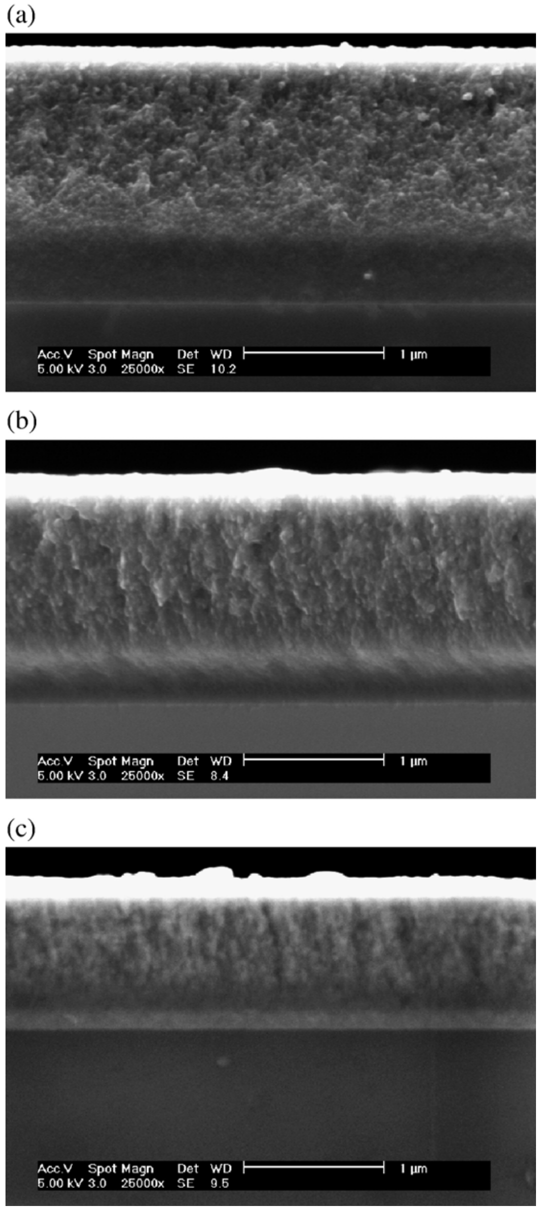

Fig. 8. SEM micrographs of the cross-sections of W-doped C-films (P_W = 120 W) deposited with Vs = −30 V: (a) at.%W = ~3 at.%, and Vs = −45 V: (b) at.%W = ~3 at.%, (c) at.%W = ~10 at.%.

– Fourth, the increasing O content in the coatings distant from the C target. Correlates well with the decrease in the Vdep values, and is related to the longer time O atoms have available to adsorb into the growing film [14]. However, there is a strange inversion in the O content when the data points closest to the center of the C target are considered. In fact, in these points, although Vdep reaches its maximum value (as a result of the superposition of sputtered fluxes coming from the opposite zones where the target is preferentially eroded), the O content is higher than in the samples placed over the grooved zone of the target (15–35 mm). This behaviour can only be explained by considering the two effects presented before, i.e. the ion (neutrals) bombardment and the deposition rate. There must be an optimum compromise between Vdep and Vs to obtain the best performance in impeding the incorporation of O in the films. Low deposition rates not only allow more time for the adsorption of O atoms but also allow more time for the action of the bombarding species. The steeper increase in the O content with the distance to the center of the C target for unbiased films in comparison to biased ones can only be explained by the synergy between both effects in biased films. In unbiased ones, strong bombardment by the Ar neutrals reflected at the target during the sputtering process is expected only in the samples directly placed over the grooved zone of the target [14]. In the other zones, only the influence of the deposition rate can be expected, which can help explain the higher O content in samples placed over the center of the C target in relation to those over the grooved zone. This is not the case for biased samples. In spite of the ion bombardment being much more intense over the grooved zones (high density plasma), the other zones also suffer bombardment since the applied bias can create a plasma all over the biased parts.

3.2.2. Structure and morphology

The evolution of the structure with increasing W content, described above for unbiased films, is repeated whatever Vs and P_W values are used in the deposition. However, in biased coatings, the detection of the carbide nanocrystals by XRD technique occurs for lower W contents (~12 at.% against the ~23 at.% for unbiased film) (Fig. 7). This must be related to the higher adatom mobility in biased depositions which enhances the segregation of W atoms from the C matrix and their precipitation under the form of β-WC_{1-x}. It should be remarked that although this phase is deficient in carbon in relation to 1/1, no other W-carbide was detected even if the equilibrium phases have higher C contents. The observation of the cross section of the films by SEM did not allow significant changes in the morphology and density of the coatings to be detected. Fig. 8 shows micrographs of films deposited at two different substrate biases (Vs = −30 V and −45 V for at.%W = 3 at.%) and W contents (at.%W = 3 and 10 at.% for Vs = −45 V). Approximately the same compact granular aspect of cross section morphology can be observed for all films, contrary to what could be expected from the literature (see e.g. [15]). In fact, with the increase of energy delivered to the substrate during

