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Crystallisation kinetics of amorphous W–Co–C sputtered films

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Abstract

The transformation kinetics from the amorphous to crystalline state in W–Co–C samples with different cobalt contents is investigated by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results show that cobalt influences the crystallisation process of the amorphous (W–C)-based system. The higher the cobalt content, the lower the crystallisation temperature. The transformation kinetics were analysed from the Kissinger equation. It was found that the crystallisation process occurs by steps and is mainly characterised by the formation of the carbide phase M_2C, controlled by diffusion. The activation energy, E, as calculated varies between 1.8 and 4.3 eV, depending on the chemical composition of the sample. With respect to the determination of the temperature vs. time transformation (TTT) diagrams, the results obtained reveal that the sample with higher content of cobalt is that which has a lower incubation time. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

From the technological point of view, transition metal carbides have attracted much attention during the last decades due to their very interesting properties. In this category, the (W–C)-based system is one of the most promising systems for surface protection in the form of hard wear-resistant coatings. Thin films of this kind of material have been made amorphous over a broad composition range by sputter deposition [1]. The amorphisation is achieved by the incorporation of a group VIIIA element during the deposition process. Cobalt has been the traditional addition element to the W–C system, although other elements, such as iron and nickel are cited as alternatives [2]. The role of these elements is to guarantee a good toughness of the films. The dependence of the thermal stability of the W–Co–C films on the cobalt content has been studied in a previous work [1]. However, nothing is known yet about the crystallisation kinetics of this system, which is crucial for an adequate technological application, since the operating temperature range will be determined by the structural changes (crystallisation) occurring with increasing temperature. Moreover, crystallisation studies are of interest since they may extend experimental information to the mechanism of crystal nucleation and growth from the amorphous phase, contributing towards obtaining crystalline structures with phase distributions required for certain applications [3–6].

In this work, results are presented on the effect of cobalt alloying on the transformation kinetics of the amorphous-to-crystalline process of the W–Co–C system, using the differential scanning calorimeter (DSC) and X-ray diffraction (XRD).

2. Experimental details

Three W–Co–C films (Table 1) were deposited on glass substrates by sputtering sintered (WC)–Co targets with cobalt contents of 4.9, 10.5 and 15.6 at.%. The sputter deposition process was the same as has been described previously [1].

To verify the amorphous state of the as-deposited samples, and to identify the structural changes with temperature, XRD investigations of the samples were carried out with an X-PERT Philips diffractometer using Co $K\alpha$

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Table 1
Chemical composition (at.%) of the W–Co–C films obtained by EPMA

Designation	Chemical composition (at.%)			
	W	Co	C	O
$W_{51}Co_6C_{43}$	49.7	5.3	41.6	3.4
$W_{48}Co_{11}C_{41}$	46.5	10.1	39.8	3.6
$W_{43}Co_{16}C_{41}$	42.3	14.9	39.3	3.5

radiation. Differential scanning calorimeter measurements were made with samples detached from the glass substrates in Polymer Science STA1500 equipment under dynamic N_2 atmosphere containing 5% of H_2. Different heating rates θ ranging from 5 to 55 K min^{-1} were utilised in the DSC measurements up to 1473 K. Isothermal annealings were performed at different temperatures below the crystallisation temperature $(T_x - 50 < T < T_x)$ during a maximum time of 180 min. Microstructural characterization of the samples was performed at room temperature after each DSC run.

3. Results

The as-deposited state of the samples was analysed by XRD (Fig. 1). The diffractograms obtained consist of two large XRD peaks characteristic of amorphous structures.

The DSC thermograms of the three W–Co–C samples are shown in Fig. 2 ($\theta = 55$ K min^{-1}). Samples $W_{51}Co_6C_{43}$ and $W_{48}Co_{11}C_{41}$ show two well-defined exothermic peaks, whereas a third peak is observed for sample $W_{43}Co_{16}C_{41}$. The temperatures at which these peaks occur depend strongly on its chemical composition, being lower if the cobalt content is higher.

