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Modification of the structural order of transition metal-carbon systems by the addition of a Group VIII element

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Abstract

ATransition-metal carbides M-C from different groups of the periodic table (IVA–VIA), doped with iron, were produced by sputtering, and their chemical composition and crystal structure were evaluated. The M-C binary thin films have different ranges of structural order depending on their heat of formation and tendency to crystallize to a structure of the NaCl type. Iron provokes a significant decrease of the range of structural order of these carbides. The iron content required for the appearing of structures with intermediate-range order is a function of the constituent transition metal of the carbide, and is higher for stronger carbide formers. \bigcirc 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sputtering; Transition metal carbides; Structural behaviour; Range of structural order

1. Introduction

In the last few decades research in the area of materials engineering has been directed towards always developing improved materials with properties tailored to must specific applications. Thin films deposition allows metastable materials to be produced, with a low degree of structural order, with promising mechanical and tribological properties. Amorphous or nanocrystal-line hard coatings based on carbides and nitrides of transition metals have been synthesised by sputtering [1-4]. In this process, evaporated atoms (ions) move for a short time on the substrate before being 'frozen-in' as a solid [5].

From the research work we have conducted to date on sputtered coatings has demonstrated that addition of a transition metal to a metal-carbon binary system can play an important role in modifying the degree of structural ordering and in turn the mechanical and tribological properties. Effectively, it is possible to significantly decrease the range of structural order of the tungsten carbide by introducing a Group VIII element such as Ni, Fe, Co or Pd; the addition of transition metallic elements of other groups does not give this effect [4,6].

In the present work the influence of iron on transition metal carbides (M-C) with different numbers of valence electrons per atom, i.e. Ti-C, V-C, Cr-C, Mo-C and W-C, has been evaluated in order to determine a general 'amorphization' criterion for these materials. The results are discussed as a function of the chemical composition of the thin films and the affinity of the transition metal for carbon.

2. Experimental details

Thin films of M–Fe–C (M = Ti, V, Cr, Mo) with \approx 2.5 µm thickness (Fig. 1) were synthesized by nonreactive radio frequency (r.f.) sputtering in a ESM 100 Edwards unit with r.f. power supplies of 1000 and 500 W, branched to the target and substrate holder, respectively.

The depositions were carried out in an argon atmosphere onto unbiased glass and heat-treated high-speed steel M2 (AISI) substrates, without substrate heating. The steel substrates were polished down to a 1 μ m diamond (final roughness lower than 0.03 μ m) and then cleaned before the depositions by ion bombardment for

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Fig. 1. Typical cross-section morphology of the thin films produced in this research work (SEM image of a Mo-Fe-C film with 5 at.% Fe).

30 min, by locating the plasma close to the substrates electrode. The depositions were carried out at a constant discharge pressure of 1 Pa and a specific power of 6.2 W cm⁻². The deposition time was kept constant at 75 min for all the systems produced. The target–substrate distance in the chamber was 6.5 cm. The films were obtained from sintered $M_x C_y$ (M = Ti, V, Cr, Mo and W) targets (Table 1) with iron plates attached. The iron was varied in the thin films by varying the relation between the exposed area of the $M_x C_y$ sintered targets and the area of the iron plates.

As will be discussed later, the introduction of iron alters the base metal/carbon relationship of the various systems, this influence being more pronounced in the thin films formed by metals of the first long period furthest from Groups VIII, i.e. Ti-C and V-C (the higher the iron content the lower the base metal/carbon ratio). To define the effect of iron on the structure of the thin films obtained, the Ti-C-Fe system was deposited in two different ways: with and without correction of the Ti/C atomic ratio. To maintain this ratio constant, as a function the iron content, it was necessary to attach foils of titanium with different areas on the TiC+Fe target to balance the enrichment in carbon of these films. The results obtained in both Ti-C-Fe systems are discussed below.

