Tribological Aspects of TiN, Ti(C,N) and (Ti,Al)N Layers Coated by PACVD on Different Tool Steels

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ABSTRACT

Coating technology, specifically thin-film technology, is one of the most prominent categories of surface treatments, among other well-known treatments like ion implantation and etching.

For wear-resistant applications, in the case of steels, a minimum deposition temperature is required in order not to disturb the previous hardened and tempered structure. Plasma activation conditions are necessary in these cases in order to excite the reactants and to be able to break bonds in the precursor or activate the precursor to react with co-reactants. For tool manufacturing, improvement of wear resistance has been achieved using coating technology. Thus, good results have been obtained for TiN, Ti(C,N) and (Ti,Al)N layers. In order to achieve these depositions, TiCl_4 , (AlCl_3) as Ti, (Al) precursor and N_2 , (CH_4) as a nitrogen (carbon) source were used.

Tribological investigations revealed that the quality of layers is very different and variable, depending on many factors like roughness and hardness of the support substrate, deposition type and quality of steel, residual stress level of the layer and lattice parameter respectively.

1. INTRODUCTION

Most of the commercial processes used to date are related to atmospheric pressure CVD in hot-wall reactors, using titanium tetrachloride (TiCl_4) as Ti precursor and N_2 or NH_3 as nitrogen source.

The reaction between TiCl_4 and N_2 proceeds in the temperature range of 900 to 1200°C, at deposition rates of 0.03 to 0.2 $\mu\text{m}/\text{min}$, yielding a hardness of 2000 to 2500 HV /1/. The relatively high deposition temperature in this process implies a considerable restriction in the range of substrates that can be coated with Ti based layers.

On the one hand, use of ammonia as a nitrogen source allows lower deposition temperatures. On the other hand, an alternative way to excite reactants and to lower the deposition temperature is by plasma activation. Direct plasma is defined here as plasma that is in direct contact with the substrate surface, such that the

precursor has to travel through the plasma itself. The substrate heated by the plasma and additional heating can provide a minimum temperature to maintain surface mobility and reactivity of the entering species (radicals and ions which have been created in the gas phase) [2,3]. Electrons, generated by the plasma, are accelerated by the applied electric field and acquire sufficient energy to cause dissociation and ionization by collisions. TiCl_4 is frequently used during plasma-assisted CVD processes (PACVD) for wear resistant applications. The high-strength electric field over the boundary layer between the plasma and the surface causes acceleration of ions to the surface.

In PACVD processes, the geometry of the reactor and the electrode configuration are very important. The plasma has to be uniformly divided over the reactor space and must uniformly surround the substrate surface. Even in the relatively simple DC plasmas this uniformity is not always reached. Furthermore, parts of the reactor may collect charge due to contamination. Thus, application of pulsed plasma may help to maintain uniformity in the reactor. Before the plasma could be disturbed, it is periodically turned off and charges are neutralized. Also, it is necessary to dose the amount of energy that dissipates in the plasma via power pulses because gas-phase chemistry plays as important a role as surface chemistry does in this kind of process. Another advantage of pulsed plasma is the possibility of applying bipolar pulses. After charges have built up on a non-conducting surface, a positive power pulse is applied.

Positive charges are then removed from the surface. During the next cycle ions arrive again at the surface to form the coating. Thus, non-conducting coatings can be deposited on non-conducting substrates.

2. EXPERIMENTAL

In order to achieve the experimental program, a large number of cylindrical samples ($\phi 55 \times 12\text{mm}$) were manufactured from three kinds of tool steels (Bohler Grade):

- a hot work tool steel W300 (0.36 %C, 1.10 %Si, 0.40 %Mn, 5.0 %Cr, 1.30 %Mo, 0.40 %V);
- a high-speed steel S600 (0.90 %C, 4.1 %Cr, 5.0 %Mo, 1.8 %V, 6.4 %W);
- a cold work tool steel K110 (1.55 %C, 0.30 %Si, 0.30 %Mn, 11.5 %Cr, 0.7 %Mo, 1.00 %V).

