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# Deposition and characterization of fine-grained W-Ni-C/N ternary films

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#### Abstract

W–Ni–C/N ternary films with 3 < at.% Ni < 14 and 0 < at.% C, N < 30 were synthesized by reactive sputtering from a W–10 wt.% Ni target with increasing partial pressures of methane or nitrogen and substrate bias. The films have been characterized by electron probe microanalysis, X-ray diffraction, ultramicrohardness and scratch testing. The results show that the degree of structural order of the films decreases with increasing nickel and metalloid element contents. The hardness values obtained vary between 25 and 55 GPa, with a maximum for films with low nitrogen and carbon contents (6–8 at.%), deposited with a substrate bias of -70 V. The Young modulus follows the same trend as hardness, with a maximum modulus value of 550 GPa. The crystalline coatings present higher critical loads than the amorphous coatings. The more adherent coatings have critical loads higher than 70 N. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ternary films; Sputtering; Substrate bias

## 1. Introduction

Advanced coating concepts, like metastable nanocrystalline or amorphous thin films, become increasingly important for protection of bulk materials surface for specific applications. Such an example is the development of (transition metal–metalloid)-based materials for applications requiring a high hardness and good wear resistance. In order to improve the toughness, these materials have been doped with other metallic elements, particularly the W–C/N systems by a Group VIII transition metal such as iron, cobalt or nickel [1].

The structure and mechanical properties of this kind of material depend on the chemical composition. The degree of structural order of the binary transition metal – carbon films depends on the type of M–C chemical bonding and on the tendency of the films towards crystallizing or not in structures of the NaCl type [2]. Moreover, the crystalline M–C films can be amorphized with the addition of small amounts of a VIII transition metal. The percentage required for amorphization is much higher, the stronger the M-C chemical bonding. In the case of the W–Ni–C system obtained from a WC-sintered target with nickel foils superimposed, the percentage of nickel required for amorphization lies in the range of 6-10 at.% [1].

All the studies referred above were carried out on films obtained in non-reactive mode from sintered metal carbides targets with fixed M/C atomic ratios (1-2) depending on the target). Moreover, as it is well known, in the field of hard coatings, sputtered nitride films present a more adequate set of mechanical properties than the carbide films, leading to a better real service behaviour. However, in spite of the importance of the nitride coatings, there no studies have been carried out on the role of a third metal transition element on the structure of these kinds of materials. Also, the influence of the metalloid element on the ability to form amorphous structures in these materials has not yet been evaluated.

The present work is devoted to ternary W–Ni–C/N reactive sputtered films with 3 < at.% Ni < 12 and 0 < at.% C,N < 30 and has two purposes: (1) to study the influence of the percentage of carbon and nitrogen on the structure and mechanical properties of W–Ni films with different nickel contents, and (2) to address the relationship of the present results to previous obtained for the W–Ni–C system deposited in the non-reactive mode.

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## 2. Experimental

Samples with a thickness of  $2-3 \,\mu\text{m}$  were deposited on high-speed substrates in a reactive d.c. magnetron sputtering system from a sintered W–10 wt.% Ni target. The substrate holder is equipped with a rotation system in order to improve the uniformity of the deposit. The total pressure was kept constant at  $3 \times 10^{-1}$  Pa, whereas the N<sub>2</sub>/Ar and CH<sub>4</sub>/Ar partial pressure ratios were varied in the range of 0–1. A specific power target of 10 W cm<sup>-2</sup> and substrate bias of -70 V were applied to obtain films with different chemical compositions and structures. In order to study the role of substrate bias on the coatings performance, this parameter was varied in the range of 0 to -120 V.

Before deposition, the substrate surfaces were cleaned

with an ion gun. The cleaning procedure included first of all electron heating up to temperatures of around 450°C and then Ar<sup>+</sup> bombardment (ion gun settings at 20 A, 40 V, substrate at -120 V). The chemical composition of the films was determined by electron probe microanalysis with a CAMECA SX50 equipment. Microstructural characterisation was performed by X-ray diffraction (Philips X'PERT apparatus) using CoKa radiation. The hardness tests were performed in an ultramicroindentation device from Fischer, with a Vickers indenter and a nominal load of 100 mN. For each load, five indentations were made using a continuous load-unload cycle. The values obtained in the tests were corrected following the procedure indicated by Trindade et al. [3]. The scratch tests were performed in a commercial scratch testing equipment (CSEM



Fig. 1. Influence of (a) the reactive gas partial pressure and (b) substrate bias on the morphology of the W–Ni–C/N films. The micrographs in (a) concern the W–Ni–N and were obtained from films deposited with a substrate bias voltage of -70 V. The micrographs in (b) were obtained from films W–Ni–C deposited with  $P_{CH_a}/P_{Ar} = 1/4$ .

