Growth kinetics of nanometric dendrites in metal-carbon thin films

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Abstract

Tungsten-carbon films deposited by pulsed-DC reactive magnetron sputtering show the formation of a dendritic structure at the nanometric scale. The structure is formed by a combination of a polycrystalline $\beta$–W phase together with a non-stoichiometric WC$_{1-x}$ phase. The nanodendrites coincide with W-rich zones, whereas C-rich regions are located at the interstices. The characteristics of this nanostructure have been modulated by varying the metal concentration of the films. Composition, structure and morphology were characterized by X-Ray Photoelectron Spectroscopy, Electron Probe Micro-Analysis, Transmission Electron Microscopy, X-Ray Diffraction and Atomic Force Microscopy, whereas mechanical and tribological properties were evaluated by profilometry, nanoindentation and microscratch. The observed growth pattern is interpreted as the result of nucleation and growth of a W phase into a W-C amorphous
matrix, whose growth is controlled by diffusion of carbon. A simulation model based in phase field modelling presenting similar morphologies is formulated. This special structure combines properties of W and diamond-like carbon films, which enlarges the scope of applications towards self-lubricant hard and low-friction coatings with improved stability.

1. Introduction

Nanostructure has a strong influence on the macroscopic properties (mechanical, electrical, optical, etc) of thin films, and the control of this structure can be a key step in the design of new coatings with improved properties [1,2]. In this context, a great deal of research has been recently devoted to the engineering of designed structures at the micro to nanometric scales. This can be achieved by means of very expensive and time-consuming techniques, as for instance nanolithography and atomic force microscopy [3], or by procedures such as varying deposition conditions during growth, with which properties such as mechanical performance of protective coatings can dramatically be enhanced [4].

An alternative approach is to provide growth conditions for which the desired nanostructure is spontaneously generated. Carbon nanotubes constitute a classical example of self-structured material grown from a reactive atmosphere in the presence of a catalyst [5,6]. Another example is provided by nanocomposites, which can be formed by thermally induced nucleation and segregation of immiscible phases. These nanostructured materials are of great interest to enhance certain film properties in view of specific applications, such as hard and tribological coatings [7-11], biocompatible coatings [12] and films with electric functionality [13]. The current investigation in
nanocomposite coatings mainly addresses the connection between the structure and the physical properties, with the aim to enlarge their scope of technological applications in optics, electronics and magnetism. A physical mechanism related to nanocomposite formation, spinodal decomposition, produces spontaneous segregation at a distinct length scale, and for instance it can form metal-carbon (Me-C) multilayers at the nanometric scale [14,15]. An interesting point in these examples is that the involved physical mechanisms act at scales at which it is difficult or expensive for a structure to be directly manipulated, and that often the level of complexity achieved is much higher than what could be obtained with other techniques. It is therefore of a capital interest to find new procedures to induce a material to generate nanostructures, but it is also crucial to identify the relevant physical mechanisms, since their control should allow for the design and fine tuning of the material’s final properties.

In this paper we study the spontaneous formation of structures during the growth of tungsten-carbon thin films deposited by pulsed-DC reactive magnetron sputtering. Most of previous research on Me-C films was devoted to the addition of a minority metal content in an essentially diamond-like carbon (DLC) matrix, in order to modulate the DLC characteristics. On the contrary, here we have explored the opposed composition range, namely that of majority metal content. Whereas pure W films show a columnar structure, we obtain that the addition of C induces the formation of a complex, branched structure of nanometric dendrites, similar to those that can be found in solidification processes but at very different scales [16]. Moreover, the characteristics of this structure can be controlled to a certain extent by varying the composition of the films. We will also present a model for the growth of a polycrystalline W phase in which dendrites appear via nucleation of W crystals, whose growth is limited by C diffusion and rearrangement of W atoms. The combination of this nanodendritic structure with the
mixture of tungsten and carbon atoms shows beneficial results on surface properties. Moreover, the presence of W makes such structures promising for high-temperature applications.

