MECHANICAL BEHAVIOUR OF SPUTTERED M-Fe-C (M = CR, MO, W) CARBIDES

B. TRINDADE*, M.T. VIEIRA*, A.M. AMARO**, J.S. CIRNE** *ICEMS, Departamento de Engenharia Mecânica da Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030 Coimbra, Portugal **CEMUC, Departamento de Engenharia Mecânica da Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030 Coimbra, Portugal

ABSTRACT

Transition metal carbides of the VI Group of the Periodic Table (M-C where M = Cr, Mo, W) doped with iron were deposited as thin films on glass substrates by magnetron sputtering and were structurally and mechanically analysed by X-ray diffraction, laser interferometry and ultramicrohardness. The results show that the structure of the M-C binary systems depends on the position of the element M in the Periodic Table. Both W-C and Mo-C systems are crystalline (fcc structure) while the Cr-C is amorphous. The hardness and Young's modulus of the films increase from the carbides of the 1st to the 3rd long Period. The addition of iron decreases the degree of structural order of the films as well as their Young's modulus. The films with higher hardness are those with a transition structure between crystallinity and amorphism.

INTRODUCTION

The development and the optimisation of coatings for wear-resistant mechanical applications is of great scientific and technological interest nowadays, particularly for metal cutting, metal forming and other fields of manufacture. Among the suitable materials for these applications, those based on transitional metals of Groups IV and VI of the Periodic Table are promising materials because of their unique mechanical, physical and chemical properties. The performance of these materials may be however increased by the addition of another metal with weak affinity to the base material. This is the case of cobalt in the W-Co-C system. This element reduces the stress level and the grain size of the deposited material, thus decreasing the probability of a premature failure of the coating [1].

The addition of a metal to a carbide / nitride system may induce materials with different degrees of structural order. It is known that the incorporation of a Group VIII metal to the W-C system gives rise to amorphous structure [2]. The atomic arrangement of these amorphous materials is not completely random but maintains a degree of short-range order (less than 20 Å). Their structure is formed by small β -MC1-x crystallites (M = mainly tungsten) with a few unity cells size, surrounded by a disordered phase rich in the Group VIII element [2].

This work concerns the synthesis and characterisation of sputtered M-Fe-C carbides (where M is a Group VI element: Cr, Mo, W) with different degrees of structural order. Films with 3-4 µm thickness have been deposited by magnetron sputtering and characterised by electron probe microanalysis (EPMA), X-ray diffraction (XRD), ultramicrohardness and laser interferometry. The Young's modulus of the films has been calculated by means of laser interferometry and ultramicrohardness. The results obtained are discussed in terms of the influence of the element iron on the structure and mechanical properties of this type of carbides.

EXPERIMENTAL DETAILS

Films of M-Fe-C (M = Cr, Mo or W) with some μ m thickness have been deposited on glass substrates (75x25x1 mm) by magnetron sputtering from M-C sintered targets (Cr₃C₂, Mo₂C and WC) partially covered by iron foils. The percentage of iron in the films was varied between

0 and 11 at% by altering the ratio between the area of the surface of the sintered target exposed and the area of the iron foils. The chemical composition of the films was determined by EPMA. The structure analysis was performed by XRD with Co K α radiation. Ultramicrohardness was utilised for mechanical analysis of the films. The Young's modulus of the films has been calculated by means of two different techniques: laser interferometry and ultramicrohardness.

