



On the growth, orientation and hardness of chemical vapor deposited Ti(C,N)



L. von Fieandt^{a,*}, K. Johansson^a, T. Larsson^b, M. Boman^a, E. Lindahl^c

^a Uppsala University, Department of Chemistry – Ångström Laboratory, Lägerhyddsvägen 1, Box 538, 75120 Uppsala, Sweden

^b Seco Tools AB, Björnbacksvägen 2, 73782 Fagersta, Sweden

^c AB Sandvik Coromant, Lerkrogsvägen 19, 12679 Hagersten, Sweden

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ABSTRACT

Chemical vapor deposition (CVD) of Ti(C,N) from a reaction gas mixture of TiCl₄, CH₃CN, H₂ and N₂ was investigated with respect to gas phase composition and kinetics. The gas phase composition was modelled by thermodynamic calculations and the growth rate of the CVD process was measured when replacing H₂ for N₂ while the sum of partial pressures H₂ + N₂ was kept constant. The N₂/H₂ molar ratio was varied from 0 to 19. Single crystal c-sapphire was used as substrates. It was found that low molar ratios (N₂/H₂ molar ratio below 0.6) lead to an increased Ti(C,N) growth rate with up to 22%, compared to deposition without added N₂. The mechanism responsible for the increased growth rate was attributed to the formation and increased gas phase concentration of one major growth species, HCN, in the gas phase. The texture of the Ti(C,N) films were also studied. <211> textured layers were deposited at N₂/H₂ molar ratios below 9. At higher molar ratios, <111> oriented Ti(C,N) layers were deposited and the grain size increased considerably. The films deposited at a N₂/H₂ ratio above 9 exhibited superior hardness, reaching 37 GPa. The increased hardness is attributed to an almost epitaxial orientation between the layer and the substrate. The absence of grain twinning in the <111> oriented layer also contributed to the increased hardness. The Ti(C,N) layers were characterized by elastic recoil detection analysis, X-ray photo electron spectroscopy, scanning electron microscopy, X-ray diffraction and nanoindentation.

1. Introduction

Modern chip forming metal cutting applications set a very high demand on the wear resistance of cutting tools. To increase the wear resistance, hard protective coatings are used. Depending on the application, the tool is coated using chemical vapor deposition (CVD) and/or physical vapor deposition (PVD). The coatings are optimized to meet a variety of different cutting applications and materials. Today the trend in the field of metal cutting is to use higher cutting speeds, but also to extend the use of the tools to materials that are difficult to machine.

State of the art cutting tools are coated with a layer combination of TiN/Ti(C,N)/Al₂O₃ with the TiN/Ti(C,N) layers being closest to the substrate. The alumina layer has continuously been optimized with respect to phase control (α or κ -Al₂O₃) and texture, e.g. (001) thereby increasing the lifetime of this type of coated tool considerably [1–3]. However, texture control has mainly been optimized on the alumina layer and a similar optimization of texture and growth direction of the intermediate Ti(C,N) layer has so far almost been overlooked.

Titanium carbonitride, Ti(C,N), has been used as a wear resistant

coating material for WC/Co cutting tools since the beginning of the 1970s [4]. Initially the coatings were deposited from TiCl₄-CH₄-N₂ reaction gas mixtures at relatively high temperatures, around 1000 °C [5,6]. At such high deposition temperatures problems with decarburization of the tool material can arise, causing formation of brittle carbon deficient phases (η -phase; M₆C or M₁₂C, M = W,Co). The introduction of moderate temperature (MT) CVD enabled deposition of Ti(C,N) at a temperature as low as 700 °C due to the use of the more reactive precursor CH₃CN instead of CH₄ and N₂. The lower deposition temperature reduced the problem of decarburization and η -phase formation [4,5]. Despite the long use of the MT CVD-Ti(C,N) process in the cutting tool industry, the mechanisms involved in the deposition process are not particularly well understood.

