

Thin Solid Films 252 (1994) 82-88



Structural stability and crystallization studies of metastable sputtered W-Ni-C films

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Received 1 March 1994; accepted 7 June 1994

Abstract

The as-deposited state and the annealing behaviour of metastable $W_{\rm Ni}$ -C films, synthesised by non-reactive r.f. magnetron sputtering, have been studied by means of electron probe microanalysis, secondary ion mass spectrometry, X-ray diffraction, differential thermal analysis and in-situ high temperature transmission electron microscopy. The results are presented and correlated with previous studies on $W_{\rm CECO}$ C films. As will be shown, the as-deposited structure of the films is dependent on chemical composition and varies from crystalline to amorphous with increasing nickel content. The transformation structures produced during annealing of the films are consistent with those anticipated from the $W_{\rm Ni}$ C equilibrium phase diagram.

Keywords: Carbides; Coatings; Crystallization: Sputtering

1. Introduction

Cemented carbides, especially those based on tungsten carbide, have been used in applications requiring high hardness and good wear resistance. In (WC)based cermets, the presence of a binder metal element in the boundaries of a fine-grained microstructure causes strain energy dissipation and increases toughness [1]. Cobalt has been the traditional binder element although other transition metals such as nickel and iron are cited as alternatives [2, 3]. Some authors claim that superior sintered and mechanical properties can even be achieved through the association of nickel with cobalt or iron (Ni Co or Ni -Fe) instead of only cobalt [4, 5].

In recent years there has been an increasing effort towards depositing sputtered thin films from (WC)based cermets on metallic surfaces, of which steels are a typical example [6-10]. In a previous work concerned with the production and characterization of W-(Fe,Co) C films obtained by sputtering, we have shown that, on the contrary to (WC)-based cermets, the structure of the sputtered films depends on the type and percentage of the addition element, varying from β -MC₁, (M = W and Fe/Co) to amorphous with increasing iron and cobalt contents [10]. The amorphization of these films was explained in terms of both distortion of the β -MC₁ , lattice owing to the difference between the atomic radii of tungsten and iron/cobalt and lower carbon affinity for iron and cobalt than for tungsten.

This work is devoted to W Ni-C sputtered films and has two main purposes: (i) to ascribe the amorphization of the W C structure to the presence of a Group VIII transition metal; and (ii) to adress the relationship of the present results to the previous obtained for the W (Fe,Co)-C systems, bearing in mind that nickel and cobalt are weaker carbide formers than iron and that the atomic radii of these elements decreases from iron to nickel ($r_{\rm Fe} > r_{\rm Co} > r_{\rm Ni}$). For this study, a set of W-Ni-C samples were prepared by non-reactive r.f. magnetron sputtering and analysed in the as-deposited state and after annealing at increasing temperatures.

2. Experimental details

A set of W–Ni C thin films (1 -2 μ m thick) was non-reactively r.f. sputtered onto high-speed steel M2 (AISI) and glass substrates from a stoichiometric WCsintered target partially covered with nickel foils.

Films on steel substrates were examined in the asdeposited state and after 1 h furnace annealing under

vacuum ($P = 10^{-5}$ Pa) at temperatures of 650 °C, 700 °C and 750 °C, by means of electron probe microanalysis (EPMA), secondary ion mass spectrometry (SIMS) and X-ray diffraction (XRD). The X-ray analysis was performed with Co Ka radiation and an incidence angle of 4°. After detachment from the substrates by hydrofluoric acid, the films deposited onto glass were chemically analysed before heat treatment and their structural behaviour with temperature followed by differential thermal analysis (DTA) and in-situ high temperature transmission electron microscopy (TEM). Films for TEM analysis were supported between grids and were 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°. A 200 keV microscope equipped with a single-tilt hot stage was used for the TEM observations.

3. Results

3.1. Chemical analysis

The chemical composition of the as-deposited and 750 °C treated W-Ni-C films on steel substrates is given in Table 1. Data for a W-C film obtained in previous work [10] is also presented as a reference. The results of chemical composition obtained from the films detatched from their glass substrates before heat treatment do not differ from those of films on steel substates. Table 1 shows carbon-deficient as-deposited films with at.% Metal-to-at.% Carbon ratios varying from 1.28 (film without nickel) to 1.62 (Ni-richest film). Comparing the chemical composition of the films on substrates before and after annealing at 750 °C one can conclude that they lose carbon during heat treatment, the loss of carbon being much important for amorphous films.