In order that each existent peak corresponds to a particular structural transformation in the DSC thermogram, the samples were subjected to thermal cycles up to different maximum temperatures as the vertical arrows in Fig. 3 indicate. The same figure also shows the results of the structural analysis of the W–Co–C samples, undertaken at room temperature after cooling. It should be pointed out that no thermal events were observed on the DSC curves corresponding to the quenching of the samples, indicating that no structural transformations occur during cooling. Based on theses results, it can be affirmed that the transformations that occur during heating are irreversible, the structure being maintained during the cooling process. As can be observed in Fig. 3, the crystallisation of the W–Co–C samples takes place with the formation of a carbide M_2C where M is essentially tungsten. The formation of M_2C depends on the chemical composition of the sample, verifying that the difference in temperature between the first and second DSC peak is higher in the case of films with higher cobalt content. The increase in temperature leads to the appearance of other crystalline structures such as MC, M_6C, the solid solution (W) and later, the carbide $M_{12}C$. In the case of the sample with 16 at.% Co, the formation of a phase rich in cobalt (Co_7W_6) for temperatures at 1273 K has been verified. Fig. 4 represents the X-ray diffractograms of this sample obtained for different maximum temperatures of the heat treatment. Besides the diffraction peaks of the phases referred to, the large peaks of the amorphous phase in the two corresponding diffractograms at temperatures of 1073 and 1223 K are visible, pointing towards a high structural stability of this phase as a function of temperature.

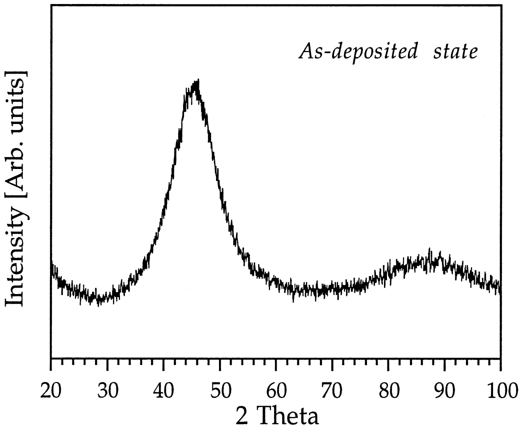

Fig. 1. X-ray diffractogram of the as-deposited samples.

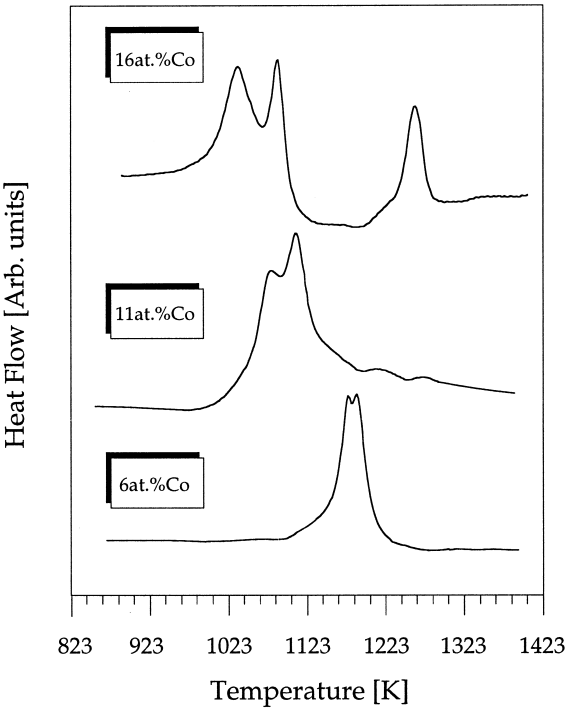

Fig. 2. DSC thermograms of the three W–Co–C samples ($\theta = 55$ K min^{-1}).

