High-temperature tribological characterization of commercial TiAlN coatings

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Abstract
This study was performed with the aim of evaluating the relative tribological behaviour at high temperature of $(Ti_{1-x}Al_x)N$ coatings commercially deposited on WC inserts. The $(Ti_{1-x}Al_x)N$ multilayered, nanostructured and single-layer coatings, which contained different Ti/Al atomic ratios varying from 7/3 to 2/3 respectively, were deposited by employing a commercial PVD cathodic arc process. The absolute hardness value for each coating is also reported and has been calculated from the Vickers microhardness measurements by using one of the models published in the literature. Standard ball-on-disc testing was conducted in order to determine friction coefficients and wear rates for these systems against a 6 mm alumina ball. These tests have been carried out in conditions that are not common in industrial use, e.g. metal cutting tools inasmuch as alumina is not a representative workpiece material. The sliding tests were performed out at 25, 500 and 700 °C with 5 N normal loads. At 25 °C, a wear volume, V, of approximately 10^{-2} mm^3 was obtained for all the tested coatings. When the test temperature increased to 500 °C, the single-layered coatings showed a wear volume of the same order of magnitude as those tested at room temperature. The multilayered coated samples decreased their wear volume by one order of magnitude, whereas the nanostructured samples showed almost no wear. At 700 °C, the wear volume values reported for all samples were similar and of the same order of magnitude as those tested at room temperature. The wear mechanism is discussed together with the morphological and compositional characteristics, determined by SEM coupled with EDX analysis.

1. Introduction

The tribological properties of a single tool material never satisfy all its performance requirements. Cutting tool wear is the result of load, friction and high temperature between the cutting edge and the workpiece. For many years, metalworking industries have shown great interest in improving the properties of the coated cutting tool materials and ceramic materials have good prospects for tribological applications, especially under severe conditions. Coatings can provide high wear resistance on the surface, increase the surface hardness of cutting tools at high temperature and provide a chemical barrier to decrease diffusion or reaction between the tool and the workpiece, thus reducing tool wear. Therefore, the demand to develop wear resistant hard coatings with good thermal stability has become crucial for the extension of tool life as machining speed increases and for die materials, where high hardness is required. Friction occurring between the tool and the component leads to an increase of the contact temperature and finally to oxidation, resulting in the wear of the coating. The increase in the temperature can also be generated by an increase in the speed of the cutting process. Titanium nitride (TiN) is widely used as a protective coating in cutting and punching tools, due to its high hardness and good wear resistance, but its use at elevated temperature is restricted due to its poor chemical stability.

It is known that (TiAl)N coatings could enhance wear and oxidation resistance of the tool overcoming the shortcomings presented by both TiN and TiCN traditional PVD coatings [1, 2]. (TiAl)N coatings have been found to form a stable and protective oxide surface layer due to rapid temperature elevation during high speed machining and therefore an enhanced resistance to oxidation [3–5]. However, it has been shown that the mechanical properties and the ability to protect the tool are strongly dependent on their chemical composition [6–8].

The present study is carried out in order to evaluate the relative wear behaviour at room and high temperature of $(Ti_{1-x}Al_x)N$ coatings against alumina. The alumina ball is not a common counterface material in industrial applications of coated tools or components, but it is chemically stable at high temperature and has been used as counterface for the standard studies of tribological behaviour of hard coatings at high temperatures [9–12]. There is some relevance of this tribosystem however, in the machining mechanisms of steels that contain hard alumina inclusions and some pre-sintered alumina ceramics.

2. Experimental details

The $(Ti_{1-x}Al_x)N$ coatings were deposited in a commercial PVD coating equipment by using a cathodic arc process on WC–6%Co cemented carbide inserts. The TiAlN-based coatings contained varying Ti/Al atomic ratios. Roughness measurements were conducted by means of a New View Zygo 200 optical profilometer. The ball cratering method (Calotest, CSEM) was used to determine the thickness of the coatings. The morphologies of the coatings and their composition were studied using scanning electron microscopy (SEM).