Laser interferometry

One of the techniques used for the calculation of the Young's modulus of films consists in the Laser evaluation of the change of maximum displacement obtained in the middle of a specimen, uncoated (y_s) and coated (y_f) , charged by an external force *P* normal to the axis. In this work, a modified Michelson's interferometer was used. A simply supported beam of glass with a distance of 50 mm between supports was considered. The load *P* was applied at the middle span. For the uncoated substrate, the maximum displacement is given in SI units by:

$$y_{s\max} = \frac{-2.604 \times 10^{-6}}{E_s I_{x_s}} \times P$$
(1)

where E_s and I_{x_s} are the Young's modulus and the inertia momentum of the glass substrate $(E_s I_{x_s} = 0.1625 \text{Nm}^2)$. For each value of *P*, the number of interference fringes that appear during the specimen bending are counted. Since each fringe corresponds to a 0.3 µm displacement of the middle line of the specimen, it is possible to calculate the maximum displacement for each load value. By Eq. (1), for each load (*P_i*) the corresponding Young's modulus (*E_{si}*) of the substrate is obtained, and the average calculated.

After deposition, the flexural rigidity is given by $E_s I_{xs} + E_f I_{xf}$ and the equation (1) becomes:

$$y_{f \max} = \frac{-2.604 \times 10^{-6}}{E_s I_{x_s} + E_f I_{x_f}} \times P$$
(2)

where E_f and I_{xf} are the Young's modulus and the inertia momentum of the film, respectively. Knowing E_s , I_{x_s} and I_{x_f} , the Young's modulus of the film, E_f , is easily calculated from Eq. (2) by the maximum displacement of the coated specimen.

Ultramicrohardness

The slope of the unloading load-depth curve in a depth-sensing indentation test can be used as the measure of the elastic properties of a material. Elastic modulus is determined from [3] :

$$\frac{dP}{dh} = \left(\frac{2}{\pi}\right)^{1/2} DE_r \tag{3}$$

where dP/dh is the slope of the unloading curve, D is the Vickers diagonal length and E_r is the "specimen + indenter" modulus given by:

$$\frac{1}{E_r} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i}$$
(4)

and where *E* and *v* are the Young's modulus and the Poisson's ratio of the sample (film + substrate) and E_t and v_i are the same parameters for the indenter. The Young's modulus and Poisson's ratio of the indenter used for calculations were taken from literature as $E_i = 1050$ GPa, $v_i = 0.07$ [4]. If one assumes that the indenter has an ideal pyramidal geometry and uses the plastic depth *hp*, instead of the *D*, we obtain:

$$\frac{dh}{dP} = \frac{1}{2h_p} \left(\frac{\pi}{24.5}\right)^{1/2} \frac{1}{E_r}$$
(5)

where dh/dP is the compliance of the equipment (reciprocal of the unloading slope).

The tests were performed in a nanoindentation device with a Vickers indenter. Young's modulus of the samples was obtained by indenting the specimens to various depths (nominal loads ranging from 5 mN to 170 mN). Five indentations were made for each load using a continuous load-unload cycle. The values of the Young's modulus of the films, E_{f} , were obtained by the following equation:

$$E - E_s = \left(E_f - E_s\right)\Phi_{Gao} \tag{6}$$

where Φ_{Gao} is a weight function, called the Gao function [5] given by:

$$\Phi_{Gao} = \frac{2}{\pi} \arctan \frac{1}{x} + \frac{1}{2\pi(1-v^2)} \times \left[(1-2v)\frac{1}{x}\ln(1+x^2) - \frac{x}{1+x^2} \right]$$
(7)

with x = a/t (a = contact radius and t = thickness of the film). With a set of measured E_j (a_j/t) values, the corresponding values of $y = E_j - E_s$ are determined, as well as the values $x_j = \Phi_{Gao}$ (a_j/t) using Eq. (7). The regression constant B (slope of the straight line) is calculated and the reduced film modulus is obtained as $E_f = E_s + B$. The Young's modulus of the glass substrate, E_s , was obtained experimentally by laser interferometry and ultramicrohardness and is equal to 78 GPa.

