Optical Monitoring and X-Ray Absorption Spectroscopy for Studies of Wear on Thin Films

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København d 17. december 2010
Abstract

This thesis is a study on thin films and coatings, some of which are of hard ceramic materials such as titanium nitride (TiN), titanium aluminum nitride (TiAlN) and chromium nitride (CrN) and some of which are of optical materials such as titanium dioxide (TiO$_2$). The films and coatings have been studied extensively in various ways ranging all the way from initial film nucleation and growth mode studies over both individual and combined wear and optical characterizations to real-time dynamical wear process experiments and possible chemical phase change detections.

Thin films of TiN and TiO$_2$ were studied with respect to the initial film nucleation and growth mode by in-situ RHEED monitoring, whereas films and coatings of TiO$_2$, TiN and TiAlN were studied by combined tribo-optical means to verify a proposed optical wear monitor system consisting of hard protective coatings with embedded nano-layers of optical signal materials. Changes in the optical reflections from a simple laser pointer are observed when the wear process reaches the embedded signal layer in the optical monitor (much like eating a layer cake from above - once you reach the layer of strawberry jam, you know that you are half way through the cake). Moreover, the dynamical wear process of hard TiAlN and CrN multi-layer coatings with an embedded CrN wear-marker layer is studied in real-time X-ray absorption spectroscopy and transmission experiments by means of specific synchrotron radiation.
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Ultra slidstærke belægninger, også kendt som tribologiske coatings, af keramiske materialer som titannitrid (TiN), titanalamuminiumnitrid (TiAlN) og kromnitrid (CrN) deponeres ofte på forskellige industrielle maskindele for at minimere det mekaniske slid, der ellers kan ødelægge eller deformere delene som følge af de mange gentagne slidbelastninger. Det slidstærke lag vil på et tidspunkt ligeledes blive slidt igennem, hvorved beskadigelser igen kan opstå med mindre delene overfladebehandles på ny.

Med et fjernbetjent optisk sensorsystem, bestående af slidstærke coatings med indlejredesignallag af optiske materialer valgt således at refleksionen fra en laser ændres når coatingen er slidt igennem til signallaget, vil gennemslidning af de tribologiske coatings kunne observeres. Den optiske sensor kan i princippet sammenlignes med at spise et stykke lagkage fra oven; når man er kommet ned til laget med jordbærsyltetøj ved man, at man er halvvejs igennem lagkagen.

Indlejret tyndfilm vil muligvis svække den slidstærke coating. Det er derfor vigtigt at undersøge om slidprocessen henover kontaktfladen mellem de to materialer i den tribologiske film påvirkes. Mekaniske tribometerstudier kan afsløre filmens tribologiske egenskaber, mens den specifikke Røntgen absorption studeret under slidprocessen kan afsløre dynamiske egenskaber i selve slidprocessen.

Keramiske nitrid film til industrielle formål fremstilles ofte ved fysisk fordampningsdeponering (PVD), mens pulset laser deponering (PLD) er en forholdsvis ny teknik til disse materialer. PLD er en meget fleksibel teknik, hvor parametre som den stokiometriske og kemiske komposition og især filmtykkelsen kan kontrolleres, hvorimod tribologiske film sædvanligvis fremstilles bedst med PVD.

Preface

The work for this thesis has been carried out in connection with both experimental and theoretical work performed mainly at DTU Fotonik, Risø Campus (initially a part of the former Optics and Plasma Research Department, Risø National Laboratory), Technical University of Denmark, while being enrolled as a Ph.D student in physics at the Niels Bohr Institute, Faculty of Science, University of Copenhagen. A significant part of the wear tests were performed at Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, in France with guidance from Matthieu Guibert and Michel Belin and the X-ray absorption experiments at the European Synchrotron Radiation Facility in Grenoble, France by the management of beamline scientist Cornelius Strohm, while the work leading to this thesis was supervised by Dr. Jørgen Schou, senior scientist and group leader at DTU Fotonik and Professor in nanophysics Robert Feidenhans’l, Niels Bohr Institute, University of Copenhagen. This study has been supported by the Danish Strategic Research Council with the NABIIT grant 2106-05-0035 (09-060711/DSF).

A list of publications is presented below, where the initial papers [1–5] have been reviewed and already published. The paper on the results from the European Synchrotron Radiation Facility [6] is in progress and will be submitted for review shortly. The final paper [7] was published in DOPS-Nyt [8], which is the Journal of the Danish Optical Society with ‘The purpose ... to provide a common forum for all optics professionals in Denmark where news about the rapidly growing optics industry as well as scientific results can be communicated’.

The author of this thesis would like to thank the main supervisors Jørgen Schou and Robert Feidenhans’l for great enthusiastic help and support during these studies, but also the other participants on this NABIIT project; Senior Scientist Henrik C Pedersen from DTU Fotonik, Head of Programme Nini Pryds from Risø DTU, Professeur Jean-Michel Martin from LTDS, Research and Development Manager Niels Jørgen Mikkelsen from CemeCon Scandinavia A/S and in particular Ingénieur d’Etude Matthieu Guibert and Ingénieur de Recherche Michel Belin from LTDS and Tine Straasø from University of Copenhagen for essential assistance.

Moreover, technical and scientific assistance from different members of the staff at Risø DTU National Laboratory for Sustainable Energy; Jørgen Stubager, Finn Saxild, Jørgen Geyti, Ove Rasmussen, Katarzyna Rodrigo, Karl Thydén and Jacob Bowen has been an important help and the rest of the former LSO-group made my time at Risø really ‘hyggelig’. Special thanks should also be placed to Maria, Kreuff, Loa-Lårbassen and Sune for vital support and assistance.

Inge L Rasmussen
December 2010
List of Publications

Journal Paper Refereed


In progress


Journal Paper Not Refereed


Conference Contributions

- Wear control of tribological hard coatings with embedded optical nano-layers (poster), The Danish Physical Society Annual Meeting, Nyborg, Denmark, 2006

- Optical Control of Tribological Nanothinfilm. A Wear Sensor (poster), The Danish Optical Society Annual Meeting, Lyngby, 2006

• Wear of Titanium Nitrides in Tribological Hard Coatings Studied by Optical Monitoring (poster), 34th Leeds-Lyon Symposium on Tribology, Lyon, France 2007

• Optical In-situ Monitoring of Wear (oral), Summer school in connection with the 34th Leeds-Lyon Symposium on Tribology, Lyon, France 2007

• A Tribological Study of Titanium Nitrides with Synchrotron Radiation (poster), NorWip Nordic Meeting for Women in Physics, Lyngby, Denmark, 2007∗

• Reflectance Measured from Worn and Unworn Surfaces of Titanium Compounds (poster), The Danish Optical Society Annual Meeting, Nyborg, Denmark, 2008

• RHEED Study of Titanium Dioxide Using Pulsed Laser Deposition (poster), European Materials Research Society Spring Meeting, Strasbourg, France, 2008

• Pulsed Laser Deposition of TiO on MgO Studied by RHEED (poster), Danish Physical Society Annual Meeting, Nyborg, Denmark 2008

• Reflection Spectrometry of Virgin and Worn Titanium Compounds Surfaces (poster), Joint Workshop of Physical & Chemical Graduate School Göttingen and Dahlem Research School of Molecular Science, Berlin, Germany, 2008


• Dynamic Study of a Sliding Interface Wear Process of TiAlN and CrN Multi-Layers by X-ray Absorption (oral), 1st Common Meeting of the Nordic Physical Societies, Lyngby, Denmark 2009

∗Awarded with Poster Prize.

Material from paper [1] is discussed in the film characterization chapter (sections 10.2 and 10.3) but also in the wear chapter (in section 11.3) and material from papers [2, 3] is presented in section 10.4 of the film characterization chapter. Moreover, material from [4] is presented in different parts of the wear chapter (sections 11.1 and 11.4), where material from the corresponding paper [5] is discussed in sections 11.5 and 11.6 and material from paper [6] is presented in chapter 12 of the dynamical wear process studies. Finally, basic ideas from paper [7] is discussed in theoretically specular reflections optics chapter in section 4.3.
Part I

INTRODUCTION
Chapter 1

Introduction

Hard films of ceramic nitride such as titanium nitride (TiN), titanium aluminum nitride (TiAlN) and chromium nitride (CrN) are frequently used, due to the materials high wear resistance, as protective coatings of industrial steel tools in order to increase the tool durability [9–12]. Nonetheless, these protective coatings will eventually wear off and as a result the coated steel tool potentially damaged [13]. Consequently, an existing request for a wear monitoring solution, which may warn an industrial production operator before the tribological coating wears out and the steel tool severely damages, is met in the NABIIT project on 'Wear control of tribological hard coatings with embedded optical nano-layers', a project, which this thesis is a part of.

One aim of the NABIIT project is to establish such a wear monitor solution, in this case consisting of hard coatings with embedded nano-layers of optical signal materials such that a change in the optical reflections by means of a simple laser pointer is observed when the wear reaches the embedded layer. But, nano-layers embedded within hard coatings may weaken the tribological properties of the layered structure and it is accordingly important to learn how and if the combination of two different materials with an interface affects a wear process.

Systematic high-speed wear experiments by means of slightly modified mechanical tribometer studies may lead to general wear properties of such multi-layered structures within reasonable time ranges. In-situ X-ray absorption studies by means of transmission of specific synchrotron radiation during the wear experiments may lead to knowledge of the dynamical wear process when simultaneously monitoring the wear of an embedded wear-marker (signal) layer. High-speed wear, as supported by the expert tribologists at Laboratoire de Tribologie et Dynamique des Systèmes in Ecole Centrale de Lyon, France is essential within the scope of this thesis, since traditional mechanical tribometer experiments on these wear resistant coatings otherwise are very time consuming and thus not feasible within a realistic time range. Naturally, this also concerns the real-time dynamical wear studies, since access to synchrotron radiation facilities is highly time-restricted.

Protective ceramic nitride coatings are often produced for industrial purposes by physical vapor deposition, a well-known ceramic film deposition technique [9], whereas pulsed laser deposition is a newer technique for production of these films. Pulsed laser deposition is a very flexible technique with great preservation of chemical composition combined with highly controllable film thickness (down to a monolayer) [14, 15], but physical vapor deposition usually results in the best protective films. As a result, either film production techniques are applied in the present work whenever best fitted.
Thus, the three main objectives of this thesis are to 1) produce thin films with the pulsed laser deposition technique, study the initial film nucleation and if possible establish growth modes, 2) characterize single-layer and multi-layer coatings – initially with respect to thickness, reflectance, refractive index and wear properties, but also with respect to combined wear and optical properties in order to verify the proposed wear monitoring system, 3) study dynamical wear processes of multi-layer coatings with in-situ X-ray monitoring of an embedded wear-marker layer and if possible to identify chemical phase changes of the embedded material when exposed to an abrasive wear process.

The thesis is divided in five parts; Introduction, Theoretical Methods, Experiments, Results and Summary. The initial part begins with a general introduction and is followed by a preliminary chapter describing the film and substrate materials studied together with descriptions and illustrations of both single-layer and multi-layer samples.

The subsequent part includes all theoretical methods and is divided into four main topics; film growth, optics, coatings tribology and X-ray physics. The different mechanisms and techniques for film deposition, growth mode and nucleation are discussed together with an introduction to the in-situ film nucleation monitoring system, RHEED. An outline of the optics involved and in particular the optical monitoring method is given as well as an introduction to coatings tribology. The final topic includes a short presentation of synchrotron radiation and gives in particular the basic concepts of the X-ray absorption monitoring.

The various experimental setups and characterization methods are discussed in part three, which is also split into three chapters. Initially, the film production setups are described together with the different schemes for film characterization. The linear tribometer, a mechanical wear tester, is also explained and illustrated together with the optical characterization methods. The final chapter displays and describes the combined wear and X-ray transmission and absorption experiment at the European Synchrotron Radiation Facility.

All results on the many different experiments and measurements are presented and discussed in the fourth part. Initially, the different films and coatings are characterized in terms of thickness, refractive index and initial film growth. This is followed by the various results obtained with respect to tribological wear tests including also both simulations and measurements on combined wear and optics, some of which are also the results on the optical wear monitor solution with the embedded optical signal layer. The results on the dynamical wear process studies with the wear-marker layer obtained at the European Synchrotron Radiation Facility are presented and discussed in the final chapter.

A summary is given in the end, which includes both concluding words on the results presented and some perspectives on possible future improvements of the various samples, setups, measurements and experiments. Additional illustrations and measurements are included in the first appendix and a complete collection of reviewed papers is found in the second appendix at the very end together with a bibliography of the references made in this thesis.
Chapter 2

Materials and Samples

An overview of the different coating and thin film materials is presented here together with the corresponding substrate materials. Also, the two multi-layer systems, TiN-on-TiO$_2$-on-Steel and TiAlN-on-TiN-on-Steel, for the proposed optical wear monitor are described and illustrated together with the third multi-layer system with the embedded wear-marker layer for dynamical wear studies, TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon.

2.1 Film Materials

Four different coating and thin film materials were studied in this work. Thin films of titanium dioxide (TiO$_2$), titanium nitride (TiN) and titanium aluminum nitride (TiAlN) were studied with respect to the wear and optics both individually and combined, whereas coatings of chromium nitride (CrN) and TiAlN were used in the X-ray absorption measurements for the dynamical wear process studies. TiN and TiO$_2$ films were also studied with respect to growth mode and initial film nucleation.

TiO$_2$

Titanium dioxide is a well known material and used in many everyday applications ranging all the way from sun blockers to window cleaning systems. It has been studied considerably due to both physical and chemical properties and has a wide range of technological application possibilities because of the dielectric, electrochemical, photocatalytic and optical features [16]. TiO$_2$ exists in three phases; rutile, anatase and brookite of different properties [17,18] as Tab. 2.8 displays. TiO$_2$ was primarily studied for optical properties but also with respect to the film growth mode. A blue transparent TiO$_2$ thin film by FerroPerm is shown in Fig. 2.1.

\[\text{Figure 2.1: Photo of 4 steel coupons. Uncoated steel (stål), } \sim 50 \text{ nm TiO}_2, \sim 2 \text{ µm TiN and } \sim 2 \text{ µm TiAlN.}\]
CHAPTER 2. MATERIALS AND SAMPLES

Color | Hardness [HV] | Temp\(^1\) [°C] | Temp\(^2\) [°C] | Friction Coefficient
---|---|---|---|---
TiN | Golden | 2300 | 450 | 600 | 0.4
TiAlN | Bluish Grey | 3600 | 450 | 1000 | 0.3
CrN | Metal Grey | 1800 | 450 | 700 | 0.5

**Table 2.1:** CemeCon A/S specifications on the tribological coatings TiN, TiAlN and CrN. Temp\(^1\) is the processing temperature and Temp\(^2\) is the maximum employment temperature. From [19].

**TiN**

The ceramic nitride TiN is a very hard, inert and protective coating material often used in production lines on steel tools, on metal drills applied in drilling machines [9, 20] but also for decorative purposes in everyday items as a golden-like coatings on (low end) jewelry and watches [13]. Figure 2.1 shows the bright golden yellow appearance of TiN, as produced by the commercial manufacturer CemeCon A/S, and the high resistance to wear and hardness [19] is specified in Tab. 2.1, where the Hardness is given in units of HV (see section 5.4.1 below), and the density below in Tab. 2.8.

Transition metal nitrides as TiN exhibit free-electron-like behavior [21] such that the material contains conduction electrons. As a result, a relatively strong absorption due to the high value of the extinction coefficient (see section 4.1.2) combined with a high reflectivity due to the comparatively small refractive index is observed in the visible spectral region, which is similar to that of metallic compounds [22, 23].

TiN was studied in a number of different contexts; primarily for both individual wear and optical features, combined wear and optical purposes but also with respect to the initial film nucleation and growth.

**TiAlN**

Another nitride, the protective coating material titanium aluminum nitride originally developed from TiN and AlN [20], is often termed \(\text{Ti}_{1-x}\text{Al}_x\text{N}\).

It is, like TiN, used as wear resistant coatings in industrial production lines and on cutting tools [9] and has a higher hardness compared to TiN (see Tab. 2.1). The color appears dark blueish grey as the photo in Fig. 2.1 displays, where the indicated [19, 24] stoichiometrically composition is \(\text{Ti}_{0.50}\text{Al}_{0.50}\text{N}\).

The density is not known from list values and thus necessarily estimated – by use of densities of TiN and the material AlN\(^1\)(aluminum nitride), which both are known. TiN displays metallic (free-electron-like) qualities and AlN dielectric, whereas TiAlN exhibit electronic properties ranging from metallic to dielectric, depending on the elemental composition – the size of \(x\) (0 \(\leq\) \(x\) \(\leq\) 1), such that optical properties with respect to the absorption range from those of metal to those of dielectrics [25]. TiAlN was studied for both individual wear and optical characteristics but also for combined wear and optical purposes and in the dynamical wear process study by X-ray absorption spectroscopy.

\(^1\)The density of AlN is 3.3 \(g/cm^3\) [17]. The difference (5.22 – 3.3) \(g/cm^3\) = 1.91 \(g/cm^3\) is used in the rough density estimation, where 0.50 is from 50% Ti and Al in the TiAlN composition, 13 and 22 is the Al and Ti mass number, respectively,

\[
\text{Density of TiAlN} = \left(3.3 + 1.91 \cdot 0.50 \cdot \frac{13}{22}\right) g/cm^3 = (3.3 + 0.56) g/cm^3 = 3.86 g/cm^3.
\]
2.2 Substrate Materials

Three very different materials were used as substrates in this study; 100Cr6 ball bearing steel, vitreous carbon and Magnesium Oxide due to different objectives of the study.

100Cr6 Steel

A high carbon chrome steel alloy, commonly known as 100Cr6 bearing ball steel, was used as substrate in both optics and wear studies. The alloy consists of a number of different compounds, where the main elements are iron, carbon and chromium with a percentaged composition as listed in Tab. 2.2. Also, very small amounts of manganese, phosphor, silicon and sulfur are included in the steel alloy. A steel coupon or substrate of $15 \times 15 \times 2 \, \text{mm}^3$ is included in Fig. 2.1, where the steel sample in the photo is labeled 'stål' – the Danish word for steel.