Composite hardness was determined by conducting standard Vickers indentations using a motorized stage Leco microhardness tester. Loads of 0.098, 0.245, 0.49, 0.98, 1.96, 2.94, 4.9 and 9.8 N were used and maintained for 15 s, respectively. Six indentations were performed for each load on the coated and uncoated substrate and an average value was reported in each case. Measurements of the indentation were carried out using image analysis. In the case of the substrate, only higher loads were employed to obtain its hardness.

A high temperature ball-on-disc tribometer (CSEM, Switzerland) was used to investigate the wear behaviour of the coated and uncoated samples. The static partners were alumina balls, 6 mm diameter, which were loaded with a normal force of 5 N.

Table 1. Elastic constants employed for the calculation of the Hertzian contact pressure.

Material	Young's modulus, E (GPa)	Poisson's constant, ν	Reference
Alumina ball	400	0.25	[14]
WC–6%Co-substrate	676	0.26	[15]
TiAlN coating	600	0.20	[16]

The Elastica 2.0.5 software package [13] was used for assessing the coating/substrate mechanical strength. The Hertzian maximum contact pressure is expressed as

$$p_0 = \left\{ \frac{6WE^{*2}}{R^2\pi^3} \right\} \tag{1}$$

where W is the normal load, R is the contact radius of the ball and E^* is the contact modulus given by

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} - \frac{1-\nu_2^2}{E_2}. \tag{2}$$

In equation (2), ν_1 and E_1 correspond to the Poisson's ratio and Young's modulus for the coating/substrate system, whereas ν_2 and E_2 correspond to the Poisson's ratio and Young's modulus of the static counterpart. Table 1 presents the elastic constants of the materials which were used to perform the calculations.

Values of 2 and 0.7 GPa were found for the Hertzian contact pressure and for the von Mises stress, respectively for the tribosystems under study.

Bouzakis *et al* [17], by applying finite element methods to the analysis of metal cutting processes, have reported equivalent von Mises stress values acting on the cutting edge of tools that are affected by the sharpness of the cutting edge and chip contact length. In typical alloy steel machining, these authors cite failures of coatings occurring at applied stresses of several GPa, at the coated cutting edge and smaller values for the flank. When VDI strip turning tests were carried out on a similar workpiece alloy, normal stresses of 0.5–1 GPa were reported [18], with effective friction coefficient values of 0.45–0.65. However, in industry, cutting forces depend on cutting speed, feed rate and depth of cut, as well as the workpiece material, so the values obtained in the laboratory wear tests could only be compared with the values obtained for a specific industrial system.

The tested specimen was rotated against the ball at a velocity of 0.1 m s^{-1} for 1000 m. The experiments were performed in air, without lubrication, at temperatures of 25, 500 and 700 °C respectively at a relative humidity of $60 \pm 5\%$.

When testing was complete, the material loss was evaluated by measuring the cross-sectional area of the wear scar on the coated discs by using a New View Zygo 200 optical profilometer, and the wear volume was calculated. The wear scar at the end of each test was studied by SEM coupled with quantitative energy dispersive x-ray analysis (EDX).

3. Results and discussion

The different structures of the $(\mathrm{Ti}_{1-x}\mathrm{Al}_x)\mathrm{N}$ coated samples on WC–6%Co were prepared for the tribological test. The surface average roughness of the hard metal substrates was $R_\mathrm{a} = 0.086 \pm 0.004\ \mu\mathrm{m}$. The Ti/Al atomic ratios, determined from the results of the EDX quantitative analysis, varied from 7/3 to 2/3, as shown in table 2. The highest percentage of Al corresponds to the single-layer coating which had approximately 60% Al, whereas the smallest value of 30% corresponds to the multilayer coating. According to earliest studies [19, 20], coatings of TiAlN with less than 70% Al have a NaCl cubic structure.
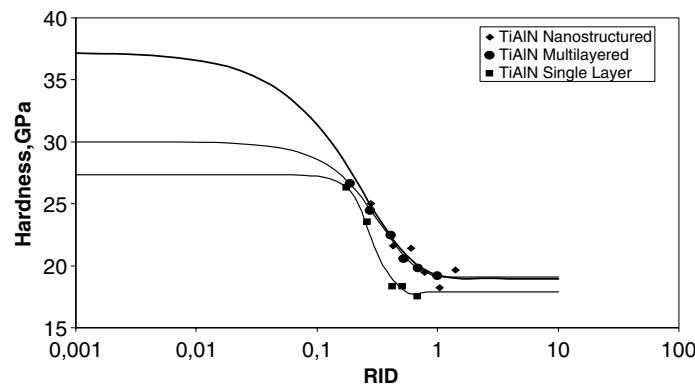
Figure 1. Change of the composite hardness with the relative indentation depth for all TiAlN coatings.