2. Experimental details and procedure

2.1. Thin film deposition and characterization

Tungsten-carbon films (W-C) were deposited by reactive magnetron sputtering of a W target in an Ar-diluted CH₄ atmosphere. The depositions were performed in a plasma reactor equipped with a load-lock chamber, and a computer-controlled gas supply and pumping system. It achieved a base pressure of 10⁻³ Pa as pumped down by a turbomolecular pumping system. The substrates were monocrystalline Si (100) wafers, placed on a sample-holder located 10 cm away from the target. The samples were biased to -200 V using RF (13.56 MHz) in order to increase the energy of ion bombardment onto the growing film. This substrate-holder (cathode) was water-cooled to keep the growth process at room temperature. An asymmetrical bipolar pulsed-DC power supplier (ENI RPG-50) was employed to drive the W target cathode, with 100 W, 100 kHz pulse frequency and 70% duty cycle as consigned values. Mass flow controllers injected Ar and CH₄ at a total gas flow of 40 sccm, yielding a pressure of 5 Pa. Composition of the films was regulated by varying the relative CH₄ flow ratio, R, from 0 to 25%, where \( R = \frac{[CH_4]}{[CH_4 + Ar]} \).

Measures of atomic composition of the films were performed by X-Ray Photoelectron Spectroscopy (XPS) by using a Perkin-Elmer PHI 5500 spectrometer, operated with the Kα line of Al (1.487 keV) as X-ray source. The atomic compositions
showed the following relationship with $R$: films grown at $R=0, 1, 2, 3, 6$ and $25\%$ presented a composition of $100, 85, 74, 65, 51,$ and $19\%$ at. W, respectively [17]. H atoms are not counted in this percentage. Additional measurements of composition by Electron Probe Micro-Analysis (EPMA) by a CAMECA SX-50 provided values of metal abundance which agreed within 15\% margin of error with respect to XPS. Such results gave bulk information, from which it was inferred that W-C films possessed a uniform composition.

Cross-section Transmission Electron Microscopy (TEM) images and Selected Area Electron Diffraction (SAED) patterns were obtained by a Philips CM30 electron microscope working at a voltage of 300 kV. On the other hand, high resolution TEM (HRTEM) images and Electron Energy Loss Spectroscopy (EELS) composition mappings were provided by an electron microscope working at 200 kV with a Jeol Jem 2010F field emission gun. The procedure of sample preparation for cross-section analysis involved several steps. Firstly, the samples were cut, and glued pairs were prepared by facing the coated surfaces. After that, plano-parallel grinding, polishing and concave grinding were performed in order to obtain very thin “sandwiches”. The process to obtain electro-transparent samples finished with ion milling carried out in a precision ion polishing system.

X-Ray Diffraction (XRD) measurements were performed by a Siemens D-500 X-ray spectrometer with Bragg-Brentano geometry using 0.15406 nm wavelength radiation. Atomic Force Microscopy (AFM) measurements of surface topography were obtained by a multimode atomic force microscope with a Nanoscope IIIA electronics from Digital Instruments operating in tapping mode at a scan frequency of 2 Hz.

A Dektak 3030 surface profilometer was employed to measure both the thickness of the films and the radius of curvature of the substrates. These latter measurements, taken
before and after the deposition and applying Stoney’s equation, permitted to determine mechanical residual stresses of the films. Hardness of the films was determined at ambient conditions by the nanoindentation method using a NanoTest 550 (MicroMaterials) characterization system, which is fitted with a sharp Berkovich diamond indenter with a tip radius of 200 nm. Indentation curves were obtained with loading and unloading rates from 0.056 to 0.56 mN/s. Finally, friction characterization was performed under ambient conditions at 40% of relative humidity by utilizing the microscratch test method, which uses a 200 μm-diameter diamond spherical tip to perform 2 mm-long scratch path with an increasing normal from 0.1 to 20 N.

2.2. Simulations

For the simulations we have employed a model for phase transformation of a polycrystalline dilute alloy, based on modifications of known phase field models for solidification [18-20]. We consider three dimensionless fields: a (phase) field $\phi(\vec{r},t)$ that distinguishes two phases (amorphous W-C and crystalline W) by taking different values (-1 and +1) in each one; a field $U(\vec{r},t)$ related to the concentration of carbon; and a field $\theta(\vec{r},t) \in [0,1)$ indicating the local crystallographic orientation. For simplicity we have adopted a 2-D lattice system. We assume that there is an effective temperature gradient in the solid, moving at the growth velocity $v_g$, due to the energy of the bombardment of particles that hit the surface while the substrate is maintained at a cool temperature. Thus the local temperature is used to modify the stability of both phases. Also, we consider that diffusion only takes place close to the surface. Then, the dynamic equations for the fields are:
\[
\tau \frac{\partial \varphi}{\partial t} = \left[ 1 - \tanh^2(\Delta T) \right] \left[ \nabla^2 \varphi + \varphi(1-\varphi^2) - \lambda \varphi \left( U + \Delta T - \alpha \nabla \vartheta \right) \right]
\]
\[
\frac{\partial U}{\partial t} = \vec{\nabla} \cdot \left[ \frac{1}{2} \left( 1 - \tanh^2(\Delta T) \right) \left( 1 - \varphi \right) \nabla U + \vec{j}_U \right] + \frac{1}{2} \frac{\partial \varphi}{\partial t}
\]
\[
\frac{\partial \vartheta}{\partial t} = \frac{1}{2} D_o \left[ M_1 (1 - p(\varphi)) + M_2 (1 + p(\varphi)) \right] \vec{\nabla} \left[ \frac{1}{4} (1 + p(\varphi)) \left( \frac{\vec{\nabla} \vartheta}{|\vec{\nabla} \vartheta|} \right) \right] + (1 - p(\varphi)) j_0
\]