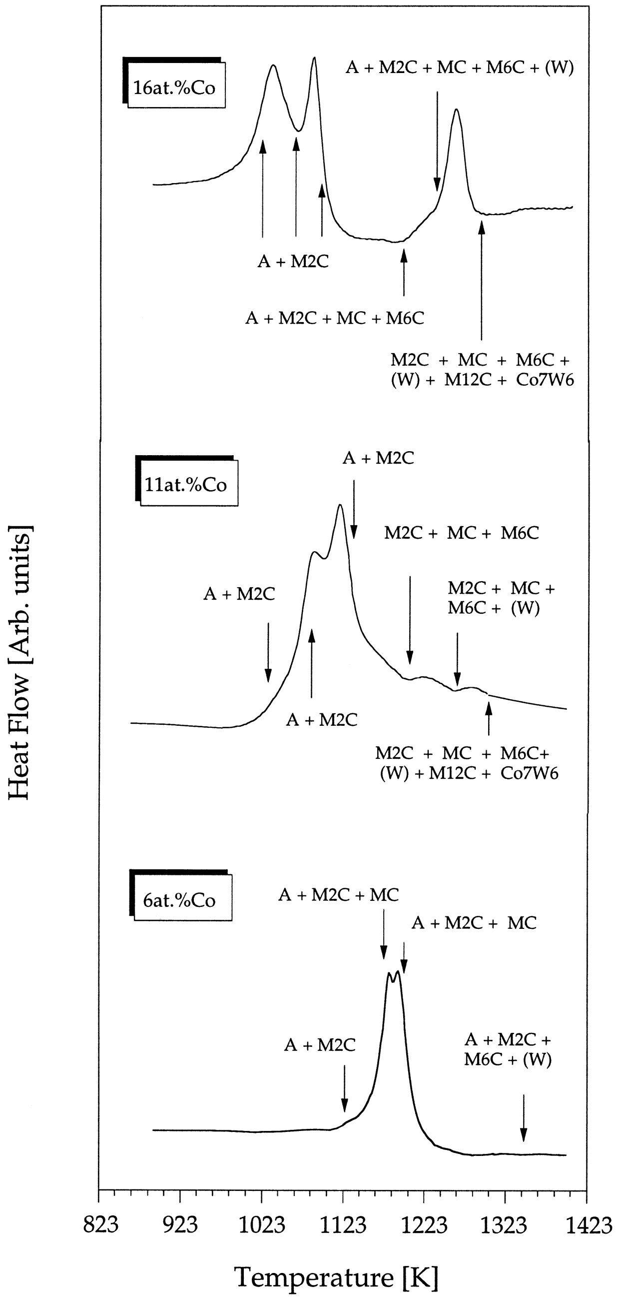

Fig. 3. Compilation of the XRD results of the three samples for different annealing temperatures (A = amorphous).

To study the crystallisation kinetics, we assume that the rate of variation of the crystallised fraction α in each stage is expressed as

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is assumed to have an Arrhenius behaviour given by

$$k(T) = A\exp(-E/kT) \tag{2}$$

A being the pre-exponential or frequency factor, E the activation energy, k the Boltzmann constant and T the absolute temperature.

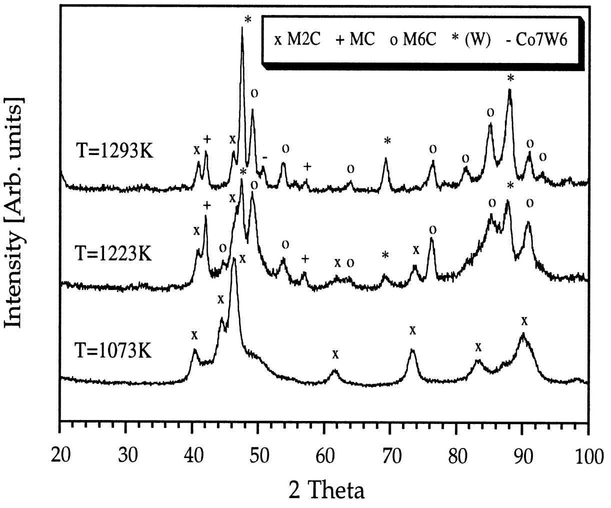

Fig. 4. Room temperature XRD results of the sample with 16 at.% Co heat-treated at different maximum temperatures.

