Mechanical and thermal stability of hard nitride coatings

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The cover image is the cross-sectional scanning electron micrograph of a mechanically damaged coating, showing the crack propagation in the multilayered coating.

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Hard coating's thermal stability is essential due to the high temperature environment of high-speed cutting applications, while the phase and microstructure evolution induced by exposing the coating to high temperature affects the mechanical properties. In this thesis, the mechanical stability of arc-evaporated, hard, transition metal nitride coatings annealed at high temperature is analyzed and related to the phase and microstructure evolution. In addition to hardness, fracture toughness is evaluated by surface and cross-sectional investigations by scanning/transmission electron microscopy of damage events following mechanical tests.

The crack resistance of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ with a range of Al content ($x = 0.23-0.82$) was studied by contact fatigue tests, where the differences in the microstructure were found to play a major role. Superior mechanical properties were found in $\text{Ti}_{0.63}\text{Al}_{0.37}\text{N}$; in the as-deposited state as a result of a favorable grain size, and after annealing at 900 °C due to the microstructure formed during spinodal decomposition.

The mechanical and high-temperature properties of hard coatings can be enhanced by alloying or multi-layering. Within this work, quaternary Ti-Al-X-N ($X = \text{Cr}, \text{Nb}$ and V) alloys were studied and superior toughness was found for $\text{TiAl}(\text{Nb})\text{N}$ in both the as-deposited and annealed (1100 °C) states. The hexagonal (h)-AlN formation in cubic (c)- $\text{Ti}_x\text{Al}_{0.37}\text{Cr}_{1-0.37-x}\text{N}$ ($x = 0.03$ and 0.16) was analyzed by in-situ x-ray scattering during annealing. The energy for h-AlN formation was found to be dependent on the microstructure evolution during annealing, which varies with the coating composition.

High Al content h-ZrAlN/c-TiN and h-ZrAlN/c-ZrN multilayers were investigated through scratch tests followed by focused ion-beam analysis of the crack propagation. A c-Ti(Zr)N phase forms in h-ZrAlN/c-TiN multilayers at high temperatures and that contributes to enhanced hardness and fracture toughness by keeping the semi-coherent sub-interfaces.

Finally, an in-situ analysis of coatings by x-ray scattering during a turning

process was carried out. It demonstrates the possibility of observation of stress evolution and thermal expansion of the coatings or the work piece material during machining. This experiment provides real-time information on the coating behavior during cutting.

Sammanfattning

Hårda skikts högtemperaturstabilitet är viktig på grund av den höga temperatur skikten utsätts för under skärande bearbetning, och den utveckling av faser och mikrostruktur som då sker påverkar skiktets mekaniska egenskaper. I den här avhandlingen har den mekaniska stabiliteten hos arcförångade, hårda metallnitridskikt som värmebehandlats vid höga temperaturer studerats. Förutom hårdhet har även skiktets seghet utvärderats genom yt- och tvärsnittsstudier av den sprickbildning som uppstår vid mekanisk provning med hjälp av svep- och transmissionselektronmikroskopi. Segheten hos $\text{Ti}_{1-x}\text{Al}_x\text{N}$ skikt med varierande Al-halt ($x = 0.23-0.82$) studerades genom utmattningsprovning och resultaten visar att förändringar i mikrostrukturen spelar en stor roll. $\text{Ti}_{0.63}\text{Al}_{0.37}\text{N}$ skikten hade överlägsna mekaniska egenskaper; på grund av en fördelaktig kornstorlek i de obehandlade skikten och efter värmebehandling som ett resultat av det spinodala sönderfall som skett. De mekaniska egenskaperna och högtemperaturegenskaperna hos hårda skikt kan förbättras genom legering eller genom multilagring. I den här avhandlingen har kvarternära Ti-Al-X-N ($X = \text{Cr}, \text{Nb}$ eller V) skikt studerats och $\text{TiAl}(\text{Nb})\text{N}$ skikten hade en överlägsen seghet i både obehandlat och värmebehandlat (1100°C) tillstånd. Bildandet av h-AlN i $\text{Ti}_x\text{Al}_{0.37}\text{Cr}_{1-0.37-x}\text{N}$ ($x = 0.03$ and 0.16) skikt studerades genom in situ röntgenspridning under värmebehandling. Den energi som krävs för att bilda h-AlN beror av mikrostrukturutvecklingen under värmebehandling vilken i sin tur beror av skiktets kemiska sammansättning. h-ZrAlN/c-TiN och h-ZrAlN/c-ZrN multilager med hög Al-halt undersöktes genom reptester följda av tvärsnittsstudier av sprickbildningen genom en analys med en fokuserad jonstråle (FIB). En c-Ti(Zr)N fas bildas vid höga temperaturer i h-ZrAlN/c-TiN multilagren och det bidrar till förhöjd hårdhet och förbättrad seghet på grund av en bibehållen koherens mellan lagren. Slutligen har in situ röntgenspridningsstudier av ytskikt utförts vid svarvning. Studien visar på möjligheten att observera spänning och värmeutvidgning av skikten eller arbetsmaterialet under bearbetning. Experimenten ger information om skiktets beteende under bearbetning i realtid.

La estabilidad térmica del recubrimiento es esencial debido a que estos recubrimientos durante su aplicación son utilizados a elevada temperatura y a alta velocidad. Durante dicho proceso, la evolución microestructural afecta a las propiedades mecánicas. En dicha tesis, la estabilidad mecánica de los recubrimientos duros base nitruro producidos mediante arco y recocidos a elevada temperatura son analizados y se correlacionado con su transformación de fase. La dureza, la resistencia a la fractura son evaluados mediante la observación tanto superficial como transversal mediante microscopia electrónica de barrido. La resistencia a la propagación de grieta de $Ti_{1-x}Al_xN$ con un contenido en Al que fluctúa entre 0.23-0.82 se estudia mediante ensayos de fatiga por contacto, donde la diferencia microestructural juega un papel importante. Las mejores propiedades mecánicas se encuentran en las muestras con un 0.63 de Ti donde se ha realizado un proceso de recocido a 900 °C debido a la descomposición espinoidal.

Las características mecánicas y de alta temperatura de recubrimientos duros pueden ser mejoradas si tenemos un recubrimiento multicapa. Aleaciones cuaternarias de Ti-Al-X-N ($X = Cr, Nb$ y V) son estudiada, y una mejor tenacidad de fractura se encuentra para la muestra $TiAl(Nb)N$ sin tratamiento de recocido como recocida a 1000°C. La formación del AlN con una estructura hexagonal en la muestra $Ti_xAl_{0.37}Cr_{1-0.37-x}N$ ($x = 0.03$ y 0.16) son analizadas mediante ensayos in-situ de difracción de rayos X durante el proceso de recocido. Cabe mencionar que la energía cinética para la formación de la AlN con una estructura hexagonal depende del proceso de recocido, la cual hace variar la composición química del recubrimiento. Multicapas de h (hexagonal)-ZrAlN/c (cúbica)-TiN con un elevado contenido de Al son estudiadas mediante ensayos de rayado y la generación de daño es observado mediante la técnica del haz de iones focalizados.

Las formas de la fase de c-Ti(Zr)N en las multicapas de (h)-ZrAlN/c-TiN formadas a elevadas temperaturas contribuyen a mejorar la dureza y la tenacidad de fractura manteniendo la semicoherencia en las intercaras entre cada capa.

Finalmente, se realiza un análisis in-situ de los diferentes recubrimientos me-

diante dispersión de rayos X durante un proceso de torneado. En este caso, se demuestra la posibilidad de observar la evolución de las tensiones residuales y de la expansión térmica durante el proceso de conformado. Dicho experimentos proporciona información en tiempo real sobre el comportamiento del recubrimiento en condiciones de servicio.

Populärvetenskaplig sammanfattning

Material spelar en stor roll i det vardagliga livet och den materialutveckling som sker gör att människor kan åtnjuta prylar och utrustning av allt högre kvalitet. Till exempel har, under bara ungefär 70 års utveckling, datorer minskat i storlek från att uppta ett helt rum till en mobiltelefon stor som en hand och som nästan alla har råd att äga. Det har skett som en följd av utvecklingen av halvledarmaterial, där transistorer kan göras mindre och mindre så att ett chip kan fyllas med fler transistorer som kan utföra fler operationer på mindre yta. Ytskikt kan förbättra produkters prestanda inom många tillämpningar. Till exempel gör keramiska ytskikt på turbinbladen i en jetmotor att bladen kan motstå högre temperaturer utan att smälta. Det gör att motorn kan köras med högre hastighet och därigenom minska bränsleförbrukningen.

Metallbearbetning som svarvning, fräsning och borrar är en viktig del av många tillverkningsindustrier, till exempel bilindustrin som måste kunna bearbeta stål med hög precision. Ett skärverktyg som används vid metallbearbetning utsätts för höga temperaturer och tryck. Genom att lägga ett tunt lager (med en tjocklek som är ungefär $1/20$ av ett hårstrås tjocklek) av ett hårt material på verktyget kan verktygets livslängd ökas väsentligt. Ytskiktet gör skärprocessen mer energieffektiv eftersom färre skärverktyg behöver användas då verktygen håller längre, mindre effekt krävs för processen och mindre kylvätska behövs.

TiAlN ytskikt är vanliga på verktyg för skärande bearbetning. Den intressanta egenskapen hos TiAlN är att dess hårdhet ökar då den utsätts för höga temperaturer. Ytskikten tillverkas genom arcförångning, en teknik där Ti och Al joner bildas från ett fast material och sedan får reagera med kvävgas och bilda ett metastabilt TiAlN skikt på ett substrat. När ytskiktet sedan utsätts för höga temperaturer vid metallbearbetning så sönderfaller det till de mer stabila TiN och AlN faserna och den mikrostruktur som bildas resulterar i en härdning av ytskiktet. Hårdheten ökar dock inte kontinuerligt med ökande temperatur. En anledning är den fastransformation av AlN som sker, från en kubiskt ordnad struktur till en hexagonalt ordnad struktur. Den mjukare hexagonala fasen gör att ytskiktets hårdhet minskar vid temperaturer

över 1000 °C.

