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Defect-engineered (Ti,Al)N thin films

Isabella Citlalli Schramm Benítez

Nanostructured Materials
Department of Physics, Chemistry and Biology (IFM)
Linköping University, Sweden

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Abstract

This thesis investigates the effect of point defects (nitrogen vacancies and interstitials) and multilayering ((Ti,Al)N/TiN) on the phase transformations in cathodic arc-evaporated *cubic* (Ti,Al)N thin films at elevated temperatures. Special attention is paid to the evolution of the beneficial spinodal decomposition into *c*-TiN and *c*-AlN, the detrimental formation of *wurtzite* AlN and the potential application as hard coating in cutting tools.

c-(Ti_{1-x}Al_x)N_y thin films with varying Al fractions and N content ($y = 0.93$ to 0.75) show a delay in the spinodal decomposition when increasing the amount of N vacancies. This results in a 300 °C upshift in the age hardening and a delay in the *w*-AlN formation, while additions of self-interstitials enhance phase separation. High temperature interaction between hard metal substrates and thin films is more pronounced when increasing N deficiency through diffusion of substrate elements into the film. Low N content films ($y = 0.58$ to 0.40) showed formation of additional phases such as Ti₄AlN₃, Ti₂AlN, Al₅Ti₂ and Al₃Ti during annealing and a transformation from Ti₂AlN to Ti₄AlN₃ via intercalation. The multilayer structure of TiN/TiAlN results in surface-directed spinodal decomposition that affects the decomposition behavior. Careful use of these effects appears as a promising method to improve cutting tool performance.

Zusammenfassung

Diese Arbeit untersucht den Effekt von Punktdefekten (Stickstoffleerstellen und Zwischengitteratome) und Multilagen ((Ti,Al)N/TiN) auf die Phasenumwandlung in lichtbogenverdampften *kubischen* (Ti,Al)N-Dünnschichten bei erhöhten Temperaturen. Besonderes Augenmerk liegt auf der Entwicklung der vorteilhaften spinodalen Entmischung in *c*-TiN und *c*-AlN und der nachteiligen Bildung von *Wurtzit*-AlN, sowie der möglichen Anwendung als Hartstoffbeschichtung von Schneidwerkzeugen.

$c\text{-(Ti}_{1-x}\text{Al}_x\text{)N}_y$ mit unterschiedlichem Al-Anteil und N-Gehalten von $y = 0,93$ bis $0,75$ zeigt mit zunehmenden Stickstoffleerstellen eine Verzögerung der spinodalen Entmischung. Dadurch verschiebt sich die Ausscheidungshärtung um $300\text{ }^\circ\text{C}$ zu höheren Temperaturen und die *w*-AlN-Bildung wird verzögert, während der Einbau von Eigenzwischengitteratomen die Entmischung beschleunigt. Die Hochtemperaturwechselwirkung zwischen Hartmetallsubstrat und Dünnschicht durch Diffusion von Substratelementen in die Schicht nimmt mit steigendem Stickstoffdefizit zu. Stickstoffarme Schichten ($y = 0,58$ bis $0,40$) zeigen während der Wärmebehandlung zusätzliche Phasen wie Ti_4AlN_3 , Ti_2AlN , Al_5Ti_2 und Al_3Ti und eine Umwandlung von Ti_2AlN in Ti_4AlN_3 durch Interkalation. Die Multischichtstruktur von TiN/TiAlN führt zu einer oberflächengerichteten spinodalen Entmischung, die das Entmischungsverhalten beeinflusst. Ein gezielter Einsatz dieser Effekte erscheint als ein vielversprechender Weg, um die Leistungsfähigkeit von Schneidwerkzeugen zu verbessern.

Sammanfattning

I denna avhandling behandlas inverkan av punktdefekter (kvävevakanser och interstitialer) och multilagring ((Ti,Al)N/TiN) på högtemperaturfasomvandlingar i tunna arcförångade skikt av kubiska (Ti,Al)N. Störst vikt har lagts på utvecklingen av det fördelaktiga spinodala sönderfallet till c-TiN och c-AlN, den ofördelaktiga omvandlingen till w-AlN och potentialen som hårda skikt i verktygstillämpningar.

Tunna $c\text{-(Ti}_{1-x}\text{Al}_x\text{)}\text{N}_y$ skikt med olika Al-andel och en N-halt mellan ($y = 0.93$ och 0.75) uppvisar ökad undertryckning av det spinodala sönderfallet med ökat kvävevakanshalt. Detta resulterar i bildandet av w-AlN skiftas upp i temperatur vilket gör att åldershärdningen höjs med $300\text{ }^{\circ}\text{C}$. Däremot medför närvaron av självinterstitialer ett snabbare sönderfall. Växelverkan mellan hårdmetallsubstraten och de tunna skikten vid hög temperatur ökar med minskad kvävehalt i skiten genom diffusion av atomer från substratet in i filmen. Filmer med låg kvävehalt ($y = 0.58$ till 0.40) bildar även andra faser så som Ti_4AlN_3 , Ti_2AlN , Al_5Ti_2 och Al_3Ti under värmebehandling och fasomvandlingen från Ti_2AlN till Ti_4AlN_3 sker via en mekanism kallad intercalation. Multilagring av TiN/TiAlN resulterar i ett ytriktad spinodalt sönderfall vilket påverkar det totala sönderfallsförloppet. Nyttjande av dessa resultat syns som lovande vägar till förbättrade verktygsegenskaper.

Populärvetenskaplig sammanfattning

En tunnfilm är ett tunt lager av ett material som oftast täcker ett större objekt av ett annat material. Att man belägger ett objekt beror på att man vill förbättra, förändra eller skydda ytan av objektet, t.ex. för att göra ytan mer motståndskraftig mot repor eller värme, filtrera UV-ljus, vara vattenavvisande, eller helt enkelt ändra dess färg. Enligt litteraturen kan en tunnfilms tjocklek kan variera från ett atomlager till flera mikrometer. Man måste klyva ett hårstrå på längden i flera hundra delar för att få samma tjocklek. Det intressanta med dessa beläggningar är att trots att det är så tunna så kan de ge stora förändringar på objekt som är betydligt större, t. ex. något om vi kan hålla i handen.

De tunna filmer som är studerade i denna avhandling har potential att användas på verktyg för metallbearbetning. När man svarvar eller fräser arbetsstycken av metall så gör med det med en relativt hög skärhastighet, vilket medför att verktyget utsätts för hög temperatur och högt tryck. Trots dessa betingelser så måste verktyget vara hårt för att skärprocessen skall fungera. Ett vanligt förekommande tunnfilmsmaterial inom verktygsindustrin är titanaluminiumnitrid som också kan skrivas som $(\text{Ti,Al})\text{N}$. I denna avhandling har detta material används som utgångspunkt och sedan förändrats för att göra det ännu bättre. En viktig egenskap som $(\text{Ti,Al})\text{N}$ har är att det vid höga temperaturer bildar som domäner av titannitrid TiN och aluminiumnitrid AlN som gör att tunnfilmen kan bibehålla sin höga hårdhet men om temperaturen blir för hög så tappar ändå materialet sin hårdhet.

I denna avhandling så har i huvudsak två saker ändrats hos $(\text{Ti,Al})\text{N}$ för att förbättra egenskaperna och trycka upp den negativa fasomvandlingen till ännu högre temperaturer. I den första delen så undersöktes effekten av att minska kvävehalten i $(\text{Ti,Al})\text{N}$ utan att förändra kristallstrukturen men en del av kvävepositionerna var tomma. I denna andra delen användes $(\text{Ti,Al})\text{N}$ som en del i en multilagerstruktur tillsammans med TiN och sedan studerades multilagrets egenskaper. Resultaten visar

att genom att ta bort en liten andel av kvävet så förbättras materialets hårdhet vid höga temperaturer och den negativa fasomvandlingen är fördröjd till högre temperaturer. Om man tar bort för mycket kväve så bildas nya faser och fasomvandlingar som gör att materialet inte längre lämpar sig som en ytbeläggning på verktyg. Slutsatsen är ändå att styrning av kväveinnehållet är en parameter som tidigare negligerats men som har stor potential att förbättra (TiAl)N-belagda verktygs egenskaper. Dessutom bör konceptet även undersökas hos andra nitridsystem.

Preface

The work presented in this thesis is a result of my doctoral studies in the *Erasmus Mundus* joint doctoral program, DocMASE, at two research groups in two Universities between 2012 and 2017. Functional materials group at Saarland University (Saarbrücken, Germany) and Nanostructured materials group at Linköping University (Linköping, Sweden) in strong collaboration with SECO Tools (Fagersta, Sweden). In addition, the work was supported by the German Research Society (DFG), the federal state government of Saarland (Germany), the European Regional Development Fund (project AME-Lab), the Swedish Research Council (VR) and the Swedish Foundation for Strategic Research (SSF).

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Included papers and my contributions

- I. *Impact of nitrogen vacancies on the high temperature behavior of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ alloys*

I.C. Schramm, M.P. Johansson Jõesaar, J. Jensen, F. Mücklich and M. Odén
***Acta Materialia* 119 (2016) 218**

Carried out the major part in the planning and characterization, besides ERDA measurements, and wrote the first draft of the paper.

- II. *Solid state formation of Ti_4AlN_3 in cathodic arc evaporated $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ alloys*

I.C. Schramm, C. Pauly, M.P. Johansson Jõesaar, P. Eklund, J. Schmauch, F. Mücklich, M. Odén
***Acta Materialia* 129 (2017) 268**

Carried out the major part in the planning and characterization, besides TEM experiments where I participated, and wrote the first draft of the paper.

- III. *Effect of nitrogen vacancies on phase stability and mechanical properties of arc deposited $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$ ($y < 1$) coatings*

I.C. Schramm, C. Pauly, M.P. Johansson Jõesaar, S. Slawik, S. Suárez, F. Mücklich and M. Odén
***Surface and Coatings Technology* 330 (2017) 77**

Carried out the major part in the planning and characterization, besides TEM and EBSD experiments where I participated, and wrote the first draft of the paper.

- IV. *Enhanced thermal stability and mechanical properties of nitrogen deficient titanium aluminum nitride $(\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}_y)$ thin films by tuning the applied negative bias voltage*

K.M. Calamba, I.C. Schramm, M.P. Johansson Jõesaar, J. Ghanbaja, J.F. Pierson, F. Mücklich and M. Odén
***Journal of Applied Physics* 122 (2017) 065301**

Took part in the experimental work, carried out the APT experiments and the SEM imaging, and contributed to the writing and discussion of the manuscript.

- V. *Surface directed spinodal decomposition at TiAlN/TiN interfaces*
A. Knutsson, I.C. Schramm, K. Asp Grönhagen, F. Mücklich and M. Odén
***Journal of Applied Physics* 113 (2013) 114305**

Took part in the experimental work, carried out the APT experiments, and contributed to the writing and discussion of the paper.

