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MICROCHEMICAL AND MECHANICAL CHARACTERISTICS OF ARC PLASMA DEPOSITED TiAlN AND TiN/TiAlN COATINGS

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Single layer TiAlN and alternate TiN/TiAlN multilayered hard coatings were deposited on Si, plain carbon steel and high-speed steel substrates by the cathodic arc technique. Chemical composition, phase composition, texture, Vickers microhardness, adhesion, bilayer period, sliding friction coefficient and wear resistance were investigated by XPS, EDX and XRD analyses, microhardness measurements, scratch and tribological tests.

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1. Introduction

The increasing demands in performance of high speed dry machining resulted in a rapid progress to produce coatings with good wear and oxidation resistance at high temperatures. Of these coatings, those made of TiAlN have successfully been applied as protective films on cutting tools [1-7]. Their better performance as compared to that of the current wear resistant films (TiN, TiC, Ti(C,N)) was attributed to the formation of an aluminium oxide layer on the film surface. Since multilayer coatings often exhibited better features for industrial applications than single layer coatings, TiAlN based multilayers such as alternate TiAlN/CrN, TiAlN/TiN or TiAlYN/VN were selected as potential candidates in protecting machine parts and tools [8-10]. In our earlier paper [11] we have shown that superlattice coating of the type TiN/ZrN exhibits a significant increase of microhardness if compared to monolayer coating.

In this work, results of microchemical and mechanical investigations on single-layer TiAlN films and alternate TiN/TiAlN multilayers prepared by cathodic arc method [12] are presented. The coatings were analyzed in terms of elemental and phase composition, texture, microhardness, compositional modulation period (Λ), adhesion and tribological characteristics.

2. Experimental

Details of the deposition system can be found elsewhere [13]. The deposition chamber was equipped with two cathodes made of Ti and Ti-Al alloy (75:25 at. %). The coatings were deposited on Si, plain carbon steel and high-speed steel substrates. The multilayer structures were prepared by using two rotating shutters placed in front of each cathode. The shutters were periodically open and close so that Ti and Ti+Al atoms were alternatively introduced in the reactive atmosphere for a certain duration. The deposition rates of TiN and TiAlN layers were chosen to be equal (~0.9 nm/s),

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different bilayer periods (Λ) being obtained with different rotating speeds of the shutters. The overall thickness of the coatings was controlled to be of about 3.5 μm. The multilayers will be denoted by TiN/TiAlN – n, where n is the number of the individual layers.

The main process parameters both for the TiAlN single layer coatings and for the TiN/TiAlN multilayers with various bilayer periods were as follows: reactive atmosphere – N_2; gas flow rate – 150 cm^3/min; arc current – 90 and 100 A at the Ti +Al and the Ti cathode, respectively; substrate bias – 220 V; deposition time - 60 min.

Both energy dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to determine the chemical composition of the coatings. EDX investigations were performed by means of a XL-30 – ESEM TMP scanning electron microscope. XPS spectra were obtained with a VG ESCA 3 MK II spectrometer, using monochromated Al K_α radiation (1486.6 eV). The spectra were calibrated with respect to the C_{1s} peak (285 eV). A 5 keV Ar^+ ion beam was used for sputter etching of the samples (20 min).

Phase composition and texture were analyzed by X-ray diffraction (XRD), with CuK_α radiation.

Vickers microhardness HV was measured at an applied load of 15 gf. Scratch tests under standard conditions were undertaken to determine the coating adhesion. The critical load L_c was measured by optical microscopy. Film thickness was evaluated by microscope examination of the cross section through the coating. The bilayer period Λ was calculated from the overall thickness of the multilayer and the number of the bilayers.

Tribological performance of the coatings (sliding friction coefficient and wear) were investigated by using a testing apparatus mainly consisted of a coated sample (disc of 18 mm in diameter) pressed on a rotated steel disc. The wear resistance was evaluated by measuring the thickness of the worn layer, using an indentation procedure with a Vickers diamond tip. The tests were performed dry, under the conditions: sliding speed – 22 m/min; load – 4 N. Geometrical considerations lead to the expression of the worn layer thickness (d):

$$d = (D_0 - D)\frac{\sqrt{2}}{4} ctg \frac{136^0}{2} \qquad \text{[mm]}$$

where D_0 and D are the diagonals of the indent before and after wear, respectively.