In these equations the carbon concentration is given by the local value of \( U(\vec{r}, t) \), through the expression:
\[
c(\vec{r}, t) = c^0(\varphi) \left[ 1 + \frac{\Delta c^0}{c^0_1} U(\vec{r}, t) \right]
\]

where \( c^0(\varphi) = c^0_1 (1 - \varphi)/2 + c^0_2 (1 + \varphi)/2 \), being \( c^0_{1,2} \) the concentrations of carbon of each of the phases, and \( \Delta c^0 = c^0_1 - c^0_2 \) is the miscibility gap. The dimensionless local temperature is given by \( \Delta T(\vec{r}, t) = (x + x_0 - v_x t)/l_T \), where \( x_0 \) marks the initial position of the film surface, and \( l_T = |m| \Delta c_0 / G \) is a characteristic thermal length related with the penetration length of the atoms. Here \( m \) is the slope of the liquidus curve of the phase diagram and \( G \) is the temperature gradient. Moreover, dynamics is only allowed in a thin layer near the surface by using the factor \( 1 - \tanh^2(\Delta T) \). The parameters \( M_1 \) and \( M_2 \) are the orientational mobilities in the liquid and the solid, \( \alpha \) reflects the change in free energy due to the presence of a grain boundary, and \( \lambda \) is a positive coupling constant.

The polynomial \( p(\varphi) = 15/8 (\varphi^5/5 - 2\varphi^3/3 + \varphi) \) is an auxiliary function of the model. We assume a fourfold anisotropy (depending on the angle between the orientation of the interface and the local crystallographic orientation \( \vartheta \)) in the kinetic term, which is related to the interfacial dissipation associated to the atomic rearrangements of the phase transformation. This anisotropy takes the form \( \tau = (1 + \epsilon \cos [4(\Theta - 2\pi \vartheta)])^2 \), where \( \epsilon \) is a parameter characterizing the magnitude of the kinetic anisotropy and \( \Theta(\vec{r}, t) \) is the local orientation of the interface given by \( \tan \Theta(\vec{r}, t) = \partial_{x} \varphi / \partial_{y} \varphi \). Finally, we have also added
two gaussian noises, accounting for compositional and thermal fluctuations, of zero mean and variances given by

\[ \langle j^r_U(r,t), j^r_U(r',t') \rangle = 2D_U F_{\delta} \delta(r-r') \delta(t-t'), \]

\[ \langle j^\theta_U(r,t), j^\theta_U(r',t') \rangle = 2D_\theta F_{\delta} \delta(r-r') \delta(t-t'). \]

As initial conditions in each lattice point we have taken for \( \theta \) homogeneously distributed random values, and \( U = 1 - \Delta + 0.1 \chi \), \( \varphi = 1 \) for \( x < x_0 \), and \( U = -\Delta + 0.1 \chi \), \( \varphi = -1 \) for \( x > x_0 \), where \( \chi \) are normalized gaussian random numbers. Therefore changes in the parameter \( \Delta \) correspond to different initial carbon concentrations. We implicitly assume a constant miscibility gap \( \Delta c^0 \) between the equilibrium values of both phases, which have been taken as \( c_1^0 = 0.5 \) (50% at. W) for the W-C phase and \( c_2^0 = 0.05 \) (95% at. W) for the W phase. In the simulations the rest of parameters were fixed as: \( D_\theta = 1, D_U = 8, I_T = 200, \lambda = 12.76, F_U = 10^{-3}, F_\theta = 10^{-4}, \alpha = 0.2, \nu_g = 1.5, M_1 = 10, M_2 = 10^{-4}, \varepsilon = 0.1 \). We have checked that the qualitative trends obtained in simulations did not depend on the specific values chosen for these parameters.