I den här avhandlingen har ytskiktens seghet studerats genom reptester eller utmattningstester. Elektronmikroskopistudier av utmattningsprovade ytskikt visar att fortplantningen av sprickor i TiAlN skikt beror på Ti/Al förhållandet och kornstorleken. Om kornstorleken är alltför liten eller alltför stor så kommer sprickorna att fortplantas rakt igenom skiktet medan om kornstorleken har ett optimalt värde så böjs sprickorna av där korngränserna korsas. Skillnaden påverkar livstiden för ett verktyg eftersom enklare fortplantning av sprickor gör att ytskiktet slits snabbare. Den här studien relaterar ytskiktens fassammansättning och mikrostruktur till skiktens mekaniska egenskaper.

Hårda, kvävebaserade ytskikt kan förbättras till exempel genom att legera TiAlN med ett fjärde grundämne. I den här avhandlingen har högtemperaturstabiliteten hos kvarternära legeringar undersökts eftersom fasutvecklingen är viktig för hur de mekaniska egenskaperna utvecklas vid höga temperaturer. TiAlNbN skikt fanns ha de bästa mekaniska egenskaperna efter att de utsatts för höga temperaturer vilket beror av att den hexagonala AlN fasen bildas senare i dessa skikt jämfört med de andra studerade legeringarna. Var i strukturen hexagonala AlN korn bildas beror på ytskiktets kemiska sammansättning. Den energi som krävs för att bilda hexagonal AlN har uppmätts för två TiAlCrN skikt med olika sammansättning och resultaten visar att den beror av var i skikten som den hexagonala fasen bildas. Den här kunskapen kan användas för att designa nästa generations hårda ytskikt med förbättrad högtemperaturstabilitet och bättre mekaniska egenskaper.

Ytskikt som har en multilagerstruktur kan också ha förbättrade mekaniska egenskaper. Genom att omväxlande växa lager av två olika material med en tjocklek som är en bråkdel av en procent av skiktets totala tjocklek syntetiseras en multilagerstruktur. Högtemperaturegenskaperna och de mekaniska egenskaperna hos ZrAlN/TiN och ZrAlN/ZrN multilager studerades i den här avhandlingen. En sekundär fas av Ti(Zr)N bildades i ZrAlN/TiN skiktet vid värmebehandling vilket resulterade i bibehållna töjningar samt koherens mellan ZrAlN- och TiN-lagren. Det resulterade i bättre seghet i ZrAlN/TiN skiktet jämfört med ZrAlN/ZrN skiktet där en liknande sekundär fas saknades.

Slutligen har en svarv i liten skala byggts vilken kan placeras vid en synkrotronljuskälla för fasanalys in situ under svarvning. Genom att använda röntgenstrålning med hög intensitet samt noggrann precision vid linjering av skärverktyget i röntgenstrålen kan fasutvecklingen i ytskiktet följas i realtid vid skärande bearbetning. Dessutom kan information om verktygets temperatur och töjningstillstånd extraheras. Studien demonstrerar potentialen för djupgående undersökningar av ytskikt vid metallbearbetning.

Preface

This thesis is a collection of results from my doctoral studies in the Nanostructured materials group at Linköping university and Department of Materials Science and Metallurgical Engineering at Universitat Politècnica de Catalunya between 2013 and 2018, with the support by the EU's Erasmus-Mundus graduate school in Material Science and Engineering (DocMASE). The experimental work has also been performed at Seco Tools AB in Fagersta and Petra III in Hamburg. The work has also been financially supported by Swedish Research Council VR, Swedish Government Strategic Research Area grant AFM - SFO MatLiU, and the competence center FunMat-II.

List of publications and my contribution

[I] Effects of decomposition route and microstructure on h-AlN formation rate in TiCrAlN alloys

Y.H. Chen, L. Rogström, D. Ostach, N. Ghafoor, M.P. Johansson-Jõesaar, N. Schell, J. Birch and M. Odén

Journal of Alloys and Compounds 691 (2017) 1024–1032

I participated in the growth of the coatings and synchrotron measurements, carried out the analysis of the results and wrote the manuscript.

[II] Thermal and mechanical stability of wurtzite-ZrAlN/cubic-TiN and wurtzite-ZrAlN/cubic-ZrN multilayers

Y.H. Chen, L. Rogström, J.J. Roa, J.Q. Zhu, I.C. Schramm, L.J.S. Johnson, N. Schell, F. Mücklich, M.J. Anglada and M. Odén

Surface & Coatings Technology 324 (2017) 328–337

I carried out the GIXRD and mechanical tests, analyzed the results, and wrote the manuscript.

[III] Enhanced thermal stability and fracture toughness of TiAlN coatings by Cr, Nb and V-alloying

Y.H. Chen, J.J. Roa, C.H. Yu, M.P. Johansson-Jõesaar, J.M. Andersson, M.J. Anglada, M. Odén and L. Rogström

Surface & Coatings Technology 342 (2018) 85–93

I planned the study, carried out the characterization, analyzed the data and wrote the manuscript.

[IV] Toughness of arc deposited $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x = 0.23\text{-}0.82$) coatings evaluated by contact fatigue testing

Y.H. Chen, J.J. Roa, M.P. Johansson-Jõesaar, R.D. Boyd, J.M. Andersson, M.J. Anglada, M. Odén and L. Rogström

In manuscript

I planned the study, carried out the characterization, analyzed the data and wrote the manuscript.

[V] A small-scale lathe for in situ studies of the turning process using high-energy x-ray scattering

L. Rogström, Y.H. Chen, J. Eriksson, M. Fallqvist, M.P. Johansson-Jõesaar, J. Andersson, N. Schell, M. Odén and J. Birch

In manuscript

I participated in the planning and measurements of the study; assisted in data analysis and paper writing.

Symbols and abbreviations

a	Lattice constant
A	Area
APT	Atom probe tomography
BF	Bright-field
c	Cubic structure
CSM	Continuous stiffness measurement
d	Plane spacing
d^*	Strain-free plane spacing
d_ψ	Plane spacing measured at a tilt angle
D	Grain size
DF	Dark-field
DFT	Density functional theory
EDS	Energy-dispersive x-ray spectroscopy
E_{hkl}	Elastic modulus in the hkl direction
FD	Flow direction
FFT	Fast Fourier transform
FIB	Focused ion beam
G	Total free energy
G_s	Surface energy
G_v	Crystal free energy
GD	Growth direction
GI	Grazing incidence
GIS	Gas injection system
h_c	Contact depth
h_s	Surface displacement
HAADF	high-angle annular dark-field
h	Hexagonal structure
HR	High-resolution
hkl	Miller index

I	Intensity
IP	In-plane
IR	Infrared
k_1	Stress constant
L_c	Critical load
Me	Transition metal
ND	Normal direction
PVD	Physical vapor deposition
P_{max}	Maximum indenter load
S	Contact stiffness
SAED	Selective-area electron diffraction
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
TEC	Thermal expansion coefficient
TEM	Transmission electron microscopy
TD	Transverse direction
XRD	X-ray diffraction
λ	Wavelength
2θ	Scattering angle
ψ	Tilt angle
ν_{hkl}	Poisson's ratio in the hkl direction
ε	Strain
ϵ	Indenter constant
σ	Stress
σ_y	Yield stress
σ_0	Stress in crystals without grain boundaries

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CHAPTER 1

Introduction

Coatings are commonly used in our daily life, including spray coatings of wood for furniture finishing; decoration or protection of luxury items and durable parts in cars. Hard coatings are used to substantially prolong the lifetime of cutting tools, where they have wide application areas such as turning, shaping and drilling. Since nitride coatings exhibit a superior hardness ~ 30 GPa, they successfully decrease the abrasive wear that tools undergo during the cutting process as TiAlN has been widely applied in the cutting industry [1, 2].

The phase evolution of TiAlN in the high temperature environment that occurs during high-speed cutting process has been extensively studied because of the strong relation with its hardness. Initially the mechanical properties improved when exposed to high temperature (> 1000 °C), due to age hardening by spinodal decomposition. However, further annealing results in degradation of its hardness due to hexagonal (h)-AlN formation.

Approaches to improve mechanical properties of TiAlN coatings at high temperatures by enhancing its thermal stability are needed. By varying Ti/Al ratio of TiAlN, the phase contents are changed, affecting the phase evolution at high temperatures [3, 4]. Accompanied with different coating microstructure, hardness in both as-deposited and annealed coatings is varied with its composition. Not only hardness is an essential property of coatings, but good fracture toughness is also required [5] to prevent failure during machining process. Thus, studies on the fracture behavior in TiAlN related with its coating composition are essential.

Further, alloying the TiAlN with a fourth transition metal (Me) is theoretically estimated to alter its thermal stability and toughness [6]. The comparison between TiAl(Me)N alloys' mechanical properties can lead to the design of superior coating that has high temperature properties. On the other hand, h-AlN formation has been found to be critical to coating's mechanical strength, as it breaks the coherency between domains in the microstructure when growing in larger grain size [7, 8]. The

kinetics of h-AlN forms during annealing are interesting to study, to discover its dependence on the coating composition and microstructure. In addition to multi-component coatings, multi-layering structures can also contribute to enhanced thermal and mechanical properties [9–11]. One of the advantages of multilayer structures is that cracks can be deflected by the sub-interfaces or propagated differently with compressive stress in sub-layers [12].

There are differences between annealing environment and the one during a real turning process, such as high pressure applied on the coatings. However, a direction observation of phase evolution during a turning process is lack of due to the complexity of in-situ measurement.

This thesis focuses on fracture toughness for TiAlN coatings with varied Ti/Al ratio, TiAl(Me)N coatings with Me = Cr, Nb and V, and ZrAlN/TiN (or ZrN) multilayers. The results are further related with their thermal stability, and energies for h-AlN formation is further extracted in TiAlCrN. Finally, a phase analysis of hard coatings during a turning process is carried out, with the aid of a small-scale of turning rig integrated with a synchrotron radiation source.

