Deposition and characterization of Ti-Al-C-N coatings

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Abstract. In the present work, Ti-Al-C-N coatings were deposited on cemented carbide substrates by lateral rotating cathodes (LARC\(^\circ\)) process using Platit π\(^{00}\)+DLC deposition unit. The effect of C\(_2\)H\(_2\) gas flow rate on elemental and phase composition, deposition rate, cross-sectional and surface morphology, mechanical and tribological properties of the coatings was studied. Following analytical techniques, namely: scanning electron microscopy (SEM) with energy and wave dispersive X-ray spectroscopy (EDS and WDS), X-ray diffraction analysis (XRD), nanoindentation measurements, Rockwell C indentation test and tribological testing were used for Ti-Al-C-N coatings evaluation. From the EDS analysis, it was found that the carbon content in the coatings increased from 0 at. % to 22.3 at. % as the C\(_2\)H\(_2\) gas flow rate increased from 0 sccm to 75 sccm. The increase in deposition rate of coatings from 0.029 \(\mu\)m/min to 0.052 \(\mu\)m/min was documented. From XRD results it was found that the coatings consist of a cubic B1-NaCl type Ti\(_1\)N\(_{0.9}\) phase. The maximum hardness was observed at C\(_2\)H\(_2\) gas flow rate of 25 sccm and the lowest friction coefficient (0.35) at the maximum C\(_2\)H\(_2\) gas flow rate. The coatings deposited at C\(_2\)H\(_2\) gas flow rates (25 sccm and 50 sccm) exhibited an excellent adhesion.

1. Introduction

Currently, hard coatings fabricated by methods of physical vapor deposition (PVD) have been strongly used to improve properties of various kinds of engineering materials and are now widely employed in numerous technical fields [1-4]. Hard coatings are characterized by excellent mechanical properties, such as high hardness, wear resistance and thermal stability [5-8]. Titanium Nitride (TiN) coatings belong to the group of the most common used PVD hard coatings today [9,10]. However, one of the major drawbacks of TiN coatings is their limited oxidation resistance (up to 500 °C) [3]. This problem has been solved by incorporation of aluminium in the cubic NaCl-type TiN matrix, which leads to creation of the Ti-Al-N metastable solid solution [11-15]. Depending on the Al content, the supersaturated Ti-Al-N phase decompose (~800 °C) via spinodal decomposition into two phases: fcc-TiN and fcc-AlN [16-18]. In addition, some researchers has shown an enhancement of tribological and mechanical properties by the addition of carbon to Ti-Al-N coatings [19-21]. Stueber et al. deposited using reactive magnetron sputtering series of Ti-Al-C-N coatings with different carbon contents (0-28 at. %). It resulted to deposition of nanocomposite coatings with a structure of a metastable hard
nanocrystalline fcc-TiAlCN phase embedded in an amorphous carbon matrix (a-C) [22]. In the work of Lackner et al., Ti-Al-N and Ti-Al-C-N coatings were fabricated by employing the pulsed laser deposition (PLD) technique. They found that the variation of the deposition parameters had caused a change of the chemical composition, the texture and the crystallinity of the coatings and, consequently, the mechanical properties and tribological behaviour, which was characterized by pin-on-disc test. The results proved the excellent industrial applicability of these coatings for cold-forming operations. Very low-wear rates were found for the Ti-Al-N coatings. In contrast, the Ti-Al-C-N coatings possessed low-friction coefficients of approximately 0.2 [21]. The effect of magnetic filtering on morphology, surface roughness, chemical composition, adhesion and corrosion resistance of Ti-Al-C-N coatings during a filtered cathodic arc deposition (FCAD) was investigated by Hsu et. al. Despite of the deposition rate of the filtered Ti-Al-C-N coating was slower compared to the unfiltered one, the former had a relatively denser structure, smoother surface and exhibited better adhesion. In addition, both coatings improved the corrosion resistance of DC53 steel in 3.5 wt.% NaCl solution. Particularly, filtered Ti-Al-C-N coating offered more effective corrosion protection than unfiltered Ti-Al-C-N [23]. Al-Bukhaiti et al. used the magnetron sputtering for a deposition of Ti-Al-C-N coatings in the form of multilayers consisted of Ti/Ti-Al-N/Ti-Al-C-N nanoscale layers. The tribological performance of the coatings was studied by a ball-on-disk test against 100Cr6 steel and Al2O3 balls. Results showed that the deposited coatings were characterized by low wear rates of 10^{-15} m^3/Nm, low friction coefficients in the range of 0.25-0.37 and satisfactory hardness in the range of 17-20 GPa [24].