Table 1 Chemical composition and structure of the targets

	Chemica	l composition	Structure	
	М	С	M/C	
TiC	50.6	48.9	1.03	fcc
V_4C_3	52.5	47.0	1.15	fcc
Cr_3C_2	57.8	41.7	1.39	Orthorhombic
Mo ₂ C	66.4	33.1	2.01	Hexagonal

The chemical composition of the thin films and targets was determined by electron probe microanalysis using CAMEBAX SX50 equipment. The experimental conditions used for the analysis were 5 kV and 40 nA for carbon determinations and 20 kV and 20 nA for all the metallic elements.

The structure of the thin films was studied by X-ray diffraction (XRD). A Philips X'Pert diffractometer with CoK_{α} radiation operated at 35 kV and 25 mA was used for the structural analysis. Microstructures of the thin films were analyzed using a 100 kV TEM microscope. The thin films were detached from the glass substrates by fluoridric acid, supported between two-nickel grids, and thinned from both sizes by ion milling in an argon atmosphere until they were electron transparent.

3. Results

3.1. Chemical composition

Tables 2 and 3 show the composition of the thin films studied in this work in atomic percentage. Fig. 2 represents the relationship between the chemical composition of the binary thin films M-C and the targets used for the depositions. The line at 45° represents the separation between thin films enriched in carbon (right hand area) and deficient in carbon (left hand area). All but the W-C systems present lower metal/carbon atomic ratios than those of the corresponding targets. The lighter the metallic element forming the carbide the higher the excess of carbon of the M-C thin films.

Fig. 3 represents the influence of the iron percentage on the base metal/carbon atomic ratio for the systems obtained from binary sintered targets. The composition of all the systems was normalized to unity, i.e. we consider the M/C ratio of all the binary systems to be equal to unit. The composition of the ternary systems was then plotted following this normalization. As can be observed, the presence of iron gives rise to a decrease of the base metal/carbon ratio, particularly in the case of the systems of the first long period of the periodic table, e.g. Ti–C, V–C and Cr–C.

3.2. Structure

Fig. 4 shows the XRD results for the M–C and M– Fe–C films. With the exception of the Cr–C system, the structure of all the other binary systems is a crystalline NaCl-type phase. The XRD pattern of the Cr–C film features two very wide peaks (a stronger broad peak and a weaker sub-peak), which are characteristic of materials with a low degree of structural order. The addition of iron to the M–C crystalline thin films leads to the appearance of structures with diffraction patterns identical to those of the base Cr–C system. The amount of

Table 2 Chemical composition of the samples synthesised in this study

Ti-Fe-C	V-Fe-C	Cr-Fe-C	Mo-Fe-C	W-Fe-C
Ti _{43.2} C _{56.8}	V _{48.2} C _{51.8}	Cr _{54.8} C _{45.2}	$Mo_{66,0}C_{34,0}$	W _{56.0} C _{44.0}
Ti _{39.5} Fe _{4.8} C _{55.7}	V _{40.3} Fe _{8.2} C _{51.5}	$Cr_{50.5}Fe_{7.0}C_{42.5}$	$Mo_{61.1}Fe_{4.7}C_{34.2}$	$W_{53,3}Fe_{4,0}C_{42,7}$
Ti _{34.7} Fe _{10.3} C _{55.0}	V _{39,2} Fe _{13,4} C _{47,4}	Cr _{40.7} Fe _{13.3} C _{46.0}	Mo _{57.0} Fe _{13.3} C _{29.7}	W _{52.3} Fe _{5.8} C _{41.9}
Ti _{30.8} Fe _{15.1} C _{54.1}	V _{26.2} Fe _{26.1} C _{46.7}	Cr _{38.9} Fe _{16.7} C _{44.4}	Mo _{53.1} Fe _{17.1} C _{29.8}	W _{46.9} Fe _{13.4} C _{39.7}
Ti _{25.0} Fe _{19.7} C _{55.3}	_	_	Mo _{44.9} Fe _{26.2} C _{28.9}	W _{43.3} Fe _{19.9} C _{36.8}
Ti _{21.6} Fe _{26.1} C _{52.3}	-	_	_	W _{36.6} Fe _{31.5} C _{31.9}
Ti _{16.0} Fe _{36.3} C _{47.7}	-	-	_	