CHAPTER 2

Material systems

TiN coatings are widely applied in cutting applications, due to its superior mechanical properties in terms of hardness. However, since improved high temperature mechanical properties are needed for high speed cutting applications, ternary and quaternary alloys are extensively used instead of binary alloys such as TiN.

2.1 Ti-Al-N

Ti_{1-x}Al_xN alloys have been demonstrated to exhibit superior mechanical properties compared to TiN, including high hardness after high temperature annealing [13] and better oxidation resistance [14]. However, Ti_{1-x}Al_xN is thermodynamically unstable, so that physical vapor deposition (PVD) techniques such as arc evaporation needs to be employed to form metastable solid-solutions. Further, different crystal structures and mechanical properties are obtained when varying the Ti/Al ratio in the metastable Ti-Al-N coatings [15]. In general, single phase cubic NaCl-structure Ti_{1-x}Al_xN is obtained with $x < 0.6$, a dual-phase structure including h-Ti_{1-x}Al_xN is formed when x is between 0.6 to 0.7. Single phase h-Ti_{1-x}Al_xN is formed at even higher Al content, due to its relatively higher stability than the cubic phase at these compositions [3, 4, 16].

As cubic (c)-Ti_{1-x}Al_xN exhibits a higher hardness than h-Ti_{1-x}Al_xN, c-Ti_{1-x}Al_xN coatings are commonly applied in the cutting industry and its mechanical properties have been studied with great interest and were found to be tunable with the Ti/Al ratio [3, 15]. The hardness increases with some addition of Al ($x < 0.6$) into TiN, which can be explained by solid solution hardening (alloy hardening) [13] and by the increase of the bulk modulus due to the decrease of lattice spacing (lattice parameters of AlN is smaller than TiN) [3]. With high Al content ($x > 0.6$), when a hexagonal phase is present, a decrease in hardness

of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ has been found in various studies [3, 13, 15]. The composition of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and its mechanical properties are related with the deposition conditions. Nevertheless, the dependence of the mechanical properties on its microstructure remains consistent.

When exposed to high temperature, the metastable $\text{Ti}_{1-x}\text{Al}_x\text{N}$ tend to decompose into thermodynamically stable phases. The decomposition process in hard coatings can enhance or deteriorate mechanical properties depending on the corresponding phase and microstructure evolution. Spinodal decomposition of c-TiAlN during annealing results into age hardening [17, 18]; on the contrary, further annealing forms h-AlN which degrades the mechanical properties [10, 19]. Thermal stability of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is closely related with the chemical composition; thus, studies of Ti-Al-N coatings with various Ti/Al ratio are important for optimization of these coatings. Therefore, studies of phases, thermal stability and mechanical properties of as-deposited and annealed $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys with various Ti/Al ratios were performed in **Paper IV**.

2.1.1 Spinodal decomposition

Spinodal decomposition is commonly observed in c- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ during post-annealing. If an alloy lies in a miscibility gap on a phase diagram, spinodal decomposition will take place during annealing. Spinodal decomposition can take place when only local composition fluctuations exist in the system, without an energy barrier to overcome for phase separation as the case in nucleation and growth (described in section 2.1.2). The miscibility gap of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is found in the concentration range of $\sim 0.25 < x < \sim 0.95$ at 1073 K (estimated operating temperature of cutting) as shown in Figure 2.1, which was calculated by considering the vibrational contribution to the mixing enthalpy [20]. The wide range of Al concentration results in that most $\text{Ti}_{1-x}\text{Al}_x\text{N}$ undergo spinodal decomposition during annealing, while the decomposition process does not involve nucleation and growth which will occur if it lies in the binodal region. Since spinodal decomposition is a continuous process, coherent interfaces form between domains with different compositions during phase separation. The coherency strain between domains contributes into varied elastic energies for the alloy [21], which gives enhancement of mechanical properties. The evolution of microstructure during spinodal decomposition is therefore essential for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings. Depending on the coating composition, the driving force toward decomposition is different; thus the evolution of mechanical properties during annealing also changes.

2.1.2 Formation and growth of h-AlN

Another phase transformation commonly observed in TiAlN-based coatings at high temperature is the formation of h-AlN. In c- $\text{Ti}_{1-x}\text{Al}_x\text{N}$, c-TiN and c-AlN phases formed by spinodal decomposition further evolve into c-TiN and h-AlN, since the coarsening of domains induces the transformation of c-AlN into h-AlN phase, which is a more thermodynamically stable phase [23]. The mechanism of this phase transformation is nucleation and growth, which starts with nuclei

Figure 2.1. Phase diagrams of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ calculated by [20] indicating the spinodal and binodal regions [22].

formation controlled by the total free energy. The total free energy (ΔG) of a nucleus includes its surface energy (ΔG_s) and the crystal free energy (ΔG_v), where the two contributions are dominant for different nucleus size. Thus, the critical nucleus size is determined when the total free energy, that is the sum of ΔG_s and ΔG_v , reaches a maximum value. The critical nucleus size means the minimum size of a stable formed nucleus that will subsequently grow in size, since the ΔG decreases with increasing nucleus size [24]. For nuclei larger than the critical nucleus size, coarsening begins in order to minimize the total free energy. Nucleation modes are classified as continuous nucleation with a constant nucleation rate and site-saturated nucleation with pre-existing nuclei [25].

The h-AlN formation is a nucleation and growth process [26, 27]; therefore, an activation energy barrier governs the formation process. Such activation energy has been studied in TiAlN with different coating compositions [28], which was found not to be the determining factor for the formation rate of h-AlN; instead, the interconnection of h-AlN domains in the microstructure is. On the other hand, as presented in **Paper I**, deviation in microstructure evolution of TiAlCrN that affects the h-AlN formation can be revealed by the differences in such activation energy, which is further discussed in section 2.2.

The formation of h-AlN has been found to alter the coating's mechanical properties. The initial h-AlN formation causes coherency strains to form due to coherent interfaces between cubic and hexagonal domains/grains which enhances the wear and toughness properties [29–31]. Further growth of this phase leads to degradation of mechanical properties due to the loss of coherent interfaces [19].

2.2 Ti-Al-X-N (X = Cr, Nb and V)

One of the methods for enhancing a coating's thermal stability is to introduce a fourth element into the Ti-Al-N system. Theoretical studies predict that Ti-Al-Me-N (Me : transition metal) systems exhibit superior thermal stability, which delays the spinodal decomposition and results in superior hardness at higher temperatures than Ti-Al-N alloys [32–36]. The thermal stability and mechanical properties of quaternary alloys are studied in this thesis, which are further discussed below.

Studies on Ti-Al-Cr-N system has shown that it exhibits enhanced thermal stability, oxidation resistance [37, 38] and cutting performance [39–42]. The driving force for decomposition dependent on the chemical composition of $\text{Ti}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}$ [43], where Lind et al has predicted by theoretical calculations that the decomposition routes would vary with different composition of $\text{Ti}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}$. Understanding the phase transformations at high temperature is essential for designing coatings with the desired mechanical properties. One of the essential factors is the h-AlN formation, which is strongly related to the coating's mechanical properties including hardness as described in section 2.1.2. Forsén et al found that h-AlN forms semi-coherent or incoherent interfaces with c-TiCrN domains depending on its domain size [37, 44]. In quaternary alloy Ti-Al-X-N systems, the h-AlN phase forms from the Al-rich domains generated during phase evolution. In $\text{Ti}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}$, such domains are CrAlN [38, 45, 46]. Thus, the mechanism forming the CrAlN phase, which is relate to the thermal stability of the coating is essential for the h-AlN formation. In **Paper I**, the activation energy for h-AlN formation was studied for $\text{Ti}_x\text{Al}_{0.37}\text{Cr}_{1-0.37-x}\text{N}$ alloys, and the decomposition routes, where CrAlN phase formed differently in the microstructures, determine the h-AlN formation rate.

Similar to the Ti-Al-Cr-N system, Ti-Al-X-N (X = Nb and V) systems are also among the interesting quaternary alloys with improved thermal stability by altering the mixing free energy [6, 43]. Though few experimental studies on thermal stability of Ti-Al-X-N (X = Nb and V) have been carried out [47], enhanced ductility of these quaternary alloys is expected from theoretically calculations [6, 48], along with superior properties for cutting applications [14, 49, 50]. Since brittleness is a common drawback of ceramic coatings [51, 52], enhancement of fracture toughness is essential for improvements of hard coating's wear or crack resistance. Experimental results also prove the enhanced toughness properties of $\text{Ti}_{1-x-y}\text{Al}_y\text{Nb}_x\text{N}$ [53], and the improved tribological properties are also found in $\text{Ti}_{1-x-y}\text{Al}_y\text{V}_x\text{N}$ [54]. In **Paper III**, the evolution of mechanical properties under high temperatures is studied and related to both spinodal decomposition and h-AlN formation, which is dependent on the thermal stability of Ti-Al-X-N alloys.

2.3 (Ti)-Zr-Al-N

$\text{Zr}_{1-x}\text{Al}_x\text{N}$ alloys exhibit similar structural and thermodynamic characteristics as $\text{Ti}_{1-x}\text{Al}_x\text{N}$. With larger miscibility gap and higher mixing energy than $\text{Ti}_{1-x}\text{Al}_x\text{N}$ [55, 56], it has a higher driving force for decomposition of its solid solution. In fact, only $\text{Zr}_{1-x}\text{Al}_x\text{N}$ with Al content lower than ~ 0.3 forms the cubic structure [56, 57]. The c- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ shows promising mechanical properties along with good

oxidation resistance at high temperatures [58–61]. With high Al content ($x > \sim 70\%$), a h- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ solid solution is formed [55, 62], which even displays superior wear behavior during cutting than c- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ coatings due to its high thermal stability [63].

