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Structural behaviour of sputtered W–C–Co coatings at increasing temperatures

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In order to evaluate the thermal resistance of sputtered W–C–Co coatings, a structural study was carried out on amorphous and crystalline coatings according to their cobalt content after having been annealed at increasing temperatures up to 800 °C. All the films were stable up to 700 °C, at which temperature the amorphous films began to crystallize as α-W_2C; for higher temperatures the α-W_2C carbide evolves to M_6C, the extent of which increases the higher the cobalt content; for low cobalt content films WC carbide was also formed. Crystalline films have similar structural transformations, although the M_6C phase is almost non-existent and α-W_2C and WC can occur with preferential orientations. In all cases, the films after annealing were carbon-deficient in relation to the results obtained for the as-deposited conditions; in spite of the fact that the phases detected after crystallization are also carbon-deficient, these results are not consistent which implies that some free carbon should exist in the annealed films.

1. Introduction

One of the possible advantages of using the W–C–Co system in the production of coatings for mechanical components is their higher hot hardness when compared with other industrial coatings such as Ti-based coatings [1]. Nevertheless, these coatings must withstand a temperature increase without suffering significant structural transformations which can create a high stress level in the films and lead to their failure. It is known that during service the temperature of the component surface can increase, particularly in applications where severe wear is present as in cutting tools, the tips of which can reach several hundred degrees centigrade [2].

In previous work [3] we have shown that sputtered W–C–Co coatings deposited on alloy steels could be obtained with very different characteristics depending on the conditions used in the deposition. Concerning the structures of the coatings, two main groups were obtained, crystalline and amorphous films according to their cobalt content. In order to evaluate the suitability of these coatings for industrial application we must study their thermal stability at increasing temperatures. However, when high-speed steel (HSS) is used as a substrate, the maximum temperature possible to be studied is near 800 °C, which is a threshold value to guarantee no important dimensional variation due to the $\alpha \rightarrow \gamma$ transformation occurs (for the HSS used in this study it is a little higher than 800 °C).

In this work, the structure of sputtered W–C–Co films is studied as a function of temperature increase. Amorphous films with different cobalt contents and crystalline films with different structures were selected to be analysed at increasing temperatures up to 800 °C.

2. Experimental procedure

The films were deposited by r.f. magnetron sputtering from WC targets with different cobalt contents (6 and 15 wt % Co) on HSS substrates (Table I). Films were also deposited by r.f. diode sputtering in order to obtain transition conditions between amorphous and crystalline character. Thus two films were selected, both with a cobalt content lower than that corresponding to the lowest cobalt content of amorphous r.f. magnetron film: one with an X-ray spectrum typically amorphous (N8) and the other with a protuberance on the characteristic peak of the amorphous structure suggesting the presence of crystallinity (N9). The substrates were austenitized at $\theta_\gamma = 1220\,°C$ for 15 min, cooled in water and triple-tempered at $\theta_T = 550\,°C$. The thickness of the deposited films (t) was approximately 2 µm.

The composition of the coatings was evaluated by X-ray photoelectron spectroscopy (XPS) and by energy-dispersive X-ray spectroscopy (EDXS) techniques.

After deposition the coated samples were isothermally annealed in a vacuum (10^{-4} Pa) for 1 h in the range 200 to 800 °C and, after cooling, the samples were analysed by X-ray diffraction. For the highest temperature, isothermal annealing for 24 h was also carried out.

3. Results

In Table I, in addition to the deposition conditions, the chemical composition and the main structural indications of the W–C–Co films analysed in this work are shown. The analysis of the structure of the films was the subject of a previous paper [3]. Fig. 1

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TABLE I W–C–Co films selected for structural study at increasing temperatures

Film No.	Co in WC Target (wt %)	Deposition pressure (Pa)	Substrate Bias (-V)	W/C (at %) from XPS	W/Co (at %) from EDXS	Structure
N1	15	1	0	1.1	2.3	Amorphous
N2	15	1	50	1.0	2.6	Amorphous
N3	15	1	100	1.2	3.0	Amorphous
N4	15	1	150	–	3.3	Amorphous
N5	15	1	200	1.2	3.8	Amorphous
N6	15	1	400	1.5	4.7	Amorphous
N7	6	0.3	0	0.9	5.3	Amorphous
N8	6	1	0	–	7.1	Amorphous
N9	6	1	50	–	9.4	Signs of crystallinity
N10	6	0.3	100	1.1	14.4	β-WC_{1-x} [3 1 1]. α-W_2C [1 0 0]
N11	6	0.3	200	1.2	19.4	β-WC_{1-x} [1 1 0], α-W_2C [1 1 0]

