Decomposition of arc evaporated Ti$_{1-x}$Al$_x$N coatings during metal machining

Sönderfall av PVD-belagd Ti$_{1-x}$Al$_x$N under svarvning

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Titel
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Sammanfattning
I arbetet undersöks sönderfallsprocessen i beläggningar av kubisk (Ti,Al)N på svarvskär under skärande bearbetning, dvs. under samtidigt högt tryck och hög temperatur. Genom att variera skärhastigheten har olika temperatur- och trycktillstånd erhållits i beläggningarna. Röntgendiffraktion (XRD) transmissionselektronmikroskop (TEM) samt sveprtransmissionsmikroskop har använts för detaljerad ytэтажäring av skärets spånsida.

Temperaturer har under bearbetningen mätts med en IR-CCD kamera och varierat mellan 750°C och 950°C, normalkrfter mellan 2 GPa och 2.5 GPa har beräknats från skärkrafters uppmätta under bearbetning. Resultaten visar också en relaxation av beläggningen, dvs. en annihilering av defekter, trots den relativt korta skärten.
**Summary**

This work investigates the decomposition process of cubic phase (Ti,Al)N coated metal cutting insert during machining, i.e., under simultaneous high temperature and high pressure. Different temperatures and normal stresses were obtained during the machining by varying the cutting speed. X-ray diffraction (XRD) and analytical transmission microscopy (TEM) including scanning TEM (STEM) were used for detail characterization of the tool-chip-interface.

Temperatures between 750°C and 950°C, measured by an IR-CCD camera and normal stresses between 2 GPa and 2.5 GPa, calculated from the measured contact force, were obtained at the tool-chip interface. The results also reveal a relaxation of the coating during cutting, i.e. an annihilation of defects, despite the rather short machining time.
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1 Introduction

This thesis is the result of a diploma work performed during autumn 2009 at Nanostructured Materials, Linköping University. The thesis is the finishing part of the master programme Materials Design and Engineering at Högskolan Dalarna and the Royal Institute of Technology.

Cutting operations by chip removal are common in the tooling industry as a technique to machine a material, henceforth referred to as the work piece, to a desired shape. In advanced metal cutting operations, the tools used are commonly made of cemented carbide (WC-Co) in combination with a well designed tool coating (material, phase and thickness) to enhance the wear properties of the tool during machining. The most frequently used tool coating, deposited with physical vapor deposition (PVD), in metal cutting applications is the cubic phase of (Ti,Al)N with thicknesses ranging from sub-micrometer up to several micrometers. (Ti,Al)N has been used since the mid-1980 when Al was added to the TiN system in order to achieve a coating more resistant to oxidation.

However, the adding of Al gave another advantage compared to TiN, when exposed to temperatures around 900°C the metastable cubic (Ti,Al)N decomposes through a spinodal decomposition into coherent cubic TiN and cubic AlN regions. Accompanying the decomposition is an increase in hardness triggered by a coherency strain mechanism. Further annealing though decomposes cubic AlN into hexagonal AlN which is followed by a decrease in hardness.

During a cutting operation the coated tool is subjected to both high temperatures and high normal stress. Earlier research on the (Ti,Al)N coating material has focused on the material properties when only temperature is considered, i.e. neglecting the effect of pressure. This diploma work is therefore a first step to investigate the (Ti,Al)N coating properties at simultaneous high temperature and pressure which will, in future, give further knowledge of the cutting tool wear.
1.1 Aims

The main aims of the present work are:

- Phase characterization of a (Ti,Al)N coating deposited on a cutting insert and exposed to the conditions prevailing at the cutting edge during metal cutting (turning)

- To compare the microstructure of (Ti,Al)N coatings exposed to high temperature anneals to the microstructure developed when exposed to simultaneous high temperature and high pressure.

1.2 Abbreviations and acronyms

The following abbreviations and acronyms are used in the thesis.

- AL40: Ti$_{0.60}$Al$_{0.40}$N
- Al67: Ti$_{0.33}$Al$_{0.67}$N
- CVD: Chemical Vapor Deposition
- EDX/EDS: Energy Dispersive X-ray Spectroscopy
- FIB: Focused Ion beam
- LOM: Light Optical Microscopy
- PVD: Physical Vapor Deposition
- SEM: Scanning Electron Microscopy
- STEM: Scanning Transmission Electron Microscopy
- TEM: Transmission Electron Microscopy
- TNMA: Triangular substrate used for cutting tests
- TPUN: Triangular substrate used for cutting tests
- XRD: X-Ray Diffraction
2 Deosition of thin films

Thin film deposition is mainly performed with either chemical vapor deposition (CVD) or physical vapor deposition (PVD). In this study, only thin films produced by PVD and more specifically by cathodic arc evaporation are used and is described in more detail in the paragraphs below.

Commonly there are three steps when depositing with both CVD and PVD. The first step is to synthesize the deposition material which includes a transition from solid or liquid phase into vapor phase. In the second step the vapors are transported from the source to the substrate where the third step takes place. The third step is a condensation of the vapors which is then followed by nucleation and growth of the film.