Prior to coating, the samples were heat-treated and polished as follows:

- W300 – hardening from 1040°C in hot oil and tempering twice at 520°C and 560°C , 54 – 56 HRC, $R_a = 0.20 \mu\text{m}$;
- S600 – hardening from 1180°C in hot oil and tempering three times at 520°C , 64 – 66 HRC, $R_a = 0.30 \mu\text{m}$;
- K110 – hardening from 1070°C in hot oil and tempering at 220°C , 60 – 62 HRC, $R_a = 0.08 \mu\text{m}$;

The coatings were made in a DC-pulsed PACVD reactor and consisted of three kind of layers: TiN, Ti(C,N) and (Ti,Al)N.

For the first variant of deposition – TiN - the parameters of the process (in its main step) were: $T=510^\circ\text{C}$, $U=490\text{V}$, $I=4\text{A}$, $p=2\text{mbar}$, $P=1000\text{W}$, pulse on/off ratio = $0.08 (\mu\text{s}/\mu\text{s})$ / negative bias, $t=10$ hours;

TiN deposition parameters												
Step/ Parameters	t [h]	T [°C]	U [V]	I [A]	p [mbar]	P* [W]	Gas flows [l/h]					
							N ₂	H ₂	Ar	TiCl ₄	CH ₄	AlCl ₃
Sputter cleaning	2	510	450	14	4	512	10.5	400	60	-	-	-
Rising	1	510	450	14	4	512	10.5	-	-	450	-	-
TiN deposition	10	510	490	2-4	2	1000	10	200	10	1600	-	-

*Plasma power dissipation

For the second variant of deposition – Ti(C,N) – the parameters of the process (in its main step) were: T=510°C, U=430V, I=4A, p=2mbar, P=1000W, pulse on/off ratio = 0.76 (μs/μs) / negative bias, t=10 hours.

Ti(C,N) deposition parameters												
Step/ Parameters	t [h]	T [°C]	U [V]	I [A]	p [mbar]	P* [W]	Gas flows [l/h]					
							N ₂	H ₂	Ar	TiCl ₄	CH ₄	AlCl ₃
Sputter cleaning	2	510	450	14	4	512	10.5	400	60	-	-	-
Rising	1	510	450	14	4	512	10.5	-	-	450	-	-
TiN deposition	2	510	490	2-4	2	1000	8	170	16	1560	-	-
Ti(C,N) deposit	10	510	430	4-5	2	1000	18	160	8	1538	5	-

*Plasma power dissipation

For the third variant of deposition – (Ti,Al)N - the parameters of the process (in its main step) were: T=540°C, U=500V, I=24A, p=2mbar, P=2900W, alternating pulse – positive on/off ratio = 8 (μs/μs), negative on/off ratio = 0.1 (μs/μs), t=9 hours.

(Ti,Al)N deposition parameters												
Step/ parameters	t [h]	T [°C]	U [V]	I [A]	p [mbar]	P* [W]	Gas flows [l/h]					
							N ₂	H ₂	Ar	TiCl ₄	CH ₄	AlCl ₃
Sputter cleaning	2	540	450	14	4	512	10.5	250	20	-	-	-
Rising	1	540	450	14	4	512	10.5	-	-	450	-	-
TiN deposition	1	540	490	2-4	2	900	8	170	16	1560	-	-
(Ti,Al)N deposition	10	540	500	24	2	2800	12	170	16	0.4	-	20

*Plasma power dissipation

Following the coating processes, first of all the microhardness of the coating variants, $HV_{0.100}$, $HV_{0.050}$, $HV_{0.025}$, $HV_{0.010}$ were measured. The average values of these measurements are presented in Table 1. In addition, the roughness values of the layers with a Talysurf profilometer were estimated. The average values of these measurements are presented in Table 2.

In order to estimate the friction coefficients of the layers, a typical method such as the *incline plan method* was used. Thus, the samples were placed with the plane surface on the inclined test plane. Then, the testing plane platform was varied for different angles until the sample started sliding.

The experimental results of these analyses are given in Table 3.

The platform of the inclined test plane device was made from Romanian OLC45 carbon steel, in annealed heat treatment conditions, STAS 880/88, with $R_a=0.6 \mu m$.

The x-ray diffraction method was employed in order to establish some aspects that depend on the internal structure:

- the main growth direction,
- the distance between the crystallographic planes ($d_{h,k,l}$) for the maximum intensity signal,
- the lattice parameter,
- the internal stress level.