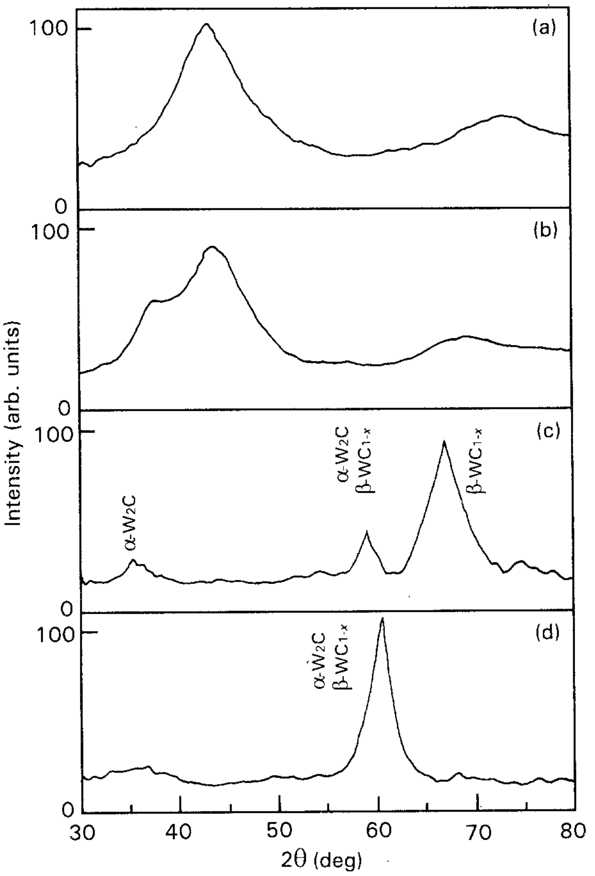

Figure 1 X-ray spectra of sputtered W–C–Co films: (a) N1, N2, N3, N4, N5, N6, N7, N8; (b) N9; (c) N10; (d) N11.

shows typical X-ray spectra of these films. Fig. 2 is a schematic presentation of the X-ray spectra of the films at increasing temperature. The results will be analysed by considering two main groups of films, the amorphous and the crystalline.

3.1. Structural transformation of amorphous films.

All the amorphous films showed an identical behaviour with temperature increase; they did not present any significant structural transformation up to 710 °C. At this temperature crystallization begins and the films present a metastable α-W_2C phase [4]. This carbide occurred generally without preferential orientation, with the exception of N5 and N6 films which showed a strong [0 0 1] orientation. In spite of the observed crystallization, the X-ray spectra of the 710 °C annealed films still showed the existence of the amorphous structure, the extent of which is dependent on the cobalt percentage of the film (compare the X-ray spectra of films N1 and N8 in Fig. 3). It is verified that the higher the cobalt content of the film, the lower is the crystalline fraction of the structure.

For the 800 °C annealing temperature ($t = 1$ h) small variations in the X-ray spectra were observed as

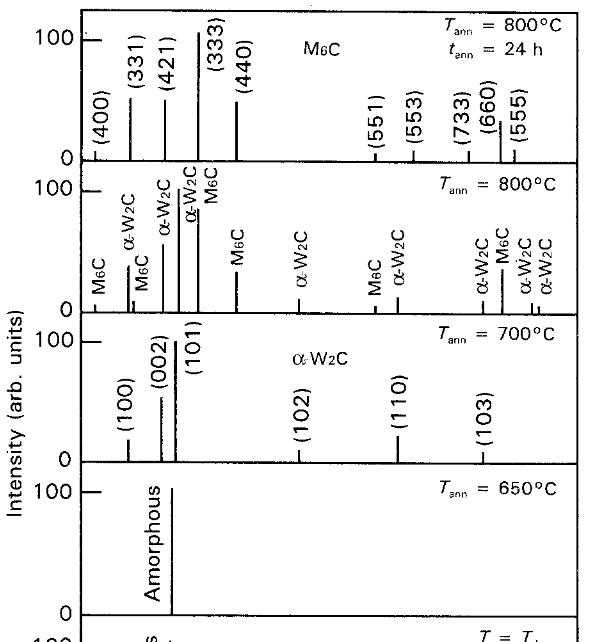

Figure 2 Schema of the characteristic X-ray spectra of sputtered W–C–Co films at increasing temperatures: (a) N1, N2, N3, N4 (ex. N1); (b) N5 (. . .), N6 (—); (c) N7, N8, N9 (ex. N9); (d) N10; (e) N11.