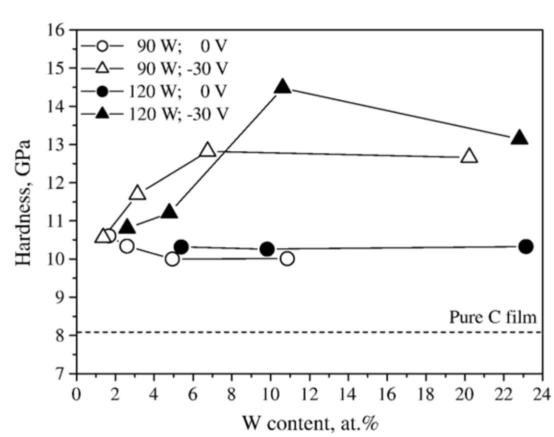

Fig. 9. Evolution of the hardness of W-doped C-films as a function of (1) their W content; (2) the substrate bias and (3) the W-cathode power applied.

film growth, smoother and denser films are usually deposited which is not true in this case as can be shown by comparing micrographs in Figs. 4 and 8. Presently, studies are being performed for the evaluation of the residual stresses and the sp^2/sp^3 contents in these films which may shed some light on the interpretation of the degree of compactness of the coatings.

3.2.3. Mechanical properties

Fig. 9 compares the hardness values for unbiased and −30 V biased films for P_W=90 and 120 W. No data are presented for higher Vs values due to the bad adhesion of the films. Although for W-poor films, no influence of Vs can be detected (H is kept close to 10 GPa) whatever P_W value is, for higher W content biased films show an improvement in the hardness that can reach 50% for W contents close to 10 at.%. On the other hand, biased films show lower adhesion, having very low Lc values (typically [6–7 N] against [12–17 N] for unbiased films) which make these coatings unsuitable for practical applications. In order to envisage testing these coatings in tribological applications, an improvement in adhesion is required by optimizing the deposition process, e.g. by using a metallic interlayer between the films and the substrate. If such a procedure is followed it will be also possible to further study higher Vs values. In a previous study with Ti-doped films [3], hardness values as high as 37 GPa could be reached but with Vs=−60 V. In that study a Ti interlayer was used allowing successful deposition of the coatings even with Vs values of −80 V.

4. Conclusions

C-based films were alloyed with W up to more than 50 at.% by magnetron co-sputtering from two individual targets of C and W. All coatings were XRD amorphous or quasi-crystalline up to W contents of ~12 and ~23 at.% when deposited with or without substrate bias, respectively. For higher W contents the presence of WC_{1-x} nanocrystallites was clearly detected by XRD.

Substrate bias was revealed to be a determining factor in both the O content and the deposition rate whereas no influence on the W/C ratio and cross section morphology was registered. An inverse trend was observed with mechanical properties, i.e. the hardness increased with substrate bias while the scratch test critical load value decreased. For the highest applied substrate bias the coatings spalled off spontaneously. The highest H values were reached for a W content of 10 at.%. No influence of the power applied to the W target on the coatings properties was detected.

For the future study of the influence of hydrogen content on the tribological behaviour of W-doped C-based films, the coatings should be deposited with the substrate negatively biased at low Vs values with W contents close to 10 at.%. Under these conditions, a good compromise between high hardness and good adhesion can be achieved.

Acknowledgments

The authors acknowledge the financial support from Programme Alβan, the European Union Programme of High Level Scholarships for Latin America, scholarship no. E04D045110BR. The authors are also indebted to Dr. A. Nossa for performing SEM analysis at Prof. J. De Hosson's group at the University of Groningen at Netherlands.

References

[1] J. Robertson, Mater. Sci. Eng., R Rep. 37 (2002) 129.
[2] A. Grill, Surf. Coat. Technol. 94–95 (1997) 507.
[3] Y.T. Pei, D. Galvan, J.Th.M. De Hosson, A. Cavaleiro, Surf. Coat. Technol. 198 (2005) 44.
[4] C. Corbella, E. Pascual, G. Oncins, C. Canal, J.L. Andújar, E. Bertran, Thin Solid Films 482 (2005) 293.
[5] C. Strondl, N.M. Carvalho, J.Th.M. De Hosson, G.J. van der Kolk, Surf. Coat. Technol. 162 (2003) 288.
[6] A.A. Voevodin, J.P. O'Neill, J.S. Zabinski, Thin Solid Films 342 (1999) 194.
[7] J.-P. Palmquist, Zs. Czigany, M. Odén, J. Neidhardt, L. Hultman, U. Jansson, Thin Solid Films 444 (2003) 29.
[8] J.C. Damasceno, S.S. Camargo Jr., M. Cremona, Thin Solid Films 433 (2003) 199.
[9] K. Vercammen, K. Van Acker, A. Vanhulsel, J. Barriga, A. Arnsek, M. Kalin, J. Meneve, Tribol. Int. 37 (2004) 983.
[10] J.V. Fernandes, A.C. Trindade, L.F. Menezes, A. Cavaleiro, J. Mater. Res. 15 (8) (2000) 1766.
[11] J.M. Antunes, A. Cavaleiro, L.F. Menezes, M.I. Simões, J.V. Fernandes, Surf. Coat. Technol. 149 (2002) 27.
[12] ENV 1071-3 Advanced technical ceramics — methods of test for ceramic coatings: Part 3. Determination of adhesion and other mechanical failure modes by a scratch test, 2002.
[13] R.E. Somekh, J. Vac. Sci. Technol., A 2 (1984) 1285.
[14] D.M. Mattox, Handbook of Physical Vapor Deposition (PVD) Processing, Noyes Publications, New Jersey, 1998.
[15] Y. Lifshitz, Diamond Relat. Mater. 5 (1996) 388.