Related papers but not included in the thesis

- VI. *Nanostructured and coherency strain in multicomponent hard coatings*
R. Forsén, I.C. Schramm, P.O.Å. Persson, F. Mücklich, M. Odén and N. Ghafoor
***Applied Physics Letters. Materials* 2 (2014) 116104**
- VII. *Tuning hardness and fracture resistance of ZrN/ZrAlN nanoscale multilayers by stress-induced transformation toughening.*
K. Yalamanchili, I.C. Schramm, E. Jiménez-Piqué, L. Rogström, F. Mücklich, M. Odén and N. Ghafoor
***Acta Materialia* 89 (2015) 22**
- VIII. *Exploring the high entropy alloy concept in (AlTiVNbCr)N*
K. Yalamanchili, F. Wang, I.C. Schramm, J. Andersson, M.P. Johansson Jõesaar, F. Tasnadi, F. Mücklich, N. Ghafoor and M. Odén
***Thin Solid Films* 636 (2017) 346**
- IX. *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
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- X. *A coated cutting tool and a method for coating the cutting tool. Nitrogen deficient TiAlN*
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Acronyms and symbols

1D	one-dimensional
3D	three-dimensional
APT	atom probe tomography
<i>c</i> -	<i>cubic</i> crystal structure
CVD	chemical vapor deposition
Da	Dalton
DSC	differential scanning calorimeter
EBSD	electron backscatter diffraction
EDS	energy-dispersive X-ray spectroscopy
EFTEM	filtered analytical transmission electron microscope
ERDA	elastic recoil detection analysis
<i>F</i>	evaporation field
<i>fcc</i>	face-centered cubic
FDA	frequency distribution analysis
FIB	focused ion beam microscopy
G	Gibbs free energy
HAADF	high angle annular dark field STEM
HRTEM	high-resolution TEM
Isosurface	iso-concentration surface
k_f	field factor
LEAP	local-electrode atom probe
μ	Pearson coefficient
m/q	mass-to-charge ratio
MAX	$M_{n+1}AX_n$
N_v	nitrogen vacancies
Proxigram	proximity histogram

PVD	physical vapor deposition
ROI	region of interest
SAD	selected area diffraction
SDSD	surface directed spinodal decomposition
SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
SZM	structure zone model
TEM	transmission electron microscopy
t_{flight}	time-of-flight
TG	thermogravimetry
T_m	melting point
TMN	transition metal nitride
ToF-E	time-of-flight energy
w-	<i>wurtzite</i> crystal structure
XRD	X-ray diffractometry

1. INTRODUCTION

TO THE FIELD

Coated cutting tools constitute the majority of tools used nowadays in material removal with geometrically defined edges [1]. The cutting tool experiences an environment of high localized temperatures ($\sim 1000\text{ }^{\circ}\text{C}$) and high stresses ($\sim 700\text{ MPa}$) during material removal [2], which makes metal machining a demanding process. It also encounters repeated impact loads (interrupted cuts) and interaction with the work piece chips. The use of a coating that withstands these harsh conditions has led to an improvement in tool lifetime and cutting performance. Ideally, this thin film should be chemically inert, stable at high-temperatures, wear resistant with low friction, oxidation resistant and harder than the substrate [2], [3]. There is a wide variety of hard coatings designed to meet the requirements of different applications on the market. Nevertheless, the appearance of new workpiece materials (difficult to cut) and the demand for higher production rates (extreme cutting conditions) lead to a strong, ongoing development in this field [1], [2], [4], [5]. In the scope of this thesis, the investigated films have the potential for their application as hard coatings for metal cutting in turning and milling tools.

TiN was the first commercial physical vapor deposited (PVD) coating used in the cutting tool industry in the late 70's, and since then, nitrides have governed most of the hard coating industry [1]. Among all available transition metal nitrides (TMNs) on the market, (Ti,Al)N is one of the most extensively investigated and used systems [1]–[3], [6]. It was the addition of Al into TiN which substantially improved its properties at elevated temperatures [7], [8]. Solid solution (Ti,Al)N coatings with a *cubic* (rock-salt)

structure, typically deposited by PVD, exhibit high hardness (~ 30 GPa), low thermal conductivity and good wear resistance [2], [3]. For medium to high Al content, a protective Al_2O_3 upper layer formed at high temperatures (above 700°C) is responsible for the good oxidation resistance [9], [10]. Furthermore, (Ti,Al)N coatings show high thermal stability and hot hardness [2], [3]. It is the evolution of hardness at elevated temperatures (age hardening) that is the key characteristic of these coatings.

The quasi-binary isostructural (rock-salt, B1) TiN-AlN phase diagram presents a miscibility gap [11], [12]. If a metastable solid solution *cubic* (Ti,Al)N is obtained inside the miscibility gap, the system will tend to phase separate into coherent *c*-TiN and *c*-AlN via spinodal decomposition instead of the thermodynamically stable phases *c*-TiN and *w*-AlN under the right conditions. The main advantage of spinodal decomposition is the formation of nanometer-sized *c*-TiN and *c*-AlN domains [3], [13]–[15]. The difference in elastic properties and lattice parameter between the different domains leads to coherency strain and a Koehler-type hardening [16]–[18], resulting in age hardening [16]. However, further annealing leads to coarsening of the domains, the formation of *wurtzite* AlN, and a degradation of mechanical properties, especially hardness [16], [19], [20]. Understanding and modifying the phase transformation in (Ti,Al)N has become a key factor to improve coating performance in the last three decades [3], [21], [22]. The use of other alloying elements, artificial layer structures, external pressure and stress are some of the proposed solutions for improving the thermal stability and suppressing the *w*-AlN formation [3], [23]–[27]. Although extensive research has been carried out on this system, there are few studies on the impact of point defects on the phase transformations in (Ti,Al)N thin films which is the main scope of this work.

This thesis investigates the unexplored effect of constitutional defects (nitrogen vacancies) and their combination with deposition-induced self-interstitials on the phase transformation of *cubic* solid solution (Ti,Al)N thin films at elevated temperatures. This was indirectly performed by reducing the nitrogen content of the as-deposited alloy and by applying a negative substrate bias voltage during film deposition in a cathodic arc

evaporation system. Herein, point defect engineering is demonstrated to significantly impact the phase decomposition pathway, the evolution of microstructure and the hardness at elevated temperatures.

In addition, a deeper understanding of the effect of artificial interfaces in a multilayer configuration (Ti,Al)N/TiN on the phase transformation on (Ti,Al)N was developed. Multilayering has been demonstrated to modify the phase transformation in a positive way [24]. Here, the internal interfaces are shown to shift the onset for decomposition to lower temperatures due to the appearance of surface-directed spinodal decomposition (SDSD).

The thesis is divided into two main parts. The first part is a background of the research that was carried out. Fundamental concepts are introduced, the employed characterization techniques are presented and the experimental setup is described. It concludes with an overview of the contribution made to the field by this work with a summary of the appended papers (manuscripts). The second part contains the result of the research in the form of scientific papers/manuscripts, which are briefly described below:

In **Paper I**, the effect of nitrogen vacancies on the thermal stability of *cubic* solid solution $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ free-standing coatings is presented for different Al metal ratios ($x = 0.26, 0.48$ and 0.60) and a N deficiency from $y = 0.92$ to 0.75 .

In **Paper II**, highly N deficient $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ ($0.58 \geq y \geq 0.40$) alloys are investigated for a wide range of Al metal fractions ($x = 0.28$ to 0.63). The transformation path is presented and a transformation mechanism from Ti_2AlN to Ti_4AlN_3 via intercalation is suggested.

In **Paper III**, substrate-coating interaction in the presence of N vacancies is investigated in $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$ coatings. Commercial cemented carbides (WC/Co based) were used as substrate and the N deficiency ranged from $y = 0.92$ to 0.46 .

In *Paper IV*, interaction and impact on thermal stability and mechanical properties when combining different types of point defects (N vacancies and interstitials) in $(\text{Ti}_{0.54}\text{Al}_{0.46})\text{N}_{0.87}$ are presented.

In *Paper V*, the effect of artificial interfaces on the thermal stability of $(\text{Ti},\text{Al})\text{N}$ is investigated in a multilayer configuration $(\text{Ti},\text{Al})\text{N}/\text{TiN}$. Surface-directed spinodal decomposition is shown experimentally and confirmed by phase field simulations.

2. PHASE TRANSFORMATION

A phase transformation describes the change in a system from an initial state to a new one. The main driving force for this to occur is the minimization of the system's Gibbs free energy. Some examples of phase transformations are the transitions from solid, to liquid, to gaseous state by increasing the temperature; the change in crystal structure by applying pressure; the transition from ferromagnetic to paramagnetic states by crossing the Curie temperature, etc. In order to understand why a system *wants* to transform, to which state and how fast will it be, thermodynamics and kinetics are needed.

In this chapter, some thermodynamic concepts regarding the phase stability and the driving force for phase transformations in alloys are discussed, followed by a description of the main mechanism of transformation in this thesis: diffusion. Finally, for this thesis, three relevant diffusional transformations in solids are presented, i.e. nucleation and growth, spinodal decomposition and coarsening, and intercalation for MAX phase transformation.

2.1 Phase stability

A system is usually defined as a mixture of one or more phases; a phase, being a part of the system where the properties and composition are homogenous and physically different from other parts (phases) [28]. Every system is described by its Gibbs free energy:

$$G = H - TS$$

H is the enthalpy, T the temperature and S the entropy. Enthalpy represents the internal energy of the system and the entropy is related to its randomness.

Figure 2.1: A schematic variation of Gibbs free energy with the arrangement of atoms. Configuration "B" has the lowest free energy, were the system is at stable equilibrium. Configuration "A" is a metastable state. Adapted from [28].

There are three main states of a system: *stable*, *metastable* or *unstable*. The equilibrium *stable* state is defined by the global minimum of the system's free energy, $dG = 0$, while a *metastable* state is any state where the energy is at a local minimum, $dG = 0$. Every other state where $dG \neq 0$ is *unstable*. A simplified example of how the Gibbs free energy changes as a function of arrangement of atoms is shown in Figure 2.1. Two minimums are observed and only one, configuration "A", has the lowest free energy of the system, the equilibrium *stable* state [28]. The system is in thermodynamic equilibrium only when the Gibbs free energy is at its minimum, if this is not the case the system will have a natural tendency (driving force) to achieve the minimum energy. It is then when a phase transformation can take place.

A phase transformation does not necessarily occur straight to the equilibrium *stable* state, but can pass through intermediate metastable states, which may last for short or indefinite periods of time. The duration of any intermediate step will depend on the energy barrier ($\Delta G_{\text{barrier}}$) that the system must overcome to change state, e.g. free energy

hump between configurations “A” and “B” (Figure 2.1). The higher $\Delta G_{\text{barrier}}$ it is, the more difficult it will be for the system to change state. Of course, the duration of these metastable states also depends on other kinetic factors (which are further described in text below).

Figure 2.2: Equilibrium of α and β phase shown by the tangent rule construction. Adapted from [28].

To predict the state to which a system wants to transform, it is important to know how the Gibbs free energy changes as a function of the parameter under consideration (e.g. composition, temperature). In alloys, different elements are mixed together and more than one phase can be stable for the same condition. Therefore, the Gibbs free energy becomes composition, temperature and pressure dependent.

A simplified example is where A and B atoms are mixed together but they do not have the same crystal structure in their pure state, one being α phase and the other β . In this case, each phase will have its own Gibbs free energy curve, G_α and G_β . The equilibrium between the two phases will be reached when the chemical potential of each component (A and B) is the same in each phase (α and β):

$$\mu_A^\alpha = \frac{\partial G_\alpha}{\partial X_A} = \frac{\partial G_\beta}{\partial X_A} = \mu_A^\beta$$

This is equivalent to the common tangent rule, where the tangents to each G curve at the equilibrium composition lie on a common line as shown in Figure 2.2. For this example, the composition range with a high amount of A atoms will present the α phase, compositions rich in B atoms will show the β phase, and a mix of both phases in between. The composition of α and β phases cannot exceed the composition dictated by the common tangent, i.e. there is a miscibility gap.

The complexity increases when more elements (A, B, C, ...) and possible phases (α , β , γ , ...) are involved in a system. Nevertheless, the common tangent rule can always be applied and a similar condition for equilibrium is imposed to the system. The chemical potential of each element must be identical in every phase [28], i.e.

$$\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \dots$$

$$\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \dots$$

$$\mu_C^\alpha = \mu_C^\beta = \mu_C^\gamma = \dots$$

For all examples above, the equilibrium state of an alloy was considered for a fixed temperature and pressure and only composition was varied. Once the temperature is taken into account, an equilibrium phase diagram can be constructed (see examples in Chapter 3).

In this thesis, phase transformations in (Ti,Al)N alloys were investigated by thermal activation at a fixed pressure, in a temperature range where the system is mainly in solid state. Therefore, most attention will be given to phase diagrams where composition and temperature are varied as shown in the following Chapter 3.

2.2 Diffusion

In this thesis, phase transformation occurs via thermal activation, and diffusion is one fundamental mechanism involved. Diffusion is the movement of atoms, and it is induced by a gradient of the chemical potential. In general, there are two types of diffusion, downhill and uphill. In the first and most common, the atoms move to eliminate concentration gradients. In the second, the movement is towards the high concentration regions. These composition gradients are directly correlated to the chemical potential gradients of the components [28].