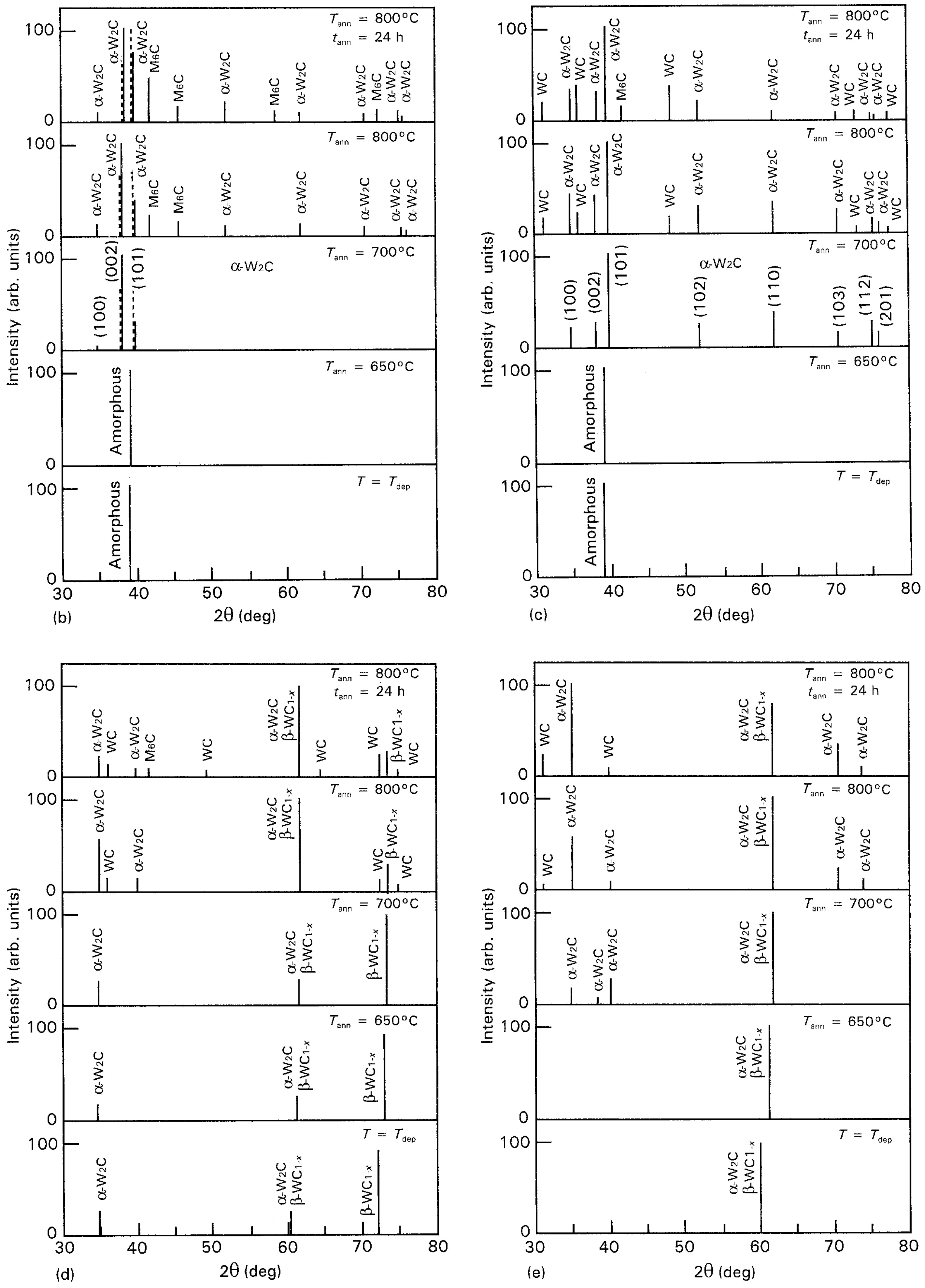

FIG. 2 b–e

follows:

(i) Besides the α-W_2C carbide in all the films, peaks were detected corresponding to the M_6C phase (M = Co, W), although 2θ values were lower than those predicted in the JCPDS standards for η-Co_3W_3C, being better correlated with θ-Co_2W_4C [4]. Nevertheless, for films with low cobalt content (N7, N8) the M_6C phase is closer to η-Co_3W_3C and the WC phase [4] was also detected.