Based on this assumption, the Kissinger equation [7] derived from the Johnson–Mehl–Avrami (JMA) method can be written as

$$\ln\left(\theta/T_{\mathrm{p}}^{2}\right) = \ln A - E/RT_{\mathrm{p}} \tag{3}$$

θ being the heat rate, T_{p} the temperature of the maximum of each DSC peak and R the gas constant. By measuring the temperature T_{p} at different scanning rates (Fig. 5) and

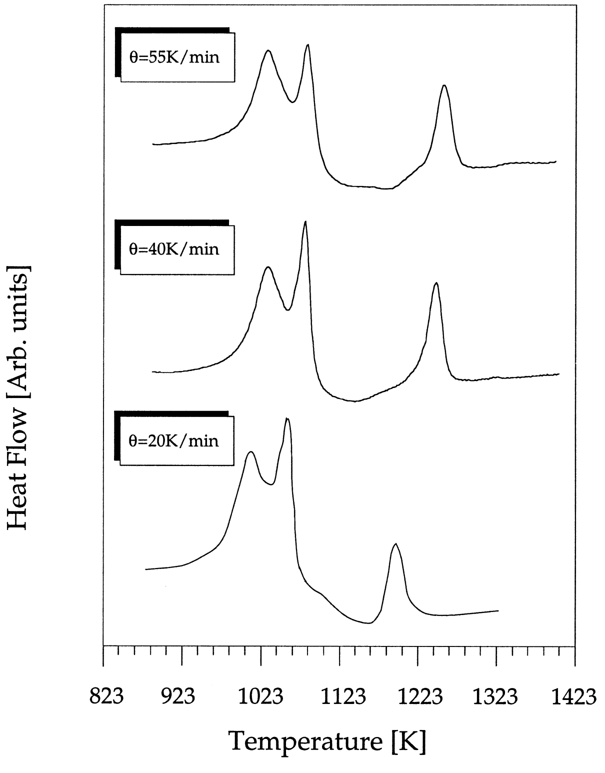

Fig. 5. Influence of the heating rate on the phase transformation temperatures.

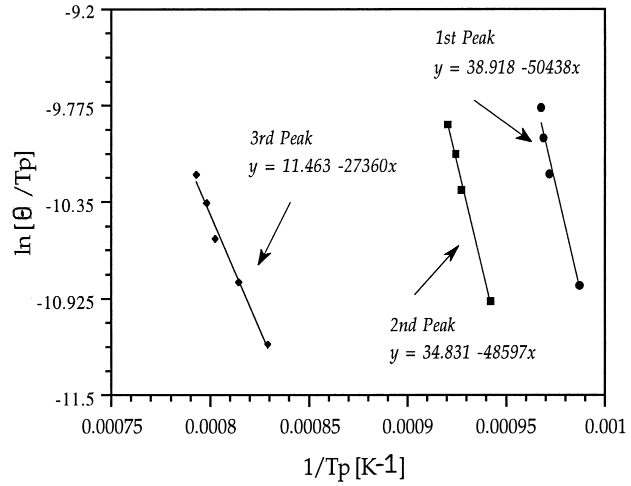

Fig. 6. Example of a $\ln(\theta/T_p^2)$ against $1/T_p$ plot obtained for the sample with 16 at.% Co.