3. Structural, morphological and surface properties

3.1. Formation of dendrites

Pure W films were obtained with \( R = 0 \). Fig. 1a presents a cross-section TEM image of a representative film. It can be seen that, similarly to previous studies, these films present a columnar structure [21,22]. Column height was limited by film thickness, whereas grain boundaries that contain void regions defined the column width. Fig. 1b shows a detail of the W film near the surface, and Fig. 1d is a dark-field micrograph of the same region. The latter image indicates the distribution of crystals with a determined
orientation within the film. As shown by the tracks performed by Bragg reflections, crystals were oriented according to column direction and formed elongated grain domains of several sizes. The crystal regions observed in the dark-field images reached up to 20 nm. SAED spectrum shown in figure 1c is typical of a polycrystalline material, where the diffraction rings revealed the presence of a polycrystalline phase. XRD scanning (Fig. 1e) confirmed that the observed phase was β-W, which showed a preferential orientation perpendicular to the substrate in (h00), indicated by the relatively high line intensities corresponding to the lines (200) and (400). According to the Scherrer’s formula, the FWHM of XRD peaks provided crystallite sizes between 10 and 12 nm. In contrast to the more stable bcc W type, β-W consists in a metastable crystalline phase presenting A15 structure, which can be induced by the presence of oxygen during growth [23,24]. Oxygen traces from the background pressure in the reactor may have promoted this growth mode.

The incorporation of C atoms within the W matrix during deposition with $R > 0$ led to the formation of dendritic W-C structures. By varying metal abundance (by changing $R$ values) this structure could be modulated. Fig. 2 corresponds to the W-C film with 75% at. W ($R=2\%$). Columns are still well defined and sidebranches appear attached to them, which allow us to identify such growth as dendritic in character. Figs. 2a and 2c account for this structure. Figure 2b is a HRTEM image, in which crystallites of nanometric size (nano-crystallites), smaller than crystal domains of W film, are observed to grow within W-rich regions. SAED spectrum (inset in figure 2a) presented only a diffuse ring surrounded by a weak halo. This pattern corresponds to an amorphous material, which may be attributed to the structural transition from columnar crystals typical of W to nano-crystalline inclusions. The W-C sample with the highest W concentration, 85% at. W, showed a similar pattern. Thus, the crystallinity of W
films was significantly reduced with minimum addition of C. Figures 2d and 2e are EELS mappings corresponding to W and C, respectively, in the same region of Fig. 2c. The darker zones have a deficit of the mapped element. We can see that the same dendritic structure observed in the TEM images (Fig. 2c) is correlated with the W mapping in Fig. 2d. In particular, the region between dendrites and side-branches clearly corresponds to W-poor zones (for instance at the locations indicated by the arrows). Furthermore, in Fig. 2e we can see that the same regions correspond to higher carbon concentrations. These images show that the W-rich zones occupy preferably the space delimited by the dendrites, suggesting that the dendritic growth is associated to the formation of W-rich regions with segregation of C towards the grain boundaries. Precisely this fact connects the dendritic structure with the composition distribution in the film. These phenomena are simulated with a phase field model in section 4.

3.2. Influence of metal concentration on film structure

Figs. 3a-e show TEM images of a series of W-C films with gradually decreasing metal concentration. We observe dendritic nanostructures similar to those presented in subsection 3.1, which in this case are modified by the variation of composition. Dendrites appeared more defined at lower W abundance, probably due to an effect of phase segregation induced by C incorporation. Indeed, C-rich regions were shifted from the axis of the columns to the grain boundaries, as it can be inferred from C and W mappings in Figs. 2d and 2e. This segregation could also inhibit crystalline growth, so it would explain the trend to amorphization of W-C films. The sample with 50% at. W (Fig. 3e) shows a structure with more packed side-branches. In this case, C and W concentrations could have achieved a critical value such that phase segregation
mechanism might not be active any longer. DLC films would show an extrapolation of this structure, in which side-branches disappear and a disordered amorphous C matrix without grain boundaries remains. This trend observed with concentration changes has been modelled in section 4 using a phase field model.