(ii) The orientations of α-W_2C observed for the 710 °C annealing temperature were the same as for

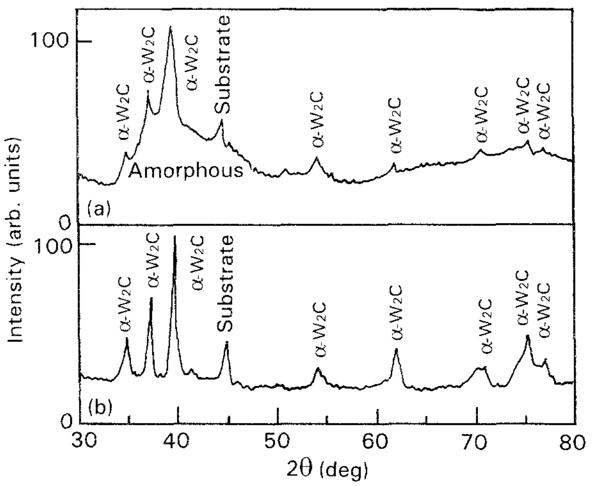

Figure 3 X-ray spectra of sputtered W–C–Co films annealed at 710 °C: (a) N1, (b) N8.

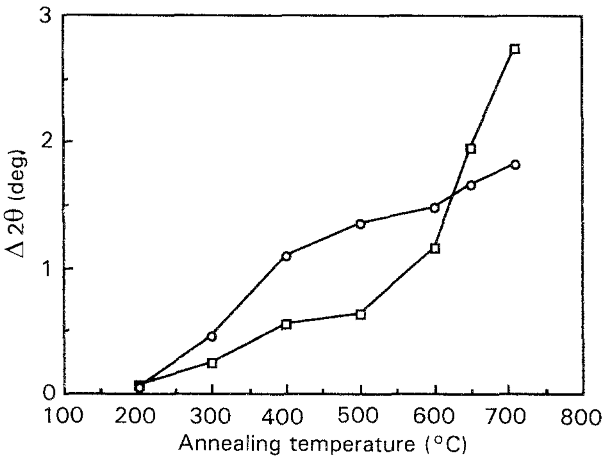

Figure 4 Shift in peak position relative to the as-deposited film value for the two main peaks of X-ray spectra of films (□) N10 and (○) N11, as a function of temperature increase.

800 °C, although in N5 and N6 films the [0 0 1] preferential orientation is less noticeable.

(iii) The peaks in the X-ray spectra corresponding to the amorphous structure have almost disappeared.

With an increase of the annealing time the structure development observed for lower times is reinforced, i.e. the importance of M_6C or WC phases increases in relation to the α-W_2C phase. The final content of M_6C carbide in the film depends on its cobalt percentage; the higher the percentage the higher the M_6C content.

As a conclusion, the sequence of crystallization of the W–C–Co amorphous films can be schematized as follows:

$$\text{W–C–Co (amorphous)} \xrightarrow{T\,=\,710\,^\circ\text{C},\ t\,=\,1\,\text{h}} \alpha\text{-W}_2\text{C}$$

$$\xrightarrow{T\,=\,800\,^\circ\text{C},\ t\,=\,1\,\text{h}} \alpha\text{-W}_2\text{C} + \text{M}_6\text{C or WC}$$

$$\xrightarrow{T\,=\,800\,^\circ\text{C},\ t\,=\,24\,\text{h}} \alpha\text{-W}_2\text{C}\downarrow + \text{M}_6\text{C or WC}\uparrow$$

In spite of the signs of crystallinity in the X-ray spectrum, film N9 has an identical behaviour to amorphous films, particularly films N7 and N8. Its sequence of crystallization can also be represented by the scheme presented above.

3.2. Structural transformation of crystalline films

Concerning crystalline W–C–Co films, it was also observed that up to 710 °C there are no structural changes. However, small variations in the peak positions were detected with increase of annealing temperature, the peaks being displaced to higher 2θ angles (Fig. 4).

