IN SITU HIGH TEMPERATURE CRYSTALLIZATION STUDY OF SPUTTER DEPOSITED AMORPHOUS W–Fe–C FILMS

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Abstract—The structural behaviour of amorphous W48Fe31C11 and W48Fe28C13 films produced by sputtering have been studied in situ during annealing up to ≈950°C by means of hot stage transmission electron microscopy. Differential thermal analysis and X-ray diffraction were used as complementary experimental techniques. The results are presented and correlated with the equilibrium phases anticipated from the W–Fe–C ternary phase diagram and with previous studies on similar films deposited and annealed onto substrates.

1. INTRODUCTION

The hardness and high melting points of the stable Group IV–VIA carbides made them potentially attractive as bases for industrial materials, e.g. to cutting tools or resistant wear devices. The impact and transient high-temperature-resistant properties referred to and fine grain size are also important factors. In recent years, metastable (W–C)-based films produced by physical vapour deposition (PVD) onto alloy steel substrates have been shown to be extremely interesting hard coatings for these tribological applications [1, 2].

Since integrity of a coating depends essentially on its adherence to the substrate, significant structural changes in service, involving high internal stresses must be avoided. Partial crystallization can improve the yield strength in detriment to ductility. Moreover, the dimensional stability and residual stress may be strongly affected, particularly for films deposited onto stable substrates.

The present work is a part of a long study concerning the role of the constitution of transition metal solutes on (W–C)-based systems obtained by r.f. sputtering from sintered cemented carbide targets. In a previous study [2, 3] on the characterization of W–Me–C (Me = Fe, Co) films synthesized onto steel substrates and their structural behaviour during annealing, we showed that iron and cobalt play similar structural roles in the as-deposited state as well as during heat treatment. Their as-deposited structure was found to be dependent on the chemical-composition, becoming progressively amorphous with increasing of iron and cobalt contents. When heat treated at temperatures higher than 650°C, these films lose carbon into the steel substrates and transform to M2C and M6C [3].

This paper reports an in situ high temperature study on the annealing behaviour of amorphous W–Fe–C films and has three main purposes: (i) to gain additional knowledge about the structural ability and crystallization mechanisms of the W–Fe–C films; (ii) to establish the similarities and/or differences in the annealing behaviour of these amorphous films synthesized by PVD and liquid-quenched alloys with similar chemical compositions; and finally (iii) to compare the results with those obtained for similar films synthesized and annealed onto steel substrates.

2. EXPERIMENTAL DETAILS

Two W–Fe–C films (1–3 μm thick) with different iron contents and similar W/C ratios, W48Fe31C11 and W48Fe28C13, were synthesized by non-reactive r.f. magnetron sputtering onto glass substrates. Table 1 shows the chemical composition of the films examined by electron probe microanalyser (EPMA). The films were found to contain small amounts of oxygen and argon (3 and 1 at.%, respectively). These elements come from the discharge gas (argon 99.995%) of the PVD process and the ultimate pressure (10–4 Pa) and they were entrapped during sputtering. After chemical characterization, the films were detached from the glass substrates by hydrofluoric acid. In order to prevent contamination of their surface by the acid, the etching was done by the glass side. Once detachment occurred, the thin films were cleaned in distilled water. Films for TEM analysis were supported between two nickel grids and thinned on both sides to electron transparency by ion-milling, using argon ions at incident energies of...
4–5 keV and incident angles of about 20°. The chemical composition of the films was examined after the process of samples preparation and no contamination from the acid or the nickel grids, was detected. After structural characterization of the as-deposited structures by X-ray diffraction (XRD) and transmission electron microscopy (TEM), the annealing behaviour of the films was followed by hot stage (TEM) and differential thermal analysis (DTA) plus (XRD). The TEM analysis was performed in a 200 keV microscope equipped with a single-tilt heating stage. DTA analysis was performed with a heating rate of 20°C min⁻¹ in a furnace with argon atmosphere. The structure of the films was examined after cooling by XRD using Co-Kα radiation.

