Self Lubrication on the Atomic Scale

Design, Synthesis and Evaluation of Coatings

MATTIAS LINDQUIST
Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångström laboratorium, Lägerhyddsvägen 1, 75121 Uppsala, Friday, March 7, 2008 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

In this thesis a new design concept of tribologically active coatings aimed for low friction applications, have been explored. Materials modeled by ab initio DFT calculations were realized through deposition of carbide and nanocomposite coatings by DC-magnetron sputtering.

The design concept employs destabilization of a carbide material by alloying with a weak carbide-forming element, which refines the structure into a nanocomposite. The destabilization creates a driving force for superficial ejection of carbon in a tribological contact, forming a lubricious graphitic carbon layer. The otherwise hard material limits the real contact area and the transformed layer accounts for low shear resistance. Hence, the ideal situation for low friction is provided by formation of an easily sheared thin surface layer on a hard material.

TiAlC was chosen as a model system for the theoretical modeling as well as for the depositions. The elemental composition, microstructure and mechanical properties of the coatings were characterized to relate the inherent properties to the experimentally achieved tribological response.

As predicted by theory, TiAlC coatings were shown to provide self-lubrication on the atomic scale by giving low friction through a tribologically induced surface restructuring.

It was shown possible to reduce the friction coefficient from 0.35 for TiC to 0.05 by addition of Al.

Alloying with Al also proved to be a potent method in tailoring residual stresses from high and often detrimental levels to acceptable levels, with no significant reduction in either hardiness or Young’s modulus.

The effect of adding Al into TiC on the oxidation resistance was also explored. The critical temperature for onset of oxidation proved to increase with the Al-content from about 350°C for TiC to about 450°C for TiAlC with about 7 at% Al. A further increase in Al content did not change the onset temperature further but reduced the oxidation rate.

Keywords: Tribology, low friction, PVD, sputtering, nanocomposite

Mattias Lindquist, Department of Engineering Sciences, Box 534, Uppsala University, SE-75121 Uppsala, Sweden

© Mattias Lindquist 2008

ISSN 1651-6214
urn:nbn:se:uu:diva-8443 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-8443)
Till Anna
List of papers

I  Design of Nanocomposite Low-Friction Coatings
   O. Wilhelmsson, M. Råsander, M. Carlsson, E. Lewin, B. San-
   yal, U. Wiklund, O. Eriksson and U. Jansson

II  Tribofilm Formation and Tribological Properties of TiC and
    Nanocomposite TiAlC Coatings
    M. Lindquist, O. Wilhelmsson, U. Jansson and U. Wiklund
    Accepted, Wear 2008

III Tribofilm Formation from TiC and Nanocomposite TiAlC
    Coatings, Studied with Focused Ion Beam and Transmission
    Electron Microscopy
    M. Lindquist, O. Wilhelmsson, U. Jansson and U. Wiklund
    Submitted, Wear 2008

IV  Tailoring the Residual Stress in Magnetron Sputtered TiC
    In manuscript

V   Oxidation Resistance of Nanocomposite TiAlC Coatings
    M. Lindquist, U. Wiklund and S. Jacobson
    In manuscript

VI  The Role of Aluminum Additions in the Oxidation and Wear
    of a TaC:C Low-Friction Coating
    D. Nilsson, N. Stavlid, M. Lindquist, U. Wiklund and S. Hog-
    mark
    In manuscript
Related work

**Deposition and Characterization of (Ti$_{1-x}$Fe$_x$)$_7$C$_3$ Thin Films Grown by DC Magnetron Sputtering**
O. Wilhelmsson, S. Biljelovic, M. Lindquist, B. André, U. Wiklund, P. Svedlindh and U. Jansson

**Tribological Testing of Ceramic Coatings Boosted for Low Friction and for use in Electrical Contacts**
In manuscript

**Conductive Ceramics as Tribological and Electrical Contact Materials**
In manuscript, will be presented at ICEC 2008

**A Comparative Evaluation Method for Low Friction Coatings in Dry Sliding Thrust Bearings**
M. Carlsson, U. Wiklund
Tribologia, 2004, 23, pp 27
The author’s contribution to the papers

These are the author’s contribution to the individual papers

<table>
<thead>
<tr>
<th>Paper</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper I</td>
<td>Part of planning, part of coating deposition, evaluation and experimental work, part of writing</td>
</tr>
<tr>
<td>Paper II</td>
<td>Most of planning, all coating depositions, most experimental work and evaluation except XPS, XRD and TEM analyses, all writing</td>
</tr>
<tr>
<td>Paper III</td>
<td>Most of planning, all experimental work and evaluation except XPS and TEM analyses, all writing</td>
</tr>
<tr>
<td>Paper IV</td>
<td>All planning and coating deposition, most of experimental work and evaluation, all writing</td>
</tr>
<tr>
<td>Paper V</td>
<td>All planning and coating deposition, most of experimental work and evaluation, most writing</td>
</tr>
<tr>
<td>Paper VI</td>
<td>Part of experimental work and discussion, part of writing</td>
</tr>
</tbody>
</table>
## Contents

1 Introduction ........................................................................................................... 13  
1.1 Surface coatings in engineering ................................................................. 14  
1.2 Research objectives ..................................................................................... 15  
1.3 Novel design concept for triboactive coatings ......................................... 15  

2 Coating properties ................................................................................................ 16  
2.1 Mechanical properties ................................................................................ 16  
  2.1.1 Hardness and Young’s modulus .......................................................... 16  
  2.1.2 Residual stresses ............................................................................. 17  
2.2 Tribological properties ................................................................................. 18  
  2.2.1 Wear resistance ................................................................................ 18  
  2.2.2 Thermal and chemical stability .......................................................... 18  
2.3 Coatings for low friction applications ....................................................... 19  
2.4 The ultimate low friction coating ................................................................. 19  

3 Coating design and deposition ........................................................................... 20  
3.1 The theoretical basis for the coating design concept .................................. 21  
3.2 Coating deposition ....................................................................................... 22  
3.3 Sputtering .................................................................................................. 23  
3.4 Coatings deposition ..................................................................................... 25  

4 Coating growth .................................................................................................... 26  
4.1 Nucleation and growth ............................................................................... 26  
4.2 Structure zone models and diagrams .......................................................... 26  
4.3 Effects from ion bombardment ................................................................. 27  
  4.3.1 Surface topography .......................................................................... 27  
  4.3.2 Defects and stresses ......................................................................... 28  
  4.3.3 Grain size and morphology .............................................................. 28  

5 Coating characterization .................................................................................... 29  
5.1 Composition, microstructure and phases ............................................... 29  
5.2 Mechanical properties ................................................................................. 32  
5.3 Tribological properties .............................................................................. 35
6 Contributions ............................................................................................................36

6.1 The new low-friction concept Coating design, evaluation and verification (Paper I-III) ..................................................................................................................36

6.2 Tailoring the mechanical properties Residual stresses, hardness and Young’s modulus (Paper IV) ..................................................................................40

6.3 Oxidation resistance Influence by Al addition in TiC (Paper V) 44

6.4 TaC:C coatings with Al addition Influence on friction, wear and oxidation resistance (Paper VI) .........................................................................................47

7 Conclusive summary ..................................................................................................50
Abbreviations

a-C  amorphous Carbon
DFT  Density Functional Theory
DLC  Diamond Like Carbon
EDS  Energy Dispersive X-ray Spectroscopy
FIB  Focused Ion Beam
PVD  Physical Vapor Deposition
SEM  Scanning Electron Microscopy
SZD  Structure Zone Diagram
SZM  Structure Zone Model
TEM  Transmission Electron Microscopy
TiC  Titanium Carbide
WCF  Weak Carbide Former
XPS  X-ray Photoelectron Spectroscopy
XRD  X-ray Diffraction
1 Introduction

Even though you might not know what the word tribology means, you have for sure encountered the effects from the phenomenon more than once today, you just didn’t think about it. It began as you woke up, rose from the bed and put your leather soled slippers on, walked carefully on the slippery wooden floor of the bedroom into the brick floored kitchen, without falling, but you probably felt the difference in grip. On your way out you had to walk carefully to avoid slipping on the icy driveway. As you got in behind the wheel of your car, you started a real complex tribological system, by just turning the ignition key and starting up the engine. What determines if you fall or not, how your engine sounds and runs etc., is the coefficients of friction in between you and the ground and between the mechanical components of your engine. Whether you put leather or rubber soled shoes on your feet or start up the engine of your car you are experiencing a number of different tribological systems. Sometimes you need high friction like when you walk, so that you don’t fall. You need high friction also to steer, accelerate and brake your car. At the same time you also need low friction, e.g. in your hip joint to swing your leg, or in the car engine to run with low wear and low fuel consumption. Sometimes you need a moderate friction, not too high and not too low. For example, you need a well tuned friction for a comfortable seating position in your car. A too high friction will cause resistance when you slide into position in the seat. On the other hand, the friction must not be too low so that you tend to slide down or off the seat. The above mentioned examples are all surface interactions determining the function and performance of everything that moves in the everyday life.