For film N10 the beginning of the structural transformation occurred at 800 °C. The [3 1 1] orientation almost disappeared and the film showed a strong [1 1 0] orientation. Besides this alteration the X-ray spectrum also has other peaks which can be identified as WC carbide. An increase of annealing time at this temperature gave rise to a small increase of the WC phase and a depletion of α-W_2C.

Concerning the N11 film, at 710 °C recrystallization of the film was observed, with new non-oriented α-W_2C carbide peaks superimposed on the original peaks in the X-ray spectrum. However, for 800 °C annealing the film was bi-oriented ([1 1 0] residual and [1 0 0] new preferential orientation) and with increase of the annealing time the [1 0 0] orientation became predominant.

For higher annealing temperature and time, both crystalline films showed traces of the M_6C phase.

4. Discussion

The discussion of the results will be carried out by considering the structural evolution of amorphous and crystalline W–C–Co films and their chemical composition.

4.1. Amorphous films

The crystallization of amorphous W–C–Co films occurs through the formation of metastable phases before the final equilibrium phases. In all the films, the first crystalline structure to be formed with increasing temperature is α-W_2C which exists in the W–C equilibrium diagram down to 1250 °C [5]; even for crystalline films this is also the phase resulting from the recrystallization of the structure.

In other structural transformations for systems including the elements carbon and tungsten, as for example in the production and subsequent heat-treatment of high-speed steels, for some particular conditions related to the chemical composition of the HSS and cooling rates of the material it is known that, before the appearance of the equilibrium phases WC and M_6C, the W_2C phase is detected [6]. Moreover, other authors [7] observed during the carbonization of small samples of pure tungsten that the first structure to be formed was also α-W_2C; only afterwards was WC carbide formed, which developed progressively until a sample completely formed by this phase was obtained. If the process was catalysed by the presence of cobalt, the formation of η-phase (Co_3W_3C) delayed the formation of WC and extended the region of W_2C formation. In the case of this study the situation is somewhat different, since the transformation occurs from an amorphous structure. Nevertheless, in the light of the following sequence it is also possible to understand the occurrence of α-W_2C as the first carbide of crystallization.

(i) If it is assumed that the amorphous structure is formed following the theory that correlates the ease of forming an amorphous material with the ratio between the atomic radii of the constituents [7, 8], during the deposition the solvent atoms tungsten and cobalt have a tendency to form a compact structure as solute atoms are inserted in interstitial octahedral sites. As the atomic radii of these solvent atoms are sufficiently different, the presence of cobalt atoms in substitution for tungsten atoms gives rise to lattice deformation and the possibility of it becoming mechanically unstable, the more so the higher the percentage of cobalt; thus an amorphous structure can be obtained. These ideas are supported experimentally by previous results. On the one hand, it was found by Mössbauer analysis that iron atoms substitute for tungsten atoms in the lattice of sputtered crystalline W–C–Fe films [9]. Considering the similarity of cobalt and iron (atomic radius, metallic character, sputtering rate etc) it is also possible to extrapolate that cobalt substitutes for tungsten either in an amorphous structure where short-range order exists, or in the long-range order of a crystalline structure. As a consequence, it would be more correct to indentify all the carbides detected in the films as M_2C and MC. On the other hand, a threshold value for the cobalt content in sputtered W–C–Co films was found, which determined their crystalline or amorphous character [3]. Moreover, as was shown above, the higher the cobalt content in the film the lower is the transformed part in the first step of crystallization, which indicates a greater difficulty in organizing the amorphous structure.

(ii) In amorphous structures the order is locally maintained and is similar to that of the crystalline phase obtained in the first crystallization step [8, 10]. In the results shown above, there is a fact which confirms this. It is well known that an increase of substrate bias during deposition gives rise to an increase of adatom mobility during the film deposition which, in some sputtered films, leads to the formation of highly preferentially oriented films; one of these orientations is [001] for h.c.p. structures [11]. Films N5 and N6, deposited with high substrate bias, present this preferential orientation in the first step of crystallization. This means that in the amorphous state there was already some short-range order with the atoms preferentially stacked in particular configurations; this particular configuration was maintained after crystallization and preferential orientations were observed. It should be remarked that although the structure of the films obtained with lower substrate bias is also amorphous, the orientation after crystallization is different. Among the different tungsten carbide phases, singular or with cobalt, those which have compact lattices and simple structures are β-WC_{1-x} (f.c.c NaCl type) [4] and α-W_2C (h.c.p). Since β-WC_{1-x} is an even higher-temperature equilibrium phase than α-W_2C, it is probable that the first crystallization phase is α-W_2C. Moreover, as will be referred to later, the chemical composition of the film after annealing is closer to M_2C than to β-WC_{1-x}.