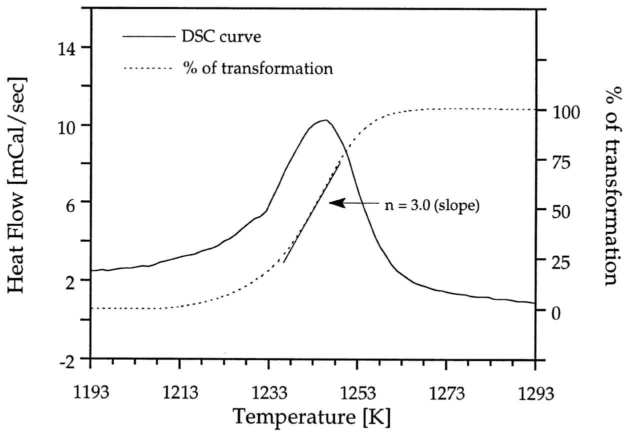

Fig. 7. Percentage of transformation as a function of temperature for the third DSC peak of sample $W_{43}Co_{16}C_{41}$.

plotting $\ln(\theta/T_p^2)$ against $1/T_p$ (Fig. 6), one can derive the values of E and A from the slope of the straight line plotted and the ordinate at the origin, respectively. These values are presented in Table 2 for the three samples.

The structural transformation mechanisms of the samples were determined from the DSC thermograms considering the transformed volume fraction as a function of temperature (Fig. 7). This is described by a sigmoid-type curve whose slope n at the linear part of the plot is called the 'Avrami exponent', which is an important parameter to describe the transformation behaviour. The values of n obtained for each exothermic peak are listed in Table 3 for the three samples.

In order to calculate the temperature vs. time transformation (TTT) diagrams for the crystallisation process, isothermal annealings were performed for the two alloys with higher cobalt contents at different temperatures below the onset of the first DSC peak during 180 min. The incubation time for the beginning of the crystallisation was determined experimentally from the DSC curves as the time when the exothermal signals deviate from the baseline. The TTT diagrams of both $W_{48}Co_{11}C_{41}$ and $W_{43}Co_{16}C_{41}$ alloys are shown in Fig. 8. The film with a higher degree of cobalt is that which has a lower incubation time. Besides this, the time necessary for the beginning of the process of crystallisation decreases as it gets closer to the temperature of crystallisation.

4. Discussion

The synthesised W–Co–C samples have X-ray diffractograms characteristic of 'metallic amorphous' materials. In a previous study on the structural characterisation of these materials by EXAFS and Mössbauer spectroscopy, it was concluded that its structure is formed by an atomically heterogeneous mixture of very small crystallites of a NaCl-type tungsten carbide phase (< 20 Å) surrounded by an amorphous phase rich in cobalt [8].

The crystallisation of the W–Co–C sample has been studied with the help of DSC and X-ray techniques. The crystallisation kinetics was investigated in a non-isothermal mode by means of the Kissinger method [7]. The validity of applying this method to heterogeneous reactions has been questioned [9], but the parameters E and A have a practical value even if their theoretical interpretation is difficult [10]. The use of non-isothermal analysis (instead of isothermal analysis) is preferred for the following reasons: (i) dynamic experiments are quicker than isothermal ones and the results are widely considered easier to inter-

Table 2
Activation energy E and frequency factor A calculated from the DSC peaks of the W–Co–C samples

	1st peak		2nd peak		3rd peak	
	E (eV)	A (s^{-1})	E (eV)	A (s^{-1})	E (eV)	A (s^{-1})
$W_{51}Co_6C_{43}$	4.0	$3E+12$	3.9	$7E+11$	–	–
$W_{48}Co_{11}C_{41}$	3.6	$7E+10$	1.8	$2E+8$	–	–
$W_{43}Co_{16}C_{41}$	4.3	$8E+16$	2.3	$1E+15$	1.4	$9E+4$

Table 3
Values of the Avrami exponent n obtained for the phase transformations of the W–Co–C samples

	1st peak	2nd peak	3rd peak
$W_{51}Co_6C_{43}$	1.4	1.6	–
$W_{48}Co_{11}C_{41}$	2.1	2.0	–
$W_{43}Co_{16}C_{41}$	1.2	1.3	3.0