Ti(C,N) coatings deposited using the MT process (CH₃CN + TiCl₄ + H₂) generally grow columnar with a <311>/<211> out of plane orientation [7–12]. The morphology of the MT-Ti(C,N) can be altered by changing the TiCl₄/CH₃CN ratio. While this change affects the morphology, the orientation of the grains remains unaffected [13].

Most cutting tools are coated with multi-layer coatings of Ti(C,N)

* Corresponding author.

E-mail address: linus.fieandt@kemi.uu.se (L. von Fieandt).

and Al₂O₃. The adhesion between the layers in the multi-layer system is crucial for a high performance tool. Layer adhesion is affected by the orientation relation between different layers, where a large mismatch between two layers can cause a poor adhesion due to a high amount of strain over the interface. The orientation relation between TiC/TiN deposited onto α -Al₂O₃ has been investigated previously [14,15], showing the epitaxial relation (111)TiC/TiN||{(001) α -Al₂O₃. Epitaxial growth is observed despite the relatively large mismatch between layer and substrate. However, no published work on the orientation relation between MT-Ti(C,N) deposited onto (001) oriented α -Al₂O₃ are known to the authors. In previous studies the carbon/nitrogen precursors for TiC/TiN were CH₄ and N₂, respectively and layers were grown at significantly higher temperatures. The assumed CVD reaction path for Ti containing layers using TiCl₄ suggests that presence of hydrogen reduces the energy requirement of Cl⁻ removal from TiCl₄ [16,17]. This is achieved through the formation of HCl instead of Cl₂. As most MT-Ti(C,N) are deposited in excess of H₂, the Cl⁻ removal is considered as a fast reaction and not as the rate determining step of Ti(C,N) formation. The assumed rate determining step is the cleavage of the $\text{C}\equiv\text{N}$ bond in the CH₃CN, which, due to its high bond strength, requires more energy than Cl⁻ removal from TiCl₄ [18].

N₂ is sometimes added to the reaction gas mixture during deposition of MT-Ti(C,N) as it is believed to improve adhesion and a more homogeneous coating thickness distribution. Furthermore, N₂ is known to increase the deposition rate, however, the mechanism has not been investigated [13]. The reactivity of N₂ in a reaction gas mixture consisting of TiCl₄, CH₃CN and H₂ at temperatures of typically 800–900 °C is low and will therefore not affect the coating composition [10,19,20]. Studies of TiN coatings grown from TiCl₄ and NH₃ at (600–900 °C) indicate that added N₂ affects the microstructure, orientation and growth rate of the deposit [21,22]. The authors discuss whether N₂ changes the growth and surface chemistry by adsorption of N₂, leading to surface blockage. Also the stability of NH₃ as a function of added N₂ was discussed. The effect of N₂ addition on growth of MT-Ti(C,N) layers has not been studied.

In this paper the H₂/N₂ ratio in the CVD reaction forming Ti(C,N) has been varied in a systematic way, both experimentally and theoretically, in order to study the effects on orientation, orientation relationships, microstructure, growth kinetics and hardness of the MT-Ti(C,N) layer.

2. Experimental details

2.1. CVD deposition

Ti(C,N) was grown on polished 10 × 10 × 0.5 mm single crystal c-sapphire (001) substrates with a surface roughness < 5 Å supplied by MTI corp. A Bernex 325 hot wall CVD reactor was used and the sapphire substrates were placed at half the tray radius and half the reactor height. Furthermore, 3 polished WC-Co control pieces were placed at the center, half radius and at the periphery of bottom, middle and top levels of the reactor, respectively. The process conditions are shown in

Table 1
Ti(C,N) deposition parameters. $T = 830$ °C, $P_{\text{tot}} = 8$ kPa, $\text{TiCl}_4 = 0.26$ kPa, $\text{CH}_3\text{CN} = 0.04$ kPa.