α-M_2C changes to the equilibrium phases M_6C and MC with increasing temperature. Both these phases have some relation to α-M_2C; for M_6C phase the carbon environment is similar to that in α-W_2C, the surrounding tungsten configuration being that of two inverted isosceles triangles [12]. In M_6C the tungsten atoms are arranged in octahedral units placed in the lattice positions of the f.c.c. cube, whereas the cobalt atoms are arranged as tetrahedra placed in the octahedral interstices of the cube. WC is also a hexagonal phase where the tungsten and the carbon atoms each form a set of interpenetrating simple hexagonal lattices, whereas in α-W_2C the tungsten atoms form an almost close-packed lattice and the carbon atoms a simple hexagonal lattice [12].

The annealing of amorphous films depends on their cobalt content, transformation occurring differently. Thus, for high cobalt content films, MC is not observed even for the highest annealing temperatures; as a result of the α-M_2C transformation, only M_6C phase is detected. A good qualitative agreement is obtained between the chemical composition (percentages of Co and W) and X-ray diffraction results. The film which presented after annealing only M_6C carbide, with a lattice parameter according to the form Co_2W_4C, has approximately a W/Co ratio of 2. As the cobalt content of the films decreased (increasing W/Co) the films showed an increasing relative quantity of α-M_2C which was not transformed into M_6C. For the amorphous films with low cobalt content, besides the M_6C phase the equilibrium MC carbide is also detected for the highest annealing temperatures. The relative contents of these phases are very low and, in contrast to that observed for the high cobalt content films, the M_6C carbide is very close to the Co_3W_3C form instead of Co_2W_4C, due to the formation of an MC phase very deficient in cobalt.

It seems that the mode of deposition, diode or magnetron, has little influence on the structure of the film. In fact, both the amorphous film and the film deposited in diode mode which showed signs of crystallinity show a behaviour with increase of annealing temperature which is very similar to that of films deposited by r.f. magnetron. The differences in the as-deposited structure arise from their cobalt content in

TABLE II Chemical composition M/C (M = W + Co) of films (at %) before and after annealing

Film No.	Before annealing	After annealing
N1	1.6	4.0
N10	1.2	2.1
N11	1.2	2.1

accordance with previous work [3]. The diode-deposited film has a cobalt content which should be close to the threshold value which defines the transition between amorphous and crystalline character for those deposition conditions. The transformations observed during its annealing are similar to those of the low cobalt content r.f. magnetron deposited film.

4.2. Crystalline films

The alterations in the X-ray spectra of crystalline films annealed up to temperatures of 700 °C are related to the stress relaxation induced by the temperature increase. It is well known that sputtered films obtained in conditions of high substrate bombardment (low deposition pressures and/or high substrate bias) can show a high compressive stress level, with a very high defect-density structure [13]. With temperature increase the structure is able to recover and the stress level decreases. This is accompanied by recuperation of the equilibrium lattice dimensions of the structure, as was observed in this study.

For temperatures higher than 700 °C the structural transformation of W–C–Co crystalline films is similar to that of the amorphous ones, particularly with those of low cobalt content; the main difference is interrelated with the phase orientation. In fact, while in amorphous films there was a tendency to obtain non-oriented structures, in crystalline films there were changes in the film orientation with temperature increase. Moreover there is also, for one of the films, a strong orientation in the MC phase resulting from the recrystallization of α-M_2C.

4.3. Chemical composition of the films

One of the most important conclusions from analysis of the results concerning the influence of the annealing temperature on the transformation of W–C–Co films is that the structures obtained after transformation are carbon-deficient relative to the initial global composition of the film, particularly for high cobalt content films (e.g. N1), for which M_6C is the predominant phase.

Since the temperature increase leads to structures which are progressively more deficient in carbon (α-$M_2C \rightarrow M_6C$), it is possible that the films lost a part of their carbon to the substrate or environment (vacuum). Chemical composition analysis of the coatings after annealing was performed in some cases and significant carbon losses were detected when their content was compared with that of the same film before annealing (Table II).