The word tribology was coined as late as in 1966. It is based on the Greek word tribos that means rubbing [1]. The scientific definition of the word tribology is: “The science and technology of interacting surfaces in relative motion and the practices related thereto”. Tribology comprises friction, lubrication and wear and describes their respective origins, causes and actions. The sentences below are referred to as the Amontons laws of friction (1699).

- The friction force is directly proportional to the applied load
- The friction force is independent of the apparent area of contact

The tribological research breakthrough came in the 1950s when Bowden and Tabor introduced physical understanding of the laws of friction on an atomic scale [2]. The technical breakthrough came in the 1960s as the scan-
ning electron microscopes were launched commercially and became more easily accessible.

Friction arises when two bodies in relative motion come into contact. Their surface roughness peaks, asperities, are intimately pressed against each other and form contact spots. Each spot deforms under loading and the contact area grows until it supports its partial load, i.e. until the applied load is balanced by the contact area times the yield stress for plastic flow. By definition, a material cannot carry a load exceeding its inherent hardness. A good approximation of the total real contact area is therefore given by taking the normal load divided by the material hardness.

Relative motion in a loaded contact promotes adhesion or even local welding as the mating surfaces in contact are rubbed against each other. In maintaining the relative motion, the junctions formed in the contact spots must be broken. The local force required to shear one such junction is defined by the yield shear stress \( \tau \) times the junction area \( A \). All the local forces required to shear all simultaneously active junctions add up to the resulting friction force. The ratio between the resulting friction force \( F_F \) and the applied normal load \( F_N \) define the coefficient of friction, often denoted \( \mu \).

\[
\mu = \frac{F_F}{F_N} = \frac{\tau A}{AH} = \frac{\tau}{H}
\]

Hence, what ultimately determines the friction is the lowest shear stress in the contact and the hardness \( H \) of the softest material determining the area \( A \).

1.1 Surface coatings in engineering

In modern engineering the need for high performance in mechanical, optical, magnetical, electrical and chemical systems etc. are usually provided by a coating composite. The primary properties are supplied by the coating while the substrate often only accounts for macroscopic load support. Well-known examples are thin (1–10 μm) nitride and carbide coatings such as TiN and TiC applied on metal cutting tools. The Nobel Prize in physics 2007 was rewarded to Albert Fert and Peter Grünberger for the discovery of Giant Magnetoresistance today used in thin films, which vastly improved the density of data memory storing. Yet another successful family of coatings is the diamond like carbon (DLC) which today is frequently applied to a variety of systems that benefit from low friction and low wear rates, such as sliding bearings, cam followers and computer hard drives. This thesis focuses on design, synthesis and evaluation of tribological coatings primarily aiming for low friction applications.

Friction and wear are not parameters that can be ascribed to single materials. They always represent a whole tribological system in which the material is only one of many components. Certain materials that frequently give low
friction in a variety of applications are often erroneously named low friction materials. Bearing this in mind the author often allows himself to use the same designation.

1.2 Research objectives

The initial aim of the thesis was to realize a design concept modeled by ab initio DFT calculations, in depositing coatings with dc magnetron sputtering. The deposited coatings were characterized for elemental composition, microstructure and mechanical properties to relate the inherent coating properties to the achieved tribological response.

The main objective was to design and deposit carbide and closely related nanocomposite coatings for low friction applications. This includes studies to increase the understanding of the deposited coatings mechanical and tribological properties in relation to their composition and microstructure.

1.3 Novel design concept for triboactive coatings

Carbide-based coatings are examples of frequently used hard and wear resistant low friction coatings [3]. A friction coefficient < 0.1 is often found in coatings with high content of amorphous carbon (a-C). The a-C forms a soft and lubricious matrix, surrounding hard wear resistant carbides. The coating hardness is usually reduced with increasing carbon fraction [3, 4]. According to the low friction concept of an easy-to-shear superficial layer on a hard substrate, the friction could be even lower by reducing the matrix fraction while simultaneously releasing carbon that segregates to the surface.

Stoichiometric carbide coatings without amorphous matrix are usually hard with strong bonds between metal and carbon. Hence, a release of carbon in a tribological contact involving such a coating is therefore difficult. The most stable transition metal carbide is TiC and the Ti-C bonds are hard to break, thus, a limited release of carbon is expected. However, for transition metals after group V in the periodic table, the bond strength to carbon decreases and the carbides becomes metastable [5]. These elements are weak carbide forming metals (WCF) and any bond to carbon is easily broken. With sufficient energy input the metastable carbide will decompose into an energetically more favourable state by releasing some of its carbon. Frictional heating occurs in the superficial surface layer and an easily sheared surface is created. Since the release of carbon is a response to the tribological contact without any additives, one might say that the coating is self-lubricating.
The tribological behavior of a considered material is dependent on a number of system properties such as contact geometry, properties of contacting materials, environment, temperature, contact pressure, sliding velocity, etc. Relevant properties influencing the friction and wear performance of coatings are the mechanical properties such as hardness, Young’s modulus and residual stress content, as well as thermal and chemical resistance. The surface roughness also has a strong influence, for hard coatings especially on friction and wear of the counter material.

Until now most research towards coatings for low friction and reduced wear have been concentrated to produce passive coatings in the sense that their properties do not change during use. In this thesis a new class of coating materials is explored. It has the potential to react to excessive tribological loading by adjusting its friction properties beneficially.

2.1 Mechanical properties

The mechanical properties are important factors for friction and wear resistance of coatings in all tribological applications. Unfortunately, nature provides a contradiction between hardness and ductility. These two properties have to be optimized for each coating application. However, an important exception confirms this contradiction; decreasing the grain size increases both hardness and ductility [6].

2.1.1 Hardness and Young’s modulus

The hardness of a material is a measure of its resistance to plastic deformation. Diamond being the hardest material today has a hardness of \( \approx 100 \) GPa. Coating materials can be classified into three coarse classes depending on their hardness, hard materials (20–40 GPa), superhard materials (40–80 GPa) and ultrahard materials (> 80 GPa) [7]. The coatings deposited during this thesis are in the upper range of the hard materials.

A crystalline material deforms through dislocation movements or twinning and grain boundary sliding. Through the Hall-Petch relation, the hardness can be tuned by controlling such mechanisms [6]. The hardness can e.g. be increased by decreasing the grain size, thereby hindering dislocation
movement. The hardness and ductility increase with decreasing grain size (or interlamellar spacing of multilayered coatings) down to \( \approx 10 \text{ nm} \) where a further decrease, for some materials, instead reduces the hardness and ductility due to a change in deformation mechanism [8]. With grains of \( \approx 5 \text{ nm} \) in size, dislocations can not form and movement along grain boundaries is hindered due to the lack of dislocation sources and slip planes. If these grains are embedded in an amorphous matrix separating the grains with 1–2 nm, i.e. a few atomic distances, this space is too small for relieving intrinsic stresses giving a high hardness, > 50 GPa [7, 9]. Amorphous materials can be hard but are usually very brittle since they cannot be deformed by dislocation glide nor twinning.

The Young’s modulus describes the resistance to elastic deformation, i.e. it reflects the atomic bond strength. The Young’s modulus may be changed by alloying, or by utilizing a composite concept. Materials with high hardness typically display high Young’s modulus [9], which implies that they are brittle. For a combined high hardness and toughness the material should have a typical grain size of about 5–50 nm and the matrix should be amorphous to restrict crack propagation. This has been shown for e.g. TiC grains embedded in matrix of a-C with a hardness of about 30 GPa and still allowing for about 40 % plastic deformation [10, 11].

Among the DLC coatings, the fraction of sp\(^3\) bonded carbon determines the mechanical properties. The higher the fraction the harder and more diamond like is the coating. Hydrogenated DLC coatings have sp\(^3\) bonds stabilized by hydrogen bonds. An increased fraction of hydrogen to carbon bonds decreases the fraction of the stronger carbon to carbon bonds and, as a consequence, influences the mechanical properties [7, 12].

### 2.1.2 Residual stresses

Coatings made by PVD most often display compressive residual stresses [13]. A certain level of compressive stress, 1–5 GPa, might be beneficial for the coating cohesion and performance by increasing the fatigue strength and resistance to tensile cracking. Too high compressive stress, 5–10 GPa or higher, can be cumbersome and increases the risk of coating spontaneous detachment [14].

The residual stress of PVD coatings are made up by one thermal and one intrinsic component which add up to the total residual stress [15]. The thermal stress originates from differences in thermal expansion between coating and substrate material. At the deposition temperature, the coating and substrate are in equilibrium. When cooling down from the deposition temperature, the difference in thermal expansion induces the thermal stresses.

The intrinsic stress occurs as a response to crystallographic defects built into the coating during deposition and is consequently closely related to the deposition parameters. At low deposition pressure or at a high negative sub-
strate bias, point-defects are introduced by an atomic peening mechanism were energetic ions and/or neutrals knock surface adatoms into interstitial sites. The coating would compensate for the corresponding volume increase by expansion if it had not been bonded to the substrate. Instead a plane state of compressive stresses is developed. Entrapped sputter gas atoms further increases the strain similarly [13, 16-20]. The total residual stress level is the sum of the thermal and intrinsic stresses as long as the total stress level is lower than the yield stress.