2.1 Introduction to PVD

PVD is often used to deposit films and coatings on substrates, as in this study, or to deposit shapes without substrates, e.g. foils. The deposition rate can vary between $10^{-3}$ to 75 $\mu$m per minute and is dependent of the deposited material and PVD technique [1]. The most common PVD technique are cathodic arc evaporation, ion plating and sputtering [1]. In this study the films have been deposited with cathodic arc evaporation.

2.1.1 Cathodic arc evaporation

Arc evaporation produces dense adherent coatings and is therefore widely used by the industry. It uses a low voltage and high current to create a plasma discharge between two electrodes. To do this, the metal source in the coating alloy, in this study TiAl, acts as a cathode and is hit by an electrical arc. The arc discharge hits small locations of the cathode surface which yields a high current density.

The high current evaporates atoms because of extremely high temperatures and emits electrons from the cathode which then collide with the atoms and ionize them. The substrates are often negatively charged and therefore attract the positive ions. At the substrate the ions condensate together and react with a gas, in this study N$_2$ [2].
A disadvantage with arc evaporation is that not only atoms and electrons are emitted from the molten cathode but also macroparticles. The macroparticles may drastically reduce the positive properties of the film and it is therefore of interest to minimize the number of particles hitting the substrate. One way to do this is the use of shields or magnetic filters [2]. However, because this decreases the deposition rate it is not commonly used in the cutting tool industry.

2.2 Nucleation and growth of the film

The growth of the film on the substrate is usually divided in three modes. The first mode is a three-dimensional growth where small clusters nucleates on the substrate and then grow as islands. The mode is also called Volmer-Weber and occurs if the film atoms are more inclined to bind to each other than to the substrate [1]. The second mode is a two-dimensional mode, also called Frank-van der Merwe, where the film atoms grow layer by layer. This mode occurs if the film atoms rather bind to the substrate than to each other [1]. Finally, there is a third mode which is a combination of the first two modes. This growth mode, called Stranski-Krastanov, begins as a layer by layer growth but changes to island growth after one or several layers are grown [1].
3 Ti$_{1-x}$Al$_x$N

Before Ti$_{1-x}$Al$_x$N was introduced as a coating for cutting tools in the mid-1980s pure TiN was used. But since TiN oxidizes at temperatures of 500°C-600°C [3] and cutting temperatures can well exceed 900°C the use as a coating for cutting tools is limited [4]. The deposition with PVD gives the possibility to deposit the coating in a metastable phase because of a low growth temperature. This is of great importance, since the maximum solubility of AlN in TiN is only about 5% at 2450°C [5].

3.1.1 Structures of Ti$_{1-x}$Al$_x$N and TiN/AlN

The as-deposited structure of Ti$_{1-x}$Al$_x$N is known as [NaCl]-Ti$_{1-x}$Al$_x$N (or c-TiAlN) where N and Ti/Al are structured in two combined fcc-structures as can be seen in Figure 1 [6]. As described in Paragraph 3.1.2 the stable configuration for AlN is though a hexagonal [wurtzite]-structure (h-AlN) which can also be seen in Figure 1 [7].

![Figure 1. [NaCl]-structure (left) and [wurtzite]-structure (right). Large atoms indicate Ti/Al and small atoms N.](image)

3.1.2 Decomposition of Ti$_{1-x}$Al$_x$N

Previous research has shown that the metastable c-TiAlN decomposes into two cubic phases, [NaCl]-TiN (c-TiN) and [NaCl]-AlN (c-AlN), through a spinodal decomposition (Paragraph 3.2) at 900°C-1100°C [3]. This decomposition has positive effects on the mechanical properties of the coating since the phases are coherent due to the small lattice
mismatch. The decomposition can therefore be seen as a hardening mechanism referred to as age hardening similar to what usually is observed in metals [7].

c-TiN is the stable configuration and does not decompose further while c-AlN is still in a metastable state. Therefore, at further annealing c-AlN decomposes to h-AlN [3]. Since the hexagonal phase differs from the cubic the decomposition leads to incoherency. This rapidly lowers the hardness of the coating since the age hardening effect decreases, i.e. the dislocation mobility is increased [10]. In summary, the phase transformations in TiAlN can be written as

c-(Ti,Al)N → c-TiN + c-AlN → c-TiN + h-AlN

3.1.3 The influence of pressure

So far, the research has been focused on decomposition induced by the temperature. However in a cutting operation the pressure obtained can reach several GPa because of the small contact area and high applied force. With this information it is of importance to further investigate the influence of pressure on the decomposition which has been performed theoretically by Alling et al [11].