<table>
<thead>
<tr>
<th>100Cr6 Compounds</th>
<th>Composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>97.0</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>0.98 - 1.10</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>1.45</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>0.35</td>
</tr>
<tr>
<td>Phosphor</td>
<td>P</td>
<td>0.03</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>0.23</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 2.2: Percentaged composition of the common tribological test material 100Cr6 bearing ball steel [26,27].
CHAPTER 2. MATERIALS AND SAMPLES

Vitreous Carbon

Vitreous Carbon, also known as Glass Carbon due to the materials appearance as black glass, is a non-graphitizing material and achieved by pyrolysis of polymers [28]. It consists of carbon in a macroisotropic microcrystalline formation [29], with almost all foreign elements evaporated during formation. A high carbon purity is necessary in the X-ray absorption experiment, where foreign and potentially heavily absorbing elements are unwanted. Moreover, the low Z number makes vitreous carbon a fine X-ray substrate. The material combines both ceramic and glass-like properties such as high temperature resistance and high degree of chemical attack resistance [30]. Figure 2.3 displays a photo of a vitreous carbon substrate and Tab. 2.8 below the density. Vitreous carbon was used as substrates in the multi-layer system TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon for the dynamic wear process study.

MgO

A single crystal substrate of the white mineral Magnesium Oxide (MgO) as Fig. 2.4 displays was used in the TiN and TiO\textsubscript{2} film growth study, since the cleaved ionic crystal make a fine substrate [31] and the lattice mismatch (0.6%) with TiN is good [2]. Periclase MgO (100), is a very hygroscopic material and must be protected from humidity in order not to absorb water from the atmosphere, but contaminants may be removed by reversed high-temperature annealing [32,33].

![Figure 2.3: Vitreous carbon for X-ray experiment.](image)

![Figure 2.4: Periclase MgO for film growth study.](image)

**Figure 2.3:** Vitreous carbon for X-ray experiment.

**Figure 2.4:** Periclase MgO for film growth study.

TiN-on-TiO\textsubscript{2}-on-Steel

![Diagram](image)

**Figure 2.5:** Golden-like TiN (tribo) with a \(~50\) nm embedded TiO\textsubscript{2} (signal) layer deposited on a polished steel coupon (substrate).

TiAlN-on-TiN-on-Steel

![Diagram](image)

**Figure 2.6:** Bluish grey TiAlN (tribo) with a \(~2\mu m\) embedded golden-like TiN (signal) layer deposited on a polished steel coupon (substrate).
2.3 Samples

A number of samples covered with either thick or thin films of different materials was studied for various purposes and a description of these samples is given here together with illustrations and photos of selected samples and series of samples.

2.3.1 PLD and RHEED Samples

Substrates of MgO was covered via pulsed laser deposition with nucleating films of either TiN or TiO$_2$ while the development and growth simultaneously were monitored with RHEED and subsequent TiN and TiO$_2$ film surface morphology with atomic force microscopy and X-ray diffraction.

2.3.2 Optics

The optical laser reflectance was measured from different sample coatings to estimate the complex refractive index but also measured from various multi layered samples with embedded signal layers to verify the concept of the optical wear monitor system.

Refractive Index and Extinction Coefficient

An uncoated polished steel coupon, a ~50 nm TiO$_2$ film on a polished steel coupon and thick coatings of TiN and TiAlN deposited on polished steel coupons are studied optically in order to estimate the refractive index and extinction coefficient of the materials. These four material samples are displayed together in Fig. 2.1.

Optical Wear Monitor System TiN-on-TiO$_2$-on-Steel

A multi-layer sample with a top TiN tribological coating on a thin optical signal layer of TiO$_2$ deposited in turn on polished 100Cr6 steel substrates was produced in order to verify the proposed optical wear monitor. Figure 2.5 illustrate the cross section of a TiN-on-TiO$_2$-on-Steel multi-layer sample. Five samples of increasing (or decreasing) top TiN coatings on ~50 nm embedded TiO$_2$ were produced to simulate a wear situation with decreasing top layer thickness and as such prove the concept of the remote

<table>
<thead>
<tr>
<th>Multi-layer Coatings for Optical Tests</th>
<th>Material</th>
<th>TiO$_2$ [nm]</th>
<th>TiN [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td></td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td>–</td>
<td>20</td>
</tr>
<tr>
<td>Sample 3</td>
<td></td>
<td>–</td>
<td>40</td>
</tr>
<tr>
<td>Sample 4</td>
<td></td>
<td>–</td>
<td>70</td>
</tr>
<tr>
<td>Sample 5</td>
<td></td>
<td>–</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2.3: Expected coating thickness of the TiN-on-TiO$_2$-on-Steel system as displayed in Fig. 2.7.
optical monitor for assumed wearing of coatings (see e.g. section 4.3.1). The optimum thickness of 50 nm TiO$_2$ layer is established below (see section 11.2.1). Figure 2.7 displays a photo of the complete sample series, where the noted thicknesses refers to the expected TiN thickness as also listed in Tab. 2.3 together with the expected TiO$_2$ thickness. The increasing TiN layer thicknesses are clearly visible with the naked eye. The human eye is actually a very fine detector, which can easily detect changes on nm scales such as those of the photo [34]. An uncoated steel substrate was also included in the photo for comparison but otherwise not used in these optical multi-layer measurements.

**Optical Wear Monitor System TiAlN-on-TiN-on-Steel**

Another wear monitor system, TiAlN-on-TiN-on-Steel, with a top TiAlN tribological coating on a thick embedded layer of TiN deposited in turn on a steel substrate is illustrated in Fig. 2.6. The TiN layer is for this sample system working as the signal layer (see e.g. section 4.3.1) similarly to the TiO$_2$ signal layer of the previous sample (Fig. 2.5). Five such samples for pure optical purposes were, as before, produced with increasing (or decreasing) top TiAlN tribological coating to simulate a wear situation with decreasing top layer thicknesses, such that this optical monitor system also could be proved. A photo of the complete sample series is shown in Fig. 2.8, in which the thicknesses noted refers to the expected top TiAlN layer thickness as also listed in Tab. 2.4 together with the expected TiN signal layer thickness.

### 2.3.3 Wear and X-Ray Absorption

A third and final multi-layer sample system TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon was used in the combined wear and X-ray absorption experiments at the European Synchrotron Radiation Facility in Grenoble, France.

<table>
<thead>
<tr>
<th>Multi-layer Coatings for Optical Tests</th>
<th>Material</th>
<th>TiN [µm]</th>
<th>TiAlN [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>30</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>–</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>–</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>–</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>–</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 2.4: Expected coating thickness of the TiAlN-on-TiN-on-Steel system as displayed in Fig. 2.8.*
2.3. SAMPLES

*TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon*

![Diagram of TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon]

**Figure 2.9:** Multi-layer sample system TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon with 1.5 µm TiAlN on 0.5 µm CrN on 1.5 µm TiAlN deposited on a vitreous carbon substrate.

*TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon* for X-ray Transmission and Absorption

Figure 2.9 illustrates a cross section of the different layers in the system deposited on top of vitreous carbon, in which the TiAlN coatings are blue, the CrN layer is bright grey and the carbon substrate black.

The multi-layer sample consists of a ~1.5 µm top TiAlN tribological coating deposited on a ~0.5 µm CrN wear-marker layer, which in turn is deposited on a ~1.5 µm embedded TiAlN tribological coating as listed in Tab. 2.5.

The CrN wear-marker Layer constitutes the signal layer of this multi-layer system, as TiO$_2$ and TiN did for the two optical multi-layer systems (see Figs. 2.7 and 2.8), since the CrN X-ray absorption k-edge around 6 keV is significantly shifted from that of TiAlN (around 5 keV) such that the signal from the latter does not disturb that of CrN in the X-ray absorption experiment [35]. An additional embedded TiAlN coating has been included in this system, since the CrN layer is supposed to be worn through, but the wear process should preferably not continue in to the vitreous carbon substrate, since this is not a wear resistant material.

### 2.3.4 Wear

Single layer coatings of TiN and TiAlN were produced with the sole purpose to be tested in the linear tribometer for abrasive wear to establish wear properties of the two materials. Table 2.6 displays the layer thickness, where 2 samples (labeled TiAlN$^*$) were covered with ~3 µm TiAlN and 4 with ~2 µm. The two TiAlN coating types are otherwise identical - only the coating thickness differs.

<table>
<thead>
<tr>
<th>Tribological Coatings for XAFS</th>
<th>Layer Thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAlN</td>
<td>1.5</td>
</tr>
<tr>
<td>CrN</td>
<td>0.5</td>
</tr>
<tr>
<td>TiAlN Embedded Tribological Coating</td>
<td>1.5</td>
</tr>
<tr>
<td>Vitreous Carbon</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Table 2.5:** Expected coating thickness of the TiAlN-on-CrN-on-TiAlN-on-Steel system shown in Fig. 2.9.
CHAPTER 2. MATERIALS AND SAMPLES

### Table 2.6: Expected coating thickness of TiN and TiAlN single layer coatings for wear tests.

<table>
<thead>
<tr>
<th>Coatings for Wear Tests</th>
<th>TiN</th>
<th>TiAlN</th>
<th>TiAlN*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Thickness</td>
<td>2 µm</td>
<td>2 µm</td>
<td>3 µm</td>
</tr>
</tbody>
</table>

#### 2.3.5 Wear and Optics

The multi-layer samples *TiAlN-on-TiN-on-Steel* (Fig. 2.6) was also tested by combined tribo-optical means. The other multi-layer system *TiN-on-TiO₂-on-Steel* (Fig. 2.5) was not tested in the combined optics and wear experiment and thus not exposed to an actual abrasive wear process as discussed (see section 11.4.1) below, however, the system did prove to work – conceptually – as an optical monitor.

**TiAlN-on-TiN-on-Steel for Combined Optics and Wear**

Three different sample types of the *TiAlN-on-TiN-on-Steel* system of different top TiAlN coating thickness as Tab. 2.7 displays, were tested with the combined optics and wear measurements. The different top TiAlN coatings of these samples should not be mixed with the samples with increasing (or decreasing) top coatings for optical studies alone as seen in Figs. 2.7 and 2.8.

### Table 2.7: Expected coating thickness of the TiAlN-on-TiN-on-Steel system as shown in Fig. 2.6.

<table>
<thead>
<tr>
<th>Coatings for Optics and Wear Tests</th>
<th>TiN [µm]</th>
<th>TiAlN [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Thickness</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

#### Table 2.8: Theoretical and measured values from literature of various coating and substrate materials studied.

<table>
<thead>
<tr>
<th>Material</th>
<th>Name</th>
<th>Stoichiometry</th>
<th>Density [g/cm³]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Titanium Dioxide</td>
<td>TiO₂</td>
<td></td>
<td>[17,36]</td>
</tr>
<tr>
<td></td>
<td>rutile</td>
<td></td>
<td>4.274</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anatase</td>
<td></td>
<td>3.895</td>
<td></td>
</tr>
<tr>
<td></td>
<td>brookite</td>
<td></td>
<td>4.123</td>
<td></td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium Nitride</td>
<td>TiN</td>
<td>5.22</td>
<td>[17,20]</td>
</tr>
<tr>
<td>TiAlN</td>
<td>Titanium Aluminum Nitride</td>
<td>Ti₀.5₀Al₀.5₀N</td>
<td>3.86</td>
<td>sec. 2.1</td>
</tr>
<tr>
<td>CrN</td>
<td>Chromium nitride</td>
<td>CrN</td>
<td>5.9</td>
<td>[17,36,37]</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium monoxide</td>
<td>MgO</td>
<td>3.58</td>
<td>[17,36]</td>
</tr>
<tr>
<td>Steel</td>
<td>AISI E 52100 Steel (100Cr6)</td>
<td>Fe₀ₓCr₀ₓ...</td>
<td>7.81</td>
<td>[27]</td>
</tr>
<tr>
<td>Glass Carbon</td>
<td>Vitreous Carbon</td>
<td>C</td>
<td>1.42</td>
<td>[38]</td>
</tr>
</tbody>
</table>
Part II

THEORETICAL METHODS
Chapter 3
Thin Film Growth

The various thin films and coatings are produced by different techniques as discussed in this chapter together with an introduction to the general properties and principles of the initial film growth and RHEED in-situ diagnostics.

3.1 Film Deposition Techniques

A description of the three film deposition techniques employed for producing the films and coatings is given, where pulsed laser deposition is discussed in greater details since this method was used in the film growth studies of TiN during deposition. The remaining two methods are employed by the commercial manufacturers, CemeCon A/S and FerroPerm, for production of tribological hard coatings and oxide films – and thus only described briefly.

3.1.1 Pulsed Laser Deposition

A pulsed laser deposition (PLD) experiment consists basically of a pulsed laser beam incident on a target situated in a vacuum chamber such that material is removed explosively from the target surface, in a process termed laser ablation, transferred and collected on a substrate [39]. The schematical drawing in Fig. 3.1 illustrates the basic principles of the PLD process, where the plasma plume (gas of ionized particles, electrons, ions, atoms and neutral particles) arises from the laser-target interaction and a subsequent accumulation of target material on the substrate surface results in film deposition.

One of the primary strengths of the PLD technique is the possibility of stoichiometric conservation of material during transfer from target to thin film [15]. Also, highly perfect interfaces and precise layer thicknesses can be achieved by controlling the number of laser pulses, the laser repetition rate and the pulse energy (combined with raster scanning of laser beam position and rotation of target and substrate during deposition) such that e.g. layer-by-layer growth may be obtained.

Other advantages of the deposition technique are the possibility of making multi-layer thin films by change of target in a multi-target PLD system and the possibility of film deposition either in vacuum – or in a reactive or inactive background gas [14]. Moreover, since the ablated target atoms and ions generally have a kinetic energy that exceeds thermal energy by more than one order of magnitude [40], the surface mobility of the target particles is greatly enhanced, which favors growth of high crystalline quality [14,41].
It is possible to describe the PLD process in a background gas within five steps; laser-target interaction, one dimensional plume expansion, 3D plume expansion, slowing down and stopping of plume and film depositing on the substrate [15]. Figure 3.2 and 3.3 illustrate the five steps separately. Each of the process steps depends on different experimental parameters such as target and substrate materials together with substrate temperature – and background gas type and pressure. Also, properties of the light source – wavelength, fluence and pulse duration influence the deposition process [42]. Typically, lasers in the UV range combined with nanosecond pulses are selected due to a strong absorption [41,43].

Laser-Target Interaction

Photons from the laser pulse are absorbed in the target surface (1) through electronic processes, by which the absorbed energy is transferred into the material either by free electron excitations in metals or by interband transitions in non-metals. The absorption may result in a heating of the outermost target surface parts – far above melting temperatures, where the absorbed energy is converted into heat much faster than the laser pulse duration (typically a few nano-seconds), and the melting surface starts vaporizing and particles ablate from the target in an explosive evaporation of ions, electrons and neutral atoms.

At further incidence UV energy photons (2) ionizes the evaporated material and a plasma plume is formed above the target, provided the laser power density is above the threshold for plasma creation. The plasma continues to absorb photons until the end of the laser pulse, which causes further heating of the plasma and it may become dense and completely opaque for the laser, such that the laser-target interactions stop [42,44]. This means that the process has an optimum for which the process runs most efficiently, very much depending on the various experimental process parameters.

Plume Expansion

The plume of target particles keeps expanding (3) in a direction normal to the target surface [45] and the originally one dimensional plume expansion changes into a 3D expansion. If the process takes place in a background atmosphere of specific elements, the surface of the 3D plume volume is enclosed by these

Figure 3.1: Laser pulses irradiate a target. Material is ejected and deposited as a thin film on substrate.
3.1. FILM DEPOSITION TECHNIQUES

Figure 3.2: Principles of PLD process I. 1) Light absorption in the solid target. 2) One dimensional plume expansion of the ablated material during laser irradiation. 3) ‘Free’ 3D plume expansion in vacuum or dilute gas.

elements (4) causing the ejected particles to collide with the background elements (grey discs) leading to scattering, attenuation and thermalization of the plume particles, where the pressure and background gas element type influence the kinetics of the deposition [42]. An inert background atmosphere (e.g. argon) in the vacuum chamber slow down the plume particles as they otherwise may damage the growing film with their high energy and a controlled partial pressure of e.g. oxygen preserves the (oxide) film stoichiometry by avoiding depletion of the volatile oxygen. Moreover, plume particles expanding in vacuum proceed with unchanged speeds.

Film Deposition

The arriving target particles gather on the substrate surface (5) and coalesce with the substrate surface either by van der Waals forces between the particles and substrate surface atoms or as a consequence of chemical bonds between the two [42]. Thus, preliminary film nucleation formation starts upon arrival as discussed further in section 3.2 below.

3.1.2 Physical Vapor Deposition

Many different process techniques are included within Physical Vapor Deposition (PVD). The project partner and commercial thin film manufacturer CemeCon Scandinavia A/S utilizes a common PVD sputtering technique; magnetron sputtering, in which the sputtering process is combined with a magnetic field.

Figure 3.3: Principles of PLD process II. 4) slowing down and stopping of plume in background gas. 5) Deposition of thin film on substrate.
Incident particles at a few tens of eV have enough energy to penetrate a target surface and as a result of mainly elastic collision processes, atoms are sputtered from the target [46]. Excited neutrals as well as ionized atoms, molecules and clusters are ejected during the sputtering process together with also secondary electrons as seen in the schematical representation in Fig. 3.4, in which an ion is incident on a target surface.

A dilute gas of typically argon is let in between the cathode and anode in the deposition camber. By applying an appropriate voltage between the electrodes, a plasma of argon ions, neutrals and electrons is formed. A confining magnetic field \( B \) in magnetron sputtering, keeps the plasma and thus also the secondary electrons close to the target such that passing neutral atoms may be ionized and consequently accelerated towards the target surface (the cathode) by the strong electric field of the plasma [47]. Magnets just below the target result in a concentration of magnetic field lines close to the center part of the target surface (as Fig. 3.5 illustrates), which in turn results in a high concentration of electrons which maintains the plasma. Ions incident on the cathode (target) produce neutral sputtered particles, which are unaffected by both the plasma and the magnetic field and proceed towards the substrate surface.

Figure 3.4: Schematics of particles emitted under ion bombardment of a metal surface. After [46].

Figure 3.5: Principles of magnetron sputtering of thin films. The concentrated \( B \)-field confines the plasma (magenta 'cloud') in the vicinity of the target surface.
3.2 INITIAL FILM GROWTH

Introducing also a reactive gas to the system during the sputtering deposition of a metallic target, sputtered neutral particles and reactive gas particles may combine in a chemical reaction to form compounds on the substrate [47, 48]. Reactive gases such as nitrogen or oxygen applied in this modified magnetron sputtering deposition method, known as Reactive Magnetron Sputtering, may result in film deposition of nitrides or oxides on the substrate.

3.1.3 Electron-Beam Evaporation

Evaporative PVD is within a different group of PVD processes, where the Electron-Beam Evaporation technique is utilized by the commercial TiO$_2$ thin film supplier, FerroPerm. A short description of the film deposition method is given here.