The decrease of the carbon content during heat treatment was confirmed by SIMS. Fig. 1 shows a typical example of the C sputter depth profiles obtained from

Table 1

Chemical composition of the as-deposited and 750 $^\circ C$ annealed W Ni-C films deposited onto steel substrates

Film designation Analysed composition

	Analysed composition					
	As-deposited state			After annealing at 750 °C		
	w	Ni	С	w	Ni	<u>с</u>
$W_{56}C_{44}[10]$	56.1		43.9	63.0		37.0
$(W_{93}Ni_7)_{60}C_{40}$	55.7	4.1	40.2	58.5	4.9	36.6
$(W_{90}Ni_{10})_{59}C_{41}$	53.2	6.1	40.7	58.0	6.8	35.2
$(W_{84}Ni_{16})_{61}C_{39}$	51.3	9.7	39.0	55.7	10.8	33.5
$(W_{79}Ni_{24})_{62}C_{38}$	47.3	14.5	38.2	51.4	16.2	32.4
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Fig. 1. Typical example of the SIMS carbon sputter depth profiles obtained for the W Ni-C films on steel substrates, in the as-deposited condition and after annealing at 650 °C and 750 °C.

the W-Ni-C films before and after furnace annealing at 650 °C and 750 °C. For the as-deposited state a well-defined film/substrate interface at about 1.3 μ m below the surface was observed. Carbon signal intensities obtained from samples annealed at 650 °C and 750 °C decrease from the surface to the film/substrate interface, signifying that the loss of carbon from the film during heat treatment is due to the diffusion of carbon into the steel substrate.

3.2. Structural analysis

3.2.1. As-deposited state

The structure of the as-deposited W-Ni-C films was examined by XRD and TEM. The Ni-poorest film (Ni = 4 at.%) exhibits an extremely fine-grained structure (10-50 nm) indexed as β -MC_{1-x} [11] (Figs. 2(a) and 2(b)). The increase of Ni content in the films lead to amorphous structures characterized by two large XRD peaks and fairly contrasted TEM images, associated with diffuse and large electron diffraction (ED) rings (Figs. 3(a) and 3(b), respectively).

3.2.2. Structural evolution with temperature

3.2.2.1. Films onto steel substrates. The structural stability of the W-Ni-C films deposited on steel substrates was studied by XRD after furnace annealing. Two different structural evolutions were observed due to the heat treatment. Films with at.% Ni < 10 transform with temperature to M₂C + MC (Fig. 4(a)), the M₂C phase being predominant. This transformation occurs at different temperatures, according to the percentage of nickel, whereas in the case of crystalline (W₉₃Ni₇)₆₀C₄₀ as-deposited film, the β -MC_{1-x} phase is still present after 1 h annealing at 700 °C, signs of the as-deposited structure are no longer detected at this



Fig. 2. (a) XRD and (b) TEM patterns obtained from the as-deposited crystalline (W₉₄Ni-)₆₀C₄₀ film.



Fig. 3. (a) XRD and (b) TEM patterns obtained from as-deposited amorphous films.

temperature in the $(W_{90}Ni_{10})_{59}C_{41}$ film. In both cases, this transformation seems to be complete after 1 h annealing at 750 C. The sequence of structural transformations during annealing of films with nickel contents higher than or equal to 10 at.% is shown in Fig. 4(b). Development of the microstructure from the single-phase amorphous condition to a two-phase structure of α -Ni + MC is observed at 650 C. XRD α -Ni peaks are shifted to lower diffraction angles when compared with those of pure Ni in JCPDS cards [11]. Annealing at temperatures ranging from 650 C to 750 C results in the formation of M₆C from the remaining amorphous phase.

3.2.2.2. Films detached from the substrates. As already mentioned, the thermal stability of the W Ni-C films detached from the substrates was followed by DTA and high temperature TEM. In spite of the occurence of the same phase transformations, these films change structurally at higher temperatures than the corresponding ones on steel substrates. DTA results reveal an important decrease of the thermal structural stability of the films with the increase of the nickel content (≈ 860 C for the Ni-poorest film against \approx 705 C for the Ni-richest film). Regarding in situ annealing in the microscope the results show that films with nickel contents lower than 10 at.% transform to a fine-grained M₂C microstructure at temperatures varying from 750 C to 850 C (Fig. 5(a)). The higher the percentage of nickel in the film the lower this transition temperature. For higher temperatures (T = 800 C) a coarser-grained M₂C structure is observed (Fig. 5(b)). Small quantities of MC were also detected in the regions close to the TEM grids for the higher annealing temperatures. The size of the M₂C precipitates ranges from 20-50 nm at 750 C and 150-200 nm at 800 C. For as-deposited films with $Ni \ge 10$ at.%, an amorphous $\rightarrow x$ -Ni \neg MC transformation was detected for temperatures close to 690 C (Fig. 6(a)). No other phase changes were observed in these films at higher annealing temperatures. It is interesting to note however a continuous growth of α -Ni and MC crystals with



Fig. 4. XRD patterns showing the structural evolution with temperature of films with (a) at.% Ni < 10 and (b) at.% Ni $\ge 10. \odot$, β -MC_{1-x}; s, Fe-x (substrate); ×, M₂C; +, MC; \ge , M₆C; ϕ , x-Ni.