The change in Gibb’s free energy of mixing can be described as [12]

$$\partial \Delta G = \Delta V \partial P - \Delta S \partial T$$  \hspace{1cm} \text{Eq. 1}

If the temperature is fixed the latter term is zero and the derivative of the Gibb’s free energy with respect to pressure is described as

$$\left( \frac{\partial \Delta G}{\partial p} \right)_T = \Delta V$$  \hspace{1cm} \text{Eq. 2}
where $\Delta G$ and $\Delta V$ are

$$\Delta M = M_{Ti_{1-x}Al_xN} - (1 - x)M_{TiN} - xM_{AlN} \quad (M = G, V) \tag{Eq. 3}$$

Therefore, $\Delta V$ is the deviation from Vegard’s law which claims that the volume is linear with respect to the concentration of the components [12]. This difference has earlier been determined to be positive for the isostructural, i.e. c-AlN and c-TiN, system in this study [13]. When the nonisostructural, i.e. h-AlN and c-TiN, case is studied the deviation instead is negative because of the large volume of h-AlN.

In the study by Alling et al, the mixing enthalpies of the cubic and hexagonal solid solutions are analyzed with respect of pressure and composition, see Figure 2. As can be seen in Figure 2 a higher pressure shifts the transformation from cubic to hexagonal to higher values of $x$. This means that even if there are regions with a higher content of AlN, the probability of a transformation from c-AlN to h-AlN will be smaller.

![Figure 2.](image)

Figure 2. a) shows the mixing enthalpy of the cubic and hexagonal solid solutions at 0, 5 and 10 GPa. b) shows the mixing enthalpy for the isostructural cubic $Ti_{1-x}Al_xN$ at different pressures [11].

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An isostructural phase diagram, Figure 3, was also constructed in the study by deriving the mixing enthalpies. The result indicate that when adding pressure to the system the spinodal region increases and at compositions below $\text{[at-\%]}_{\text{Al}}=40$ the effect is larger. This can be seen as the shoulder in Figure 3 and is a result of the asymmetric mixing enthalpies.

In summary the study concludes that an applied pressure, e.g. as in a cutting operation, will probably improve the positive properties of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ compared to when only annealing at atmospheric pressure is performed. This is due to an increased probability for spinodal decomposition and a decreased probability for the transformation c-AlN to h-AlN [11].
3.2 Spinodal decomposition

Spinodal decomposition is a transformation without an energy barrier to nucleation. The Gibbs free energy ($G$) describes the thermodynamic stability of a solid solution as a function of composition ($x$) and temperature ($T$), $G(x,T)$. As can be seen in Figure 4 the curvature of the free energy, i.e. the second derivative with respect to $x$, can be either positive or negative. The area in the miscibility gap where the curvature is negative is called the spinodal.

![Figure 4. Upper diagram shows Gibbs’s free energy ($f$) vs. composition at $T=T_0$ and lower diagram shows a phase diagram for the same components.](image)

If an alloy with a composition inside the spinodal gap in Figure 4 is solution treated and quenched at temperature $T=T_0$ the composition will initially be the same. However the composition is unstable which will cause the phases to separate into coherent phases spontaneously. This decomposition is done by small fluctuations which produce A-rich and B-rich regions. The diffusion flow is therefore “up-hill” diffusion where atoms diffuse towards areas rich of the same atoms.
Outside the spinodal, where the Gibbs free energy curvature is positive, small variations in composition instead increases the free energy. This means that the alloy is metastable and the free energy can only be decreased if nuclei with a composition different from the matrix are formed. This mechanism is called nucleation and growth and includes “down-hill” diffusion [13].
4 Characterization techniques

Several techniques have been used in this work to characterize the properties of the coatings. X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used for phase characterization. The mechanical properties of the coating have been investigated with nanoindentation. TEM and scanning electron microscopy (SEM) were used for microstructural and morphological characterization.

4.1 X-ray Diffraction

XRD is a non-destructive technique used for structural characterization. As can be seen in Figure 5 X-rays are directed against the surface and scattered by the atomic planes. At specific incident angles (θ) the diffracted beams interfere with each other according to Bragg’s law in Eq. 4.

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

Eq. 4

where \( d \) is the spacing between atoms, \( n \) an integer (order of reflection) and \( \lambda \) is the X-ray wavelength. Since \( n \) and \( \lambda \) are constants the spacing between atoms can be determined when knowing the incident angle when interference occurs. Besides lattice parameters XRD can also be used to obtain information about phase composition, film thickness, grain size, residual stress and crystallographic orientation.

Figure 5. X-ray diffraction planes [14].
When performing an XRD measurement the angle of an incident beam and a detector is varied simultaneously. The detector detects the intensity of the interfering X-rays, hence when constructive interference occurs the intensity is increased. This results in a diffractogram, which can be seen in Figure 6. Since the sampling depth can be a few \( \mu \text{m} \) signals from the substrate are shown in the diffractogram as well (in Figure 6 denoted by \( s \)) [2].

