Structural characterization of arc evaporated TiAlN/TiN multilayers

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Sammanfattning

Tunnfilm med multilagrad struktur av TiN och Ti$_{0.34}$Al$_{0.66}$N har undersökt. Beläggningarna gjordes med två rotationshastigheter, 1 och 5 varv per minut vilket resulterade olika lagertjocklekar. Proven värmeebehandlades i 900°C i 2h med konstant argonflöde. Mikrostrukturen undersöktes med transmissionelektronmikroskop (TEM), sveptranmissionelektronmikroskop (STEM) och röntgendiffraktion (XRD). Restspännningar i proven analyserades med röntgendiffraktionsmetoden sin$^2\psi$. Kemiska sammansättningen undersöktes med XRD och energy dispersive spectroscopy (EDS). Resultaten från de obehandlade proven av båda rotationshastigheterna visade homogena att lager av TiN och Ti$_{0.34}$Al$_{0.66}$N. Filmen med tjockare lager (1rpm) visade högre restspänningsvärden än provet med tunnare lager. Efter värmeebehandling visar STEM bilderna och EDS mappen från 1rpm provet en tydlig segregation av Al i form av sfäriska områden med en storlek på ~7nm. Detta syns även i röntgendiffraktionsresultaten som uppvisar en ökning av TiN och minskning av Ti$_{0.34}$Al$_{0.66}$N och dessutom nya AlN toppar. Efter värmeebehandling har det även skett en spänningsrelaxation i filmerna.
Abstract

Multilayer TiN and Ti$_{0.34}$Al$_{0.66}$N thin film deposited with arc evaporation from Ti – Al and Ti cathodes in a N$_2$ atmosphere has been investigated. The depositions were performed with two different rotation speeds, 1 and 5 rotations per minute, resulting in different layer thicknesses. Samples were heat treated at 900°C for 2 hours in constant argon flow. The microstructure of both the as deposited samples and the heat treated samples were studied using transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and x-ray diffraction (XRD). Residual stresses were investigated with XRD using the sin$^2\psi$ method. Chemical composition was determined with XRD and energy dispersive spectroscopy (EDS). The STEM, EDS and XRD revealed homogenous layers of single phase TiN and Ti$_{0.34}$Al$_{0.66}$N. After heat treatment the Ti$_{0.34}$Al$_{0.66}$N layer was decomposed to TiN and spherical locking AlN areas with size of ~7nm. The split was also seen in the X-ray spectra as an increase TiN and AlN peaks and decrease in (Ti, Al)N peaks. Residual stress measurements reveal bigger values in the thin 1rpm sample compared to the 5rpm sample. The XRD results show that the thin films undergo stress relaxation during heat treatments.
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1 Introduction

Ceramics was used already seven thousand years ago to form vessels of clay. Today ceramics are used in a wide range of high technological applications. It is a fascinating class of materials with some remarkable properties in sense of heat resistance, hardness and thermal shock resistance. These special properties of the ceramics make them attractive for thin film applications within the metal cutting industries. [1]

1.1 Background

During the 1970s and -80 extensive research were done on titanium nitride (TiN) thin films on cutting tools applications. TiN is a golden-coloured ceramic with high hardness and stiffness which find extensive use as coating materials in wear protective applications as diffusion barriers, corrosion protection and decorative coatings. However for cutting tool applications TiN has a shortcoming in stability at temperatures over 600°C where severe oxidation of the coating is initiated. The work temperature of cutting tools is typically between 600-1200°C degrees which created a big interest and need in develop methods and materials for a more stable thin film.

In the pioneer work of Beenoh-Marchwicka aluminium was added to the TiN to improve the high temperature behaviour. The new compound Ti$_{1-x}$Al$_x$N significantly increased oxidation resistance and overall machining performance, a comparison between TiN and Ti$_{1-x}$Al$_x$N hardness at elevated temperatures is seen in Figure 5. TiN oxidizes severely at temperatures higher than 500-600°C whereas the oxidation of Ti$_{1-x}$Al$_x$N starts between 750-800°C. The reason for the increase in performance of the Ti$_{1-x}$Al$_x$N was at first associated only with increased oxidation resistance of the coating. However later research showed that the increased oxidation resistance is not the only reason of increased performance but also age hardening plays an important role. The age hardening is a quite complex and involves several steps and transformation mechanism which will be discussed later.

1.2 Pervious Works

Besides several articles there has also been complete doctoral thesis made in the field of TiN and Ti$_{1-x}$Al$_x$N. In 2005 Anders Hörling, Linköpings Univeristet, presented his doctoral thesis
“Thermal stability and age hardening of TiN-based Thin Film” which has been one of the most important sources for this work. Mark Terner, Luleå Tekniska Universitet, performed SAXS measurements on Ti<sub>1-x</sub>Al<sub>x</sub>N which is the reason for the further studies of SAXS found in this work.

1.3 Purpose

As mention in section 1.1 there has been extensive research on TiN and Ti<sub>1-x</sub>Al<sub>x</sub>N and their high temperature behaviors. However the assumed AlN precipitations have never been visualized which should be possible with today’s TEM equipment. To find and gain knowledge of the growth, size and shape of the AlN precipitations is the main purpose of this work.

1.4 Aim

- Greater understanding of the AlN precipitations as result of heating arc evaporated Ti<sub>1-x</sub>Al<sub>x</sub>N
- Connect results with earlier performed SAXS experiments
2 The Ti$_{1-x}$Al$_x$N System

Cutting tools with thin films of Ti$_{1-x}$Al$_x$N has been used in the industry since late 1980s. Compared to TiN, TiC, CrN the coating has higher stability at high temperatures, higher hardness and better oxidations resistance. This chapter gives the theoretical information about the Ti$_{1-x}$Al$_x$N structure, phase transformations and mechanical properties but starts with basic theories about metastable equilibriums and spinodal decomposition.