Fig. 5. TEM bright field micrograph and the associated SAEDP obtained during in situ annealing in the microscope at (a) 750 °C and (b) 800 °C from films with at.% Ni < 10.

increasing temperature (Fig. 6(b)): both the α -Ni and MC crystals were found to be faulted. Twinning is observed for the α -Ni crystals on the {111} planes (Fig. 7). MC structure defects consist of a high density of stacking faults on the {1100} planes (Fig. 8).

4. Discussion

Closer analysis of the results obtained in this work for the W-Ni-C films and those previously obtained for W-Me-C (Me = Fe,Co) films [10] reveals obvious



Fig. 6. TEM bright field micrograph and its associated SAEDP obtained during in situ annealing in the microscope at (a) 750 °C and (b) 800 °C from films with at $^{9}\sigma$ Ni \ge 10.



Fig. 7. TEM bright field micrograph and the associated SAEDP (zone axis - [110]) obtained from a \times -Ni crystal.



Fig. 8. TEM bright field micrograph and the associated SAEDP (zone axis = [0001]) obtained from a MC crystal.

similarities between these systems. Concerning the asdeposited state, this work shows that in fact it is possible to synthesize metastable ($W \cdot C$)-based films by sputtering from sintered targets. Furthermore, it confirms that the amorphization of the films is due to the presence of a Group VIII transition metal, utilized as a binder element in the (W-C)-based cermets. The struc-

ture of W Ni-C films was found to vary from β - MC_{1} , to amorphous with increasing nickel content. β -MC₁, is a high temperature phase [12] with a fcc NaCl-type structure [13]. This may exist over a wide range of composition, where x extends from near unity down to about 0.5. The occurrence of β -MC₁, in films obtained by non-reactive r.f. sputtering has been claimed in other works (see for example Refs. [7, 9, 10]) and it seems to be due either to its great compactness or to its large solubility domain. The amorphization of the sputtered (W-C)-based films by the addition of small amounts of a Group VIH transition metal such as iron, cobalt or nickel seems to be the result of two different phenomena: distortion of the W Me C (Me = Fe, Co, Ni) lattice owing to the difference between the atomic radii of these metals ($r_{\rm te} = 1.26$ Å, $r_{\rm Co} = 1.25$ Å, $r_{\rm Ni} = 1.24$ Å) and that of tungsten ($r_{\rm W} =$ 1.42 Å) and/or lower carbon affinity for iron, cobalt and nickel than for tungsten.

The chemical analysis of the as-deposited and treated W-Ni-C films deposited onto steel substrates revealed that they lose carbon during annealing, the flux of carbon atoms occuring into the steel. This can be explained by the characteristics of the carbon atom (interstitial type) and the different carbon percentages of the various W-Ni C films and the M2 steel ($\approx 7.4at.\%$).

When heat treated, the metastable as-deposited W Ni-C films tend to reach equilibrium giving rise to fine-grained multiphase microstructures. Similar structural evolutions with temperature were observed for both crystalline W Ni-C and W (Fe,Co) C systems, i.e. β -MC_{1-x} \rightarrow MC \leq M₂C (Table 2). In contrast to crystalline films, the structural evolution of amorphous as-deposited W-Ni-C films differs from that of W (Fe,Co)-C films with similar addition element content: whereas the crystallization mechanism of the amorphous as-deposited W-Ni-C films is essentially characterized by the formation of α -Ni + MC, W-(Fe,Co)-C Table 2 Comparison between the structural evolution of the W- Ni C and W -(Fe,Co) -C films during annealing

$$\overrightarrow{\mathbf{z}} \left[\begin{array}{c} \text{Amorphous} \rightarrow (\text{Ni}) + \text{MC} \rightarrow (\text{Ni}) + \text{MC}^{\text{a}} \\ \beta - \text{MC}_{1-x} \rightarrow \beta - \text{MC}_{1-x} + \text{MC} \rightarrow \text{MC} + \text{M}_2\text{C} \\ \end{array} \right] \\ \overrightarrow{\mathbf{z}} \left[\begin{array}{c} \text{Amorphous} \rightarrow M_2\text{C} + \text{M}_6\text{C} \rightarrow \text{M}_2\text{C} + \text{M}_6\text{C} + \text{MC}^{\text{b}} \\ \beta - \text{MC}_{1-x} \rightarrow \beta - \text{MC}_{1-x} + \text{MC} \rightarrow \text{M}_2\text{C} \\ \end{array} \right]$$

^aSmall amounts of M_6C were also observed for W-Ni-C films annealed with substrate.