Sample	H ₂ (kPa)	N ₂ (kPa)	Ar(kPa)	Deposition time (min)	Growth rate (μm/h)
0	7.7	0	0	70	1.24
1	6.5	1.2	0	60	1.52
1A	6.5	0	1.2	80	1.01
2	4.9	2.8	0	70	1.43
3	2.8	4.9	0	70	1.16
4	0.7	7.0	0	150	0.67
5	0.4	7.3	0	360	0.24

Table 1.

In the experiments, excess hydrogen was reduced and replaced with nitrogen in a stepwise approach as shown in Table 1. Argon was used instead of N₂ in one experiment (sample 1A), this sample was only characterized with respect to the growth rate. The total gas flow was kept constant at 2400 l/h in all the depositions. Deposition times were adjusted in order to deposit layers of equal thicknesses (about 1.5 μm).

2.2. Thermodynamic modelling

In order to increase the understanding of the deposition process and the main growth species, thermodynamic modelling was employed. The gas phase composition at the process conditions presented in Table 1 was modelled by thermodynamic calculations. A free-energy minimization technique was used (Program: Ekvicalc) [23]. TiCl₄, CH₃CN, N₂, H₂ and Ar were used as reactants in the calculations. For an accurate estimation of the gas phase composition prior to deposition all condensed phases were suppressed in the calculations and a total of 69 gaseous species were used in the calculations (for a complete list see Appendix A, Table A1). This is a common approach to model gas phase reactions in CVD [24]. Thermodynamic calculations can predict a chemical system only if the chemical reactions can reach equilibrium. Since gas phase reactions at 830 °C are fast, the gases are preheated and mixed at an earlier stage in the reactor and the residence time of the gas phase in the reactor is long (about 2–3 s depending on the total pressure), this approximation can be used. The results in this investigation were used to clarify the experimental results by modelling which gas phase species are most abundant and most likely the main contributor to the growth of a CVD coating.

2.3. Characterization

The crystallography of the thin films, phase compositions and the out-of-plane orientations were evaluated by θ – 2θ X-ray diffraction using a Philips MRD-XPRT diffractometer equipped with a primary hybrid monochromator and a secondary X-ray mirror. In addition, pole figures in the Ψ range 6–89° were acquired using a Philips MRD-XPRT diffractometer operating in point focus mode and equipped with a primary X-ray poly-capillary lens with crossed slits, a secondary flat graphite monochromator with parallel plate collimator, and a nickel filter. Cu K α -radiation was used for all X-ray measurements. The pole figure measurements were performed on the Ti(C,N) (200) diffraction peak, i.e. at 42.1° in 2θ . In addition to the pole figure measurements the poly-capillary set-up was used to determine residual stresses in the layers. The stress states were calculated using the cell parameters determined from (111) planes parallel to the surface and (422) planes 90° from the surface. The stress was calculated with Hooks law using the elastic modulus from the hardness measurements described below [25].

Top surface morphologies, cross section film thicknesses and microstructures were examined using a Zeiss Merlin High resolution scanning electron microscope (HR-SEM) operated at an acceleration voltage of 3 kV.

The compositions were investigated by X-ray photoelectron spectroscopy (XPS) using a PHI-Quantum 2000 scanning ESCA microprobe with monochromatic Al K α radiation. For all layers, sputtered depth profiles were acquired to determine the average bulk composition. The profiles were attained by 4 kV Ar⁺ ions on areas of 1 × 1 mm². The compositions were determined using sensitivity factors for Ti, C and N, obtained from reference measurements of two Ti(C,N) samples by elastic recoil detection analysis (ERDA). Calibration allowed atomic concentration to be determined within 0.4% at.

Mechanical evaluation through nanoindentation was performed using a CSM UNHT Nanoindenter with a Berkovich tip diamond indenter. The indentations were made at a constant linear loading of 3 mN/min to a depth of 110 nm. Hardness was measured after gentle surface polishing (with 6 μm diamond slurry) to decrease the surface

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