2.1 Metastable equilibrium

A system is in equilibrium when it is in its most stable and shows no desire to change ad infinitum. The system has the lowest possible value of Gibbs free energy, mathematically described as $dG = 0$. However there are systems which have configurations that show local minimums in the free energy curve and therefore also satisfy $dG = 0$. Such configurations are in a so called metastable equilibrium state. The metastability means that the Gibbs free energy of the system is at a local minimum but not at the lowest possible G value of the system, illustrated as point B in Figure 1. An often used simplified explanation of the metastable state is a standing milk package which is stable but has not the lowest potential energy until its lying. If as result of thermal fluctuation or some other energy influence, a system in local minimum will rapidly rearrange into a state with the lowest possible Gibbs free energy, illustrated as point A in Figure 1 [2].

![Figure 1: Stable (A) and metastable (B) equilibrium][2]
2.2 Spinodal Decomposition

Spinodal decomposition is a phase transformation mechanism that occurs without that the material system has to overcome an activation energy barrier. The transformation is distinctly different from the more well known nucleation and growth process in the way that the new phases forms by a continuous process and the phases therefore remains coherent during the separation process [2].

One criteria of spinodal decomposition is a miscibility gap in the phase diagram. A miscibility gap arise when to atoms in a system “dislike” each other and therefore the free energy curve for a solid assumes a negative curvature in the middle at low temperatures. The solid solution will be most stable as a mixture of two phases $\alpha'$ and $\alpha''$ with composition $e$ and $f$, Figure 2. When the temperature increases $e$ and $f$ will approach each other and eventually disappear. The $\alpha' - \alpha''$ region is knows as the miscibility gap of a system.

![Figure 2 Miscibility gap[2]](image)

An alloys with composition $X_0$ in a binary phase diagram with a miscibility gap, heat treated and quenched into the two phase $\alpha' + \alpha''$ region will initially be homogenous with free energy $G_0$, Figure 3. Small fluctuations in compositions produce A-rich and B-rich regions that cause the total free energy of the system to decrease. As a result of the free energy decrease a uphill diffusion occurs to minimize the $G$ and a equilibrium of $X_1$ and $X_2$ are reached. If the material system does not fulfill the prerequisite of spinodal decomposition instead the traditional nucleation and growth by downhill diffusion will occur. Schematic composition profile of spinodal decomposition from initial composition at time $T_1$ to final composition $T_4$ is seen in...
Figure 3 c. Compared to the case of the downhill diffusion the spinodal decomposition show no sharp edged in the composition profile during decomposition. [2]

Figure 3. (a) Phase diagram (b) corresponding free energy (c) and schematic composition profiles at increasing time at spinodal decomposition [2]

2.3 Surface-Directed Spinodal Decomposition (SDSD)

If spinodal decomposition occurs at the surface a segregation of one component over the other can occur in the early stages of the transformation. This segregation will results in a fluctuation in the composition field perpendicular to the free surface which grows as it forms alternating A-rich and B-rich layers parallel to the surface. The evolved microstructure can become aligned with the geometry of the surface if the chemical interaction of a competent with the surface is sufficiently strong. This alignment with the surface geometry can affect the specimen even far into the interior regions. This phenomenon is known as surface directed spinodal decomposition (SDSD). [3,4]
2.4 Structure of Ti$_{1-x}$Al$_x$N

The structure of Ti$_{1-x}$Al$_x$N is based on the structure of [NaCl]-TiN with $x$ amount of the titanium atoms substituted with aluminium atoms. However, the structure of Ti$_{1-x}$Al$_x$N has been shown to be dependent of the size of $x$, i.e. the alumina content. As deposited coatings with $0 \leq x \leq 0.52$ have a metastable cubic NaCl structure (Figure 4a) whereas $0.59 \leq x \leq 0.90$ yields a two phase structure consisting of cubic NaCl and hexagonal Wurtzite structure (Figure 4b). However, the cathodic arc plasma technique (section 3.2) allows synthesizing of single phase [NaCl]-Ti$_{1-x}$Al$_x$N with an alumina content as high as $x=0.66$. This is possible because the atoms’ ability to redistribute themselves in the growing film during ion bombardment, the ability to create fully ionised plasma and low substrate temperatures [5].

![Figure 4](image.png)

(a) NaCl structure  (b) Wurtzite structure

2.5 TiAlN Phase diagrams

By estimation and calculation of the free energies of formation for the [NaCl] and [Wurtzite] structures it was possible to construct a phase diagram and with free energy graphs of the TiN-AlN. The phase diagram shows that the solid solubility of AlN in TiN seems limited and at 2700K the AlN only reaches ~5mol%. At temperatures below 1500K the TiN-AlN has a two phase structure of TiN and AlN structure. This can however be changed by incorporate Al in the TiN structures with later described physical vapour deposition techniques. The structure of such deposition is expected to be [NaCl] which also has been confirmed experimental [6].


2.6 Phase Transformations

The as deposited Ti$_{1-x}$Al$_x$N is expected to transform into the equilibrium cubic TiN and hexagonal AlN during heat treatments. When the thin film of Ti$_{1-x}$Al$_x$N is annealed at 900°C it will however first transform through spinodal decomposition into c-TiN and c-AlN which is indicated by asymmetric broadening of the [200] Ti$_{1-x}$Al$_x$N XRD peak. This intermediate transformation step into the metastable c-AlN occurs because the transformation into the stable h-AlN is associated with a high nucleation barrier due to larger atomic volume and incoherent interfaces with TiN. Annealing at 1100°C results in a small fraction of the c-AlN formed at 900°C transforms into their stable hexagonal structure. Annealing at 1200°C supply enough energy to overcome the energy barrier and complete the transformation to the equilibrium two phase structure of c-TiN and h-AlN [7]. The complete transformation of Ti$_{1-x}$Al$_x$N can simply be written as

\[ c-(Ti, Al)N \rightarrow c-TiN + c-AlN \rightarrow c-TiN + h-AlN \]. \hspace{1cm} Eq. 1

2.7 Influence of phase transformations on mechanical properties

The improvement of mechanical properties when using Ti$_{1-x}$Al$_x$N thin films was earlier connected only to the high oxidation resistance. However the two steps of phase transformation mention in section 2.6 have been shown to have considerable effect on the hardness of cutting tools with thin Ti$_{1-x}$Al$_x$N films. This has mainly been investigated by Hörling et.al [8] and will be explained in this section.