Above $T/T_m > 0.2$, where $T$ denotes the absolute deposition temperature and $T_m$ denotes the melting temperature, recovery and recrystallization yield intrinsic stress relaxation and limits the stress accumulation during coating deposition [16, 17]. The temperature of most PVD processes is below this level.

2.2 Tribological properties

2.2.1 Wear resistance

Wear resistance is not a material property; it depends on all the parameters that make up the tribological system in which the coating is only one component. For instance, it is usually sufficient that the hardness of the coating exceeds that of the counter material. For coatings, the adhesion to the substrate and the ability to comply with any substrate deformation may be the most important properties.

In many technical applications the counter material is hardened steel with a typical hardness below 10 GPa. However, most modern steels contain carbides and nitrides having a hardness exceeding this value by far. Since the coating usually is very thin microabrasion by these particles have to be considered, and the coating hardness should exceed the particle hardness.

In most technical applications of thin coatings a wear rate $<< 10^{-6}$ mm$^3$/Nm is required, which, for instance, means that a 1 μm coating loaded with 1 GPa would wear through after $>> 10^3$ m in dry sliding.

2.2.2 Thermal and chemical stability

On the microscale the thermal and chemical conditions in the tribological contact are very harsh. Typically the localised friction temperature may approach the melting temperature of the contacting material with the lowest $T_m$. Used in contacts against steel, these flash temperatures may even exceed 1000°C in dry sliding. Consequently, thermal and chemical stability are desired properties of tribological coatings. The most common unwanted chemical reaction for PVD coatings is oxidation.
2.3 Coatings for low friction applications

A typical friction coefficient in boundary lubricated contacts for many materials is about 0.1. This is also the typical level in dry sliding of systems using coatings such as DLC, MoS₂, WS₂ and diamond. In dry contacts, without lubricants, high demands on the wear resistance are also put on the coatings.

Coatings or solid lubricants that generate low friction in dry sliding often have a lamellar structure, or form a layered structure under tribological load. Examples are graphitic carbon and transition metal dichalcogenides like MoS₂ and WS₂ [21-24]. During use the lamellae arrange in parallel to the surface providing an easily sheared surface layer. However, MoS₂ and WS₂ suffer from being sensitive to humidity and oxidation, which limits their use considerably [23-26]. Another example of coatings generating low friction is made up by a matrix of DLC with embedded WS₂ particles [27].

The low friction properties of carbon coatings originate from a transformation from the initial sp³ bonded carbon in the coating to a surface layer of sp² bonded carbon. Carbon in the sp³ phase, as in diamond, has strong bonds to adjacent atoms. The sp² configuration has strong bonds within the same plane and weak bonds between the planes [14]. The sp² superficial layer is not only lubricious but also protects the counter surface from wear [4, 28]. Hence, the phase transformation described gives an example of an ideal system for reduction of friction and wear according to Eq. 1 above.

The mechanical and tribological properties of DLC coatings can be tuned by incorporation of a carbide forming metal [4, 29]. A nanocomposite microstructure is formed with carbides embedded in the DLC or a-C matrix [10]. Decreased friction coefficients and significantly decreased counter surface wear rates due to increased amounts of transfer layer have been reported. Also the mechanical properties could be increased with the addition of a metal while the coating wear rates increased when exceeding a certain metal content, depending on metal [4, 30].

2.4 The ultimate low friction coating

The present knowledge in coating properties and design for low friction application can be summarized as below.

- Optimized hardness to minimize the contact area and abrasive wear resistance
- Ability to provide a thin and easily sheared superficial layer
- Substrate and coating properties matched to enhance coating adhesion and compliance with substrate deformation
- Optimized residual compressive stresses for high cracking and fatigue resistance
- High thermal and chemical resistance to function in dry sliding
Coating design and deposition

Today there are powerful tools available for modeling important properties of selected material compositions. At the same time there are powerful tools for synthesizing and characterizing the suggested materials. Thus, an initial series of calculations might be useful as guidance for a subsequent deposition series in the development of novel coatings.

In theoretical studies of solids a complete description of an electron’s quantum mechanical behavior requires that the time-independent Schrödinger equation is solved. This is in practice impossible since the potential experienced from one electron is affected by the other electrons present in the solid. The many body-problem arises where wave functions are employed to describe the exchange interactions and correlations. This, however, rapidly becomes very complicated since it is necessary to describe the wave functions using about $10^{23}$ equations [31, 32].

In 1998 Kohn received the Nobel Prize in chemistry for his development of density functional theory. He had shown that there is a total-energy functional that exactly yields the ground state energy for an exact ground state electron density [33]. That means the many-body problem could be vastly simplified and the ground state is actually described by an equivalent set of one-electron equations. Hence, the electron density functional can be used to describe properties of the system ground state, its total energy and electron density distribution. It is thereby possible to calculate e.g. bond strengths, atomic arrangements at surfaces and interfaces, lattice parameters as well as electrical properties [31, 32].

In this context DFT was used for two purposes. The first to calculate the density of states (DOS) that describes the energy level distribution. In such a DOS plot overlapping well defined peaks below the Fermi level, where electrons are occupying the states, indicate strong hybridization, i.e. strong bonds as seen for TiC in Fig. 1. The second purpose was to obtain a charge density plot, which in real space illustrates the electron distribution, i.e. the location and directionality of bonds in a certain crystallographic plane, see inset in Fig. 1.
3.1 The theoretical basis for the coating design concept

The design concept of the novel tribologically active coatings developed in this thesis utilizes alloying of a binary carbide with a weak carbide forming (WCF) transition metal. WCF transition metals are those in period V or higher in the periodic table [5]. Calculations based on DFT predict alloying with a WCF metal will lower the stability of the carbide phase (Me-C bonds) relative to the amorphous carbon (C-C bonds). Despite this, it is desirable to deposit a coating in a mechanically stable carbide structure that changes character locally under tribological load. This implies that the coatings must be made metastable with an inherent driving force to form amorphous carbon. Such coatings can be produced e.g. by physical vapor deposition (PVD) under vacuum conditions at fairly low temperatures, where compositions far from a thermodynamic equilibrium can be created.

With energy transferred in a tribological contact, friction heating or mechanical stress, the material closest to the surface will rearrange and if possible decompose to obtain an energetically more favorable state. Since the diffusion rate of WCF metal is much lower than that of carbon, the latter is driven out from the carbide. The superficial carbon can transform into graphitic carbon, forming an easily sheared surface layer in the tribological contact. Some of the metal atoms in the contact are oxidized and worn off but the major part remains. Since the migration and transformation of carbon is a response to the tribological contact, one might say that the coating is self-lubricating.
Figure 2 schematically shows a comparison between a tribologically passive monocarbide coating, an as-deposited metastable coating and a corresponding tribologically activated coating. In this thesis, TiC being a common PVD coating and Al being a typical WCF was used.

![Comparison of coatings](image)

*Figure 2. Schematic illustrations of a) monocarbide, b) WCF-alloyed carbide and c) tribologically activated WCF-alloyed carbide coatings. (red–metal atom, black–carbon atom, yellow–WCF metal atom)*

### 3.2 Coating deposition

PVD is a versatile method for producing dense well adhering coatings aimed for low friction or wear resistance with thicknesses in the range 1–10 μm. It comprises several different deposition methods, which have in common that the source material is in a solid form. The source materials are brought into a vapor like state by arc evaporation, sputtering or by thermal heating. Thereby, it is possible to produce coatings of almost all materials at low temperatures, typically below 500°C. Since the composition can be easily tuned, PVD methods are well suited for experimental work, especially for deposition of metastable coatings. In this thesis, sputtering has been used.

Of great importance for a successful deposition is the removal of surface contaminants like grease or dust that might interfere with the coating adhesion. A thorough cleaning process of the substrates is therefore required.
3.3 Sputtering

In order to have as little coating impurities and unwanted reactions as possible, like oxidation, all deposition processes start out under vacuum conditions. After evacuation an inert gas, often argon, is leaked back into the chamber. An applied electric field, accelerates electrons towards the anode and inelastic collisions ionize the gas atoms and create more electrons and ions, a plasma is formed.

Sputtering needs a plasma to accelerate ions towards the source material (in sputtering called target). The ions strike the target and source material is ejected through the collisions. If their energy exceeds the targets binding energy, target atoms are ejected and secondary electrons are created, contributing to further gas ionization, see Fig. 3.

![Figure 3. Schematic illustration of sputtering with Ar⁺-ions.](image)

The sputtering rate can be greatly improved by the employment of a magnetron. A magnetic field is applied perpendicular to the electric field, forcing the secondary electrons emitted from the target surface to drift in a closed helical motion in front of the target, see Fig. 4. A magnetron thus increases the electron density and the probability for ionization of the gas atoms which in turn increases the target bombardment.

![Figure 4. The sputtering setup used in the thesis, with a circular and a rectangular magnetron. Illustrations after [34].](image)
Sputtering enables evaporation of almost any material irrespective of melt temperature. Composite targets can be used to evaporate several elements at the same time but the elemental composition has to be adjusted since the sputter yield varies between elements.