Technical data for XRD experimental conditions:

$2\theta/\theta$ locked-Start 20.000° -Step 0.010° -Step time 1s-Temp.= $25^\circ C$ -CuK α 1- λ : 0.15406 nm.

The d_{hkl} distances were estimated according to Bragg's relation /4/:

$$d_{hkl} = \frac{\lambda}{2 \cdot \sin \theta} \quad [nm] \quad (1)$$

The lattice parameters $\langle a \rangle$ for cubic microstructures were estimated from the equation /4/:

$$a = d_{hkl} \cdot \sqrt{h^2 + k^2 + l^2} \quad [nm] \quad (2)$$

Considering the main (200) orientation and the plane stress state, an impression of the stress levels in the coatings by XRD analysis could be obtained by using the following formula /5/:

$$\sigma = \frac{a_0 - a}{a} \cdot \frac{E_f}{(1 - \nu_f)} \quad [GPa] \quad (3)$$

where:

a_0 – the parameter of the crystallographic lattice in non-stressed conditions [nm];

a – the parameter of the crystallographic lattice considering the residual stress state [nm];

E – Young's modulus of the coating [GPa];

ν_f – Poisson's ratio of the coating;

σ_f – the residual stress (in the coating plane) [GPa].

The following relation gives the deviation from the standard lattice parameter value:

$$\varepsilon_{hkl}^* = \frac{a_{hkl} - a_0}{a_0} \cdot 100 \text{ [\%]} \quad (4)$$

The following relation (average values) estimated the grain size for each type of layer:

$$D = \frac{0.9\lambda}{B \cos \theta} \text{ [nm]} \quad (5)$$

The experimental results of the XRD analysis are given in Table 4.

Glow-discharge optical emission spectrometry has been used to find the chemical composition profiles of the coatings in depth. Thus, a minimum of 30% titanium has been considered as an inside boundary of the layer thicknesses.

The GD-OES analysis results are presented in Table 5.

Wear testing was carried out using an SAE type machine, in hertzian-line contact conditions. The experimental samples consisted in tool-steel wheels, 55 mm in diameter and 12 mm thick.

The contact conditions were arranged so that the upper wheel was fixed and made from OLC45 Romanian steel in annealed heat-treatment conditions (0.45% C, with $R_a=0.6 \mu\text{m}$ on the cylindrical contact surface) and the lower wheel (the coated wheel) was rotated at 50 rpm, such that 100% sliding conditions occurred between the two contact surfaces.

Table 6 shows the wear results average obtained for various coating specimens and tool-steel substrates under an applied load of 110 daN.

3. RESULTS

Table 1

The results of hardness tests following the coating processes

<i>Layer type</i>	<i>HV_{0.100}</i> <i>[daN/mm²]</i>	<i>HV_{0.050}</i> <i>[daN/mm²]</i>	<i>HV_{0.025}</i> <i>[daN/mm²]</i>	<i>HV_{0.010}</i> <i>[daN/mm²]</i>
TiN1	1470	1700	1878	2253.6
TiN2	1533	1724	1912	2294.4
TiN3	1523	1720	1900	2280
TiN4	1512	1715	1880	2256
TiN5	1490	1756	1896	2275.2
TiN6	1510	1722	1904	2284.8

Table 1 (continued)

The results of hardness tests following the coating processes

<i>Layer type</i>	<i>HV_{0.100}</i> <i>[daN/mm²]</i>	<i>HV_{0.050}</i> <i>[daN/mm²]</i>	<i>HV_{0.025}</i> <i>[daN/mm²]</i>	<i>HV_{0.010}</i> <i>[daN/mm²]</i>
Average	1506.33	1722.83	1895	2274
Ti(C,N)1	946	1250	1650	1980
Ti(C,N)2	1098	1284	1695	2034
Ti(C,N)3	1067	1298	1713	2056
Ti(C,N)4	996	1285	1696	2035
Ti(C,N)5	1108	1300	1716	2058
Ti(C,N)6	1122	1278	1687	2024
Average	1056.16	1282.5	1692.83	2031.16
(Ti,Al)N1	1630	2250	2696	3335
(Ti,Al)N2	1690	2288	2622	3146
(Ti,Al)N3	1712	2278	2614	3137
(Ti,Al)N3	1678	2290	2634	3161
(Ti,Al)N3	1633	2268	2600	3120
(Ti,Al)N3	1658	2212	2644	3173
Average	1666.83	2297.66	2635	3178.66