As seen in Figure 5 the hardness of a Ti$_{1-x}$Al$_x$N coating increase between 600 - 1000°C. At higher annealing temperatures a steep decrease in hardness can be observed. This coincides with the steps of phase transformations in Eq.1 and has also been shown to be directly connected [9].
The split into c-AlN and c-TiN, which is the first step of phase transformation in Ti$_{1-x}$Al$_x$N, leads to a mismatch of approximately 4% in the thin film. The precipitation of second phase particles throughout the matrix increases the difficulty of motion through the lattice and the hardness increase. The increase is explained by lattice misfit caused by the difference in lattice parameter between the two phases results in the development of elastic strain fields surrounding the coherent phase boundaries that hinder motions. At higher annealing temperatures the c-AlN will start to transform to h-AlN. The h-AlN is incoherent with the matrix which results in a nonhomogeneous distribution of Al in the matrix. This will decrease the hardness because of stress relaxation and decrease in oxidation resistance [8, 9].
3 Thin Film Deposition

Besides painting, thin films are synthesized by mainly two deposition techniques; chemical vapour deposition (CVD) and physical vapour deposition (PVD). This work will only involve thin films deposited by PVD. The PVD can be divided into three methods; cathodic arc evaporation, sputtering and pulsed laser deposition. In this present work thin film synthesized with cathodic arc evaporation was investigated.

3.1 PVD in general

The physical vapor deposition is a deposition method in which material is vaporized from a solid or liquid source in the form of vapor through vacuum or low pressure gaseous or plasma environment to a substrate where it condensates. The method is typically used to deposition thicknesses in the range of three up to thousands of nanometers but can also be used for multilayer coatings and freestanding structures. The substrate size range is from millimeters to large as 25 x 25 cm (for example glass panels on buildings). The deposition rate varies between 10-100Å per second. Elements and alloys can be deposited using a reactive deposition process. In reactive processes the compounds are formed by a reaction between the depositing material and a surrounding gas environment, for example titanium in a nitrogen atmosphere results in a deposition of TiN. [10]

3.2 Arc Evaporation

Arc evaporation is used as PVD method at SECO Tools AB. This method has an efficient source of highly ionized material for producing dense and adherent coatings having a wide range of compositions. A big advantage with arc evaporation is the possibility to control the fully ionized plasma with electric and magnetic fields.
The metal vapour vacuum arc is formed when a plasma discharge occurs and conducts electrons in a vacuum. A micrometer sized cathode spot with high current density ($10^6$ A/cm$^2$) is formed by concentrate the arc discharge on the cathode surface. The arc spot with high local surface temperature creates a molten pool on the target material (cathode) from which vigorous evaporation and electron emission occurs Figure 6. Above the molten pool is an acceleration zone in which an electric field accelerates the emitted electrons. After a mean free path the accelerated electrons collide and ionise the metal vapour atoms in an ionisation zone. This means that dense fully ionised plasma is formed. Because of strong concentration gradients a diffusion driven flow of the electrons and ions starts away from the ionisation zone and onto the anode. This model is called the stationary cathode spot model [10, 11, 12].

### 3.3 Nucleation and growth

How the growth of thin film occurs at an atom level is complicated but though of big interest to understand to be able to improve the deposition of thin films. The nucleation and growth process is mainly understood with help of complicated computer modelling and in this rapport only the basic theories are explained. Because of industrial demands of low temperatures at thin films deposition (20-30% of melting temperature) the synthesis is often done in conditions far from the thermodynamic equilibrium of the system. The relatively low temperature of Ti$_{1-x}$Al$_x$N deposition will, because of competitive growth, make it possible to
control the synthesis of the metastable phases and create artificial structures. Typical atomistic processes during epiaxed growth are illustrated in Figure 7. The deposition is done with a flux of (a) on a perfect substrate. The deposited atoms can move on the surface (b), form dimers (c), or attach to islands (d), move as a dimer (f), form second layers on top of islands (h) and in high energetic growth some atoms can re-evaporate and leave the substrate. All atoms movement are results of minimizing the energy of the system. The growth is often divided into the three modes Stranski-Kranstankov (S-K), Volmer –Weber (V-W) and Frank-van der Merwe (F-M). S-K is the most complicated and involves wetting layers and three dimensional islands. F-M growth is layer-by-layer and V-W is three-dimensional islands [3, 13].

![Figure 7 Nucleation and growth of thin film [13]](image)

### 3.4 Epitaxial mechanisms

The word epitaxy derives from the Greek where *epi* means “over” or “upon” and *taxis* “order” or ”arrangement”. Physically epitaxy is an interference that occurs in the interface between a thin film and the substrate or in the interfaces of multilayer thin films during growth. The interference involves that the atoms in the epitaxial layer partly inherits the arrangements of the neighbour layer. Figure 8a shows a monolayer thin film A with no disturbance and Figure 8b show a multilayer deposition where both layer A and B affects each other. Only the first atomic layers are affected in this illustration but epitaxial mechanism can cover complete layers. The lattice B is stretched and lattice A is contracted with a result of tensile and compressive stresses. The introduced stresses in the material often change the mechanical properties of a system. However there is a breaking point where epitaxial
mechanism is no longer possible and the lattice parameter differences are too big and the semicoherence will break, this is illustrated in figure Figure 8c [b, 14].

**Figure 8** Monolayer thin film b. Multilayer with epitaxy c. Multilayer with coherency loss [14].
4 Small angle X-ray diffraction

This work has also involved studies of the material analyse method SAXS, small angle x-ray diffraction. Earlier work has been done with this technique on Ti$_{1-x}$Al$_x$N with the Advanced Photon Source (APS) at Argonne National Laboratory in Illinois, USA. The goal was not only to understand the theoretical part of SAXS but also the experimental setup and how the raw data is analysed. Information about the shape and size of macromolecules, characteristic distances of partially ordered materials and pore size is some of the features that SAXS can give information about.