A delocalized plasma is used for both preheating and etch cleaning of substrates before the deposition starts as well as heating during coating growth. In cases where the gas atoms are not completely ionized, the atoms will end up in an excited state. As they go back to their ground state the excess energy from the de-excitation will be emitted as photons, which creates the characteristic glow from the plasma, as shown in Fig. 5.

![Figure 5. Substrates rotating over the magnetron through the plasma. Note the plasma being most intense close to the magnetron surface. Note also how the thermionic arc source (upper right) contributes to an increased ionization.](image)

Any object placed inside the plasma will be bombarded by both electrons and ions. By applying a negative or positive substrate bias, the type and extent of bombardment can be controlled. For example a high negative bias gives an intense ion bombardment during etch cleaning, which removes the native oxide on the substrate surface. A smaller negative substrate bias can be used to increase the surface mobility. This will however also increase the amount of introduced point defects such as surface adatoms being knocked into interstitial sites and/or sputter gas being entrapped. In contrast, a positive bias can be used to suppress the ion bombardment during the deposition. An auxiliary thermionic arc current can be employed to increase the amount of ions and electrons, i.e. to increase the plasma density.

Coating growth during deposition can to a large extent be resembled with boiling water on the stove. The vapor will condense on all colder surfaces in the vicinity. If the surface temperature is below 0°C, the water will freeze into a solid coating of ice. The same thing happens as the source material is evaporated, moves through the chamber and hits the substrate forming a solid coating.
3.4 Coatings deposition

In this thesis a Balzers BAI640R PVD coating system was employed for magnetron sputtering. Elemental targets of C and Ti both with purities of 99.995% were used. When depositing the Al containing coatings, the Ti-target and/or the C-target was partially covered with Al-foil of 99.0 % purity, fastened with conductive carbon based adhesive, a method developed by Nilsson et al. [35].

All substrates for mechanical characterization and tribological tests were made of powder metallurgical high speed steel (ASP, Erasteel Kloster AB designation) with a hardness of about 66–69 HRC [36]. The substrates were polished to a surface roughness $R_a$ 5–10 nm. Before coating deposition they were ultrasonically degreased for 5 minutes in an alkali solution (UPON [37]) heated to 60°C, rinsed in deionized water and ultrasonically cleaned in ethanol. The remaining surface contaminants were removed by 30 min pre-heating at the process temperature of 250–300°C and a short etching process with a -200 V substrate bias, which also removed any native oxide.

The base pressure was $2 \times 10^{-5}$ mbar and the deposition pressure was $3.5 \times 10^{-5}$ mbar. An initial Ti-interlayer, thermally evaporated, was deposited for increased adhesion. Magnetron co-sputtering of two targets was employed for 100 to 500 min with a substrate bias ranging from -110 to +50 V. The coating thicknesses ranged from 1 to 1.5 μm.
4 Coating growth

The coating microstructure and the composition are the most important variables determining the coating properties. The microstructure is dependent on deposition parameters in a complex way as will be described below.

4.1 Nucleation and growth

The coating grows through clustering of highly mobile, loosely bonded atoms, so called adatoms. The most stable cluster nucleates in islands on the substrate surface and as the growth continues the island density saturates. A coalescence phenomenon forms open surfaces where new nucleation sites occur. As the coalescence continues, a network of unfilled channels is formed in between the growing islands. With proceeding growth the channels are covered, sink in and shrink. As a consequence isolated voids will form. If the voids are filled completely during the growth process the coating becomes continuous [38]. In contrast, if the voids of some reason are not completely filled, they are built in as defects.

4.2 Structure zone models and diagrams

During island coalescence, less favorable energetic grains will be out-conquered and overgrown. The formation of columns is strongly dependent on for example temperature and pressure and the resulting microstructure can be described by so called Structure Zone Models (SZM) as first proposed by Movchan and Demchishin. Thornton developed this model for sputtering and illustrated the dependence on Ar-pressure and homologue temperature, i.e. the ratio of absolute substrate temperature T and the source material melting temperature T_m in Structure Zone Diagrams (SZD), see Fig. 6a [16, 39]. In zone 1, T/T_m < 0.3, the mobility of adatoms is low due to low temperatures. Shadowing effects due to e.g. a rough substrate surface will give a columnar microstructure with dome-capped columns separated by open boundaries, resulting in poor mechanical properties. In zone 2, 0.3 < T/T_m < 0.5, the higher temperature increases the adatom mobility giving increased surface and grain boundary diffusion and a dense columnar structure is formed. Zone T is a transition zone in between zone 1 and 2 with
a dense array of fibrous grains. Zone 3, $T/T_m > 0.5$, is characterized by bulk diffusion, i.e. recrystallization and grain growth. The coating consists of equiaxed grains or columns.

A decreased deposition pressure increases the mean free path and increases the energetic particle bombardment. Additional nucleation sites are formed and consequently the structure becomes denser. An increased ion bombardment can produce microstructures otherwise only attainable for higher $T/T_m$ ratios. The revised SZD by Messier [40], in Fig. 6b, illustrates the effect from employing a substrate bias with preserved Ar-pressure. An increased substrate bias increases the ion bombardment, i.e. a similar effect as expected from a decrease in pressure.

**Figure 6.** Structure zone diagrams of coating growth during sputtering. a) the original SZD proposed by Thornton [16], b) the revised SZD proposed by Messier [40].

The SZD can be used to interpret the growth mechanisms. Hence, it might be a useful tool in the design of new coatings since it provides a prediction of the resulting microstructure for a certain set of deposition parameters.

### 4.3 Effects from ion bombardment

Ion bombardment provides more than the increased adatom mobility above. It also affects the surface topography, introduces defects and stresses and changes the grain size and morphology.

#### 4.3.1 Surface topography

An increased ion bombardment can have a smoothening effect on the coating surface. This is due to, e.g. filling of surface depressions and taking off edges. Most affected are surface atoms loosely bound to the coating or at exposed positions. The process is called resputtering and the atoms often land nearby the initial site and smoothen the surface on an atomic level [38].
4.3.2 Defects and stresses

The net defect density most often increases with increased ion-energy. However, since increased energetic bombardment also increases the surface mobility, there is usually a competition between defect creation and healing. Entrapment of sputter gas atoms in the growing coating due to the extensive rate of impinging ions, gives a compressive stress contribution. Implantation of energetic backscattered neutrals and forward sputtered adatoms at interstitial sites often cause a lattice parameter expansion and contribute to a compressive residual stress level [19, 38].

4.3.3 Grain size and morphology

The increased bombardment also favors forward sputtering of coating adatoms into the boundary void regions [38, 41]. The filling of voids contributes to a denser structure. Impurities like incorporated gas atoms and/or precipitates can segregate to grain boundaries. These locally pin the grain boundary, and hinder grain boundary migration and prevent further grain growth [38].
5 Coating characterization

There are a large number of different methods for characterization of material and coating properties. To obtain the best possible information, it is essential to use the right set of experiments and to use the proper equipment. The instruments and the methods used throughout this thesis to probe different properties of the coatings are shortly described below. The headers include references in Roman numbers to the papers in which they are used.

5.1 Composition, microstructure and phases

X-ray Diffraction – XRD

A Philips X’Pert X-ray diffractometer with a Cu Kα X-ray source was employed for determination of phase compositions and grain sizes. Grazing incidence (GI) scans with 0.5° angle of incidence were used to maximize the diffraction volume and suppress the substrate influence. The Scherrer equation was employed to estimate the crystallite sizes from full width half maximum values [42]. Coating texture was investigated using θ-2θ-scans where crystallographic planes parallel to the sample surface, fulfilling Bragg’s law of diffraction, gave diffraction peaks with an intensity distribution that revealed information on any preferential growth direction.

X-ray Photoelectron Spectroscopy – XPS

A PHI Quantum 2000 was used for analyses of the chemical state and the elemental composition of coatings, wear tracks and tribofilms. The samples are irradiated by monochromatic Al Kα X-rays, which excite core electrons by the photoelectric effect. A detector collects the ejected photoelectrons and a spectrometer determines their energies. The measured energy, i.e. the difference between X-ray energy and the kinetic energy of the photoelectron represents the energy required to release the electron which constitutes an elemental fingerprint. When two atoms bond together, the electron distribution changes, i.e. the electron binding energies of an atom depend on how the atom is bonded to other atoms. This enables identification of which elements have bonded to each other. Depth profiling is performed via alternating analysis and material removal by sputtering using Ar⁺-ions. The information depth is about 50 Å and the spot size can be varied between 10–50 μm, which comfortably enables analysis of features like coating wear tracks and
transfer layers. XPS C1s spectra from a TiC coating, a wear track and a corresponding transfer layer on the counter surface with peaks revealing bonds to both C and Ti are shown in Fig. 7.

Figure 7. XPS C1s spectra obtained from a TiC coating, coating wear track and the transfer layer on the counter surface.