In this study, Ti-Al-C-N coatings with different C2H2 gas flow rates were deposited by lateral rotating cathodes method (LARC®). The influence of C2H2 gas flow rate on microstructure, morphology, chemical and phase composition, nanoindentation hardness, adhesion and tribological properties of Ti-Al-C-N coatings was studied.

2. Experimental details

2.1. Deposition

PLATIT π80+DLC deposition unit that uses technology of lateral rotating cathodes arc (LARC®) was utilized for depositions of Ti-Al-C-N coatings. The LARC® technique has two major advantages over the conventional planar vacuum arc deposition systems. The first advantage comes from the unique design and positioning of cylindrical cathodes, which results in a maximum effective cathode surface and longer cathode lifetime. The second advantage comes from the Virtual Shutter function, which makes it possible for in situ cathode cleaning before coating deposition without a plasma interruption. This two features result in superior adhesion and smooth, droplet free surfaces of the as-deposited coatings [25]. Mirror polished tungsten carbide disks (WC-10 wt.% Co) of 12 mm in diameter were used as substrates. Prior to the depositions, the substrates were ultrasonically cleaned in acetone, dried in a hot air and mounted onto a rotational substrate holder. The deposition chamber was pumped down to a pressure of 10^{-2} Pa by using rotary and turbomolecular pumps and heated up to the temperature of 470°C. The substrates were cleaned by Ar⁺ glow discharge and then, a thin TiN layer was deposited in order to improve the coatings adhesion before the deposition. The constant deposition parameters were following: Ti cathode current 132 A, Al cathode current 95 A, substrate bias −90 V, substrate holder rotation 12 rpm and N2 gas flow rate 100 sccm. C2H2 gas flow rate was varied from 0 to 75 sccm in order to adjust the carbon content in the coatings. The influence of C2H2 gas flow rate and thus carbon content in the coatings on their chemical and phase composition and mechanical and tribological properties was evaluated. Deposition time (90 min.) was the same for all deposition cycles.

2.2. Characterization

The elemental composition of the Ti-Al-C-N coatings was simultaneously measured with INCA X-Max 50 mm² energy dispersive X-ray spectrometer to determine heavier elements (Ti and Al) and INCA Wave wave energy dispersive spectrometer (light elements C and N), both manufactured by Oxford Instruments Company. The fracture areas, surface morphologies and indents after Rockwell C indentation test were observed by JEOL JSM 7600F high resolution scanning electron microscope in
secondary electrons imaging mode. Parameters during observation were following: $U = 20$ keV, $I = 2$ nA and $WD = 15$ mm. Identification of phases present in the deposited coatings was performed by X-ray diffraction analysis using an Empyrean diffractometer from Panalytical Company with a CoK$_\alpha$ anode ($\lambda = 0.178897$ nm). The analysis was carried out in Bragg-Brentano geometry. The parameters for the Co anode used during the measurement were following: $U = 40$ kV, $I = 40$ mA, angular interval 20-130° 2θ and step size 0.026° 2θ. Nanoindentation measurements were performed using Anton Paar NHT2 device with Berkovich diamond indenter. The load was gradually increased to 20 mN at a loading rate of 60 mN/min and was held at the maximum value for 5 s. Continuous stiffness method was employed to assure that the indentation depth was within the 5-10% of the coating thickness. The indentation curves were processed with Oliver & Pharr method. The average friction coefficient was measured using ball-on-disc sliding test with a Bruker UMT TriboLab device. Tungsten carbide balls with diameter of 6.3 mm were used as a counterpart material. The sliding tests were performed with a sliding speed of 0.15 m/s under a load of 5 N. For purposes of the Rockwell C indentation test, a common hardness tester produced by Škoda Company was utilized.

3. Results and discussion

3.1. Elemental composition

Elemental composition of the Ti-Al-C-N coatings deposited with increasing C$_2$H$_2$ gas flow rate is documented in Figure 1. Not surprisingly, as C$_2$H$_2$ gas flow increased, the C content in the coatings increases from 0 at.% to 18.72 at.%, while N content decreases from 54.28 at.% to 47.34 at.%. Meanwhile, the Ti content also decreases correspondingly from 22.89 at.% to 12.35 at.%. The Al content remains basically unchanged (~21 at.%).

