

PROPERTIES OF TITANIUM BASED HARD COATINGS DEPOSITED BY THE CATHODIC ARC METHOD

I. MICROCHEMICAL AND MICROSTRUCTURAL CHARACTERISTICS

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TiN, TiC and Ti(C,N) hard coatings were deposited on Si substrates by a cathodic arc system. Various investigation techniques (ERDA, XPS, and XRD) were used to analyze the microchemical and microstructural characteristics of the films (surface chemistry, chemical composition, texture) prepared under different deposition conditions.

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1. Introduction

Ti based hard coatings, in single or multilayer structures, have wide range applications in various fields, since they significantly increase the lifetime and performance of tools and machine parts that are subjected to severe working conditions [1] – [3]. Different PVD or CVD methods were used to prepare Ti based films, whose properties depend on the deposition method and conditions. Considerable attention has been given in the last years to the cathodic arc deposition technique because it is a versatile, efficient and high productivity system, which is able to prepare a large variety of binary and multiphase hard compounds [4] – [9].

In the present work we report on the synthesis and characterization on TiN, TiC and Ti(C,N) single and multilayer hard coatings, deposited on different substrates (Si, various types of steels, cemented carbides) by the cathodic arc technique. The majority of the investigations have been carried out on TiN, which is one of the most studied and used coatings to date.

Part I of the paper deals with some microchemical and microstructural properties of the films (surface chemistry, chemical composition, texture), whereas Part II covers the results of the experimental investigations on the film characteristics directly related to the performance of coated tools and machine parts (microhardness, adhesion, film thickness, corrosion and wear resistance).

2. Experimental

2.1 Deposition unit and procedure

A schematic diagram of the deposition set-up is shown in Fig. 1. The system was equipped with two arc evaporators, but for the work presented here only one evaporator was used. The base pressure in the deposition chamber was of about 10^{-3} Pa. Specimens to be coated were ultrasonically cleaned with trichlorethylene and mounted on a rotating holder inside the deposition chamber. Prior to deposition, the samples were sputtered by Ti ion bombardment (1000 V; 5 min).

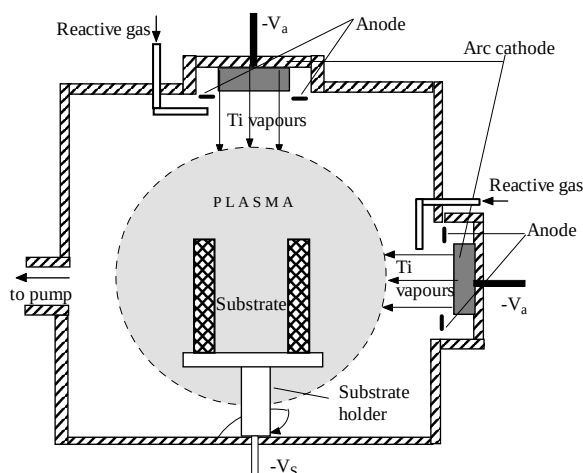


Fig. 1. Schematic illustration of the deposition setup.

The main process parameters for the various coatings were as follows: substrate material - Si, cathode material - Ti; reactive atmosphere - N_2 , CH_4 and $N_2 + CH_4$ for TiN, TiC and Ti(C,N) coatings, respectively; total gas pressure 2×10^{-3} - 1 Pa; arc current 60 - 130 A; substrate bias voltage 0 - 225 V; deposition temperature 160 - 340 °C; deposition time: 15 - 120 min.

For Ti (C,N) deposition, the composition of the gas mixture was controlled through the relative gas flow rates of N_2 and CH_4 . Two gas compositions were chosen: 80 vol. % N_2 + 20 vol. % CH_4 and 30 vol. % N_2 + 70 vol. % CH_4 . As it was reported (e.g. [5]), the chemical compositions of the Ti(C,N) films were almost the same (within 5 - 10 %) as those obtained by ratio of the gas compositions, so that the two Ti(C,N) coating types will be noted hereafter as $TiC_{0.2}N_{0.8}$ and $TiC_{0.7}N_{0.3}$, respectively.

For Ti(C,N) coating deposition the substrate bias and arc current values were 225 V and 90 A, respectively.

2.2 Investigation techniques

X-ray Photoelectron Spectroscopy (XPS) and Elastic Recoil Detection Analysis (ERDA) were used to investigate surface chemistry and chemical composition of the TiN films, respectively.

