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Characterization Using XPS and XRD of Ti(C,N) Coating Properties for Cutting Tool Applications

ABSTRACT

The properties of titanium carbonitride (TiCN) are a result of its composition, which can be adjusted by controlling the material's C-N ratio to a precise level. An experimental study was conducted to vary the composition and properties of TiCN. The substrate used for cathodic arc physical vapour deposition (CAPVD) was tungsten carbide (WC-6Co), which was prepared in-house by a powder metallurgy process. Pure titanium (Ti) was used as a cathode and source of Ti. Methane (CH₄) and nitrogen

(N₂) gases were used as sources of C and N to form the Ti(C,N) coating applied in the CAPVD process. Tests showed that the composition and properties of Ti(C,N) were successfully varied by controlling the CH₄-N₂ ratio. The surface microhardness of coated carbide samples improved and the coefficient of friction declined as the carbon content incorporated within the Ti(C,N) coating increased.

1. Introduction

A hard thin layer deposited on a cutting tool can improve its wear resistance and prolong tool life. Worldwide, more than half of metal cutting tools are coated [1–3]. For over 30 years, the most popular coating materials have been hard films, such as titanium nitride (TiN) and diamond-like carbon (DLC). These films provide high hardness and low friction to resist wear, thus increasing tool life [4]. Despite differences in coating material properties, the coating chosen for any application is highly dependent on the purpose and desired characteristics of the tool. If the selection of a coating is incorrect, the life of a coated tool could actually be shorter than that of an uncoated tool [4].

TiN is a popular gold-colour coating that is applied on high-speed steel and carbide cutting tools [5, 6]. TiN is the first-generation hard coating for carbide tools that used physical vapour deposition (PVD) [7]. TiN possesses useful properties, such as high hardness, strength, chemical stability and adhesivity on carbide substrates, and low coefficient of friction with excellent resistance to built-upedge (BUE) formation [8, 2, 6]. Thus, TiN coating improves wear resistance and prolongs the lifespan of high-speed steel and carbide cutting tools, particularly at extreme cutting speeds and feed rates [8, 2, 6]. However, TiN does not provide a barrier to diffusion wear when it cuts against stainless steel despite acting as a heat barrier [9]. Moreover, TiN and DLC protective films employed in high temperature applications or high-speed machining suffer from severe damage because of poor resistance to high temperature oxidation. Oxidised films are brittle in nature and easily fracture. Fractured oxidised films cannot provide protection for the substrate and alter tool geometry. These effects result in drastic reduction of the life of the coated tool [4].

Inclusion of carbon atoms in the TiN lattice substantially increases a film's hardness and lowers its friction coefficient. TiCN (titanium carbonitride) has high chemical stability and superior mechanical properties, such as low friction coefficient, excellent wear resistance, and high elec-

trical conductivity, hardness (HV 2500–3000), toughness, and melting point (3,050 °C) [8, 10, 11]. Researchers report that TiCN is a solid solution for TiC and TiN which takes on the excellent characteristics of both face-centred cubic (FCC) materials [11, 12, 10]. Thus, TiCN has better anti-wear capabilities and higher hardness than either TiN and TiC [13, 11, 8, 14, 2, 15, 12], which allow it to replace conventional TiN in cutting tools and cold forming applications [12].

The properties of TiCN can be tailored by controlling its composition through changes to the C-N ratio. Cheng et al. found that the CH₄ fraction has significant effects on the composition and properties of TiCN when it is produced by the large area filtered arc deposition (LAFAD) technique [10]. Narasimhan et al. improved the hardness, wear resistance and surface smoothness (surface properties) of TiCN coating by providing a carbon-rich top layer [8].

In this study, the composition and bonding structure of in-house deposited Ti(C,N) coatings were characterized using XRD and XPS to assess the effect of variations in the C-N ratio. Ball on disc and microhardness tests measured the coefficient of friction and surface microhardness of the deposited coatings.