A beam of electrons discharged thermionically from a hot filament may melt and evaporate material from a target by impact [49]. The target is placed in a crucible (target holder) located above the filament and the substrate is placed above the target such that evaporants are collected as a thin film on the substrate surface as Fig. 3.6 illustrates.

The electron beam is emitted from the filament situated below the target such that evaporants from the target will not reach the filament and thereby destroy it. The direction of the electron beam is controlled by a magnetic field, $B$, which causes the electrons to move in a circular path as illustrated. In order to achieve good uniformity of the deposited thin film, the electron beam impact position on the target is usually scanned across the surface by controlling the magnetic field.

3.2 Initial Film Growth

The early stages of film formation – the very initial nucleation and growth modes, as deposited by the film deposition methods; e-beam evaporation, PVD or PLD, but studied only through pulsed laser deposited films, are discussed here. In film growth and deposition, target particles collect on the substrate
CHAPTER 3. THIN FILM GROWTH

Deposition, Time
Stranski - Krastinov
Frank - Van der Merwe
Volmer - Weber

Figure 3.7: Three basic thin film growth modes develop during deposition. After [50].

(see Fig. 3.3 above), where they coalesce with the surface atoms. When the particles reach the substrate they may diffuse some distance on the surface before attractive interactions eventually dominate over diffusion and subsequently start nucleation formation [42].

3.2.1 Growth Modes

Figure 3.7 illustrates three typical [31, 44] growth and nucleation modes describing the development or coalescence of deposited films, where the film growth develop in time with the direction of the arrow.

3D Island Growth Film structures grow in three dimensions through island formation in the Volmer-Weber nucleation and growth mode as the illustration shows. Different atomic processes are possible as film atoms arrive on the substrate surface [44]. They may diffuse across the substrate or cluster surfaces, come across other mobile film atoms to start cluster nucleation, attach to or detach from existing clusters, re-evaporate of the surface or of a cluster nucleation. This variety of atomic nucleation processes is shown in the schematic diagram in Fig. 3.8, in which (a) is atom depositing on the substrate, (b) atom re-evaporating from the substrate, (c) two atoms initiating cluster nucleation, (d) atom diffusing towards an already existing cluster, (e) atom depositing on the existing cluster (f) atom re-evaporating from the cluster and finally (g) atom dissociating away from the cluster.

2D Monolayer Growth In a two dimensional growth a full monolayer completely covers the substrate before the subsequent nucleation formation initiates a 2\textsuperscript{nd} monolayer (a monolayer is one atomic layer thick). Consequently, the film grows in two dimensions in a mode also known as Frank-Van der Merwe growth (see Fig. 3.7).

Figure 3.8: Atomic nucleation processes of 3D clusters in Volmer-Weber growth of deposited film atoms [44].
2D Monolayer and 3D Island Growth  The *Stranski-Krastinov* growth mode is a combination of the first two modes; the film initially starts formation of two dimensional atomic monolayers and then continues with 3D island formation. The change from 2D to 3D may be influenced by modifications in the energy situation due to the full grown monolayers, which could be due to an increased stress level as a result of lattice mismatch between the substrate lattice and the lattice of the growing 2D film. If the lattice mismatch between the substrate and the thin film is large an increased stress level is seen.

3.3 RHEED

RHEED, an abbreviation for *Reflection High-Energy Electron Diffraction*, is a method frequently utilized to study film surface morphology. Mechanisms and processes during deposition and growing of thin films by PLD are studied by analyzing the electron beam diffraction from the surface of a growing film.

A schematic overview of a typical PLD setup with a high-pressure RHEED system is seen in Fig. 3.9, in which the deposition chamber is sketched together with the electron source, the e-gun. The electrons are generated at a low pressure, where differential pumping between the electron source and the chamber makes deposition at high-pressure possible.

The electron beam is incident on the substrate surface at a very low angle. A grazing angle tilt of $0^\circ - 3^\circ$ between incident e-beam and substrate surface ensures a small penetration depth of the electrons and only the top few atomic monolayers of the combined thin-film and substrate surface are monitored. This makes RHEED an extremely surface sensitive diffraction method and one can observe how the electrons are scattered by surface steps and terraces. The RHEED pattern is instantaneously displayed on the phosphor screen, the diffraction pattern may be used to determine crystallographic substrate structures and more interestingly – an instantaneous crystallographic structure of the growing thin film.

![Schematic view of a typical PLD setup with high-pressure RHEED. The electron beam is generated by the electron gun and detected via the screen on the left hand side. Adapted from [51].](image-url)
CHAPTER 3. THIN FILM GROWTH

3.3.1 Geometry and Ewald Sphere

Electrons incident on the substrate strikes the surface at the grazing angle $\Theta_i$ seen in the geometrical representation in Fig 3.10, where the diffracted beams are monitored on the screen. $\Theta_i$ ($\Theta_f$) and $\phi_i$ ($\phi_f$) are the incident and azimuthal angles of the incident (diffracted) e-beams, $R_s$ is the distance between substrate and screen and $s$ the distance between the diffraction spots or streaks appearing on the screen.

An Ewald sphere can be used to show the allowed diffraction conditions for the elastically scattered electrons. The diffraction spots can together with the electron energy and the RHEED geometry ($R_s$) be related to the Ewald sphere geometry as Fig. 3.11 sketches, such that the reciprocal lattice of the surface can be found by relating the spot geometry and spacing of a RHEED pattern to an Ewald sphere. Only the top few monolayers interact with the electrons and the RHEED pattern arises thus essentially from a 2D crystal. The reciprocal lattice of a bulk crystal consists of a set of points in 3D space, whereas the reciprocal lattice for a 2D crystal surface is a series of infinite rods extending perpendicularly to the substrate surface as illustrated. The diffraction conditions are satisfied when the reciprocal lattice rods intersect the 2D Ewald disc as seen in Fig. 3.12, where the sphere is centered on the substrate surface with a radius equal to the size of the wavevector of the incident beam, $k_0$. $k_0 = 2\pi/\lambda$, where $\lambda$ is the

[Figure 3.10: Schematic view of a typical RHEED geometry. Adapted from [51].]

[Figure 3.11: Three dimensional Ewald sphere construction with reciprocal lattice rods. From [51].]

[Figure 3.12: 2D Ewald sphere of radius $k_0$ situated at the substrate surface. $k_s$ is the allowed diffraction conditions and here also the specular beam. $G$ is the difference between $k_s$ and $k_0$.]
3.3. RHEED

Figure 3.13: RHEED patterns for different surface ‘imperfections’ on single crystal substrate. After [52, 53].

The electron wavelength\(^1\). This means that the magnitude of any \(k_s\) from the sphere origin to any intersection (see Figs. 3.11 and 3.12) equals that of \(k_0\); \(|k_0| = |k_s|\). Furthermore, the diffraction spots or streaks are produced when the momentum of the incident and diffracted beams differs by the reciprocal lattice vector \(G\) such that

\[
k_0 - k_s = G
\]

\(k_0\) is the wavevector of the incident beam and \(k_s\) the wavevector of the diffracted beam. \(G\) is also drawn.

Surface Imperfections

Two different types of surface roughness result in two different characteristics of the RHEED pattern [51]. A rough surface with a random distribution of terraces and steps leads to broadened reciprocal lattice rods, where streaks occur due to intersections with the Ewald sphere and a rough surface with small three dimensional islands or asperities on the surface leads to transmission spots. The reciprocal lattice rods are in that case replaced by the bulk reciprocal lattice points in 3D where streaks are replaced with spots.

Different modes, including, a flat surface and surface imperfections such as terraces, mosaic structures and islands are shown in Fig. 3.13 with the possible corresponding RHEED patterns. For a perfectly flat crystal the reciprocal lattice rods (see Fig. 3.12) have zero width and the corresponding diffraction spots appear sharp and distinct [52] as illustrated in the top part of the figure, in which the mirror beam, i.e. the specular beam, and the direct beam (not visible in real RHEED images) also are included.

\(^1\)The electron wavelength can be found through the approximate relation \(\lambda(\text{Å}) = \sqrt{150/E}\), where \(E\) is in eV.
A crystal mosaic structure consists of domains with small crystal misorientations with respect to each other and stepped surface structure is one crystal with a terraced surface structure (see center part, Fig. 3.13). Both the mosaic and weakly stepped (terraced) structures result in broadening of the reciprocal lattice rods such that the diffraction spots observed for the ideal flat surface are changed into diffraction streaks or elongated spots instead [53]. Both strongly stepped surfaces with large terraces and deep valleys (bottom part, Fig. 3.13) may lead to diffraction patterns, which essentially are caused by transmission through parts of the bulk surface, where streaks are replaced with spots [51]. The bottom RHEED pattern also applies for surfaces with 3D island nucleation formations.

Substrate Preparation

An extremely clean and flat substrate surface is required for good RHEED measurements. One method for crystal substrate preparations is thermal heat treatment. If thermally annealed in an oxygen atmosphere, impurities on an oxide substrate surface may be removed and possible oxygen vacancies re-filled. An initial rough surface may also be smoothed by the treatment, since the surface atoms may re-associate in the hot oxygen atmosphere to an almost atomically flat surface with a terrace-like surface structure [51].

3.3.2 Intensity Oscillations

RHEED may be used especially to monitor homoepitaxial growth, where 2D Frank-Van der Merwe (layer-by-layer) growth is expected, due to the perfect lattice match between film and substrate, i.e. the growing thin film and substrate materials are identical in homoepitaxial growth [51]. The intensity of the specular spot is seen in Fig. 3.14 to oscillate during a 2D monolayer deposition. Initially, the RHEED intensity decreases as few atoms are collected and the decrease continues until the monolayer is half grown and the intensity is at a minimum, where interference between the beams from the flat, full layer and the growing incomplete layer causes the intensity decrease [52]. The atoms keep gathering to complete the monolayer and the RHEED intensity increases until the layer is complete. Completion of one full monolayer leaves the intensity back at maximum. One oscillation is seen for each monolayer completed and as several monolayers are grown, oscillations (see Fig. A.3 in the appendix) continue during the growing of 2D monolayers. Only 2D monolayer growth results in these oscillations. Other types of growth modes result in a continuous decrease of the specular beam intensity as e.g. nucleating islands roughen the surface.

![Figure 3.14: RHEED oscillations from Frank-Van der Merwe monolayer growth depending on the level of film atoms covering the substrate. From [54].](image)
Chapter 4

Specular Reflections Optics

The theoretical basis for the optical wear monitor – the principles of reflection and refraction between different media, including the refractive index for conductors and non-conductors are discussed together with the reflectance from multi-layers and the principles in the optical Warning System.

4.1 Reflection and Refraction

4.1.1 Refractive Index

The refractive index $n$ of a material is defined as the ratio of the speed of an electromagnetic wave in vacuum, $c$, to that in the medium or material, $v$ [55]. This leads to an expression for the refractive index

$$n \equiv \frac{c}{v} = \sqrt{\frac{\epsilon \mu}{\epsilon_0 \mu_0}}, \quad (4.1)$$

where $\epsilon_0$ is the electric permittivity and $\mu_0$ is the permeability, both in vacuum. $v = 1/\sqrt{\epsilon \mu}$; $\mu$ and $\epsilon$ are within the medium. The refractive index is thus merely a factor by which the electromagnetic phase velocity in the material relative to that in vacuum is reduced. The refractive index when crossing a boundary between two media is also described in the Law of Refraction [22], where the relation between the refractive indices and the angle of incidence and refraction is known as Snell’s Law

$$\frac{\sin \theta_i}{\sin \theta_r} = \frac{v_1}{v_2} = \frac{n_2}{n_1}, \quad (4.2)$$

Figure 4.1: An interface boundary between the two different media. All beams are in the plane of incidence.
\( \theta_i \) and \( \theta_t \) are the angles of the incident and refracted (transmitted) beams, respectively, \( n_1 \) and \( n_2 \) the refractive indices of the two media involved as Fig. 4.1 displays, in which \( v_1 \) and \( v_2 \) are the wavefront velocities in the two media. The beam incident (in the figure) on an interface; the blue boundary surface between two different media, is transmitted through but also reflected off of the interface, where the incident, reflected and refracted beams all are propagating within the (green) plane of incidence. The angle of the reflected beam equals the incident angle; \( \theta_i = \theta_r \), whereas the transmitted \( \theta_t \) depends on the refractive indices of the two media involved such that for instance

\[
\theta_i > \theta_t \quad \text{when} \quad n_1 < n_2
\]

and vice versa (see Snell’s Law, Eq. (4.2)). The above situation is also the case depicted in the figure. The refractive index is dependent on the wavelength of light\(^1\) [55, 56]. This means the that the refractive indices are not universal constants but only valid for a specific wavelength. However, few changes are usually seen within the visible light range.

### 4.1.2 Complex Refractive Index

The refractive index defined above (Eq. (4.1)) is described for light propagating within a non-conducting media (conductivity \( \sigma = 0 \)). Looking at conducting materials, such as metals (with conductivity \( \sigma \neq 0 \)), a number of electrons within the material are unbound in the sense that an \( E \)-field applied will cause a flow of a current in the material, where the conducting electrons will oscillate with the harmonic wave (\( E \)) but also collide with lattice imperfections or the lattice and thereby cause conversion of electromagnetic energy into joule heat [55]. Thus, the conductivity of a metal results in absorption of the radiant energy. By defining the refractive index as a complex index

\[
\tilde{n} = n + ik
\]  

in which \( n \) and \( k \) are real numbers, the absorption of conducting materials is included [56, 58]. \( n \) is the refractive index as defined above in Eq. (4.1) and \( k \) is known as the attenuation index or the extinction coefficient. \( k \) describes the materials ability to transform incident light into thermal energy, i.e. to absorb light incident on the material surface. Thus, \( k \) determines the rate of light absorption in the material.

---

\(^1\)This is also the reason for a ray of sunlight being split into a ‘rainbow’ when passing through e.g. a glass prism.
4.1.3 Polarization of Light

The orientation of the oscillations of the electromagnetic light waves is described by the polarization. A plane electromagnetic wave is linearly polarized as seen in Fig. 4.2a, where the transverse electric field wave is oscillating vertically – up and down. The electric field wave is accompanied by a magnetic field wave (in blue) but only the linear E-field motion is included in the small diagrams.

Two plane electromagnetic waves of equal amplitude but with a difference in the phase by 90° are circularly polarized as illustrated in Fig. 4.2b, in which the end of the electric field vector \( \mathbf{E} \) would appear to be moving in a circle during propagation. The electric field vector makes one complete revolution, i.e. one full circle rotation as the light advances one wavelength. The direction of the rotation determines the orientation of the polarization. Linearly polarized light (see Fig. 4.2a) is separated in two types; TE polarized light also known as the \( s \)-polarization and TM, known as the \( p \)-polarization. TE is for Transverse Electric Wave, which means that the electric vector is perpendicular to the plane of incidence and TM is for Transverse Magnetic Wave, which means that the magnetic vector is perpendicular to the plane of incidence – and thus the electric vector is parallel to the plane of incidence [22]. TE corresponds to the \( \perp \)-notation and TM corresponds to the \( \parallel \)-notation, an illustrative notation form. Both notation forms are used.

It is possible to select either of the two polarizations (TE or TM) by use of a linear polarizer as Fig. 4.3 illustrates, where only the horizontal component of the laser beam is transmitted. The polarizer consists essentially of many parallel conducting wires which absorb all electromagnetic wave components (see section 4.1.2) propagating parallel to the wires. The part of light propagating perpendicular to the wires is basically transmitted unaltered.

4.1.4 Fresnel’s Equations

Fresnel’s Equations describe the behavior of light as it reaches an interface. For an \( \mathbf{E} \)-field propagating \( \perp \) to the plane of incidence for dielectrics with a permeability \( \mu_i \approx \mu_t \approx \mu_0 \), the Fresnel Equations are

\[
\begin{align*}
    r_\perp &\equiv \left( \frac{E_{0t}}{E_{0i}} \right)_\perp = \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\
    t_\perp &\equiv \left( \frac{E_{0t}}{E_{0i}} \right)_\perp = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_t}
\end{align*}
\]

(4.4)\hspace{1cm}(4.5)

in which \( r_\perp \) is the amplitude reflection coefficient and \( t_\perp \) the amplitude transmission coefficient. For an
CHAPTER 4. SPECULAR REFLECTIONS OPTICS

E-field propagating parallel (∥) to the plane of incidence, a similar pair of Fresnel equations \( r \) and \( t \) are given

\[
r_∥ = \frac{n_2 \cos \theta_i - n_1 \cos \theta_r}{n_1 \cos \theta_i + n_2 \cos \theta_i}
\]

\[
t_∥ = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i}
\]

in which the two media on each side of the interface are assumed to be non-magnetic.

4.2 Reflectance and Transmittance

A laser beam incident on an interface illuminates a surface area \( A \) due to the cross-sectional area of the laser beam not being a sizeless mathematical point. Figure 4.4 displays the incident beam reflected of the interface and simultaneously transmitted. \( I_i, I_r \), and \( I_t \) are the incident, reflected and transmitted flux densities (intensities), respectively, and the corresponding cross-sectional areas of the incident, reflected and transmitted laser beams are \( A \cos \theta_i \), \( A \cos \theta_r \), and \( A \cos \theta_t \). The incident power arriving at the surface over the area \( A \) is \( I_i A \cos \theta_i \); the energy per unit time flowing in the incident beam. Correspondingly, the reflected and transmitted power is \( I_r A \cos \theta_r \) and \( I_t A \cos \theta_t \), respectively. The reflectance is defined as the ratio of the reflected power to the incident

\[
R \equiv \frac{I_r A \cos \theta_r}{I_i A \cos \theta_i} = \frac{I_r}{I_i}
\]

in which the waves are propagating within the same media such that \( v_r = v_i \). Additionally, the angles cancel out, since \( \theta_i = \theta_r \). Similarly, the transmittance is defined as the ratio of the transmitted power to that of the incident

\[
T \equiv \frac{I_t A \cos \theta_t}{I_i A \cos \theta_i}
\]

To uphold conservation of energy during the reflecting and transmitting of light, the total energy incident on the area \( A \) (Fig. 4.4) per unit time must equal the energy reflected of and transmitted through the area \( A \); i.e. \( I_i A \cos \theta_i = I_r A \cos \theta_r + I_t A \cos \theta_t \) leading to \( 1 = R + T \) such that the reflected intensity together with the transmitted cannot exceed unity.

Figure 4.4: A beam incident on an interface illuminates a surface area \( A \).