3. RESULTS

3.1. As-deposited state

As is characteristic of amorphous materials, the as-deposited state of these W–Fe–C films is characterized by fairly contrasted TEM images associated with diffuse and large electron diffraction (ED) rings [Fig. 1(a) and (b), respectively] and two large XRD peaks (Fig. 2). Double exposed images in dark field at different defoci using the brightest ED ring did not reveal further structure details.

3.2. In situ annealing

3.2.1. TEM analysis. The microstructural and phase transformation during annealing of the W–Fe–C films in the microscope was temperature dependent. The massive crystallization of the amorphous W–Me–C films occurred for temperatures between 700 and 800°C in the vicinity of the nickel grid lines. This is explained by the in situ annealing procedure itself, in which the heat transfer from the sample holder to the thin foils takes place essentially by conduction through the TEM grid lines. However, in order to avoid artefacts due to an eventual reaction of the films with the nickel at high temperatures, the TEM analysis were confined to the regions away from the grids. The morphology of the first crystals appeared more or less globular [Fig. 3(a)]. The SAEDPs obtained in this stage of crystallization from the film W₇ Fe₂ C₁ show, in addition to the large ED rings of the amorphous phase, some reasonably well defined rings ascribed to M₇ C [4] [Fig. 3(b)] whereas the film W₅ Fe₂ C₁₁ reveal ED rings associated with a two-phase structure of M₇ C + M₄ C [4] [Fig. 3(c)]. Continued heating resulted in an intensive formation of M₇ C, in particular for the W₅ Fe₂ C₁₁ and grain growth of both W–Fe–C films (Fig. 4). The SAEDPs obtained at 850°C exhibit ED rings corresponding to the M₄ C and M₄ C phases. The M₇ C seems to be the predominant phase in the iron-poor film whilst M₄ C is the major phase in the iron-rich film.

Isothermal in situ annealing at temperatures close to 900°C led to the appearance of big crystals, indexed as MC [4] (a great number of these crystals were observed in the iron-poor film), with essentially two morphology types: prismatic-shape and rod-shape (Fig. 5). Both crystals exhibited a high density of defects [Figs 6(a) and 7(a), respectively]. The most frequent SAEDPs obtained from the prismatic

| Table 1. Chemical composition of the W–Fe–C films (at.%) |
|-----------------|-----|-----|-----|-----|
| Film designation | W   | Fe  | C   | O   | Ar  |
| W₇ Fe₂ C₁      | 45.5| 12.3| 39.6| 1.5 | 1.1 |
| W₅ Fe₂ C₁₁     | 35.4| 28.5| 31.0| 3.8 | 1.3 |

Fig. 2. XRD diffraction pattern of the amorphous as-deposited films.
Fig. 3. TEM bright field micrograph (a) and the associated SAEDP obtained at the beginning of the crystallization from film $W_{84}Fe_{11}C_{41}$ (b) and film $W_{8}Fe_{35}C_{31}$ (c).

crystals [Fig. 6(b)] showed a zone axis very close to the $c$-axis and streaks along the $\langle 1100 \rangle$ directions indicating that the WC structure defects consist of a high density of stacking faults lying on $\{1100\}$ planes.

The rod-shape MC crystals [Fig. 7(b)] present two different structure defects, one large defect on the $\{1100\}$ planes and a high density of smaller defects on the $\{0001\}$ planes.

3.2.2. DTA and X-ray analysis. The DTA results obtained during annealing of the as-deposited structures are presented in Fig. 8. The phase transform-
ations of the amorphous films were found to give rise to two exothermic peaks at temperatures in the range 700–850°C. The first peak is, for the two cases, stronger than the second one. Both DTA peaks are shifted towards lower temperatures for the iron-rich film.