3. Results and discution

3.1. Chemical composition

The chemical binding state and elemental composition of the TiN and TiAlN monolayers were investigated by XPS. The film composition was determined from Ti 2p, Al 2p, N 1s, O 1s and C 1s peaks.

For a TiN coating, typical Ti 2p spectra taken from the as-deposited and the sputter etched sample are shown in Fig. 1. According to the literature values [13-15], the Ti $2p_{3/2}$ peak assignments were as follows. Ti $2p_{3/2}$ peaks at 455, 456.5 and 458.1eV were associated with TiN, Ti_2O_3 (TiO) and TiO_2, respectively. Ti $2p_{1/2}$ peaks corresponding to the same compounds were found at 460.6, 461.9 and 463.7 eV, respectively. Comparing the data in Fig. 1a and b, one must notice the significant differences in the film composition before and after sputter etching: both Ti_2O_3 and TiO_2 concentrations decreased (from 31.4 to 27.9 at.% and from 37.9 to 24.1 at.%, respectively), while TiN amount increased (from 30.8 to 48.7 at.%). Considering the N 1s, O 1s and C 1s spectra, besides the above mentioned compounds, important amounts of adsorbed C and O_2 were detected, which is a typical contamination phenomenon when coatings are exposed in atmosphere.

Similar composition depth profiles were found for the TiAlN films, except for the presence of Al in the film composition. The Al content was measured to be in the range from 5.2 to 6.1 at.%, with a slight increase after etching.

The XPS results are consistent with the following chemistry model of the monolayers. On the coating surface, a mixture of TiN (or TiAlN), Ti_2O_3 and TiO_2 compounds, together with high amounts of adsorbed oxygen and carbon, are present. Below the surface, a graded layer, with increasing TiN (or TiAlN) and decreasing TiO_x, O_2 and C is formed. The coating bulk consists mainly of an almost stoichiometric TiN (or TiAlN) compound (N/Ti=0.92 – 1.05; N/(Ti+Al)=1.02 – 1.11)

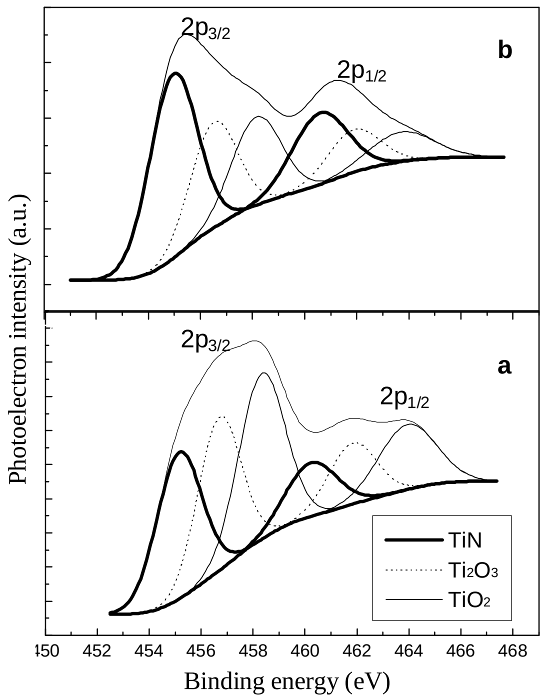

Fig. 1. XP Sspectra of a TiN coating a) as-deposited; b) – after sputter etching.

The elemental composition of the TiAlN and TiN/TiAlN coatings was determined by EDX technique. An EDX spectrum of a TiAlN film is shown in Fig. 2. The elemental concentrations from a TiAlN monolayer and a TiN/TiAlN multilayer (with 720 layers) is given in Table 1. The coatings are slightly overstoichiometric (in agreement with the XPS data) and the Al/Ti ratios were found to be of 0.20 (for TiAlN) and 0.11 (for TiN/TiAlN). On the other side, the measured oxygen content was significantly lower than that obtained from the XPS analysis.