Furthermore, the capability of an atom to move in a system is defined as diffusivity. It depends on the type of element, the host phase and its surroundings (e.g. a surface). The differences depend on conditions such as the mechanism of diffusion (substitutional and interstitial), the probability of jumping to a vacant site, the number of vacancies, the chemical potential gradients and the temperature, among others. In an alloy, where differences in element diffusivity can exist, it is more complex to describe how atoms will move (diffuse).

One more important aspect to take in consideration for phase transformation is the presence of defects like grain boundaries, interfaces, dislocations, free surfaces, etc. In the vicinity of these defects, the diffusivity and the equilibrium conditions of a system may change, since they have a more open structure and the movement of atoms along them is much faster than in the lattice. These defects are also called high-diffusivity paths and under certain circumstances, they can be the dominant diffusion path and may control the phase transformation [28].

2.3 Diffusional transformations in solids

In the scope of this thesis, where the phase transformation path of (Ti,Al)N alloys was investigated at elevated temperatures, three diffusional transformations in solids are of relevance and discussed in more detail below.

2.3.1 Nucleation and growth

Nucleation is the self-organization of elements, structural and/or compositional, into a new phase. It occurs via formation of a small nucleus (embryo) inside a region of the system and it is the first step for phase transformation. It can be homogenous or heterogeneous. The first is the ideal case and it takes place randomly inside the system. The second is the most common and it occurs at suitable sites where the energy needed to form an embryo is lower than the homogenous case. Those places can be dislocations, grain boundaries, stacking faults, excess vacancies, inclusions, and free surfaces.

In order to form a stable embryo, there is an energy barrier (ΔG^*) for nucleation to be overcome (Figure 2.3 (a)). This is related to three main contributions: volume generation, interface formation and a strain energy mismatch between the initial phase and the new phase. The first contribution minimizes the free energy of the system and is dominant above a critical embryo radius (r^*). The other two add additional energy to the system and are responsible for the nucleation barrier.

Once the nucleus of the new phase is stable, it will grow in order to decrease the Gibbs free energy of the system. This stage is called growth. A schematic view of how the composition varies with time in a nucleation and growth process is shown in Figure 2.3 (b). It starts with the nucleation of a phase with composition X_2 , in the matrix with composition X_0 , and it ends with two phases (X_1 and X_2), where X_1 is the composition of the depleted matrix.

Sometimes the energy cost for nucleation is too high and intermediate phases are formed before reaching the equilibrium state. These phases may not have the lowest free energy but a low nucleation barrier, making them energetically favorable. This stepwise transformation occurs especially if there are differences in the crystal structure between initial and final state, e.g. formation of Guinier-Preston zones.

Figure 2.3: (a) Variation of Gibbs free energy with embryo radius r for a homogenous nucleus, where ΔG^* is the nucleation activation barrier. (b) Schematic composition profiles at increasing time during nucleation and growth of precipitates with X_2 composition. Modified from [28].

2.3.2 Spinodal decomposition and coarsening

Spinodal decomposition is a mechanism where an initial phase separates into two phases without a nucleation barrier (nucleation free). The condition for this to occur, is that the free energy of a given alloy must have a negative curvature, $\partial^2 G / \partial X^2 < 0$, as shown schematically in Figure 2.4 (b) for the composition X_0 at the temperature T_2 . Small fluctuations in composition will decrease the free energy of the system, and uphill diffusion will take place until equilibrium composition of both new phases, X_1 and X_2 , is reached [29]. The only limitation is the diffusion which can be activated with temperature.

Figure 2.4: (a) Schematic phase diagram of a binary alloy presenting a miscibility gap and (b) the corresponding free energy curve at the temperature T_2 . Modified from [28].

Spinodal decomposition possesses the following characteristics [30], as shown schematically in Figure 2.5:

- It occurs homogeneously throughout the system (except near lattice defects) and it results in a finely disperse microstructure.
- The compositional fluctuations exhibit a certain wavelength during segregation, and the amplitude should increase continuously until a metastable state is reached.
- The interfaces between phases are diffuse.

Figure 2.5: Schematic representation of an alloy during spinodal decomposition (into X_1 and X_2) as a function of time in a (a) 1D composition profile [28] and (b) phase field simulated 2D microstructure [31], obtained by solving a modified Cahn-Hilliard equation.

This mechanism of transformation was first proposed by Hillert [29], and later improved and expanded to three dimensions by Cahn [30], [32] and Hilliard [33]. It occurs in

systems that present a miscibility gap in their phase diagram, e.g. Au-Ni, which is usually defined by two regions: spinodal and binodal as shown schematically in Figure 2.4 (a). Nucleation-free decomposition occurs only inside the spinodal region, while in the binodal region, a phase separation through nucleation and growth takes place. The line dividing them is called spinodal and it is defined by a zero curvature of the Gibbs free energy $\partial^2 G / \partial X^2 = 0$ (Figure 2.4). Cahn proposed that near the limit, yet still within the spinodal region, decomposition will be too slow so that the compositional fluctuations will reach a metastable state, and competing mechanisms like nucleation and growth will take over [30].

The kinetics describing the phase separation via spinodal decomposition are defined by the Cahn-Hilliard equation [33]:

$$\frac{dc}{dt} = D \nabla^2 (c^3 - c - \gamma \nabla^2 c)$$

D is the diffusion coefficient, c is the concentration, and γ is the surface energy. As the time advances, the concentration approaches a sinusoidal composition profile with a wavelength (λ). The amplitude of the composition profile increases with time with a fixed λ until a metastable equilibrium is reached as shown schematically for one dimension in Figure 2.5 (a).

An important parameter that determines the rate of spinodal decomposition is λ , i.e. the smaller λ is, the faster the system decomposes. However, λ cannot be predetermined for a system (alloy composition) since it depends on the initial intrinsic compositional fluctuations and on the principle of selective amplification (fluctuations with $\sqrt{2} \lambda_{\text{critical}}$ will grow faster and dominate) [30]. Only an upper limit in the spinodal decomposition rate can be set, the critical wavelength ($\lambda_{\text{critical}}$), which depends on the interfacial energy and the coherency strain energy of the system. Therefore, below this $\lambda_{\text{critical}}$ decomposition cannot occur [28].

Once a wavelength dominates in the phase separation, this λ will persist and the amplitude will increase until the system has reached the final composition of the phases, X_1 and X_2 (Figure 2.5 (a)) [28]. The following stage is called coarsening, where a growth of the domains with composition X_1 and X_2 will take place in order to minimize the interfacial and strain energy of the system [32]. During coarsening, there is no wavelength defining the evolution of the domain growth.

Only systems that present a miscibility gap in their phase diagram can be candidates for spinodal decomposition. The system studied in this thesis, metastable (Ti,Al)N with a B1 structure, is one of the systems presenting a miscibility gap which is shown and described in the following Chapter 3.

2.3.3 Intercalation

The ability to accommodate an elements or molecule by insertion between layers in a layered material is called intercalation [34]. There are different chemical and physical methods for activating this insertion and diverse inorganic hosts (graphite, clays, carbides, etc.) [34]–[37]. Only one is of interest in this thesis: the thermal activation of intercalation in transition metal nitrides/carbides for MAX phase formation. First, a brief introduction into MAX phases is given, followed by the description of the process of intercalation as a mechanism of phase transformation.

MAX phases ($M_{n+1}AX_n$ phases, $n = 1, 2, 3$) are a class of hexagonally structured nitrides and carbides that present a characteristic layered structure with M_6X octahedral layers separated by A-element layers. M is an early transition metal (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta), A is an A-group element (Al, Si, Ga, Ge, As, In, P), and X is carbon or nitrogen. The nomenclature depends on the amount of M layers separated by A layers, e.g. M_2AX ($n = 1$), M_3AX_2 ($n = 2$) or M_4AX_3 ($n = 3$) as shown in Figure 2.6 [38]. Their layered structure makes them a good candidate for intercalation.

Intercalation in MAX phases was proposed for the first time by Zhou *et al.* [39], and presented later by Riley *et al.* as a low temperature solid state method for MAX phase synthesis without the formation of intermediate phases [40], [41]. In general, intercalation starts with a solid-state binary precursor ($M_{1-n}X_n$) and an A-element source. Through thermal activation, a spontaneous rearrangement of the precursor into a layered structure makes the insertion of the A-element possible, and finally the formation of a MAX phase [40]. Intercalation is a reversible process [39], [42].

Figure 2.6: Crystal structures of the different MAX phase stacking sequences: M_2AX , M_3AX_2 , and M_4AX_3 from Högberg *et al.* [43] adapted from Barsoum [44].

In order for intercalation to occur, a proper selection of the binary precursor must be done in which a rapid and highly selective diffusion can take place. The precursor must have crystallographic similarities with the MAX phase structure, and it must allow an unrestricted motion of constituent elements through sufficient diffusion “pathways” [41]. Examples for precursors are MX binaries with NaCl (B1) structure, like TiC_x ($x < 1$) and TiN_x ($x < 1$), where the sub-stoichiometry in the non-metallic lattice

enhances the X-element diffusivity [3]. The structures present similarities in the shared edges between M_6X octahedral in MAX phases and the ones in the B1 structure [38], [45].

Once the precursor exists, the next step is the thermal activation in the presence of an A-element source, where a sequence of steps must occur spontaneously. These steps start with (a) the initial random distribution of X-element vacancies, (b) ordering of the vacancies, (c) twinning of the precursor sublattice, and finally (d) intercalation of A-element [41]. A schematic view of the transformation is shown in Figure 2.7.

Figure 2.7: Proposed reaction mechanism of the intercalation of silicon into the customized solid state precursor, $\text{TiC}_{0.67}$ by Riley *et al.* [41].

MAX phase formation via intercalation has been reported in different ternary systems, e.g. Ti_3SiC_2 , Ti_2AlC , Ti_3AlC_2 [46]–[48]. Until now it has only been shown in ternary systems containing carbon as the X-element.

3. TI-AL-N SYSTEM

The Ti-Al-N system has received considerable attention in the last three decades due to the technologically relevant materials obtained from this system either as bulk or as thin film. Various applications include TiN thin film diffusion barriers, AlN in electronic semiconductor devices, (Ti,Al)N wear-resistant coatings, high temperature composites like Ti₂AlN, Al₃Ti, AlN, and TiN enhancing Al-base alloys, TiN embedded in steels preventing grain growth, etc [3], [6], [38], [49].

In order to obtain the desired material, it is important to understand and predict the phases formed in the system at different compositions, temperatures, pressures, etc. For that task, phase diagrams are of great help since they predict the thermodynamically stable phases for the different conditions. In the case of thin films, where it is possible to synthesize alloys far from thermodynamic equilibrium (like in the case of this thesis), additional data of the metastable phases is needed.

The prime material investigated in this thesis is the metastable *cubic* solid solution B1-(Ti_{1-x}Al_x)N_y alloy with a rock salt structure deposited as thin film, in a very wide metal and non-metal compositional range ($0.28 \leq x \leq 0.63$ and $0.40 \leq y \leq 1.0$). To understand the thermal stability and the phase transformation of this alloy at high temperatures (up to 1400 °C) and ambient pressure, all available data was revised. Therefore, the chapter is divided in two parts. Firstly, the thermodynamic stable phases in the multicomponent Ti-Al-N system are examined in terms of composition and temperature variation at fixed pressure (1 atm). Secondly, the available thermodynamic data of the metastable *cubic* solid solution B1-(Ti_{1-x}Al_x)N_y is presented. Additionally, as a guide for the reader, the most relevant phases in this work, stable and metastable, and their structure data are presented at the end of this chapter.

3.1 Stable phases in the Ti-Al-N system

Figure 3.1: (a) Ti-Al phase diagram by Kainuma et al. [50], (b) Al-N phase diagram assessed by Hillert and Jonsson [51] and (c) Ti-N phase diagram assessed by Chen and Sundman [52].