![Figure 6. X-ray diffractogram after a 0-2\( \theta \)-scan on Ti\(_{0.33}\)Al\(_{0.67}\)N.](image)

### 4.2 Nanoindentation

Nanoindentation is a method commonly used to measure the hardness and elastic modulus of a material, though it can also be used to measure hardening exponents, creep parameters and residual stresses [15]. Ordinary methods for measuring hardness, e.g. Vickers and Rockwell, are not possible to use when measuring the hardness of thin films. This is because the penetration depth of these methods, may exceed the film thickness thus affecting the underlying substrate which consequently will influence on the measured hardness value. As a rule of thumb, the penetration depth should therefore not exceed 10% of the film thickness [2].
In nanoindentation an indenter tip is used together with sensors to measure mechanical load and indenter displacement. The indenter tip is usually a so called Berkovich indenter which is a diamond tip formed as a three-sided pyramid. The indenter tip penetrates the film while the sensors record the force and displacement, as can be seen in Figure 7 [15].

![Figure 7. Example of a load-displacement curve during nanoindentation.](image)

The film hardness (H) can then be evaluated for a Berkovich indenter using Eq. 5.

$$H = \frac{P_{\text{max}}}{A}$$  \hspace{1cm} \text{Eq. 5}

where A is the projected contact area and $P_{\text{max}}$ the maximum indentation load. Since the indent is small, the area has to be estimated according to Eq. 6 (yields for a Berkovich tip).

$$A = 24.56 \cdot h^2 + \delta$$  \hspace{1cm} \text{Eq. 6}

where h is the total displacement and $\delta$ a tip correction factor obtained from a calibration procedure [2,16].
4.3 Electron Microscopy

4.3.1 Basic principles
An electron microscope uses, as the name implies, electrons which hits a sample. The high energy primary electrons interact with the sample which irradiates secondary electrons, backscattered electrons and characteristic X-rays. These signals are detected by different detectors which obtain information about the sample, e.g., surface topography/morphology, phase content, crystal orientation and element composition [17].

4.3.2 Resolution
One of the main reasons to use electron microscopy instead of light optical microscopy (LOM) is the limited resolution in LOM. The resolution in LOM is expressed by the Rayleigh criterion in Eq. 7.

\[ \delta = \frac{0.61\lambda}{\mu \sin \beta} \tag{Eq. 7} \]

where \( \delta \) is the resolution, \( \lambda \) the radiation wavelength, \( \mu \) the refractive index and \( \beta \) the semi angle of collection of the magnifying lens. For a good microscope the denominator can be approximated to unity which gives a resolution to about half the wavelength of light. Green light in the middle of the visible spectrum has a wavelength of about 550 nm which gives a resolution of around 300 nm.

For electrons, the wavelength is given by their energy according to de Broglie’s equation in Eq. 8 (the equation is modified to include relativistic effects).

\[ \lambda = \frac{h}{2m_0eV \left( 1 + \frac{eV}{2m_0c^2} \right)^{1/2}} \tag{Eq. 8} \]

where \( h \) is Planck’s constant, \( m_0 \) the electron rest mass, \( e \) the electron charge, \( V \) the acceleration voltage and \( c \) the speed of light in vacuum. This gives a wavelength of about
0.0037 nm for 100 keV electrons which is a major resolution advantage compared to LOM. The value is though only theoretical because of non perfect electron lenses but can be seen as guiding for the electron microscopy resolution [18].

### 4.3.3 Transmission Electron Microscopy

As the name implies, in a TEM the electron beam transmits through the sample, the electron energy is often in the order of several hundred keV. This requires an electron transparent sample, which often means a thickness less than 100 nm. The transmitted electrons are detected with a detector which translates electron intensity into a screen picture of the sample.

The most powerful capability with TEM is the possibility to create a selected area diffraction (SAD) pattern. Compared to XRD the electrons are scattered by the electrons and nuclei which gives a stronger scattering than X-rays do. The diffraction pattern can be used to obtain information about crystallinity, e.g., lattice distance and crystal structure and hence the possibility to determine phases in a sample [18].

### 4.3.4 Scanning Transmission Electron Microscopy

In scanning transmission electron microscopy (STEM) an electron beam is scanned across the sample. The electron beam is scanned by adjusting the scan coils and the image is viewed on fluorescent screen. Since the image has to build up scan lines the image creating is slower than TEM imaging where the image is static. This also generally gives a noisier image when using STEM instead of TEM.

### 4.3.5 Scanning Electron Microscopy

A SEM scans an electron beam across the area to be analyzed. The electron energy ranges from a few keV to 50 keV and the beam size is typically 10 Å in diameter. Often used together with SEM is the EDS which is described below [19].

### 4.3.6 Energy Dispersive X-Ray Spectroscopy

Energy Dispersive X-Ray Spectroscopy (EDS) is a method to perform an elemental analysis of a sample. When the electron beam interacts with the sample some of the
sample electrons are ejected. This leaves the atom as an ion in an excited state and when the atom relaxes it sends out a photon of electromagnetic radiation, X-ray. The energy of these photons is of a characteristic value for each element. Therefore it is possible to determine the sample element composition when detecting the X-rays [17].