XRD analysis in the Bragg-Brentano geometry was performed along with TEM observations. Agreeing with SAED patterns, only one weak and broad peak was detected in W-C films, which was identified as a sum of two contributions: the (111) reflection from WC_{1-x} phase plus the (210) from β-W, because this peak lies between predicted angles for both phases. Such a peak appeared already at very low C concentration, showing a degradation of the initial crystallinity of the W film; this can be inferred by comparing the XRD scans of figures 1e and 3f. The instability of β-W phase may explain the fragility of W crystallinity when it is mixed with other elements. The monotonic reduction of XRD peak intensity as metal content decreased showed that crystals tend to grow in metal-rich films, so C-rich samples contain a more diluted crystallite distribution. This phenomenon was accompanied by a decrease of Bragg angle towards WC_{1-x} (111) reflection site. In this way, the amorphous matrix of W-C film with 51% at. W lodges mainly WC_{1-x} crystallites. An average crystallite size of about 2 nm in all cases was inferred from the Scherrer’s formula [17]. This small size and the detection of only one weak Bragg peak pointed out to a very poor crystallinity, even for the sample with 85% at. W (Fig. 3b). As reported in other works, the formation of a dendritic-like columnar structure of W could be a route to the amorphous state [21,22]. Hence, W amorphization enhanced by C inclusion could be related to dendrite generation. The fact that the growth occurs at room temperature and the high melting point of W may explain the small crystallite size. Indeed, both factors yield to lower
mobility of depositing W atoms by surface diffusion and, therefore, only nano-scaled clusters are formed.

3.3. Surface properties

The surface properties have been characterized and also connected to film structure. Surface topography is influenced by the dendritic growth of W-C films. Indeed, AFM scans revealed a roughening of W-C film surface by formation of spikes compared with flat DLC films. This result was quantitatively displayed by RMS roughness: 0.21 and 5.86 nm for DLC and W-C with 50% at. W, respectively [17]. Regarding stress results, the high compressive stress typical of DLC films was not observed in W-C. The intrinsic stress of -3.0 GPa of DLC films decreased and was maintained to less than -0.1 GPa when W was incorporated [17]. Contrary to the packed structure of DLC, the formation of dendritic-like structures appears to contribute to stress relaxation, which can be of relevance for film stability. Moreover, the lodging of relatively small crystals in an amorphous matrix of carbon contributes to minimize crack formation and propagation, and therefore to increase film toughness and to relieve stress [25]. On the other hand, hardness suffers a monotonic decrease from the typical values of DLC, 24 GPa, to approximately 10 GPa. The plasticity increase due to W inclusion could be justified by a collateral effect of metal incorporation in DLC, which consists in a decrease of sp³/sp² ratio and leads therefore to material softening [26]. Finally, these microstructural rearrangements did not affect appreciably the friction coefficient. DLC showed a coefficient of 0.05, whereas 0.03 was found for the W-C film with 75% at. W. Since the error bars were approximately 0.01, we can conclude that such coefficient has not undergone a significant variation by adding W to DLC films.
4. Modelling of dendritic nanostructure formation

The formation of the dendritic structure can be interpreted as the nucleation and growth of a polycrystalline W phase inside an amorphous W-C matrix, controlled by the diffusion of C. In this scenario, the nucleation process is produced because the composition of the film as directly deposited is not thermodynamically stable. In fact, there is a compositional gap in the W-C phase diagram from 0% to 50% at. C for temperatures below 1250°C. Furthermore, the different atomic ordering of the amorphous matrix and the polycrystalline W would exclude spinodal decomposition as alternative phase separation mechanism. For the growth of the W phase, expelled C atoms should be able to diffuse, which would be allowed by the energy excess of the deposited atoms in the superficial layer of the film, equivalent to a locally higher temperature. The involved physical mechanisms are then similar to those of solidification processes, in which the interplay between interfacial surface tension and diffusion is known to produce morphological instabilities and dendritic growth. Using this analogy, a rough estimate of the length scales at which structures are expected to appear can be obtained from the diffusion length, defined as $l_D = D/v_g$ being $D$ the diffusion coefficient and $v_g$ the growth velocity. Values such as $D \approx 10^{-19}$ m$^2$/s for the diffusion of C in W at 1000 K [27] and $v_g \approx 0.1$ nm/s for the growth velocity of the film give diffusion lengths at the nanometric scale, thus consistent with the observed structures. Here we apply the model described in section 2.2 to account for the formation of such structures.