The Ti-Al-N system presents a large variety of stable binary and ternary phases. The majority of the binary compounds are mixtures of Ti and Al, and only three of them contain nitrogen. The Ti-Al mixtures are intermetallic phases: Al₃Ti, AlTi, AlTi₃, Al₂Ti and Al₅Ti₂. Some have a wide compositional range of existence like TiAl and AlTi₃, while others have a very narrow one like Al₃Ti and Al₂Ti, as shown in Figure 3.1 (a). Their crystal structures are varied, e.g. γ -TiAl (L1₀), α_2 -AlTi₃ (DO₁₉), Al₃Ti (DO₂₂).

The three binary phases containing nitrogen are AlN, TiN and Ti_2N . AlN has a hexagonal (*wurtzite*) structure and a very narrow compositional range as shown in Figure 3.1 (b) [51]. This phase is a wide-band-gap (6.3 eV) semiconductor which does not accommodate any excess nitrogen or aluminum under thermodynamic equilibrium. Ti_2N presents a tetragonal structure with a narrow compositional range and it is stable only at low temperatures as shown in Figure 3.1 (c) [52]. Finally, TiN belongs to the transition metal nitrides (TMN) with a rock salt (B1) structure, which can be seen as two face-centered cubic (*fcc*) structures with one unit cell shifted half an *a*-axis towards the other. One *fcc* lattice is occupied by Ti atoms and the other by N atoms. One main characteristic of TMNs is that they can accommodate a large quantity of nitrogen deficiency via nitrogen vacancies in the N lattice [3], [53], making TiN stable over a large compositional range as it is shown in Figure 3.1 (c). TiN can also accommodate N overstoichiometry through metal vacancies [54].

Figure 3.2: Schematic stacking sequence along *c*-axis of MAX phases Ti_2AlN and Ti_4AlN_3 .

Only three ternary compounds are stable in the Ti-Al-N system: Ti_2AlN , Ti_3AlN and Ti_4AlN_3 . Ti_3AlN has a L1_2 -type structure and can be obtained after prolonged annealing at relatively low temperatures, i.e. 1000 °C [52]. Ti_2AlN and Ti_4AlN_3 belong to the MAX phases (for more details on MAX phases see Chapter 2 section Intercalation). Their structure is constituted by Ti_6N octahedral layers separated by Al layers, and depending on the amount *n* of Ti_6N layers separated by A layers, it will be Ti_2AlN (*n* = 1 layer) or Ti_4AlN_3 (*n* = 3 layers) [38]. The schematic view of their structure is shown in Figure 3.2.

Figure 3.3: Isothermal sections of Ti-Al-N at (a) 1300 °C assessed by Procopio *et al.* [55]. Insert on the left corner is the old phase diagram reported by Chen and Sundman [52]. (b) 900 °C and (c) 1200 °C calculated by Chen and Sundman [52].

For the Ti-Al-N system both MAX phases have shown to accommodate N vacancies [56]–[58], making their compositional range broad. Among the ternary compounds Ti_2AlN exists over a large temperature and composition range, i.e. 700 to 1600 °C (e.g. see Figure 3.3) [52]; while Ti_4AlN_3 has a very narrow temperature range around 1300 °C, as shown by Procopio *et al.* in Figure 3.3(a) [55]. As side note, Ti_4AlN_3 was wrongly believed to be $\text{Ti}_3\text{Al}_2\text{N}_2$ until Barsoum *et al.* showed that it is the MAX phase TiAlN_3 [59].

3.2 Metastable *cubic* solid solution ($\text{Ti}_{1-x}\text{Al}_x$) N_y

Metastable solid solution $c\text{-(Ti}_{1-x}\text{Al}_x)\text{N}_y$ alloys with a B1 structure can be obtained as thin films in a wide compositional range with an aluminum metal fraction $x < 0.7$ [3] and a nitrogen to metal ratio $0.37 \leq y \leq 1.02$ [54], [60], [61]. Their structure is similar to that of TiN, where two *fcc* sublattices are interpenetrated. One *fcc* lattice is randomly occupied by Ti and Al atoms, and the other by N atoms. Due to the technological relevance of this alloy as hard coating for cutting tools, extensive investigations on its thermal stability and phase transformations have been conducted. For the scope of this work, two relevant thermodynamic assessments are presented. The first is the quasi-binary TiN-AlN isostructural *cubic* phase diagram (N stoichiometric case) which has been optimized lately by Shulumba *et al.* (Figure 3.4) [12]. The second is the phase decomposition pattern of the metastable *cubic* $\text{Ti}_{1-x}\text{Al}_x\text{N}_{1-y}$ in the presence of nitrogen vacancies (N sub-stoichiometric case) calculated by Alling *et al.* via first principle calculations (Figure 3.5) [62].

The calculated phase diagram for $c\text{-(Ti}_{1-x}\text{Al}_x)\text{N}$ shows a miscibility gap, and three regions can be distinguished: spinodal, binodal and the solid solution (Figure 3.4) [12], [63]. The first one corresponds to the spinodal region, where the metastable $c\text{-(Ti}_{1-x}\text{Al}_x)\text{N}$ is subject to nucleation-free, isostructural phase separation into $c\text{-TiN}$ and the metastable $c\text{-AlN}$ (spinodal decomposition). In the binodal region, separation is also expected, but the phases $c\text{-TiN}$ and $c\text{-AlN}$ are formed via nucleation and growth. Finally, the solid solution region can be observed at high temperatures. The miscibility gap has an asymmetric shape with the maximum located at high Al content ($x \approx 0.8$) which is explained by the electronic structure mismatch between TiN and AlN, stronger in the Al-rich side [63]. Therefore, the driving force for segregation increases for alloys with high Al content. Furthermore, Shulumba *et al.* showed that lattice vibrations have a strong impact on the calculated B1- $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ phase diagram by lowering the maximum of the miscibility gap from 6560 to 2860 K and increasing the solubility of AlN in TiN as shown in Figure 3.4 [12].

Figure 3.4: Calculated quasi-binary TiN-AlN phase diagram for B1-(Ti_{1-x}Al_x)N by Shulumba *et al.* [12]. Adapted figure showing only the miscibility gap calculated with the SIFC TDEP method where the anharmonic vibrational entropy contribution is included. The dash-dotted lines correspond to the spinodal metastable region and the solid line to the binodal. Abbreviations: SIFC = symmetry-imposed force constants; TDEP = temperature-dependent effective potential method.

Cubic AlN is a metastable phase with a B1 structure and a small volume mismatch with *c*-TiN in comparison to *w*-AlN with *c*-TiN, since a volume difference of 22.5 % between *c*-AlN and *w*-AlN exists [64]. Under specific circumstances (e.g. solid solution *c*-(Ti,Al)N inside the miscibility gap), spinodal decomposition can take place. The formation of *c*-AlN is energetically favorable as an intermediate step during the phase transformation of *c*-(Ti,Al)N into the stable phases *c*-TiN and *w*-AlN following the path:

If enough energy is given to the system, *c*-AlN will eventually transform into the thermodynamic stable phase *w*-AlN via nucleation and growth [13], [63]. This

transformation is not accounted for in the B1-(Ti_{1-x}Al_x)N phase diagram presented by Shulumba *et al.* (Figure 3.4), nor in the following decomposition pattern map, since only isostructural phase separation is considered and of relevance to predict.

The effect of nitrogen substoichiometry on the phase stability of the metastable *cubic* B1 (Ti_{1-x}Al_x)N_y ($y < 1$) alloys has been investigated by Alling *et al.* using static *ab initio* calculations [62]. They predicted the preferred isostructural decomposition pattern of *c*-(Ti_{1-x}Al_x)N_y in the x-y compositional space as shown in Figure 3.5. The length of the arrows represents the magnitude of the driving force for nucleation-free phase separation, and the arrows point toward the preferred decomposition direction. A point represents no driving force for nucleation-free phase separation. The map can be divided in three major regions according to Alling *et al.*, which were schematically drawn in the map for a better visualization:

- (1) High Al content, between N-rich and N-poor regions: Most energetically unstable compositional range. There are no reports of synthesis of stable or metastable *cubic* (Ti,Al)N alloys. Nevertheless, the use of epitaxial growth, pressure or a multilayer configurations could help obtain alloys in this range [65], [66].
- (2) Close to N stoichiometry and medium-high Al content: Nitrogen tends to stick preferably to aluminum due to unfavorable accommodation of N vacancies in AlN which presents a semiconducting bonding [62]. On the other hand, TiN can accommodate the N vacancies due to its broad stable composition range in the N deficient side (see Figure 3.1 (c)), as has been shown experimentally [67].
- (3) The N-poor, Ti-rich region: Strong driving force for precipitation of metallic Al or Al-Ti mixtures and tendency of N to stick to Ti. AlN formation is not energetically favorable since the phase does not accommodate N vacancies (see comment on region (2)), and all compositions between Al metallic mixtures and AlN are unfavorable. Alling *et al.* also mention that the formation of Ti-Al alloys

or compounds has the same driving force as foret. stabilizing hexagonal MAX phases and cubic Ti_3AlN perovskite [62].

Figure 3.5: Energetically preferred decomposition pattern of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ in x - y composition space calculated by Alling et al. [62]. The arrows point in the direction in which a phase separation would be most energetically favorable. Their length indicates the magnitude of this energy. Dot indicates no driving force for phase separation. Map modified from the original by adding a division of three regions.

3.3 Summary of relevant phases

The information presented in this chapter should serve as a guide to predict and understand the phase evolution of metastable *cubic* solid solution $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ thin films, when the composition of the alloys is varied and the material is subjected to high temperatures. The relevant phases for this thesis and their respective structures are listed below:

Phase	Crystal structure	ICDD #	Space group	Lattice parameter (Å)
(Ti,Al)N*	Cubic	Al-dependent	Fm3m (225)	$4.120 < a < 4.241$
TiN	Cubic	00-038-1420	Fm3m (225)	$a = 4.241$
AlN*	Cubic	00-025-1495	Fm3m (225)	$a = 4.120$
AlN	Hexagonal	00-025-1133	P63mc (186)	$a = 3.111$ $c = 4.979$
Ti₂AlN	Hexagonal	00-055-0434	P63/mmc (194)	$a = 2.989$ $c = 13.614$
Ti₄AlN₃	Hexagonal	04-010-5108	P63/mmc (194)	$a = 2.988$ $c = 23.372$
Ti₆Al₂N₄*	Hexagonal	This work	unknown	$a = 2.988$ $c = 56.2$
Al₃Ti	Tetragonal	01-072-5006	I4/mmm (139)	$a = 3.853$ $c = 8.583$
Al₅Ti₂	Tetragonal	03-065-9788	P4/mmm (123)	$a = 3.905$ $c = 7.4$

* *Metastable phase.*

4. THIN FILMS

According to literature, a thin film is broadly considered as a layer of material with a thickness that can vary from an atomic monolayer up to several microns [3]–[5], [68]. It must show a difference of at least one order of magnitude between the lateral dimensions and the layer thickness, and it can be on a substrate (partially confined), confined between two materials or free-standing. Moreover, a multilayer is referred to as a stack of thin films. The process of synthesizing a thin film atom by atom from a source on a growth surface is called deposition, common methods of which are physical vapor deposition (PVD) and chemical vapor deposition (CVD) [4], [69]. The method and deposition parameters produce distinct microstructures and, consequently, properties. A deep understanding of this strong process-microstructure-properties correlation must thus be developed to achieve the desired properties, rendering the characterization of the thin film a crucial task.

In this thesis, a PVD process called cathodic arc evaporation was used for depositing (Ti,Al)N thin films, which is currently used for coating cutting tools [1], [2], [70]. The main focus lies on the characterization of the film microstructure and hardness in as-deposited and annealed (up to 1400 °C) states. Therefore, the chapter is divided in two main sections: in the first one, the steps involved in the synthesis of a thin film by cathodic arc evaporation are described, as well as the employed experimental setup; the second part briefly introduces the characterization techniques used. Due to its relative novelty, atom probe tomography (APT) will be described in more detail as a nonstandard technique, as well as the different data analysis methods and graphical representations employed in this study.