Figure 4.5: Reflection and transmission of a laser beam (red arrow) through a multi-layer sample.
4.2. REFLECTANCE AND TRANSMITTANCE

4.2.1 Reflectance from Multi-Layer Sample

The reflectance, $R$, from a multi-layer structure with many interface boundaries may be derived [22,59,60] from Fresnel’s reflection laws (Eq. 4.4 - 4.7)

$$R_{1234} = |r_{1234}|^2 = \frac{r_{12} + r_{234} \exp[i2k_zd_2]}{1 + r_{12}r_{234} \exp[i2k_zd_2]}$$  (4.9)

The indices, $i = 1-4$, correspond to the layers of the multi-layer sample in Fig. 4.5. The laser (red arrow) is incident on the sample surface at $z = 0$, between layer 1 and 2, where 1 is in air. The amplitude reflection coefficients $r_{12}$ and $r_{234}$ are

$$r_{12} = \frac{n_2^2k_z1 - n_2^2k_z2}{n_2^2k_z1 - n_2^2k_z2}$$  (4.10)
$$r_{234} = \frac{r_{23} + r_{34} \exp[i2k_zd_3]}{1 + r_{23}r_{34} \exp[i2k_zd_3]}$$  (4.11)

in which $\rho=0$ (or $\rho=1$) corresponds to the TE (or TM) polarization and $d_i$ is the thickness of layer $i$. The normal wave vector component of the two reflection amplitude coefficients is

$$k_{z,i} = \frac{2\pi}{\lambda} \sqrt{n_i^2 - N^2}$$  (4.12)

in which $\tilde{n}_i = n + ik$ is the complex refractive index of medium $i$ (see Eq. (4.3)) and $\lambda$ the wavelength of the laser beam. $N = n_i \sin \theta_i$ is the normalized tangential component of the wave vector and seen to be independent of the medium due to Snell’s law (Eq. (4.2)). This means that $k_{z,i}$ depend on both the refractive index $n_i$ and the angle of incidence $\theta_i$. Thus, $R_{1234}$ of Eq. (4.9) also depends on the complex refractive index and the angle of the incident laser beam – and on the layer thickness and polarization of the light. A corresponding expression for the transmittance also exists, but only $R$ is studied here.

4.2.2 Brewster Angle

A laser beam incident on a boundary surface (Fig. 4.1) will be completely transmitted through the interface at a particular angle of incidence $\theta$, such that the reflectance will go to zero at this specific angle – the Brewster angle for TM polarized light. TE polarized light is both reflected and transmitted for that angle. The phenomenon only occurs for non-conducting materials with no absorption, i.e. the extinction coefficient $k = 0$. The reflectance calculated (by Eqs. (4.9) - (4.12)) for a laser beam incident on an interface between two media with refractive index $n_1 = 1$ (refractive index of air) and $n_2 = 2$ is plotted as a function of the incident angle $\theta_i$ in Fig. 4.6 for TE (red) and TM (blue squares) polarized light. The reflectance of the TE polarized light increase with $\theta_i$, whereas the TM reflectance initially decrease until the Brewster Angle where all light is completely transmitted. After the Brewster Angle the TM reflectance increase to reach the TE reflectance at 90$^\circ$.

Similarly, the TE and TM reflectance from an interface between a non-conducting material ($n_1 = 1$) and a conducting material ($n_2 = 2 + i2$) is calculated and plotted in Fig. 4.7, in which the TM polarized light (blue) initially decreases with the incident angle until the Brewster angle. The reflectance does not reach zero at this point, since a part of the light is absorbed in the conducting material due to the extinction coefficient $k = 2$ of the second media and is eventually converted into thermal energy. The TM polarized light is thus not completely transmitted through a conductor at the Brewster angle due to absorption.
4.2.3 Diffraction, Scattering and Roughness

A laser beam incident on a smooth surface will be reflected in one collimated and well-defined beam as Fig. 4.8a illustrates, if the size of the ridges and valleys on the surface are small compared to the wavelength of the incident beam, $\lambda$. In contrast, the incident laser beam will not be reflected into a single collimated beam, when the sample surface is rough, i.e. when the size of the ridges is large compared to $\lambda$, but rather reflected in many directions as shown in Fig. 4.8b [55, 61]. The divergence of the diffused reflected beam depends on the surface roughness where the extreme case shown illustrates the principle.

4.3 Optical Monitor of Coatings

The reflectance $R$ measured of a sample surface depends on the complex refractive index $\tilde{n}$ of the surface material, the wavelength $\lambda$, the angle of incidence $\theta$ and polarization (TE or TM) of the incident laser beam – and also the thickness $d$ of the surface material layer (see section 4.2.1). Naturally, $R$ also depends on the properties of the underlying layers (see Fig. 4.5) when the top coatings become transparent for the laser beam. It is thus possible to estimate the layer thickness $d$ of the top coating simply by measuring the reflectance – if of course $\tilde{n}$, $\lambda$, the polarization and $\theta$ are known in advance. A slight variation of this perception has been utilized in the principles of an optical monitor for wear control. It is possible to optically monitor the wear of the steel tool surface by having the mould piece or steel tool coated initially with a signal layer and subsequently with a top tribological coating. If the two coating materials are carefully selected with significantly different optical properties – that is with respect to the complex refractive index $\tilde{n}$ and the wavelength $\lambda$ at which the system is monitored, it is then possible to achieve
4.3. OPTICAL MONITOR OF COATINGS

a significant change in the optical reflection when wearing through the tribological and signal coatings. This is seen in Figs. 4.9 and 4.11, in which the theoretical reflectance \( R \) from two individual warning systems has been calculated with \( \lambda = 633 \text{ nm} \) and \( \bar{n} \) as obtained (Tab. 10.7) by use of Eqs. (4.9) - (4.12).

4.3.1 Warning Signals

Both the TE and TM reflectance of the first warning system calculated as function of a top TiN layer thickness with an embedded TiO\(_2\) signal layer, \( R(d_{TiN}) \) is shown in Fig. 4.9. The reflectance level is unchanged for large TiN layer thicknesses. But, as the TiN top coating reaches zero thickness and thus the embedded signal layer, \( R(d_{TiN}) \) suddenly drops. This significant change is caused by the different optical properties of the two specific coating materials selected for the first system and it can thus be utilized in a warning system with more than one signal layer embedded in the tribological coating. Adding several embedded TiO\(_2\) signal layers to the tribological coating, several warning signals in terms of a significantly decreased reflectance signal will be achieved as Fig. 4.10 displays, in which two TiO\(_2\) signal layers are embedded within the tribological TiN coating, leading to a 1\(^{st}\) and a 2\(^{nd}\) warning signal. Thus, these two abrupt dips in the TE reflectance correspond to the position of the embedded signal layers.

Figure 4.9: The reflectance starts decreasing for a specific TiN layer thickness on top of TiO\(_2\).

Figure 4.10: Two TiO\(_2\) signal layers lead to two warning signals.

Figure 4.11: The reflectance starts increasing for a specific TiAlN layer thickness on top of TiN.

Figure 4.12: Two TiN signal layers lead to two warning signals.
A similar but opposite system is seen in Fig. 4.11, where the TE and TM reflectance is also calculated as a function of, in this case, a top TiAlN layer thickness with a TiN signal layer embedded beneath the top TiAlN tribological coating, i.e. $R(d_{TiAlN})$. The reflectance is in this case seen to have a fairly low level for large TiAlN layer thicknesses, but as the TiAlN top coating reaches zero and thus the embedded TiN layer, both the TE and TM reflectance rises significantly. This significant rise is caused in a similar manner by the difference in the optical properties of the two specific coating materials selected, but in a reverse way. This 'opposite' system can also be used in a warning system for an optical monitor, when adding several signals to the tribological coating. Again, having several embedded signal layers in the tribological coating of this system, several warning signals in terms of significant rises in the reflectance signal will be observed. In Fig. 4.12 two TiN signal layers are embedded in the tribological coating causing two sudden peaks in the reflectance – a 1st warning and a 2nd warning. The two significant peaks correspond, as in the previous case, to the position of the two embedded signal layers, which thus act as – signal layers.

The principles of the two types of warning systems seen in Figs. 4.10 and 4.12 are basically identical. A steel tool or mould piece is coated with a tribological coating where signal layers, as the two examples illustrates, are embedded within the tribological coating. The key point of the system is the difference in the optical properties of the two coating materials selected for the warning system such that the difference in the reflectance is also significant when going from the tribological coating to the signal layer, as in either of the two system types seen in the figures. Thus, it is in this way theoretically possible to optically monitor the coatings of a steel tool or mould piece as the coating layer thickness is decreasing.
Chapter 5

Tribology of Coatings

Initially, the concept of friction between two objects is discussed, followed by a description of some properties in the wear mechanisms in coatings tribology. Additionally, a short discussion on tribological hard coatings and the concept of hardness and other material parameters are given in the end.

5.1 Friction

Two bodies in contact, with one of the bodies moving tangentially over the other, experience friction as Fig. 5.1 illustrates. The forces acting the moving body are drawn schematically; W is the force of the body, N the normal force, F an externally applied force and \( F_{\text{friction}} \) is the friction force [62], where friction experienced during a sliding motion is known as sliding friction. \( \mu \), the friction coefficient describes the degree of friction in a contact, between the two bodies and is given by the tangential frictional force \( F_{\text{friction}} \) divided by the normal force, N

\[
\mu = \frac{F_{\text{friction}}}{N},
\]

where \( F_{\text{friction}} \) is the force required to initiate or sustain the sliding motion of the body [63], i.e. \( F > F_{\text{friction}} \) in order for the body to move. The friction coefficient is not a 'true' physical constant but an empiric quantity, which means that large variations may occur.

5.1.1 Adhesion and Deformation Friction

Generally, \( F_{\text{friction}} \) consists of two components; friction due to adhesion between the two contacting surfaces, \( F_a \), and friction due to deformation of the surfaces, \( F_d \) [64]. The latter component is in turn

Figure 5.1: Diagrams of forces acting on a body on a flat surface.
divided into deformation friction due to ploughing $F_{d_1}$ and friction due to asperity deformation $F_{d_2}$, leading to

$$F_{friction} = F_a + F_{d_1} + F_{d_2}.$$ 

These three components constituting the friction force of a sliding friction contact are illustrated together in Fig. 5.2, in which the specific friction types are drawn individually on a large scale.

**Adhesion**

Adhesion friction is a result of continual formation and breakage of bonds between asperities of the sliding surfaces, such that asperities on the surface of one body come in contact with surface asperities of the opposing body and form welded junctions, which must be cut or sheared to uphold the sliding movement [65]. Figure 5.2 display such a contact between asperities in the ‘adhesion’ part. The bonds are formed by interatomic forces between the atoms in the contact interface, which depend on the surface composition and the degree of surface asperities, i.e. if sharp peaks from each body penetrate the other surface [63]. In order for the sliding to occur the friction force must ’cut’ the weakest tangential planes at areas of contact – areas where the two bodies actually touch each other. Thus, $F_a$ depends on the shear strength between the interfacing bodies and on surface energy characteristics of the contacting materials, rather than on properties of a single component [63].

**Ploughing**

In a sliding contact, with one of the contacting surfaces being harder than the other, asperities such as sharp roughnesses on the harder surface may penetrate or plough into the other body of a softer surface material [65]. This ploughing into the softer material is resisting the sliding movement of the contact and thus adding to the friction between the two bodies in the contact. Also, wear particles impacted or squeezed together in the contact interface may plough into the softer surface as the center part of Fig. 5.2 illustrates. A foreign particle is ’peeling’ a large chunk of the softer material or ploughing its way into the softer body, which naturally also resists the sliding and thus adds to the friction force. Thus, the ploughing component of friction, $F_{d_1}$, depends on general material properties (e.g. soft, hard) and on the geometry of the surface asperities ploughing into the softer surface, but also on the geometric properties of the penetrating wear particles [63].
Asperity Deformation

Two approaching asperities in a sliding contact (see Fig. 5.2) must inevitably undergo some kind of deformation for the two asperities to pass each other and the sliding movement of the contact to continue. The two asperities move towards each other; the top asperity move to the right and the bottom asperity to the left. The degree of deformation depends on e.g. the normal load acting on the system [65].

The two deformation components of friction, $F_{d1}$ and $F_{d2}$, differ in the size scale of the involved asperities [64]. The deformation of asperities occurs only for asperities with sizes measured on a micro-scale, whereas the ploughing takes place with larger asperities and with wear particles measured on a macro-scale. Actually, detailed studies of microscopic friction mechanisms showed that in most sliding situations, deformation friction as a result of surface ploughing by wear particles (center part Fig. 5.2) is the most important component of the parts constituting friction [66]. This means that wear particles, such as either harder surface asperities ploughing into a softer surface or regular particles ploughing the surface, are responsible for the main friction contribution in a sliding friction contact.

5.1.2 Development of Friction in Time

A sliding contact experiences a number of phases of friction mechanisms during a sliding experiment as Fig. 5.3 illustrates. The friction coefficient of a sliding steel contact, plotted as a function of time, develop in time with 6 phases identified [65]. The relative contributions to the friction from adhesion, ploughing and asperity deformation depend on the specific materials used, the surface topography, the environment and on the condition of the contact, which in turn is influenced by the sliding history.

**Stage 1** Friction is mainly due to ploughing by asperities. Also asperity deformation takes place, which results in a polishing of the surface. Friction due to adhesion is insignificant during the initial phase due to the presence of surface contaminants, as these prevent contacting materials to form bonds.

**Stage 2** The previous contaminants have been removed by polishing wear processes causing areas of bare contacting interfaces (see Fig. 5.2 left) to appear. As a result, a slight increased friction due to adhesion is seen.

**Stage 3** A fast increase in the number of wear particles trapped in the contact, as a consequence of higher wear rates, causes a fast increase in the friction due to ploughing and larger clean areas result in an additional increased effect on the friction from adhesion. Friction due to asperity deformation also contributes as long as these are present in the contact.

![Figure 5.3: 6 stages of friction mechanisms in a steel sliding contact. Adapted from [64, 65].](image-url)
Stage 4  The number of wear particles leaving the contact equals the number of new particles entering. This leads to a steady-state condition combined with a steady-state situation for the asperity deformation and adhesion friction. Asperity deformation continues to contribute, since new sharp asperities may form due to wear by delamination. This steady-state situation continues when two identical materials slide against each other.

Stage 5  A hard surface material sliding against a softer surface may cause asperities of the harder material to be removed leading to a very smooth surface. The deformation of asperities are thus decreasing together with ploughing by wear particles, since wear particles cannot easily anchor in a polished surface.

Stage 6  Both the hard and soft surfaces have been polished to a mirror-smooth surface and the friction coefficient reaches a steady-state value where few changes occur.

5.2  Wear Mechanisms

Wear is the removal of material when two solid surfaces move against each other in a contact (see Fig. 5.2), which makes both friction and wear a result of the same tribological sliding contact processes [64]. Four basic wear mechanisms are responsible for the removal of material; adhesive, abrasive, fatigue and chemical wear as Fig. 5.4 illustrates, where most wear situations involve a combination of mechanisms.

**Adhesive Wear**  Two counter facing asperities in a contact may stick together or adhere to each other and form a junction as illustrated in Fig. 5.4A. The sliding motion of the contact may subsequently cause a separation in the bulk of the softer asperity leading to material removal from the softer surface asperity.
5.2. WEAR MECHANISMS

**Abrasive Wear and Asperity Deformation** Abrasive wear takes place in contacts with one surface being considerably harder than the other, in which both hard asperities (Fig 5.4B, left hand side) and hard wear particles introduced in the contact (Fig 5.4B, right hand side) cause removal of material from the softer surface.

**Fatigue and delamination Wear** Growth of fatigue cracks as a result of continuous loading and unloading on a surface, at stress levels such that the surface material cannot sustain the repeated loadings, consequently cause surface parts or wear debris, to detach due to fatigue as shown in Fig. 5.4C. Delamination wear takes place on a microscopic scale, where small fatigue cracks nucleated below the surface tend to propagate parallel to the surface leading to plate-like wear debris.

**Chemical Wear** This wear process is dominated by destructive chemical reactions in the contact causing removal of surface material as Fig. 5.4D illustrates. The most typical chemical wear process is oxidational wear. A thin oxide layer present on surfaces causes friction on these materials to be relatively low. However, if the oxide layer is continuously removed in a sliding contact the formation of a new oxide layer is speeded up leading to increased wear of the surface material.

### 5.2.1 Tribological Test Machines – Sliding Wear

Wear tests in a sliding configuration may be performed in several different ways with different geometrical configurations of the test machines [67].

**Pin-on-Disc**

'Pin-on-disc’ is a well known and frequently used test configuration in sliding wear tests due to the setup flexibility with a large number of variable parameters, such as attached heat stages and controlled isolated atmospheres. Figure 5.5 illustrates the basic principles of the set-up, in which a pin incident on the surface of a rotating disc induces a circular wear track on the surface of the disc. The normal load is applied either through the pin as indicated by the vertical arrow or via the base sustaining the disc.

**Linear Reciprocative Tribo-Tester**

A linear reciprocating tribometer is commonly used in sliding wear tests due to the simplicity of the set-up configuration and the variety of external parameters. It consists essentially of a pin and a sample surface as the schematical drawing in Fig. 5.6 displays, where the pin moves in a reciprocating motion back and forth across the surface – or the sample correspondingly moves while the pin is fixed. The normal load is applied either from above via the pin or from below via the base supporting the test sample.

![Figure 5.5: Pin on rotation disc. From [67].](image1)

![Figure 5.6: Reciprocating pin on flat. From [67].](image2)
It should be mentioned that the friction force is largely independent of the sliding velocity [68], which generally means the friction force in the two different tribological test machines is unaffected by the movement of the contact. Consequently, the friction force is not influenced by the varying contact velocity in the reciprocating motion of the linear tribometer.

5.3 Tribologically Coated Surfaces - Hard Coatings

Introducing a second layer to a surface means that the tribological surface behavior is most likely altered – this is quite commonly known since for instance adding a second coating by oiling a bicycle chain changes the ride significantly. Other protective tribological coatings, which are not soft or greasy as oil, are for example hard coatings. These are used more and more frequently [69] due to the possible improvements of the mechanical and chemical properties of a surface, for which a variety of such coatings exists, some of which are based on nitrides, borides or carbides. Other coatings based on carbon such as diamond-like carbon (known as DLC) are also frequently used.