The XPS measurements were performed on a SSX-100 spectrometer (*Surface Science Instruments*) using monochromated Al $K\alpha$ radiation (1486.6 eV). Spectra were acquired at room temperature, in a vacuum of about 5×10^{-7} Pa, and with a take-off angle with respect to the sample normal of 55°. The analyzed area was about 1.4 mm², and the pass energy was set to 150 eV. In these conditions, the resolution, as determined by the full width at half maximum (FWHM) of the Au 4f_{7/2} peak of a standard gold sample, was around 1.6 eV.

For ERDA experiments an incident 80 MeV Cu^{10+} ion beam was used. The detector of the elastically scattered recoils consisted in an ΔE pulse ionization chamber and a residual energy silicon detector placed inside the ionization chamber. Both the angle of incidence and the angle of exit were 75° relative to the sample normal.

Phase composition and texture of the coatings were determined by X-Ray Diffraction (XRD) technique using an X-ray DRON diffractometer with Cu $K\alpha$ radiation.

3. Results

3.1 Surface chemistry

The deposition parameters for the TiN films analyzed by XPS are listed in Table 1.

Table 1. Deposition parameters: nitrogen pressure P_{N_2} , arc current I_a , substrate bias voltage V_s ,

deposition time t .

Sample	Deposition parameters			
	P_{N_2} (Pa)	V_s (V)	I_a (A)	t (min)
1	2×10^{-2}	225	60	15
2	8×10^{-2}	225	60	15
3	5×10^{-1}	225	60	15
4	8×10^{-2}	50	60	15

The XPS Ti 2p, N 1s and O 1s peaks recorded on the different samples have similar shapes, suggesting that the TiN coatings have approximately the same surface composition. The detailed analysis of the XPS lines was done by a peak-fitting procedure, using a linear background and mixed Gaussian/Lorentzian (85 % G/L) peak shapes. The peak decomposition, with similar results for the investigated samples, was shown for the sample 1, in Fig. 2.

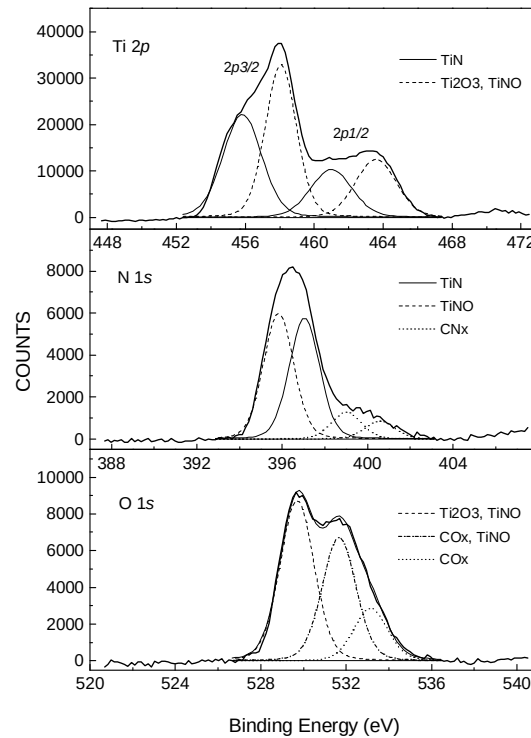


Fig. 2. Peak decomposition exemplified for the sample 1. The spectra were shown after background subtraction. TiNO designates the Ti oxynitride (see the text).

The coating bulk is described by the Ti $2p_{3/2}$ and N 1s peaks at 455.8 and 397.0 eV (Table 2), respectively, specific to TiN [10,11]. The corresponding Ti/N ratio, calculated by peak quantification, is close to one, indicating the stoichiometric bulk TiN.

The major contribution to the Ti $2p_{3/2}$ peak, at 458.1 eV, is close to the binding energy of Ti $2p_{3/2}$ in Ti_2O_3 (458.5 eV [12]), while the component of O 1s at 529.7 eV lies at the position characteristic of the same compound (529.6 eV [13]). These peaks correspond to an oxidized layer on the top of the coating, with the chemical composition (or titanium valence) close to that in Ti_2O_3 .

Table 2. The binding energies (in eV) of the XPS peaks and the atomic concentration of the corresponding phases. TiNO abbreviates the titanium oxynitride.