The X-ray diffraction results obtained at room temperature after DTA analysis are illustrated in Fig. 9. Both films are crystallized during heat treatment. The diffraction pattern obtained from the $W_{84}Fe_{11}C_{41}$ films consists of well defined peaks ascribed to $M_7C$, $MC$ and $M_6C$ [4]. The structure of the $W_{8}Fe_{35}C_{31}$ film is formed by $MC$ and $M_6C$.

4. DISCUSSION

The W–Fe–C films produced in this study are amorphous in the as-deposited state. The amorphization of these films is due to the presence of iron. In previous work [2, 3] on the structure and chemical composition of W–Me–C (Me=Fe, Co) sputtered films, it was shown that the as-deposited structure of the films ranges from crystalline phases such as $MC$, $\beta$-$MC_{1-x}$, and $M_7C$, to amorphous with

Fig. 4. TEM bright field micrograph showing the morphology of the $M_7C$ and $M_6C$ crystals formed during annealing ($T \sim 850°C$).

Fig. 5. TEM bright field micrograph obtained after annealing at 1000°C, showing geometrically shaped large MC crystals embedded in matrices of $M_7C$ and $M_6C$. 
carbide and it may only dissolve a small amount of iron (7.5 at.% at 1100°C [9]), a gradual enrichment of the matrix in iron during the amorphous → M₇C transition is conceivable. This may explain the appearance of the M₇C phase early in the crystallization process of the iron-rich coating WₓFe₉Cₓ3. The formation of the first M₇C crystals in this film was so rapid that it is not possible to determine whether the crystallites grow simultaneously with the M₇C phase from the amorphous phase, or sequentially as a result of an M₇C + iron-rich matrix → M₇C reaction. However, considering the intensive development of the M₇C phase to the detriment of the M₇C phase occurring for higher annealing temperatures, one can consider the second hypothesis as the most probable.

Extensive annealing at high temperatures undergoes the formation of MC + M₇C from the M₇C phase. According to the DTA results (2nd peak) this reaction takes place at ~845°C for the iron-poor film and ~750°C for the iron-rich film. The decomposition of M₇C during annealing of W–Fe–C films confirms that this carbide is metastable at these temperatures. It is known that the same reaction occurs during long isothermal annealing of tungsten-rich high speed steels for temperatures between 900 and 1200°C [9]. The crystallization process passing by a metastable phase, such as M₇C in our case, is known in other systems [10] and is a mean to obtain increasing cobalt and iron contents. The crystalline/amorphous transition was found to occur in the range 5–10 at.%Me. The amorphization of the sputtered (W–C)-based films is due to the addition of a late transition metal [5], iron/cobalt in this case. On the contrary, other authors [8] found that substituting a late transition metal (group VIIA or VIII A) by an early transition metal (Group IVA, VA or VIA metal) in a transition metal–non metal system may render a very difficult amorphous former. In the Fe–Cₓ₁₅ₓ₃₀ system, iron may be partly substituted (up to 50%) by various combinations of molybdenum, chromium and/or tungsten, without amorphization of the structure.

The as-deposited amorphous W–Fe–C phases crystallize during high temperature annealing. DTA results reveal an important decrease of the thermal structural stability of the films with the increase of the iron content. The first peak (associated to the crystallization from amorphous to the M₇C phase) indicates a crystallization temperature of ~758°C for the WₓFe₉Cₓ3 film and ~695°C for WₓFe₉Cₓ3. The decomposition process of the amorphous phase occurs by the precipitation of the M₇C phase and it can be classed as a primary-type crystallization in which one phase precipitates resulting in an enrichment of the remaining elements in the amorphous phase. Taking into account that M₇C is a tungsten-rich
either new metastable phases, such as new carbides for example [11, 12], or to attain the final stable phases (MC and M₄C in this study) predicted from the phase equilibrium diagrams.