Table 2. Sample characteristics.

Sample	Structure	Ti/Al	Roughness R_a (μm)	Thickness (μm)
Substrate	WC–6%Co	—	0.09 ± 0.004	—
$Ti_{0.4}Al_{0.6}N$	Single layer	2/3	0.07 ± 0.011	3.1
$Ti_{0.6}Al_{0.4}N$	Nanostructured	3/2	0.12 ± 0.004	4.4
$Ti_{0.7}Al_{0.3}N/TiN$	Multilayered	7/3	0.09 ± 0.005	4.8

Results from the microhardness measurements, carried out for normal load values changing from 0.098 to 9.8 N, are shown in figure 1. This figure illustrates the change in the composite hardness, H, for three different systems as a function of the relative indentation depth, $\beta = d/7t$, according to the model advanced by Puchi Cabrera [21], which is expressed as

$$H = H_s + (H_c - H_s) \exp[-(\beta/\beta_0)^n] \qquad (3)$$

where d represents the indentation diagonal, t the coating thickness, H_s the substrate hardness, H_c the coating hardness and β_0 and n constants characteristic of the coating–substrate system. H_c, H_s, β_0 and n were determined simultaneously by using non-linear least square analysis. The substrate hardness, measured independently, was determined to be 18.8 GPa at 0.3 kgf.

Table 3 summarizes the hardness values obtained for the coatings, as well as the corresponding constants which are characteristic of the coating/substrate system. It can be observed that in the case of the $Ti_{0.6}Al_{0.4}N$ nanostructured coatings a higher value of H_c of 37.2 GPa is obtained, as expected, since it has been shown that an improvement in the mechanical properties can be achieved by grain refinement down to the nanometre length scale. In the case of the ($Ti_{0.7}Al_{0.3}N/TiN$) multilayered coatings, the calculated H_c value of 30 GPa was obtained, which is only 3 GPa higher than the H_c value determined for the single $Ti_{0.4}Al_{0.6}N$ coating.

It has to be recalled that the hardness values, as well as the Young's modulus, are a function of the Al concentration in the $Ti_{1-x}Al_xN$ [20], i.e. they both increase with the Al content until 50% Al and then drastically decrease due to the formation of a hexagonal wurtzite phase. In this case, the aluminium content in the single-layer coating could explain the decrease in the hardness value.

Table 3. Parameters from equation (1) derived from composite Vickers microhardness data.

Coating	H_c (GPa)	H_s	β_0	n
Single layer $Ti_{0.4}Al_{0.6}N$	27.3	18.0	0.31	3.72
Nanostructured $Ti_{0.6}Al_{0.4}N$	37.8	18.9	0.35	1.56
Multilayered $Ti_{0.7}Al_{0.3}N/TiN$	30.0	19.1	0.25	1.40

Table 4. Results from the sliding wear tests.

Sample		Test temperature		
		25 °C	500 °C	700 °C
Substrate	V (mm^3)	0.6×10^{-3}	1.6×10^{-3}	—
	μ_f	0.4	0.7	0.6
Single layer	V (mm^3)	12.5×10^{-3}	45.0×10^{-3}	20.5×10^{-3}
$Ti_{0.4}Al_{0.6}N$	μ_f	0.6	0.8	0.9
	S_{fd} (m)	180	—	250
Nanostructured	V (mm^3)	15.0×10^{-3}	—	16.0×10^{-3}
$(Ti_{0.6}Al_{0.4}N)$	μ_f	0.85	—	0.9
	S_{fd} (m)	550	—	195
Multilayered	V (mm^3)	18.0×10^{-3}	3.5×10^{-3}	19.5×10^{-3}
$(Ti_{0.7}Al_{0.3}N/TiN)$	μ_f	0.94	0.9	0.9
	S_{fd} (m)	800	—	50

The parameters n, associated with the slope of the curve, and β_0, associated with the position across the β axis, represent indicators of the degree of plastic deformation undergone by the substrate and the coating during indentation, respectively. Better coating–substrate systems would be characterized by low n and large β_0 values.