Scanning Electron Microscopy – SEM I-VI
A Leo 1550 SEM with a FEG and an in-lens secondary electron detector was used for measurement of coating thickness, microstructure investigation of fractured cross-sections and for investigation of transfer layers, Fig. 8a. A LEO 440 SEM with a LaB6-filament was employed for characterization of coatings after scratch testing and for elemental analysis of coatings using an attached unit for Energy Dispersive X-Ray Spectroscopy (EDS). This complements XPS as the analysis area in EDS is much smaller, roughly 1 μm.

Focused Ion Beam – FIB II-IV
The FEI Strata DB235 dual beam instrument combines an SEM and a Focused Ion Beam (FIB). The ion beam can be used for imaging in resemblance with an SEM as there are detectors available for collecting both ions and electrons. What distinguishes ion imaging from ordinary SEM is the surface interaction where the ions are capable of penetrating the surface. The penetration varies between grains, providing crystallographic contrast. Ion imaging is however accompanied by material removal already at low ion beam currents. By increasing the ion energy, ion milling commences and depth profiling and sample cross-sectioning is possible. This was used for investigation of changes in the microstructure within steel ball counter surfaces used in the tribotests.

The FIB also enables sample preparation for Transmission Electron Microscopy (TEM) from specific regions of interest such as transfer layers on
counter surfaces, as shown in Fig. 8a. The TEM sample preparation using the FIB starts with deposition of a Pt layer to protect the region of interest. The ions are used to dig into the material, at the end leaving a sample disc below the Pt layer. The sample is cut free on the sides and in the bottom, see Fig. 8b. The sample is picked up and mounted onto a TEM grid and further ion beam polished to a thickness of approximately 100 nm. It is thereby ready for analysis in the TEM. Samples for TEM analysis were produced from both coating wear tracks and counter surface transfer layers.

**Transmission Electron Microscopy – TEM**

Microstructure investigations of coating cross-sections as well as cross-sections from transfer layers/tribofilms were performed using a FEI Tecnai F30 ST High Resolution TEM (HR-TEM) as exemplified in Fig. 8c. Energy Filtered TEM (EF-TEM) and Scanning TEM (STEM) for EDS analysis were employed for cross-section overviews with atomic contrast and for investigation of elemental composition at high resolution, respectively. As the analysis area in TEM EDX is about 10 nm this technique is vastly superior to XPS and EDS for high resolution elemental analysis.

![Figure 8. a) SEM image of a transfer layer tribofilm on the counter surface steel ball after a tribotest, with region of interest marked. b) FIB milling of the marked region, and the cut free sample. c) Cross-section TEM image of the steel ball tribofilm.](image)

**Raman Spectroscopy**

A Renishaw Micro-Raman system equipped with a green laser (514.5 nm) and a notch filter for suppression of the incident laser light was employed for revealing the carbon and oxide types in as-deposited coatings, wear tracks, counter surface transfer layers/tribofilms and oxides formed at elevated temperatures.

The spot size is approximately 1 μm and the incident photons stimulate different molecular vibrational states. This causes inelastic scattering of photons resulting in a gain or loss in energy, a Raman shift, depending on the initial molecular state.
Figure 9 shows the Raman spectrum after a tribotest with TiC. Two peaks originate from the TiO$_2$ phase (rutile) denoted R. Carbon have two significant Raman active modes corresponding to disordered graphite (D) around 1350 cm$^{-1}$ and graphite (G) around 1580 cm$^{-1}$ respectively. Peak positions and widths are affected by e.g. bond disorder and clustering, [14, 43, 44].

![Raman spectrum of TiC coating after tribotest showing carbon with graphite (G) and disordered graphite (D) peaks and TiO$_2$ (R) peaks.](image)

**Figure 9.** Raman spectrum of TiC coating after tribotest showing carbon with graphite (G) and disordered graphite (D) peaks and TiO$_2$ (R) peaks.

### 5.2 Mechanical properties

**Nanoindentation**

The coating hardness $H$ and Young’s modulus $E$ were evaluated by nanoindentation employing a Nanoindenter XP equipped with a three-sided pyramidal Berkovich diamond tip with a tip radius of 200 nm. The material hardness is the material’s resistance to plastic deformation due to an applied peak load $P$ and the projected load carrying area $A$

$$H = \frac{P_{\text{max}}}{A}$$  \hspace{1cm} (2)

The indentation depth must not exceed 1/10 of the coating thickness to avoid influence from the underlying substrate. Hence, thin coatings require very shallow indent depths and the residual indent geometry is hard to investigate, even in an SEM, for measurements of the area $A$. In here lies the strength of the nanoindentation technique in that it does not rely on microscopic observations. The load $P$ and indent depth $h$ are continuously measured, as illustrated by the load-displacement plot in Fig. 10, showing a complete loading – unloading sequence.
Figure 10. A load-displacement plot as obtained from nanoindentation, after [45].

The area $A$ is calculated by inserting the contact depth $h$ into a tip area function $A = F(h)$. From Eq. 2, $H$ can then be obtained at maximum indent depth $h_{\text{max}}$ and $E$ can be obtained from the stiffness $S$ i.e. the initial slope of the unloading curve, in accordance with Oliver and Pharr [45].

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

(3)

**Scratch testing**
A CSM Revetester equipped with a Rockwell C diamond stylus with a tip radius of 200 μm was employed for scratch testing. The diamond stylus was slid over the coating surface at a constant velocity of 10 mm/min and under a load continuously increasing at a rate of 100 N/min. The SEM was used for characterization of the scratches, where the presence of cracks, substrate exposure and plastic deformation provide information on e.g. fracture mechanisms and coating adhesion [46].

**Residual stress**
Residual stress analyses were performed using two different methods. The first, based on XRD, measures the strain in a specific crystallographic orientation in a coating for various $\psi$-angles. Figure 11 schematically shows how the $\psi$ angle relates to the more commonly encountered angle in XRD, the $\theta$ angle.
Figure 11. XRD set-up for residual stress measurements [47].

The sample is tilted to different $\psi$-angles for which a detector scan in $\theta$ is performed. If a bi-axial stress tensor is assumed the strain is related to the angle $\psi$ according to

$$\varepsilon_\psi = \frac{d_\psi - d_0}{d_0} = \frac{1 + \nu}{E} \sigma \sin^2 \psi - \frac{2\nu}{E} \sigma$$

where $\sigma$ is the stress component in the plane of the coating, with Young’s modulus $E$ and Poisson’s ratio $\nu$, that gives the measured strain $\varepsilon$, i.e. the change in cell parameter or lattice d-spacing along the surface normal. The unstressed lattice spacing $d_0$ is calculated for $\psi = 0$. The method is consequently called the $\sin^2 \psi$-method [47].

The second method used is the plate deflection technique [48]. A coated sample roughly 5×5 mm$^2$ in size, was cut out and ground and polished from the backside to reach a coating to substrate thickness ratio of approximately 1/100. The curvature of the coated surface was subsequently measured using light interference microscopy, WYKO NT-1100, and applying the well known Stoney equation

$$\sigma_c = \frac{E_s t_s^2}{6r(1-\nu_s)t_c}$$

where $\sigma_c$ is the residual stress in a coating of thickness $t_c$, $r$ is the radius of curvature of the deflected sample and $t_s$ is the thickness of the substrate with Young’s modulus $E_s$ and Poisson’s ratio $\nu_s$ [49].
5.3 Tribological properties

The tribological properties were evaluated in a simple but versatile ball-on-disc test. A coated disc is rotating at a continuous velocity in contact with a ball pressed against the disc by a normal load $F_N$, see Fig. 12. The resulting tangential friction force $F_F$, is measured and the friction coefficient is given by the ratio $F_F/F_N$. Steel balls were used as steel is a very common counter surface to low-friction coatings. A normal load of 5 N and a ball diameter of 6 mm were used, resulting in a Hertzian contact pressure of about 1 GPa. This was higher than for typical mechanical contacts, at the order of a few MPa, i.e. the test was more severe than that of a real case.

![Figure 12. Schematic illustration of the ball-on-disc test setup.](image)
6 Contributions

6.1 The new low-friction concept
Coating design, evaluation and verification
(Paper I-III)

Aim
The aim was to realize a design concept modeled by ab initio DFT calculations, by depositing coatings with DC magnetron sputtering and to verify the design concept by tribological testing and material analysis.

The concept is based on substituting some Ti with Al in TiC to destabilize the carbide phase and furnish an inherent ability to form graphite in tribological contacts, as described in Ch. 3.1.

Experimental
DFT calculations were employed for predicting how the substitution of Ti with Al will affect the type of chemical bonds and to estimate the compositions required for graphite formation. It was found that the prerequisites for a spontaneous formation of graphite were fulfilled for an Al content exceeding 12.5 at%. Four test coatings, see Fig. 13, were deposited by DC magnetron co-sputtering and characterized by XRD, XPS, Raman, SEM and TEM. Tribotests were performed in ambient environment in dry sliding with a loaded steel ball on a rotating coated disc.

Figure 13. Illustration of test coatings composition.