Table 2

The results of roughness measurement tests

Layer/ substrate	R_a[μm] before deposition	R_a[μm] Sample no. 1	R_a[μm] Sample no. 2	R_a[μm] Sample no. 3	R_a[μm] average values	Roughness changing grade* [%]
TiN/K110	0.08	0.09	0.11	0.12	0.106	+32.50
TiN/W300	0.22	0.30	0.33	0.38	0.336	+52.72
TiN/S600	0.32	0.36	0.35	0.30	0.336	+5.00
Ti(CN)/K110	0.08	0.11	0.11	0.13	0.116	+45.00
Ti(CN)/W300	0.22	0.44	0.42	0.40	0.420	+90.90
Ti(CN)/S600	0.32	0.40	0.42	0.40	0.406	+26.87
(TiAl)N/K110	0.08	0.19	0.16	0.15	0.166	+108.33
(TiAl)N/W300	0.22	0.24	0.28	0.27	0.263	+19.54
(TiAl)N/S600	0.32	0.37	0.32	0.36	0.350	+9.37

* $(R_{a\text{ final average}} - R_{a\text{ initial}})/R_{a\text{ initial}}$

Table 3

The results of friction coefficient measurements

<i>Deposition type</i>	<i>The roughness R_a of the deposition on the sample plane surface [μm]</i>	μ_s <i>experimental tribosystem 1</i>	μ_s <i>experimental tribosystem 2</i>	μ_s <i>average values</i>
TiN 1	0.80	0.3205	0.3222	0.3213
TiN 2	0.78	0.3203	0.3210	0.3206
TiN 3	0.80	0.3211	0.3231	0.3221
Ti(C,N) 1	0.48	0.3147	0.3182	0.3164
Ti(C,N) 2	0.45	0.3123	0.3170	0.3146
Ti(C,N) 3	0.56	0.3179	0.3193	0.3186
(Ti,Al)N 1	0.20	0.3900	0.3948	0.3924
(Ti,Al)N 2	0.23	0.3917	0.3970	0.3943
(Ti,Al)N 3	0.26	0.3961	0.3981	0.3971
Non-coated sample 1	0.74	0.4689	0.4672	0.4680
Non-coated sample 2	0.43	0.4646	0.4666	0.4656
Non-coated sample 3	0.20	0.4633	0.4635	0.4634

Table 4

The results of XRD analysis

Deposition/ substrate	$\langle d_{200} \rangle$ [nm]	$\langle a \rangle$ [nm]	$\varepsilon_{(200)}$ [%]	D [nm]	E_f [GPa]	ν_s	σ [GPa]
TiN/K110	0.2126	0.4252	0.35	32.90	≈ 600	0.25	-2.8321
TiN/W300	0.2132	0.4264	0.63	33.24	≈ 600	0.25	-5.0979
TiN/S600	0.2130	0.4260	0.54	33.04	≈ 600	0.25	-4.3426
Ti(CN)/K110	0.2139	0.4279	0.99	11.61	≈ 525	0.25	-6.9388
Ti(CN)/W300	0.2140	0.4280	1.01	11.66	≈ 525	0.25	-8.1189
Ti(CN)/S600	0.2141	0.4282	1.06	11.84	≈ 525	0.25	-8.4965
(TiAl)N/K110	0.2045	0.4090	-3.46	68.46	≈ 450	0.25	+20.8166
(TiAl)N/W300	0.2043	0.4086	-3.56	68.45	≈ 450	0.25	+21.3830
(TiAl)N/S600	0.2047	0.4094	-3.37	67.87	≈ 450	0.25	+20.2501

*The standard interplane distance for the (200) orientation of TiN compound is 0.2111 nm and the standard lattice parameter of TiN, a_0 , is 0.4237 nm.