4.1 Basic SAXS

Small angle x-ray diffraction analysis is a technique for studying structural features of colloidal size; capable of delivering structural information of macromolecules between 5 and 25 nm of repeat distances in partially ordered systems of up to 150 nm. Any scattering process is characterized by a reciprocal law which gives an inverse relationship between particle size and scattering angle [15]. The dimension of the colloidal particles is always significantly larger than the wavelength of the X-ray which makes the angular range of scattering small, typically between 0.1 - 10°. The X-rays are primarily scattered by electrons which means that the small angle x-ray scattering is only observed when sample electron density has inhomogenetis of colloidal size. The electrons in the inhomogeneitie (particle) resonate with the frequency of the X-rays passing through and emit coherent secondary waves which interfere with each other. This can be visualized with a spherical particle (Figure 9a) that is assumed to scatter waves only at the indicated points (electrons) to an angle of 20 with path different of $1\lambda$ [16].

Figure 9 Illustration of simplified SAXS [15]
If scattering from all electrons are included the superposition of waves with all phases should lead to that no scattering occurs in the 20 direction because of destructive interference. If instead small angles are assumed the phase differences becomes smaller and constructive interference will occur. A maximum of scattered waves will be seen in the direction of the zero scattering angle where all the waves are in exactly the same phase. The intensity versus the scattering angle of this case is clearly visualized with curve 1 in Figure 10.

![Figure 10 Scattering intensity versus angle [15]](image)

If the same theories are applied to a bigger sphere path differences of 1λ will occur at smaller scattering angels as shown in Figure 9b and result in a steeper curve (2). Small angle x-ray diffraction will occur when the particles are big compared to the wavelength. This scattering of isolated particles, called “particulate scattering”, was postulated by Guinier in 1938. This “particulate scattering” is a part of Guinier’s law where electron density is used as mass density, equation Eq.2, where $I$ is the scattered intensity, $n_e$ number of low angle electrons in an atom and

\[ q = \frac{\sin(\theta)}{\lambda}. \]

The law makes it possible to calculate the gyration radius $R_g$ of the particle. $R_g$ is similar to the moment of inertia for the particle using the electron density instead of the mass as weighting factor. The radius of gyration makes it possible to calculate an average particle size with special scattering functions.

\[ I_1(h) = (\Delta n_e)^2 e^{-q^2 R_g^2/h^3} \quad Eq. 2 \]

The previous simplified model assumes particles surrounded by vacuum which means that the scattered amplitude will be proportional to the electron density $\rho$, numbers of mole of electrons per unit volume. For the more realistic case of dissolved particles the difference of the electron density of the solute $\rho_2$ and the solvent $\rho_1$ will be effective. The scattered amplitude will then be proportional to $\rho_2-\rho_1$ and the scattered intensity to $(\rho_2-\rho_1)^2$. 
The radius of gyration is often the main parameter obtained by SAXS analysis, it is however possible to obtain a number more of parameters from a scattering curve. Volume and particle molecular weight is example of such parameters. There is also a possibility to get information about the particle interface using Porod's law which is not being explained in this work [15, 16].

4.2 HE-XRD (High Energy X-ray Diffraction) Experiment on Ti$_{1-x}$Al$_x$N

4.2.1 Experimental

The phase transformation of Ti$_{1-x}$Al$_x$N described in Eq.1 was investigated with SAXS. The aim was to study the decomposition of Ti$_{1-x}$Al$_x$N films in-situ during heating via simultaneous SAXS & WAXS measurements. The Ti$_{1-x}$Al$_x$N was deposited onto WC-Co substrates in a commercial chamber at Seco Tools AB (described in 5.1). To investigate the influence of bias deposition was performed at both -20 and -40V. The thickness of the films was increased to 8µm which is thick compared to the films in production. The samples was cut into 1mm thick sections and clamped into wolfram sample holder to get an even heat distribution. The 80,72keV X-rays was focused to a height of 1µm and width of 100µm using a slit and a silica lens. The heating rate was 5°C/min and sampling was performed every 20 second. The vacuum in the furnace was approximately 5x10$^{-3}$τ during the experiments. A simple drawing of the experimental setup can be seen in Figure 11. The sampling was done on a 2D detector. Figure 12 illustrates raw results from the detector. The small red/yellow area in the middle represents the SAXS, the surrounding rings the WAXS. Its also possible to see the disturbances from the sample holder and the chamber glass. Because of the differences in electron density of AlN and TiN only the AlN was visible to SAXS (explained in section 4.1).
The wanted raw data for different angle sections is selected and converted with matlab. The plots, one for every sampling, from matlab are then fitted with Igor pro and the Irena package. This is an anisotropic system with correlations which uses 2-level Unified Fit model.

![Experimental SAXS setup](image)

**Figure 11 Experimental SAXS setup**

4.2.2 Results

The presented result are a summary of fits done by Mark Terner, Lina Rogström and the author. The fitting procedure and the outcome is highly affected by manual chosen factors,
therefore it’s important to get similar results from several operators to confirm the results. At higher temperatures (~1000°C) the curves are often too noisy to achieve a proper fit. In general the results show an almost linear increase in Rg. The results from the 50% Al and 40% Ti sample however show a distinct change in growth rate at around 18Å, Figure 13. This is believed to be connected with the transformation of cubic to hexagonal AlN discussed in section 2.6. The results give valuable information about the growth rate and particle size. However to be able to use the SAXS results to the full more detailed information about the particle shape is needed which is one of the aims in this work.

\[ \text{Figure 13 Saxs fits of sample 50%Al and bias -40V} \]
5 Experimental Metod

X-ray diffraction (XRD section 5.8) was performed at Seco Tools AB with a Bruker AXS D8-advanced X-ray diffractometer with a line-focus and a Cu Kα X-ray source. The peaks in the spectra were fitted using a pseudo-Voigt function. Transmission electron microscope (TEM, section 5.5) was performed in an FEI Tecnai G² TF20UT 200kv field emission gun (FEG) microscope. Samples were examined primarily with high resolution transmission electron microscopy (HRTEM, section 5.5.1) and scanning transmission electron microscopy (STEM, section 5.5.2) with a nanoprobe. Compositional variations across the sample were obtained with in situ energy dispersive spectroscopy (EDS, section 5.6) while the microscope was in STEM mode. This chapter also contains theoretical information about electron energy loss spectroscopy (EELS, section 5.7) which has not been used in this work but will be a powerful complement in future works.