Table 1	
Results of chemical composition, structure and mechanical analysis of the studied W–Ni–C/N fi	ms <sup>a</sup>

	Deposition Partial pressure ratio and bias	Chemical composition				Structure			Mechanical analysis		
		at.% W	at.% Ni	at.% C or at. % N	(W+Ni)/ (N or C)	Phases present	$d_{(110)}$ of the (W) phase (Å)	Width (110) peak (2θ)	H (GPa)	E (GPa)	Lc (N)
System W–Ni–G	2										
Bias = -70 V	0	97.3	2.7	_	_	α-W	2.265	0.79	$25 \pm 1.7$	$400 \pm 30$	60-65
	1/5	85.6	7.0	7.4	12.5	α-W	2.266	0.49	$27 \pm 2.8$	$391 \pm 25$	>70
	1/4	84.8	7.0	8.2	11.2	α-W	2.264	0.48	$39 \pm 3.7$	$555 \pm 53$	>70
	1/3 <sup>b</sup>	78.3	7.1	14.6	5.8	$\alpha$ -W+A	2.275 (2.236)	0.83 (5.48)	$25 \pm 1.5$	$305 \pm 27$	45-55
	1/2	78.4	7.6	14.0	6.1	$\alpha$ -W+A	2.272 (2.259)	0.77 (5.97)	$26 \pm 1.2$	$370 \pm 31$	55-65
$P_{\rm CH_4}/P_{\rm Ar} = 1/4$	0 V	77.9	8.3	13.8	6.2	α-W	2.257	0.42	$28 \pm 1.5$	$300 \pm 18$	>70
	-50  V	84.0	6.4	9.6	9.4	α-W	2.263	0.47	$37 \pm 2.5$	$397 \pm 22$	>70
	-70  V	84.8	7.0	8.2	11.2	α-W	2.264	0.48	$39 \pm 3.7$	$555 \pm 53$	>70
	-120 V	88.2	4.8	7.0	13.3	α-W	2.268	0.54	$35 \pm 1.7$	$463 \pm 24$	60-65
System W-Ni-N	N										
Bias = -70 V	0	97.3	2.7	_	_	α-W	2.265	0.79	$25 \pm 1.5$	$400 \pm 21$	60-65
	1/5	86.7	8.3	5.0	19.0	$\alpha$ -W+W2N	2.271	0.61	$55 \pm 5.0$	$510\pm35$	>70
	1/4	76.2	12.8	11.0	8.1	$\alpha$ -W+W2N+A	2.277 (2.254)	0.75 (7.06)	$29 \pm 2.0$	$305 \pm 25$	>70
	1/3	67.3	14.2	18.5	4.4	А	(2.270)	(6.91)	$31 \pm 1.0$	$310 \pm 20$	55-60
	1/2	66.5	12.1	21.4	3.7	А	(2.272)	(7.11)	$28 \pm 2.0$	$307 \pm 18$	55-60
	1/1.5	61.4	14.3	24.3	3.1	А	(2.272)	(7.08)	$30 \pm 3.0$	$320 \pm 21$	45-50
	1/1	57.5	13.8	28.7	2.5	А	(2.283)	(7.01)	$27 \pm 1.5$	$304 \pm 15$	55-60
$P_{\rm CH_4}/P_{\rm Ar} = 1/5$	0 V	82.4	12.2	5.4	17.5	α-W	2.261	0.54	$40 \pm 1.5$	$500 \pm 29$	55-60
	-70  V	86.7	8.3	5.0	19.0	α-W	2.271	0.61	$55 \pm 5.0$	$510\pm35$	>70
	-120 V <sup>b</sup>	89.0	7.7	3.3	29.3	α-W	2.279	0.66	$25\pm4.0$	$350\pm26$	55-60

<sup>a</sup> Values in parentheses concern the amorphous phase and were obtained from the main amorphous peak.