2. Methodology

Coating deposition was done with the Hauzer Techno Coating (HTC) 625/2 ARC system. All substrates used in the study were 14 × 14 × 3 mm WC-6Co tungsten carbides, which were prepared in-house through a powder metallurgy process [16]. The substrates were cleaned ultrasonically in isopropanol for 15 minutes prior to the 2 hour cathodic arc physical vapour deposition (CAPVD) process (Fig. 1 [17]). 99.9 % purity titanium (Ti) target was used as a cathode. The reactor chamber was evacuated to ~0.0001 Pa (10⁻⁶ mbar). The substrates were then heated up to the 300 °C deposition temperature and etched via ion bombardment for 10 minutes before methane (CH₄) and nitrogen (N₂) gases were introduced into the chamber. The ion bombardment was performed to remove any contamination on the surface of the tungsten carbide and increase the adhesive strength between coating and substrate [18]. The arc current of the cathode was maintained at 100 A throughout the process, while the substrate bias was set at 1000 V during ion bombardment and 50 V during coating deposition. The deposition process was carried out in residual pressure with range 0.1–0.01 Pa (10⁻³–10⁻⁴ mbar). The ratios of CH₄-N₂ used in the deposition process are summarised in Table 1.

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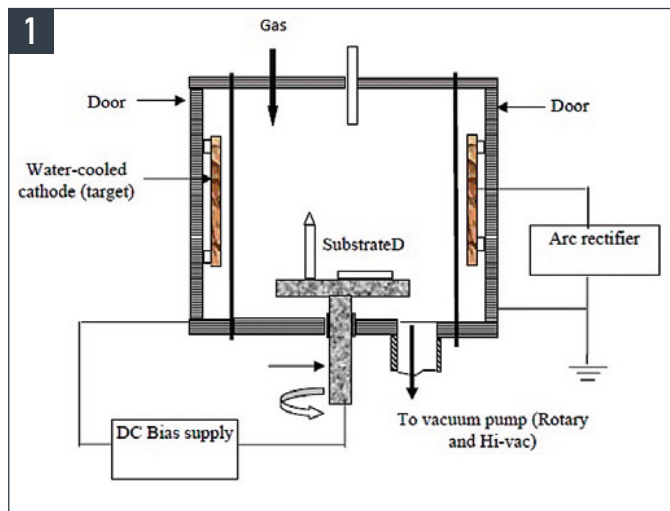


Fig. 1 • Schematic diagram of CAPVD processing

Uncoated carbide sample (H1) was included to allow comparisons with the mechanical properties of the TiCN coatings. Our previous studies and cross-sectional examinations revealed that the growth rate of the coating was approximately 0.75 μm/hour (Fig. 2).

The composition, bonding structure and amount of each element present within a coating are functions of the CH₄-N₂ ratio. These properties were characterized using a Bruker D8 X-ray diffractor (XRD) and an Omicron DAR 400 X-ray photoelectron spectroscope (XPS). The source for XRD was Cu-K_α with a wavelength of 0.15406 nm, while the source for XPS was Al-K_α with 1486.7 eV and a wavelength of 0.83386 nm.

The surface roughness of the samples was measured with a Shimadzu SPM 9500 J2 scanning probe microscope. The coefficient of friction of the samples was evaluated by ball on disc tests performed with a CSEM tribometer. During the test, an uncoated 6 mm 100 Cr6 chrome steel ball was dry-turned on the samples at 10 cm/s for 1,000 m under 10 N normal loads with a turning radius of 4 mm. The surface microhardness of coatings was determined by an AFFRI microhardness tester at 50 gf.

3. Results and discussion

During CAPVD, high cathodic arc current passes through the Ti target, causing it to vaporise and discharge a large amount of highenergy Ti⁺ ions and electrons. CH₄ and N₂ gases in the deposition chamber are ionised by the electrons, which generates reactive CH_xⁿ⁺ and N⁺ ions. Reactions among Ti⁺, CH_xⁿ⁺, and N⁺ ions create three possible Ti-coatings: TiC, TiN, and TiCN (Equation 1), which are then deposited on the surface of the substrate. Moreover, CH₄ is ionised to form CH_xⁿ⁺ and H⁺ (Equation 2). H⁺ ions may diffuse and combine with each other to form H₂ [10] or incorporate with titanium to form titanium hydride [19].