4.3.7 Focused Ion Beam

A focused ion beam (FIB) is a feature in SEM but scans ions instead of electrons. When the ions collide with the sample ions, atoms and electrons are emitted. This gives the possibility to both create an image but also remove selected material with a high spatial resolution and used for TEM sample preparation [20].
5 Experimental

5.1 Coating deposition

The coatings were deposited in a commercial Sulzer Metaplas MAXIT® PVD System Model MZR-323 reactive cathodic arc evaporation system at Seco Tools AB in Fagersta. Different insert geometries were used as substrates. These were namely triangular flat inserts (ISO geometry TPUN160308 and ISO geometry TNMA160408) intended for cutting tests as well as polished square inserts (ISO SNUN120408) for coating characterization purposes, see Figure 8. The substrates were made of cemented carbide, WC-Co with a hardness of 1690 HV and before deposition, the substrates were ultrasonically cleaned and degreased.

Figure 8. From left to right is the TPUN, TNMA and SNUN substrate.


Ti$_{0.33}$Al$_{0.67}$N (Al67) film was deposited with six cathodes with analogous cathode composition. The substrates were placed by magnets in the PVD chamber with the polished side facing the cathodes. In order to obtain (Ti,Al)N-films with the desired composition of Ti$_{0.60}$Al$_{0.40}$N (Al40) a number of substrates were placed at four different positions with respect to two different cathodes, see Figure 9. The two cathodes were composed of pure Ti and Ti$_{0.50}$Al$_{0.50}$ respectively thus obtaining films covering the desired composition.

Except for different cathodes the depositions was performed under the same conditions. The atmosphere was N$_2$ and the substrate bias was -40 V and a substrate temperature of 400°C. The drum was rotating with 3 rpm.

### 5.2 Heat treatment

Samples were heat treated in a Sintervac Furnace from GCA Vakuum Industries at Seco Tools AB in Fagersta. The samples were annealed to 700, 800, 900 and 1000°C in a protective argon atmosphere at ambient pressure. Until 40°C below the wanted temperature, $T_{\text{max}}$, the heating rate was 7°C/min and above it was decreased to 5°C/min. The temperature was held isothermally at $T_{\text{max}}$ for 2 hours and then cooled to 500°C in ~1.5 h and from 500 °C to 100 °C in ~4 h.
5.3 SEM/EDS studies

EDS analyses were performed on the films with four different compositions to conclude which one to use in cutting tests, i.e. the coating with a composition below 40% Al. The analyses were performed at three different spots at the film, one in the middle of the substrate and two at the edges to study a possible gradient in the film. The two edge spots examined were those closest to the bottom and top in the PVD chamber.

5.4 Cutting tests

The cutting tests were performed at Seco Tools AB in Fagersta using a quenched and tempered steel (SS2244, 230 HB) as work material. The normal rake angle was 6° for the TPUN inserts and -6° for the TNMA inserts. Both longitudinal and orthogonal turning tests were carried out and the cutting parameters can be found in Table 1 in Appendix 1. During turning, the axial, radial and tangential force components were measured and documented.

5.5 Tool stress

The stress state distribution at the cutting edge was analytically calculated according to the model described in [21] which has been used in previous cutting tests at Seco Tools AB. The parameters used in the model are tangential and radial force ($F_t$ and $F_r$), chip thickness ($h_c$) and plastic contact length ($l_{pl}$). The chip thickness and contact length were measured in a LOM. The edge was approximated to a sharp edge, i.e. the effect of any rounding of the edge during cutting is neglected. The stresses calculated by the model are the normal stress and the tangential stress and their distribution along the total contact length.

5.6 Tool temperature

The tool temperature was measured with an IR-CCD camera as described in [22]. When the data is analyzed the temperature can be obtained from the IR intensity, a brighter intensity yields a higher temperature. The data was analyzed to find the peak temperature, i.e. the highest temperature at the cutting edge. Also, for some cutting parameters, the temperature distribution was derived.
5.7 Nanoindentation

5.7.1 Sample preparation

Pieces with a thickness of approximately 3 mm were cut from the substrates with Struers Accutom-5 (feed 0.02 mm/s, speed 3000 rpm). The pieces were then moulded in bakelite with an inclination of the film. This was made by placing the pieces with the film down on a plate with an elevation. The sample was ground with abrasive grains of SiC with 12 µm size until a third of the substrate was visible. In the final steps the sample was polished with a polishing cloth and diamond slurry with sizes 6, 3 and 1 µm until no scratches were seen.

5.7.2 Experimental setup

The hardness measurements were performed with an UMIS nanoindentor equipped with a Berkovich diamond tip. Approximately 20 indentations were made in each film in order to sustain a mean value of the film hardness. The software used to analyze the indentations to achieve the hardness results was Ibis 2. When the data was analyzed extreme values which differed heavily from the average values was removed.
5.8 TEM

For TEM analyzes only the coating called Al40 was analyzed. The reasons for this were twofold, firstly to improve our understanding of the Al40 composition and secondly the limited times for this diploma work.