<sup>b</sup> These films present a low thickness compared to the other W-Ni-C/N films. The values of H, E and Lc of these films are given in italics.

Revestest) fitted with an acoustic detector. Detailed morphologies of scratch channels were observed by means of a scanning electron microscope (Jeol JSM-T330) equipped with energy dispersive X-ray analysis (TRACOR).

## 3. Results and discussion

Fig. 1 shows the cross-section morphologies of the W–Ni–N films as a function of the  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratio and substrate bias. As can be observed, there is an increase in the compactness of the films with increasing partial pressure of reactive gas and substrate bias. This typical behaviour [4] is due to the incorporation of the interstitial element and to the higher bombardment of the biased films occurring during their growth process.

Table 1 presents the results of chemical composition, structure and mechanical analysis of the studied films. In the case of the W–Ni–C system, no characterisation could be performed on the films obtained with  $CH_4$  flows of 1/1.5 and 1/1 since these films showed a very poor adhesion, flaking off from the substrates.

## 3.1. Chemical composition and structure

As a general trend, one can say that the increase in the  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratio gives rise to a gradual increase

in the nickel percentage in the films. This can be explained by the resputtering of the species during the growth of the films. In the case of the binary W–Ni film, nickel is preferentially resputtered due to the higher mass of tungsten [5]. When nitrogen or carbon is added to the system, the number of tungsten species arriving at the growing films is lower than in the binary films, contributing to a smaller resputtering of nickel. The analysis of the films obtained with different substrate biases confirms this theory. In fact, for the same  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratio, the higher the substrate bias (bombardment with more energetic ions), the higher the preferential Ni resputtering and thus the lower the nickel content of the films (Table 1).

Concerning the structural results, the films without nitrogen or carbon are formed by the  $\alpha$ -W phase. Since no other phases were observed, it is assumed that nickel is dissolved in the tungsten solid solution. This result contradicts the W–Ni equilibrium diagram in which nickel is insoluble in the tungsten even at high temperatures [6]. However, the ability of the sputtering technique to form structures with enlarged solubility domains is well known [7]. The diffraction peaks of the  $\alpha$ -W phase are shifted to higher interplanar distances when compared to those of the  $\alpha$ -W ICDD card<sup>1</sup>. Taking into account that the atomic radius of nickel is

<sup>&</sup>lt;sup>1</sup> International Centre for Diffraction Data, card 4-806.



Fig. 2. Influence of  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratio on the structure of the W–Ni–C and W–Ni–N films.

lower than that of tungsten, the increase of the lattice parameter of the  $\alpha$ -W phase might be explained by the argon incorporation (discharge gas) in the films during deposition. The structural results of the films W–Ni– C/N deposited with different substrate biases confirm this idea. Indeed, the film deposited without a substrate bias presents the lowest value for the lattice parameter (Table 1), closer to that of the ICDD card for bcc tungsten.

The increase of carbon or nitrogen contents in the films gives rise to (1) an increase in the lattice parameter of the  $\alpha$ -W phase and (2) a broadening of the diffraction peaks, i.e. a decrease in the degree of structural order (Table 1).

The W–Ni–C films are formed by an  $\alpha$ -W phase. However, in the X-ray diffractograms of the carbonrich films (Fig. 2), a broad peak in the base of the  $\alpha$ -W (110) peak can be observed, which is attributed to the existence of an amorphous phase. There is an increase in the  $d_{(110)}$  distance of  $\alpha$ -W when the amorphous phase is formed, which might suggest a compositional change of the former phase. The chemical composition of the amorphous phase should also change with increasing  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratio since the position of its main diffraction peak increases with the nickel and metalloid element contents.

Nitrogen leads initially to the appearing of a preferential orientation ([110] direction) of the  $\alpha$ -W phase and later to the formation of the W<sub>2</sub>N and amorphous phases. This last phase is easily detected in the W-Ni-N film deposited with  $p_{N_2}/p_{Ar} = 1/4$ . Similar to the W-Ni-C system, the appearing of the amorphous phase leads to an increase in the  $d_{(110)}$  distance of  $\alpha$ -W and therefore leading to a compositional change of this phase. For higher partial pressure ratios, complete amorphisation of the W-Ni-N films occurs. The values of full width at half height obtained from the diffractograms of the amorphous phase are in the order of  $2\theta =$ 7 and seem to be independent of the chemical composition of the samples. However, the increase in the  $P_{N_2}$ partial pressure gives rise to an increase in bonding length due to the incorporation of more nickel and nitrogen in the lattice.