CH ₄ -N ₂ ratio	Coating
0.04	TiCN1
1	TiCN2
2	TiCN3
Uncoated	H1



Fig. 2 • Cross-section of the coating after 2 hours of deposition

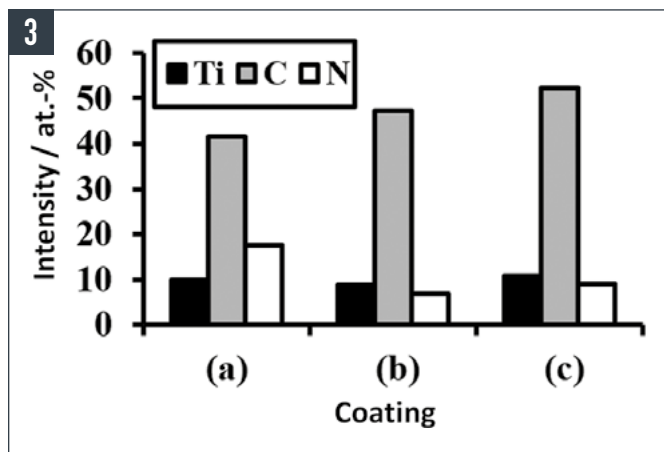
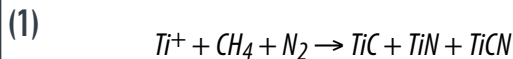


Fig. 3 • Intensities of Ti, C and N in coating (a) TiCN1, (b) TiCN2 and (c) TiCN3



XPS and XRD characterized the bonding structure and composition of the coatings. Different intensities of Ti, C, and N were observed in the deposited Ti(C,N) coatings with different CH₄-N₂ ratios (Fig. 3). The intensities of C, N, and Ti for ratio 0.04 (TiCN1) were 41.44, 17.50, and 9.99 atom-% (relative atomic percentage), respectively. Increasing the CH₄-N₂ ratio to 1 (TiCN2) increased the percentage of C to 47.24 atom-%, but decreased N and Ti to 6.80 and 8.77 atom-%. A further increase of the CH₄-N₂ ratio to 2 (TiCN3) resulted in C, N, and Ti values of 52.19, 9.06, and 10.84 atom-%. The initial increase in CH₄-N₂ ratio produced more CH_xⁿ⁺ but less N⁺, which led to more C and less N being incorporated into the deposited coating. However, the deposition with CH₄-N₂ ratio 2 resulted in increases of intensity for C, N and Ti compared to the sample with ratio 1. Adding more CH₄ into the chamber promoted the reactivity of the ions and resulted in more C and N atoms in the coating. In contrast, Cheng et al. found that adding more CH₄ gas into the chamber decreased the reactivity of ions in the plasma, which resulted in the incorporation of fewer C and N atoms into TiCN coatings when they were applied via LAFAD [10].

Figure 4 shows the Ti 2p, C 1s, and N 1s XPS spectra of the deposited coatings. The XPS spectra of Ti 2p for TiCN1 showed two main peaks at 457.8 and 462.09 eV and a shoulder peak at 455.36 eV. The peak at 457.8 eV was attributed to 2p_{3/2} splitting from an intermediate phase of Ti₂O₃, while the shoulder peak at 455.36 eV was attributed to 2p splitting as-

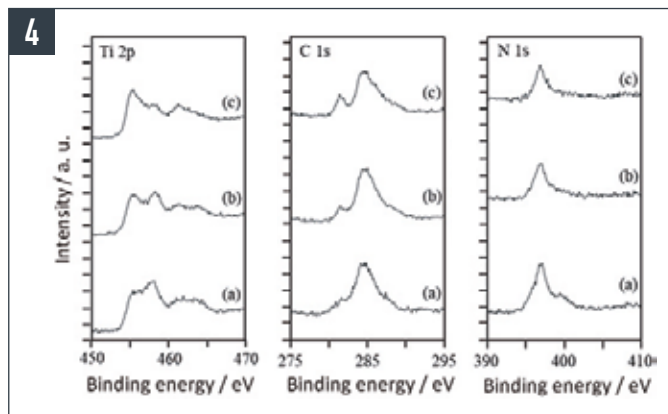


Fig. 4 • XPS spectra for Ti 2p, C 1s, and N 1s: (a) TiCN1, (b) TiCN2, and (c) TiCN3

