

Available online at www.sciencedirect.com



Surface and Coatings Technology 174-175 (2003) 68-75



www.elsevier.com/locate/surfcoat

# Influence of Ti addition on the properties of W-Ti-C/N sputtered films

A. Cavaleiro\*, B. Trindade, M.T. Vieira

ICEMS, Departamento de Engenharia Mecânica - FCTUC, 3030 Coimbra, Portugal

#### Abstract

Thin films of W-Ti-C/N were deposited by d.c. reactive magnetron sputtering from W-Ti targets with 0, 10, 20 and 30 wt.%Ti. The influence of titanium and interstitial element (carbon and nitrogen) contents on the structure, hardness and adhesion of the coatings was evaluated by X-ray diffraction analysis, ultramicroindentation and scratch-testing, respectively. The results show different compositional dependencies of the structure and grain size of the films. Hardness was related with the structure of the films, including lattice distortion and grain size. The higher hardness values ( $\approx$  50 GPa) were obtained for W-Ti-N films with 40–45 at.%N deposited from the W-20 wt.%Ti target in a reactive N<sub>2</sub> atmosphere. However, these films present relatively low adhesion to the substrates with critical loads of 30 N. The best compromise between hardness and adhesion was reached for W-Ti-N films with low nitrogen and titanium contents.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: W-Ti-C/N hard coatings; Sputtering; Structural analysis; Hardness; Adhesion

#### 1. Introduction

In the last two decades, much research work was carried out on the development of coatings based on the W-Ti system. The driving force for these studies were originally the good thermal behavior of this system making it suitable as a diffusion barrier in integrated circuits (e.g. Refs. [1-10]). In spite of the multiple references in the literature concerning the development of coatings based on Ti or W nitrides or carbides for mechanical applications only few coatings involving simultaneously W and Ti were studied [11-14]. From these, two studies [11,12] dealt with multilayer films and two other concern the deposition of W-Ti-N/C mixing films. Nevertheless, only a very limited range of the ternary W-Ti-N/C chemical composition diagram was covered (Fig. 1-circle points). Shaginyan et al. [13] studied the deposition from a W + 10 wt.% Ti target with increasing partial pressure ratios of N2 in the deposition chamber. Neither other Ti contents nor Ccontaining thin films were analyzed. By their side, Koutzaki et al. [14] although have analyzed Ti contents from 0 to 100 at.% only studied C-containing films with atomic contents in the range from 35 to 50 at.%C.

Regarding our studies on the W-Ti-C/N system, several papers with results concerning particular films have been published up to date, either on their oxidation/corrosion behavior [15–19] or mechanical properties [20–24].

This research study has two objectives: (i) to extend the zone of the ternary W-Ti-N/C system diagram to other chemical composition films as it is shown in Fig. 1 (square points) and (ii) to compile the results obtained so far on the ternary W-Ti-N/C system. Results concerning the structure, hardness and scratch test behavior of the coatings will be presented and discussed.

## 2. Experimental procedures

## 2.1. Deposition technique

The films were deposited by d.c. reactive magnetron sputtering with a specific target power density of 10 W cm<sup>-2</sup> and a negative substrate bias of 70 V. Targets of W–Ti alloys with 0, 10, 20 and 30 wt.%Ti were sputtered in a mixed Ar+CH<sub>4</sub>(N<sub>2</sub>) atmosphere with CH<sub>4</sub>(N<sub>2</sub>)/Ar partial pressure ratio in the range 0–1. The total deposition pressure was  $3 \times 10^{-1}$  Pa. The substrates of M2 (AISI) high-speed steel were heat-treated in order to reach a final hardness of 9 GPa. After grinding they were polished with diamond pastes down to a particle

<sup>\*</sup>Corresponding author. Tel.: +351-239-790700; fax: +351-239-790701.

E-mail address: albano.cavaleiro@dem.uc.pt (A. Cavaleiro).