Multilayered structures can further enhance thermal stability and mechanical properties [9–11] of the coatings. In the Zr-Al-N material system, c- $\text{Zr}_{0.65}\text{Al}_{0.35}\text{N}$ /TiN multilayers have been shown to have superior thermal stability, as hardness enhancement is retained at annealing temperature up to 1100 °C [64]. The secondary phase TiZr(Al)N is formed during annealing, which contributes to the improved mechanical properties, while such phase does not exist for c- $\text{Zr}_{0.65}\text{Al}_{0.35}\text{N}$ /ZrN multilayers. Therefore, it is interesting to study how a multilayer system of h- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and c-TiN (or ZrN) perform in thermal and mechanical properties, as was done in **Paper II**. The secondary phase Ti(Zr)N forms in h- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ /TiN and keeps the semi-coherency at sub-interfaces at 1100 °C annealing. Such phase is also found to be able to sustain the compressive stress in the c-TiN phase so that enhanced fracture toughness is observed; on the contrary, the stress is relaxed and evolves into tensile stress finally in h- $\text{Zr}_{1-x}\text{Al}_x\text{N}$ /ZrN, where no secondary phase presents.

3.1 Cathodic arc evaporation

The deposition of hard coatings in this work was performed by cathodic arc evaporation, which is widely applied for large-scale production in the cutting industry [65]. The process is started by applying a high current, low voltage arc discharge on the metallic cathodes, resulting in cathode spots of high power density ($\sim 10^{13}$ W/m²) on the cathode surface. With an extremely high local temperature, the material is transformed from solid phase into fully ionized plasma [66]. The high density of ion flux brings high kinetic energy to the substrate with the aid of a negative substrate bias. The high kinetic energy of the ionized plasma allows the possibility of depositing coatings at low (~ 300 - 500 °C) temperatures and for forming metastable compounds [4]. The high plasma density also provides the advantage of high deposition rate.

When a reactive gas is introduced during the cathodic arc evaporation process, e.g. nitride or oxide compound coatings can be deposited depending on the reactive gas. In this thesis, the deposition was carried out as in Figure 3.1, in 1-5 Pa N₂-atmosphere or N₂ mixed with Ar, with substrate temperature of 400-550 °C and substrate bias voltage of -30 to -20 V. During deposition, two or three cathodes with different materials/compositions are used. For example in **Paper I**, TiAl and CrAl cathodes with specific compositions are used for TiAlCrN coatings. Changing the vertical position of substrate on the holder and the cathode composition, various coating compositions could be deposited. The compositions of samples were determined after deposition and samples with the desired composition were chosen for experiments. A rotating substrate holder was used during deposition, which results in homogeneous deposition, and it can also be used for growing multilayered structures. For depositions of multilayered structures, on each side of

the deposition chamber a certain set of cathodes for the desired material of the sub-layers in the multilayered samples is mounted. In **Paper II**, the ZrAlN/TiN (or ZrN) multilayers were deposited by placing a ZrAl cathode and a Ti or Zr cathode on the opposite side of the chamber.

Figure 3.1. A schematic illustration of cathodic arc evaporation.

The substrates are predominantly cemented carbide (WC-Co) with 12 wt% Co. The depositions were also done on iron foils for preparation of free-standing coating powder, to prevent chemical reactions between coating and substrate materials during in-situ annealing experiments at ~ 1100 °C (**Paper I**). Powder samples were prepared by dissolving the iron substrates in hydrochloric acid, a procedure that completely removes the Fe while retaining the coating structure [67].

3.2 Microstructure of deposited coatings

The microstructure of coatings deposited by arc evaporation is affected by deposition parameters such as cathode composition, bias voltage [68] and substrate temperature [69]. In general, columnar microstructures of arc deposited films are formed due to intense ion bombardment [70].

The chemical composition is the critical parameter in this thesis to change the microstructure of the deposited coatings. Taking the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys as an example, transition from a cubic to a hexagonal $\text{Ti}_{1-x}\text{Al}_x\text{N}$ phase takes place with increasing Al content ($x > 0.71$) [71]. However, the limit of the Al content for the phase transition varies with the deposition process. The main reason is the difference in the atom's mobility on the sample surface, as atoms deposited by arc evaporation have higher mobility than other deposition methods due to the higher kinetic energy [72]. On the other hand, the coatings are also under higher ion bombardment during deposition in the arc evaporation. The microstructure of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ also evolves with the Al content. Hörling et al [4] has compared the microstructures between $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys with $x = 0.67$ and 0.75 . With ~ 10 % of increase in Al content, the microstructure of the as-deposited coatings changes significantly from columnar to fine grain structures. In **Paper IV**, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys with a range of Al content ($x = 0.23, 0.37, 0.63$ and 0.82) were studied. As shown in Figure 3.2, from the coating cross-sections, we can clearly observe the

trend of decreasing grain size with increasing Al content. A dual-phase of c-TiAlN and h-TiAlN is present in samples with an Al content of 0.63 and 0.82, while low Al content coatings are single phase c-TiAlN. The small grain size in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ with high Al content is due to the competitive growth of the two-phases structures [16]. It's due to the second phase (h-TiAlN) grains act as nucleation sites for grain growth so that the columnar structure with large grain size is not formed [73].

Figure 3.2. Microstructure overview of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ with $x =$ (a) 0.37, (b) 0.63 and (c) 0.82 from TEM investigations.

3.3 Residual stress

High residual stress is common for arc-deposited films [68, 74, 75]. The sources of which are the differences in thermal expansion coefficient between the coating and the substrate and the introduction of compressive stress by ion bombardment [76]. In TiAlN alloys, different Ti/Al ratio results into varied residual stress [3, 74]. For quaternary alloys TiAl(Me)N alloys (Me = Cr, Nb and V) and ZrAlN/TiN (or ZrN) multilayers studied in **Paper II** and **III**, the residual stress is also found to be different between with varied coating compositions. The origin of such variations may be a result of different ion flux and ion bombardment during deposition of different elements, since the bonding energy of an element affects the evaporation from the cathode [69, 77, 78]. Ion bombardment leads to defect generation in the coatings leading to higher compressive residual stress.

The residual stress can affect the mechanical behavior in various aspects, for example in the damage of coatings during scratch tests [79]. In **Paper II**, the residual stress which sustains in ZrAlN/TiN multilayers during annealing is found to be beneficial for the coating's fracture toughness. The mechanism behind it is that the crack propagate in different directions depending on the residual stress of the coatings [12]. Therefore, to deposit coatings with adequate properties for their desired applications is important [80]. For example, high compressive stress is usually regarded as beneficial for hardness; however, it is sometimes results into higher degree of damages from scratch or wear tests [74, 81]. One way to control the residual stress in the coating is by changing the substrate bias, as higher negative bias results in higher kinetic energy of the ions for bombardment. Thus, higher

compressive stress is found with higher substrate bias [74].

Characterization techniques

Determining phase content and microstructure of hard coatings is essential to understand their mechanical properties and cutting performance, especially at high temperature because the temperature in high-speed cutting processes may exceed 1000 °C [82]. In this section, the characterization techniques used in this thesis are presented.

4.1 X-ray diffraction

X-ray diffraction (XRD) is a rapid and non-destructive method to determine crystal structures. As shown in Figure 4.1, the path difference of x-rays with a specific wavelength (λ) scattering on atomic planes in a crystalline structure with a plane spacing (d) can be described as

$$\Delta_1 + \Delta_2 = 2d \cos(90^\circ - \theta) = 2d \sin \theta. \quad (4.1)$$

Constructive interference takes place when the path difference equals to an integral (n) multiply with the wavelength as described by Bragg's law, which can be expressed as,

$$n\lambda = 2d \sin \theta. \quad (4.2)$$

When constructive interference takes place, maximum scattering intensity is achieved.

For lab-source XRD experiments, a constant x-ray wavelength is usually used, $\text{Cu K}\alpha = 1.54 \text{ \AA}$ in this thesis. In a " $\theta - 2\theta$ " measurement, the incident angle (θ) is kept as half of the 2θ , where 2θ is the angle between incident x-ray beam and the detector, i.e. the scattering angle. Then, when the incident angle (θ) fulfill the Bragg's condition, a diffraction "peak" is resulted due to constructive interference,

Figure 4.1. The illustration of Bragg's diffraction. (Based on the figure in Ref. [83])

where the d value can be obtained from Eq. 4.2. Further, the obtained d can be assigned to specific phases and diffracted planes, as each atomic plane of a crystal has a specific d , which is related with its lattice constants and the hkl index of the plane. Taking a cubic crystal structure for example, it can be expressed as

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \quad (4.3)$$

where a is the lattice constant of the cubic phase and (hkl) is the Miller index of the atomic diffraction plane. The experimental results are shown in Figure 4.2, demonstrating that XRD can be effectively used for phase determination of coatings after annealing.

4.1.1 Grazing incidence x-ray diffraction

When keeping the incident angle low ($\sim 2-5^\circ$) but above the total reflection angle, the grazing incidence (GI) XRD experiments are performed. The advantage of the GIXRD technique is especially observed for thin films, when the substrate's diffraction signal is much stronger than the film. With higher incidence angle, the penetration depth of x-ray into the sample increases [84], resulting into more diffraction signal from substrate instead of the film. Therefore, the advantage of using grazing incidence angle is to increase the signal from the film by keeping the penetration depth low to avoid substrate signal.

Poly-crystalline films consists of grains with various directions, where the plans are not always parallel to surface normal. Therefore, with a fixed θ , Bragg's condition can still be fulfilled with various 2θ values for poly-crystalline films, since the diffraction planes are not only originated from the planes that are perpendicular to the surface normal (as indicated in Figure 4.1). In **Paper II**, coating signals are successfully investigated by GIXRD without strong interference from the substrate, as shown in Figure 4.2.

Figure 4.2. Phase analysis of as-deposited (a.d.) and annealed ZrAlN/TiN multilayers by XRD; "s" indicates the signal from the substrate.

4.1.2 In-situ x-ray scattering during high temperature annealing

Compared with lab-source x-ray instruments, synchrotron x-ray sources have the advantages of high brightness, high photon energy and the capability of integration with desired experimental equipment for in-situ measurements. For studies of phase evolution which need high time resolution, a synchrotron source is an essential tool. Due to high photon flux from synchrotron source, rapid diffraction scans can be done with faster rate than an in-house x-ray equipment. High energy x-rays (~ 80 keV) also has the advantage of penetrating samples, since the absorption is low. The in-situ measurements during high temperature annealing are done by the integration of a furnace in the beamline, which can heat samples to ~ 1000 °C, shown in Figure 4.3. The x-ray beam is aligned with the sample and passes through the glass windows located on each side of the furnace and the openings on the graphite heater tube. The furnace is under vacuum of around 10^{-5} torr to prevent oxidation of films during annealing.