5.8.1 Sample preparation

The samples were cut with a Struers Accutom-5 (feed 0.02 mm/s, speed 3000 rpm) and a low speed diamond wheel saw into pieces measuring 1.8×0.5×0.5 mm\(^3\). Two pieces were fitted in a titanium grid with the thin films facing each other as can be seen in Figure 10. The grid was then baked at 200ºC in a mixture of araldite and graphite for two hours. After baking, the excessive amount of araldite and graphite was removed before polishing. The polishing was made with diamond abrasive films in four steps with grain sizes of 16, 6, 3 and 1 µm. After the final step the grid was approximately 50 µm with no visible scratches.

![Figure 10. Two pieces fitted in a titanium grid with the thin films facing each other.](image)

5.8.2 Precision Ion Polishing System

A precision ion polishing system (PIPS) was used in the TEM preparation after diamond polishing. PIPS shoots argon ions towards the center of the rotating sample from the top and bottom. The ions collide with the sample and removes material from it. This is performed in two steps. In the first step the energy is 5 keV with an ion beam modulation set to double until a hole is obtained. The energy is then reduced to 3 keV with a single modulation for 20 minutes. For both steps the rotational speed was 3 rpm.
5.8.3 FIB

A TEM sample was prepared with FIB on an insert used in a cutting operation and to do this the lift out technique was used. The first step was to deposit a platinum strap over a selected area (2×25 μm), the area chosen was where the highest temperature was obtained, as seen in Figure 19 and Figure 20. In the second step a trapezoid was milled on each side of the strap which creates a cross section specimen between the trapezoids. A needle is then attached on the specimen with platinum. The specimen is then cut off from the sample and lifted off with needle. In the final step the specimen is attached to a specimen holder and thinned with ions until electron transparent.

![TEM sample](image)

Figure 11. LOM picture of cutting edge showing where the TEM sample was taken from in FIB. Also in the figure is the distance from cutting edge, indicated by the vertical arrow.

5.9 XRD

XRD was performed at Seco Tools in Fagersta. The beam diameter was 2 mm and to minimize the effect from the unaffected area the cutting zone was delimited with tape, see Figure 12. In order to find the area a scan at a specific angle in the x- and y-direction was performed respectively. Since the intensity is lowered when the tape is scanned the cutting zone could easily be found at the maximum intensity peaks. A 2θ-scan was then
performed at fixed x- and y-values. Most of the scans were performed with a variation of the \(2\theta\) angle from 30 to 45 degrees with steps of 0.1 degrees and an analyze time of 4 seconds per step. In order to get more accurate results a few scans were also performed with a time of 200 seconds per step.

![Figure 12. The method used to delimit the cutting zone which can be seen in the bottom right corner of the cutting insert.](image)
6 Results

6.1 SEM/EDS

6.1.1 Chemical analysis of as-deposited samples

Figure 13 shows the composition at the three spots of each insert as was described earlier. Figure 14 shows the mean values of the EDX examination, calculated from the results in Figure 13. If compared to Figure 9 the values from left to right correspond to the inserts from bottom and top of the placement in the PVD chamber. The numbers in the inset correspond to the vertical distance from the TiAl cathode, see Figure 9.

![Graph showing variation in Al content of (Ti,Al)N films with vertical distance from the TiAl cathode at three different spot locations at substrate.](image-url)
Figure 14. Variation in Al content of the (Ti,Al)N films (as measured by EDX) with vertical distance from the TiAl cathode (compare with Figure 9) during coating deposition.
6.2 Tool stress

Table 2 in Appendix 2 gives the parameters used in the analytical stress model. The normal and tangential stress for three different geometries and/or compositions is shown in Figure 15-16 below at different speeds. The distance from the cutting edge is defined in Figure 11.

Figure 15. Normal ($\sigma$) and tangential ($\tau$) stress for Al40 deposited on a TPUN geometry. The distance from edge is measured at the chip flow direction.

Figure 16. Normal ($\sigma$) and tangential ($\tau$) stress for Al67 deposited on a TPUN geometry. The distance from edge is measured at the chip flow direction.
Figure 17. Normal ($\sigma$) and tangential ($\tau$) stress for Al67 deposited on a TNMA geometry. The distance from edge is measured at the chip flow direction.
6.3 Tool temperature

6.3.1 Peak temperature

The peak temperatures for three different geometries and/or compositions are shown in Figure 18.

![Figure 18. Peak temperatures as a function of the cutting speed for Al40 deposited on TPUN and Al67 deposited on TPUN and TNMA.](image)

6.3.2 Thermal maps

Thermal maps for Al67 at 200 m/min and the two geometries TPUN and TNMA can be seen in Figure 19. Thermal maps for Al40 at three different cutting speeds (100, 200 and 400 m/min) can be seen in Figure 20.
Figure 19. Thermal maps for AL67 at speed 200 m/min. The left map is TNMA and right is TPUN.