In the literature, hardness values of (TiAl)N coatings obtained by cathodic arc plasma deposition were reported as high as 29.4 GPa for an atomic ratio of Ti/Al of 1:1 [22]. Also, it was reported that superhard (TiAl)N film with two-phase nanocrystalline (nc-) TiAlN/amorphous (a-) AlN structure presented a hardness as high as 47 GPa [23], irrespective of the fact that both TiN and AlN alone have a considerably lower hardness of 21 and 12.3 GPa, respectively. Moreover, it was found that the hardnesses of $Ti_{1-x}Al_xN$ films strongly correlate with the film structure [24].

Table 4 shows the values obtained for the wear volumes, V, from the sliding wear tests for both the substrate and (TiAl)N coatings against an Al_2O_3 ball under a load of 5 N. Friction coefficient values of the end of the test, μ_f, are also reported. In some conditions, a sudden change in the friction coefficient values has taken place during the test as a result of the coating penetration and the exposure of the substrate. In these cases, the corresponding sliding distance (S_{fd}) is also indicated in the table as a measure of the film durability under the tested conditions. However, it has to be recalled that the coatings had a different thickness.

The friction coefficient obtained for the WC–6%Co substrate/Al_2O_3 ball pair at 500 °C was high, approximately 0.7, compared to the value of 0.4 corresponding to the friction coefficient at room temperature. At 500 °C, the samples showed a small amount of oxidation and the formation of a non-uniform thin grey oxide layer, which leads to a considerable amount of debris.

The morphology of the film is similar to that reported in previous studies [25], which were related to the oxidation of WC based hard metals in the temperature range of 500–600 °C.
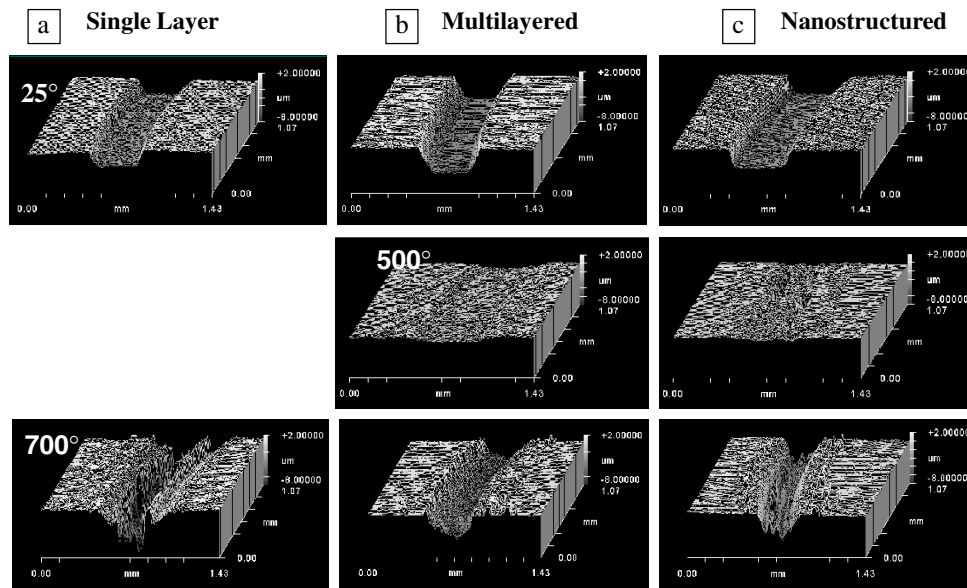
Figure 2. Wear track 3D profiles at different testing temperatures: (a) single-layer TiAlN; (b) multilayered TiAlN coating and (c) nanostructured TiAlN coating.