Sample	C		Ti		N			O	
	C-C	C-(O, N) bonds	TiN	Ti_2O_3 TiNO	TiNO	TiN	C-N bonds	Ti_2O_3 TiON	C-O bonds
1	284.8 45.0%	286.2, 288.4 10.7%	455.8 4.9%	458.1 5.9%	395.8 4.5%	397.0 4.4%	399.0, 400.6 1.6%	529.7 10.9%	531.7, 533.1 12.0%
2	284.8 37.9%	286.2, 288.4 10.5%	456.1 6.4%	458.2 7.2%	396.0 6.1%	397.2 5.7%	399.1, 400.8 1.9%	529.9 12.5%	531.7, 533.3 11.8%
3	284.7 33.5%	286.2, 288.3 8.8%	455.9 6.2%	458.1 9.5%	395.9 7.0%	397.2 6.1%	399.0, 400.8 2.0%	529.9 14.6%	531.6, 533.1, 535.4 12.3%
4	284.7 37.9%	286.3, 288.4 9.2%	455.6 6.4%	458.0 8.6%	396.0 4.6%	397.1 8.6%	398.9, 400.5 2.5%	529.8 11.9%	531.7, 533.3 10.4%

N 1s component at 395.8 eV could be attributed to a highly oxidized Ti oxynitride in the outermost layer, as earlier proposed by Ernsberger et al. [14]. Moreover, the Ernsberger's model assigned the Ti $2p_{3/2}$ and O 1s peaks at 458.2 and 529.9 eV, respectively, to the same oxynitride phase. Our XPS results are, however, more consistent with a mixture of Ti_2O_3 and Ti oxynitride on the coating surface. According to this model, the O 1s peak at 531.7 eV is partly contributed by a less oxidized oxynitride, as an intermediate layer between the outermost layer and the bulk TiN.

The other contributions to N 1s (at 399.0 and 400.6 eV) and O 1s (531.7 and 533.1 eV) correspond to bonds with carbon within a contamination layer on the sample surface. The former peaks are very close to those earlier reported for the N 1s spectra of CN_x films [15]. The high amount of adventitious carbon, despite the high vacuum during the XPS measurements, suggests that carbon was deposited on the coating surface during the deposition process or sample storage.

One must notice that the different conditions of the coating deposition should induce changes of the surface chemistry of the coatings. Some differences were found between the samples here discussed, meaning a higher N/Ti ratio for the sample 4, as well as a slightly higher concentration of the oxynitride phases in the samples 3 and 4. However, one could not establish a clear relationship between the chemistry of the passive layer and the nitrogen pressure. This means either that the reactive gas pressure alters the coating surface to a less extent than e.g. the oxygen and water levels during the reaction [14], or that the variation range of this parameter was not wide enough to induce stronger, systematic changes of the passive layer.

3.2 Chemical composition

Chemical composition of TiN films prepared on Si substrates under different deposition conditions was investigated by ERDA. A quantitative analysis of the energy spectra, using a special program [16], has been carried out.

A typical example of ERDA spectra from a TiN film is shown in Fig. 3, where the computer simulation curve is also plotted (deposition conditions: $p_{N_2} = 1 \times 10^{-3}$ Pa, $V_s = 225$ V, $I_a = 90$ A). In this case the film composition was: Ti – 42.09 %, N – 56.10 %, O – 0.39 %, C – 1.40 %, from which N /Ti ratio of 1.3 was calculated.

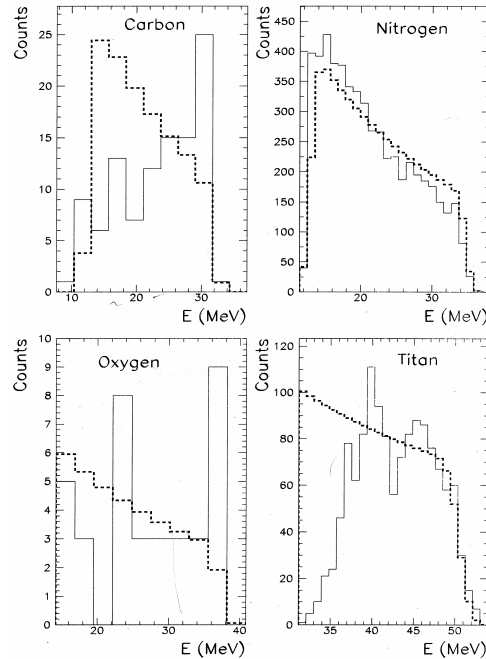


Fig. 3. ERDA spectra of Ti, N, O and C for TiN coating.