4.1 Synthesis

In general, the synthesis of a thin film by a PVD process requires three main steps; the first is the creation of a material vapor from a source, followed by the transport of the vapor phase to the substrate and, finally, the film growth through condensation of vapor species and nucleation. All three steps can be controlled independently to some extent, making PVD techniques versatile tools to control the microstructure and properties of the deposited films.

4.1.1 Cathodic arc evaporation

Cathodic arc evaporation belongs to the PVD processes where the vapor phase of the desired material source (cathode target) is obtained by heating it with a high current (30 - 400 A), low voltage (tens of volts) arc discharge that moves along the cathode surface either controlled or randomly [4], [69], [70]. The arc spot (10^{-8} to 10^{-4} m diameter) carries high current densities ($\sim 10^8$ to 10^{12} A/m²) which erode the cathode by melting and vaporization as well as particle ejection. The ionized plasma generated by the process consists of electrons, multivalent ions, neutral vapor atoms and droplets, where the desired species are the metal ions and neutrals. A schematic view of a cathodic arc evaporation system is shown in Figure 4.1. The arc is usually ignited by a mechanical striker and confined to the cathode surface by a boundary shield. The vapor with multivalent ions is responsible for sustaining the arc. While the arc spot movement is governed, to a certain extent, on cathode composition, gas species and pressure, presence of magnetic fields, etc. with a typical velocity of ~ 100 m/s [4]. Furthermore, the ions ejected from the cathode surface are typically accelerated towards the substrate by applying a negative bias voltage to the substrate, thus controlling the energy of the condensing species.

The relatively high possible ionization of the material atoms in the plasma (30 - 100 %) [70], high kinetic energies (10 - 200 eV) [71], and multiple charge states of the ions [70]

are crucial parameters for the resulting microstructure and properties of the coating. These characteristics are responsible for relatively high deposition rates (e.g. 200 nm/min), a dense structure and good adhesion [2], [6], [70].

Figure 4.1: Schematic view of a cathodic arc deposition system with a model of the source emission. Adapted from Ohring [4].

Deposition of compound materials (nitrides, oxides, etc.) by cathodic arc evaporation is usually performed in a reactive atmosphere where some of the compound elements are evaporated from the cathode target, followed by their reaction with a gas (e.g. N_2 , O_2) to form the desired compound. This variation of the technique is called reactive cathodic arc evaporation [69], [70]. It is preferably used for deposition of compound materials since evaporation of a compound target does not necessarily result in a vapor phase with the same composition, but rather a dissociation of the vapor species into fragments of the compound [69]. It is one of the most common deposition processes used for refractory nitrides, carbonitrides, and carbides in the cutting tool industry [1], [2], [4].

Figure 4.2: (a) SEM micrograph of (Ti,Al)N film surface roughness due to macroparticles and (b) cross section in SE contrast of (Ti,Al)N thin film with embedded macroparticles.

One of the main disadvantages of this technique is the generation of macroparticles (droplets), which arise from the erosion of the cathode when the arc stays too long on one spot, locally melting the cathode [69]–[71]. The droplets arise from the ejection of liquid or solid particles due to thermal shock and hydrodynamic effects [4], resulting in a thin film with randomly embedded macroparticles. This leads to a disrupted film growth, an increase of the nucleation sites for new grains, a reduction in adhesion of the coating, an increase in surface roughness, and the creation of voids beneath and above them [2], [72], [73] as shown in Figure 4.2. Moreover, their composition tends to be more metallic compared to the reacted compound film (e.g. nitrides) [70], which can degrade the mechanical properties of the thin film. Size and density of the macroparticles can be controlled by the arc movement, deposition parameters or cathode target [69], [71], [74]. They can also be removed by the usage of a filter due to the differences in mass and properties, or by producing a diffuse arc [71], [75]. However, the deposition rate drops substantially and it becomes less attractive for industrial scale deposition. Therefore, no filter is used during industrial scale depositions, nor for the thin films deposited in this thesis.

A second disadvantage of the cathodic arc evaporation process is the relatively high residual compressive stress caused by the high kinetic energy of the impinging ions, which generates lattice defects [3], [76], [77]. The compressive residual stresses are responsible for the increase in hardness since they also act as obstacles for dislocation movement and have a crack closing effect. Nevertheless, if the stresses are too high, delamination of the thin film can occur [3], [78].

4.1.2 Film growth

The final step involved in the synthesis of a thin film is its growth. This consists in consecutive nucleation, island growth, coalescence of islands, competitive grain growth, formation of a continuous structure, recrystallization and film thickness growth [79], [80]; making the evolution of the thin film structure a rather complex phenomenon. Therefore, a lot of effort has been put into understanding the correlation between deposition parameters and thin film microstructure, leading to the development and refinement of structure zone model (SZM) diagrams. SZMs should be a guideline to understand the mechanisms dominating the film growth, and thereby enable tuning of the deposition process parameters in order to obtain the desired microstructure and film properties.

There is no specific SZM for cathodic arc evaporated coatings, nevertheless a good approach is the model presented by Barna *et al.* for PVD thin films which is shown schematically in Figure 4.3 [79]. It was constructed by considering the role of impurities in addition to the most determinant atomic processes controlling the microstructure evolution: surface and bulk diffusion. Three main zones can be distinguished according to Barna *et al.*: *Zone I*, with low deposition temperatures, where porous and low density thin films are obtained with thin columns (1-10 nm) due to low surface and low bulk diffusion; *Zone T*, where surface diffusion is activated and a competitive columnar growth of the different crystal orientations takes place (here, texture changes with the film thickness); and *Zone II*, where surface and volume diffusion are active and high

due to the high deposition temperatures, leading to wide columnar growth with similar orientation.

Cathodic arc evaporation films are typically located in the intermediate zone (*zone T*) since they present a dense columnar microstructure [2], [80]. A competitive columnar growth takes place at the beginning of the film growth and with increasing thickness, a dominant crystallographic orientation of the columns is observed [80].

Figure 4.3: Structure zone model for PVD film growth for (a-c) different film thickness. Adapted from Barna et al. [79].

Surface and volume diffusion during film growth are primarily affected by the temperature. However, in the case of deposition of transition metal nitrides by PVD processes (cathodic arc evaporation), the synthesis temperature is low in comparison to the melting point of the material ($0.2 - 0.3 T_m$ of the material deposited) [3], [70] and the energetic particle bombardment can be used to modify the adatom mobilities and nucleation rates during deposition [80]. These factors lead to kinetic limitations during growth of thin films far from thermodynamic equilibrium conditions. Therefore, by using PVD processes, it is possible to have controlled synthesis of metastable phases or artificial structures [3], [80]. A good example, and the base of this thesis, is the deposition of metastable *cubic* solid solution *c*-(Ti,Al)N thin films with compositions

inside the miscibility gap, where in thermodynamic equilibrium a demixing into c -TiN and w -AlN would be expected [52].

The appropriate selection of the deposition parameters (substrate negative bias, gas atmosphere, deposition pressure, substrate temperature, etc.) is crucial to achieve the desired microstructure and film properties.

4.1.3 Experimental setup

The deposition configuration used during this thesis consists of three circular cathodes of 100 mm in diameter mounted next to each other, facing a rotating cylinder where the substrates are placed, as shown schematically in Figure 4.4. During deposition, the cylinder is set to rotate, maintain a growth temperature of ~ 450 °C and a deposition rate $0.1 \mu\text{m}/\text{min}$, while the total gas pressure is kept at 2 Pa. A negative bias of - 30 V is used in all depositions unless stated otherwise. In order to study the effect of aluminum metal fraction when changing a deposition parameter, cathodes with different metal ratios (Ti:Al) were selected: 33:67, 45:55 and 100:0. Two different substrates were used: Fe foil and cemented carbide (ISO SNUN120408) comprising tungsten carbide (WC) with a 12 wt. % Co binder and less than 2 wt.% of other carbides, e.g. tantalum carbide. The first substrate was used for obtaining free-standing thin film since the Fe foils can be dissolved in HCl. The second one was selected so as to measure hardness and determine film-substrate interaction.

Three main deposition conditions were used in this thesis:

1. A mixed reactive gas atmosphere. Ar and N₂ gas were mixed in different ratios at a fixed total gas pressure, in order to reduce the nitrogen content of the deposited thin films.
2. An increase in negative bias voltage on the substrate. The kinetic energy of the ions arriving at the substrate was varied by changing the bias voltage in order to change the microstructure of the thin film.

3. A multilayer configuration. Deposition of (Ti,Al)N/TiN multilayers was implemented in order to have a predefined artificial structure and observe the effect of increasing interfaces.

For the (Ti,Al)N multilayer deposition, pure Ti cathodes were placed on the opposite side of the rotating cylinder (sample holder) in relation to the Ti:Al cathodes (Figure 4.4). This way, a multilayer configuration was obtained. The bilayer thickness was varied with the speed of the cylinder.

Figure 4.4: Schematic view of the deposition setup used for the synthesis of the thin films investigated in this thesis.

4.2 Characterization techniques

The characterization of thin films is not a trivial task. Challenges arise from the combination of the material and the limited dimensions of the film with the limitations and pre-requirements of the characterization technique. More specifically: the thickness of the thin film, the amount of material available for analysis, the change in microstructure along film thickness, the substrate used, the difficulty of quantitative chemical analysis (especially light elements) and structural analysis, the sample preparation and other challenges must be overcome for unambiguous characterization of the thin film microstructure and properties [81]. Therefore, it is of great relevance to choose the appropriate characterization techniques and to combine different techniques that cover different scales and information about the thin film.

The techniques used during this study are presented below with a description of the setup and parameters used. The main focus was on microstructure and hardness characterization of as-deposited and annealed thin films.

4.2.1 Differential scanning calorimetry

The thermal response of (Ti,Al) N_y alloys and (Ti,Al)N/TiN multilayers was measured in a differential scanning calorimeter (DSC) Netsch STA 449C operating with an argon flow of 50 ml/min. An alumina crucible holding 50 mg of the sample in powder form was used for each measurement. A zirconium oxygen getter was placed in the vicinity of the sample to avoid oxidation of the samples. First, samples were outgassed at 250 °C for one hour, directly followed by heating to 1400 °C with a rate of 20 °C/min. A second run was used as baseline and subtracted from the first measurement [82]. In some cases, a thermogravimetry (TG) measurement was coupled in order to obtain information about mass change attributed to phase transformations. Following the convention in the hard coating field, exothermic reactions are plotted upwards.

In addition, the DSC was used to heat powder samples to intermediate temperatures under the same conditions as stated above, to track the phase transformation sequence. A single heating cycle up to the desired temperature and 15 mg of powder were used. The maximum temperatures ranged from 700 to 1400 °C in 100 °C or 50 °C steps, when necessary.

Powder samples were obtained by deposition of the thin film material on Fe foils followed by a removal of the latter. First, the Fe foil was thinned mechanically by backside grinding, and then dissolved in hydrochloric acid (37 %). A magnet was used to confirm complete dissolution of the substrate. The recovered coating flakes were cleaned with distilled water and acetone and ground into a fine powder. The particles presented a flake-like shape approximately 30 - 80 μm long, fulfilling the criteria of a free-standing thin film. This Fe foil removal process has proven to yield a powder with the same stoichiometry and crystal structure as the deposited coating [83]. It also achieves a complete dissolution of the macroparticles generated during cathodic arc deposition, since the composition is of a more metallic nature.

4.2.2 X-ray diffraction

Phase analysis, preferred orientation (texture) and stress measurements were carried out in a PANalytical X'Pert PRO MPD and a PANalytical Empyrean diffractometer using Cu K_α radiation. A focusing, symmetric Bragg Brentano configuration was used for phase analysis. In this setup, only lattice planes parallel to the sample surface contribute to the diffraction peaks. Additional low-background optics were used in the PANalytical Empyrean diffractometer. The diffractograms were recorded at room temperature either as-deposited or after annealing. A silicon zero diffraction plate was used as sample holder in order to reduce background signal. Stress measurements were performed on the 422 diffraction peak of $c\text{-(Ti,Al)N}$ by using the $\sin^2\psi$ method. The elastic constants used to convert the strain measurements to stress are: $E = 460$ GPa and $\nu = 0.20$, obtained from *ab initio* calculations [18]. Pole figure measurements were

performed in the main reflections 111, 200 and 220 of the c -(Ti,Al)N structure with a resolution of three degrees for ψ and ϕ .