![Figure 1. Elemental composition of Ti-Al-C-N coatings as a function of C$_2$H$_2$ gas flow rate in at.%.](image)

3.2. Cross sections and surface morphology

The morphology of the cross sections of Ti-Al-C-N coatings fabricated at different C$_2$H$_2$ gas flow rate is given in Figure 2. A thin TiN adhesive layer was deposited to the substrate in order to improve the adhesion of the coatings. Each of Ti-Al-C-N coatings are characterized by the smooth surface topography and columnar structure with the columns diameter widens as the coatings grow. Higher deposition rate (from 0.029 μm/min to 0.052 μm/min) was documented with increasing of C$_2$H$_2$ gas flow rate. The maximum coating thickness of ~4.71 μm was observed at C$_2$H$_2$ gas flow of 75 sccm (Figure 2d). The presence of micro-droplets that are associated with the LARC$^\circledR$ process was documented as well (Figure 3). Micro-droplets are being formed during the deposition process due to
the ejection of liquid metal particles from the cathodes and may negative affect the coating during its growth [26].

Figure 2. Cross-sections of Ti-Al-C-N coatings deposited at different C$_2$H$_2$ gas flow rate, a) 0 sccm, b) 25 sccm, c) 50 sccm and d) 75 sccm.

Figure 3. Surface morphology of Ti-Al-C-N coatings deposited at different C$_2$H$_2$ gas flow rate, a) 0 sccm, b) 25 sccm, c) 50 sccm and d) 75 sccm.
3.3. Structure

XRD patterns of Ti-Al-C-N coatings deposited at different C$_2$H$_2$ gas flow rates are given in Figure 4. Identification of peaks confirmed the assumption that the Ti-Al-C-N coatings consist of a cubic B1-NaCl type Ti$_{1}N_{0.9}$ phase (ICSD 98-000-1547) with a maximum intensity of (111) diffracting plane at a Bragg angle of 42.876° 2Θ. The unit cell parameters are following $a = b = c = 4.239$ Å, $\alpha = \beta = \gamma = 90^\circ$. The carbon free coating is strongly oriented in the [111] direction. The increase in the C$_2$H$_2$ gas flow rate caused a substitution of N atoms by C atoms and decrease in intensity of (111) Ti$_{1}N_{0.95}$ and (022) Ti$_{1}N_{0.95}$ diffracting planes, because C could act as a diffusion inhibitor that restrains the growth of the coating grains, what can result in presence of randomly oriented grains in the coatings [27]. Because of the atomic volume of C is larger compared to that of N, the Ti-Al-N unit cell increased with increasing of the C$_2$H$_2$ gas flow rate. In addition, the peaks position shift to a lower diffraction angles is caused by increase of carbon content, which leads to the d-spacing expansion. The expected expansion of the coating unit cell may be also explained by the substitution of Al into the Ti lattice positions [28]. The h-WC (ICSD 98-061-9096) and c-Co (98-062-2439) phases are the contribution of the substrate to the overall diffraction pattern of Ti-Al-C-N coatings. The expected amorphous a-C phase has not detected because of its non-crystalline character [29].

![Figure 4. XRD patterns of Ti-Al-C-N coatings as a function of C$_2$H$_2$ gas flow rate.](image)

3.4. Hardness and adhesion

Figure 5 shows the values of nanoindentation hardness (H$_{IT}$) of Ti-Al-C-N coatings deposited at different C$_2$H$_2$ gas flow rate. The hardness of Ti-Al-C-N coatings slightly increases as the C$_2$H$_2$ gas flow rate increased to the value of 25 sccm and reaches the maximum hardness of 33 GPa in the coating which contains 14.59 at.% C. This effect can be explained with the increase of C content in the coating, because more and more C atoms replace N atoms to form Ti(C,N) solid solution. Because of the influence of the solid solution effect, the hardness of the coatings is expected to increase. After that, the hardness values decreases with a further increase in C$_2$H$_2$ gas flow rate. Decrease in hardness at higher C$_2$H$_2$ gas flow rates is probably related with a creation of amorphous a-C phase [30]. The Young's modulus of elasticity (E$_{IT}$) of Ti-Al-C-N coatings is documented in the same plot in Figure 5. As C$_2$H$_2$ gas flow rate increased from 0 sccm to 50 sccm, Young’s modulus of the coatings increase from 426 GPa to 441 GPa. Further increase in C$_2$H$_2$ gas flow rate from 50 sccm to 75 sccm caused a significant decrease in Young’s
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...modulus to a value 384 GPa. This decrease could be explained by the different chemical compositions in those coatings, because Young’s modulus is sensitive to density and atomic structure of coating [3].