sociated with the TiN and $2p_{3/2}$ splitting from intermediate phases such as TiO. The other main peak at 462.09 eV was attributed to $2p_{1/2}$ splitting from an intermediate phase such as Ti_2O_3 . TiCN2 showed three main peaks at 455.30, 458.37 and 461.05 eV, and a shoulder peak at 463.60 eV. The peaks at 455.30 and 458.37 eV were attributed to 2p and $2p_{3/2}$ splitting, respectively. These values correspond to TiN and other intermediate phases such as TiO_2 .

The last main peak at 461.05 eV and its shoulder peak at 463.60 eV were attributed to $2p_{1/2}$ splitting, related to TiN and intermediate phases of Ti_2O_3 . Finally, TiCN3 exhibited two main peaks at 455.4 and 461.16 eV, and a shoulder peak at 458.18 eV. The peak at 455.4 eV was attributed to 2p and $2p_{3/2}$ splitting associated with TiN and TiC. The shoulder peak at 458.18 eV came from 2p and $2p_{3/2}$ splitting, corresponding to an intermediate phase of TiO_2 . The other main peak at 461.16 eV was attributed to $2p_{1/2}$ splitting, linked to TiN and intermediate phases of Ti_2O_3 .

All N 1s spectra exhibited slightly symmetrical main peaks at 396.9 to 397.2 eV and shoulder peaks from 399.26 to 399.30 eV. The main peaks showed the existence of N-Ti and N-C bonds, while the shoulder peaks confirm the presence of N-C, N-C-H, N-H, and N-O bonds. The C 1s spectra similarly exhibited fairly symmetrical main peaks from 284.55 to 284.96 eV and shoulder peaks from 281.40 to 281.51 eV across all samples. The main peaks reflect C-C, C-N, C-H, C-H-O, and C-H-N bonds and the shoulder peaks reveal the existence of C-Ti bonds.

Overall, the XPS results indicated the presence of Ti-N, Ti-C, Ti-O, C-C, C-N, C-H-N, C-H and N-H bonds in the deposited TiCN coatings. Unfortunately, the exact binding energy and bonding structure of Ti-C-N is undetermined [20]. However, TiCN was believed to have been successfully manufactured.

As a next step, XRD was used to characterize the composition and crystalline structure of the deposited coatings (Fig. 5). Five peaks corresponding to the (111), (200), (220), (311) and (222) TiN planes were observed in the XRD patterns. The highest intensity TiN (111) peak indicates that all the Ti(C,N) coatings grew preferentially along the (111) orientation.

TiCN1 was an FCC $TiC_{0.2}N_{0.8}$ coating, but TiN was also present within deposited TiCN1. This result may be due to the high N content in the chamber. Ti^+ ions react easily with N^+ ions to form TiN coating. TiN is a stronger and more stable structure than TiCN, because the lattice parameters and atomic distances of TiCN are larger than for TiN. Moreover, TiN (osbornite) exists naturally. The larger size of C atoms compared to N atoms causes a distortion of the lattice [10]. Therefore, residual C content can form amorphous carbon within the deposited TiCN1 coating. This ex-