Equipped with a two-dimensional area detector as in this thesis, diffraction signals in a wide range of scattering angles can be captured within a single exposure. By image processing, a line scan of d can be extracted, by converting the 2θ angle, which is the angle between the incident beam and the diffracted signal, by Eq. 4.2. Line scans can be obtained in various directions between the growth direction (GD) and the in-plane (IP) direction by choosing a tilt angle (ψ). Such results are very useful for stress measurements (section 4.1.3) and texture analysis.

In **Paper I**, the formation of h-AlN was investigated by in-sit x-ray diffraction analysis during annealing, since the h-AlN phase has dominant effects on coating's

Figure 4.3. Experimental setup for in-situ x-ray diffraction during high temperature annealing.

mechanical properties [29, 30, 85]. As shown in Figure 4.4, the phase transformation can be observed from the changes in the diffraction pattern, while the exact phases can be identified from the extracted line scans. With an image exposure taken every four seconds, the phase evolution and also the intensity of the h-AlN signal can be monitored during the annealing process. The activation energy for the phase transformation can then be extracted and was found to be related with the coating's microstructure.

Figure 4.4. (a) Diffraction patterns on the area detector and (b) line scans from the TiAlCrN coating in various states (**Paper I**).

4.1.3 Stress measurements

The residual stress of coatings can be measured by x-ray diffraction using the $\sin^2\psi$ method [86]. In this thesis, two different geometries for stress measurements are used. Reflection geometry, shown in Figure 4.5, is done with an in-house

x-ray source (Cu $K\alpha$). The corresponding angles for transmission geometry using synchrotron radiation are shown in Figure 4.3. The principle of stress measurement is the same for two geometries. Assuming a bi-axial stress state of the films, where the two in-plane stresses are the same ($\sigma_x = \sigma_y = \sigma$) and the out of plane stress (σ_z) equals to 0, the strain ($\varepsilon = \varepsilon_x = \varepsilon_y$) can be then calculated as

$$\varepsilon = \frac{d_\psi - d^*}{d^*} , \quad (4.4)$$

where d^* is the strain-free plane spacing and d_ψ is the plane spacing measured at a specific tilt angle, ψ . The strain can also be expressed as [87]

$$\varepsilon = \frac{1 + \nu_{hkl}}{E_{hkl}} \sigma \sin^2 \psi - \frac{2\nu_{hkl}}{E_{hkl}} \sigma , \quad (4.5)$$

where ν_{hkl} is the Poisson's ratio and E_{hkl} is the elastic modulus for the specific crystallographic direction (hkl). Combining Eq. 4.4 and 4.5, a linear dependence between d_ψ and $\sin^2 \psi$ and be obtained by:

$$d_\psi = d^* \left(\frac{1 + \nu_{hkl}}{E_{hkl}} \sigma \sin^2 \psi - \frac{2\nu_{hkl}}{E_{hkl}} \sigma \right) + d^* . \quad (4.6)$$

Therefore, by plotting the data of d_ψ versus $\sin^2 \psi$ from XRD measurements, the stress states of the films can be calculated from the slope. The tilt angle (ψ) for

Figure 4.5. Geometry of x-ray diffraction with reflection geometry.

observing d^* can be obtained by setting Eq. 4.5 to $\varepsilon = 0$, as it can be calculated as

$$\sin^2 \psi = \frac{2\nu_{hkl}}{1 + \nu_{hkl}} . \quad (4.7)$$

When d^* is known, the strain can be calculated in various tilt direction such as in-plane strain ($\psi = 90^\circ$) without using the E_{hkl} , by Eq. 4.4. As in **Paper II**, the in-plane strain is extracted by the in-situ x-ray diffraction during annealing. As defect annihilation or phase transformation can be induced during annealing, strain may be affected accordingly and can be monitored.

To further extract the stress states, the elastic modulus (E_{hkl}) needs to be known as shown in Eq. 4.6. Averaged elastic constants were used for stress

calculations in a poly-crystalline material. The (111) and (200) planes are two extreme orientations i.e. the stiffest and the softest depending on anisotropy, thus they are not ideal choices for calculating the stress state in the coating [88]. The stress is assumed to be equal for all grain in this measurement. In **Paper III**, the stress information of as-deposited coatings are extracted from c-220 planes. The used elastic modulus is estimated from theoretical calculations as TiAlN ($E = 432$ GPa); TiAl(Nb)N ($E = 420$ GPa); TiAl(V)N ($E = 429$ GPa) with Hill's average combining the Voigt and Reuss model [89].

4.2 Electron microscopy

Electron microscopy utilizes the interaction between incident electrons and the investigated sample for imaging and identification of phases and microstructure. In general, electron microscopy provides visual images for direct comparison or determination of grain sizes existed in the films, and investigations of surface topography for as-deposited or damaged coatings by mechanical tests. The microscopy techniques used in this thesis are the following.

4.2.1 Scanning electron microscopy

Scanning electron microscope (SEM) is used for analysis of the topography of the surface and cross-sectional investigations in this thesis. A focused electron beam with a specific energy (typically 3-10 keV) is incident onto the sample. The electron beam is rastered across the sample and interact with the atoms in the sample, resulting into the emission of secondary electrons which are collected by a detector for imaging. The signal contains information of the topography and composition. For example, the investigation of the droplet density on the coating surface can be investigated. Further, studies on surfaces deformed by nano-indentations, contact fatigues imprints and scratch tests can also be done by SEM. In Figure 4.6, the damage events from the same nano-scratch on ZrAlN multilayers with TiN and ZrN show clear differences. The deformation of the coatings is different between two coatings, as coating spallation with multiple small crack events observed on the scratch track in ZrAlN/TiN multilayers. For the ZrAlN/ZrN multilayer, larger area of coating spallation with longer cracks is observed instead. Together with higher penetration depth recorded for ZrAlN/ZrN multilayers during scratch tests, it shows that higher degree of damage occur in this coating during the nano-scratch tests.

4.2.2 Transmission electron microscopy

Details in the cross-sectional structures or crystallographic relations can be investigated by transmission electron microscopy (TEM). In TEM, a wild beam of coherent, high energy (200 keV) electrons are penetrated through thin samples (~ 100 nm). Bright-field (BF) TEM images are constructed by recording direct beam passing through the sample, which includes information of mass and crystalline orientation [90]. For example, columnar or fine grain structures of hard coatings

Figure 4.6. SEM imaging of the nano-scratch tracks of (a) ZrAlN/TiN and (b) ZrAlN/ZrN multilayers.

can be revealed by TEM using cross-sectional samples. Further, by introducing an objective aperture and selecting a diffracted electron beam, a dark-field (DF) TEM image can be obtained. From DFTEM, regions with a specific crystallographic orientation can be revealed and compared. High-resolution (HR) TEM images reveal atomic structure contrast, which is generated from the interference of coherently scattered electron waves passing through a periodic crystalline structure. Coherent interfaces can be revealed by lattice fringes, which are continuous across the interfaces. Figure 4.7 reveals coherent sub-interfaces between multilayers, while the difference in contrast between c-TiN and h-ZrAlN sub-layers distinctly indicates the two phases in the multilayering structures. As indicated by the white dash lines, the lattice fringes are continuous across the sub-layer interfaces. Fast Fourier transform (FFT) can be done on the HRTEM images to extract the reciprocal space pattern, then the zone axis and the crystal structure of the sample can be determined.

Selective-area electron diffraction (SAED) is another useful tool for determining the crystal structure from a specific area of the film in TEM. By inserting a selective aperture in the image plane, diffraction patterns from specific areas of the sample are obtained. The advantage of this technique is that the crystal structure can be determined from a several hundred nanometers area. Diffraction signal from the substrate can be avoided by SAED since the aperture is centered on the coating. Therefore, the structures of coatings can be clearly observed as shown in Figure 4.8 (**Paper II**). First, one can observe that after annealing at 1100 °C for 2h, there is more overlap of the h-(0002)/c-(111) and h-(11-20)/c-(220) signals compared to the as-deposited sample. It indicates that there is a change of the d . From the diffraction pattern obtained by SAED, the d can be extracted by Bragg's law as mentioned in section 4.1. Therefore, the crystal structure can be determined for certain grains or features by TEM investigation. In this thesis, the lattice parameters and crystal structures are defined by combining SAED and XRD for example in ZrAlN/TiN multilayers study. In addition, from Figure 4.8, we can observe higher degree of texture of the h-ZrAlN than the c-TiN phase, which may explain why only h-ZrAlN (0002) that has texture along the growth direction is observed from XRD.

Scanning transmission electron microscopy (STEM) is an advanced technique

Figure 4.7. HRTEM micrograph of the h-ZrAlN/c-TiN multilayer in its as-deposited state with the FFT of the two sub-layers.

for imaging using a highly focused electron beam (diameter ~ 0.2 nm) that is rastered across the sample. When collecting the scattered electrons with the high-angle annular dark-field (HAADF) imaging detector, images showing mainly mass contrast are obtained. In **Paper I**, STEM was used for tracking the location of AlN formation in coatings as shown in Figure 4.9. Since AlN has lower mass than (Ti, Cr)N, it appears with darker contrast in the HAADF-STEM image due to relatively lower scattering intensity than higher mass materials. The regions with dark contrast were further investigated by FFT, and a hexagonal crystal structure was confirmed. Further, there are also compositional modulation of Al-rich and Al-deficient domains shown in the inset of Figure 4.9, indicating the Al atoms diffuse from the inside of the grains into columnar boundaries during phase evolution.

4.2.3 Energy-dispersive x-ray spectroscopy

Energy-dispersive x-ray spectroscopy (EDS) is used for identification of elements in specimens. The principle is to detect the characteristic x-rays emitted from the material excited by the incident electrons. This technique is integrated with SEM and TEM, which is beneficial for determining elemental distribution directly in parallel to recording of the electron images. In this thesis, EDS is mainly used for the determination of coating composition and to study certain features of mechanically tested samples such as coating spallation or oxidation. The major difference between EDS in TEM and SEM is the detection volume. As the sample thickness is much lower in TEM than SEM, the element distribution on cross-sections of samples can be identified by TEM at much higher resolution (1-2 nm).