Two TiC coatings, one pure carbide and one with an excess of carbon were included. To form coating pairs for comparison, Al was added to substitute Ti in such a way that the C/Me ratio remained. An experimental comparison
between coating A and C indicates any positive effect of having an excess of carbon in conventional TiC coatings. Comparing A and B yield any effect from Al substitution. D alone shows any effect from combining excess of carbon and Al substitution.

**Results**

As predicted, coatings B and D give significantly lower friction than the corresponding coatings A and C. The combined effect of Al addition and carbon excess was outstanding, giving a smooth curve at a friction coefficient of about 0.05 in dry sliding, see Fig. 14. Note that carbon in excess alone seems to be detrimental for the friction behavior.

![Friction recordings from the ball-on-disc testing. Four coatings A–D (on the disc) with compositions given in Fig. 13.](image1)

**Figure 14.** Friction recordings from the ball-on-disc testing. Four coatings A–D (on the disc) with compositions given in Fig. 13.

To confirm that the low friction obtained for coating B was due to the predicted graphite formation, XPS and Raman analyses were performed on the wear tracks of coatings A and B in parallel, see Figs. 15 and 16, respectively.

![XPS analyses of the C1s peak from coating A, pure TiC (a) and coating B, TiAlC (b).](image2)

**Figure 15.** XPS analyses of the C1s peak from coating A, pure TiC (a) and coating B, TiAlC (b).
Comparing coatings A and B in dry sliding, significantly more carbon was released in the wear track for the coating with Al addition. Raman spectroscopy revealed that the released carbon was graphitic, see Fig. 16. The large difference in signal intensity between TiC and TiAlC reflects the much larger amount of graphite formed during wear of TiAlC.

Figure 16. Raman spectra of TiC (a) and TiAlC (b). D = disordered graphite and G = graphite.

The tribological contact of the ball-on-disc configuration is characterized by tribofilm formation. Both ball and disc were successively covered with thin layers of transformed coating material, see Figs. 17 and 18.

Figure 17. FIB cross-sections of the ball contact area of TiC (a) and TiAlC (b).
Note that the plastically deformed layer of the ball contact area, beneath the tribofilm, is much thinner for the TiAlC than for the TiC, indicating that much lower shear forces are associated to the corresponding lower friction, cp. Fig. 14.

In higher magnification the tribofilm of the ball tested against TiAlC reveals a relatively homogeneous material with thin amorphous carbon rich strokes, see Fig. 18.

Figure 18. a) TEM cross-section through the tribofilm on the ball tested against TiAlC. b) EDX scan between 1 and 2, along the line indicated in (a).

Tribofilms on balls tested against both TiC and TiAlC display similar structure. However, the tribofilms formed from TiC contained nanometer-sized carbide grains originating from the coating wear track, whereas the tribofilm from TiAlC was mainly composed of transformed coating material, see Fig. 19.

Figure 19. HR-TEM cross-sections of tribofilms on the ball tested against TiC (a) and TiAlC (b). The crystallite size is indicated in a). The brighter regions correspond to the carbon rich strokes.
Both tribofilms contained mainly graphitic carbon and some TiO₂, as indicated by XPS and Raman. The tribofilm on the ball run against TiC displayed a larger influence from Ti-C bonds in XPS and the presence of TiO₂ was more pronounced in Raman analyses, in comparison to the tribofilm on the ball run against TiAlC.

Main conclusions
A novel concept of designing low friction coatings, using Ti-Al-C coatings as a model system, has been explored.

- The hypothesis of substituting Ti with Al in TiC coatings to obtain a self lubricating effect proved to be valid.
- A significantly lower friction was recorded for the new coating materials. Friction coefficients of typically 0.05 were obtained in dry sliding, which is half the value usually obtained in boundary lubricated contacts. The explanation is that the tribological contact stimulates the formation of easily sheared tribofilms.
- The excellent tribofilms are formed by the mechanism postulated by DFT. The strong Me-C bonds become weaker with the addition of Al and carbon release is facilitated.

6.2 Tailoring the mechanical properties
Residual stresses, hardness and Young’s modulus
(Paper IV)

Aim
Unacceptably high compressive residual stresses were noticed for the PVD TiC coatings. On the other hand, with the Al containing coatings problems such as cracking and delamination were never experienced. This motivated further studies of the possibility to tailor the residual stress levels.

The aim was to explore the possibility to tailor the residual stresses and mechanical properties (hardness and Young’s modulus) of TiC by Al alloying and by changing the bias voltage during coating deposition with DC magnetron sputtering.

Experimental
Two test series of coatings were deposited by DC magnetron co-sputtering, see Table 1. The first series was pure TiC with varying bias, ranging from -110 V to +50 V. In the second series the bias was -50 V and the Al substitution was varied. In practice, floating potential corresponds to a bias voltage of about -5 V. The coatings were characterized by nanoindentation, XRD (GI, θ-2θ), XPS and SEM. The residual stresses were measured both by
XRD employing the \(\sin^2 \psi\)-method and by the sample deflection technique calculating the residual stress from the well known Stoney equation.

Table 1. Composition [at\%] from XPS and thickness [\(\mu\)m] of deposited coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Bias [V]</th>
<th>Ti</th>
<th>C</th>
<th>Al</th>
<th>O</th>
<th>C/Me</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-110</td>
<td>-110</td>
<td>61.8</td>
<td>36.7</td>
<td>0.0</td>
<td>1.5</td>
<td>0.59</td>
<td>1.02±0.05</td>
</tr>
<tr>
<td>TiC-50</td>
<td>-50</td>
<td>59.8</td>
<td>38.7</td>
<td>0.0</td>
<td>1.6</td>
<td>0.65</td>
<td>1.35±0.05</td>
</tr>
<tr>
<td>TiC0</td>
<td>floating</td>
<td>65.7</td>
<td>32.5</td>
<td>0.0</td>
<td>1.8</td>
<td>0.49</td>
<td>1.27±0.05</td>
</tr>
<tr>
<td>TiC+50</td>
<td>+50</td>
<td>62.6</td>
<td>34.5</td>
<td>0.0</td>
<td>2.9</td>
<td>0.55</td>
<td>1.25±0.05</td>
</tr>
<tr>
<td>TiAlC0</td>
<td>-50</td>
<td>59.8</td>
<td>38.7</td>
<td>0.0</td>
<td>1.6</td>
<td>0.65</td>
<td>1.35±0.05</td>
</tr>
<tr>
<td>TiAlC4</td>
<td>-50</td>
<td>53.7</td>
<td>41.5</td>
<td>3.7</td>
<td>1.1</td>
<td>0.72</td>
<td>1.20±0.05</td>
</tr>
<tr>
<td>TiAlC7</td>
<td>-50</td>
<td>51.2</td>
<td>40.6</td>
<td>7.2</td>
<td>1.0</td>
<td>0.70</td>
<td>1.31±0.05</td>
</tr>
<tr>
<td>TiAlC13</td>
<td>-50</td>
<td>49.2</td>
<td>36.8</td>
<td>13.0</td>
<td>1.1</td>
<td>0.59</td>
<td>1.26±0.05</td>
</tr>
<tr>
<td>TiAlC17</td>
<td>-50</td>
<td>42.6</td>
<td>37.8</td>
<td>17.2</td>
<td>2.4</td>
<td>0.63</td>
<td>1.32±0.05</td>
</tr>
</tbody>
</table>

Note that the TiC-50 is used also in the Al-series as a coating with 0 at\% Al, i.e. TiAlC0. The bias-series reveals any effect on the coating properties from varying the substrate bias and consequently the energetic ion-bombardment. The Al-series reveals any effect from increasing Al content with maintained substrate bias.

Results

All TiC coatings in the bias-series displayed a columnar microstructure with a grain size of 110–160 Å. When substituting some Ti with Al, the columnar microstructure was replaced by a fine granular structure, see Fig. 20. There was a drastic decrease in crystallite size with increasing Al-content, from about 160 Å for TiAlC0 to 30 Å for TiAlC17. All coatings were entirely carbidic, i.e. there were no indications of C-C bonds from the XPS analyses.
In the bias series, the residual stress level displayed a significant decrease when changing the bias polarity from negative to positive, Fig. 21a. For negative substrate bias, the stress level was found to be unacceptably high. For the TiAlC coatings, there was a gradual decrease in the stress level for increasing Al-content, Fig. 21b.

In comparing the two methods used for measuring the residual stress, a significant difference in absolute values was found. The trends were however similar and the effects from a change in bias or by Al-substitution, as measured by two completely different methods, were proved.

The change in bias polarity caused a drop in hardness and a significant decrease in Young’s modulus. The Al-series displayed a gradual decrease in both Young’s modulus and hardness with increased Al content, see Fig. 22.
In scratch testing, TiC coatings deposited with negative bias displayed compressive cracks that extended beyond the rim of the scratch. These cracks display characteristic inclined fracture surfaces associated with chip formation during crack growth. For floating potential the cracks never extended beyond the rim and for positive bias there were mainly tensile cracks in the scratch.

For the Al-series, which was deposited at -50 V bias, the compressive cracks decreased in length and number with addition of 4 at% Al. For 7 at% Al, there were additional tensile cracks, and with 13 and 17 at% Al, there were mainly tensile cracks and very limited chipping.