These studies have shown that the film produced during oxidation consisted mainly of $CoWO_4$ complex oxide and small amounts of both $WO_{2.9}$ and WO_3 oxides.

When testing was carried out at higher temperatures, the morphology of the scale formed changed and at a temperature of 700 °C the behaviour was completely different, i.e. the friction coefficient of WC–6%Co at the end of the test decreased to a value of 0.6. In this case, the samples presented on their entire surface a green cracked scale, which is a typical colour for the formation of a WO_3 oxide [25]. Due to this scale formation, it was impossible to determine the worn volume of the samples tested at this temperature.

On the other hand, the sliding wear results at 25 °C for the (TiAl)N coatings against the alumina ball indicated an abrasive wear mechanism, with a production of a high quantity of debris in the contact, which could be confirmed by the progressive wear loss of the material in the wear tracks, as shown in figure 2. At this temperature, the track depth has overcome the coating thickness for all the coatings.

The static counterparts (alumina balls) also showed a considerable abrasive wear loss as a consequence of the contact with a material of higher hardness. For all the tests conducted at room temperature, smooth flat ball wear scars were obtained, which contributed to the maintenance of a uniform contact stress with the formation of a wide wear track in the coated sample. The behaviour of the multilayered and nanostructured coatings was very similar at room temperature, presenting similar values for the friction coefficients at the end of the test, μ_f, and wear volumes, as shown in table 4. However, it has to be recalled that the single-layer coating had a thickness of more than 1 μm less than the other coatings.

When the test temperature was raised to 500 °C, the single-layer $Ti_{0.4}Al_{0.6}N$ coating wear volume measured by means of the profilometer was found to be markedly different in comparison with the wear volume of the multilayered and nanostructured coatings. When compared to the wear volume of the multilayered coatings, its value was almost one order of magnitude higher, whereas the nanostructured coatings showed no wear volume loss.
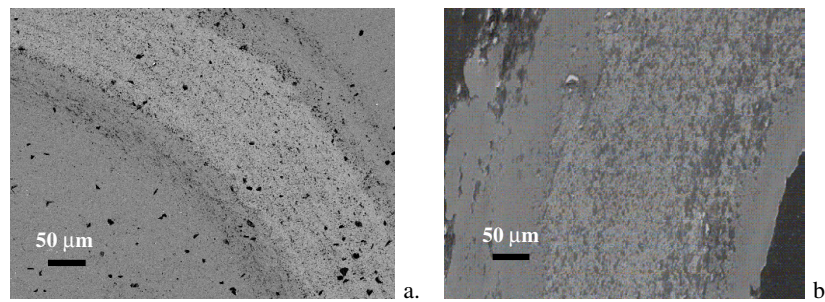
Figure 3. SEM micrographs (back-scattering mode) of the wear track at 500 °C: (a) multilayered coating; (b) single-layer coating, where a transferred layer is observed.
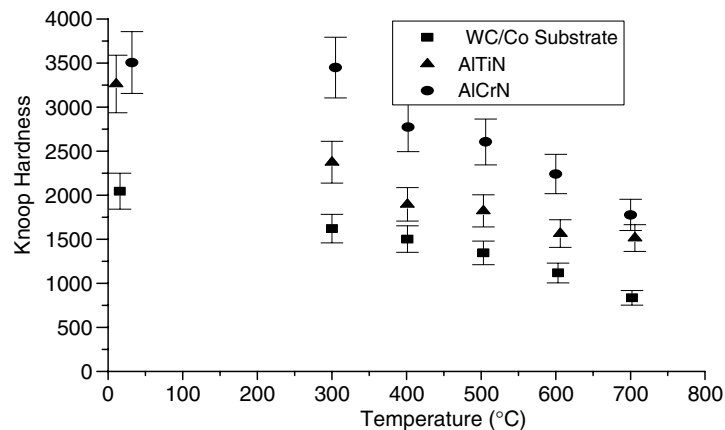

Figure 4. Hot microhardness measured under vacuum using a Nikon model QM high-temperature microhardness tester employing a high-temperature diamond Knoop indenter (information supplied by Balzers, Amherst, NY, USA).