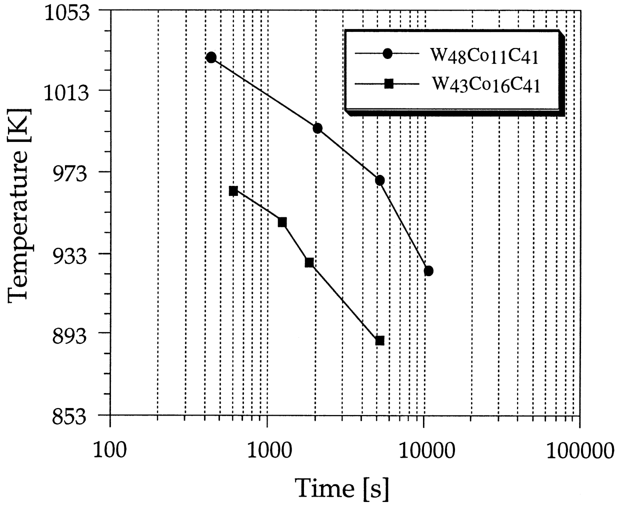

Fig. 8. Partial TTT diagrams of the $W_{48}Co_{11}C_{41}$ and $W_{43}Co_{16}C_{41}$ samples.

pret; (ii) the reaction process can be followed over a wide temperature range, and (iii) several reaction steps can be observed in a single experiment.

The DSC curves obtained during heating of the films up to the maximum temperature of 1473 K show the dependence of the crystallisation temperature on the heating rate (Fig. 5), which means that crystallisation occurs with diffusion and requires an activation energy. On the basis of the classical nucleation theory [11], one may state that the difference between the real and the theoretical transformation temperatures depends on the heating rate, the crystallisation taking place at higher temperatures for higher heating rates.

Concerning the structural stability of the films with temperature, the results obtained confirm that cobalt influences the crystallisation process of the amorphous (W–C)-based system, particularly the temperature at which it occurs. The higher the cobalt content in the films, the lower the crystallisation temperature. The structural stability of these films has been discussed on the basis of several parameters such as: chemical composition, bonding energy, degree of structural order, structural defects and diffusion of chemical elements [12].

The crystallisation of all the W–Co–C samples occurs by steps, the extension of which depends on the cobalt content. The first two DSC peaks correspond to the formation of a carbide phase M_2C. According to the literature, this carbide may exist in three different crystallographic structures with similar *d* spacings: an ordered hexagonal structure α-(M_2C), an orthorhombic structure β-(M_2C) and finally a disordered hexagonal structure γ-(M_2C). The careful analysis of the X-ray diffractograms for temperatures within the range of the first two DSC peaks do not reveal any splitting of the diffraction peaks of the M_2C phase, characteristic of the orthorhombic structures. Therefore, it can be affirmed that the crystallographic structure of the M_2C phase corresponds to one of the hexagonal forms: α- or γ-. The fact that no other phase besides the M_2C carbide was detected at the beginning of crystallisation, leads us to put forward the following possibilities: (i) the first two DSC peaks are a result of the crystallisation of the amorphous phase and correspond to the two crystallographic forms of the M_2C carbide; (2) the second DSC peak is the result of the total or partial recrystallisation (order → disorder transformation) involving the structures α- (ordered phase) and γ-M_2C (disordered phase). The first possibility seems to be more viable, keeping in mind the earlier results obtained by in situ observation of the crystallisation of the W–Fe–C amorphous films by transmission electron microscopy at high temperatures [13]. Effectively, it has been mentioned in this study that crystallisation occurs in a gradual manner with the formation of M_2C there being an increase in the percentage of the crystallised phase in detriment to the amorphous phase. Besides this, the existence of an order → disorder transformation ($\alpha \rightarrow \gamma$) does not seem to be very likely since no alterations in the DSC curves were detected during the cooling of the samples.