It was not possible in this work to determine the precise crystal structure of the M₄C carbide formed during annealing of the W-Fe-C films. According to the literature [13] this carbide may exist in three different crystallographic structures with similar d spacings: α-(W₄C), an ordered hexagonal or pseudo-

hexagonal structure stable between 1250 and 2100°C; β-(W₄C), an orthorhombic structure existing from 2100 to 2400°C and finally γ-(W₂C), a disordered hexagonal structure stable between 2450°C and the melting point. No superlattice reflections resulting from an eventual order of the carbon atoms in the M₄C phase were observed by TEM. However, careful X-ray diffraction measurements did not show any distortion of the metallic sublattice of this phase, which could induce a splitting of some X-ray peaks, characteristic of the orthorhombic phases. In conclusion one can notice that the crystal structure of the M₄C carbide formed from the amorphous W-Fe-C phase is ascribed to one of the hexagonal forms: α- or γ-. Taking into account this assumption, one can assert that there are some structural relations among the phases formed during annealing of the W-Fe-C films [14]. The two carbides MC and M₄C, which are both of hexagonal structure, are partially insoluble, and differ from the fact that in MC the tungsten and the carbon atoms each form a set of interpenetrating simple hexagonal lattices, whereas in M₄C the tungsten atoms form an almost close-packed lattice, and the carbon atoms a simple hexagonal lattice. M₄C is a complex cubic carbide with the same carbon environment as that of M₄C (i.e. the surrounding tungsten configuration is that of two isosceles triangles inverted). Moreover, as well as the M₄C structure, both the MC and the M₄C structures are able to dissolve a certain amount of iron [9].

The MC crystals formed during annealing showed a high density of stacking faults. If it is true that MC and M₄C carbides are partly insoluble, such defects can occur during the M₄C → MC + M₄C...
transition and be due to the difference of the unit cell volumes of the two carbides (127.5\,Å³ for \( \text{M}_2\text{C} \) against 74.2\,Å³ for \( \text{MC} \)) [14]. One other plausible explanation for these structural faults is related to the MC chemical composition. An excess tungsten or iron in this carbide might introduce imperfections in the manner of stacking of the lattice planes, destroying the anisotropy along the direction parallel to hexagonal basal planes. The deformation mechanisms and the structural defects of WC have been the subject of some papers [15, 16]. Two types of stacking faults have been proposed for the WC structure, one lying on the prismatic \{1\overline{1}00\} planes with a \{1\overline{1}23\} displacement vector (the one most frequently observed) and the other on the pyramidal \{1\overline{1}23\} planes with a displacement vector of \{0\overline{1}10\}. In the present work, the streaks observed along the \langle1\overline{1}00\rangle directions in the SAEDPs of the prismatic crystals confirm the existence of stacking faults lying on the \{1\overline{1}00\} planes of the WC structure. However, another type of defect was now observed lying perpendicular to the largest growth interfaces of the rod-shape WC crystals with the matrix, i.e. on the \{0001\} planes.

In light of the present results it is possible to discuss the stability of the phases formed during annealing of the films, in terms of the W–Fe–C ternary diagram [17]. The liquid–solid equilibria of this diagram are complex, with nine binary surfaces of crystallization: \( \delta\text{-Fe}, \gamma\text{-Fe}, \text{Fe}_6\text{W}_5, (\text{W}), \text{W}_7\text{C}, \text{WC}, \beta\text{-WC}, \ldots \), \( \text{M}_2\text{C}(\tau_\gamma\text{-phase}) \) and C. All but one, the \( \text{M}_2\text{C} \) phase, are derived from the binary axes [18]. There is no consistent equilibrium data of the W–Fe–C system at temperatures lower than 1000°C. The few studies available were performed by Sato et al. [19] and by Kuo [20] on alloys isothermally transformed for various periods of time at 700°C, after austenitization at 1100 and 1300°C, respectively. Moreover, there is only moderately good agreement between these two works, in particular concerning the composition range of the \( \text{M}_2\text{C} \) carbide and the eventual existence of complex carbides such as \( \text{Fe}_6\text{W}_5\text{C} \) (\( \tau_\gamma\text{-phase} \)) and \( \text{FeW}_2\text{C} \) (\( \tau_\gamma\text{-phase} \)). The \( \tau_\gamma\text{-phase} \) was detected by Sato et al. by means of electrolytic extraction of carbides from high-tungsten low carbon alloys, but Kuo did not observe it. Nothing is said about the \( \tau_\gamma\text{-phase} \).