5.3.1 Tribological Mechanisms of Coated Surfaces

The tribological properties and mechanisms of coated surfaces are different from non-coated surfaces. A hard coating covering a soft surface separates the soft substrate material from a counterface and may in this way reduce the wear by prevention of surface ploughing. Hard coatings are thus particularly useful in abrasive wear situations. Properties influencing the tribological processes in a contact, which has one or two coated surfaces, are the coating thickness, the surface roughness and the size and hardness of wear debris in the contact [64]. Figure 5.7 schematically represents six tribological contacts where a hard spherically shaped slider moves over soft substrates (light grey) covered with hard coatings (dark grey).
A hard smooth sphere slides in Fig. 5.7 over a soft substrate covered with either a thick (a) or a thin (b) hard film without any debris present in the contact, where the thick film support the softer substrate during the load such that deformation is at a minimum. This reduces the contact area and wear due to ploughing and shear is decreased. The thin film may on the other hand may not sustain the load and the combined film and substrate surface consequently deform such that repeated surface deflection may cause fractures and fatigue cracks that will destroy the thin coating.

A rough slider moving over a rough surface coated with a thick hard coating may show no surface deformations as Fig. 5.7c illustrates. The sphere is moving over a number of small asperities and this continues only for very hard spheres and coatings, since the contact pressure at each asperity is very high. Surface deformations are on the other hand seen if the hard coating is thin (d), in which case an increased number of asperity contacts are seen. The repeated loadings of the asperities (as the slider moves across the surface) result in an increased probability of fatigue fractures.

Wear debris and loose particles, originating from the environment or developed in the contact by different wear mechanisms, are often present in sliding contacts. Particles in a contact may hide in valleys and gorges as seen in Fig. 5.7e, where the wear process take place on the asperity tops in the contact, such that the particles show no or little influence on the actual wear. Increased friction and wear is, on the other hand seen, if the contact roughness is removed such that the particles no longer can hide in the asperity gorges. Depending on the hardness of the particles, they may either be crushed and destroyed under the load in the contact if the particle hardness is smaller than the hardness of the surfaces, or the particles may be trapped by the surface roughnesses and cause ploughing and scratching in the contact if the particle hardness is higher than the surfaces’ hardness.

5.4 Material Parameters in Tribology

The tribological behavior such as properties of friction and wear of materials depends on several different properties, some of which depend on either surface characteristics or on characteristics of the bulk material.

5.4.1 Mechanical Properties in Bulk Material

Tribological and mechanical properties of bulk materials are connected to characteristics of the material such as the deformation behavior and the response to surface loading. The most important parameters describing these characteristics are the elastic modulus, the material strength, the hardness and the toughness [64], even if several other material properties [63] also influence the tribological properties of bulk materials.

Young’s modulus, also known as the elastic modulus, describes the elastic deformation of a material. Elastic materials are characterized by a reversible deformation when unloaded, which means that the materials return to the initial shape without changes. Materials such as rubber has a very low elastic modulus, whereas e.g. ceramics have a very high value for the elastic modulus. The material strength describes the plastic deformation of a material, which is the opposite of the elastic deformation, such that a plastically deformed material remains permanently deformed after the unload [64]. The hardness H characterizes the material resistance to permanent deformation and depend on properties as structure,
CHAPTER 5. TRIBOLOGY OF COATINGS

chemical bonding, grain size of the coating [9,70]. It is defined by an indenter’s normal force (or applied load) \( L \) divided by the area of indentation \( A \), i.e. \( H = L/A \) and is as such an unsophisticated method for measuring the material strength [71]. Extremely hard coatings are measured with the specialized Vickers Hardness Test and the Vickers number \( HV \) is found by the relation

\[
HV = 1.854 \frac{F}{A^2},
\]

where \( F \) is the applied load and \( A^2 \) is the area of indentation measured in mm\(^2\) [72].

Surface Properties

The tribological properties with respect to the surface conditions of materials depend on various characteristics such as the surface roughness, the degree of purity and surface contaminations. Also, adsorbates due to interactions with the environment and the degree of surface oxidation influence the tribological properties of materials.

5.4.2 Wear Rate

Material wear may be characterized by a more general value for the amount of wear, a standardized wear quantity [73,74] also known as the specific wear rate. The different rates may then be compared regardless of e.g. different experimental parameters. It is defined as the worn volume divided by the normal load times the distance [64]

\[
k = \frac{V}{Fd}, \tag{5.1}
\]

where the volume of removed material (corresponding to the volume of the 'halfpipe' shaped wear scar) is given by \( V (= L_x \cdot L_y \cdot L_z = A \cdot L_y) \). The area of removed material \( A (= L_x \cdot L_z) \) is usually found in a cross section of the scar. \( F \) is the normal load applied to the contact during the wear process and \( d \) the sliding distance. For a reciprocating motion \( d \) is the total traveled sliding distance. Thus, \( d = 2 \cdot s \cdot n \), where \( s (= L_y) \) is the scar length, \( n \) the number of cycles and the factor 2 arising from the reciprocating motion (back and forth) during the wear process in the linear tribometer [75]. Accordingly, the wear rate for a reciprocating wear test, normally given in units of \( 10^{-6}mm^3/Nm \) [64], may be expressed in terms of

\[
k' = \frac{A}{F \cdot 2 \cdot n}. \tag{5.2}
\]
Chapter 6

X-Ray Radiation

Synchrotron radiation is discussed in this chapter together with X-ray Absorption Spectroscopy (XAS) and in particular XANES and EXAFS. A description of the XAS during the wear process is also included.

6.1 Synchrotron Radiation

Synchrotron radiation is known as radiation from charged particles traveling at relativistic speeds in magnetic fields, which force them to follow a curved path [76]. An electron (or positron) moving at relativistic speeds in a uniform linear motion does not radiate. But when the electron is forced to follow a curved path, e.g. by an applied magnetic field, \( B \), the electron accelerates as a result of Newtons 2\textsuperscript{nd} law;

\[
F = |e| v \times B = ma.
\]

Thus, the electron accelerates and radiation is emitted when the electron path is changed. Figure 6.1 shows a typical storage ring with straight sections followed by circular arc segments, in which bunches of electrons circulate such that beams of X-ray photons (blue fans) are emitted during a bend due to the applied magnetic field, \( B \).

6.2 Photoelectric Absorption

An X-ray photon may, when interacting with matter, move an atomic electron from a shell into the continuum of free states by simultaneously annihilating the photon, if the photon has an energy larger

\[
\text{Figure 6.1: Principles of a synchrotron. Collimated X-ray beams (blue fans) are emitted at each bend.}
\]
than the binding energy of that specific atomic electron. A schematic atomic energy level diagram in Fig. 6.2 shows the inner atomic shells and subshells, in which the incoming X-ray photon is absorbed, the atomic K-shell electron kicked out and a hole created. This is possible only, when the photon energy is above a certain threshold value – the electron binding energy. Atomic electrons are bound to an atom with specific discrete energies, binding energies, leading to discrete jumps, when the absorption, is measured as a function of the X-ray photon energy. An example of this discrete jump in the absorption is shown in Fig. 6.3. X-ray absorption is strongly dependent on the atomic number, \( Z \), of the elements contained in the absorbing material, as it approx. varies with \( Z^4 \) [76]. The transmission through a material of thickness \( t \), seen in Fig. 6.4 is given by the exponential decay of the absorption coefficient of the material, \( \mu_a \):

\[
T = \frac{I}{I_0} = e^{-\mu_a t},
\]

i.e. determined through the ratio of the radiation intensity measured before \( (I_0) \) and after \( (I) \) the sample. The absorption coefficient is also related to the absorption cross-section, \( \sigma_a \), by the mass density of the material, \( \rho_m \), Avogadro’s number, \( N_A \), and the atomic number of the material, \( A \), through the relation;

\[
\mu_a = \left( \frac{\rho_m N_A}{A} \right) \sigma_a,
\]

which means it is possible to achieve the absorption cross-section or the absorption coefficient of the material by measuring the transmission \( T \) of the X-ray photons through a material – if the thickness of the material is known and vice versa.

### 6.2.1 XAS – XANES and EXAFS

An x-ray absorption spectrum (XAS) is often divided into two regions [78]: the X-ray Absorption Near Edge Structure (XANES) and the Extended X-ray Absorption Fine Structure (EXAFS) as the absorption spectrum (Fig. 6.3) with annotated regions shows. The two regimes have identical physical origin, but the spectrum is split for easier analysis and interpretation, since the two methods are used differently.

XANES is also known as Near Edge X-ray Absorption Fine Structure (NEXAFS). It is typically measured within some decades of eV of the main absorption edge, i.e. the discrete jump in the absorption. Furthermore, XANES is sensitive to the chemistry of the absorbing atom, since many elements show significant edge shifts with oxidation states as Fig. 6.5 displays for Chromium III and VI.
6.3. ABSORPTION DURING WEAR

EXAFS is often measured within some hundred of eV of the absorption edge [79] and the spectrum usually examined with analytical approximations, once the edge step and the background absorption are removed and only the isolated wiggles, corresponding to near neighbor coordination shells, are studied [80]. It will not be elaborated further here on that, since EXAFS was used solely for a detector pixel to X-ray photon energy calibration.

XANES is quite useful in e.g. oxidation studies as the position of the absorption edge is determined by the chemical bonds, while EXAFS is useful for e.g. species determination. The wiggles or oscillation-like structures in the XAS spectrum (Fig. 6.3) are caused by scattered waves interacting with neighboring atoms [76]. Thus, wiggles are not observed from free atoms in gases. Only a sharp increase in the absorption (an edge) is seen in this case.

K-edge The discrete jump in the absorption observed around energies corresponding to the binding energy of an atomic electron in the K shell is known as an K-edge, where the edge is caused by the photo electric absorption just discussed. An iron K-edge is seen in Fig. 6.3 and chromium K-edges in Fig. 6.5.

6.3 Absorption During Wear

The transmission and thereby also the absorption depends on the thickness $t$ of the material, the photons pass through (see Eq. (6.1)), such that the total transmission $T$ increases as the thickness $t$ decreases. This is valid for all energies and materials. The decreasing or thinning of the sample thickness could, as in this case, be due to a wear process, where material is removed. Looking then, for instance, at specific X-ray energies combined with specific materials, a more significant signal is seen (Fig. 6.7).

6.3.1 Wear-Marker Layer

A small cartoon illustrates in Fig. 6.6 different stages of a TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample (see Fig. 2.9) exposed to a wear process while simultaneously being probed with X-ray photons. Initially, the top TiAlN coating is exposed to the wear process while simultaneously being probed with X-ray photons. Initially, the top TiAlN coating is exposed to the wear process and removed (1). After TiAlN is removed, the underlying CrN wear-marker layer is also exposed to the continued wear process and consequently also removed (2). Finally, the CrN layer is worn away and the embedded TiAlN layer exposed (3). Two different schemes are possible when probing the wear process with X-ray photons;

![Figure 6.4: The intensity of the X-ray beam before, $I$, and after, $I_0$, the sample with absorption coefficient $\mu$ and thickness $t$.](image)

![Figure 6.5: XANES on the chromium K-edge for $Cr^{3+}$ and $Cr^{6+}$ show significant shifts in the edge and pre-edge appearance and position. From [77].](image)
either to measure the total absorption or the specific absorption. The total absorption at energies away from the chromium K-edge, will according to Eq. (6.1) decrease continuously during the wear process, i.e. during the thinning of the sample material. This is depicted in orange in the principle drawing of Fig. 6.7, in which the total absorption decreases evenly as the sample thins out during the three stages.

It is also possible to measure the specific absorption, where the X-ray photon energies are kept on the chromium K-edge. In this case the specific absorption (green line) is initially unaffected, since the thickness of the CrN wear-marker layer is untouched (1) at this point. When the wear reaches the CrN layer (2) a decrease in the specific absorption is seen, since the wear-marker layer is wearing out. The specific absorption continues consequently to decrease until all chromium is removed. Finally, the complete CrN layer is worn off (3) and the specific absorption stops decreasing as seen in Fig 6.7.

Figure 6.6: X-ray probing of wear process. 1) Initially, the TiAlN top coating is removed, subsequently 2) the CrN wear-marker Layer and finally 3) the embedded TiAlN layer is exposed to the wear process, while the complete wear process is measured in-situ by X-ray absorption.

Figure 6.7: The total absorption (orange line) decreases during the complete wear process due to thinning of the sample, while the specific absorption (green line) at the chromium K-edge only decreases during wear of the CrN wear-marker layer; situation (2) of Fig. 6.6.
Part III

EXPERIMENTS
Chapter 7

Film Production & Characterization Methods

Different experimental methods for producing the various films used in this work (TiO$_2$, TiN, TiAlN and CrN) are described in this chapter together with employed thin film characterization methods, such as e.g. RHEED, CASINO and The Laser Reflectance method.

7.1 Film Production

TiO$_2$ and TiN thin films were produced with PLD for RHEED studies, whereas TiN, TiAlN and CrN films were produced by PVD and TiO$_2$ by e-beam evaporation for the combined optics and wear study.

7.1.1 Pulsed Laser Deposition

Thin films of TiN and TiO$_2$ were deposited in a large area PLD setup as illustrated in Fig. 7.1 and previously discussed in [81]. The setup consists basically of a ultra high vacuum (UHV) chamber with a base pressure of $10^{-9} - 10^{-7}$ Pa, in which the film deposition takes place, some optical parts placed outside the chamber, and a KrF (krypton fluoride gas) excimer lasing at wavelength $\lambda = 248$ nm. An additional

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**Figure 7.1:** Drawing of the PLD setup.  
**Figure 7.2:** Photo of the PLD setup placed at Risø.
chamber connected to the main UHV chamber was used as a load station (not included in Fig. 7.1), through which substrates and targets are transferred to the main (deposition) chamber without breaking the ultra high vacuum. The two chambers are disconnected during deposition to avoid contamination of the subjects stowed inside. Figure 7.2 shows a photo of the complete PLD setup.

The laser beam was focused on either a target of TiO$_2$ or TiN as Fig. 7.3 shows, where the substrate was kept at a constant temperature of 700 °C and located 88 mm above the target during the film deposition. Ablated target material (multicolored object) gather and accumulate as a thin film on the substrate (see sections 3.1 and 3.2). A rotational motion of the target combined with a rastering motion of the beam spot position on the target prevent the laser from ‘drilling’ a hole in the target surface.

**TiO$_2$**

A target of synthetic rutile TiO$_2$ ($\varnothing = 24.5$ mm) [82] was irradiated with 20 ns laser pulses of fluence 0.5 - 1 J/cm$^2$ and frequency of 1 Hz (see Tab. 7.1). An oxygen background pressure of 0.1 mbar was introduced in the vacuum chamber during the deposition process (to maintain the stoichiometry of the grown TiO$_2$ films) together with an inert background gas of argon.

<table>
<thead>
<tr>
<th>PLD Settings</th>
<th>TiO$_2$</th>
<th>TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser frequency</td>
<td>1 Hz</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Fluence</td>
<td>0.5 - 1 J/cm$^2$</td>
<td>4 J/cm$^2$</td>
</tr>
<tr>
<td>Laser pulse duration</td>
<td>20 ns</td>
<td>20 ns</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>700 °C</td>
<td>700 °C</td>
</tr>
<tr>
<td>Distance (target - substrate)</td>
<td>88 mm</td>
<td>88 mm</td>
</tr>
<tr>
<td>Target material</td>
<td>TiO$_2$</td>
<td>TiN</td>
</tr>
<tr>
<td>Background pressure</td>
<td>0.1 mbar</td>
<td>0.02 mbar</td>
</tr>
<tr>
<td>Background gas</td>
<td>O$_2$</td>
<td>N$_2$</td>
</tr>
<tr>
<td>Inert background gas</td>
<td>Ar</td>
<td>Ar</td>
</tr>
</tbody>
</table>

**Table 7.1:** Various settings for depositing TiO$_2$ and TiN films by PLD.
The MgO substrates (Fig. 2.4) were prior to the TiO₂ film deposition heat treated in a 100% O₂ atmosphere at a temperature of 1050 °C for 5 hours with a ramp of 100 °C pr hour from 0 to 900 °C, followed by a ramp of 50 °C pr hour from 900 to 1050 °C. The substrates were cooled down with a reverse ramp (see Fig. 7.4 of the temperature as a function of the time) and after the annealing quickly transferred from the furnace to the preparation chamber. This specific MgO annealing process has been showed by Dégardin et al. [83] to result in optimal conditions for monitoring of layer growth by use of RHEED.

TiN

Thin films of TiN were also grown on MgO substrates but with slightly different parameters, where a stoichiometric TiN target (⌀ = 24.5 mm) [82] was irradiated with 20 ns pulses at a fluence of 4 J/cm² and a frequency of 10 Hz (see Tab. 7.1). Additionally, a background gas of nitrogen at 0.02 mbar was present in the deposition chamber in order to keep the stoichiometry of the deposited TiN film. The MgO crystals (⌀ = 24.5 mm) [82] were prior to the deposition process and RHEED study also thermally annealed, in this case at 1000 °C for 40 hours with a temperature ramp similar to that of Fig. 7.4. The substrates were afterwards quickly transferred to the preparation chamber.

7.1.2 Physical Vapor Deposition And E-Beam Evaporation

Coatings of TiN, TiAlN and CrN were produced in an industrial magnetron sputtering setup from CemeCon AG by the commercial manufacturer and project partner, CemeCon A/S, and thin TiO₂ films were commercially produced by electron beam evaporation in an argon gas by the commercial manufacturer, FerroPerm. The principles of PVD were previously discussed in section 3.1.2 together with a short e-beam evaporation description in section 3.1.3 above (see e.g. Fig. 3.6).

A photo in Fig. 7.5 displays the CC 800/9ML magnetron sputter interior with the array of TiN coated samples pointed out and Fig. 7.6 illustrates the basic concept of the specific PVD process employed by CemeCon A/S for TiN coatings. Argon ions (green) are accelerated by the plasma (bluish cloud) towards the titanium target. As a result, Ti atoms (blue) are sputtered from the target, where a simultaneous inlet (left chamber wall) of a reactive N₂ (red) background gas lead to a chemical reaction between Ti and N such that compound molecules of TiN are formed and gathered on the substrate surface with a deposition rate of ∼1 nm/sec [19]. The substrate temperature was kept between 220 and 240 °C.
CHAPTER 7. FILM PRODUCTION & CHARACTERIZATION METHODS

7.2 Film Characterization

Several methods were applied in characterizing the various films, due to the difference in the properties and applications of the films. A description of the various characterization methods are given here.

7.2.1 RHEED

A high pressure RHEED system with typical parameters, electron energy of 35 keV and beam current of 1 µA, was used in the in-situ film growth study of TiN and TiO₂. The pattern, arising from the electrons diffracted of the MgO substrate surface, is reproduced on the fluorescent phosphor screen (see e.g. Fig. 3.10) and simultaneously observed by use of a CCD camera monitoring the screen. The recorded movies were analyzed with the commercial software KSA 400, which simply converts pixel values in the CCD images into an intensity such that a bright pixel leads to a high number and a dark pixel leads to a low number. Different areas of the CCD images of special interest for the RHEED analysis, are possible to select for individual intensity analysis.