<sup>0257-8972/03/\$ -</sup> see front matter @ 2003 Elsevier Science B.V. All rights reserved. doi:10.1016/S0257-8972(03)00328-1



Fig. 1. Chemical composition of the W–Ti–C/N films studied in the literature (circle points) and in the present work (square points).

size of 1  $\mu$ m. Before deposition, the substrate surfaces were ion cleaned with an ion gun. The cleaning procedure included a first electron heating, up to temperatures close to 450 °C and afterwards Ar<sup>+</sup> bombardment for 8 min (ion gun settings at 20 A, 40 V, substrates at -100 V). The deposition time was 30 min and the final thickness of the films was in the range from 2.5 to 5  $\mu$ m.

#### 2.2. Characterisation techniques

The structure of the films was analyzed by X-ray diffraction (XRD) using a Siemens diffractometer with Co K $\alpha$  radiation. A Cameca SX-50 electron probe microanalysis apparatus was used to determine the chemical composition of the coatings.

The hardness of the coated samples were evaluated using ultramicroindentation (Fischer Instruments— Fischerscope), with an indentation load of 50 mN. The testing procedure, including the correction of the experimental results for geometrical defects in the indenter, thermal drift of the equipment and uncertainty in the initial contact, was described elsewhere [25].

The scratch tests were performed in a commercial scratch-testing equipment (CSEM Revetest) fitted with an acoustic detector. Detailed morphologies of scratch channels were observed by means of scanning electron microscopy (Jeol JSM-T3330) equipped with energy dispersive X-ray analysis (TRACOR).

# 3. Results and discussion

#### 3.1. Chemical composition

Fig. 2a–d shows the evolution of the chemical composition of the films as a function of the  $CH_4$  and  $N_2$ 

partial pressure ratios. As it would be expected the increase of the reactive gas partial pressure in the chamber during the deposition gives rise to a progressive increase of the C and N contents in the films (Fig. 2a and b). However, particularly for films of the system W-Ti-N, the incorporation of the reactive element is much easier for Ti-containing targets. For example, for  $p_{\rm N_2}/p_{\rm Ar} = 0.35$ , the N content in the films deposited from the W and the W+30 wt.%Ti targets varies from 5 to 50 at.%, respectively. This is in agreement with the great difference of the heat of formation between tungsten and titanium nitrides [26]. For the W-Ti-C films, the carbon contents measured do not differ so much as for N-containing films, which can be explained by the lower differences in the chemical affinities of W and Ti to C in comparison to N [26].

Concerning the W/Ti ratios, it can be concluded from the analysis of Fig. 2c and d that the films have higher tungsten content than what would be expected from the targets composition. This is due to the preferential resputtering of Ti atoms from the film due to the bombardment by either the  $Ar^+$  ions induced by the negative substrate bias or the fast neutrals atoms reflected at the target [13,27]. Moreover, the presence of C or N in the films leads to a decrease of W/Ti ratio in relation to W-Ti film. When these elements are added to the films, the higher affinity of Ti for these elements leads to the formation of strong Ti–N(C) bonds making harder the preferential re-sputtering of Ti (lighter element) in relation to W and thus leading to smaller W/Ti ratios.

#### 3.2. Structure

#### 3.2.1. W-Ti binary system

Fig. 3 shows the XRD patterns of the various W-Ti films. The main phase indexed is b.c.c. and can be regarded as a metastable solid solution of Ti in the  $\alpha$ -W phase. With the increase of the Ti content there is a progressive shift of the diffraction peaks for lower angles, corresponding to an increase of the interplanar distance, induced by the presence of the larger Ti atoms. However, the film deposited from the W+20 wt.%Ti target does not follow exactly this trend. A close analysis of the XRD pattern of this film (see the insert in Fig. 3 in a root scale) allows detecting a small peak that can be ascribed to the low temperature h.c.p. Ti phase. This suggests the depletion of Ti from the b.c.c. phase, which can explain the reason why the XRD pattern of this sample shows an  $\alpha$ -W (1 1 0) diffraction line at almost the same  $2\theta$  value as the film deposited from the W+ 10 wt.%Ti target. The h.c.p. Ti phase has also been detected by Ramarotafika and Lemperiere [7] in W-Ti sputtered films synthesised with low deposition rates.