Figure 20. Thermal maps for Al40 at 100 (top left), 200 (top right) and 400 (bottom) m/min.
6.4 XRD

6.4.1 Heat treated

The results from XRD measurements on heat treated and as deposited samples can be seen in Figure 21. When as deposited, there are two major peaks at around 36.5 and 42.5 if the substrate peaks (denoted in Figure 21 and 22 by an s) are disregarded. If the heat treated samples (to 700°C and 800°C) are studied a clear shift to large angles is observed.

At 900°C and 1000°C the diffractograms are somewhat different since there is also a peak at 43.8 degrees. Finally, an examination of the sample heat treated to 1000°C shows a peak at around 33.2 degrees which is not detectable at the other diffractograms. This peak is visualized by the inset to the right in Figure 21.

![Figure 21. XRD scans of untreated sample and samples heat treated to 700°C, 800°C, 900°C and 1000°C, aluminum content 40%. The inset shows a zoomed view between 32.5 and 34 degrees to visualize the hexagonal peak. If non colored, the graphs are ordered in the same way as in the legend.](image)
6.4.2 Cutting tests

The results after XRD measurements on inserts used in longitudinal cutting can be seen in Figure 22 (Al40) and 22 (Al67). The interesting peaks can be found at approximately 36.5-37.5 and 42.5-43 degrees. There is a clear shift to larger angles for both peaks when compared to the as deposited sample.

![Figure 22](image1.png)

**Figure 22.** Two XRD scans of untreated samples (bottom and black) and cutting edges (top and red) for Al40.

![Figure 23](image2.png)

**Figure 23.** Two XRD scans of untreated samples (bottom and black) and cutting edges (top and red) for Al67.
6.5 Nanoindentation

6.5.1 As deposited

In Figure 24 the results after nanoindentation can be seen for as deposited samples and samples heat treated to 900°C.

![Graph showing hardness values vs. aluminum content for heat treated and as-deposited coatings.](image)

Figure 24. The hardness values obtained from nanoindentation plotted against the aluminum content for heat treated and as-deposited coatings.
6.6 TEM

In Figure 25 below one overview TEM picture of the as deposited Al40 coating is shown together with a SAD pattern.

Figure 25. A TEM picture of the film in its as deposited state and a SAD pattern in the top left corner.
Figure 26 below shows three TEM micrographs from three Al40 coatings, as deposited, annealed to 900°C and machined coatings.

![Figure 26. TEM micrographs showing the coating when it is as deposited, annealed to 900°C and machined.](image)

Below, in Figure 27, is an EDS map of an Al40 coating annealed to 900°C, taken in STEM mode, from a small area (40×40 nm). The STEM image shows the variation in Z (Z-contrast) of the imaged region where lighter regions indicates a higher Z component. The EDS maps (Ti and Al) show the variation in composition with respect to Ti and Al, respectively. Here, a brighter area indicates a larger fraction of the mapped element.

![Figure 27. STEM image and EDS maps, of an Al40 coating annealed to 900°C, with respect to Al and Ti showing the spinodal decomposition.](image)
7 Discussion

7.1 Cutting stress
As can be seen in Figure 15 to Figure 17 the peak normal stress appears at the tool tip and ranges between 2 and 2.5 GPa for all different cutting parameters. The friction shear stress has its maximum around half the total contact length and then decreases to zero. A comparison between the different speeds reveals that the normal stress does not vary much. This is not the case for the friction stress which is lowered at a larger speed. An explanation for this could be that since the cutting temperature is increasing at larger speed the work material is softened which lowers friction shear stress.

7.2 Cutting temperature
As can be seen in Figure 18 the peak temperature is more dependent on the cutting speed and the effect of geometry (change in rake angle from -6 to +6 deg.) and/or composition appears to be marginal. The peak temperature ranges from about 780°C to 950°C as the feed increases from 100 m/min to 400 m/min. When comparing TNMA and TPUN in the thermal maps it seems that the area with high temperature is larger when cutting with TNMA. This might be a result of the rake angle but since the effect is rather small and the uncertainty of the temperature measurement (around 25°C) is large it is hard to draw any conclusions.

7.3 Nanoindentation
The hardness results after nanoindentation seen in Figure 24 is a bit peculiar when comparing to previous studies [4]. First of all, the measurements indicate a much harder material than previous studies have shown. Secondly, the trend shows that the hardness values decreases when aluminum is added to the coating. Earlier studies show the opposite trend, an increase of aluminum content also increases the hardness. However, it is possible that the results have been affected by the sample preparation. After annealing to 900°C the hardness trend is reversed, and the values are more consistent to previous studies. As shown earlier this hardness increase originates from the spinodal decomposition which acts as an age hardening effect.
7.4 XRD

7.4.1 Heat treated samples

The shift to larger angles at the scans at 700°C and 800°C in Figure 21 indicates a relaxation of compressive stresses. The compressive stress in the film is likely to originate from the deposition of the coating. The relaxation is not as clear at 900°C and 1000°C since the peaks at 42.8 and 43.8 degrees are probably a result of spinodal decomposition into c-TiN and c-AlN, i.e. the coating was relaxed before the decomposition. The final peak at 33.2 degrees on the sample heat treated to 1000°C can be explained by a further decomposition of c-AlN into h-AlN as that peak corresponds to the lattice parameter of 100 (10-10) h-AlN.