Table 5

The results of GD-OES analyses by GDL evaporation

Deposition type	The average thickness [μm]	The average molar formula of the coatings (at the middle of the GD-OES profiles)
TiN	3.70	TiN _{1.33}
Ti(C,N)	3.33	Ti(C _{0.2} N _{0.57})
(Ti,Al)N	4.16	(Ti _{0.3} Al _{0.35})N

Table 6

The results of wear tests in dry conditions for sliding-line contact

Coating type	Substrate steel	Coating roughness value R_a [μm]	Initial weight of test specimen [gr.]	Testing time [min.]	Final weight of test specimen [gr.]	Weight loss percentage [%]*
TiN	S600	0.30-0.36	173.5590	20	173.5542	0.002766
TiN	K110	0.09-0.12	188.1860	20	188.1810	0.002657
TiN	W300	0.30-0.38	182.4918	20	182.4890	0.001534
Ti(CN)	S600	0.40-0.42	173.2123	20	173.2011	0.006466
Ti(CN)	K110	0.11-0.13	188.3456	20	188.3410	0.002442
Ti(CN)	W300	0.40-0.44	182.6310	20	182.6204	0.005804
(TiAl)N	S600	0.32-0.37	172.6955	20	172.6740	0.012450
(TiAl)N	K110	0.16-0.19	188.0103	20	188.0042	0.003245
(TiAl)N	W300	0.24-0.28	182.9060	20	182.8517	0.029687

*Weight loss percentage is given by the relation: $[(W_i - W_f)/W_i] \times 100$ [%]

4. CONCLUSIONS

According to the experimental results, after the deposition processes, the roughness values increased compared to the previous substrate roughness values. The smallest increase in roughness was observed for TiN.

If the substrate roughness value exceeds 0.30 μm , the increase in roughness after the deposition is not spectacular.

The maximum microhardness values were recorded for (Ti,Al)N coatings and the minimum values for Ti(C,N) coatings.

The Ti(C,N) depositions presented the lowest values of friction coefficient, although for the roughness values of the support substrate medium values were recorded.

The diffraction patterns revealed a cubic structure for all the coatings, similar to that of TiN /6/. The difference in the measured peak intensity is remarkable. Coatings 1 (TiN) and 2 Ti(C,N) have a strong (200) reflection and weaker (111), (220) and (311) reflections. In the case of the (Ti,Al)N coating, the presence of aluminum leads to a change in the (200) peak position compared to the normal (200) TiN position. This could be explained through the substitution of Ti atoms in the coating matrix by Al atoms. In this case, the other reflections (111), (220) and (311) are very little developed.

The preferred orientation of a deposited coating under ion bombardment is assumed to be dependent on the total energy of the coating. This total energy is defined as the sum of the internal or cohesive energy of the crystals in the coating and the surface energy /7/. The contribution of the surface energy to the total energy is relatively high compared to the cohesive energy in very thin layers. If the surface energy contribution to the total energy is predominant, then the coating exhibits a preferred (200) orientation due to the low number of open bonds at the surface. However, as the layer grows and becomes thicker, the contribution of the internal to the total energy increases.

The experimental XRD results revealed that $\langle a \rangle$ lattice parameters were lowest in the case of (Ti,Al)N variant and highest in the case of the Ti(C,N) variant.

From the point of view of residual stresses, the most favorable aspect was characteristic of the Ti(C,N) coating variant, which presented the highest values of compressive stresses. At the same time, poor results were obtained for the (Ti,Al)N coatings, which are characterized by a residual tensile stress level.

According to the SEM micrographs, the cross-section shows a complete phase transition of the top layer of the substrate and a density gradient over more than 80-100 μm into the bulk material. GD-OES applied in order to evaluate the depth concentration profiles clearly shows a decreasing carbon percentage in the substrate compared to the initial steel values. This means that a light decarburation phenomenon has taken place during the plasma assisted deposition process.

Generally, the wear tests revealed good and similar results for the Ti(C,N) and TiN layers. However, if we compare the deposition variants for K110 steel, we note that the lowest weight loss was found for samples coated with Ti(C,N).

From the tribological point of view, the experimental results show that Ti(C,N) depositions offer the best test piece qualities.

Acquiring high qualities of the layers depends on the roughness and microhardness values of the support substrates. Thus, if the substrates present low values of roughness and high microhardness, higher qualities can be obtained for the coatings.

The presence of supplementary Al-atoms, besides the Ti-atoms, in the coating matrix, leads to the changes in the lattice parameter in such a way that a residual tensile stress level is induced. This is a real disadvantage for the wear behavior of coatings.

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