Figure 4.8. Diffraction patterns of ZrAlN/TiN multilayers under as-deposited and annealed states obtained by SAED.

With SEM, quick confirmation of exposed substrate on the surface due to scratch tests can be carried out as in **Paper III**. In **Paper IV**, further examination of the oxidation layer underneath the surface formed by contact fatigue tests could only be achieved by TEM due to the need of better resolution.

4.3 Focused ion beam

Focused ion beam (FIB) is a technique that uses a heavy ion beam for imaging, milling and metal deposition. Ga^+ ions are used for cross-sectional milling and Pt are deposited by a gas injection device (GIS) for protection of the surface from damages that can occur during milling, as shown in Figure 4.10 (a). The lift-out technique by FIB is a method to prepare cross-sectional samples for TEM analysis. With the aid of FIB, a cross-sectional sample at a specific area e.g. close to an indentation or a mechanically resulted feature can be done with much higher precision compared to sample preparations of mechanical grinding. As shown in Figure 4.10 (b), an area of interest can be prepared as cross-sectional lamella with milling out surrounding materials followed by final polishing with sample thickness down to ~ 100 nm.

In this thesis, FIB was used for obtaining cross-sectional views of the crack behavior or phase information by further TEM studies in sub-surface regions of the coatings after indentation or scratch tests. Modern FIB instruments are equipped with a SEM system, which means the cross-sections can be directly imaged with SEM. Cross-sections close to scratch or indentation damages were prepared with FIB and crack propagation underneath the damage was further analyzed. The surface view of some damages, for example, the scratch damages shown in Figure 4.6, does not always reveal the distinct differences in coating's fracture behavior. But from Figure 4.11, the cross-sectioned images clearly reveals the different crack behaviors in the coatings. From such results, studies on fracture toughness properties and its relation to the internal stress of the multilayers was

Figure 4.9. STEM images of the $\text{Ti}_{0.16}\text{Cr}_{0.36}\text{Al}_{0.48}\text{N}$ coating annealed at 1150 °C for 10 min, with the inset shows the higher magnification image taken within the white square region.

carried out as in **Paper II**. Further, differences in phase content or defect density between as-deposited and samples after fatigue tests was studied by FIB/TEM in **Paper IV**.

4.4 Atom Probe Tomography

Atom Probe Tomography (APT) is a technique which maps out the chemical composition in 3D at the atomic scale. The samples are first prepared as an extremely sharp tip with a 30 nm radius by focused ion beam (FIB) milling. After applying a laser or high voltage pulse, ions are evaporated from the sample and are collected by a 2D detector. The difference in time between the pulse and the detection of the evaporated ion can then be used to extract the mass-to-charge ratio. With the (X, Y) coordinates on the detector from the ions, the reconstruction of a 3D image can be done by extracting the original place of the atoms on the tip. Phase transformations, which are common in hard coatings during high temperature annealing, is a relevant example where APT studies are useful for extracting chemical distribution in samples under various states. As shown in

Figure 4.10. (a) Schematic figure of FIB experimental set-up; (b) The cross-sectional view of a coating (top) and the lamella prepared by FIB for TEM investigations (bottom), with dashed squares indicating the crack present in the coating.

Figure 4.12 (from the work in **Paper II**), the compositional profile changes after annealing in ZrAlN/TiN multilayers samples. This change is hard to observe by STEM due to lower resolution and sample preparation issues; however, APT analysis can clearly show such variations.

Figure 4.11. Cross-sectional view of scratch damages on (a) ZrAlN/TiN and (b) ZrAlN/ZrN multilayers.

Figure 4.12. APT 2D contour plots of ZrAlN/TiN under (a) as-deposited and (b) 1100 °C annealed states.

Mechanical properties of hard coatings

Mechanical properties of materials are related to various aspects, such as hardness or fracture toughness. While high hardness of ceramic coatings leads to improved tool life due to low wear rate, poor toughness is usually found [51, 91], which leads to high degree of crack propagations and subsequent failure of coatings [92, 93]. Therefore, toughening hard coatings is essential for coating development, and has been approached by various methods such as alloying TiAlN [33, 42, 48, 94], where *ab initio* density functional theory (DFT) can predict with elements choice for avoiding brittle coatings [89]. Simulation results of toughness properties can further explain the different behavior of hard coatings in mechanical tests [95, 96].

However, most studies focus on the hardness or wear rate of the coatings; thus, the evaluation of toughness properties has not been fully developed. Although scratch and contact fatigue tests have been used to analyze the tribological properties of coatings [75, 97–99], most studies are limited to surface damages such as shape of damage features or critical load resulting in failure [100, 101]. Detailed studies of how cracks propagate in the coatings are important for resolving toughness properties [102–105], which are strongly related to their cutting performances. The knowledge can be used for designing of next-generation of hard coatings. The following are the main analysis techniques for determining mechanical properties used in this thesis.

5.1 Hardness

Hardness is one of the most frequently used properties for evaluation of coatings. High hardness can result in low wear rate in abrasive wear processes [1, 106], which has been demonstrated with improved life time and performance of tools [107–109]. In this thesis, the hardness was measured by nanoindentation. The technique

is based on the use a diamond tip, which is indented into the sample with an increasing load to the maximum indenter load (P_{max}), resulting in a residual area (A) of the imprint. From a load-displacement curve during nanoindentation test shown in Figure 5.1, the hardness (H) can be calculated as

$$H = \frac{P_{max}}{A} . \quad (5.1)$$

Figure 5.1. Experimental results of a load-displacement curve during a nanoindentation test.

If a Berkovich indenter is used as in this thesis, the residual area of the indenter can be then estimated as

$$A \approx 24.5 h_c^2 , \quad (5.2)$$

where h_c is the contact depth of indentation. In order to obtain h_c , the surface displacement (h_s) needs to be determined as shown in Figure 5.2,

$$h_s = \epsilon \cdot \frac{P_{max}}{S} = \epsilon \cdot \frac{P_{max}}{dP/dh} . \quad (5.3)$$

ϵ is a constant that depends on the shape of the indenter ($\epsilon = 0.75$ for Berkovich indenter) [110] and S is the contact stiffness which can be determined from the unloading curve shown in Figure 5.1.

In this thesis, two different methods of hardness measurements are used, hardness determination only at the maximum applied load [110] and continuous stiffness measurement (CSM) [111]. In **Paper III**, hardness is measured when applying $P_{max}=50$ mN, resulting in penetration depth of 0.20 to 0.24 μm for ~ 3 μm thick coatings. The maximum displacement into the surface fulfills the rule of thumb of nanoindentation, 10% displacement of total coating thickness to avoid substrate influence to the results [110]. As the arc deposited coatings exhibit high surface

Figure 5.2. A schematic figure of a cross-section during indentation. (Based on the figure in [110])

roughness from macro-particles, 20-30 indents were done on polished tapered cross-sections and an average hardness value was calculated.

CSM, which was used in **Paper II** and **IV**, is done by applying a small oscillation of applied force during indentation and measuring the corresponding displacement during each oscillation. The advantage of CSM is that hardness information is obtained continuously with increasing penetration depth. As shown in Figure 5.3, the hardness changes with displacement into the sample are observed from samples resulting in three regions. For displacements lower than ~ 400 nm, the large variation of hardness and high scattering are due to macro-particles on the coating surface. Hardness values become stable and are less scattered between displacements of 500 and 900 nm, where the values correspond to coating's hardness. As the coating thickness is around $6\text{ }\mu\text{m}$ in the ZrAlN/ZrN multilayered coatings shown here, we find that the 10 % rule is not totally valid. Studies show that the critical indentation depth for correct coating information varies for different coating systems [112, 113]. With higher indentation depth, the hardness starts to decrease, due to the influence of the substrate (WC-Co), exhibiting hardness of 15-20 GPa [114].

5.2 Fracture toughness

The wear behavior of hard coatings is usually complicated, and hardness is not the only factor. While transition metal nitride coatings exhibit high hardness, they are also well known of their brittleness. Since cracking can lead to subsequent failure or spallation of coatings, the crack behavior essentially affects the tool life time for machining applications [115, 116]. However, methods evaluating fracture toughness of thin coatings are not yet fully established.

Scratch tests and contact fatigue tests are the techniques used in this thesis for studying fracture toughness of hard coatings. Combined with FIB/SEM analysis of the damaged coatings, differences in spallation or crack propagation can be revealed. As fracture toughness is related to the amount of energy needed for crack propagation [80] in the coating, investigations of crack lengths of a damage event

Figure 5.3. CSM results of ZrAlN/ZrN multilayered coatings on a WC-Co substrate.

are critical [117, 118]. TEM studies on the cross-sectional lamella can further reveal differences of crystallite size or phases between samples, as described in section 4.3. Since grain size and phase contents are important factors for mechanical properties of materials [119, 120], studies on correlating the microstructure with coating's fracture toughness are carried out in this thesis.

5.2.1 Scratch testing

Scratch testing is a technique commonly used for evaluation of the coating's adhesion and toughness properties [101, 121, 122]. It can be done in nano- and micro-scales [123]. In this thesis, nano-scratch tests with loading force up to 500 mN were used to study ZrAlN/TiN (ZrN) multilayers (**Paper II**), which can be very useful for observing smaller scale of damage events during sliding tests. An SEM surface view of nano-scratch tracks on the as-deposited and annealed ZrAlN/TiN multilayers is shown in Figure 5.4, where changes in the track appearance reveal different fracture toughness of the coatings. On the other hand, micro-scratch tests were carried out, using a spherical diamond indent and loads in the range of 0-150 N for Ti-Al-X-N coatings in **Paper III**. It is commonly used for determination of the critical load (L_c) for chipping events in the scratch track or coating delamination, which are related with elastic strength and ductility of the coatings [124, 125]. The results can be directly linked to the coating's cutting performance and tool life.