Although not many temperatures have been systematically studied, an almost completed equilibrium diagram of the system W–Fe–C is available at 1000°C (Fig. 10). At this isothermal section, the films synthesized in this work lie in two different structural domains: \( \tau_\gamma \) + MC for the film \( \text{W}_9\text{Fe}_{13}\text{C}_{44} \) and \( \gamma\text{-Fe} + \tau_\gamma + \text{MC} \) for the film \( \text{W}_{10}\text{Fe}_{15}\text{C}_{33} \). The \( \text{M}_2\text{C} \) phase is not accepted at this temperature even for higher carbon contents. Unlike the \( \gamma\text{-Fe} \) phase, these equilibrium phases are in accordance with these ones obtained in this study. The absence of \( \gamma\text{-Fe} \) in the W–Fe–C films annealed at 950°C can be related to the homogeneity of the \( \tau_\gamma \) phase. It is known that this phase has a negligible range of homogeneity with respect to carbon, but a quite wide variation in the Fe/W ratio, varying from 1 (Fe\(_6\)W\(_5\)C) to 2 (Fe\(_8\)W\(_7\)C). It is probable that, in contrary to what is predicted from the W–Fe–C equilibrium diagram, the \( \text{M}_2\text{C} \) phase formed by the reaction \( \text{M}_2\text{C} \rightarrow \text{M}_2\text{C} \) + MC is of the type \( \text{Fe}_6\text{W}_5\text{C} \) and not \( \text{FeW}_2\text{C} \), which would impede the formation of the other iron-rich phases such as the \( \gamma\text{-Fe} \) phase.

Finally a discussion regarding the relationship of the present results and those obtained for films on steel substrates is possible and useful. There are some differences in the thermal behaviour between W–Fe–C films annealed onto steel substrates in a vacuum furnace and annealed without substrate in an electronic microscope. The crystallization of the films onto steel substrate occurs at lower temperatures than films without substrate. Moreover their crystallization processes do not follow exactly the same steps: the development of the MC phase from the \( \text{M}_2\text{C} \) phase observed for films without substrates was not observed for films onto steel. This is understood by the diffusion phenomena occurring during the successive isothermal annealings of these last films. The loss of carbon into the steel substrates enhances the decomposition of the amorphous phase and impedes the formation of carbon-rich phases such as MC. Thus, it is our opinion that the application of the W–Me–C films deposited onto steel as hard films for mechanical applications should require in the future either the existence of an additional layer.
between the film and the substrate in order to act as a barrier to the migration of carbon atoms into the steel or the incorporation of an additional chemical element capable of stabilizing chemical and structurally the as-deposited structure at high temperatures.

5. CONCLUSIONS

1. Both the $W_{\text{Fe}}\text{Fe}_{15}\text{C}_{40}$ and the $W_{\text{Fe}}\text{Fe}_{15}\text{C}_{15}$ films were found to be amorphous in the as-deposited condition.

2. Crystallization of these films occurred during annealing at high temperatures and is characterized by an initial precipitation of the metastable phase $M_2\text{C}$. With increasing temperature, this phase gives rise to equilibrium phases $\text{MC} + M_6\text{C}$, predicted from the ternary $\text{W-Fe-C}$ equilibrium phase diagram.

3. Precipitation of the MC carbide results in different structure defects depending on its morphology. Prismatic WC crystals contain stacking faults on the \{100\} planes. Regarding the rod-shape WC crystals they present two different structure defects, one large defect on the \{100\} planes and a high density of smaller defects on the \{001\} planes.

4. The crystallization process of films annealed with and without steel substrates do not follow exactly the same steps: due to carbon diffusion into the steels substrates, the crystallization of films onto substrates occurs at lower temperatures and is characterized by the absence of carbon-rich phases such as MC.

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