We will consider the growth of a polycrystalline W phase into the forming film of an amorphous W-C phase which, at low temperature, is inside the compositional gap.
The W phase is initially nucleated on the substrate, and grows by expelling C atoms to the W-C matrix where they diffuse. Simulation results of the model are shown in Fig. 4. In this figure we show films grown for different initial C concentrations, maintaining constant the other parameters. We see that while for low C the structure is more columnar (Fig. 4a), the increase in concentration makes dendrites to form thinner and more structured sidebranches (Figs. 4b and 4c). The resulting patterns are very similar to experiments, and the observed trend is correct. Regarding the orientational field $\theta(\vec{r},t)$, simulation results indicate that the crystalline domains correspond to columns for the lower C case, and to individual dendrites for higher concentrations. These domains compete during growth, in such a way that some of them can invade neighboring domains which cease to grow. This competition is manifest in the final shape of columns and dendrites.

A detailed view of the region around a dendrite tip is shown in Fig. 5 for the case with $\Delta=0.2$ (initial composition of 59% at. W). Local concentration values are indicated by a color scale. Note that, being the model formulated for a dilute alloy, high concentration values are only qualitative, and for instance points with $c$ values higher than 1 could be found. It can be seen that composition in the bulk of the dendrite is quite uniform and close to that of equilibrium of the W phase. In the interstices the C concentrations are very large, much higher than the equilibrium value for the W-C phase. In this, concentration values present large variations. Indeed compositional gradients in the region ahead the dendrite promote diffusion of C atoms into the W-C phase, which is the mechanism that permits the phase transformation to progress. The final pattern is formed by a dendritic structure of W, grown by expelling the excess C atoms, surrounded by a shield with high C concentration.
5. Conclusions

In conclusion, spontaneously structured W-C films containing nanodendrites have been deposited by pulsed-DC reactive magnetron sputtering. It is observed that columnar W films acquire a dendritic-like structure when C atoms are added. Such an arrangement, as well as surface topography and mechanical properties, is sensitively modified at different metal concentrations. A two-level structure in W-C films was discovered. Firstly, we distinguished a nanoscale architecture consistent of dendritic-like columns, rich in W, shielded by grain boundaries rich in C. This structure tends to vanish when W content decreases down to 50% at. Secondly, a dominant amorphous phase with embedded nano-crystallites dominates the nanoscale structure of W-C. A combination of a polycrystalline $\beta$-W phase and a non-stoichiometric WC$_{1-x}$ phase is detected for concentrations above 50% at. W. By contrast, DLC features would be achieved at high C concentrations. The dendritic growth is interpreted as a morphological instability of the interface between the polycrystalline and the amorphous phase. Simulations of a phase field model for polycrystalline growth present indeed similar dendritic structures, and are expected to provide valuable information for the design of new experiments. The structure acquired by W-C films could improve the performance of DLC coatings in many tribological applications. Spontaneous structure formation appears then as a valuable and economical strategy for the design of new nanostructured materials, and the research on the associated physical mechanisms should become a key step in the control of this technology.

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References


Figure captions

Figure 1
Cross-section TEM micrograph of a W film (a), where a detail near the surface is shown in bright- (b) and dark-field (d). The SAED spectrum indicates the presence of a polycrystalline phase (c). The XRD diffractogram is typical of β-W phase and the peaks are labelled (e).

Figure 2
W-C film with 75% at. W. TEM micrograph showing the dendritic-like structure (a), and HRTEM image with some circled nano-crystallites (b). In (c) we show a magnified TEM image of a region close to surface. EELS analyses for the same region are shown providing compositional mappings of W (d) and C (e). The arrows highlight morphological features, which can be correlated with changes in composition.

Figure 3
Cross-section TEM images corresponding to the W film (a), and W-C samples with 85% (b), 75% (c), 65% (d) and 50% (e) at. W. The XRD spectra show the trend to amorphous state as W content decreases (f).

Figure 4
Simulations of the model for polycrystalline phase transformation for different values of initial carbon concentration: a) Δ=0.8 (86% at. W), b) Δ=0.4 (68% at. W), c) Δ=0.2 (59% at. W). Grey levels correspond to carbon concentrations, and have been normalized in such a way that black corresponds to the equilibrium concentration of the
W phase, and white corresponds to concentrations equal to or larger than equilibrium concentration of the W-C phase.

Figure 5
(Color online) Carbon concentration for a selected area of the dendrite pattern obtained in simulation of the case Δ=0.2 (59% at. W). To calculate $c$ values we have taken as equilibrium values of both phases $c_1^0=0.5$ (50% at. W) for the W-C phase and $c_2^0=0.05$ (95% at. W) for the W phase (see text).
Figure 1
Figure 2
Figure 3
Figure 4