The atomic percentages of nickel and nitrogen required to obtain amorphous structures are 14.5 and 18.5%, respectively. This nickel percentage is higher than that found in a previous study on the amorphous forming ability of tungsten carbide by nickel [1]. However, in this study, the W/X (X=interstitial element) atomic ratio was close to unity, whereas in the present study, W/X = 3.6. On the basis of this result, it could be suggested further that both nickel and nitrogen elements contribute to the amorphisation of the structure. However, the lower the percentage of the interstitial element, the higher the percentage of the substitutional element required for amorphisation. In spite of this, it is not possible to affirm that carbon has a lower ability than nitrogen to form amorphous (W-Ni)-based structures since, for similar percentages of interstitial elements, the W-Ni-N system contains more nickel than the W-Ni-C system.

### 3.2. Mechanical analysis

### 3.2.1. Hardness and Young's modulus

The hardness of the W–Ni film  $(25\pm1.5 \text{ GPa})$  is higher than that of pure tungsten (18 GPa [8]) obtained in a previous work with the same deposition parameters. The hardening of the  $\alpha$ -W phase must be attributed to the presence of nickel and to a decrease in grain size.

The addition of carbon/nitrogen to the W–Ni system has two different effects on hardness:

1. For low  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratios, there is an hardness increase with nickel and metalloid contents. The higher values of hardness were obtained for partial pressures ratios of 1/4 (system W–Ni–C) and 1/5 (system W–Ni–N). The highest hardness obtained for each system corresponds to films with (W+Ni)/C=11.2 and (W+Ni)/N=19.0. This might explain the differences of the maximum values



Fig. 3. End of a scratch channel where only very small cracks are visible.

obtained for the W–Ni–C and W–Ni–N systems (39 GPa against 55 GPa). The presence of the  $W_2N$  phase in the W–Ni–N system may also contribute to an increase in film hardness.

2. For high  $p_{\text{reactive gas}}/p_{\text{Ar}}$  ratios, similar hardness values were obtained for the films ( $\approx 30$  GPa), independently of the chemical composition. It should be noted that these hardness values correspond to films entirely or partially amorphous.

Concerning the influence of substrate bias on the hardness of the films, the results show that the films with the highest hardness are those obtained with -70 V. Two different phenomena contribute to this situation: the chemical composition of the samples and their bombardment during sputtering. As is known, the higher the substrate bias, the lower the percentage of the lighter elements in the films and the higher the percentage of argon trapped in them. Whereas the reduction of nickel and interstitial element contents leads to a decrease in hardness, the decrease in argon content has a contrary effect. These two effects conjugated give rise to maximum hardness values for intermediate substrate bias values.

With respect to the Young modulus, the values calculated for the various films are related to the hardness values: as the hardness increases, the modulus of elasticity increases and vice versa.

### 3.2.2. Adhesion

The values of critical load presented in Table 1 concern adhesive failures. These consist of small chipping failures on the cracks characteristic of buckling. Some coatings do not reveal any important cracking up to the maximal charge applied (Fig. 3). No extensive spalling was observed in any of the studied films. The results indicate that the crystalline coatings have higher critical loads than the amorphous coatings. However, no significant differences were observed between the adhesion of the W–Ni–C and the W–Ni–N films.

## 4. Conclusions

Characterisation studies have been carried out on the structure and mechanical properties of W–Ni–C/N ternary films deposited by reactive sputtering with increasing partial pressures of reactive gas  $(CH_4 \text{ or } N_2)$  and substrate bias. The degree of structural order of the films decreases with increasing nickel and metalloid element contents. The hardness of the various films varies between 25 and 55 GPa. The higher values were obtained for partial pressures ratios of 1/4 (system W–Ni–C) and 1/5 (system W–Ni–N). The Young modulus follows the same trend as hardness, with a maximum modulus of 550 GPa. Crystalline coatings have higher critical loads than the amorphous coatings.

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