Table 3

Chemical composition of the $\mathrm{Ti}{-}\mathrm{C}{-}\mathrm{Fe}$ samples with constant $\mathrm{Ti}{/}\mathrm{C}$ atomic ratio

System	Ti-l	Fe-C	(Ti/C	ratio	controlled)
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 $\begin{array}{l} Ti_{48.3}C_{51.7}\\ Ti_{45.0}Fe_{10.5}C_{44.5}\\ Ti_{39.3}Fe_{23.1}C_{37.6}\\ Ti_{34.3}Fe_{31.5}C_{34.2}\\ Ti_{31.0}Fe_{39.2}C_{29.8} \end{array}$



Fig. 2. Relationship between the chemical composition of the binary M-C thin films and that of the corresponding targets.

iron required depends on the type of base transition metal carbide and is higher for stronger carbide formers. This structural transition occurs gradually, accompanied by a widening of the diffraction peaks. The Mo–C and W–C systems present a compositional range in which the XRD patterns are formed by three wide peaks.

Fig. 5 shows the influence of iron on the d_{111} spacing of the M–Fe–C crystalline thin films. In the same figure are plotted the ICDD values for the fcc M–C binary carbides used as targets, TiC_{1-x}, V₄C₃, Mo₂C and WC_{1-x} [7] are also shown. As can be observed, the d_{111} values obtained from the binary sputtered thin films are higher than those of the ICDD files (particularly for the



Fig. 3. Influence of the iron percentage on the specific transition metal/ carbon atomic relationship.



Fig. 4. Influence of iron on the structure of the thin M-Fe-C films. NC, nanocrystalline; T, transition; QA, quasi-amorphous.

Ti-, Mo- and W-based systems), which might be due to stresses and/or off-stoichiometric chemical compositions. The addition of iron has two contrasting effects on the position of the diffraction peaks. In contrast to the Ti-C system, the addition of small quantities of iron to all the others M-C systems results in a slight increase in the d_{111} value of the fcc structure which make up the crystalline thin films; the opposite situation occurs for higher quantities of iron (Ti-Fe-C and V-Fe-C



Fig. 5. Influence of iron on the interplanar distance d_{111} of the M-Fe-C nanocrystalline thin films.

systems). These two systems can accommodate the highest quantities of iron in the crystalline domain.

Fig. 6 shows typical TEM images and the corresponding selected area diffraction patterns (SADP) of the thin films obtained in this work. The TEM image of the films with larger grain sizes (Fig. 6a) consists of fine grains, about 50 nm in diameter, and the corresponding SADP consists of five relatively large diffraction rings, characteristic of fcc nanocrystalline materials. The thin films



Fig. 7. X-ray diffraction patterns of the Ti–C–Fe samples with a Ti/C atomic ratio ≈ 1 .

with a shorter range of structural order (Fig. 6b) are characterized by low-contrast TEM images associated with diffuse and broad diffraction rings. These films can be described as formed by nanoparticles about 20 Å in diameter, embedded in an amorphous matrix.

Fig. 7 shows the XRD patterns of the Ti-C-Fe system with a controlled Ti/C atomic ratio. The d_{111} values are also shown in this figure. The structural order of the thin films decreases with increasing iron content, the films having a fcc structure. The film of the Ti-C-Fe system with 39.2% Fe and a Ti/C ratio ≈ 1 has a



Fig. 6. Typical TEM and SADP images of the nanocrystalline and quasi amorphous thin films produced in this work. (a) $W_{56.0}C_{44.0}$, (b) $W_{46.9}Fe_{13.4}C_{39.7}$.

larger range of structural order than the corresponding film with Ti/C < 1. Further, the thin films with a Ti/C \approx 1 have lower d_{111} spacings than similar films with the same iron content but with lower Ti/C ratios.