This different performance of the single-layer coatings could, probably, be attributed to the elevated Al content of these coatings (more than 50%Al) in comparison with the other two. Similar studies have shown that the wear rate of (TiAl)N coatings increases with increasing Al content [25], as their hardness also decreases. During the test, a higher amount of material transfer occurs from the coating towards the ball and back (figure 3(b)).

Furthermore, the increase in the coating ductility at 500 °C could explain the increase in the friction coefficient value, where additional plastic work is required for a softer contact region. The behaviour of the single-layer coatings could be corroborated by analysing the results shown in figure 4, where the hot microhardness variation with temperature of WC/Co, AlTiN and AlCrN coated systems is presented.

These results, which have been obtained by measuring the hot hardness under vacuum using a Nikon model QM high-temperature microhardness tester employing a high-temperature diamond Knoop indenter, were supplied by Balzers, the coating manufacturers. From these experimental findings it seems that the single-layer AlTiN coating softens at a faster rate than the carbide substrate, so that the difference in coating/substrate microhardness is less at temperatures higher than 400 °C.

Studies conducted by means of SEM coupled with energy dispersive x ray analysis (EDS) of the nanostructured and multilayered coatings tested at 500 °C showed that inside the wear
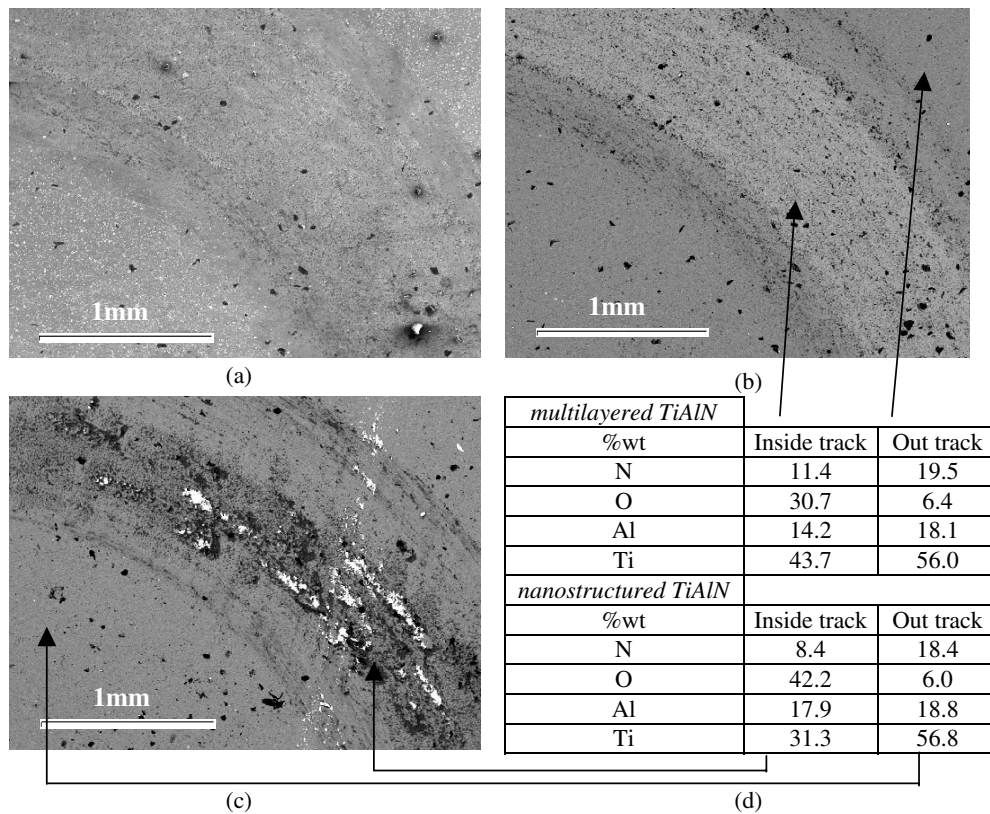
multilayered TiAlN		
%wt	Inside track	Out track
N	11.4	19.5
O	30.7	6.4
Al	14.2	18.1
Ti	43.7	56.0
nanostructured TiAlN		
%wt	Inside track	Out track
N	8.4	18.4
O	42.2	6.0
Al	17.9	18.8
Ti	31.3	56.8