5.1 Deposition Conditions

In this work cemented carbide (WC-Co) [Seco Tools “HX”, chemical composition (wt. %) WC 93.5-Co 6-(Ta,Nb)C 0.5] pieces of size 13x13x4mm and hardness of 1635 HV10 were used as substrate with the big surface facing the cathode. The average grain size of the substrate was 1µm. The substrates were deposited in the commercial arc evaporation system Metaplas MR323. Before placing the samples in the PVD machine the substrates were grinded by a diamond wheel of grain size 150µm and finally ultrasonically cleaned by a degreasing agent. The depositions were carried out in a 99.995% pure N₂ atmosphere and the substrates were negatively biased (-55V) and kept at temperature of 500°C. TiN and Ti₁₋ₓAlₓN layers was achieved by equipping the evaporation system with separated Ti₀.₃₃Al₀.₆₇ and pure Ti cathodes (Figure 14). The samples were, because of the rotation, moved in and out of the deposition zones of the different cathodes which resulted in multilayer deposition. Different layer thicknesses were achieved by using different rotation speeds, 1 and 5prm. Immediately after deposition the chamber was vented with dry N₂. The main reason to produce multilayer is the incoherency of AlN and TiN. This incoherency means that the AlN will be “locked up” in the original Ti₁₋ₓAlₓN layers and though will be theoretically easier to find compared to a regular thin film.
5.2 Isothermal annealing

Heat treatments were performed in a Centor Vacuum Industries furnace with constant argon flow. Each sample was heated from room temperature in a sequence with two heating rate steps, 6°C/min to 850°C and 5°C/min to 900°C where the samples were held for 2 hours.

5.3 Sample preparation

The TEM samples are prepared by a combination of mechanical abrasion and ion etching. Samples are cut into 1.8x0.5x0.5mm pieces with an acutom 5 saw (feed speed 0.020mm/s, 3000rpm) and a DBT low speed diamond wheel cutter model 650. The pieces are then placed in a titanium grid with the thin films facing each other. The grid is baked in a mixture of graphite and araldite for two hours at 175°C. After removal of unnecessary graphite/araldite mixture de samples is mechanical polished on both sides with diamond abrasive papers of grid sizes 16, 6, 3 and 1µm. Every step of mechanical polishing affects the material proportional to the grid size which means that suitable thickness of sample material has to be removed. This mechanical polishing is performed to a mirror like surface and a thickness of 40-60 µm. The sample is then ion milled with a Precision Ion Polishing System (PIPS, section 5.4) with
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double modulation at 5keV until a hole obtained. Further the sample is polished with single modulation at 3kev for 3 minutes and final polished ~2keV for 45min.

5.4 PIPS

A Gatan Precision Ion Polishing System (PIPS) is used in the final step of TEM sample preparation. Ion milling with PIPS is a non mechanical thinning method where energetic argon ions collides with the centre of a rotating specimen and “sand blast” it. There is a risk of resputtered material soiling the sample, this is avoided with a low incident angels around 5° and final polishing at low acceleration voltage with single modulation that sputters all the soiling amorphous material to one side of the sample and removing it from the center.

5.5 Transmission Electron Microscopy

Transmission electron microscopy is a very powerful analysis technique because of its ability of both giving a physical image of the sample as well as an electron diffraction pattern. Compared to an optical microscope, which illuminates the sample, the TEM instead irradiates the samples with electrons. A vacuum environment increases the mean free path of electrons giving a more accurate picture. After transmitted through the specimen the electrons hits a fluorescent screen or a CCD where an image is visualized. The TEM can not use traditional optical lenses and instead have electromagnetic lenses controlling the electron beam.

A powerful analyse feature of the TEM is the possibility to get an electron diffraction pattern (DP). When the electron beam is incident on the sample, scattering will occur since all illuminated parts of the sample will act as scattering sources. When Braggs law is fulfilled interference will cause coherently scattered beams that are recorded as a “spot” pattern residing in the back focal plane of the objective. The DP can give answers to if the specimen is crystalline or amorphous. If crystalline it’s possible to investigate the lattice parameter, symmetry etc. If the specimen is monocrystalline it’s possible to investigate the grain morphology, how large the grains are, the grain size distribution etc. A key requirement for TEM is thin electron transparent sample. A thick sample would cause too many interactions leaving no intensity in the transmitted beam. A thin sample also minimise the risk of two different grains overlapping in the path of the beam giving a false projected image [17, 18].
5.5.1 **High Resolution Transmission Electron Microscope**

High Resolution Transmission Electron Microscopy (HRTEM) is actually not an extra feature of the microscope but a specification if it’s possible to imaging the crystallographic structure of a sample. Such magnification is of course very powerful when analysing defects, interfaces etc. One example of a high resolution TEM picture is seen in Figure 22. To be able to get good results from HRTEM it is of big importance that the projection of the picture is down in an index direction so the atoms are on top of each other [a].

5.5.2 **Scanning Transmission Electron Microscope**

A scanning transmission electron microscope is a relatively new feature implemented in the traditional TEM. In STEM mode the electron beam is focused in a spot that scans over a limited chosen sample area. The principles of forming an image in scanning mode are fundamentally different from that for traditional static beam TEM image. In TEM a selected portion of electrons irradiated through the sample is distributed on the screen. In STEM conversely the electron beam instead is focused in a spot and scanned over the specimen by adjusting the scan coils. Scanning mode is significantly slower than the TEM images because every point scan lines have to “build up” the image. The STEM signal generated at a point on the sample is detected, amplified and a proportional signal is displayed as a pixel of the image. The image process is similar to method used in a scanning electron microscope (SEM) and makes it suitable for energy dispersive spectroscopy (EDS, section 5.6). The images from STEM are created from the direct electron hits, the low angle scattered electrons (annual dark field, ADF) or the high angle scattered electrons (high angle annular dark field, HA-ADF). In this work only HA-ADF is seen. [17, 18]

5.6 **Energy Dispersive Spectroscopy**

Incident electrons will lose energy by knocking out electrons in inner shells from the atoms in the specimen. These atoms are then excited, and in order to return to their equilibrium state electrons from other shells will occupy the electron hole. To do this the electrons have to give up energy to reach a lower energy state which is done by emitting an X-ray. The atoms of
every element have unique amounts of energy that is released during the electron movements. The energy of the emitted x-ray also depends on from which shell it comes and which shell it finally occupies. The EDS collects and analyses the X-ray and identify from which element they where emitted. The results are shown in an EDS spectrum (Figure 15) which shows how frequently an X-ray of specific energy is detected. Each peak represents a unique element and higher peaks correspond to higher concentration of the specific element. The EDS is an extra feature in TEM which only can be used in STEM mode [19].