4. Discussion

The M-C (M = Ti, V, Cr, Mo) binary thin films produced in this study contain more carbon than the targets from which they are originated. This is in contrast to the W-C system [4]. The chemical composition of a sputtered coating obtained in a non-reactive mode depends, obviously, on the composition of the target used for the deposition. However, two effects can play an important role on the final composition of a coating: (i) resputtering; and (ii) recoil implantation and cascade mixing [8,9]. The former phenomenon leads to thin films enriched in elements with higher atomic weights and the latter to thin films enriched in contaminant elements present in the chamber atmosphere. Resputtering occurs because the surface of the growing film is constantly bombarded by the reflected neutral species during sputtering. This leads to a preferential resputtering of the lighter elements of the thin films, which, in this study, was carbon. In contrast, recoil implantation and cascade mixing processes give rise to thin films enriched in contaminant elements, such as carbon. This can be explained as follows: if impinging ions reach the surface with high energy, adsorbed carbon atoms from the residual atmosphere (ultimate pressure = 10^{-4} Pa) can penetrate the lattice and become trapped (recoil implantation). Besides collisions between adsorbed carbon atoms and the cascade of moving target atoms can also cause carbon to diffuse from the surface towards the interior of the film (cascade mixing). For the energies of the argon ions used in this study, the resputtering effect dominates in W-C system (heavy metal [10]), while the recoil implantation and cascade mixing effects dominate in systems made of lighter metals.

Iron alters the base metal/carbon relationship of the various systems, the influence being more pronounced in thin films formed by metals of the first long period furthest from Group VIII, i.e. Ti-C and V-C. This confirms previous results on multicomponent materials [4], where a direct dependence of the atomic weight of the nearest neighbours to the carbon on its sputtering yield was observed.

The structural analysis conducted in the present study shows that the structure of the M-C thin films does not depend on the structure of the corresponding targets. Further, the degree of structural order of the films decreases as the content of iron increases.

The binary thin films have different ranges of structural order depending on the type of system

studied. The formation of structures with reduced range of structural order appears to be related to the stability of the metal-carbon systems, which decreases from Group IVA to group VIA of the periodic table [11], and to the tendency of the systems to crystallize in the NaCl structure. This structure has an important number of interstitial positions, which permit structurally identical thin films, but of very different chemical compositions, i.e. with extensive solubility domains. This may explain why the fcc structure occurs often in carbide-based thin films obtained by sputtering. Thus, it is logical that systems which may have this structure are generally crystalline, even in the metastable state (high-temperature structures). All but the Cr–C systems studied in this work can crystallize in the NaCl structure (see the corresponding phase diagrams [12]). This might be one of the reasons why the Cr-C system has a low range of structural order while the others consist of nanograins of about 50 nm in diameter. Further, it is in the VIA group of the periodic table that the structural differences between the thin films and their respective targets used in deposition can be verified: the Cr_3C_2 target has an orthorhombic structure while Mo2C and WC are hexagonal. It can be concluded that all the M-C thin films studied are metastable, their structure being either quasi-amorphous (Cr-C system) or nanocrystalline (all the other binary systems). The occurrence of metastable structures by sputtering is due to the process of deposition. During synthesis the atoms condense in an intermixed state, after which the system tends towards a low free energy. Structural order in a thin film is produced largely by the mobility of the adatoms. In the case of sputtering without substrate heating, the very high cooling rates ($\approx 10^8$ K s⁻¹ [13]) do not give the adatoms time to rearrange to a stable configuration. Thus metastable structures occur, with a reduced structural order and with higher solubility domains than those predicted from the phase diagrams.