From the results of Table II it is possible to conclude that the loss of carbon is higher in the amorphous structures than in the crystalline, probably as a result of the easier diffusion of this element in the amorphous structure.

In spite of the carbon losses of the films after annealing, the mismatch between structural and chemical composition results continues to exist. As an example, for N1 film only M_6C phase is detected but the M/C ratio evaluated by XPS is only 4.0 instead of 6.0. A comparison between the C_{1S} XPS peak spectra of N1 film before and after annealing (Fig. 5) allows us to conclude that the contribution of the shoulder in the C_{1S} peak at binding energies corresponding to unbonded carbon is much higher in the annealed than in the as-deposited film [14]. This means that a part of the carbon was not combined in the carbide form and some free carbon must exist. Thus, the slightly higher carbon content of the films, if only the M_6C phase is considered, can be explained by this unbonded carbon.

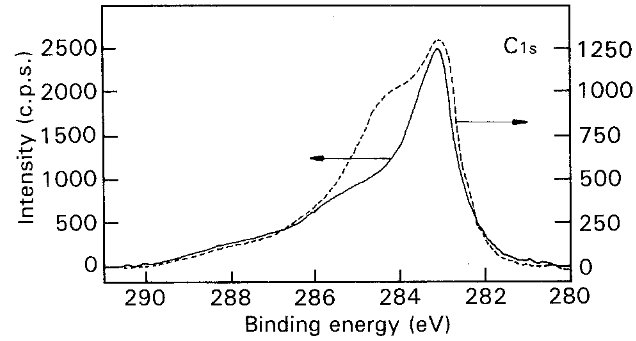

Figure 5 C_{1S} XPS spectra of a W–C–Co sputtered film, (—) before and (. . .) after 800 °C annealing.

5. Concluding remarks

Unless there are some changes in the interreticular distances, sputtered amorphous and crystalline W–C–Co coatings are structurally stable up to a temperature of 700 °C. At this temperature amorphous films began to crystallize as α-M_2C carbide, which progressively changed to M_6C and MC (M = W, Co) phases with increasing temperature. The amount of M_6C was greater the higher the cobalt content of the film, and the MC phase only occurred for low cobalt content films. Crystalline films showed a similar structural transformation, although only traces of the M_6C phase were detected and α-M_2C and MC carbides could occur with preferential orientations.

Particularly for high cobalt content films, which are formed after annealing almost exclusively of M_6C, significant losses of carbon were detected. XPS showed that some free carbon is present in the films, which justifies the discrepancies between X-ray diffraction and chemical composition results.

References

1. B.M. KRAMER and P. K. JUDD, *J. Vac. Sci. Technol. A* **3** (1985) 2439.
2. E. LENZ, Z. KATZ and A. BER, *ASME. J. Engng for Industry* (February 1976).
3. A. CAVALEIRO, M. T. VIEIRA and G. LEMPERIERE, *Thin Solid Films* **197** (1991) 237.
4. Joint Committee on Powder Diffraction Standards, Powder Diffraction Files Cards 20–1316, 35–776, 27–1125, 6–0611, 25–1047 (International Center for Powder Diffraction Data, Swarthmore, Pennsylvania).
5. E. RUDY and J. R. HOFFMAN, *Plansee Pulveromet* **15** (1967) 174.

6. M. T. VIEIRA, These d'Etat, Université de Paris-Sud, Centre d'Orsay (1983) p. 19.
7. C. F. DAVIDSON, G. B. ALEXANDER and M. E. WADSWORTH, *Metall. Trans. A.* **10** (1979) 1059.
8. T. EGAMI and J. WASEDA, *J. Non-Cryst. Solids* **64** (1984) 113.
9. B. TRINDADE and M. T. VIEIRA, *Thin Solid Films* **206** (1991) 318.
10. J. M. DUBOIS and G. Le CAER, *Acta Metall.* **32** (1984) 2101.
11. D. N. LEE, *J. Mater. Sci.* **24** (1989) 4375.
12. H. J. GOLDSHMIDT, *J. Iron Steel Inst.* (December 1948) 345.
13. D. S. RICKERBY and P. J. BURNETT, *Thin Solid Films* **157** (1988) 155.
14. C. D. WAGNER, W. H. RIGGS, L. E. DAVID, J. F. MOULDER and G. E. MUILENBERG, in "Handbook of X-ray Photoelectron Spectroscopy" (Perkin-Elmer Corp., Eden Prairie, Minnesota, 1979) p. 38.

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