#### 3.2.2. W-Ti-C/N systems

The structural results obtained for the W-Ti-C/N coatings deposited from the W+10 wt.% Ti target in a



Fig. 2. Chemical composition results of the W–Ti–N/C sputtered films as a function of the partial pressure ratio  $p_{CH_4(N_2)}/p_{Ar}$ ; (a) C content; (b) N content; (c) W/Ti ratio for W–Ti–C films and (d) W/Ti ratio for W–Ti–N films.



Fig. 3. XRD patterns of W–Ti films deposited by sputtering W targets alloyed with different Ti contents ( $2\theta$  from 44 to  $51^{\circ}$ ).

reactive atmosphere do not differ from those obtained for the binary W-C/N systems [28,29]. Carbon or nitrogen contents lower than 20 at.% give rise to the formation of an interstitial solid solution which is



Fig. 4. Evolution of the lattice parameter and grain size of W–Ti–C/N sputtered films, deposited from the W+10 wt.%Ti target, as a function of the interstitial element(s) content.



Fig. 5. XRD patterns of W–Ti–N/C sputtered films deposited from the W+30 wt.%Ti target with increasing: (a) C content; (b) N content.

confirmed by the progressive shift of the diffraction peaks of b.c.c. W-phase to lower angles. For the W-Ti-N coatings, nitrogen contents in the range 20–35 at.% leads to the formation of  $\alpha$ -W and f.c.c. NaCl-type W<sub>2</sub>N phases. For higher N contents only this last nitride was detected.

The concentration dependence of lattice parameter and grain size of the  $\alpha$ -W phase is given in Fig. 4. This plot corresponds to films obtained from the W–10 wt.%Ti target, as a typical example of all the other films. As can be seen, there is a good linear relationship between the lattice parameter of the b.c.c.  $\alpha$ -W phase, calculated from the (1 1 0) diffraction peak, and the content of the interstitial element (C and/or N) in the films. The same is true for the evolution of the grain size, calculated by the Scherrer's formula from the integral width of the  $\alpha$ -W (1 1 0) diffraction peak [30]. However, in this last case, the higher is the interstitial content the lower is the grain size of the tungsten solid solution. The lattice distortion induced by the presence of increasing amounts of C/N in the interstitial positions of the b.c.c.  $\alpha$ -W phase is responsible for the reduction of the range of structural order of the films.

Significant structural differences induced by C and N were detected in films obtained from targets with Ti contents higher than 20 wt.% (Fig. 5a and b). Analysis of the XRD patterns of the W-Ti-C/N films, obtained from the W-30 wt.% Ti target in reactive atmospheres, reveals a shift of the XRD lines of the films with low interstitial contents (<20 at.%) to lower diffraction angles, indicating that an interstitial solid solution is being formed for these compositions. In spite of the lack of experimental evidence we are convinced that up to 20 at.% of interstitial elements no significant precipitation of nitride/carbide phase is expected as was referred by Shaginyan et al. [13]. On the basis of XPS results, these authors stated the formation of Ti-N bonding (titanium nitride) before the appearing of the tungsten nitride phase. In fact, besides the detection of Ti-O bond due to surface contamination, only Ti-N bonds were identified in the Ti 2p XPS spectrum of the N-containing film. On the other hand, the deconvolution of the W 4f peak allowed concluding for the existence of free W and vestiges of tungsten nitride phase (W-N bonds). This can be explained as Ti has a higher affinity for C and N than tungsten [26]. Therefore, if any precipitation is formed in the Ti-W-C/N films containing lower interstitial contents, it should be a Ti-rich nitride/carbide instead of W-rich phase(s). In this case, a depletion of Ti and C/N would be expected in the b.c.c.  $\alpha$ -W phase and, consequently, the gradual shift in the position of the  $(1\ 1\ 0)$  diffraction line with increasing N/C content would not occur. However, as can be observed in Fig. 6, a gradual increasing in the lattice parameter of the b.c.c. W-phase of all the W-Ti-C/N coatings is observed with increasing N/C contents, as observed for binary W-N/C films. Consequently, if one assumes that precipitation of nitrides/carbides might