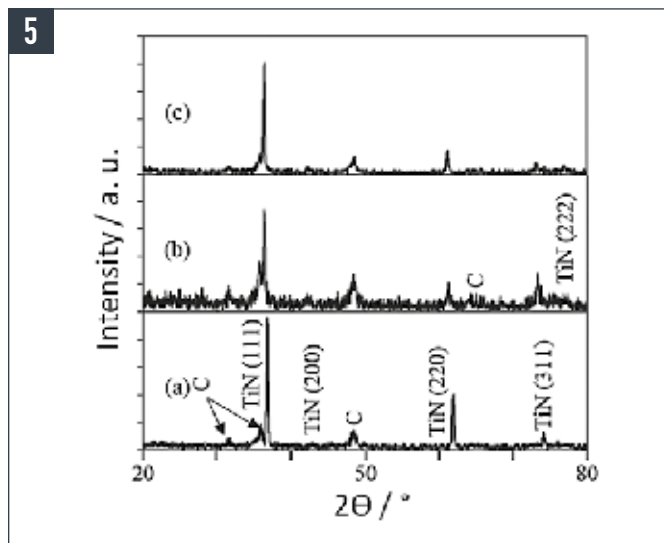


Fig. 5 • XRD patterns of (a) TiCN1, (b) TiCN2, and (c) TiCN3

plains why amorphous carbon was observed in the XRD pattern of TiCN1 even though only a small amount of C (0.04 CH_4-N_2 ratio) was added to the chamber (Fig. 5 a). Although amorphous carbon was detected and XPS showed a C-Ti bond, no diffraction peaks originating from TiC phases were observed in the XRD pattern of TiCN1. The C-Ti bond shown in the XPS results may be due to C-Ti bonding in TiCN.

The XRD pattern of TiCN2 (Fig. 5 b) showed that deposited TiCN2 still grew preferentially along the (111) orientation, despite the increase in CH_4-N_2 ratio from 0.04 to 1. The TiN (220) peak had reduced intensity but the magnitude of the (200), (222), and (311) peaks increased. This finding indicates slight adjustments in favoured orientation from (220) to (200), (222) and (311), with preferential growth of deposited TiCN2 along the (111) orientation. It reveals that TiCN2 was an FCC $TiC_{0.3}N_{0.7}$ coating, which is consistent with the XPS result that the C content and intensity increased and N decreased as the CH_4-N_2 ratio increased from 0.04 to 1. A small amount of TiC was observed within TiCN2 by XPS and XRD. Due to decreased Ti intensity, the remaining C formed amorphous carbon within the deposited TiCN2 coating, which caused more carbon peaks to be observed in the XRD pattern.

The XRD pattern of TiCN3 (Fig. 5 c) shows very low intensities of the TiN (200), (220), (311) and (222) peaks compared to the (111) peak. The deposited TiCN3 coating still grew preferentially along the (111) orientation, similar to the other two deposited Ti(C,N) coatings. The XRD pattern reveals that the deposited TiCN3 was an FCC $TiC_{0.7}N_{0.3}$ coating. The carbon content in the deposited coating increased as the CH_4-N_2 ratio went up from 1 to 2. A small amount of amorphous nitrogen was found in the XRD pattern of TiCN3, which explains the larger N content in the XPS result. As with the TiCN2 coating, amorphous carbon and TiC were also observed in TiCN3.

With increased carbon content in the coating, there is a decrease in the amount of Ti-N bonding and an increase of Ti-C and C-N bonding in the coatings. The shoulder peak accounts for only a small fraction of the total C 1s spectra compared to the first peak, indicating that only a small fraction of C atoms bond to Ti atoms and most of the C atoms exist as amorphous carbon. Some C-C bonds also originate from adventitious carbon [21, 10]. The fact that amorphous carbon increases with increasing C content will significantly affect the coating's mechanical and wear properties. These findings are in agreement with other studies [21, 10].

Table 2 · Results of the mechanical properties tests

Tests	Inserts			
	TiCN1	TiCN2	TiCN3	H1
Coefficient of friction / μ_t	0.49	0.46	0.45	0.90
Microhardness / 0.05 HV	2650	2800	2900	1600
Surface roughness, R_a / nm	103.89	124.79	100.17	53.56

Table 2 shows the surface roughness, coefficient of friction, and surface microhardness of the samples. The uncoated carbide sample (H1) had a higher friction coefficient, despite having lower surface roughness than the coated carbide samples. TiCN3 had the lowest coefficient of friction among the deposited Ti(C,N) coatings. The results showed CAPVD-coated Ti(C,N) significantly reduces the coefficient of friction by 45 % to 50 %, an indication that the coating could enhance surface lubricity of cutting tool inserts and reduce friction wear.