Figure 15 EDS spectra of 1rpm heat treated sample

5.7 Electron Energy Loss Spectroscopy

The transmitted electron beam contains a wealth of information. This information can be collected with Electron Energy Loss Spectroscopy (EELS). Most electrons pass through the sample without any energy loss which gives the zero-loss peak in the EELS spectra as seen in Figure 16. This peaks provides information regarding the energy coherency of the electron source and hence the energy resolution in any particular EELS experiment. Next peaks in the figure corresponds to the low-loss region which is a result of something called plasmons. A plasmon is a quantum of a plasma oscillation, and may be excited when a electron passing through a thin metallic film. The transmitted electron will show an energy loss equal to integral multiples of the plasmon energy. The thicker samples the more plasmons will be detecteted. The plasmons provides information about the density of the valance electrons and
the width of the rate of decay for a particular mode. Electron energy loss near-edge structure (ELNES) is a region that provides structure and bonding information. After this region in the spectra come the extended energy loss fine structure (EXELFS) that contains information regarding the bond distance and the coordination of the atoms. Highest in the spectra is the Compton profile that is a result from large angle scattering and can provide information regarding bonding [20, 21].

![Typical EELS spectra](image)

**Figure 16** Typical EELS spectra [21]

### 5.8 X-Ray Diffraction

XRD is a technique that is widely used in material science and has advantages as its non-destructive and can be applied to any solid sample without any complicated sample preparation. The technique is powerful for microstructural investigation and can be used for characterisation of crustal structure, phase transformations, residual stress, thickness measurements etc. The information from XRD is provided from the interpretation that each atom in a periodic structure acts as a point of scattering for waves, Figure 17. The scattered waves may interfere constructively to form peaks in intensity. This constructive interference is created from the conditions from Bragg’s law *Eq. 3* which requires that the path difference between the travelled x-rays is equal to an integer number of wavelengths.

\[
2d \cdot \sin \theta = n\lambda
\]

*Eq. 3*
In Bragg's law \( d \) is the atomic plane spacing of the specimen crystal, \( \lambda \) the wavelength of the x-rays and 2\( \theta \) the angle of diffraction [18].

![Figure 17 Principles of X-ray diffraction [18]](image)

### 5.8.1 Residual stress measurements with XRD

X-ray diffraction also gives possibility to non-destructive measurements of residual stresses in thin films. The most frequently used is the \( \sin^2 \psi \) method which measures the strain in the thin film under assumption of a biaxial stress state. The biaxial stress state means that \( \sigma_{xz} = 0 \) when \( x \) and \( y \) axis are in the plane and \( z \) is perpendicular to the thin film. The method is based on Hook's law Eq.4 which describes the strain in the \( z \)-direction of a biaxial stress state in an elastically isotropic material.

\[
\varepsilon_r = \frac{d_\psi - d_0}{d_0} = \frac{1 + v_{hkl}}{E_{hkl}} \sigma_\phi \sin^2 \psi - \frac{v_{hkl}}{E_{hkl}} (\sigma_{xx} - \sigma_{yy})
\]

\( E \) and \( v \) represent Young’s modulus and poisons ratio respectively, \( \sigma_{xx} \) and \( \sigma_{yy} \) the principle stresses, \( \sigma_\phi \) the stress in the \( x-y \) plane at angle \( \phi \), \( d_\psi \) the lattice spacing at tilt angle \( \psi \) and \( d_0 \) the unstrained lattice distance. By assuming \( \psi = 0 \), \( d_0 = d_{0\psi} \) and isotropic stresses in the \( x-y \) plane giving \( \sigma_{xx} = \sigma_{yy} = \sigma_\phi \) and \( \psi = 0 \) Eq.4 can be simplified to
Structural characterization of arc evaporated Ti$_{0.34}$Al$_{0.66}$N / TiN multilayer

\[
\frac{d_{\phi\psi} - d_0}{d_0} = \frac{\nu_{hkl}}{E_{hkl}} \sigma_\phi \sin^2 \psi \quad \text{Eq. 5}
\]

where then $d_{0\psi}$ is the lattice spacing parallel to the surface. The unstrained lattice parameter is generally unknown but can be substituted with $d_{0\psi}$ only giving an error of approximately 1%. The $d_{0\psi}$ is measured at different $\psi$ and the plotted versus $\sin^2 \psi$, which shall give a linear graph. From the intercept with the $d_{0\psi}$-axis, the slope $m$ of a straight line (fitted by the least mean square method) and Eq.6 it’s possible obtain a value of the residual stress $\sigma_\phi$ [11, 22].

\[
m = \frac{(1 + \nu_{hkl})}{E_{hkl}} \cdot \sigma_\phi \quad \text{Eq. 6}
\]
6 Results

6.1 Sample Colour

The colours of the as-deposited the samples differs significantly depending on rotation speed during deposition and heat treatment. The samples with deposition made at 1rpm show a blue-violet colour while the 5rpm sample has a copper gold colour, Figure 18. After heat treatments the violet colour of the 1rpm sample was no longer visible, instead a dark brown colour had occurred. The 5rpm sample on the other hand did not show any particular change apart from a slight darker colour.