Fig. 6. Evolution of the lattice parameter of the b.c.c.  $\alpha$ -W phase of W–Ti–C/N sputtered films with increasing C and N contents.



Fig. 7. Evolution of (a) hardness and (b) grain size of W-Ti-C sputtered films with increasing C content.

occur in low N/C content films, their total amount shall be negligible.

Another important feature of the XRD patterns of the Ti-W-C/N coatings is their asymmetry (see e.g. the film with 20 at.%N in Fig. 5b), which might be justified by three main factors: (1) the precipitation above referred to, but, as concluded, in a negligible amount; (2) the result of different grain sizes and residual stresses across the thickness of the films, as referred by Koutzaki et al. [14] and (3) the formation of two solid solutions with different Ti and W contents, as a result of the high temperature miscibility gap existing in the W–Ti phase diagram.

The XRD patterns of the W-Ti-N coatings shown in Fig. 5b indicate a precipitation of a Ti-rich nitride (detected at the right side of the (110) diffraction peak) for films with high N contents. This nitride must contain a certain amount of tungsten because a progressive vanishing of the (1 1 0) peak of the  $\alpha$ -W phase up to its total disappearing occurs with increasing N content. It should be remarked that TiN and W2N nitrides are isomorphous phases with similar lattice parameters, which means that they are extensively miscible [26]. A progressive shift of the (200) diffraction line of the (Ti,W)-N nitride to higher diffraction angles can be observed as a consequence of the lower atomic radius of W in relation to Ti. Regarding the W-Ti-C films, the XRD patterns shown in Fig. 5a prove the existence of the W-phase for carbon contents as high as 40 at.%. The  $(1\ 1\ 0)$  diffraction line of this phase is progressively shifted to lower angles with increasing C contents. For 55 at.%C, a NaCl-type  $(Ti,W)C_{1-x}$  phase is undoubtedly indexed from the (200) diffraction line at  $2\theta = 48.3^{\circ}$ . The precipitation of this f.c.c. phase occurs along the [1 1 1] direction, which the diffraction peak superimposed to the  $(1 \ 1 \ 0)$  peak of the  $\alpha$ -W phase.

The structural analysis of the N and C-containing films agrees with the results of the W-Ti-N/C system

available in the literature. In fact, Shaginyan et al. [13] in their studies on W–Ti–N films also detected the first precipitates oriented preferentially following [200] direction. As in our case, the (1 1 1) plane of the f.c.c. phase was only detected in films with very high N contents. By their side, Koutzaki et al. [14] observed a strong preferential orientation along the [1 1 1] direction in W–Ti–C films with carbon contents from 40 to 56 at.%. The (200) diffraction peak was only observed for the film with 56 at.%C and had a very low intensity.

## 3.3. Hardness

#### 3.3.1. C-containing films

The influence of carbon content on the hardness and grain size of the W-Ti-C films is illustrated in Fig. 7a and b, respectively. In all but the W-C films the increase of C content gives rise to increasing hardness values. The hardness of the W-C films deposited in the present study reaches a maximum for  $\approx 10$  at.%C and decreases thereafter. This result is in accordance with other works on the W-C system [28,31-36]. The highest value of hardness referred in the literature for carbon-poor W-C coatings was obtained by Quesnel et al. [34] and is slightly higher than the value obtained in this study (35) GPa against 30 GPa, respectively). For carbon-richer coatings, in which the carbide phase was detected, hardness values of 40 GPa are reported in Refs. [31,35]. Unfortunately, in the present work it was not possible to scan C contents higher than 20 at.% since the coatings flaked off spontaneously after deposition.