The influence of the nitrogen pressure on the N /Ti ratio is illustrated in Fig. 4. It should be noted that, in agreement with XPS data, a variation in the nitrogen pressure in the range 1×10^{-2} - 1 Pa has no significant influence on the N/Ti ratio. For N_2 pressures below 10^{-2} Pa, a decrease of the pressure (from 10^{-2} to 5×10^{-3} Pa) results in a decrease of the N/Ti ratio from 1.2 to 0.7. The experiments also showed that N/Ti ratio is practically constant for substrate bias voltages ranging from 50 to 225 V.

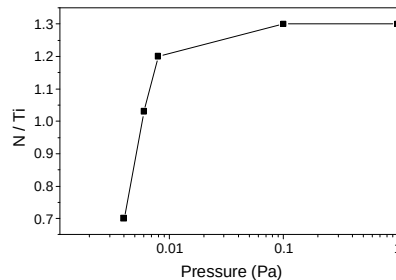


Fig. 4. N/Ti ratio as a function of N_2 pressure.

There are nevertheless certain differences between the results of XPS and ERDA investigations, arising from the specific physical processes involved in each method.

Firstly, XPS data showed that high amounts of oxygen and carbon are present in the film composition (approx. 20 % and 40 % for O and C, respectively), whereas ERDA measurements revealed relative small amounts of O and C (up to 1.5 % for each element). This can be explained by the fact that XPS analysis extends within about 15 Å of the film surface, while for ERDA, the investigated layer has a thickness in the range of 1 µm. Combining XPS and ERDA results, one may conclude that the incorporation of oxygen and carbon in the film is not due to the deposition process itself, but to the film contamination during the time elapsed between the film preparation and the composition analysis.

Secondly, the N/Ti ratio calculated from ERDA spectra were of 20 – 30 % higher than those obtained by XPS analysis. This difference is more difficult to be accounted for. Anyhow, one has to keep in mind that, as it is known [17], ERDA requires flat and smooth film surfaces, as well as good lateral uniformity. Otherwise the interpretation of the experimental data becomes difficult. More important it seems to be the fact that ERDA results depend on the knowledge of the energy loss of the elements in various compounds. In particular, data about the energy loss of Ti ions in TiN [18] are not accurately known at present. Further experiments are needed to compare ERDA results with those provided by other investigation techniques (e.g. AES, RBS or EDX).

3.3 Phase composition and texture

TiN coatings

The influence of the main deposition parameters on the phase composition and texture can be seen in Table 3, where relative intensities of the X-ray diffraction peaks are schematically shown. One may observe that the films contain mainly TiN phase. Ti was also detected (a slight (011) line), but only for low pressures ($\leq 2 \times 10^{-2}$ Pa). It is worth noting the absence of Ti₂N phase, whatever deposition were tried (even for low nitrogen pressure, high arc currents and high bias voltage, for which Ti₂N phase was expected to be present, as in the cases of other PVD deposition methods, such as ion plating, magnetron system etc [19]-[21]). This fact is not surprising if we take into account the results of the chemical composition analysis which revealed that stoichiometric or overstoichiometric TiN compound (N/Ti ≥ 1) was formed over a wide range of the deposition conditions. As it is known, in order to create Ti₂N phase, several special conditions are required, including N/Ti ratio in the range 0.3–0.4 [19].

Table 3. Relative intensities of X - ray diffraction peaks for TiN coatings
($I_{(111)} / I_{(200)} = 0.77$ for a TiN random polycrystalline sample).

Sample No	Deposition conditions			Texture for TiN $I_{(111)} / I_{(200)}$
	P_{N_2} (Pa)	V_s (V)	I_a (A)	
1	7×10^{-3}	120	60	0.64
2	2×10^{-2}	120	60	7.50
3	7×10^{-2}	120	60	18.00
4	7×10^{-1}	120	60	6.64
5	2×10^{-2}	15	60	4.14
6	2×10^{-2}	50	60	5.43
7	2×10^{-2}	225	60	9.22
8	2×10^{-2}	225	90	9.22
9	2×10^{-2}	225	130	3.88

For TiN phase, only (111) and (200) diffraction peaks were detected. Under the most deposition conditions, the diffraction patterns exhibit a strong (111) orientation, as it was reported in the existing studies [4], [7]. However, for low pressures ($< 10^{-2}$ Pa) or low bias voltage (< 20 V), no

preferred orientation was observed. A decrease of the arc current (from 130 to 60 A) leads to a stronger (111) orientation.