![Graph](image)

**Figure 5.** The effect of C$_2$H$_2$ gas flow ratio on nanoindentation hardness (H$_{IT}$) and Young’s modulus of elasticity (E$_{IT}$) of Ti-Al-C-N coatings in GPa.

The adhesion of the Ti-Al-C-N coatings was evaluated with Rockwell C indentation test. Character of cracks and failures was classified according to the VDI 3198 standard. Surprisingly, the carbon free coating deposited without C$_2$H$_2$ gas was characterized by presence of cracks and cohesive failure around the indentation mark and it can be classified in the failure mode HF4 (Figure 6a). This coating still belongs to the group of acceptable adhesion level.

![Images](image)

**Figure 6.** Failure modes of indentation marks of Ti-Al-C-N coatings deposited at different C$_2$H$_2$ gas flow rates, a) 0 sccm, b) 25 sccm, c) 50 sccm and 75 sccm.
The coatings deposited with increased \( \text{C}_2\text{H}_2 \) gas flow rates (25 and 50 sccm) were classified as HF1, because no cracks around the indentation marks were observed (Figures 6b and 6c). According to the standard, these results are considered as an excellent adhesion. However, an increase in \( \text{C}_2\text{H}_2 \) gas flow rate caused a significant deterioration of the adhesion behaviour of the coatings. In this case, a strong delamination of the coating associated with the failure mode HF6 was documented (Figure 6d).

3.5. Tribological properties

The friction coefficients curves of the Ti-Al-C-N coatings with different \( \text{C}_2\text{H}_2 \) gas flow rates are given in Figure 7. The average friction coefficient of coatings considerably decreased from 0.80 to 0.35 with increasing C content. The reduction in friction coefficient is probably related to the formation of the amorphous phase (a-C). Amorphous carbon phase exhibits low friction coefficient and from this point of view can be used as a solid lubricant [31].

![Figure 7](image_url)

**Figure 7.** Coefficient of friction (COF) as a function of \( \text{C}_2\text{H}_2 \) gas flow rate of Ti-Al-C-N coatings.

4. Conclusions

The Ti-Al-C-N coatings were deposited on cemented carbide substrates by lateral rotating cathodes (LARC®) process. The effect of \( \text{C}_2\text{H}_2 \) gas flow rate on elemental and phase composition, deposition rate, cross-sectional and surface morphology, mechanical and tribological properties of the coatings was studied. As the \( \text{C}_2\text{H}_2 \) gas flow increased, the C content in the coatings increased from 0 at.% to 18.72 at.%, while N content decreased from 54.28 at.% to 47.34 at.%. All deposited Ti-Al-C-N coatings were characterized by the columnar structure of their fracture surfaces. Higher deposition rate (from 0.029 μm/min to 0.052 μm/min) was documented with increasing of \( \text{C}_2\text{H}_2 \) gas flow rate. The maximum coating thickness of ~4.71 μm was observed at \( \text{C}_2\text{H}_2 \) gas flow of 75 sccm. The presence of micro-droplets on the surfaces of all coatings was documented as well. The Ti-Al-C-N coatings consisted of a cubic B1-NaCl type Ti\(_1\)N\(_{0.9}\) phase with a maximum intensity of (111) diffraction plane at a Bragg angle of 42.876° 2\( \Theta \). The peaks position shift to a lower diffraction angles is caused by increase of carbon content, which led to the d-spacing expansion. The hardness of Ti-Al-C-N coatings slightly increased as the \( \text{C}_2\text{H}_2 \) gas flow rate increased to the value of 25 sccm and reached the maximum hardness.
of 33 GPa, which can be explained by the increase of C content in the coating, because more and more C atoms replace N atoms to form Ti(C,N) solid solution. After that, the hardness values decreased with a further increase in C₂H₂ gas flow rate. Decrease in hardness at higher C₂H₂ gas flow rates is probably related with a creation of amorphous a-C phase. The best adhesion (HF1) exhibited the coatings deposited with increased C₂H₂ gas flow rates (25 and 50 sccm). The average friction coefficient of coatings considerably decreased from 0.80 to 0.35 with increasing C content. The reduction in friction coefficient is probably related to the formation of the amorphous phase a-C, which can be used as a solid lubricant.

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