The values obtained for the W–Ti–C coatings (Fig. 7a) are higher than the majority of the values reported in the literature by Koutzaki et al. [14]. Among the coatings studied by this author, only two films had hardness values higher than 15 GPa, one containing 47 at.%C (24 GPa) and the other containing 34 at.%C (30



Fig. 8. Evolution of (a) hardness and (b) grain size of W-Ti-N sputtered films with increasing N content up to 35 at.%.

GPa). This last coating was the one with the lowest range of structural order.

Fig. 7b shows that contrarily to hardness, the grain size of the coatings decreases with increasing carbon content, i.e. there is a decrease of the range of structural order of the films with increasing carbon content. There is a good agreement between the increase in the hardness and the decrease in the grain size, as can be confirmed by the simultaneous analysis of Fig. 7a and b.

In the light of the influence of structural parameters on the hardness of hard coatings, both the grain size and the lattice distortion have been the most utilized parameters to establish empirical correlations. The referred lattice distortion induced by the presence of increasing amounts of C/N in the interstitial positions of the b.c.c.  $\alpha$ -W phase (Fig. 6) might be responsible for the reduction of the range of structural order of the films and for the increase of hardness.

#### 3.3.2. N-containing films

Fig. 8a and b show the evolution of the hardness and grain size of the W-Ti-N films, with nitrogen contents lower than 40 at.%, as a function of N content, respectively. The values found by Shaginyan et al. [13] for films deposited from a target with 10 wt.%Ti are also plotted in Fig. 8a. In the case of W-N films, the maximal hardness is obtained for coatings with nitrogen contents in the range 4-9 at.%. Similar to the carboncontaining films, there is a decrease of hardness for higher nitrogen contents. The hardness of the W-Ti-N films with high titanium contents increases as the nitrogen content increases. However, the hardness of the films deposited from the target containing 10 wt.%Ti reaches a maximum for  $\approx 16$  at.%N and decreases, monotonically with increasing N contents. This is in accordance to the results of Shaginyan et al. [13] (see curve in Fig. 8a). In a previous work [29], we attributed this behavior to an heterogeneous distortion in the b.c.c.  $\alpha$ -W phase lattice. In that work it was suggested that

the distortion of the lattice could only influence positively the hardness of the films if all the lattice planes had approximately the same distortion degree. When the dilatation occurred along a particular direction, a decrease in the hardness was observed. It should be remarked that the lattice parameters values shown in Fig. 6 were calculated from the position of the (1 1 0) diffraction line of the b.c.c.  $\alpha$ -W phase. The positions of the other diffraction lines were not taken into account. Shaginyan et al. [13] also justified their maximum hardness values by a high level of microstrain in the films, in spite of their reduced residual stresses values.

Fig. 9 shows the hardness values obtained for the W– N and W–Ti–N films with high nitrogen contents. The higher hardness values were obtained for films deposited from the W+20 wt.%Ti target ( $W_{32}Ti_{26}N_{42}$  and  $W_{30}Ti_{25}N_{45}$ ) with chemical compositions close to the stoichiometry and formed by a NaCl-type W<sub>2</sub>C/TiN nitride phase. For these films, values as high as 50 GPa were reached. In fact, it is known [37] that a decrease in the hardness of f.c.c. transition-metal nitride sputtered films occurs for over- or sub-stoichiometric chemical



Fig. 9. Evolution of the hardness of W–Ti–N sputtered films containing the NaCl-type nitride phase, for N contents higher than 30 at.%.



Fig. 10. Evolution of the scratch-test critical loads of (a) W-Ti-C and (b) W-Ti-N sputtered films, as a function of the C/N contents.

compositions, which corroborates the results obtained in this study.