Phase analysis was performed in all as-deposited and annealed powder samples and coatings on cemented WC/Co-based substrates. Due to the predominant flake-like particle shape of the powder samples, preferred crystallographic orientation was measured in as deposited c -(Al,Ti)N_y powder samples. This way, the effect of a reminiscent preferred orientation could be separated from the change in structure factor caused by the N vacancies accommodated in the B1 crystal structure. Stress measurements were performed only in the as-deposited c -(Ti,Al)N_y coatings on WC/Co substrates where the applied substrate bias was varied, since a change in the residual compressive stresses was expected.

4.2.3 Transmission electron microscopy

Transmission electron microscopy (TEM), scanning TEM (STEM) and selected area diffraction (SAD) were used to characterize the microstructure and crystal structure of some samples in more detail. For samples in paper I to III, TEM imaging and selected area diffraction were performed in a JEOL JEM 2010 at an acceleration voltage of 200 kV. TEM/STEM analysis was carried out using a cold field emission gun JEOL JEM-ARM 200F at 200 kV equipped with a STEM Cs corrector (CESCOR, CEOS GmbH). A high angle annular dark-field (HAADF) detector was used for Z-contrast STEM imaging (paper II). Some of the FIB-prepared TEM thin lamellae received an additional thinning with an Ar Ion gun (Nanomill Mod. 1040, Fischione) for high-resolution imaging (paper II). The Ar ion beam current used was 125 pA for 20 min at a tilt angle of $\pm 10^\circ$.

For paper IV and V, cross sectional TEM samples were prepared through mechanical grinding and polishing, followed by Ar ion beam milling in a Gatan 691 precision ion polishing system until the sample was electron transparent (< 100 nm). These samples were investigated in an energy-filtered analytical transmission electron microscope

(EFTEM) using a cold field emission gun JEOL JEM-ARM 200 operated at an acceleration voltage of 200 kV. STEM imaging was performed in a FEI Tecnai G2 TF 20 UT microscope at an acceleration voltage of 200 kV using a high angle annular dark field detector.

4.2.4 Scanning electron microscopy

A scanning electron/focused ion beam (SEM/FIB) microscope, FEI Helios NanoLab600, was used for surface morphology imaging, cross section preparation, scanning transmission imaging (in SEM), energy dispersive X-ray analysis (EDS), and electron backscatter diffraction (EBSD). In situ lift-out techniques were used to prepare samples for transmission electron microscopy [84] and atom probe tomography (APT) [85] with a final cleaning step of 2 kV FIB milling. More details on APT sample preparation will be given in the respective section of this chapter.

Investigations of the chemical and phase distribution were performed by EDS and EBSD in some samples in paper III complementary to APT, due to the relatively large size of the inhomogeneities across the film thickness.

4.2.5 Nanoindentation

Hardness measurements of (Ti,Al) N_y thin films on WC/Co-based substrates were performed with an UMIS nanoindenter using a Berkovich diamond tip. To avoid effects of surface topography on hardness measurements, the samples were prepared as tapered cross sections (taper angle $\sim 10^\circ$ relative to the sample surface) by mechanically grinding and polishing to a mirror-like finish using a 1 μm diamond suspension in the final step. A maximum load of 50 mN and 30 to 50 indents for each sample were used with fused silica as reference. The indentation depths for this amount of load were around 250 nm, which is less than 10 % of the film's thickness. Average hardness values were obtained using the Oliver and Pharr method [86].

The hardness behavior at high temperatures was obtained from post-annealing hardness measurements of coatings on WC/Co-based substrates (paper III and IV). The annealing was performed in a tube furnace at a vacuum of 7×10^{-4} Pa. Isothermal annealing treatments were performed at $T_{\max} = 700, 800, 900, 1000, 1100,$ and 1200 °C for 15 min with heating and cooling rates of 20 °C/min.

4.2.6 Elastic recoil detection analysis

Elemental composition of some as-deposited (Ti,Al)N_y samples on WC/Co based substrates was measured by Time-of-Flight Energy (ToF-E) Elastic Recoil Detection Analysis (ERDA). The measurements were performed using a 36 MeV ¹²⁷I⁸⁺ ion beam with an incident angle of 67.5° relative to the surface normal and a spot size of 2 mm x 2 mm. Forward scattered recoil ions were detected with a time-of-flight energy detector at an angle of 45° with respect to the incoming ion beam [87]. The measured recoil ToF-E spectra were converted off-line into relative atomic concentration profiles using the CONTES code [88].

The technique requires a surface roughness in the nanometer range and inhomogeneities smaller than the ion beam spot cannot be detected. This is why the technique does not yield reliable results of samples containing high amounts of macroparticles, i.e. *c*-(Ti,Al)N_y (*y* < 0.9). However, it was mainly use to cross-validate compositional measurements of the *cubic* solid solution phase with atom probe tomography for samples with low amount of macroparticles (paper I), i.e. *c*-(Ti,Al)N_y (*y* > 0.9).

4.3 Atom Probe Tomography

Atom probe tomography (APT) is a powerful destructive technique that gives chemical and spatial information with near-atomic resolution (at least 0.04 nm in depth and 0.20 nm laterally) [89], [90]. It combines a 3D visualization of atomic-scale microstructure with quantitative data analysis. One of the strengths of APT is the ability to measure all the elements (light to heavy) with an equivalent efficiency. A wide range of materials including metals, semiconductors, ceramics and limited biological or organic materials [91]–[93] can be measured [94]–[96]. The volume investigated is usually small (approx. 100 nm x 100 nm x 200 nm) meaning that the scientific questions to be solved with atom probe must be in the nanometer scale.

4.3.1 Principle of operation

The main principle is the controlled field evaporation ($\sim 10 - 50$ V/nm) atom by atom from a very sharp tip (~ 50 nm radius) in ultra-high vacuum ($\sim 10^{-11}$ mbar) at cryogenic temperatures (> 15 K). Atoms at the surface of the tip are ionized and field evaporated with the combined effect of a laser or voltage pulse applied to the specimen and a static electric field that accelerates the ions toward a 2D detector. The experimental setup for atom probe tomography is shown in Figure 4.5.

The evaporation field (F) required for ionization depends on the elements, phases and their atomic bonding (crystal structure and bond type) and typically ranges from 10 to 50 V/nm. The field at the apex of an APT sample is calculated as follows [96]:

$$F = \frac{V}{k_f R}$$

where V is the applied high voltage, R the tip radius and k_f is a field factor that takes into account the tip shape and its electrostatic environment [97]. The evaporation field during the measurement can be estimated from the ratio of different charge states of an

ion by using the Kingham curves [98]. This can be combined with SEM images before and after run of the APT tip, in order to obtain tip shape information.

Figure 4.5: Experimental setup for local electrode atom probe tomography with a 2D detector, after [96].

Once the ions are field evaporated, they are accelerated towards a microchannel plate in front of the detector where the signal is amplified by converting a single ion into a cloud of electrons. These reach a delay-line detector and the positions in x and y are recorded. Since the ions are field evaporated by a controlled pulse and accelerated by a known electrostatic field, the time of flight (t_{flight}) of the ion can be used to determine its mass-to-charge ratio (m/q):

$$\frac{1}{2} m v^2 = q V \quad ; \quad v = \frac{L}{t_{flight}} \quad \Longrightarrow \quad \frac{m}{q} = 2 V \left(\frac{t_{flight}}{L} \right)^2$$

where v is the velocity, m is the mass and q is the charge of the ion, V is the total voltage and L the flight length.

The collected time-of-flight information (independent of the ion position) during an APT measurement is generally represented as a histogram called mass-to-charge spectrum or mass spectrum (Figure 4.6). The units of m/q are commonly expressed in Daltons (Da). The elemental nature of the ions can be identified by measuring the mass-to-charge-state ratio, since every element has a characteristic number of isotopes with a fixed natural abundance.

Figure 4.6: Mass-to-charge spectrum of a (Ti,Al)N sample.

The 3D reconstruction requires post-processing of the acquired data with specialized software based on an algorithm (protocol) that calculates the original position of the detected ions by a reverse-projection onto the surface of a virtual specimen. The basic protocol used in most software was published by Bas *et al.* [99]. It assumes that the tip is a truncated cone with a hemispherical cap, that the ions are projected along a straight trajectory (point-projection) and that the atoms are field evaporated layer-by-layer from the outermost shell inwards. That way, the z position of the ions can be calculated from the sequence of detection, and in combination with the detected x, y coordinates and the *time-of-flight*, a 3D reconstruction with chemical information can be made. Four fundamental parameters are required for a reconstruction: the evaporation field, the field

factor (tip geometry and electrostatic field dependency), the image compression factor (tip shape dependent) and the detection efficiency of the instrument.

The reconstruction of the APT tip is the first approach of a visual analysis of the data and depending on the type of information to be extracted, different algorithms and analysis tools are implemented. The tools used in this thesis are presented at the end of this chapter.

4.3.2 Limitations in APT

As any technique, APT has its limitations and it is important to have them in mind when performing data analysis and visualization. Artifacts in a reconstruction can arise due to the nature of the material such as presence of phases with different evaporation fields, grain boundaries, interfaces, clusters/segregations, bad thermal transport at cryogenic temperatures, etc. [96]. Also, a bad choice of measurement parameters, the specimen tip shape (no perfect hemisphere and shank angle) or a wrong choice of reconstruction parameters can lead to misleading results. Some of the main limitations encountered in this thesis and how they were mitigated are listed below.

Thermal tails in mass-to-charge peaks

They appear in laser mode when the heat from the laser pulse is not carried away fast enough. A longer cooling time of the tip can cause ions to be emitted shortly after the pulse (peak tail) and between pulses (background). Thermal tails can affect the accuracy of composition measurements since peaks may overlap or be completely hidden in the tail of another peak [96]. Tip shape (large shank angles) and measurement parameters (laser power and repetition rate, specimen temperature) can help to mitigate the effect.

Complex ion evaporation

The evaporation of complex ions (e.g. TiN^+ , CN^+ , N_2^+ , Ti_2N^+) in compound materials containing nitrides, carbides and oxides is commonly observed (e.g. Figure 4.6). This process reduces the depth resolution of the atom probe [100]. It also leads to additional peaks in the mass spectrum, making unambiguous assignment more complicated and potentially causing peak overlap. Reduction in the laser power (in laser mode) decreases the amount of complex ions when measuring nitrides [101].

Multiple event detection

It is a common limitation in the delay-line position-sensitive detectors. It takes place when multiple events (i.e. ions) arrive close in time or/and in location. The extension of the signal loss is difficult to quantify since the exact number of ions emitted is unknown and some get lost in the detection efficiency of the detector [96]. In this work a range of 40 - 50 % of the detected ion events were multiple events, consistent with literature [102], [103]. The amount can be reduced by increasing the laser power, nevertheless, this will increase the complex ion evaporation and degrade the compositional accuracy in nitrides [101].

Underestimation of N and C content

An underestimation of carbon and nitrogen contents of up to 5 at. % in carbides and in some nitride materials when using APT has been reported in literature [61], [102]. The carbon deficiency was suggested to be strongly correlated with the detector dead time, the chemical bond and the carbon sites in the carbide lattice [102], which is similar in some nitrides, e.g. $w\text{-AlN}$ [61]. Additionally, an overlap between complex and single carbon (nitrogen) isotope ion peaks contribute to the underestimation, e.g. C_2^+ , C_4^{2+} and Ti^{2+} , or N^+ and N_2^{+2} . The N and C deficiency in the total composition of a given volume (not the spatial information) can be corrected in some cases by using isolated isotopes (if they are resolved in the mass spectrum) and calculating the concentration of the other

isotopes from the natural abundance [102], e.g. by using ^{13}C for calculating ^{12}C or $^{14.5}\text{N}_2^{2+}$ to calculate the overlap between $^{14}\text{N}^+$ and $^{14}\text{N}_2^{2+}$. Cross-validation of compositional measurements with other techniques can also be of great help.