Thus, the RHEED system, which basically is the combination of the electron-gun and the screen/camera detector, monitor the changes in the substrate surface structure as target material is transferred to the substrate by the plasma plume as Fig. 7.7 illustrates. The electron beam (green arrow from the e-gun) is diffracted of the substrate surface and into several beams of different directions, while target material is deposited on the substrate. Meanwhile, the camera is recording all changes in the diffraction pattern reproduced on the fluorescent screen.

7.2.2 SEM, EDX Spectroscopy and CASINO

Scanning Electron Microscopy (SEM) was used to estimate the layer thickness by two individual but both quite simple methods – a non-destructive method and a destructive method. The non-destructive method employs a combination of SEM, EDX\(^1\) spectroscopy and the open domain program CASINO v2.42 [85], whereas the destructive method is utilized by simply cutting the sample in two such that a sample cross section is exposed for direct visual inspection.

\(^1\)EDX (sometimes also known as EDS) is short for Energy Dispersive X-ray Spectroscopy. It is an analytical method for identification of different elements within a sample together with the relative ‘amount’ of the specific elements found. The method is based on characteristic energy being emitted (see e.g. photoelectric absorption and characteristic emission in section 6.2 and Fig. 6.2) from different element species, where the emission stimulation is caused by an incident high-energy beam of charged particles, e.g. an electron beam in a SEM as Fig. 7.9 illustrates.
In the destructive method, the sample cross section is placed in a special holder, cast into epoxy and covered with a very thin carbon coating as seen in Fig. 7.8. The carbon tape and coating ensure electron conduction of the sample surface to prevent SEM electrons from disturbing the imaging, where a LV-SEM, TM1000 SEM and Supra SEM were used. A subsequent analysis of the SEM images with the open source software 'ImageJ' [86] gives a layer thicknesses, through a pixel to µm conversion by use of the SEM included distance scaler.

The non-destructive method is very simple and compares basically EDX signals measured from the sample with CASINO simulated signals (calculated results) such that a thickness of the measured film may be obtained. Thus, in the simulations the film thickness of the sample is varied until an intensity matching the measured intensity is found. This non-destructive method is previously described [81] and used in the present study to determine the layer thicknesses of the two multi-layer sample series, TiN-on-TiO$_2$-on-Steel and TiAlN-on-TiN-on-Steel, since the film thicknesses of these films are within the nanometer range (see e.g. Tab. 2.3 and 2.4) and thus not feasible in the destructive method just discussed.

A sample (thin film on substrate) is placed in the SEM vacuum chamber with the e-beam ($E_0$) incident normally on the sample surface as Fig. 7.9 illustrates. The characteristic X-ray photons emitted (see e.g. Fig. 6.2) from the sample interaction volume are detected and the EDX intensity from a specific element $A$ in the film $I_A^{\text{film}}$ ($A$ is e.g. titanium in a TiN film) is measured together with the intensity from a specific element $B$ in the substrate $I_B^{\text{substrate}}$ ($B$ is e.g. magnesium in a MgO substrate), where the substrate and film elements should differ. The ratio of these measured intensities

$$ I_A^{\text{film}} / I_B^{\text{substrate}} \quad (7.1) $$

is compared with the corresponding ratio of simulated intensities $I'$ from film and substrate

$$ I_A^{\prime \text{film}} / I_B^{\prime \text{substrate}} \quad (7.2) $$

i.e. with CASINO’s Monte Carlo simulations of the characteristic X-ray emission intensity from film and substrate.
A snapshot of a Monte Carlo simulation by CASINO [87, 88] is seen in Fig. 7.10, in which electron trajectories are calculated for 48 nm TiN film on top of a MgO substrate, with mass densities as listed in Tab. 2.8. The blue trajectories correspond to electrons absorbed in the sample – leading to emission of X-ray photons of characteristic energies, whereas the red trajectories corresponds to electrons backscattered from elements in the sample. The direction of the incident e-beam of energy $E_0$ is noted in the figure together with the materials and film thickness used in the simulation. Table 7.2 displays other CASINO settings such as the electron beam energy and the number of electron trajectories to simulate.

### 7.2.3 X-Ray Diffraction

XRD, which is short for X-Ray diffraction, was used to analyze and determine the structure of the TiN films deposited on MgO substrates by PLD for the RHEED study. The X-ray diffraction from the TiN films was studied using a STOE & CIE $\theta/\theta$ powder diffractometer with an energy dispersive Kevex detector in a Bragg-Brentano geometry. The radiation used in the specific diffractometer was CuK$_\alpha$.

<table>
<thead>
<tr>
<th>CASINO Settings</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Energy, $E_0$ [keV]</td>
<td>10</td>
</tr>
<tr>
<td>Electron Beam Radius [nm]</td>
<td>10</td>
</tr>
<tr>
<td>Electron Beam Sample Tilt $^\circ$</td>
<td>0$^\circ$</td>
</tr>
<tr>
<td>Number of simulated electron</td>
<td>200</td>
</tr>
<tr>
<td>Number of drawn electron trajectories</td>
<td>200</td>
</tr>
</tbody>
</table>

**Table 7.2:** Settings for the CASINO simulations of the electron trajectories in the film and substrate.
7.2. FILM CHARACTERIZATION

7.2.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) was used in the surface analysis of the thin films produced by PLD for the RHEED studies. The morphology and roughness of the MgO substrate samples and deposited TiN and TiO$_2$ films were measured with an AFM of the type Dualscope$^\text{TM}$/Rasterscope$^\text{TM}$, which is a SPM microscope from Danish Micro Engineering A/S. The subsequent analysis of the AFM images was performed with the corresponding software DME SPM version 1.6.1.0, also from Danish Micro Engineering.

AFM was measured in tapping mode, in which the AFM cantilever oscillates with a frequency close to its resonance frequency. Atomic interaction forces such as Van der Waals, electrostatic forces, etc act on the cantilever as it gets close enough to the sample surface causing the oscillation amplitude of the cantilever to change. These continuous changes in the cantilever amplitude is imaged as the surface topography while the cantilever is scanning across the different structures on the sample surface.

7.2.5 Laser Reflectance, $R$

The laser reflectance $R(\theta)$ as a function of the incident angle, $\theta$, was measured and the refractive index, (see section 4.1.2) determined from numerous samples, such as the TiO$_2$, TiN and TiAlN films and steel (100Cr6) substrate coupons. $R(\theta)$ is measured of a sample as the drawing in Fig. 7.11 sketches, where a laser source basically is reflected of a sample surface and the intensity measured – relative to the initial intensity. The setup consists of a linearly polarized HeNe laser source (HRP050 from Thorlabs) at wavelength $\lambda = 633$ nm, two mirrors, a TE/TM polarizer, a lens, a power meter and a rotational stage.

<table>
<thead>
<tr>
<th>Fixed Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
</tr>
<tr>
<td>Refractive Index</td>
</tr>
</tbody>
</table>

Table 7.3: The reflectance is measured from media 1 or ‘layer’ 1, which is air as seen in Fig. 4.5.
Variable Settings

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angel of incidence</td>
<td>$\theta_i$</td>
<td>[degrees]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>$n_i$</td>
<td></td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>$k_i$</td>
<td></td>
</tr>
<tr>
<td>Layer thickness</td>
<td>$d_i$</td>
<td>[µm]</td>
</tr>
</tbody>
</table>

Table 7.4: Entities of the laser reflectance (Eq. 4.9) which are possibly varied. The indices $i=2, 3$ or 4 corresponds to the layers of Fig. 4.5.

The two mirrors of the optical setup ensure a correct beam line with respect to the center of rotation of the sample, the TE/TM polarizer transmits either TE or TM polarized light (see Fig. 4.3), while the lens diminishes the beam spot size on the sample surface from an initial diameter of $\sim 1$ mm down to $\sim 100$ µm (at $\theta = 0^\circ$), since the spot size is extremely elongated on the surface at $\theta$ close to $90^\circ$. The power meter detector is placed such that the complete beam spot is incident on the detector head. $\theta$ is chosen by the rotational stage, where the sample is placed such that the center of rotation is exactly on the center of sample surface.

7.3 Method for Simulations/Calculations

The theoretical laser reflectance, $R$, was calculated by use of the program Mathematica version 6.0 from Wolfram and Eq.s (4.9) - (4.12), where the fixed parameters ($\lambda$ and $n_i$) are listed in Tab. 7.3 and the parameters possibly varied in Tab. 7.4. The refractive index of media 1 is fixed, since it is the media in which the reflectance is measured – air (see e.g. Fig. 4.5).

Not only the laser reflectance was found by Eq.s (4.9) - (4.12) for the reflectance, but also refractive indices $n$, attenuation coefficients $k$ and different top layer thicknesses $d_2$ were found by initially measuring $R(\theta)$ from a sample and then calculate either of the prospect values – layer thicknesses, refractive indices or extinction coefficients. Obviously, only one parameter at the time could be found by this method - all other parameters of all the layers should be known in advance. This is discussed further in sections 10.2 and 10.3, where the method results in estimated values on refractive indices, but also in sections 11.2 and 11.3, where simulations on layers and wear in terms of decreasing top layer thickness is discussed.
Chapter 8

Wear on Samples

The linear tribometer used in the wear experiments on TiN and TiAlN single layer samples and the TiAlN-on-TiN-on-Steel multi-layer samples is described together with different parameters and settings for the experiment. Additionally, the optics for measuring reflectance of worn TiAlN-on-TiN-on-Steel multi-layer samples is presented together with the camera and image analysis scheme.

8.1 Linear Tribometer

An abrasive wear process via a dry sliding friction was induced on the coated samples by use of a linear tribometer, designed by Guibert et al. [89] and built at Laboratoire de Tribologie et Dynamique des Systèmes (LTDS) in Ecole Centrale de Lyon, France, where it is located. The specific tribometer consists basically of a base, an arm with the contact, an oscillator and a sensor as Fig. 8.1 illustrates.

A sample is mounted between the base and counterpart and a normal load is applied to the sample surface via the base and the steel ball counterpart. The sensor, situated between the arm with the counterpart and the oscillator detects diverse information such as normal load, movement speed, etc. The oscillator controls the horizontal reciprocating movement of the contact and is situated to the right of the sensor but not included in the figure. A feedback loop keeps the applied normal load on a constant level by controlling the deflection of the sensor combined with a vertical movement of the base toward or away from the contact.

![Figure 8.1: Schematics of the linear tribometer with the steel ball counterpart.](image-url)
A photo of the essential parts of the tribometer is displayed in Fig. 8.2a, in which a TiN coated steel sample is exposed to the wear process. The sample is attached to the base by two clamps. This is also visible in Fig. 8.2b, in which a closer view of the contact zone with the arising wear scar is seen. The white substance surrounding the scar is wear residue.

8.1.1 Continuous Varying Amplitude

The highly controlled reciprocating contact movement is executed by the oscillator, which also controls the continuously varying amplitude (CVA) of the steel ball. This is a special tribometer motion, in which the amplitude is slightly reduced for each cycle, i.e. the reciprocating amplitude is continuously reduced for each stroke such that the scar depth continuously increases while the scar length continuously decreases. The CVA movement of the contact returns a right-angled trapezoid shaped wear scar as Fig. 8.3 illustrates. The top coating is removed from a TiAlN-on-TiN-on-Steel multi-layer sample (see Fig. 2.6) by the CVA wear process (Fig. 8.3) such that the TiAlN thickness decreases along the scar and the embedded TiN signal layer appear in the bottom of the scar. Table 8.1 displays the CVA maximum (initial) and minimum (final) amplitudes, $A_{\text{max}}$ and $A_{\text{min}}$, respectively, together with other fixed settings. A small number of cycles leads consequently to a small number of steps along the residual top TiAlN layer thickness and larger cycle numbers result in more steps. This, in turn, may result in an increased roughness along the scar, due to the increased number of steps along the scar.

<table>
<thead>
<tr>
<th>Fixed CVA Wear Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Load, $F$, $[N]$</td>
</tr>
<tr>
<td>$A_{\text{max}}$, $[\text{mm}]$</td>
</tr>
<tr>
<td>$A_{\text{min}}$, $[\text{mm}]$</td>
</tr>
<tr>
<td>Repetition Frequency, $[\text{Hz}]$</td>
</tr>
<tr>
<td>Diamond Grain Size, $[\mu\text{m}]$</td>
</tr>
<tr>
<td>Ratio, resin to diamond powder, $[N]$</td>
</tr>
</tbody>
</table>

Table 8.1: Fixed settings for the CVA wear process. The ratio is between the resin and diamond grains.
8.1. LINEAR TRIBOMETER

8.1.2 Wear Contact

A bearing ball made of 100Cr6 bearing steel (see section 2.2) with a diameter of 12.7 mm was used as the counterpart. However, due to the extreme wear resistance and hardness of the ceramic TiAlN and TiN coatings, a reinforcement of the much softer counterpart is crucial [26, 90], since the steel ball will wear down instead of the tribological coating if the ball surface is not reinforced.

Resin (powder and solvent, MECAPREX KM-EM and KMR) and powdered diamond grains (DIPROTEX MSY 0-0.2 μm) mixed into a viscous paste was applied to the steel ball as a reinforcement. The paste covers the contact zone, dries and hardens within a few hours and results in a uniform coverage almost matching the steel ball surface as Fig. 8.4 shows. The diamond grain size has a maximum diameter of 200 nm and causes an extremely harsh and abrasive wear environment somewhat dissimilar from usual (industrial) wear patterns. But, the purpose of the wear experiment is mainly to remove the top layer such that the embedded signal layer is ideally exposed (see Fig. 8.3) within a realistic time range (hours). Table 8.1 displays the resin to diamond ratio.

8.1.3 Parameters and Settings

A number of fixed parameters such as the applied normal load, the repetition frequency etc. were used for all samples in the wear experiment. Only the number of cycles were changed for the different samples (see Tabs. 8.2 and 8.3). A normal load of 5 N and a repetition frequency of 10 Hz were chosen to achieve a convenient wear rate such that a complete experiment could finish within a few hours including the wear scars induced with a higher number of cycles.

Single Layer TiN In order to establish an understanding of the wear of TiN, a few tests were carried out with ∼2 μm TiN coated samples (see section, 2.3.4). The samples were worn with a different number of cycles (see Tab. 8.2) to facilitate a relation between the wear and the number of cycles, since the aim of the preliminary wear tests is to find the number of cycles needed to wear through the TiN coatings.

Single Layer TiAlN TiAlN was also exposed to the abrasive wear process and necessarily worn through to the substrate, since TiAlN is the top coating material of the TiAlN-on-TiN-on-steel multilayer samples, which must be removed in the CVA process. Two TiAlN sample types of different layer thickness; ∼2 μm and ∼3 μm (see Tab. 2.6), were worn with a different number of cycles ranging from 20 000 cycles up to 90 000. The large number of cycles were required to wear completely through the almost solid layer of ∼3 μm TiAlN and into the steel substrate.
Table 8.2: Variable wear parameter; the number of cycles in a wear test for ~2 µm TiN on steel together with ~2 and ~3 µm TiAlN on steel.

Multi-layer TiAlN-on-TiN-on-Steel The aim of the wear process of the TiAlN-on-TiN-on-steel multi-layer samples (see Fig. 2.6) was to reach wear scars matching the right-angled trapezoid shaped wear scar (of Fig. 8.3) in the best way possible. Thus, the top TiAlN coating should be worn with a specific number of cycles such that the embedded TiN signal layer is just reached in the bottom of the wear scar. Three TiAlN-on-TiN-on-steel multi-layer sample series were worn as Tab. 8.3 displays.

8.1.4 Dektak Profilometer – Wear Scar Characterization

A Dektak scan profilometer (Veeco 200VI) was used to measure the scar depths introduced in the different coatings. This is a standard profilometer, where a very fine needle (stylo) scans across the sample surface in a one-dimensional sample surface measurement. The induced wear scars were also visually inspected by the use of an ordinary light microscope, to possibly establish a direct connection between the diamond grain size in the reinforced counterpart and the large wear scar grooves.

Table 8.3: Variable wear parameter; the number of cycles in a wear test for the three TiAlN-on-TiN-on-steel multi-layer samples of ~0.3, ~1 or ~3 µm TiAlN coating (see section 2.3.5).
8.2 Optical Characterization of Wear Scars

The induced wear scars were studied with a linearly polarized HeNe laser and a simple optical setup described above (see section 4.2). Figure 8.5 illustrates the principle of the reflectance measurement, where the laser beam scans the surface along the wear scar to record the decreasing residual TiAlN layer thickness. Actually, the sample position was translated during the reflectance detection, such that the incident angle was fixed at $\theta = 60^\circ$ during the complete reflectance measurement, since the laser reflectance level (see Eqs. (4.9) - (4.12)) also depend on $\theta$.

Figure 8.6 shows the optical setup for measuring the laser reflectance $R$. It is essentially identical to that of Fig. 7.11, except from the sample translator and the additional lens placed in front of the power meter detector head. The second lens (of a large diameter) collects the reflected (but also much scattered) light and focuses the beam on the detector. The optical setup of Fig. 7.11 measure the reflectance as a function of the incident angle, $R(\theta)$, whereas $\theta$ is fixed while scanning the sample surface in Fig. 8.6.

8.3 Camera and Image Analysis of Wear Scar

A separate wear scar investigation by means of a camera detection and an image analysis was also performed on selected wear scars of the TiAlN-on-TiN-on-steel multi-layer series. The image analysis was done in addition to the laser reflectance, since a camera generally is able to detect much larger surface areas than a laser beam, which in principle is a one dimensional detection scheme (see Figs. 8.5 and 8.6). The two dimensional surface area of the wear scar, illustrated in Fig. 8.7, shows how the embedded golden-like TiN starts to appear along the residual top TiAlN coating and completely visible in the bottom of the wear scar. The image is in principle Fig. 8.3 seen from a top view with identical parameters.

A photo of the wear scar sample, including a ruler, was taken with a standard camera (in this case a Canon EOSD Digital camera) and loaded into a LabView program, the software programming language from National Instruments. A LabView calibration from number of pixels to mm’s was done initially by use of the included ruler. Subsequently, a masked area surrounding the wear scar in the photo, as illustrated in Fig. 8.8, is selected and all pixels within that rectangular selection examined by the program. Each pixel in the selected area is examined in terms of the Red-Green-Blue (RGB) values such that the program reads out an 8-bit number (0-255) for the red, green and blue pixel value, respectively. Thus, three numbers for the RGB values are assigned to each pixel in the selected rectangle. But, only the red and blue pixel values have been used in this study for the two specific material components TiN and TiAlN and their colors.
CHAPTER 8. WEAR ON SAMPLES

Figure 8.7: Top view of Fig. 8.3, with corresponding initial and final amplitudes. Golden TiN layer emerges in the bottom of the wear scar as seen from above.