## 3.4. Scratch-testing results

The critical loads  $(L_c)$  values obtained from scratchtesting W–Ti–C and W–Ti–N films, are plotted in Fig. 10a and b, respectively. These values regard cohesive failures from which some examples are presented in Fig. 11. Up to the maximum applied load of 70 N, no spalling or flaking off failures were found in the scratch tracks. Many coatings show excellent behavior with no failures up to 70 N. However, the films deposited in CH<sub>4</sub> reactive atmosphere from the targets with low Ti contents show extensive spalling for high C contents. As can be seen in Fig. 10a, sudden decreases in the  $L_c$ value arise in C-containing films for C contents in the range 25–45 at.%, until the spontaneous flaking off of the films after deposition is observed.

In N-containing films (Fig. 10b) decrease in the  $L_c$  values was detected for high nitrogen contents. No spontaneous spalling was observed, whatever the N and

Ti contents in the films. The highest  $L_c$  values were reached for low or very high N contents.

Finally, taking into account the hardness values and the critical loads recorded, one may say that the best compromise between these two parameters was reached for the W–Ti–N films with low nitrogen contents, deposited from the targets with also low Ti contents. On the contrary, the films with high Ti contents in spite of presenting higher values of hardness show a deficient scratch behavior. In these films, the best compromise should be attained for N contents close to 50 at.%. Although a lower hardness value has been measured, the  $L_c$  is excellent in these films.

# 4. Conclusions

W-*x*Ti targets with x=0, 10, 20 and 30 wt.% were used to deposit W-Ti-C/N coatings by d.c. reactive magnetron sputtering in reactive CH<sub>4</sub> and N<sub>2</sub> atmospheres. The XRD analysis reveals different compositional dependencies of the structure and grain size of the films. The binary W-Ti films are formed by a metastable solid solution of Ti in the  $\alpha$ -W phase. This phase was also found to exist in the W-Ti-C/N coatings for





Fig. 11. Typical cohesive failures observed in the scratch tracks of W-Ti-C/N sputtered films; (a) tensile cracking; (b) conformal cracking.

low and medium C/N contents. W–Ti–C films with high carbon contents are formed by a NaCl-type (Ti,W)C<sub>1-x</sub> phase. Nitrogen contents in the range 20– 35 at.% leads to the formation of  $\alpha$ -W and f.c.c. NaCltype W<sub>2</sub>N phases in the W–Ti–N coatings. For higher N contents only this last nitride was detected. The higher hardness values ( $\approx$  50 GPa) were obtained for W–Ti–N films with 40–45 at.%N deposited from the W–20 wt.%Ti target. However, the adhesion of these films to the substrates is relatively low (critical loads of 30 N). The best compromise between hardness and adhesion was reached for W–Ti–N films with low nitrogen and titanium contents.

## References

- [1] M. Witmer, J. Vac. Sci. Technol. A 2 (1984) 272.
- [2] A.G. Dirks, R.A.M. Wolters, A.J.M. Nellissen, Thin Solid Films 193/194 (1990) 201.
- [3] C.E. Wickersham Jr., J.E. Poole, J.J. Mueller, J. Vac. Sci. Technol. A 10 (1992) 1713.
- [4] A.G. Dirks, R.A.M. Wolters, A.E.M. De Veirman, Thin Solid Films 208 (1992) 181.
- [5] F.-M. Yang, M.-C. Chen, J. Vac. Sci. Technol. B 11 (1993) 744.
- [6] J.H. Moser, F. Tian, O. Haller, et al., Thin Solid Films 252 (1994) 445.
- [7] H. Ramarotafika, G. Lemperiere, Thin Solid Films 266 (1995) 267.
- [8] B.R. Rogers, T.S. Cale, Y.K. Chang, J. Vac. Sci. Technol. A 14 (1996) 1142.
- [9] F. Clenet, P. Briaud, G. Turban, Surf. Coat. Technol. 97 (1997) 528.
- [10] C.-F. Lo, P. Gilman, J. Vac. Sci. Technol. A 17 (1999) 608.
- [11] T. Hurkmans, T. Trinh, D.B. Lewis, J.S. Brooks, W.-D. Munz, Surf. Coat. Technol. 76/77 (1995) 159.
- [12] J.S. Yoon, H.S. Myung, J.G. Han, J. Musil, Surf. Coat. Technol. 131 (2000) 372.
- [13] L.R. Shaginyan, M. Misina, J. Zemek, J. Musil, F. Regent, V.F. Britun, Thin Solid Films 408 (2002) 136.