Figure 5. SEM micrograph of samples tested at 500 °C: (a) multilayered coatings (secondary electron mode); (b) multilayered coating (back-scattering mode); (c) nanostructured coating (back-scattering mode) and (d) wt% of the multilayered and nanostructured coatings inside and outside the wear scar, respectively.

track there was an increase of the oxygen level in comparison with the outside region of the track, just as shown in figure 5. The exact nature of the oxide could not be found by means of this technique; however, due to the higher affinity of aluminium with oxygen, a layer of Al_xO_y or a mixture of Al_xO_y and Ti_xO_y could have been formed at this temperature according to their thermodynamic behaviour.

Vaz *et al* [8] used a Rutherford back-scattering spectroscopy (RBS) technique in order to determine the oxidation resistance of (TiAl)N coatings in air, at temperatures ranging from 500 to 900 °C. They showed that at 500 °C the RBS measurements revealed the formation of a homogeneous oxide layer composed of about 10 at.% of nitrogen and an Al/Ti ratio similar to that measured in the as-deposited sample, exhibiting a relatively sharp oxide–nitride interface. On the other hand, when the oxidation temperature increased, the nitrogen content started to disappear.

In our studies, the increase in the friction coefficient value and the low wear volume of these coatings at 500 °C suggest the formation of an oxide layer rich in Al inside the track. At this stage of the experiment, the analysis conducted by EDS revealed an oxide free surface of the samples outside the track and the presence of a higher amount of oxygen inside the wear track, accompanied by Al and Ti, indicating the formation of a mixture between Ti and Al oxides. Similar results were reported by Rebouta *et al* [3] where the samples oxidized at

600 °C in air showed a homogenous mixed oxide layer consisting of Al_2O_3 and TiO_2. On the other hand, Mclntyre *et al* [7] has also observed that the oxide layer on sputter deposited $Ti_{0.5}Al_{0.5}N$ coating consisted of a bi-layered structure of Al_2O_3 and TiO_2 at temperatures ranging between 750 and 900 °C. The growth rates of Al_2O_3 and TiO_2 were similar when TiAlN coatings were oxidized below 850 °C, whereas the morphology of the coatings determined the growth rates above 850 °C.

According to previous studies [26], the friction coefficient of α-alumina against itself is approximately 0.85 in the temperature range of 200–600 °C and this value corresponds to the friction coefficient determined during our wear tests conducted at 500 °C.

At 700 °C, the wear behaviour was similar for all the coatings. Further increase of temperature from 500 to 700 °C still does not induce detectable oxidation of the samples surface. However, in the wear track the rate of oxidation, additionally activated by friction, increases. The wear track showed a hard abrasive wear mode with deep grooves along it and with an appreciable quantity of debris accumulated outside it. In all cases, the depth of the wear tracks was higher than the coating thickness.

Another factor that can influence the wear behaviour of these coatings is the thermal softening of both (TiAl)N coatings and substrate. Softening of PVD coatings with temperature is well known [27], and it has been attributed to the relaxation of residual stresses as well as grain boundary sliding in very fine-grained materials. EDS analysis of the wear debris generated at 700 °C showed the presence of mostly W and O and minor quantities of Ti and Al, which could explain the drop in the value of the friction coefficients. Similar results were reported by Han *et al* [3], who conducted wear tests based on a ball-on-disc method, on (TiAl)N coated M2 steels in the temperature range of 400–600 °C. A smaller wear volume was found at temperature in the range of 400–500 °C, where the wear resistance was 20 times higher than at 600 °C.

4. Conclusions

The high temperature wear performance of three $(Ti_{1-x}Al_x)N$ hard coatings deposited on WC–6%Co inserts by the PVD cathodic arc process has been presented.