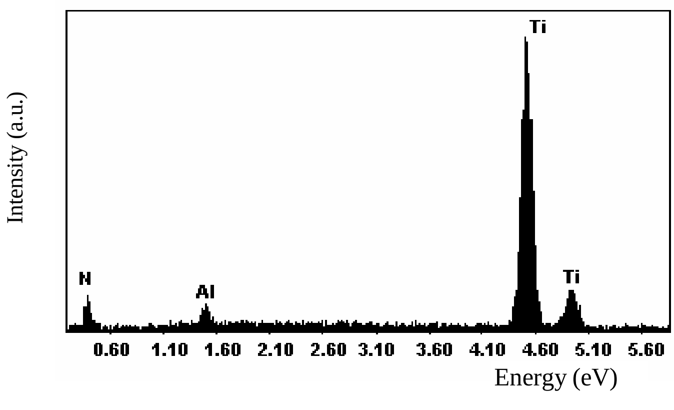

Fig. 2. EDX spectrum of a TiAlN film.

Table 1. Elemental composition of the coatings.

Coating	Elemental concentration (at %)					N/(Ti+Al)	Al/Ti
	Ti	Al	Fe	N	O		
TiAlN	35.00	6.90	2.20	46.10	9.80	1.10	0.20
TiN/TiAlN-720	39.10	4.30	2.60	44.90	9.10	1.03	0.11

3.2. Phase composition and texture

The X-ray spectrums of TiN/TiAlN multilayer coatings with two different bilayer periods (10 and 600 nm) are shown in Fig. 3. For comparison, diffraction patterns of TiN and TiAlN monolayers are also illustrated. Both single layer coatings and multilayers exhibit a strong (111) orientation. As it was expected, the diffraction lines of the TiAlN film are shifted towards higher Bragg angles as compared to the TiN lines, because the substitution of Ti atoms with Al atoms in the B1 – NaCl structure of TiN results in a decrease of the lattice parameter. Since the aluminium content in the film composition is relatively low (~7 at.%), the shift is not significant (about 0.5^0 for the (111) line). As for the multilayers, it is interesting to note that the diffraction patterns from the coatings with small and large bilayer periods are similar with those for TiAlN and TiN single layer films, respectively.

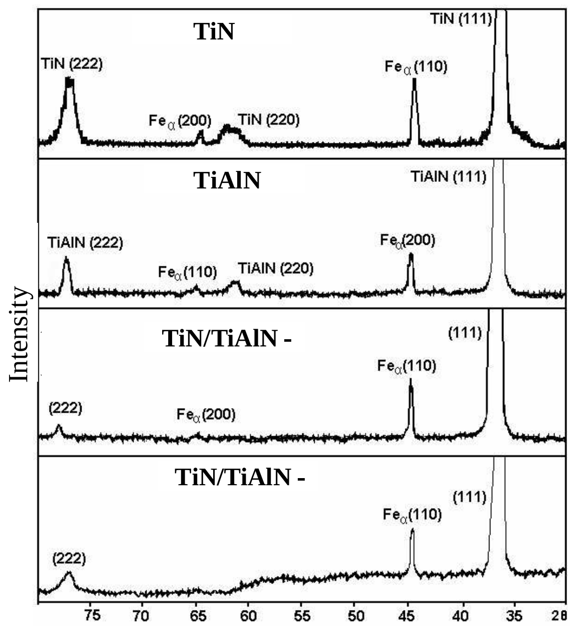

Fig. 3. X-ray diffraction patterns from TiN, TiAlN and TiN/TiAlN coatings.

3.3. Mechanical and tribological characteristics

The main mechanical properties of the coatings (microhardness, adhesion, bilayer period) are summarized in Table 2. One may note that TiAlN films had higher microhardness than that of the TiN, as usually reported. As for the multilayers, the microhardness values first increase (from 26.2 to 29.4 GPa) with the decreasing bilayer period (from 600 to 10 nm), folowed by a decrease to 23.5 GPa for Λ = 4.5 nm. A similar behavior was reported for other superlattice coatings (e.g. TiN/CrN, [16]).