Figure 8.8: Masked area selects the wear scar, with the emerging TiN coating. Only the selection was used in the image analysis of the wear scar.

The RGB values in a pixel are counted within specific wavelength ranges, which could vary from camera to camera depending on the specification of the particular camera. For the Canon EOSD Digital the red pixel values are approximately counted in a wavelength range from 550 – 700 nm with a peak around 600 nm and the blue pixel values are roughly counted from 400 – 525 nm with a peak around 450 nm [91] as Fig. 8.9 displays, in which the green range is also seen.

Figure 8.9: The RGB response from Canon EOSD Digital camera with respect to wavelength in nm. From [91].
Chapter 9

X-Ray Studies During Wear

The experiment at the ESRF is discussed in this chapter, including an initial short introduction to the X-ray source and the beamlines employed. Also, XANES, EXAFS and the transmitted intensity measuring are described together with the portable linear tribometer employed in the in-situ wear experiment.

9.1 ESRF - European Synchrotron Radiation Facility

The European Synchrotron Radiation Facility (ESRF) situated in Grenoble, France, is a 3rd generation X-ray source, which means it has a brilliance (an expression describing the brightness or intensity of the synchrotron) around $10^{20}$ [76]. A number of bending magnets combined with straight sections and insertion devices leads to a total of 40 beamlines and a circumference of 844 m. A sketch of the ring is shown in Fig. 9.1. Initially, electrons from an electron gun are accelerated in the linac, then transferred to the booster synchrotron where the electrons accelerate until an energy level of $E_e = 6$ GeV is reached. Subsequently, the high-energy electrons are injected into the main storage ring, where they circulate at a nearly constant energy for several hours. The storage ring electron current is typically $I = 200$ mA and the bending magnets produce magnetic fields of $B = 0.8$ T with an opening angle of the synchrotron beam of 0.08 mrad [76,92].

A typical beamline consists of an optics, experimental and control cabin as seen in Fig. 9.2. The optics in the optics cabin manipulate the X-ray beam into required experimental characteristics. The sample is placed in the experimental cabin together with detectors and support mechanism. Finally, the control cabin is employed in controlling the experiment and managing the collected data.

Figure 9.1: Storage ring with initial linear (linac) and circular (booster synchrotron) accelerators and beamlines. From [92].

Figure 9.2: Typical beamline cabins. From [92].
CHAPTER 9. X-RAY STUDIES DURING WEAR

9.1.1 Energy Dispersive XAS Beamline – ID24

The synchrotron radiation measurements at the ESRF were mainly performed at ID24, an energy dispersive XAS beamline [93], in principle consisting of a bending crystal to focus and disperse the polychromatic X-ray beam and a position sensitive detector. Figure 9.3 displays the beamline detector and optics and an additional photo of the bending silicon polychromator crystal is displayed in Fig. 9.4, in which the crystal bend is quite pronounced. XANES and the transmitted intensity were measured at this beamline station with the experimental settings listed in Tab. 9.1.

EXAFS Beamline – BM29

One sample was measured in the BM29 beamline spectrometer, for a subsequent calibration of the XANES measurements (at ID24), since EXAFS is possible at the chromium K-edge. The beamline station was previously described by Filipponi et al. [94] and the diagram in the appendix (see Fig. A.1) displays an overview of the spectrometer.

9.2 XANES

XANES was measured around the chromium K-edge at the energy dispersive ID24 beamline, where the bending polychromator crystal (Fig. 9.3) is both focusing the X-ray beam on the sample and simultaneously dispersing the photons with different energies into different beam paths. Each beam path has a slightly different direction such that photons of different energies reach different areas (pixels) of the position sensitive detector. The detector consists of an array of 2048 pixels where each pixel, due to the polychromator geometry, corresponds to a very short energy range and thus actually measures the amount of photons that are absorbed for the different energies of the X-ray photons.

It was possible to measure XANES (but not EXAFS) at ID24 due to the configuration of the energy dispersion and geometry of the highly focused beam. At the low energy of the Cr K-edge (around 6 keV) the range of the detector corresponds to a relatively short energy range (~150 eV) due to the energy dispersion of the beam path such that only the absorption edge and a few wiggles was observed. At larger energies the range of the detector corresponds to much larger energy ranges and the EXAFS tail may then be measured. A XANES spectrum is plotted as a function of the pixel number in Fig. 9.5.

Figure 9.3: Detector and optics of ID24 beamline, in which the X-ray beam is focused on the sample surface. The figure is from [93].

Figure 9.4: Photo of the dismounted polychromator crystal in ID24. The bending oblong piece in the bottom is the Si polychromator crystal.
9.3 TRANSMISSION

The intensity of transmitted X-ray photons was measured across the wear scar to relate the decrease of the Cr absorption edge in the XANES spectra during the wear process to the amount of removed material. The transmitted intensity, $I$, was measured (as sketched in Figs. 6.4 and 9.3) prior to each XANES measurement for a number of positions across the wear scar and simultaneously at four different pixel (corresponding to energy) intervals as seen in Fig. 9.6. The four pixel intervals are from 0 - 512 (red circles, $I_{\text{section 1}}$), 512 - 1024 (pink triangles, $I_{\text{section 2}}$), 1024 - 1536 (blue squares, $I_{\text{section 3}}$) and 1536 - 2048 (green pluses, $I_{\text{section 4}}$), i.e. 4 different ranges of the pixel array detector as indicated in different shades of green in Fig. 9.5. The intensity of transmitted photons is discussed further in section 12.1.

9.4 EXAFS

EXAFS measured (at BM29) from a TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample (Fig. 2.9) was used to calibrate from pixel number to energy. Initially, the EXAFS setup was calibrated to the Cr K-edge (around 6 keV) of a chromium metal foil, which then was used as a reference (see Fig. A.2). Subsequently, the pure chromium EXAFS measurement was compared to EXAFS measured of the multi-layer sample to achieve an EXAFS measurement as a function of X-ray photon energy. The conversion from pixel number to energy is discussed further in the appendix (see section A.5).

\[^1\]The pixel intervals $I_{\text{section}}$ correspond to the energy intervals from 5.955 - 5.996 keV, 5.996 - 6.037 keV, 6.037 - 6.078 keV and from 6.078 - 6.119 keV, which lead to a total energy range of 163.7 eV corresponding to the XANES energy range.
9.5 The Nomad, an *In-Situ* Tribometer

A portable linear tribometer (the Nomad) was used in the dynamic X-ray absorption wear process study. It was designed and built at Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon in France to be carried along and possibly inserted into many experimental detection schemes as described by Joly-Pottuz *et al.* [95, 96]. It consists basically of a stationary part where the sample is placed, and a moving part where the wear part is placed. A normal load is applied between the sample and the wear part as sketched in Fig. 9.7 and drawn in Fig. 9.9A. The reciprocating motion of the tribometer is produced by an oscillator, onto which an arm with the wear part is attached. The sensor measures speed, friction force etc during the wear process.

The Nomad was placed in the ID24 beamline such that the X-ray beam only passes through the sample in the contact zone, thus only probing the wear process. A photo of the tribometer placed in the beamline is seen in Fig. 9.8, in which the beam path of X-ray photons, as it emerges from the optics cabin (Fig. 9.2), is indicated with the light green line. The tribometer is, in the photo, open due to visual inspection of the sample after the end of a wear experiment.

<table>
<thead>
<tr>
<th><strong>Settings at the ID24 beamline</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam size (FWHM)</td>
</tr>
<tr>
<td>X-ray photon energy</td>
</tr>
<tr>
<td>$\rightarrow$ X-ray wavelength</td>
</tr>
<tr>
<td>Detector range</td>
</tr>
<tr>
<td>Integration time, transmission</td>
</tr>
<tr>
<td>Integration time, XANES</td>
</tr>
</tbody>
</table>

*Table 9.1: Fixed experimental settings for measuring XANES and transmitted intensity, I.*
The wear sphere (counterpart) moved back and forth with a frequency of 5 Hz corresponding to an average velocity of 15 mm/s and with a running length of 1.5 mm leading to halfpipe shaped wear scars, where a constant amplitude (running length) was used. The CVA wear process (Fig. 8.3) was not used in this experiment. A normal load of 3 N was applied to the contact but other values were also used as listed in Tab. 9.2.

### 9.5.1 Probing the Wear Process

A special configuration of the wear scar and X-ray beam was used in order to measure only the contact zone of the wear scar. The sample was placed on the stationary part of the tribometer and the wear sphere on the moving part (see Fig. 9.9), in which the contact is probed by the beam (light green arrow) while the wear sphere is out of the beam path. The wear sphere and wear sphere holder (of vitreous carbon) are cut off allowing the beam to pass by the wear sphere and through only the contact zone. The wear sphere counterpart consist of a hemispherical molded resin pad with embedded diamond grains made from a two component resin (Mecaprex KM-EM and KMR), in which a powder of diamond grains (Diprotex diamond powder) of grain size 2 - 4 µm was dispersed.

All real-time wear probing experiments were initiated by having the contact closed, the normal load applied and the wear sphere situated to the right-hand side (see Fig. 9.9). At first, the transmitted intensity and XANES were measured and the oscillator would initiate the reciprocating sliding motion of the wear sphere had produced a wear scar in the contact zone. After a few thousand cycles the Nomad oscillator was stopped, the wear sphere placed to the right-hand side – and XANES and the transmitted

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**Figure 9.9:** A) The sample and beam configuration from top view. The X-ray photons are only passing through the sample in the contact zone. The small insert in the upper left corner B) shows schematics of the portable tribometer with the stationary part and the reciprocating part.
intensity measured across the wear scar in a line scan map. The procedure, with a specific number of wear cycles, was succeeded by the transmitted intensity and XANES measured, and continued for thousands of cycles until the sample was worn beyond CrN layer in the center of the scar. Thus, the number of cycles in one complete wear experiment depends on the specific wear process of that experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hz [s(^{-1})]</th>
<th>Cycles, (n)</th>
<th>Length [mm]</th>
<th>Applied Load, (F) [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>5</td>
<td>0</td>
<td>70 000</td>
<td>1.5</td>
</tr>
<tr>
<td>(II)</td>
<td>–</td>
<td>0</td>
<td>–</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>30 000</td>
<td>–</td>
<td>1.5</td>
</tr>
<tr>
<td>(III)</td>
<td>–</td>
<td>0</td>
<td>55 000</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>45 000</td>
<td>68 500</td>
<td>–</td>
</tr>
<tr>
<td>(IV)</td>
<td>–</td>
<td>0</td>
<td>36 000</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 9.2: The experimental settings for the wear experiments on samples I, II, III and IV.
Part IV

RESULTS
Chapter 10

Film Characterization

The various films and coatings are characterized in a number of different ways. An important parameter is the film thickness, established through both direct and indirect methods. But, also the refractive indices of some film materials are obtained from the measured laser reflectance and the very initial growth of TiN films is characterized by RHEED.

10.1 Film Thickness

Different methods for film thickness estimation were applied as a result of the large variety of sample types, where one method may apply to one sample type but not the others. A few samples were studied with more than one thickness measuring method as a confirmation.

10.1.1 Cross Sectional Cutting

Sample cross sections of two multi-layer sample series with thick coatings, TiAlN-on-TiN-on-Steel and TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon, were studied with SEM in the destructive method (see section 7.2.2) to find values for the layer thicknesses. Subsequently, the different coating thicknesses in the SEM images were estimated by use of ImageJ [86]. The third multi-layer system TiN-on-TiO$_2$-on-Steel was not studied by cross sectional SEM views due to the thin (∼50 nm) embedded TiO$_2$ layer being difficult to image with the SEM. This also accounts for the optics series of Fig. 2.8.

TiAlN-on-TiN-on-Steel

Cross sections of each sample (see Tab. 2.7) are displayed in Fig. 10.1. The images show samples with ∼0.3 µm top TiAlN coating (a), ∼1 µm top TiAlN coating (b) and ∼3 µm top coating (c) together with coating notations of the different layers. Also, the destructive nature of this method is clearly visible as parts of the coatings broke of during the cutting, casting and polishing process. The thickness was measured in a couple of positions along a cross section such that the estimated thicknesses are average values with corresponding errors arising from the blurry SEM images and errors on averaging the thicknesses.

Table 10.1 displays the obtained thicknesses, where the values diverge a little from the expected thicknesses (Tab. 2.7) and especially the embedded TiN thickness is much thicker than expected and the TiAlN coating of the 3 µm sample is much thinner. In addition, the TiAlN thickness of the ∼0.3 µm sample was also found by the combined EDX and CASINO method (see sections 7.2.2 and 10.1.2) to be 317 nm (±19.8 nm) when using material densities as listed in Tab. 2.8.
Figure 10.1: SEM (LV-SEM or TM1000) images of three sample cross sections, where the expected top TiAlN coating is 0.3 µm (a), 1 µm (b) and 3 µm (c).
10.1. FILM THICKNESS

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>TiAlN 0.3 µm</td>
<td>0.35 (± 0.05)</td>
<td>2</td>
<td>1.75 (± 0.05)</td>
</tr>
<tr>
<td>TiAlN 1 µm</td>
<td>0.90 (± 0.05)</td>
<td>2</td>
<td>1.60 (± 0.10)</td>
</tr>
<tr>
<td>TiAlN 3 µm</td>
<td>1.90 (± 0.10)</td>
<td>2</td>
<td>1.60 (± 0.05)</td>
</tr>
</tbody>
</table>

Table 10.1: TiAlN and TiN layer thickness of TiAlN-on-TiN-on-Steel multi-layer samples (~0.3 µm, ~1 µm and ~3 µm top TiAlN) derived by ImageJ [86] combined with cross sectional SEM views (see Fig. 10.1).

TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon

High resolution SEM images of the different layers constituting the ESRF samples (Fig. 2.9 and Tab. 2.5) were used in the ImageJ thickness estimation. Figure 10.2 display the cross sectional image view with coating layers as annotated. Scratches from the sanding process are clearly visible but not destructive as for the TiAlN-on-TiN-on-Steel samples.

Five SEM images were taken at five different positions along the sample cross section such that the layer thickness obtained are average values of these five positions. The thicknesses were found with a high accuracy, as a result of the high resolution SEM images by the SUPRA SEM, and listed in Tab. 10.2 together with the corresponding errors arising from any blurry transitions between the interfaces – from one layer to the next. A high accuracy on the layer thickness is necessary for the dynamical wear process evaluations discussed (see chapter 12) below.

![Cross sectional view of a TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon sample taken with a SUPRA SEM. The different layers and the substrate are annotated.](image-url)
10.1.2 SEM, EDX and CASINO

SEM, EDX spectroscopy and CASINO simulations were applied in the non-destructive method (see section 7.2.2) to estimate the layer thicknesses of the two multi-layer series, TiN-on-TiO$_2$-on-Steel and TiAlN-on-TiN-on-Steel (see Figs. 2.7 and 2.8). The EDX intensities (of Eq. (7.1)) were obtained in steps of mainly 1 mm across the sample surface during 100 s of measuring to achieve good statistics on the film thickness estimation.

**TiN-on-TiO$_2$-on-Steel**

Figure 10.3 displays the intensity ratios from titanium of the thin film and iron of the steel substrate measured across the surface of the 20 nm sample (magenta), 40 nm sample (grey), 70 nm sample (cyan) and 100 nm sample (dark cyan). The EDX signals are measured in both the x-direction (crosses) and y-direction (triangles) to reach average values on the film thickness, since it may not necessarily be uniform across the sample surface. But, the ratios measured are actually quite similar for each sample and as a result the films almost uniformly distributed across the samples. Since the substrates are identical for each sample they do not influence the EDX signals with respect to the measured ratios, which means the intensity ratios increase with increasing amount of Ti present in the films and thus with increasing film thickness. The 0 nm sample (purple) has no top TiN coating, but the EDX measurement was used to initially establish the embedded TiO$_2$ layer thickness in the non-destructive method. Naturally, the

<table>
<thead>
<tr>
<th>Layer thickness</th>
<th>Thickness [$\mu m$]</th>
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<tbody>
<tr>
<td>TiAlN (top coating)</td>
<td>$t_1$</td>
</tr>
<tr>
<td>CrN</td>
<td>$t_2$</td>
</tr>
<tr>
<td>TiAlN (embedded coating)</td>
<td>$t_3$</td>
</tr>
</tbody>
</table>

**Table 10.2:** Layer thickness of TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer samples as found by cross sectional view in SEM (Fig. 10.2) and with ImageJ [86].
Ti signals from the different layer thicknesses contain signals from the embedded layer as well, but this is accounted for in the CASINO simulations, in which the TiO\(_2\) signal layer is included as an additional individual embedded layer of 47 nm such that the correct top TiN thickness is found when comparing measured intensity ratios with simulated intensity ratios.

Ratios of simulated intensities (see Eq. (7.2)) arising from each sample of different top TiN layer thickness are plotted (grey triangles) in Fig. 10.4 together with the average ratios (full lines) of measured Ti and Fe intensities (see Eq. (7.1)), where the related error (dotted line) corresponds to one standard deviation of the average measured intensity ratios. Each layer thickness was simulated 5 times such that each triangle corresponds to the average of 5 CASINO simulations with an error of one standard deviation of the 5 simulations. Subsequently, the simulations were fitted with a linear line to find the top TiN thickness of the different samples. Table 10.3 display the values, which correspond very well with the expected ones. The obtained thickness of the embedded TiO\(_2\) signal layer is also included in the table. Densities of

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1*</td>
<td>50</td>
<td>47</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>41</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
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<td>69</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>107</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 10.3: TiN layer thicknesses by EDX spectroscopy and CASINO. The error is determined as one standard deviation of the linear fit of the simulated ratios (grey triangles, Fig. 10.4). *Estimated TiO\(_2\) layer thickness.
100Cr6 steel, TiN and TiO$_2$ (see Tab. 2.8) were used in the CASINO simulation, where the most common of the TiO$_2$ phases anatase was anticipated. However, assuming either of the three different TiO$_2$ phases; anatase, rutile or brookite a corresponding TiO$_2$ layer thickness of 47 ($\pm$1) nm, 41 ($\pm$1) nm or 44 nm, respectively, is obtained.