The activation energy, *E*, calculated for the first two DSC peaks of the W–Co–C films, varies between 1.8 and 4.3 eV. Although there is no significant difference between the values of *E* relating to the first peak of the three films, the same is not evident for the second peak, in particular for the film with the lowest cobalt content. This fact is an index that the separation of the two first DSC peaks corresponding to the formation of M_2C is due to cobalt, the influence of this element being more important in the films with greater cobalt content. In what is referred to as the frequency factor *A*, the situation is identical to that observed for the activation energy. These two kinetic parameters show the same behaviour, i.e., the greater the value of the activation energy, the greater the frequency factor and vice versa (the effect of kinetic compensation).

The determination of the ‘Avrami exponent’ *n* referring to the amorphous → M_2C transformation mechanism was performed based on the downward slope of the curves of the percentage of transformation as a function of temperature. The values obtained vary between 1 and 2, signifying lamellar and spherical growth controlled by diffusion [10].

The analysis of the DSC curves obtained upon continuous heating reveal that the process of structural evolution of the W–Co–C films do not terminate with the formation of the M_2C carbide. In fact, this carbide is structurally metastable in the temperature range of the crystallisation of the films, functioning only as an intermediate stage between the amorphous one and the formation of more stable stages. This evolution is particularly visible in the case of films with a higher percentage of cobalt, where an important peak is detected, at a temperature close to 1223 K. This peak is attributed to the formation of phases containing cobalt, i.e. $M_{12}C$ (M = W, Co) + Co_7W_6. The values of *E* and *A* obtained for this peak are quite different from those obtained for the first two DSC peaks, which could be due to a recrystallisation phenomena involving one or more of the following crystalline phases: M_2C, MC and M_6C. In effect, it should be pointed out that the quantity of the amorphous phase in this range of temperatures is practically nil, such that the formation of the new crystalline structures should necessarily take place involving other crystalline phases. Moreover, the value of n of this transformation is approximately 3, which corresponds to the morphology of volume growth [10].

Besides the phases referred to earlier, the phases MC, M_6C and (W) were also detected through X-rays, leading to small variations in the DSC curves, which could be detected after the second exothermic peak. It should be noted that the formation of MC and M_6C after that of M_2C has already been referred to in earlier studies [1,8] with regard to the structural evolution of these types of films with temperature. With respect to the determination of the TTT diagrams, the results obtained reveal that the film with higher content of cobalt is that which has a lower incubation time. Besides this, the time necessary for the beginning of the process of crystallisation decreases as it gets closer to the temperature of crystallisation, determined during continuous heating, which is in accordance with the theory of nucleation and growth controlled through the diffusion of chemical species. As a result, the rate of nucleation is a direct function of diffusion and increases with temperature. In fact, the amorphous state being thermodynamically metastable, the increase in temperature implies its transformation into more stable crystalline structures, reducing considerably the time necessary for the process.

Lastly, it should be mentioned that the maximum time of permanence in the diverse isothermal stages was not sufficient for the total extinction of the amorphous phase, the final structure being formed by the amorphous phase $+M_2C$, MC and M_6C. All these phases were observed in continuous heating, for temperatures higher to those of isothermal permanence which, once again could be explained by the compensation of temperature by time. Effectively, it is possible to obtain the same phases at different temperatures, provided that the time for each isothermal stage is also different.

5. Conclusions

The transformation kinetics and the TTT diagrams for the amorphous-to-crystalline process in W–Co–C samples with different cobalt contents were studied by using DSC and XRD. The results obtained confirm that cobalt influences the crystallisation process of the amorphous (W–C)-based system, particularly the temperature at which it occurs. The higher the cobalt content in the samples, the lower the crystallisation temperature. The crystallisation occurs by steps and is characterised by formation of the carbide phase M_2C, controlled by diffusion. The activation energy, E, calculated, varies between 1.8 and 4.3 eV, depending on the chemical composition of the sample. With respect to the determination of the temperature vs. time transformation (TTT) diagrams, the results obtained show that the film with a higher degree of cobalt is that which has a lower incubation time. Besides this, the time necessary for the beginning of the process of crystallisation decreases as it gets closer to the temperature of crystallisation.

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