The highest critical load to first coating crack was provided by the TiC coating deposited at floating potential. The highest critical load to substrate exposure was displayed by the TiAlC coatings with the largest Al content.

Main conclusions
The possibility to tailor residual stresses by varying the substrate bias or by alloying with Al has been explored. Both investigated methods provided a possibility to change the residual stress levels. However, by varying the bias the change was more or less discrete when going from -50 V to floating potential, whereas the addition of Al provided a gradual change. Both methods also affect hardness and Young’s modulus.

- The gradual change in residual stress, by substituting Ti with Al, enables tailoring of the residual stress level.
- The gradual decrease in hardness and Young’s modulus for increasing Al addition enables tuning of the mechanical properties.
- No indications of amorphous carbon were found in any of the coatings. Hence, the decrease in hardness and Young’s modulus can not
be attributed to a softening amorphous carbon phase surrounding the crystallites. For a lowered bias the change is attributed to a less dense structure due to decreased ion bombardment and less filling of voids during coating deposition. With increasing Al content, and -50 V bias, the decrease is probably attributed to weakened intra- and intergranular bonds.

- The fact that no coating detached in connection with the compressive cracks in scratch testing indicates good adhesion.

6.3 Oxidation resistance
Influence by Al addition in TiC
(Paper V)

Aim
The aim was to investigate the influence on oxidation resistance by alloying TiC coatings with Al.

Experimental
One test series of TiAlC coatings were deposited by DC magnetron co-sputtering with increasing Al addition from 0 to 17 at% Al, see Table 1. The oxidation was performed in laboratory air in a temperature interval ranging from 300°C to 600°C. No temperature ramps were used and the oxidation time was set to 5 h for all samples. Small samples (5x5x4 mm³) were used to allow for rapid heating and cooling. Depth profiles were acquired with XPS and coating cross-sections were analyzed with FEG-SEM.

Results
With increasing Al content the onset temperature for oxidation increased from below 300°C for TiAlC0 to close to 400°C for TiAlC4 and about 450°C for coatings with higher Al content, as seen in Fig. 23.
One interesting observation was that TiAlC0 and TiAlC4 were less oxidized at 600°C than at 500°C. The explanation is a transition from the less dense anatase (3.89 g/cm³) to the denser rutile (4.25 g/cm³) above 500°C. Oxygen diffusion in rutile is obviously more difficult than in anatase.

The oxidized coatings displayed an increase in thickness, see Fig. 24. This was mainly due to a contribution from the oxide layer but a slight expansion was also noticed for the non-oxidized layer. The latter is probably associated to a relief in residual stress and possibly also to recrystallization.

Depth profiling by alternating XPS analysis and Ar⁺-sputtering for TiAlC17 oxidized at 400°C and 500°C, respectively, shows the increasing oxide depth, see Fig. 25. At 500°C, the depth profile revealed three compositional zones, indicated in Fig. 25b. These zones displayed different variations in composition as seen in the stacked XPS C1s and Ti2p spectra of Fig. 26.
In zone I, most carbon was removed as CO$_2$ (g) and the remnants formed C-Ti bonds, of the same type as the original coating material indicating the depth to which oxidation has not yet reached. In zone II, the formation of C-C bonds caused an asymmetric broadening towards higher binding energies in the C1s spectra stack, see Fig. 26a. Within each zone there are gradual shifts in the C-Ti binding energy, indicating that the oxide layer is not homogeneous. The Ti2p spectra displayed a change in bonds from a dominating contribution from TiO$_2$ in zone I, via an intermediate oxycarbide phase, TiO$_x$C$_y$ in zone II, to a dominating TiC phase corresponding to the original coating, see Fig. 26b. Throughout zone I and II, all Al was bonded in Al$_2$O$_3$ with no specific regions of enrichment or depletion.

Figure 26. Stacks of XPS C1s (a) and Ti2p spectra (b) from depth profiling of coatings heat treated at 500°C. The highest peaks represent the original coating material.
Main conclusions
This work shows that the addition of Al does not only affect the mechanical and tribological properties, but also provides increased oxidation resistance.

- The addition of Al increases the onset temperature for oxidation.
- Interestingly, the oxidation rate of TiAlC0 and TiAlC4 is lower at 600°C than at 500°C. The explanation is that the denser rutile dominates at the higher temperature.

6.4 TaC:C coatings with Al addition
Influence on friction, wear and oxidation resistance (Paper VI)

Aim
The aim was to investigate the influence on friction, wear and oxidation resistance by alloying TaC:C coatings with Al.

Experimental
A test series of TaC:C:Al coatings were deposited by DC magnetron co-sputtering with a constant Ta content of 15 at% and increasing Al content, from 0–12 at%, at the expense of carbon. The structure of as-deposited coatings was analyzed using XRD and the composition was determined with EDS. Tribotests were performed in ambient environment in dry sliding with a loaded steel ball pressed against a rotating coated disc. The oxidation tests were performed in laboratory air with heating of 5 °C/min to the maximum temperature, a holding time of 1 h at this temperature, and cooling down with 0.5 °C/min. The maximum temperatures were ranging from 300°C to 500°C. All samples were deposited on silicon wafers. Composition depth profiles were acquired with XPS and coating thickness and structure were obtained from cross-sections in FEG-SEM.

Results
TaC:C:Al coatings with addition of 6 at% Al yielded the lowest friction, close to 0.05. At 12 at% Al the friction became irregular, see Fig 27. The wear rate increased with increased addition of Al.
The coating hardness decreased from 17±1 GPa for pure TaC:C to 15±1 GPa for 12 at% Al. The Young’s modulus did not show any clear trend. All coatings displayed values of 210±5 GPa.

The oxidation tests revealed that the addition of Al did not affect the onset temperature but significantly decreased the oxidation rate, see Fig. 28. Note that the ramping time during heating and cooling also takes place in an oxidizing environment. A complex mixture of oxides and suboxides was found in both Ta4f and Al2p XPS analyses.

**Figure 27.** Friction recordings from the ball-on-disc testing.

**Figure 28.** Oxide thickness after oxidation obtained from fractured cross-sections in SEM.
Main conclusions

- All TaC:C:Al coatings displayed a friction level in dry sliding lower than typical levels of boundary lubricated contacts ($\mu \approx 0.1$).
- The lowest friction ($\mu \approx 0.05$) was obtained with 6 at% Al.
- The wear rate increased significantly for $\geq 6$ at% Al.
- The hardness and Young’s modulus were scarcely unaffected by addition of Al.
- The onset temperature for oxidation of the TaC:C coatings were not affected by addition of Al, but the oxidation rate decreased with increasing Al content.
7 Conclusive summary

This thesis presents a new ceramic coating material intended for mechanical components and tools. The coating provides extremely good low-friction properties ($\mu \approx 0.05$ in dry sliding against steel), while being hard and wear and oxidation resistant. The concept for achieving low-friction properties is the now classical: put a thin layer – providing low shear stress – on top of a hard surface – providing a small area of real contact.

The unique idea behind the present incarnation of this concept is that the superficial easy-shear layer is now automatically formed when the coated part is exposed to friction contact, and it is formed from the underlying coating by being ”sweated out” on the atomic scale. The development of the new coating has involved the complete chain from tribological concept, atomic scale theoretical calculations, synthesis by physical vapour deposition, analysis and microscopy using state of the art electron microscopy and spectroscopic techniques, and finally testing of the tribological properties.

- A triboactive system based on metastable, metal alloyed, TiC materials were suggested from theoretical calculations.
- One such system was realized by using PVD magnetron sputtering and deposit coatings similar to TiC but with some of the Ti substituted with Al.
- The predicted triboactive properties of the new TiAlC coatings were confirmed by tribological testing.
- A significant reduction in friction evolved for the TiAlC coatings compared to conventional TiC.
- The mechanism behind this phenomenon was a generation of an easily sheared graphitic tribolayer through release of carbon from the metastable TiAlC coating.
- Substituting TiC with Al also enables tailoring of the residual stress levels in TiAlC, maintaining hardness and Young’s modulus.
- The oxidation resistance is also improved by Al substituted in TiC and TaC:C.
The new coatings offer important advantages in many tribological systems, for instance, by reducing energy consumption, enabling removal of lubricants and lubrication systems, lowering the friction generated temperature in thermally sensitive applications etc. They also open up possibilities to design entirely new tribological systems and components for applications where lubricants never can be used, for instance in medical and food processing, in vacuum applications, electronic systems etc. At the same time, their high hardness will contribute to an overall high wear resistance.
Future outlook

The work performed for this thesis is restricted to a limited number of coatings. To apply the new concept and to optimize systems for more specific applications, coatings of different compositions and also other material systems have to be investigated.

No direct comparisons with state of the art coatings of today have been made. However, the test results suggest that the new triboactive coatings definitely perform at a competitive level.

Commercial competitors of today are coatings based on MoS$_2$ or DLC (diamond like carbon). They increasingly widen their areas of application, for instance in critical components of automotive engines, but also on tools for cutting and forming.