RESULTS

Table I shows the atomic chemical composition of the films determined by EPMA as well as their thickness measured by observation of the cross-section on a SEM (figure 1).

thickness of the M-Fe-C (M=W, Mo, Cr) films					
Films's designation	М	С	Fe	t (µm)	
WC WFeC1 WFeC2	55.2 52.4 47.4	44.8 43.0 42.1	4.6 10.5	3.9 3.8 3.8	
MoC MoFeC1 MoFeC2	65.2 62.5 59.0	34.8 32.4 31.2	- 5.1 9.8	3.8 3.7 3.9	
CrC CrFeC1 CrFeC2	59.9 52.5 49.6	45.1 42.8 40.8	- 4.7 9.6	2.9 2.8 2.9	

Table I - Chemical composition (at.%) and



Figure 1 - SEM image of the W-C film cross-section.

Figures 2 and 3 compile the results of the structural analysis of the M-C and M-Fe-C films. The binary W-C and Mo-C films are constituted by a crystalline NaCl-type fcc structure; the Cr-C film presents a diffractogram characteristic of amorphous materials (Fig.2). The addition of iron to the W-C and Mo-C systems leads to the appearance of amorphous structures with diffractograms identical to those of the Cr-C system (Fig. 3). A structural transition zone is visible



between the crystalline and the amorphous domains, whose films present three considerably wide X-ray diffraction peaks.



Figure 3 - Influence of iron on the structure of W-Fe-C films as a typical example of both W-Fe-C and Mo-Fe-C systems.

Figure 3 shows a plot of Φ_{Gao} (a_j/t) as a function of $E_j - E_s$ for the three M-C binary systems. Table II compiles the results of the Young's modulus obtained from the two techniques: laser interferometry and ultramicrohardness. In the same table the hardness of the films is also indicated.



Table I - Young's modulus and hardness of the M-Fe-C (M=W, Mo, Cr) films

Coating's designation	E _f *	E _f **	H
	[Gpa]	[Gpa]	[Gpa]
WC	532	460	20.5
WFeC1	507	440	21.1
WFeC2	-	428	19.4
MoC	346	280	15.3
MoFeC1	315	257	15.6
MoFeC2	323	242	14.7
CrC	288	240	12.8
CrFeC1	265	218	12.5
CrFeC2	261	210	10.9

Figure 3 - Φ_{Gao} (*a_j*/*t*) as a function of E_j - E_s for the three M-C binary systems

* Laser interferometry ** Ultramicrohardness

The values of E_f obtained by laser interferometry are higher than those obtained by ultramicrohardness. The Young's modulus and the hardness of the films increase from the 1st to the 3rd long Period, *i.e.* from the Cr-C to the W-C carbide. The Young's modulus of the films decreases as the iron content increases. The films with higher hardness are those with a transition structure between crystallinity and amorphism, *i.e.* with an iron content of about 5 at.%.

DISCUSSION

The structural results obtained in this study confirm the ability of the sputtering technique to produce metastable structures from structurally stable targets. This can be explained by the process of deposition itself. During sputtering, the atoms condensing in an intermixed state try to find a stable configuration with a low free energy of formation. However, the very high cooling rates ($\approx 10^8 \text{ °C/s}$ [6]) do not give the adatoms time to organise themselves in stabe structures, giving rise to high temperature structures, broad solubility domains or structures with a short

range order (nanocrystalline or amorphous). The films under study are structurally metastable, either because they present high-temperature structures at room temperature (fcc phases such as WC_{1-x} and Mo_2C) or because they are amorphous. Moreover, their structures differ from that of the targets used in the deposition. The target Cr_3C_2 has an orthorhombic structure while Mo_2C and WC are hexagonal. The formation of amorphous structures seem to be related to the stability of the metal-carbon systems, which decreases from the 3^{rd} to the 1^{st} Long Period of the Periodic Table, and to the tendency of the systems towards cristallising or not in structures of the NaCl-type. This structure has a high compactness and allows extensive solubility domains. This might be the reason why the fcc structure is the predominant structure of the transition metal carbides obtained by sputtering. Thus, it is natural that the systems whose equilibrium diagrams foresee the existence of this type of structure would have better conditions to be crystalline, even in a metastable condition. Contrary to the Cr-C system, the fcc NaCl-type phase exists in both Mo-C and W-C systems at room temperature (phase Mo₂C) or at high-temperatures (phase WC_{1-x}), respectively.