7.4.2 Cutting tests

Also in Figure 22 the shift to larger angles at the peaks at 36.5-37.5 and 42.5-43 degrees can be related to a relaxation of residual compressive stresses in the film. No signs of decomposition can be seen in the scan, and a comparison with the heat treated samples shows that the cutting edge is similar to samples heat treated to 700°C or 800°C. The similar behavior can be seen in Figure 23 where Al67 is analyzed even though the 2θ angles are somewhat different.

Why no decomposition, neither the spinodal nor the c-AlN to h-AlN, can be observed may be due to the relatively short time in cut in the turning operation. This was at most two minutes which, compared to the annealing time, could be too short for the decomposition to start. Alternatively, if the spinodal decomposition has started, the accuracy of the XRD is not good enough to detect the two cubic phases because of the rather high intensity from unaffected material.

Finally, the peak at around 39.5 degrees which can be seen in both Figure 22 and Figure 23 is probably from the tape used. This peak can also be seen in Figure 28 in Appendix 3 where a comparison is made between scans with or without tape.
7.5 TEM

Figure 25 of the as deposited coating shows a defect rich columnar structure with a column width typical for (Ti,Al)N. The SAD pattern has been indexed as cubic (111), (200) and (220). When comparing the as deposited coating with the heat treated coating in Figure 26 the defect density has decreased due to the relaxation of the coating which was discussed above in the XRD paragraphs. This is also seen in the machined coating despite the short machining time of approximately 2 minutes.

Finally, Figure 27 of the STEM EDS map with respect Al and Ti shows the typical appearance of the spinodally decomposed Ti-rich and Al-rich regions. The size of the regions is around 5 nm which is consistent with previous studies [23].

7.6 Summarized discussion

The annihilation of defects, i.e. relaxation of residual stresses, is seen both in the XRD measurements and in TEM examinations. This occurs in the heat treated coatings as well as in the cutting inserts even though the cutting time was approximately 2 minutes. For the annealed coatings an increase in hardness is observed despite the defect annihilation. This is observed in several previous studies and is a result of a spinodal decomposition, which can also be seen in both the XRD measurements and in TEM examinations.

A problem with analyzing coatings used in cutting operations is that during cutting the pressure and the temperature are coupled, i.e. it is not possible to choose a specific temperature and/or pressure. Therefore, a direct comparison between annealed and worn coatings is hard since the temperatures are not exactly the same. This might be a problem from a strictly scientific point of view if a better understanding of the material properties is wanted.
8 Conclusions

- The temperature and normal pressure acting on the cutting insert during machining can be estimated with the above approach.

- The temperature and stress distribution vary with cutting parameters, a variation of the cutting speed between 100 and 400 m/min alters the temperature between 750 and 950°C and the normal stress between 2 and 2.5 GPa.

- There is an annihilation of defects in both annealed and machined coatings if compared to the as deposited coatings despite the short machining time.
9 Future work

Since this diploma work is intended to be a beginning of a PhD position there are a lot of work left in this area. Some of this is listed in the points below.

- Extensive studies on inserts used in cutting operations with different composition.

- Studies on inserts used in cutting operations for a longer period of time.

- Pure pressure/temperature studies, i.e. heat treatments during high pressure/s. Both *ex situ* and, if possible, *in situ* measurements.
10 References


[2] Flink A. Growth and characterization of Ti-Si-N thin films. Department of Physics, Chemistry and Biology (IFM); 2008.


[8] NaCl polyhedra


## 11 Appendix

| Appendix 1 | Cutting test parameters | II |
| Appendix 2 | Measured parameters for analytical stress | III |
| Appendix 3 | Illustration of tape effect | IV |
11.1 Appendix 1

In Table 1 the parameters used during cutting tests are shown. The trial numbers are not consecutive since other cutting operations were performed but not included in this diploma work.

Table 1. Cutting parameters in cutting tests.

<table>
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<th>Trial number</th>
<th>Coating</th>
<th>Geometry</th>
<th>Cutting speed [m/min]</th>
<th>Feed [mm/rev]</th>
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<td>TPUN</td>
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<tr>
<td>32,33</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200</td>
<td>&quot;</td>
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<td>34,35</td>
<td>&quot;</td>
<td>&quot;</td>
<td>400</td>
<td>&quot;</td>
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<td>&quot;</td>
<td>200</td>
<td>&quot;</td>
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</table>

II
11.2 Appendix 2

Table 2 contains information about the measured values obtained during and after the cutting tests.

Table 2. Measured values during and after cutting tests.

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<th>$h_c$ [mm]</th>
<th>$l_{pl}$ [mm]</th>
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</tbody>
</table>
11.3 Appendix 3

Figure 28 shows four XRD diffractograms on two different inserts with and without tape.

![Figure 28. XRD scans performed on two different inserts with and without tape.](image)