The sliding tests carried out at 25 °C indicated that a wear volume, V, of approximately 10^{-2} mm^3 was obtained for all the tested coatings. However, when the test temperature was increased to 500 °C, the single-layered coatings presented a wear volume of the same order of magnitude as those tested at room temperature. The multilayered coated samples decreased their wear volume by one order of magnitude, whereas the nanostructured coated samples showed almost no wear. At 700 °C, the wear volume values reported for all samples were similar and of the same order of magnitude as those tested at room temperature.

Also, the crucial role of both the oxide formation during the wear tests from room temperature up to 700 °C and the coating and substrate softening process, which becomes dominant as the temperature increases, explaining the abrasive damage produced on the coated systems, has been shown.

Acknowledgments

References

[1] Lee S H, Ryoo H-J and Lee J-J 1994 *J. Vac. Sci. Technol.* A **12** 1602
[2] Mencer D E Jr, Hess T R and Mebrahtu T 1991 *J. Vac. Sci. Technol.* A **9** 1610

[3] Rebouta L, Vaz F, Andritschky M and da Silva M F 1995 *Surf. Coat. Technol.* **76/77** 70–4

[4] Komanduri R 1989 *Int. J. Refract. Metal. Hard Mater.* **8** 125

[5] Gu J, Barder G, Tung S and Gu R-J 1999 *Wear* **225/229** 273–84

[6] Stock H R, Schulz A, Kopnarski M and Gross T 1998 *Surf. Coat. Technol.* **98** 918–24

[7] Mclntyre D, Greene J E, Hakansson G, Sundgren J E and Munz W D 1990 *J. Appl. Phys.* **67** 1542–53

[8] Vaz F, Rebouta L, Andritschky M, da Silva M F and Soares J C 1998 *Surf. Coat. Technol.* **98** 912–7

[9] Sun Y and Bell T 1998 *Wear* **218** 34–42

[10] Kutschej K, Mayrhofer P H, Kathrein M, Polcik P and Mitterer C 2004 *Surf. Coat. Technol.* **188/189** 358–63

[11] Martín A, Rodríguez J, Fernández J E and Vijande R 2001 *Wear* **251** 1017–22

[12] Badisch E, Stoiber M, Fontalvo G A and Mitterer C 2003 *Surf Coat. Technol.* **174/175** 450–4

[13] Chudoba T, Schwarzer N and Richter F 1999 *Thin Solid Films* **355/356** 284–9

[14] Munro R G 1997 *J. Am. Ceram. Soc.* **80** 1919–28

[15] Roberts S G, Lawrence C W and Bisrat Y 1999 *J. Am. Ceram. Soc.* **82** 1809–16

[16] Hörling A, Hultman L, Odén M, Sjölén J and Karlsson L 2005 *Surf. Coat. Technol.* **191** 384–92

[17] Bouzakis K D, Michailidis N, Skordaris G, Kombogiannis S, Hadjiyiannis S, Efstathiou K, Pavlidou E, Erkens G, Rambadt S and Wirth I 2003 *Surf. Coat. Technol.* **163/164** 625–30

[18] Klocke F, Krieg T, Gerschwiler K, Fritsch R, Zinkmann V, Pöhls M and Eisenblätter G 1998 Improved cutting processes with adapted coating systems *Ann. CIRP* **47/1** 69–72

[19] Zhou M, Makino Y, Nose M and Nogi K 1999 *Thin Solid Films* **339** 203–8

[20] Kimura A, Hasegawa H, Yamada K and Suzuki T 2000 *J. Mater. Sci. Lett.* **19** 601–2

[21] Puchi Cabrera E S 2002 *Surf. Coat. Technol.* **160** 109–13

[22] Holleck H 1999 *J. Vac. Sci. Technol.* A **17** 2401–20

[23] Musil J and Hruby H 2000 *Thin Solid Films* **365** 104–9

[24] Navinsek B, Panjan P, Cekada M and Quinto D T 2002 *Surf. Coat. Technol.* **154** 194–203

[25] Vancoille E, Celis J P and Roos J R 1993 *Wear* **165** 41–9

[26] Dong X, Jahanmir S and Hsu S M 1991 *J. Am. Ceram. Soc.* **74** 1036–44

[27] Quinto D T, Wolfe G J and Jindal P C 1987 *Thin Solid Films* **153** 19–36