TiC coatings

X-ray analysis showed that films consisted of TiC and Ti phases (an example of a diffraction pattern is given in Table 4), where deposition conditions were: $p_{\text{CH}_4} = 10^{-1}$ Pa, $V_s = 225$ V, $I_a = 30$ A. A (111) orientation was observed for TiC phase, which became more pronounced with the increase of the bias voltage. Beside (111) peak, (200) and (220) lines were also detected.

Ti(C,N) coatings

For Ti(C,N) coatings, the diffraction lines were positioned between TiC and TiN lines. Under our deposition conditions, diffraction peaks in the case of $\text{TiC}_{0.7}\text{N}_{0.3}$ were in proximity of the TiC peaks positions given in ASTM. With the increasing $p_{\text{N}_2} / p_{\text{CH}_4}$ ratio ($\text{TiC}_{0.2}\text{N}_{0.8}$ as compared to $\text{TiC}_{0.7}\text{N}_{0.3}$) a displacement of the lines towards higher Bragg angles took place (e.g., for the line (111) the shift was of 0.43°). This effect can be accounted for by the replacement of the carbon atoms in the TiC lattice by nitrogen atoms, which have smaller dimensions.

Relative intensities of X-ray diffraction peaks ((111), (200) and (220)) are shown in Table 4 where Ti(C,N) lines were noted as belonging to TiC compound. As can be observed, an increase of the $p_{\text{N}_2} / p_{\text{CH}_4}$ ratio resulted in a stronger (111) orientation.

Table 4. Relative intensities of X-ray diffraction peaks for TiC and Ti (C,N) coatings ($I_{(111)} / I_{(200)} = 1.56$ and $I_{(111)} / I_{(220)} = 2.78$ for a TiC random polycrystalline sample).

Sample	Coating	Texture for TiC and Ti(C,N)	
		$I_{(111)} / I_{(200)}$	$I_{(111)} / I_{(220)}$
10	TiC	5.00	2.92
11	$\text{TiC}_{0.7}\text{N}_{0.3}$	5.80	1.45
12	$\text{TiC}_{0.2}\text{N}_{0.8}$	35.00	9.33

4. Summary and conclusions

XPS, ERDA and XDS techniques were used to investigate surface chemistry, chemical composition, phase composition and texture of TiN, TiC and Ti(C,N) hard coatings prepared on Si substrates under various deposition conditions.

XPS analysis revealed the elemental composition and chemical bindings existing at the surface of the TiN films. It was pointed out that the coatings, with a stoichiometric TiN bulk, are covered by an oxidized layer consisting of a mixture of Ti_2O_3 and Ti oxynitride. Within the variation range of the nitrogen pressure from 2×10^{-2} to 5×10^{-1} Pa one could not be observed systematic changes of the surface chemistry.

ERDA investigations allowed to find out the chemical composition and the stoichiometric coefficient (N/Ti ratio) of the TiN films. Experimental results showed that the films consisted preponderantly of Ti and N (in close proportions). Small amount of O and C (approx. 1% for each element) were also detected. However, an unexpected high values for N/Ti ratios were obtained, if we take into account both XPS results, the film characteristics (phase composition, color, microhardness) strongly related to film stoichiometry and the existing research on this deposition method. This could be explained by an inaccurate knowledge of the stopping cross-sections of the ions in the TiN compound, that were found in literature and used in the computational model.

It is interesting to note that for this deposition method, unlike other systems, the stoichiometry of the TiN compound does not change for variations of the N_2 pressure over a relatively wide range

(from 10^{-2} to 1 Pa). As a consequence, other film characteristics such as phase composition, texture, microhardness and deposition rate depend only slightly on these parameters within the above mentioned range.

XRD analysis revealed that the TiN and TiC films consisted of TiN+Ti and TiC+Ti phases, respectively (only small amounts of Ti were detected). For Ti(C,N), the diffraction lines were positioned between those of TiC and TiN lines, depending of the C/N ratio. Under the usual deposition conditions, a strong (111) orientation was observed.

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