Besides investigation of damage events on surface, cross-sectional analysis of the coating can be very important for revealing different toughness properties. The cracks can be appear similar on the surface, while the propagation through the coating and into coating/substrate interface can only be revealed by a cross-sectional view. In **Paper III**, the fracture toughness of quaternary Ti-Al-X-N ($X = \text{Cr}, \text{Nb}$ and V) alloys and TiAlN were studied by cross-sectional images

Figure 5.4. SEM investigation of nano-scratch tracks on as-deposited, 900 °C and 1100 °C annealed ZrAlN/TiN multilayers. From **Paper II**.

of damages event that occur during scratch tests. As shown in Figure 5.5, clear differences in the coating's deformation and crack propagation below the surface are observed. At similar scratch load, the TiAlN coating presents the highest degree of coating deformation with almost complete detachment although cracks exist at coating/substrate interface in all samples. These differences were found to be related to the ductility of the phases formed during high temperature annealing.

Figure 5.5. FIB cross-sections from the scratch tested regions for 900 °C annealed (a) TiAlN, (b) TiAl(Cr)N, (c) TiAl(Nb)N and (d) TiAl(V)N. From **Paper III**.

Another factor affecting the crack propagation is the internal stress of the coatings [12], while tensile stress results in easier crack propagation perpendicular to coating surface, contributing to further coating spallation. As shown in **Paper II**, the variation in crack propagation between as-deposited and annealed coatings is linked to the strain evolution of ZrAlN/TiN (ZrN) multilayers during annealing.

5.2.2 Contact fatigue testing

Tests with cyclic indentations are one of the methods for revealing the fatigue properties of coatings. Repetitive contact loading can be related to interrupted cutting or cold forming applications [126]. The contact fatigue behaviors of TiN

coatings has been evaluated by extracting critical cyclic times for circular cracks to appear on the surface [127]. Cross-sectional investigations further show how cracks propagate below the surface in different microstructures [105, 128].

In **Paper IV**, a 2.5 mm diameter hard metal spherical indenter was used for studying contact fatigue properties of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x = 0.23$ to 0.82) coatings. Damages such as circular cracks [105, 129] are observed at the edge of the indenter imprints on the surface. Contact fatigue properties are revealed by crack propagation on both surface and underneath the surface. While differences in fracture toughness are correlated with their grain size and phase contents among $\text{Ti}_{1-x}\text{Al}_x\text{N}$. Grain boundaries are found to deflect the cracks in the coatings, so that smaller grain size should present better fracture toughness. However, a critical grain size is found for the best crack resistance since the grain boundaries become too populated to alter the crack directions with a sub-micrometer grain size. In addition, h-(Ti)AlN formed in high Al-content $\text{Ti}_{1-x}\text{Al}_x\text{N}$ can have lower fracture toughness due to high brittleness from h-AlN phase [89]. Further, oxidation or carbonization of films [99, 130, 131] is usually observed from the fatigue tests, which is dependent on $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coating's susceptibility to oxidation [132]. The formation of such phases may actually decrease the damages of circular cracks on the surface, due to their low friction coefficient. However, the oxidation formation is generally not preferable for cutting applications since high thermal stability of the coatings are needed at high operating temperatures

5.3 Engineering the mechanical properties by tuning microstructure

Mechanical properties of the coatings described above can be further modified by changing microstructures. Engineering of grain size or arranging materials in multilayers structures can remarkably modify the hardness or toughness properties of hard coatings [15, 67, 133].

Grain size has been found to directly affect the yield stress of a material and this can be described by the Hall-Petch relation [119, 134],

$$\sigma_y = \sigma_0 + k_1 D^{-1/2} \quad (5.4)$$

where σ_y is the yield stress, σ_0 and k_1 are constants, and D is the grain size. Since the yield stress is related to the hardness and fracture toughness of hard coatings [135, 136], smaller grain size can result in enhanced mechanical properties of hard coatings. However, this is not the case when the grain size falls below a certain size. In nano-crystalline coatings, the yield stress has been found to be proportional to $D^{1/2}$ instead, which leads to lower hardness with smaller grain size [137, 138]. The mechanism behind it is that the high density of grain boundaries result in easier grain boundary sliding or dislocation motion through grains [139, 140] under loading. Fracture toughness has been found to be related to the grain size, but the exact dependence on D can vary between different deformation mechanisms [120]. In **Paper IV**, a demonstration of different contact fatigue properties of coatings

with varied grain size was carried out. The knowledge of how the microstructure affects the fracture toughness is essential for design of wear-resistant coatings.

The design of multilayer architecture in hard coatings has been shown to result in greater thermal stability [9, 141] and better mechanical properties [64, 75, 142]. The enhancement can be explained by the microstructures modification, including confinement of dislocation movement by the sub-layer interfaces [143], or residual stress in the coatings changing the direction of the crack propagation [12]. In **Paper II** it was found that the coherent interfaces between sub-interfaces and the secondary phase c-Ti(Zr)N contributes to the superior fracture resistance of ZrAlN/TiN compared to ZrAlN/ZrN multilayers, as previously shown in Figure 4.11.

Real-time analysis during a turning process

Previously mentioned in-situ measurements at high temperature (section 4.1.2) can only provide an indication of how coatings behave during the cutting process ($\sim 1000^\circ\text{C}$). Studies at high temperature and high pressure, to simulate cutting process conditions for hard coatings have extensively improved the understanding of thermal stability and decomposition [82, 144]. Further, investigations of the relation between the cutting properties of hard coatings and their phase evolution have also drawn much research interest [145–147]. Considering the importance of the relation between microstructure, phase content and mechanical properties of hard coatings, a preferable way to link these two properties would be by monitoring the phase and microstructure evolution during real time turning processes.

6.1 Design of the lathe and facing challenges

Coating wear or chip formation during a cutting process have been investigated by finite element simulation [148, 149] and TEM [150]. However, direct studies during a real-time turning process are rare, due to the difficulty of analyzing the small contact zone between the cutting tool and the work piece material. The area of the contact zone varies with different cutting parameters, and in this study, the contact zone on the tool is $\sim 200 \times 300 \mu\text{m}^2$ on the flank side and $\sim 100 \times 250 \mu\text{m}^2$ on the crater side, shown in Figure 6.1. With the aid of a high brilliance x-ray from synchrotron source and a strongly focused beam, the investigation of phase information from a specific area is achievable.

Here, a small-scale turning rig with the capacity to be integrated into an experimental station at a synchrotron source was built, as shown in Figure 6.2 (a). An x-ray beam hits the edge of the cutting tool, which is in contact with the work piece during the turning process. The scattered x-rays travel to the 2D

Figure 6.1. The SEM image of a worn cutting tool at the regions of (a) the flank side and (b) the crater side, with the dashed areas indicating the contact zone.

detector and the diffraction signals from the phases in the coating was measured. In-situ x-ray diffraction studies during a turning process demonstrate the ability of monitoring phases and stress evolution in real time cutting applications.

Figure 6.2. (a) Schematic figure of in-situ x-ray scattering during a turning process, with the inset (top left) shows the x-ray path through the cutting tool. (b) Top view of the measurement geometry for studies on the (i) flank side and (ii) crater side of the tool.

The selection of the correct coating/substrate combination is essential for carrying out investigations of interesting areas. From the top view of the cutting insert during measurements (Figure 6.2 (b)), it is shown that x-rays are scattered both from the coating and the tool substrate since the coating is only $\sim 3 \mu\text{m}$ (beam size is (i) $200 \times 50 \mu\text{m}^2$; (ii) $200 \times 200 \mu\text{m}^2$). With the geometry (i) where the flank side of the coating is the focus of the study, a heavy mass substrate was chosen to prevent diffraction signals from unaffected area of the coating, since the

heavy substrate materials would absorb the x-rays that do not go through the edge. To study the crater side of the coating or the formed chips, low mass substrate materials were chosen to decrease the absorption of the x-rays penetrating the tool substrate as shown in geometry (ii). The exposure time was set to be long enough to collect enough intensity, but also short enough to have a reasonable time resolution for studying what happens during a turning process.

The coating area of highest temperature and stress is expected to be located on the crater face of the tool, thus this is the part of the tool where the largest change in microstructure and phase content would be expected [82, 151, 152]. However, even with light substrate materials such as c-BN and Si_3N_4 , the signal from the coating on the crater side was not observable using the existing set-ups. The diffraction signal from the coating was evaluated by measurements on coated Si_3N_4 substrates shown in Figure 6.3, different geometries of "transmission" and "GI". The same illuminated volume of the coatings was used for both geometries by changing the beam size. Thus, the geometries of measurements of the (i) flank side and (ii) crater side shown in Figure 6.2 (b) are simulated with GI and transmission tests respectively. Nevertheless, coating signals can only be observed with the GI geometry and not with the transmission geometry.

Figure 6.3. d-spacing spectra of on the uncoated and coated substrates with transmission and grazing incidence (GI) geometries, which are illustrated with respect to the incident x-ray and the detector.

The major difference between the two geometries is the volume of the substrate illuminated by x-rays, which is nearly two orders larger in the transmission geometry with the beam size used in the test. This indicates that the substrate affects the coating signal. One potential reason for such phenomenon is the background of the substrate to the intensity of the coating signal, as the scattered x-rays pass through both coating and the substrate before reaching to the detector.

6.2 Stress/temperature distribution

The high pressure and high temperature environment that a hard coating experiences during a turning process remains as an interest topic as it substantially influences the properties of hard coatings. Studies of these parameters are difficult to be carried out due to the complexity of the turning process that involves a cutting tool, work piece and chips. With the aid of analytical modeling, the distribution of the normal stresses along the cutting edge of the tool has been measured and shown to be its maximum at the tool edge, which is around 2 GPa, and is similar for cutting speed from 100 m/min to 400 m/min[82].

The temperatures of cutting tool during the turning process has been measured using various methods including thermocouples/pyrometer [151] or depositing a temperature sensor coating on the tool [153, 154]. Norrby et al [82] used an infrared (IR) CCD camera to map the temperature distribution on a cutting insert and found that it increases with cutting speed [155]. The maximum temperature was at a cutting speed of 400 m/min and is around 1000 °C. However, the temperature distribution can also be affected by the cutting feed and the depth-of-cut so that turning processes with different parameters can have varied temperature environment on the cutting tool.