For an unambiguous interpretation and reconstruction of the APT data, it is important to use other techniques to adjust the reconstruction parameters and to validate the observations. SEM images before and after running an APT tip are of great help and a preceding characterization of the sample with other techniques like XRD, SEM, TEM is highly recommended.

4.3.3 Sample preparation

All APT tips in this thesis were prepared by a FIB-based wedge lift-out technique [85]. Due to the presence of compressive stress in the films, an additional rectangular cut around the region of interest was performed. This way, a release of stress is obtained and issues regarding bending fracture during lift-out are avoided.

Figure 4.7: SEM image of an atom probe tip. Tilted view (52°).

The main requirements of an APT tip is a radius of 50 to 100 nm, smooth surface (free of cracks, grooves or protrusions) and an appropriate shank angle [96]. The majority of

the APT tips measured in this thesis fulfilled these requirements and were produced with a large shank angle, e.g. at a depth of 500 nm from the tip, a diameter of 350 - 400 nm was typically obtained (Figure 4.7). This was found to be most suitable for minimizing thermal tails and increasing the quality of the mass-to-charge spectrum (Figure 4.6).

4.3.4 APT measurement

APT measurements in this thesis were performed using a local electrode atom probe (Cameca LEAP 3000 X HR) in laser mode (10 ps pulse length, 532 nm wavelength), an evaporation rate of 5 atoms per 1000 pulses, and a laser repetition frequency of 200 kHz with a pulse energy of 0.5 nJ. The cryostat temperature was set to 60 K (base temperature). The detection efficiency of this instrument is of 37 % [96].

Data reconstruction was carried out with the commercial software package IVAS (version 3.6.8, Cameca) using voltage-based tip shape reconstruction. The reconstruction parameters such as evaporation field and the geometry factor (k_f) accounting for tip shape were obtained from the mass spectrum using Kingham curves [98] in combination with SEM images before and after run from which the length of the reconstructed tip could be estimated. A fixed image compression factor of 1.65 was used. For the majority of the *c*-(Ti,Al)N samples an evaporation field of 40 V/nm was obtained (consistent with literature [103]). k_f was set from 3.3 to 4.1 individually for each tip due to varying tip shank angles.

4.3.5 Visualization and data analysis

The most common data analysis and visualizations tools used in this thesis are presented in the following:

1D concentration profiles

Composition in APT is measured from the proportion of ions/atoms of each species in a volume (voxel). Therefore, a 1D profile is a plot of the composition along a volume also called region of interest (ROI) which can have a cuboid, sphere or cylinder shape. The ROI is divided into voxels with either a fixed amount of counts (ions) or a fixed volume from which the composition is calculated and plotted in a 1D concentration profile. Only statistical variations are considered in the uncertainty (error bar).

A critical step when calculating 1D concentration profiles is the selection of the voxel size. If it is too small, then the statistic will be low and it can even contain no ion counts. If the voxel is too large, fine details or composition fluctuations may be lost from the analysis. The selection of the voxel size involves a balance between positional error and statistical error.

Iso-concentration surfaces

An iso-concentration surface (isosurfaces) is a 3D visualization of an element distribution within the reconstructed tip. The analysis tool is based on isolating blocks with a specific composition (or ion density) and connecting them to a 3D surface within the reconstructed volume [96]. This helps to identify different phases, grain boundaries, precipitates and microstructure morphologies within the tip (Figure 4.8 (a,b)). Isosurfaces have no physical meaning, but are helpful for visualization or as a reference point for a proximity histogram calculation.

Proximity histograms

A proximity histogram (proxigram) is an algorithm that calculates a composition profile in 3D relative to a reference surface [104]. The first step is the creation of an isosurface which highlights the microstructure feature to be analyzed (Figure 4.8 (a, b)). Then, the composition is examined normal to the isosurface in layers (shells) at increasing/decreasing distances (Figure 4.8 (c)), therefore no restriction in the surface geometry is imposed. Then, from each shell a concentration distribution profile (histogram) of each element present is generated. Finally, the data extracted from the histograms (average composition) is plotted as a proxigram composition profile (Figure 4.8 (d)). Proxigram have no restrictions on the surface morphology (geometry) [104]. However, it is very sensitive to the choice of the isosurface concentration used to describe the feature of interest.

Figure 4.8: Proxigram analysis. (a) Several isoconcentration surfaces, (b) a specific surface selected for the analysis, (c) a 2D illustration of how the proxigram analysis measures the average composition normal to the surface and (d) the resulting proxigram composition profile. Adapted from [96].

Frequency distribution analysis

A FDA is a histogram obtained by dividing an APT dataset into small volumes (voxels) containing a fixed amount of n ions (e.g. $n > 50$) [96]. The procedure consists in: (1) dividing the data set into small volumes (voxels), (2) extracting the composition of each voxel, (3) plotting the composition of any element present (e.g. Ti, Al, N) or any desired ratio (e.g. Al metallic ratio, $\text{Al}/(\text{Ti}+\text{Al})$). The selection of the number of ions per voxel is a critical step in FDA. Optimized voxels are needed to minimize convolution effects, since the amplitude of the measured compositional fluctuations (especially for spinodal decomposition) depend on the voxel dimension and the amount of ions per voxel [105].

Figure 4.9: Aluminum composition histogram of as-deposited and 1200 °C annealed $(\text{Ti}_{0.74}\text{Al}_{0.26})\text{N}_{0.82}$. Calculated random distribution (binomial) is shown for comparison. Pearson coefficient of both measured distributions is given, where 0 indicates random distribution and 1 complete segregation [61].

Histograms were normalized to the total number of voxels of each analyzed volume for comparison purposes. For visual comparison, a random discrete distribution (binomial distribution) was calculated by using the average composition of the analyzed volume. An example of an Al composition histogram from this work with its corresponding binomial distribution of an as-deposited sample and after annealing at 1200 °C is shown in Figure 4.9 [61].

Pearson coefficient

The Pearson coefficient (μ) is a qualitative indicator of the deviation of a measured chemical composition distribution (histogram) from a binomial (random) distribution. In order to calculate μ , the average composition of the volume analyzed, the total number of voxels and the measured composition histogram are needed. Pearson coefficient is calculated using the chi square statistics, χ_e^2 , and normalized by the total number of voxels [96], [106]. It ranges from 0 to 1, where 0 indicates a random distribution and 1 complete segregation. μ is a qualitative indicator of segregation, since it does not distinguish between different levels and morphologies of segregation. In this study, it was interesting for the as-deposited (Ti,Al)N_y samples since chemical fluctuations can be investigated (paper I and II).

5. SUMMARY OF RESULTS

In this chapter, a summary of the most relevant results of this thesis is presented. Taken together, this work contributes mainly to the understanding of the effect of point defects on the phase transformations in *cubic* (Ti,Al)N alloys. It experimentally confirms theoretical predictions by Alling *et al.* on the effect of N vacancies on the decomposition pathway in *c*-(Ti,Al)N_y ($y < 1$) [62]. Furthermore, this work increases the understanding of the predicted mechanism behind the early decomposition onset of (Ti,Al)N/TiN multilayers by surface-directed spinodal decomposition. The specific contributions to the field are presented in greater detail below.

Paper I. Impact of nitrogen vacancies on the high temperature behavior of (Ti_{1-x}Al_x)N_y alloys

This is the first study of the thermal response and structural evolution in nitrogen deficient *cubic* solid solution (Ti_{1-x}Al_x)N_y ($y < 1$) thin films for different Al metal ratios ($x = 0.26, 0.48$ and 0.60) and a N deficiency from $y = 0.92$ to 0.75 . In order to reduce complexity, free-standing coatings were used in this investigation. The results show a substantial improvement of the thermal stability by reducing the nitrogen content for alloys with a Al metal fractions of $x = 0.48$ and 0.60 . Alloys with $x = 0.28$ presented nucleation and growth of Al-Ti clusters inside the grains and *w*-AlN formation at grain boundaries. The decomposition paths shown in this study are consistent (with minor deviations) with predictions performed by Alling *et al.* on *c*-(Ti,Al)N_y ($y < 1$) via static *ab initio* calculations [62].

The nitrogen deficiency is mainly accommodated through N vacancies in the *c*-(Ti_{1-x}Al_x)N_y phase in as-deposited thin films. At elevated temperatures, alloys with Al metal fraction $x = 0.48$ and 0.60 show spinodal decomposition into *c*-AlN and *c*-TiN

which is delayed with increasing N deficiency (Figure 5.1). As a consequence, the detrimental transformation of c -AlN into w -AlN is shifted to higher temperatures. It is suggested that the mixing energy of the system is reduced by the presence of N vacancies, due to a reduction of the mixing enthalpy and an alteration of the entropy. Collectively, this reduces the miscibility gap and brings the spinodal line to lower temperatures.

Figure 5.1: Reconstructed 3D APT tips of $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$, with $y = 0.92, 0.87$ and 0.75 , in their as deposited state, and after heat treatments at $900\text{ }^\circ\text{C}$, $1200\text{ }^\circ\text{C}$ and $1400\text{ }^\circ\text{C}$. Tips were extracted from single grains and no grain boundaries are present. Only Al and Ti ions are presented for clarity [61].

In addition, the suppressed spinodal decomposition leads to a concurrent phase separation into c -TiN and w -AlN via nucleation and growth. This happens preferably

along grain boundaries at high temperatures and even inside the grains at high vacancy concentrations ($y = 0.75$). The positive impact of N vacancies led to further studies on the potential application as hard coatings in cutting tools.

Paper II. Solid state formation of Ti_4AlN_3 in cathodic arc evaporated $(Ti_{1-x}Al_x)N_y$ alloys

As a complement to the first paper, the decomposition pathway in highly nitrogen-deficient solid solution *cubic* $(Ti_{1-x}Al_x)N_y$ ($0.58 \geq y \geq 0.40$) alloys was investigated for a wide range of Al metal fractions $x = 0.28$ to 0.63 . This is the first study showing the formation of Ti_4AlN_3 (MAX phase) in thin films via solid state reaction in nitrogen deficient *c*- $(Ti_{1-x}Al_x)N_y$ alloys. A transformation mechanism from Ti_2AlN to Ti_4AlN_3 via intercalation is suggested and it is confirmed by the presence of an intermediate $Ti_6Al_2N_4$ phase (Figure 5.2). $Ti_6Al_2N_4$ has an intergrown structure whose unit cell consists of Ti_2AlN and Ti_4AlN_3 half unit cells.

Figure 5.2: Graphical abstract [107]. (Left side) Atomic scale model of the transformation mechanism from Ti_2AlN to Ti_4AlN_3 via intercalation and detwinning. (Right side) High resolution z-contrast STEM image displaying the coexistence of Ti_2AlN , Ti_4AlN_3 , and $Ti_6Al_2N_4$ along the $[1-210]$ direction in sample $(Ti_{0.52}Al_{0.48})N_{0.40}$ annealed at $1300^\circ C$. Labels indicate the number of adjacent N-rich basal planes.

Highly N-deficient single-phase *c*- $(Ti_{1-x}Al_x)N_y$ thin films were grown by cathodic arc deposition for a wide composition range ($y = 0.40$ to 0.58 with $x < 0.55$). In a first

approach, free-standing thin films and heat treatments under Ar atmosphere were used in this study. A general model of the solid state reaction path is suggested and phases such as Al_5Ti_2 , Al_3Ti , $c\text{-TiN}$, $w\text{-AlN}$, Ti_2AlN and Ti_4AlN_3 are present. Their quantity can be varied with the as-deposited composition of the thin film. The phases observed are consistent with predictions performed by Alling *et al.* on N-poor $c\text{-(Ti,Al)N}_y$ [62]. In the reaction, it is shown that the formation of Ti_4AlN_3 takes place inside the preformed Ti_2AlN (MAX phase) grains by a thermally activated diffusion process above 1200 °C. The Ti_4AlN_3 formation mechanism proposed is the intercalation of Al layers for N layers along Ti_2AlN basal plane accompanied by a simultaneous detwinning process (Figure 5.2). This is confirmed by the presence of the intermediate $\text{Ti}_6\text{Al}_2\text{N}_4$ phase. This study extends the mechanism of intercalation to a ternary phase. In this case, the precursor is a MAX phase of a low n order (Ti_2AlN) and by fulfilling several conditions, a transformation to the next thermodynamically stable MAX phase with a higher n order (Ti_4AlN_3) takes place.