![Figure 18 As deposited samples](image)

6.2 XRD

The XRD pattern of the 1rpm and 5rpm, as deposited and heat treated samples are shown in Figure 19. All pattern show consistent substrate peaks corresponding to WC and Co. The general change between the patterns from the as deposited and heat treated samples is; decrease in Ti$_{0.34}$Al$_{0.66}$N peaks and increase in TiN and AlN peaks.
However other changes are also present in the 1rpm deposited sample as a shift to lower 2\( \theta \) for all TiN peaks. Also the Ti\(_{0.34}\)Al\(_{0.66}\)N seems to be shifted but to slight bigger 2\( \theta \). However this shift behaviour is only present in the 1rpm and not in the 5rpm sample. All these mentioned changes of the 1rpm sample are better visualized in Figure 20. The AlN peak of the heat treated sample is not significant in the figure but there is still a relatively clear broadening of the Ti\(_{0.34}\)Al\(_{0.66}\)N peak around the position of c-AlN, 2\( \theta \)=44.17. More detailed data from the fitted peaks can be found in Table 1 and 2 in appendix 2.

**Figure 19** Diffraction patterns from 1rpm, 5rpm samples, as deposited and heat treated.

**Figure 20** As deopsited and 900°C XRD spectra
6.3 Residual stress scan

Residual stress measurements with XRD were performed for both TiN and Ti$_{0.34}$Al$_{0.66}$N peaks. The stress scans shows that the as deposited 1rpm have higher stress values of both the TiN and the Ti$_{0.34}$Al$_{0.66}$N layer compared to the 5rpm sample, Figure 21.

![Residual stress scan of 5rpm and 1rpm AD samples](image)

**Figure 21** Residual stress scan of 5rpm and 1rpm AD samples

6.4 TEM

Because of limited time only the 1rpm sample has been investigated in TEM. The traditional TEM mode was only used to receive high resolution TEM pictures (HRTEM). Figure 22a show a picture of an interface (marked red) of the 1rpm sample with the Ti$_{0.34}$Al$_{0.66}$N layer in the lower part of the picture. There was no significant change in the FFT pattern (Figure 22b) when a line from TiN over the interface and into the (Ti, Al)N layer was investigated. However detailed investigation of the lattices close to the interface show a slight “bended” structure [23].
6.5 STEM and EDS

The STEM was used both to get pictures of the multilayer but also together with EDS doing element characterisation. The EDS results were always divided manually into Al and Ti content.

6.5.1 1rpm as deposited

Figure 23a.1 shows an overview picture of the 1rpm as deposited sample. The layers have a homogenous look and have layer thicknesses of approximately 48nm and 26nm. The performed EDS line scan (a.2) show relatively sharp edges between the Al and Ti content in the layers and the curve is in general quite smooth. The overall intensity increase in the graph is a result of an increased sample thickness. The EDS map (Figure 28, appendix 3) show homogenous distribution of Al and Ti. Both as deposited and the heat treated sample show large single crystal grains over several interfaces as seen in Figure 29.
6.5.2 1rpm heat treated

Figure 23 shows an overview picture of the 1rpm sample heat treated at 2h. The thinner dark layer is no longer homogenous and instead seems to be segregated into darker and lighter areas. The thicker layer was still homogenous. Higher magnification picture (Figure 24) shows that the layers have separated into that the relatively distinct dark areas.

Figure 24 High magnification STEM picture.
The EDS line scan (Figure 23b.2) shows a more disturbed curve compared to the as deposited sample. Especially the thin layers has been more affected during the heat treatments. An EDS element map was performed with results seen in Figure 25. A dark pixel corresponds to a lower percent of the chosen element and a bright pixel on the contrary. Figure 25 also contains the original STEM picture (leftmost) of the chosen element map area. The Ti and Al maps clearly show that there are areas in the original STEM picture that contains higher present of Al than Ti. The TiN layers at top and bottom in the pictures show as expected high Ti content and low Al content. The STEM overview pictures (appendix 3) reveal that grains has formed during deposition that stretches over several layers. EDS spectra in Figure 15 corresponds to a point in one of the higher Al content areas.

Figure 25 Original STEM picture and EDS map of Ti and Al contents of 1rpm heat treated sample.
7 Discussion

Discussion of the result is divided into structure and chemical composition and residual stresses. The discussion will mainly concern the 1rpm sample because of the more complete amount of results. Also a short discussion that connects the results to the previous SAXS results can be found.

7.1 Structure and Chemical Composition

7.1.1 As Deposited

The XRD spectra shown in Figure 19 reveals that at both the deposition rotation speeds the as deposited Ti$_{0.34}$Al$_{0.66}$N has a [200] preferred orientation. Because of the multilayer structure it’s however impossible to determine from the XRD data whether it’s a single phase [NaCl] structure or not as it has been reported in several articles regarding single layered thin films of Ti$_{1-x}$Al$_x$N [7, 8, 11]. Noticeable is though that there is no signs of AlN peaks at all. From EDS line scan of the as deposited sample in Figure 25 it’s clear that the thinner dark areas have a higher Al content and lower Ti content then and represents the Ti$_{0.34}$Al$_{0.66}$N layers. The EDS element map of as deposited sample (appendix 3) also confirms this and shows a homogenous distribution of Al and Ti. The results from the EDS and the XRD together show that the Ti$_{0.34}$Al$_{0.66}$N [200] peak corresponds to a single phase layer in the as deposited state.

7.1.2 Heat Treated

By comparing the EDS line scans of the heat treated and the as deposited 1rpm samples the first mentioned seem to have sharper interfaces. This is however an affect from the position of the thin film relatively to the EDS detector. The as deposited sample was mounted in the sample holder in a way that the layers can affect each other and result in misleading information regarding the Ti$_{0.34}$Al$_{0.66}$N / TiN layers. It’s more likely that the as deposited sample has even sharper interfaces than the heat treated sample.

The line scans of the two samples also show a general difference in smoothness in parts of the curve corresponding to the Ti$_{0.34}$Al$_{0.66}$N layers. The heat treated sample has a clearly disturbed curve where the Al content seem to be inversely proportional to the Ti content, i.e. when the
Al curve increase the Ti curve decrease (Figure 23b.1). Also in the STEM picture the layers look non homogenous (Figure 24). The EDS elements map (Figure 25) reveals more detailed information about this segregation where the map from the heat treated sample show areas with high Al content and low Ti content surrounded by areas of high Ti content and low Al content. The segregation is also confirmed in the X-ray diffractograms which show peaks corresponding to both h-AlN and c-AlN. The h-AlN is seen as a very small peak at \(2\theta=33.30^\circ\) and the c-AlN is mainly seen as asymmetric broadening of the more distinct \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) peak at \(2\theta=43.5^\circ\). The results from the EDS element map and the XRD reveals that the \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) has decomposed into c-TiN and mainly c-AlN as explained in Eq.1. Decomposition to TiN is confirmed by an increased intensity in the already existing TiN peaks. After heat treatment at 900°C the area with rich Al content cover not more than ~50% of the \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) layers. This means that there is approximately still 16% of Al in the original matrix, which is also confirmed by the still present \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) peaks.