- [14] S.H. Koutzaki, J.E. Krzanowski, J.J. Nainaparampil, Metal. Mater. Trans. A 33 (2002) 1579.
- [15] C. Louro, A. Cavaleiro, Surf. Coat. Technol. 74–75 (1995) 998.
- [16] C.M.A. Brett, A. Cavaleiro, Mater. Sci. Forum 192–194 (1995) 797.
- [17] C.M.A. Brett, A. Cavaleiro, Thin Solid Films 322 (1998) 263.
- [18] C. Louro, A. Cavaleiro, J. Mater. Process. 92-93 (1999) 162.
- [19] J.C. Oliveira, A. Cavaleiro, C.M.A. Brett, Corros. Sci. 42 (2000) 1881.
- [20] A. Cavaleiro, M.T. Vieira, F. Ramos, J.P. Dias, Thin Solid Films 290–291 (1996) 238.
- [21] K. Abourayak, S. Fayeulle, L. Vincent, C. Ribeiro, A. Cavaleiro, M.T. Vieira, Surf. Coat. Technol. 80 (1996) 171.
- [22] A. Cavaleiro, C. Louro, J.V. Fernandes, C. Brett, Vacuum 52 (1999) 157.
- [23] M.T. Vieira, A. Cavaleiro, B. Trindade, Surf. Coat. Technol. 151–152 (2002) 495.
- [24] E. Le Patezour, A. Cavaleiro, Key Eng. Mater. 230–232 (2002) 627.
- [25] J.M. Antunes, A. Cavaleiro, L.F. Menezes, M.I. Simões, J.V. Fernandes, Surf. Coat. Technol. 149 (2002) 27.
- [26] H.O. Pierson, Handbook of Refractory Carbides and Nitrides, Noyes Publications, New Jersey, 1996.
- [27] H.F. Winters, J. Vac. Sci. Technol. 3 (1982) 493.
- [28] J.M. Castanho, M.T. Vieira, Surf. Coat. Technol. 102 (1998) 50.
- [29] C. Louro, A. Cavaleiro, Surf. Coat. Technol. 116/119 (1999) 121.
- [30] A. Niederhofer, P. Nesladek, H. Mannling, K. Moto, S. Veprek, M. Jilek, Surf. Coat. Technol. 120/121 (1999) 173.
- [31] G. Keller, I. Barzen, R. Erz, et al., Fresen. J. Anal. Chem. 341 (1991) 349.
- [32] Y. Pauleau, Ph. Gouy-Pailler, Mater. Lett. 13 (1992) 157.
- [33] D. Garg, P.N. Dyer, D.B. Dimos, S. Sunder, H.E. Hintermann, M. Maillat, J. Am. Ceram. Soc. 75 (1992) 1008.
- [34] E. Quesnel, Y. Pauleau, P. Monge-Cadet, M. Brun, Surf. Coat. Technol. 62 (1993) 474.
- [35] A. Cavaleiro, M.T. Vieira, Surf. Eng. 10 (1994) 147.
- [36] I.N. Mihailescu, E. Gyorgy, G. Marin, et al., J. Vac. Sci. Technol. A 17 (1999) 249.
- [37] J.E. Sundgren, Thin Solid Films 128 (1985) 21.