Paper III. Effect of nitrogen vacancies on phase stability and mechanical properties of arc deposited $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$ ($y < 1$) coatings

Based on the first paper, a medium Al metal fraction in the $c\text{-(Ti}_{1-x}\text{Al}_x)\text{N}_y$ was selected ($x = 0.48$), and the thermal stability in terms of $w\text{-AlN}$ formation was studied for a larger N-to-metal range $0.92 \geq y \geq 0.46$. In this study, a typical cutting tool substrate (cemented carbide WC/co based) was used in order to investigate the film-substrate interaction in the presence of N vacancies. The results show a clear age hardening effect (due to spinodal decomposition) upshifted by 300 °C when reducing the N fraction in coatings with a $y \geq 0.75$ (Figure 5.3). This upshift is consistent with the enhanced thermal stability in terms of suppressing $w\text{-AlN}$ formation. High N deficiency ($y = 0.46$) in the coating leads to a change of phase evolution and a strong interaction with WC and Co at elevated temperatures.

As deposited coatings present an increase in composition fluctuations, lattice defects and macroparticles when reducing the N content, which reduces the column width and changes the preferred orientation from 200 to 111 to 220 planes parallel to the substrate.

Figure 5.3: Graphical abstract [108]. Ex situ hardness versus annealing temperature up to 1200 °C of $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$ samples with $y = 0.92$, $y = 0.87$, $y = 0.75$ and $y = 0.46$. APT reconstructions from the interior of a column of $(\text{Ti}_{0.52}\text{Al}_{0.48})\text{N}_y$ coatings annealed at 1200 °C for 15 min: $y = 0.92$, $y = 0.87$, and $y = 0.75$. Only Al and Ti ions are shown for clarity.

At elevated temperatures, interdiffusion of substrate elements (Co and C) and nucleation and growth of c -TiN and w -AlN take place mainly along column boundaries for coatings with $y \geq 0.75$. These processes seem not to be detrimental to the coatings hardness. Conversely, high N deficiency ($y = 0.46$) leads to significant diffusion of Co, C, W and Ta throughout the coating at elevated temperatures due to the increased amount on N vacancies and column boundaries. Substitution of N by C in the non-metal lattice, and substitution of W and Ta in the metal lattice is observed, e.g. formation of c -Ti(N,C), c -(Ti,W,Ta)(C,N). The overall hardness in sample $y = 0.46$ is lower than for coatings with $y \geq 0.75$ (Figure 5.3). Nevertheless, an increase in hardness is observed above 1000 °C, and bond strengthening and solid solution hardening are suggested to be responsible for that. Base on this study, it is concluded that film-substrate interaction is a limiting factor for coating design by N deficiency. The most substantial improvement in hardness evolution was observed for $y = 0.87$.

Paper IV. Enhanced thermal stability and mechanical properties of nitrogen deficient titanium aluminum nitride ($Ti_{0.54}Al_{0.46}N_y$) thin films by tuning the applied negative bias voltage

Base on the third paper, a fixed Al metal and N-to-metal fraction in the $c-(Ti_{1-x}Al_x)N_y$ was selected ($x = 0.46$ and $y = 0.87$), and the effect of point defects (interstitials and anti-sites) generated during film growth was investigated in terms of phase stability and hardness. The defect density was varied by applying a negative substrate bias from -30 to -80 V. The results show an improvement in the as-deposited hardness for the highly biased films (-80 V). At elevated temperatures, the hardness behavior shows age hardening shifted to higher hardness values and to lower temperatures by increasing the negative bias (Figure 5.4). Highly bias films present an increased driving force for phase separation at elevated temperatures.

Figure 5.4: Hardness at different temperatures of $(Ti_{0.54}Al_{0.46})N_{0.87}$ films biased at -30 V, -55 V, and -80 V and a reference sample [108] which contains a higher N content ($y = 0.92$) [109].

The microstructure and the point defect density (interstitials and anti-sites) is modified in cathodic arc deposited $c-(Ti_{0.54}Al_{0.46})N_{0.87}$ thin films by tuning the applied negative bias, since the kinetic energy of the impinging ions is altered. In the as-deposited state, films deposited with high bias (-80V) show an increase in compressive stresses and

thus in hardness due to the increase in defect density. At elevated temperatures, it is shown that the defects caused by high ion energy bombardment (high bias) are more stable in the presence of N vacancies than the ones generated at low energy bombardment. This effect leads to a delayed annihilation of point defects (interstitials), an increase of the system's internal energy and a retention of the hardness in high bias films (Figure 5.4). With a further increase in temperature, the release of the stored lattice strain energy in the system takes place and the decomposition of the $c\text{-(Ti}_{0.54}\text{Al}_{0.46})\text{N}_{0.87}$ into $c\text{-TiN}$ and $w\text{-AlN}$ is accelerated. Thus, a shift of the age hardening effect to lower temperatures is observed (Figure 5.4). In this study, it is shown that point defect concentration generated during deposition is critical in designing N deficient (Ti,Al)N coatings.

Paper V. Surface directed spinodal decomposition at TiAlN/TiN interfaces

This work investigates the mechanism behind the early onset of spinodal decomposition in arc evaporated $(\text{Ti}_{1-x}\text{Al}_x)\text{N}/\text{TiN}$ multilayers, and the positive effect of artificial interfaces on the hardness. Two compositions ($x = 0.50$ and 0.67) were investigated in a combined study of experiments and phase-field simulations. The results show that the decomposition is initiated at the multilayer interfaces, consistent with surface-directed spinodal decomposition (SDSD) (Figure 5.5). Regardless of the composition, the same decomposition onset temperature is observed since the internal interfaces are responsible for the SDSD.

SDSD consists in the formation of a layered microstructure parallel to the interface i.e. a dominant wave vector directed normal to the surface. Phase field simulations predicted the effect of composition, internal interfaces and intrinsic composition fluctuations (induced during growth) on the microstructure and thermal stability of the multilayer system. Decomposition is initiated at the interfaces by SDSD at similar temperatures, regardless of the composition, and at earlier temperatures compared to monolithic $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$, whereas larger intrinsic fluctuations generate a more randomly oriented decomposition structure. Both mechanisms compete with each other and the resulting

microstructure is a combination of both effects. In the case of $(\text{Ti}_{0.34}\text{Al}_{0.66})\text{N}/\text{TiN}$ multilayers, the results show a clear SDSD at the interfaces which vanishes inside the layers due to a random decomposition (Figure 5.5). Moreover, the presence of interfaces generates coherency strains between TiN and $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ due to lattice mismatch. This effect prolongs the decomposition over a longer period of time and it decreases the driving force in comparison to the monolithic layers, resulting in a prolonged age hardening.

Figure 5.5: APT proxigrams from isosurfaces of a $(\text{Ti}_{0.34}\text{Al}_{0.66})\text{N}/\text{TiN}$ multilayer interfaces in (a) as-deposited state and annealed at (b) 800 °C and (c) 850 °C, showing Al, Ti, and N. (d)–(f) show 1D concentrations corresponding to a cylinder with a diameter of 5 nm of the same interfaces as in (a)–(c) [110].

6. FUTURE WORK

Based on the results obtained in this thesis, an outlook of possible research trends is presented in this chapter.

Elastic properties and electronic structure of (Ti,Al)N_y (y < 1) alloys

It has been shown previously that spinodal decomposition, hardness and age hardening of (Ti,Al)N alloys are strongly affected by the evolving elastic properties as a function of Al content [18], [111] and of the Al distribution in the metal sublattice [112]. The increase in Al content increases the directional (covalent) character of the bonds, resulting in an increase in elastic anisotropy [18] and change in the electronic structure [112]. The elastic anisotropy results in a change in the nature of (Ti,Al)N decomposition and in the resulting microstructure as pointed out by Chan [30].

In this study, it is suggested that the introduction of nitrogen vacancies in the B1 structure of (Ti,Al)N alloys leads to a change in bonding toward a metallic situation [61]. The results are in accordance with prediction of Alling *et al.* via *ab initio* calculations [62]. Therefore, it is expected that the elastic properties change with the N content. New insight into the understanding of the spinodal decomposition and age hardening in N-deficient (Ti,Al)N_y (y < 1) alloys can be obtained by the calculation of elastic properties and electronic structure.

Isostructural phase diagram of cubic (Ti,Al)N_y (y < 1) alloys

Based on the results of this work, it is suggested that the enhanced thermal stability of (Ti,Al)N_y (y < 1) via N vacancies is related to a reduction of the mixing enthalpy and an increase in the entropy. Collectively, this reduces the miscibility gap to lower

temperatures. In order to prove this, the calculation of the isostructural phase diagram of *cubic*-(Ti,Al) N_y for different N contents should be performed. Where vibrational contributions including anharmonicity and temperature dependence of the mixing enthalpy should also be taken into account for a good approximation. The N content effect on the miscibility gap will lead to a deeper understanding of the effect of N vacancies on thermal stability of (Ti,Al) N_y ($y < 1$), and to the selection of an optimized Al metal fraction.

It is important to note, that the calculation of an isostructural phase diagram of B1-(Ti,Al) N_y is not a trivial task since two phases must be selected, i.e. *c*-Al N_y and *c*-Ti N_z where y and z must not necessarily be equal. An alternative could be the calculation of a pressure-temperature diagram of the *cubic* solid solution (Ti,Al) N_y phase.

Oxidation and wear behavior in (Ti,Al) N_y ($y < 1$)

The improved thermal stability and hardness evolution of N-deficient *c*-(Ti,Al) N_y ($y < 1$) thin films appear promising for an application as hard coating in cutting tools. In order to obtain a functional coating, further investigation of other properties must be studied such as cutting performance, wear resistance and oxidation resistance. These questions were beyond the scope of this thesis but should be investigated when considering industrial application of such coatings.

Point defect engineering combined with multilayering and alloying

As mentioned in the introduction, improving the thermal stability of (Ti,Al)N at elevated temperatures has become a key factor in hard coatings research in the last three decades. Some of the approaches were the use of multilayer configurations [2], [24], [113] or alloying elements (e.g. Cr, Hf, Ta) [23], [83], [114].

The addition of alloying elements have shown to delay the decomposition by the appearance of several intermediate phases and by changing the activation energy for

diffusion [83], [115]. The combination of alloying and N vacancies could lead to an enhancement of thermal stability in $(\text{Ti,Al})\text{N}_y$ ($y < 1$) alloys, since alloying elements like Cr or Ta are introduced in the metal sublattice and N vacancies in the non-metal sublattice.

In this study, the use of artificial interfaces by a multilayer stack $(\text{Ti,Al})\text{N}/\text{TiN}$ has been shown to prolong the spinodal decomposition over a longer period of time and to decrease the driving force for decomposition [110]. The generation of coherency strains due to the presence of interfaces is the main mechanism behind the enhanced age hardening. It appears interesting to explore the combined effect of artificial interfaces with N vacancies for a further improvement of the thermal stability and mechanical behavior of $(\text{Ti,Al})\text{N}_y$ ($y < 1$) alloys.

MAX phase formation via intercalation in thin films

In this study, the mechanism of intercalation was extended to a ternary phase, where the precursor is a MAX phase of a low n order which transforms into a MAX phase with a higher n order, i.e. Ti_2AlN into Ti_4AlN_3 [107]. In order for this transformation to take place, several conditions must be fulfilled (see paper II). According to the mechanism, the origin of the precursor MAX phase of low n order is independent of transformation mechanism. It is suggested that it is possible to obtain MAX phases of high n order in thin films which have not been previously obtained by direct nucleation and growth, like Ti_4GaC_3 , Nb_4AlC_3 and V_4AlC_3 . Exploring this possibility seems a promising path to continue research.

7. REFERENCES

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