Various models have been proposed to predict the range of composition for amorphous transition metal alloys, which are based on the size differences of the constituent elements, on the enthalpy of mixing [14], or on information obtained from the phase diagrams. Giessen [15] proposed an amorphization criterion based upon the heat of formation and on the atomic size ratio. This model predicts that two elements will form an amorphous structure if they have very different sizes and a negative heat of formation. This criterion has been criticized by other authors [16] who have pointed out the existence of several examples of amorphous phases where the elements present either exhibit a positive heat of formation or atomic size ratios close to unity. Clements and Sinclair [14] and Clemens [17] have proposed a classification of the metal-carbon systems according to the thermodynamic driving force for solidstate amorphization reactions. According to this criterion, various transition metal-carbon systems lie in a region associated with solid-state amorphization. Van der Kolk et al. [16] claims that the range of relatively stable amorphous phases is determined by three factors: one is the elastic mismatched energy, whose contribution in the case of systems with large size mismatches is important. The second factor favouring the formation of an amorphous phase is a structural contribution. A large positive contribution to the enthalpy is expected for systems that consist of two elements, one with a number of valence electrons per atom Z = 5 or 6 and the other with Z = 8 or 9. For alloys in which one of the constituents has five or six valence electrons and the other has eight or nine, the structural term tends to raise the enthalpy of the solid solution relative to the enthalpy of the amorphous phase. Consequently, a wide composition range is observed where amorphous phases are found, even when the size mismatch is small. The third factor takes into account the difference in enthalpy between the solid solution and the amorphous phase, i.e. the enthalpy of fusion minus the decrease in enthalpy, which is caused by the structural relaxation of the amorphous phase. Structural relaxation strongly favours the formation of amorphous phases. All these models have been developed only for binary alloys and in some systems do not agree with the experimental observations. Further, the difference between the predictions and the experimental results is smaller in the case of systems obtained by rapid quenching than in the case of systems obtained by vapour-deposition (e.g. sputtering) [5].

The incorporation of iron to the binary crystalline M-C binary systems modifies the degree of structural order. As the iron content increases, the thin films tend towards an amorphous state; the iron content required is higher when the M-C based system is more stable. A study of the influence of the addition of transition metallic elements to the W-C system was the goal of a previous study [4], in which the authors claim that the amorphous phase forming ability in tungsten-carbon sputtered thin films is exclusive of group VIII metals, such as iron or palladium. The explanation for this was related to a set of factors connected to the electronic configuration of these elements, not only to the atomic size of the element added, but also to the crystalline structure and its affinity for carbon. This appears to be in agreement with the criteria of Van der Kolk et al. [16]. However, it should be pointed out that in contrast to Van der Kolk's study, the present study concerns carbides with a mixture of covalent/metallic bonding between the metallic element and carbon. The addition of iron decreases the covalent character of the chemical bonding and induces distortion of the crystallographic lattice tending towards amorphization. All the studied carbides are possible to be amorphizised, the percentage of iron required for the amorphization of the various systems depending on the specific transition metal forming the carbide.

Finally, it should be pointed out that the presence of carbon in the thin films might be an additional factor favouring amorphization due to the formation of metastable structures with a lower degree of structural order. Comparing the Ti-Fe-C systems obtained with different sputtering targets, with and without constant Ti/C atomic ratios, it appears that carbon also influences the structural order of these films, since the higher the carbon content, the lower the iron percentage required for amorphization. This observation has been reported in other studies on the deposition of this type of material [18]. Moreover, the large values of d_{111} obtained from the Ti-Fe-C thin films with Ti/C ratios as a function of the iron content (Ti/C < 1) can be explained by a higher concentration of carbon in interstitial positions. In fact these films obtained from sintered TiC target are richer in carbon than the ones obtained from the TiC target with Ti plates superimposed.

5. Conclusions

The results obtained show that the sputtered M-Fe-C (M = transition metal) thin films are either crystallineor amorphous according to the type of system under consideration. In the case of binary systems, all but the Cr-C thin films are nanocrystalline (grain size of about 50 nm) formed by a NaCl-type structure. Iron influences the degree of the structural order of the thin films, with quasi-amorphous structure being formed as the iron content increases. The iron content required for the occurrence of this structure depends on the specific transition metal forming the carbide, the required iron content increasing as the affinity of the transition metal for carbon increases. Carbon itself also influences the structural order of the thin films; higher carbon contents are required for amorphization as the iron content is reduced.

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