The coefficient of friction of the deposited Ti(C,N) coatings declined as the carbon content incorporated within the Ti(C,N) coating went up. TiCN3's lowest coefficient of friction was mainly due to the higher carbon content incorporated within its coating. The coefficient of friction of TiCN2 was reduced by 6 % from 0.49 to 0.46 when the C content formulaically increased by 0.1, from $TiC_{0.2}N_{0.8}$ of TiCN1 to $TiC_{0.3}N_{0.7}$ of TiCN2, although surface roughness increased from 103.89 to 124.79 nm. The coefficient of friction of TiCN3 was reduced by a further 2 % to 0.45 as the carbon in the formula increased by 0.4, from $TiC_{0.3}N_{0.7}$ of TiCN2 to $TiC_{0.7}N_{0.3}$ of TiCN3. This was accompanied by a decrease in surface roughness to 100.17 nm. The uncoated sample (H1) had the lowest surface roughness of 53.56 nm but the highest coefficient of friction of 0.90. Since surface roughness had no apparent influence on reducing friction, the coefficient of friction of the coatings was therefore strongly dependent on surface lubricity rather than on the surface roughness of the coating material.

Ti(C,N) coatings were proven to increase the surface microhardness of cutting tool inserts because the surface microhardness of the carbide substrate samples increased by 65 to 81 % when they were CAPVD-coated with a thin layer of Ti(C,N). Among the in-house deposited Ti(C,N) coatings, TiCN3 had the hardest surface, followed by TiCN2 and lastly TiCN1. The surface microhardness of the Ti(C,N) coatings increased with the amount of carbon incorporated within the material. The 0.1 C increase from $TiC_{0.2}N_{0.8}$ of TiCN1 to $TiC_{0.3}N_{0.7}$ of TiCN2 improved the surface microhardness by 5 %, from 0.05 HV2650 to 0.05 HV2800. However, the surface hardness of TiCN3 was 0.05 HV2900, only slightly higher than TiCN2. Increasing the C content to $TiC_{0.7}N_{0.3}$ of TiCN3 did not increase the hardness of the film significantly. This result may be due to the formation of a large amount of TiC and amorphous carbon within the TiCN3 coating. Similarly, the low surface microhardness of TiCN1 may be a result of the TiN formed within the coating. Several researchers have reported that TiCN had higher surface microhardness and better wear resistance than TiN and TiC [13, 11, 8, 14, 2, 15, 12].

4. Conclusions

1 The composition of TiCN was successfully varied by controlling the CH_4-N_2 ratio applied in CAPVD coating. XRD results showed that TiCN1 was structurally $TiC_{0.2}N_{0.8}$, TiCN2 was $TiC_{0.3}N_{0.7}$, and TiCN3 was $TiC_{0.7}N_{0.3}$. As the CH_4-N_2 ratio increased, the content of C incorporated within the deposited Ti(C,N) coatings increased and the N content decreased.

2 TiN (111) was the preferred growth orientation for all the deposited Ti(C,N) coatings. Amorphous carbon and TiC were present in both the TiCN2 and TiCN3 coatings and a small amount of amorphous nitrogen was traced in TiCN3. The amount of amorphous carbon and TiC increased with increases of C content and CH_4-N_2 ratio.

3 The Ti 2p spectra of coatings contained peaks at various eV values. These peaks corresponded to the TiN and TiC phases and other intermediate phases, such as TiO_2 and Ti_2O_3 . Peaks occurring below 460 eV were attributed to 2p or $2p_{2/3}$ splitting and peaks above 460 eV were associated with $2p_{1/2}$ splitting.

4 Ti(C,N) coating could enhance the surface lubricity of carbide cutting tool inserts. It can significantly lower the coefficient of friction, by a factor of 45 to 50 %, and increase surface microhardness from 65 to 81 %. As the carbon content incorporated within deposited Ti(C,N) coating increases, surface microhardness improves and coefficient of friction decreases. Moreover, the coefficient of friction of a Ti(C,N) coating strongly depends on its lubricity rather than its surface roughness.

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