^bThe MC carbide was observed for $W \cdot (Fe,Co) - C$ films annealed without substrate.

films mainly undergo the crystallization of $M_2C + M_6C + MC$ (this last phase was only detected in films annealed without substrates). The higher solubility of tunsgten in nickel (12 at.% at 700 °C [14]) compared with that of iron or cobalt (2 at.% and 1.5 at.% at 700 °C, respectively [14]) promotes the precipitation of carbonrich phases (MC) in detriment of carbon-poor phases such as M_6C . Small amounts of this last phase were however detected in the final structure of the W-Ni-C films annealed onto steel substrates as the result of the carbon diffusion into the substrates during heat treatment.

Although not many temperatures have been systematically studied, a completed W-Ni-C equilibrium diagram is available at 1300 °C [15]. At this isothermal section, the films synthezised (considering their initial chemical percentages) lie in different structural fields: $MC + M_2C + Ni_3W_{10}C_{3,4}$ (κ carbide) for nickel-poor films and α -Ni + MC + Ni₂W₄C (η or M₆C carbide) for nickel-richer films. Unlike the κ carbide the other phases are in accordance with those obtained in this study. However, it is not yet well established whether the κ phase exists as an equilibrium phase in the W-Ni-C phase diagram. Some authors claim that this carbide crystallizes from the melt in the Fe-Ni-W-C system but not in Ni-W-C [15]. In fact, large amounts of this carbide were obtained by sintering (24 h at 1400 °C) in a specimen having an Fe-to-Ni ratio of 1 [16].

Different structural stabilities were observed for W-Ni-C films with and without substrates. Carbon diffusion enhances the phase transformations with temperature and explains the lower structural stability of the W-Ni-C films deposited onto steel substrates.

There are some structure relations among the phases formed during annealing of the W-Ni-C films [13]. The two carbides MC and M₂C, which are both of hexagonal structure, are partially intersoluble, and differ in so far as in MC the tungsten and the carbon atoms each form a set of intepenetrating simple hexagonal lattices, whereas in M₂C the tungsten atoms form an almost close-packed lattice, and the carbon atoms a simple hexagonal lattice. M₆C is a complex cubic



Fig. 9. Structure of the twin in the Ni fcc metal. The plane S (a) is the plane of the figure in (b), and corresponding triangles in (a) are shaded. The plane K1 is the (111) composition plane, PQ in (b).

carbide with a W content varying from $(Fe,Co,Ni)_2$ - W_4C to $(Fe,Co,Ni)_4W_2C$. Its carbon environment is already identical with that in tungsten carbide M_2C (i.e the surrounding tungsten configuration is that of two isoceles triangles inverted).

The crystals of both the α -Ni and MC phases formed during annealing in the microscope were found to be extremely faulted. Concerning α -Ni, twinning is observed on the {111} planes, typical of fcc structures (Fig. 9). MC structure defects consist of a high density of stacking faults on the $\{1\overline{1}00\}$ planes. The deformation mechanisms and the structural defects of WC have been the subject of some work [17, 18]. Two types of stacking faults have been proposed in the literature for the WC structure: one lying on the prismatic $\{1\overline{1}00\}$ planes with a $1/6[11\overline{2}3]$ displacement vector (the one most frequently observed) and the other on the pyramidal $\{11\overline{2}3\}$ planes with a displacement vector of $1/3[01\overline{1}0]$. In the present work, the streaks observed along the $\langle 1\overline{1}00 \rangle$ 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 (Fig. 10).

Finally, it is important to refer to the use of nickel (10-15 at.%) as an additional alloying element to (W-C)-based sputtered films, which may lead in the future to attractive W-Ni-C coatings for mechanical applications. One possible advantage of W-Ni-C films over W-(Fe,Co)-C films with similar carbon/metal ratios may reside in the segregation of nickel observed during heat treatment. This segregation effect gives rise to a fine-grained structure of $WC + \alpha$ -(Ni), similar to that of sintered submicron WC--Ni materials, but certainly superior in mechanical properties.

5. Conclusions

The results shows that it is possible to synthesize metastable W-Ni-C films, either in a crystalline or



Fig. 10. Projection of the perfect (a) and faulted structures (b) of the MC onto the (1120) slip plane according to Hibbs and Sinclair [18]. The fault is creating by moving the top layer of the W atoms across the C atom layer with the displacement vector $\mathbf{R} = 1/6[1123]$.

amorphous state, by non-reactive r.f. sputtering. When heat treated, these films tend to attain equilibrium giving rise to fine-grained multiphase structures of $M_2C + MC$ (films with less than 10 at.% Ni) or α -Ni + MC (films with at.% Ni \ge 10 at.%). The W-Ni-C films, in particular those in the range 10-15 at.% Ni, may have, in the future, a potential as coatings for mechanical application.

Acknowledgements

Sponsorship for one of the authors by the Junta Nacional de Investigação Científica, given in the framework of a Portuguese-French research network, is gratefully acknowledged.

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