The new coatings have not been evaluated in lubricated contacts or in atmospheres free from oxygen or humidity. If a lubricant is to be used, the compositions might have to be changed to better adopt for the new contact situation and the new chemical environment.
Självsmörjning på atomär nivå

design, syntes och utvärdering av beläggningar

Den här avhandlingen beskriver ett nytt sätt att designa tunna funktionella skikt för applikationer där man vill åstadkomma låg friktion i tuffa kontaktsituationer, exempelvis i osmorda glidande kontakter.

När två kroppar pressas samman och utsätts för en relativ rörelse är det friktionen mellan de två kropparnas ytor som avgör hur mycket kraft som krävs för att åstadkomma en glidande rörelse. Denna kraft, kallad friktionskraften, motsvarar det arbete som krävs för att bryta (skjuva) de lokala bindingar som uppstår i kontaktfläckarna mellan de två ytorna. Friktionskraften bestäms alltså av kontaktarea och skjuvmutståndet i gränsytan mellan kropparna och friktionen är kvoten mellan friktionskraft och normalkraft.

För att nå riktigt låg friktion krävs med andra ord en liten kontaktarea och ett lågt skjuvmutstånd. Det mjukaste materialet i systemet bestämmer kontaktareans storlek och det mest lätt skjuvade materialet i kontakten bestämmer skjuvmutståndet.

Ett sätt att åstadkomma låg friktion är att ytbelägga en av de ingående komponenterna i kontakten med ett tunt lätt skjuvat skikt, ca. 1–10 μm tjockt, vilket kan jämföras med tjockleken av ett hårstrå som vanligen är kring 100 μm. Komponentens mekaniska egenskaper bestämmer kontaktnivean, och det tunna skiktet bestämmer ytans egenskaper. Problemet med lätt skjuvade skikt är att de ofta är mjuka och därmed riskerar att repas och förbrukas fort, varpå dess funktion upphör. Härda skikt kan ge problem med slitage av den obelagda motytan vilket också kan ge hög friktion.

Denna avhandling går ut på att med nytänkande design framställa och karakterisera tunna skikt med en tjocklek om ca. 1 μm. Skiktet är kolbaserade och består av titan (Ti) och kol (C) vilka tillsammans bildar så kallad titankarbid (TiC). Karbider av denna typ karakteriseras av mycket starka bindingar mellan de ingående elementen vilket medför en hög smälttemperaturen (>3000°C) som ger termisk stabilitet och en hög hårdhet (fyra gånger högre än stål) som ger nöttingsbeständighet. För skikt med överskott av kol omges de hårdare karbidpartiklarna av en mjuk kolmatris. I en glidande kontakt bildar kolet en lätt skjuvad så kallad tribofilm mellan ytor vilket ger goda förutsättningar för låg friktion. En kolmatris medför emellertid oftast
en försämring av de mekaniska egenskaperna hos skiktet och dessutom blir skiktens känsliga för oxidation.

Genom att istället utgå från en karbid där ingen kolmatris bildats och byta ut en del av titanatomerna mot t.ex. aluminiumatomer (Al) bildas en så kallad metastabil fas, TiAlC utan kolmatris, se figur 29 a-b. Detta skikt har i stort sett bibehållna mekaniska egenskaper. Bindningarna i skiktet försvagas något av aluminiumatomer, precis så mycket att den metastabila fasen omvandlas, med hjälp av den energi som tillförlts i form av friktionsvärme och mekaniskt arbete, i exempelvis en glidande kontakt mot en belagd stålkula. Omvandlingen frigör kol och eftersom energitillförseln är lokal och ytnära tar sig det fria kolet lätt ut till ytterytan. Ovanpå det hårdskikt bildas ett tunt, tribologiskt genererat lättskjutat kolskikt, dvs. skiktet är självmörjande, vilket åskådliggörs schematiskt av kulmodellen i figur 29c.

![Figur 29. Schematisk illustration av a) ett rent karbidskikt, b) ett legerat karbidskikt före test och c) efter test då kol bildat ett tunt yttskikt. (röd – Ti-atom, svart – C-atom, gul – Al-atom)](image)

Ett tunt lättsskjuvat skikt ovanpå ett hårt basmaterial utgör grunden för den ideala lågfriktionskontakten. I detta arbete har TiAlC-skikt tillverkats, vilka har goda mekaniska egenskaper samt ger låg nötning och låg friktion mot stål, ungefär hälften så hög friktion som en smord kontakt med två stålytor.

Det finns flera sätt att framställa dessa skikt. I detta arbete har en beläggningsmetod kallad physical vapor deposition (PVD), närmare bestämt sputtering, använts. Fritt översatt till svenska blir det fysisk ångfasdeponering och går till enligt följande; proverna placeras i en vakuumkammare där en ädelgas t.ex. argon (Ar) läcks in. En pålagd potential mellan anod (positiv) och katod (negativ), där katoden utgörs av beläggningsmaterialet, joniserar argongasen och ett plasma bildas. I plasmat finns bl.a. positivt laddade argonjonter vilka accelereras mot katoden, kallad target. När jonerna slår in i targe- ten frigörs beläggningsmaterial likt en sprängning i biljard, detta kallas sputtering. Det frigjorda materialet transporteras genom kammaren och kondenserar, likt vattenånga som kondenserar på en kallare yta, på alla omkringliggande ytor inklusive den komponent som ska beläggas, kallad substrat, se Fig. 30.
Allt som är placerat i plasmat utsätts för större eller mindre bombardemang av elektroner och joner beroende på dess polaritet. Med en negativ potential på substraten erhålls t.ex. ett jonbombardemang. Detta ger ofta ökad skikt-täthet men ökar också mängden inbyggda defekter i form av t.ex. inneslutna argonatomer och ytatomer som krockats in på felaktiga platser. Dessa fakto-
rer kan medföra höga kompressiva spänningar i skiktet, dvs. skiktet vill exp-
pandera och skulle, om det var möjligt, kröka substratet med skiktet på den
konvexa sidan. Till viss del kan sådana spänningar vara bra då de ökar skik-
tets mekaniska egenskaper, nötningsmotstånd och motstånd mot böjsprickor
vid töjning samt bromsar bildandet av ytsprickor. Alltför höga spänningar
kan dock leda till att skiktet flagar av spontant.

Genom att minska jonbombardemanget kan spänningarna reduceras, men
samtidigt sänks också t.ex. skiktens hårdhet och elasticitetsmodul. Med bi-
behållet jonbombardemang och inblandning av aluminium i TiC-skikten kan
den kompressiva spänningen styras, utan att sänka hårdheten och elasticit-
tetsmodulen nämnvärt. Detta medför också en möjlighet att anpassa skiktets
mekaniska egenskaper t.ex. efter substratet. Kolbaserade skikt lider ofta av
att kolet lätt oxiderar och lämnar skiktet i gasfas. Med tillsats av aluminium
till skikt av TiC och TaC:C sänks oxidationstakten markant. Dessutom höjs
också temperaturen vid vilken oxidationen startar.

Sammanfattningsvis, i jämförelse med ren TiC uppvisar de TiAlC-skikt
som tillverkats i detta avhandlingsarbete lägre friktion, möjlighet att styra
restspänningar med bibehållna mekaniska egenskaper, reducerad oxidation-
takt och förhöjd starttemperatur för oxidation.
Acknowledgements

This work has been carried out at the Tribomaterials group, Ångström Laboratory, Uppsala University.

The Swedish Research Council (VR) and Swedish Governmental Agency for Innovation Systems (Vinnova). The Strategic Research Centre for Materials Science for Nanoscale Surface Engineering (MS2E) funded by The Swedish Foundation for Strategic Research (SSF) are gratefully acknowledged for their financial support.

Erasteel Kloster AB is gratefully acknowledged for providing substrate materials.

Thank you Sture and Staffan, my professors, for introducing me to the world of tribology, for your encouragement and for the never ending suggestions on what to do next and especially the “last minute” improvements…

Thank you Urban, my supervisor, for your support, inspiration and for all the late hours of work during the last months. It has been quite a productive time, but next time I think we can start writing the papers a little bit earlier…

Ola, thank you for being the best colleague imaginable and for being the most inspiring team mate, always guiding me when I’m lost (in the forest with no map or compass). Piff&Puff rule!

Åsa and Frida, thank you very much for your enthusiastic proofreading.

Thank you Ulf and Erik, for adding chemistry-thinking to the world of low-friction and for your guidance in the chemical analysis.

Janne, Rein and Fredric, thank you for keeping the analysis equipment running. Without you, the lab would not be close to as competitive as today.

Anja, Caroline and Carin, thank you for keeping this place together, and all the scientists on the right track, at least most of the time.

Thank you all present and past colleagues at the Materials Science department for all nice “sofa-time”, Mombasa nights and travelling, I have had so much fun together with you guys.

Last but definitely not least I would like to thank my family for their support and love. And most of all, Anna, with you by my side everything is possible. I could not have made this without you. Your never ending love and support keep me up and running, I cannot live without you!

Uppsala, January 2008

/Mattias


37. Upon 5800, Henkel, Batch no: SW70324994.


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)