Table 2. Mechanical characteristics.

Coating	$HV_{0.015}$ (GPa)	L_c (N)	Λ (nm)
TiN	21.8	52	-
TiAlN	23.3	47	-
TiN/TiAlN-12	26.2	46	600
TiN/TiAlN-360	29.1	49	20
TiN/TiAlN-720	29.4	48	10
TiN/TiAlN-1500	23.5	47	4.5

Only slight differences (~ 6N) in the L_c values for different coatings were found and no systematic dependence of the adhesion on the bilayer period was observed. TiN single layer coatings exhibited the best adhesion (L_c = 52 N).

The wear behavior of the various coatings can be examined in Figs. 4 and 5, where dependences of the friction coefficient and of the worn layer thickness on sliding distance L_c are illustrated. It would be noticed that the coated samples exhibit higher wear resistance and lower friction coefficient than those of the uncoated specimen. In the first stage of the test (L <100 m), a marked increase of the wear with the sliding distance can be observed. This can be understood as a consequence of the decrease of the surface roughness occuring at the beginning of the wear process. In the following stage, the friction coefficients of the coatings remain practically constant, whereas the worn layer thickness increases, with a slope depending on the coating type. The best wear resistance and the lowest friction coefficient were measured for the TiN/TiAlN-720 multilayer (Λ = 10 nm).

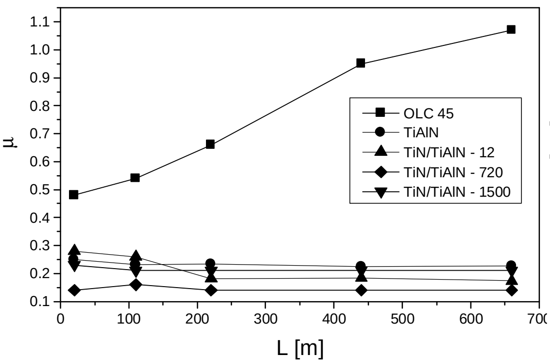

Fig. 4. Friction coefficint μ vs. sliding distance L.

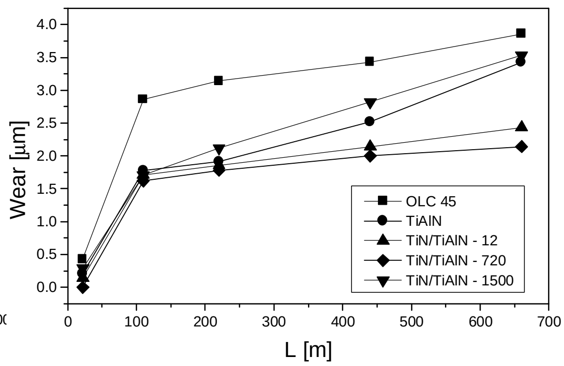

Fig. 5. Worn layer thickness vs. sliding distance L.

4. Summary and conclusions

Single layer TiAlN and TiN/TiAlN multilayered coatings (bilayer periods from 4.5 to 600 nm) were prepared by the cathodic arc deposition method, using Ti and Ti+Al (Ti/Al = 3/1) cathodes.

The analysis of the film composition showed that the TiAlN coatings were slightly overstoichiometric (N/(Ti+Al) ≈ 1.1), with a relatively low Al content (~ 7 at.%). For the TiN/TiAlN multilayers, N/(Ti+Al) ratio was close to one and the Al content decreased to 4 – 5 at.%. All the coatings were covered with a highly ionized layer, consisted of TiN (or TiAlN), Ti_2O_3 and TiO_2 compounds, together with important amounts of adsorbed carbon and oxygen. For both single layer coatings and multilayers a strong (111) preferred orientation was observed.

TiAlN films had a slightly higher microhardness as compared to the TiN (1.5 – 2GPa higher). Of all the coatings, the highest microhardness values (~30 GPa) were measured for the TiN/TiAlN multilayers with Λ = 10 nm. This coating exhibited also the best tribological performance (the lowest friction coefficient and the best wear resistance).

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