The addition of iron to the binary M-C (M = Cr, Mo, W) systems leads to a decrease of the degree of structural order of the films (Fig. 3). This result is in keeping with results of earlier studies on the deposition of doped tungsten carbide with elements of Group VIII of the Periodic Table and confirms the idea that amorphisation does not only occur in transition metal carbides of the 3^{rd} long period but also in carbides of other systems such as MoC. There isn't any one single factor to explain the high ability of the Group VIII elements towards amorphisation of transition metal carbides. Earlier studies undertaken on the subject lead us to believe that amorphisation is due to a set of physio-chemical characteristics of these elements and not related only to the difference in atomic size, crystalline structure or affinity for carbon between the different metallic elements of the carbide.

Regarding mechanical properties of the produced binary systems, the hardness and the Young's modulus of the films increase from the 1st to the 3rd long period, i.e. towards a greater metal-carbon bonding stability. This is similar to what happens in bulk carbides.

Increasing iron contents lead to a progressive decrease of the elastic modulus of the films and an increase in their hardness for iron contents of about 5 at.%, followed by a decline for higher percentages. This evolution can be explained by the type of chemical bonding between the different elements within carbide and by the degree of structural order of the films. The addition of iron reduces the number of covalent bonds, leading to a reduced Young's modulus. On the other hand, one might expect that iron would lead to a decrease of film hardness since it is a soft element compared to M-C based carbides. However, this is not true for M-Fe-C systems with medium iron contents, which could be due to a distortion of the crystal lattice by the presence of iron atoms in substitutional positions.

The Young's modulus values calculated by Laser Interferometry are higher than those obtained by Ultramicrohardness. Both methods have their advantages and disadvantages. In the former it is crucial that the substrate and the coating have constant thickness throughout the sample section, and don't present any initial curvature. This is not always possible since their deposition induces films with internal stresses that tend to distort the substrate. As for the 2^{nd} technique, the application of mathematical methods to the elastic modulus values of the composite (film + substrate) in order to calculate E_f of the film might induce more or less important errors, depending on the case in study and the type of method used. This study used the Φ_{Gao} weight function, which, according to many authors [6] gives the best results for thin films with different mechanical properties than the substrates

CONCLUSIONS

All the M-C binary (M = Cr, Mo, W) systems obtained by are structurally metastable. The W-C and Mo-C films are crystalline with a NaCl-type fcc structure, while the Cr-C is amor-

phous. The hardness and Young's modulus of the films increase from the 1st to the 3rd long Period, *i.e.* from the chromium to the tungsten carbide. The addition of iron decreases the degree of structural order of the M-C systems as well as their Young's modulus. The films with higher hardness are those with a transition structure between crystallinity and amorphism.

REFERENCES

[1] B.Trindade, M.T.Vieira and E.B.Grosse, Acta Materialia, 46,5 (1998) 1739.

[2] B. Trindade, M.T. Vieira and E.B. Grosse, Acta Materialia, 46, 5 (1998) 1739.

[3] M. F. Doerner and W.D. Nix, J. Mater. Res. 1 (4), (1986) 601.

[4] H. Gao, C.H. Chiu and J. Lee, Int. J. Solids Structures 29, (1992) 2471.

[5] H.A.Davies, in Amorphous Mettalic Alloys, edited by F.E.Luborsky (Butterworths Monographs in Materials, 1983), pg.27.

[6] J. Mencik, D. Munz, E. Quandt and E.R. Weppelmann, J. Mater. Res., 12, 9, (1997) 2475.

ACKNOWLEDMENTS

The authors would like to thank J.V. Fernandes for many useful discussions on the determination of elastic and plastic properties of thin films by ultramicrohardness.