The transformation of (Ti, Al)N from the metastable cubic state to the equilibrium two-phase structure has been reported before but has never been illustrated as in Figure 25. The picture gives information not only about shape of the precipitations but also the decomposition process active during annealing. One theoretical visual indication of spinodal decomposition is the lack of sharp interfaces between the decomposed materials as illustrated in the composition profile in Figure 3. Inspection of both the high magnification STEM picture (Figure 25) and the EDS element map reveals that the high Al content areas show diffuse boundaries to the surrounding matrix. Of course there is a possibility that this is a result from overlapping, but because of the overall consistency of this appearance it is highly unlikely. Thus, the diffuse boundaries are definitely an indication of that a spinodal decomposition process has been active in the \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) layers during heat treatment. As earlier mentioned, another indication of spinodal decomposition is the reported asymmetrical broadening of the single phase layer [200] \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) peak [7]. However this is not completely obvious in this multilayer because of the interference from the nearby TiN peak. It is though likely that the same behaviour is present also in a multilayer thin film.

Measuring of angels in the extracted FFT pattern (Figure 22b) reveals that it corresponds to the single crystal spot transmission electron diffraction pattern fcc structure as seen in Figure 26 in appendix 2. When a line from the \(\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}\) into the TiN layer was investigated by measuring the difference of angels and distance of the points in the FFT pattern, only
negligible changes in the positions of the points was seen. This indicates that both the layers has fcc structure with low mismatch and thus are coherent. The HR-TEM picture confirms the coherency and shows a slightly bended structure probably caused by the mismatch between the layers. FTT pattern was also investigated only in the $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ where no changes could be measured. This shows that there is coherency also between the $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$, the decomposed TiN and the decomposed AlN. However the mismatch between $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ and AlN has been calculated to $\sim4\%$ which is considerably higher than the mismatch between $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ and TiN. Thus, it is possible that the precipitation of AlN and the resultant coherency strain generates higher stresses in the layer than the coherency between the TiN and $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$.

### 7.2 Residual stresses

From the $1\text{rpm}$ residual stress measurements it seems that the TiN layer has compressive stresses and the TiAlN layer tensile stresses (Figure 21). If the TiN is compressive stressed it will show peaks at lower angles (Braggs law Eq.3). The (Ti,Al)N layer, if tensile stressed on the other hand will show peaks at higher angles. This theory coincides with the X-ray diffractograms and it seems that the lattices try to adopt to each other with resultant tensile and compressive stresses (also confirmed with HR-TEM). This means that the layers have coherence stresses, explained in Section 3.4. After heat treatments the TiN and $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ peaks are closer to the stress free $2\theta$ positions which indicates that stress relaxation is effective during the heat treatment. However, no conclusions can be drawn from these results until further stress investigations are performed on the samples. Even though if there is a stress relaxation between the layers it is possible that the higher mismatch between the $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}/\text{TiN}$ matrix and the AlN (discussed in section 7.1.2) compensate for the relaxation and introduce even higher stress states. Such effect has been seen in single layer thin film of $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ as reported by A.Hörling et al. in [8]. However, it is not impossible that a multilayer structure give an even higher stress state than a single layer thin film after decomposition because of the possibility of a higher percent of coherence contact areas between the AlN precipitated and the unaffected TiN layers than in a completely composed single layer with 66% AlN and 34% TiN.
7.3 SAXS

Measurements in Figure 24 reveals that the AlN precipitation has an average size of ~7nm and a spherically shape at 900°C. With information about the shape of the particles it’s possible to recalculate the electron radius of gyration $R_g$ from the SAXS result to the real radius $R$ with Eq. 8 [25, 26].

$$R = \frac{R}{1.29} \quad Eq. 7$$

From the SAXS results in graph in Figure 13 the real $R$ was calculated to ~11nm at 900°C. The calculated result is however not completely true because of different bias during the deposition of the SAXS samples and not identical heating properties. The result is though powerful for future SAXS work.
8 Conclusions

- There is coherency between the Ti$_{0.34}$Al$_{0.66}$N and the TiN layers.
- There is nothing in this work that contradicts the presence of spinodal decomposition in Ti$_{0.34}$Al$_{0.66}$N during heat treatments.
- There is coherency between the c-AlN precipitates and the Ti$_{0.34}$Al$_{0.66}$N / TiN matrix.
9 Future work

There are parts in this reports that, because of the limited time of a diploma work, has to be closer investigated both experimental and theoretically. First of all should the 5rpm samples be investigated in the same way with HRTEM, STEM and EDS as the 1rpm sample. The test matrix also has to be complemented with more annealing temperatures and rotation speeds, both higher and lower. Single layer of TiN and TiAlN should be investigated as reference materials. The samples should also be investigated with EELS to be able to get more information about the AlN phases and the nitrogen. Another method that could be a relevant complement is DSC measurements that would give information about the thermal stability. From an industrial point of view both nanoindentation and work tests are interesting.
References


[16] Methods of X-Ray and Neutron Scattering in Polymer Science ROE


Electronic links:


[b] www.britannica.com/
## Appendix

### Appendix 1

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Table 1: *As deposited data from XRD*
Structural characterization of arc evaporated Ti$_{0.34}$Al$_{0.66}$N / TiN multilayer

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Table 2: As deposited data from XRD
Appendix 2

Figure 26: Single crystal spot transmission electron diffraction pattern for f.c.c. crystal structure.
Appendix 3

Figure 27: As deposited 1rpm sample STEM picture

Figure 28: EDS element map as deposited sample
Structural characterization of arc evaporated Ti$_{0.34}$Al$_{0.66}$N / TiN multilayer

Figure 29: Heat treated STEM overview picture