Flank wear of a cutting tool is a phenomenon that occurs during metal cutting and limits the tool lifetime [156], and influences the surface finish of the work piece material [157]. Stress evolution or phase transition in the coatings during the turning process can strongly affect its hardness, which is strongly related with the abrasive wear resistance. In this thesis, the geometry of the flank side measurement is shown in Figure 6.2 (a) with the beam (indicated as (i)), positioned at the edge of the cutting tool. As shown in Figure 6.4, the in-plane strain and the strain-free d spacing (d^*) of a TiAlNbN coating is measured during three contacts of turning, with the method mentioned in section 4.1.2 and 4.1.3. For the as-deposited coating, a compressive strain is measured while there is a higher strain during contact. This behavior can be explained by the compressive stress from mechanical load during cutting [158]. Further, from the d^* values of TiAlNbN, the coating temperatures can be estimated to ~ 350 °C for both 230 and 320 m/min cutting speed. This is found much lower than the expected operating temperatures, which can be a result of that a relatively larger volume of the coatings is measured than the real contact area on the edge of the tool. Since the thickness of the tool (along the flank side) is around 4 mm and the width of the contact zone at the same direction is only ~ 200 μm , much of the coatings volume is not heated during the turning process.

6.3 Study of the chips produced during a turning process

Chips generated from work piece play an essential role for a turning process. The formation of the chips and the stress distribution on the built-up edge [159, 160] at the chip formation zone are important to study for optimization of the cutting parameters. For example, the prediction of the chip flow direction has been studied

Figure 6.4. (a) In-plane strain and (b) strain-free d spacing for TiAlNbN during and after turning runs.

in order to design with a chip breaker on the cutting tool [161, 162], so that the chips will not interfere with the turning process. The choice of work piece materials and cutting speeds affects the chip formation and stress state, which further influences the wear of the cutting tool [160]. Thus, the understanding of the stress states on the chips during the turning process contributes to better design of a cutting process. Due to the difficulty of such experiments, only few studies on the chips generated at lower cutting speed have been carried out [159, 163].

Figure 6.5. (a) Schematic figure of the defined directions on the chip respective to the x-ray beam. (b) Lattice spacings of the chips with respect to the angle between chip flow direction (FD).

Here, the exact values of the strain in the chips could not be obtained due to the lack of the x-ray scattering information from its normal direction (ND) as shown in Figure 6.5 (a). Instead, the lattice spacings of the work piece material (Fe) from the chip flow (FD) to the transverse direction (TD) can be extracted, as shown in Figure 6.5 (b). From our results, the relative higher compressive stress

found in the FD is consistent with specific crystallographic orientations. Though this finding does not agree with what work from Uhlmann et al [159], different cutting parameters such as cutting speed may result into the differences. The temperature of the chip can also be estimated using a thermal expansion coefficient (TEC) of 1.4×10^{-5} 1/K [164], to be approximately 620-710 °C, which is close to the predicted temperature for chips at the secondary cutting edge [164].

Summary of the results

7.1 Kinetics of the h-AlN formation in TiAlCrN

h-AlN formation is an intrinsic part of cubic TiAlN-based coating's evolution of mechanical properties at high temperatures [19, 29–31], as large grains of this phase degrades the coating's hardness. The formation rate of h-AlN is therefore an important aspect when designing coatings with enhanced thermal stability.

In **Paper I**, the formation of h-AlN in $\text{Ti}_{0.03}\text{Al}_{0.59}\text{Cr}_{0.38}\text{N}$ and $\text{Ti}_{0.16}\text{Al}_{0.48}\text{Cr}_{0.36}\text{N}$ coatings was investigated during isothermal annealing experiments. The decomposition route is different in each of these coatings, while spinodal decomposition takes place for $\text{Ti}_{0.16}\text{Al}_{0.48}\text{Cr}_{0.36}\text{N}$, nucleation and growth of h-AlN, c-TiN and c-CrAlN occurs in $\text{Ti}_{0.03}\text{Al}_{0.59}\text{Cr}_{0.38}\text{N}$. This difference results in faster formation rate of h-AlN in $\text{Ti}_{0.03}\text{Al}_{0.59}\text{Cr}_{0.38}\text{N}$, which corresponds to a lower activation energy (88 ± 36 kJ/mol) for h-AlN formation than in $\text{Ti}_{0.16}\text{Al}_{0.48}\text{Cr}_{0.36}\text{N}$ (304 ± 7 kJ/mol). Since h-AlN is formed from the CrAlN phase for both coatings, the location and size of CrAlN domains determine its varied thermal stability. By spinodal decomposition, the CrAlN phase is stabilized in a coherent structure with the TiCrN phase in $\text{Ti}_{0.16}\text{Al}_{0.48}\text{Cr}_{0.36}\text{N}$. By contrast, larger size of CrAlN domains are formed in the $\text{Ti}_{0.03}\text{Al}_{0.59}\text{Cr}_{0.38}\text{N}$ by nucleation and growth. In addition, the extremely low activation energy of h-AlN formation in $\text{Ti}_{0.03}\text{Al}_{0.59}\text{Cr}_{0.38}\text{N}$ is a result of direct precipitation of h-AlN at grain boundaries.

7.2 Thermal stability of multilayers and quaternary alloys

To improve the thermal stability of hard coatings at high temperatures, multilayered structures (**Paper II**) and multi-component alloys (**Paper III**) were grown and studied. The low Al content c-Zr_{0.65}Al_{0.35}N/TiN multilayer with superior thermal stability studied in Ref. [64] inspired the work on h-Zr_{0.25}Al_{0.75}N multilayers with TiN or ZrN that was investigated in **Paper II**. A secondary Ti(Zr)N phase is formed during annealing, which assists to sustain the compressive stress in the coatings and coherency at sub-interfaces partially is partially retained after annealing. The retained strain and coherency leads to better fracture resistance in the h-Zr_{0.25}Al_{0.75}N/TiN multilayer, which does not exist for h-Zr_{0.25}Al_{0.75}N/ZrN multilayer.

For TiAlN-based coatings alloyed with Nb, Cr or V, the phase evolution at high temperature was studied in **Paper III**. Different thermal stabilities were revealed by varied initial temperatures for spinodal decomposition and h-AlN formation, which is affected by the difference in the mixing free energy of coatings [6, 43]. Since spinodal decomposition and h-AlN formation are the main mechanisms taking place at high temperatures [23], the contribution of these phase transformations to the coating's mechanical properties is different. In sum, TiAlNbN exhibits the highest thermal stability in terms of the highest annealing temperature for initiating the h-AlN formation, which reflects its superior mechanical properties at 1100 °C, especially its fracture toughness.

7.3 Fracture behavior in hard coatings

Fracture toughness is an essential property for wear resistant coatings, as the brittleness of hard transition metal nitride coatings leads to easy failure of the coatings during cutting [115, 116]. The crack behavior in hard coatings was studied by indentations, scratch tests or contact fatigue analysis followed by characterization of the different toughness properties. Multilayers of ZrAlN/TiN and ZrAlN/ZrN were studied using nano-scratch and cube-corner indents, and clear differences in cracks propagation and critical load for crack initiation were found (**Paper II**). Despite a similar critical load for coating spallation, higher crack resistance is found from sub-surface studies for ZrAlN/TiN multilayers annealed up to 1100 °C, along with its higher hardness than ZrAlN/ZrN multilayers. The superior mechanical properties after annealing at high temperatures are related to the secondary phase, Ti(Zr)N that forms at the sub-interfaces.

Quaternary alloys of TiAlN alloying with Cr, Nb or V were compared to a reference alloy TiAlN by micro-scratch tests in **Paper III**. Though the damage on the surface reveals little difference between the samples, sub-surface investigations by FIB cross-sectional analysis show clear variations in the mechanism of coating failures. Cracks tend to propagate differently in the coatings, which is found to be related with the ductility of coatings estimated by the theoretical calculations [6].

In **Paper IV**, the fracture toughness of Ti_{1-x}Al_xN with x = 0.23 to 0.82 was

studied using contact fatigue tests. Rings cracks were found around the imprints only for certain samples, revealing differences in fracture toughness. Cross-sections on the ring cracks around the fatigue imprints were investigated, and varied crack propagation was found between $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings. The differences are related to the grain size. The $\text{Ti}_{0.63}\text{Al}_{0.37}\text{N}$ coating exhibits the highest degree of crack deflection by grain boundaries, due to its smaller grain size (i.e. higher density of grain boundaries) compared to $\text{Ti}_{0.77}\text{Al}_{0.23}\text{N}$. $\text{Ti}_{1-x}\text{Al}_x\text{N}$ with higher Al content than 0.37 has too small grain size (nanometer range) so that the density of grain boundaries is too high for crack deflection to take place. In addition, an oxide layer forms on $\text{Ti}_{0.18}\text{Al}_{0.82}\text{N}$ and prevents crack formation in the coating. Such oxidation may lead to easier coating failure during machining process and is absent for the other coatings.

7.4 In-situ analysis during a turning process

A cutting process is different from high temperature annealing for hard coatings. For instance, high pressure is an important factor affecting the coatings during cutting [82, 144]. Therefore, information related to turning processes is obtained by directly observing changes in the phase and microstructure that occur during machining.

Paper V demonstrates the in-situ x-ray scattering analysis of tool coatings or the chips from the work piece during a turning process. With the aid of a small scale turning rig that can be placed in a synchrotron radiation facility, determination of the temperature and stress during a turning process can be performed. PVD grown TiAlNbN and CVD grown Al_2O_3 coatings were tested and the strain and the strain-free d spacing (d^*) were investigated during the turning process. For all coatings, higher compressive strain is found during contact in the turning process, with the estimated operating temperatures as 350-430 °C. The measured temperature can be influenced by diffraction signal from coating outside the contact zone. A study on the formed chips shows higher compressive strain in the chip flow direction. The estimated chip temperature was between 720-820 °C, revealing that the measured area is in the chip formation zone.

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