**TiAlN-on-TiN-on-Steel**

Similar evaluations were conducted on the other multi-layer series. Ratios of measured intensities (see Eq. (7.1)) from aluminium of the thin film and titanium of the embedded (thick) TiN signal layer, which in the simulations were treated as the substrate, were measured across the surface of the 20 nm (magenta), 40 nm (grey), 70 nm (cyan) and the 100 nm sample (dark cyan) as Fig. 10.5 displays. An even distribution of measured ratios across the samples indicate fairly uniform film thicknesses, except the 100 nm sample, which seems a little bumpy in both x and y directions. The embedded TiN layer was treated as the substrate due to its bulky thickness, which is impossible for the SEM electron beam to pass through – the steel substrate is thus not reached and subsequently ignored for this sample series.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>30</td>
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<tr>
<td>34</td>
<td>100</td>
<td>134</td>
<td>12</td>
</tr>
</tbody>
</table>

**Table 10.4:** TiAlN layer thicknesses by EDX spectroscopy and CASINO. The error includes the error from the measured intensity ratios (see Fig. 10.6) together with the error arising from an estimated 10% deviation on the roughly determined TiAlN density of 3.86 g/cm$^3$. 

**Figure 10.5:** EDX intensity ratios of Al (TiAlN layer) and Ti (TiN layer) measured across sample surface of TiAlN-on-TiN-on-Steel multi-layer sample series (Fig. 2.8).
The corresponding ratios of simulated intensities (see Eq. (7.2)) arising from each sample of different top TiAlN layer thickness are plotted (grey triangles) together with the average ratios (full lines) of measured Al and Ti intensities in Fig. 10.6, where the related error (dotted lines) corresponds to one standard deviation of the average measured intensity ratios. Each layer thickness was as before simulated 5 times and fitted with a line to find the thicknesses. These are listed in Tab. 10.4, where the thicknesses obtained all are above the expected values. This is most likely caused by TiAlN having a slightly higher deposition rate than TiN in the process, since the production parameters used by CemeCon A/S, i.e. deposition times used in the PVD process for this sample series, were identical to those of the previous studied multi-layer series, TiN-on-TiO$_2$-on-Steel.

A possible 10% deviation in the TiAlN density, caused by the rough density estimation above (see section 2.1), may result in the fairly substantial thickness errors in the CASINO simulations of these samples and the errors on the obtained TiAlN thickness include as such both the uncertainty of the TiAlN density and, as before, the errors arising from the measured EDX intensities. The estimated density of TiAlN was listed in Tab. 2.8 together with that of TiN.

### 10.2 Reflectance

By measuring the laser reflectance as a function of the incident angle, $R(\theta)$, from bulky TiN, TiAlN and 100Cr6 bearing steel a characterization in terms of the complex refractive index ($\tilde{n}$ of Eq. (4.3)) including both the usual refractive index, $n$, and the extinction coefficient, $k$, may be derived as discussed below. But, also the laser reflectance measured as a function of the top layer thickness $R(d_1)$, if transparent for the laser light, may characterize the samples in terms of the top coating thickness. The principles of the reflectance was discussed previously (see sections 4.2 and 4.3) and measured as a function of the incident angle as section 7.2.5 describes and Fig. 7.11 illustrates.
**Figure 10.7:** R-level, measured from the 5 samples of the TiN-on-TiO$_2$-on-Steel multi-layer series (see Fig. 2.7), increases with increasing TiN thickness. The individual measurements are compared with theoretically calculated curves in the appendix in Fig. A.5, in which the subsequent (see section 10.3) complex refractive indices, $\tilde{n}_{\text{TiO}_2}$, $\tilde{n}_{\text{TiN}}$ and $\tilde{n}_{100\text{Cr}_6}$ (Tab. 10.7) are employed. Also, the principles of $R(d_{\text{TiN}})$ is evaluated further (see sections 11.2 and 11.3) for the optical wear monitor below in Fig. 11.21.

**Figure 10.8:** R-level, measured from the 5 samples of the TiAlN-on-TiN-on-Steel multi-layer sample series (see Fig. 2.8), decreases with increasing TiAlN thickness. The individual measurements are compared with theoretically calculated curves in the appendix in Fig. A.6, in which the subsequent (see section 10.3) complex refractive indices, $\tilde{n}_{\text{TiN}}$, $\tilde{n}_{\text{TiAlN}}$ and $\tilde{n}_{100\text{Cr}_6}$ (Tab. 10.7) are employed. Also, the principles of $R(d_{\text{TiAlN}})$ is evaluated further (see sections 11.2 and 11.3) for the optical wear monitor below in Fig. 11.22.
10.2. REFLECTANCE

Figure 10.9: $R(\theta)$ measured from thick TiN (dark grey triangles), steel (light grey squares) and thick TiAlN (grey discs) plotted together with the corresponding theoretical curves (full lines) as calculated with subsequent $\tilde{n}$’s (of Tab. 10.7). $R_{100Cr6}$ was measured closely (cyan crosses) around $\theta_{\text{Brewster}}$ to achieve a good value on $\tilde{n}_{100Cr6}$.

TiN-on-TiO$_2$-on-Steel Multi-Layer Sample Series

$R$ measured of the TiN-on-TiO$_2$-on-Steel multi-layer series (see Fig. 2.7, Tab. 10.3) is plotted for the 5 individual samples; 0 nm (purple), 21 nm (magenta), 41 nm (grey), 69 nm (light cyan) and 107 nm (dark cyan) as a function of $\theta$ in Fig. 10.7 for both polarizations, TE (full) and TM (open). $R$ increases with the top TiN thickness such that a high reflectance is measured for thick layers and vice versa. This means the samples become increasingly opaque as the TiN thickness increases. TiN is almost non-transparent at a layer thickness of 69 nm, since the $R$-level (light cyan) is equivalent to that of the thick coating (dark grey) displayed in Fig. 10.9. This $\sim$0% transmission above 100 nm corresponds to previous observations by Roquiny et al. [55,97]. Also, the presence of the embedded TiO$_2$ signal layer is observed in the difference between reflectance curves of the 0 nm sample (purple) and the 21 nm sample (magenta), since the position of the Brewster angle (see section 4.2.2) shifts.

TiAlN-on-TiN-on-Steel Multi-Layer Sample Series

$R$ measured from the individual samples of the other multi-layer series is plotted in Fig. 10.8 as a function of the incident angle $\theta$. All samples (magenta, grey, cyan and dark cyan) display a fairly low reflectance level due to low absorption of TiAlN (see discussion, section 10.3), whereas the level of the 0 nm sample (purple) is high, since this is pure TiN – and the reflectance for TiN is high compared to TiAlN (see e.g Fig. 10.9). The optical wear monitor and the reflectance vs. the top TiAlN layer thickness, $R(d_{TiAlN})$, are discussed (see sections 11.2 and 11.3) further – for both multi-layer series.

TiN, 100Cr6 and TiAlN

Figure 10.9 displays the reflectance measured (symbols) from a thick TiN sample (dark grey), a non coated steel substrate (light grey) and a thick TiAlN coating (grey), including both TE (filled symbols) and TM (empty symbols) reflections, together with the corresponding theoretical (full lines) curves (by Eqs. (4.9 - 4.12)) with $\tilde{n}_{TiN}$, $\tilde{n}_{100Cr6}$ and $\tilde{n}_{TiAlN}$ as obtained below. The difference in theory and measurement arises for most parts from the errors in the refractive indices (see Fig. A.7). Also, both TiN and 100Cr6 steel show a high level of reflectance, whereas TiAlN displays a low reflectance.
CHAPTER 10. FILM CHARACTERIZATION

**Figure 10.10:** TE (a) and TM (b) curves, corresponding to all TiN reflections \((R_{TE}, \theta)\) and \((R_{TM}, \theta)\) of Fig. 10.9 (dark grey triangles), calculated (by Eqs. (4.9) - (4.12)) and plotted together as a function of \(n\) and \(k\), the refractive index and the extinction coefficient, respectively, of the complex refractive index (Eq. (4.3)). Each curve (each color) correspond to one reflection \((R, \theta)\).

**Figure 10.11:** Selected curves, corresponding to the selected reflections \((R_{TM}, \theta)^*\) of Tab. 10.5, cross each other within a small area, from which \(n\) and \(k\) of the complex refractive index \(\tilde{n}\) is obtained (see Tab. 10.7). The Brewster angle (thicker dark blue line) is at 65°. A close up of Fig. 10.10 b.
10.3 Refractive Index

A thick 3 µm TiN coating is completely non-transparent for the laser light such that no reflections arise from the underlying layers or interfaces. This makes it rather simple to estimate \( n \) and \( k \) of the complex refractive index (\( \tilde{n} \) of Eq. (4.3)) from the measured reflectance in a type of ellipsometry [55]. Each reflection \( (R, \theta) \) corresponds to a curve in the \( (n, k) \)-space and \( \tilde{n} \) is found in the point where all these curves cross, when plotted together. Thus, the reflectance is measured as a function of the incident angle \( (R(\theta) \text{ of Fig. 10.9}) \) for a non-transparent coating or material and a curve in the \( (n, k) \)-space subsequently calculated (by Eqs. (4.9) - (4.12)) for each measured reflection \( (R, \theta) \). The curves obtained from all reflections are plotted on top of each other and at the point of the crossing curves, the complex refractive index \( \tilde{n} \) read off. Naturally, this is possible with other thick and non-transparent materials as well such as the polished steel substrate and thick TiAlN coating.

10.3.1 TiN

All curves as derived from reflections \( (R, \theta) \) measured from the thick TiN coating (dark grey triangles, Fig. 10.9) are plotted together in Fig. 10.10, in which the TE (a) and TM (b) curves are displayed individually. Each curve (each color) corresponds to one reflection and the TM curves (b) demonstrate the curves crossing each other at a certain point, from which \( n \) and \( k \) of the complex refractive index may be determined. The displayed curves are calculated for a 3 µm TiN thickness together with fixed parameters (see Tab. 7.3).

Curves corresponding to specifically selected reflections (see Tab. 10.5) cross each other within a limited area as Fig. 10.11 shows, in which the selected reflections \( (R_{TM}, \theta^*) \) all are measured around the lowest reflection value, the Brewster angle at \( \sim 65^\circ \), of the TM reflection. Only the selected and plotted curves are for simplicity used in the evaluation of \( n \) and \( k \) such that all TE reflections (Fig. 10.10a) are excluded, since they seem to follow the green shaded lines of the TM curves (Fig. 10.10b) and as such also cross within the area of interest.

The complex refractive index \( \tilde{n} \) of TiN was estimated from the selected crossing curves (Fig. 10.11) to be

\[
\tilde{n}_{TiN} = 0.92 + i \ 2.63,
\]

where \( n \) and \( k \) are found as the center point of the area spanned by the crossing curves. The corresponding errors (see Tab. 10.7) are determined by the outer most boundaries of the area spanned by the crossing curves.

<table>
<thead>
<tr>
<th>Incident Angle, ( \theta )</th>
<th>55°</th>
<th>65°</th>
<th>70°</th>
<th>75°</th>
<th>80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Reflectance, ( R_{TM} )</td>
<td>0.507</td>
<td>0.470</td>
<td>0.471</td>
<td>0.491</td>
<td>0.560</td>
</tr>
</tbody>
</table>

Table 10.5: Selected TM reflections as measured around the Brewster angle (at \( \sim 65^\circ \)) from the thick TiN coating (dark grey triangles, Fig. 10.9) and used in deriving corresponding curves (see Fig. 10.11).
Figure 10.12: TE (a) and TM (b) curves, corresponding to all TiAlN reflections ($R_{TE, \theta}$) and ($R_{TM, \theta}$) of Fig. 10.9 (grey discs), calculated (by Eqs. (4.9) - (4.12)) and plotted together as a function of $n$ and $k$, the refractive index and the extinction coefficient, respectively, of the complex refractive index (Eq. (4.3)). Each curve (each color) correspond to one reflection ($R, \theta$).

Figure 10.13: Selected curves, corresponding to the selected reflections ($R_{TM, \theta}^*$) of Tab. 10.6, cross each other within a small area, from which $n$ and $k$ of the complex refractive index $\tilde{n}$ is obtained (see Tab. 10.7). The Brewster angle (thicker blue line) is at 60°. A close up of Fig. 10.12 b.
10.3. REFRACTIVE INDEX

Selected Reflections ($R_{TM}, \theta^*$)

<table>
<thead>
<tr>
<th>Incident Angle, $\theta$</th>
<th>50°</th>
<th>55°</th>
<th>60°</th>
<th>65°</th>
<th>70°</th>
<th>75°</th>
<th>80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Reflectance, $R_{TM}$</td>
<td>0.058</td>
<td>0.045</td>
<td>0.038</td>
<td>0.040</td>
<td>0.061</td>
<td>0.116</td>
<td>0.318</td>
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</table>

Table 10.6: Selected TM reflections as measured around the Brewster angle (at $\sim 60^\circ$) from a thick TiAlN coating (grey discs, Fig. 10.9) and used in deriving the corresponding curves (see Fig. 10.13).

10.3.2 TiAlN

TiAlN was treated similarly, where all curves as derived from the reflections measured off the thick TiAlN coating (grey discs, Fig 10.9) are plotted together in Fig. 10.12 for the TE (a) and TM (b) reflections, in which each curve (each color) corresponds to one reflection. Clearly, the TM curves (b) cross each other within a well defined area from which $n$ and $k$ of the complex refractive index for TiAlN easily may be obtained. The TE curves (a), excluded for simplicity from the subsequent refractive index estimation, follow the green shades of the TM curves and cross as such also within this area of attention. $n$ and $k$ were, as before, derived by the crossing of a small number of curves, where Fig. 10.13 display the few selected curves, corresponding to selected reflections ($R_{TM}, \theta^*$) all measured close to the Brewster angle at $\sim 60^\circ$ (see Tab. 10.6). The curves cross within a limited area from which the complex refractive index was estimated to be

$$\tilde{n}_{\text{TiAlN}} = 1.76 + i 0.93,$$

where $n$ and $k$ are the center point of the area spanned by the crossing curves. The corresponding errors (see Tab. 10.7) are determined by the outermost boundaries of the area spanned by the crossing curves.

10.3.3 TiO$_2$ and 100Cr6 Steel

A similar approach for 100Cr6 steel, in which reflections (light grey squares, Fig. 10.9) leads to curves similar to those of TiN, resulted in a complex refractive index (see Tab. 10.7) and reflections measured from the 47 nm TiO$_2$ coating sample (purple, Fig. 10.7) ultimately lead to $\tilde{n}_{\text{TiO}_2}$. This is possible once the TiO$_2$ layer thickness (Tab. 10.4, sample 30) and $\tilde{n}$ of the steel substrate are determined specifically, since both values are necessary in the curve calculations when the coating is so thin it becomes transparent and the laser light may reach the embedded interface boundary. $\tilde{n}$ is otherwise obtained as before with and almost non-existing extinction coefficient due to TiO$_2$ being a non-conductive material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index, $n$</th>
<th>Extinction Coefficient, $k$</th>
<th>$n_{\text{ref}}$</th>
<th>$k_{\text{ref}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{n}_{\text{TiN}}$</td>
<td>0.92 (± 0.04)</td>
<td>2.63 (± 0.12)</td>
<td>0.8 - 0.9</td>
<td>2.4 - 2.7</td>
<td>[98,99]</td>
</tr>
<tr>
<td>$\tilde{n}_{\text{TiAlN}}$</td>
<td>1.76 (± 0.07)</td>
<td>0.93 (± 0.07)</td>
<td>1.8 - 2.6</td>
<td>0.4 - 0.9</td>
<td>[25,100]</td>
</tr>
<tr>
<td>$\tilde{n}_{\text{100Cr6}}$</td>
<td>2.21 (± 0.56)</td>
<td>3.07 (± 0.59)</td>
<td></td>
<td></td>
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<tr>
<td>$\tilde{n}_{\text{TiO}_2}$</td>
<td>2.79 (± 0.05)</td>
<td>0.02 (± 0.01)</td>
<td>2.1 - 2.6</td>
<td>0.005 - 0.15</td>
<td>[101–103]</td>
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</table>

Table 10.7: Refractive indices and extinction coefficient derived for TiN, TiAlN, steel and TiO$_2$ (see Fig. 2.1) at $\lambda = 633$ nm. $n_{\text{ref}}$ and $k_{\text{ref}}$ are values from the literature.
The obtained refractive indices and extinction coefficients for the four materials agree with those of the literature, where Valkonen et al. [99] found $\tilde{n} \approx 0.9 + i 2.7$ and Jedrzejowski et al. [98] found $\tilde{n} \approx 0.9 + i 2.4$ for TiN, while Schüler et al. [25] for TiAlN showed large fluctuations in both $n$ and $k$ with respect to wavelength and stoichiometry, but reached $\tilde{n}_{\text{Ti},0.52\text{Al},0.48\text{N}} \approx 1.9 + i 0.4$ and Mardare et al. [102] found $\tilde{n} \approx 2.45 + i 0.005$ for TiO$_2$ with the anatase phase predominating over the rutile phase. The deviations between values obtained here and those of the literature may be caused by differences in production methods and parameters, since films and materials not produced after exactly the same process parameters may change the stoichiometry and thereby also the refractive index [23, 25, 104]. Naturally, the film thickness of the TiO$_2$ is also an issue and could account for the relative large deviation, but also limitations within the calculations of the huge expression for the reflectance (Eq. 4.9 - 4.12) by Mathematica may cause inconsistent results on the refractive indices and extinction coefficients.

TiN display metal-like properties with a strong absorption as also observed above (see Tab 10.7) together with a high reflectivity as shown in Fig. 10.9. TiO$_2$, in contrast, is a non-conducting material and absorbs as such very little, which agrees well with the obtained results. Moreover, the absorption ($k$) of TiAlN is low (but not almost non-existing as for TiO$_2$), as a result of TiAlN’s half-metal half-dielectric properties. It should be noted that TiN have almost opposite optical properties – values of $n$ and $k$ with respect to both TiO$_2$ and TiAlN – the two other materials in either of the proposed wear monitor systems of Figs. 2.5 and 2.6, such that large optical differences should be obtained when going from one of these materials to TiN.

### 10.4 Film Growth Mode by PLD and RHEED

The purpose of the thin film production and study with PLD was initially to produce very precise layer thickness samples (since this is one of PLD’s primary forces [14, 15]) of TiO$_2$ and TiN for the optical wear monitor multi-layer series (Fig. 2.7 and 2.8), together with a film nucleation and growth mode study. But, it turned out that commercially acquired TiO$_2$ thin films from FerroPerm were very fine and as such satisfied the requirements on quality (refractive index) and layer thickness. This, combined with the fact that the project partner CemeCon managed to develop process parameters for deposition of very thin TiN (and TiAlN) films (which is otherwise not a standard production at CemeCon), made the production of precision films by PLD unnecessary in terms of the optical wear monitor. Even so, a film growth study was carried out to gain knowledge of the film development and growth mode and thin films of primarily TiN but also TiO$_2$ were produced by PLD and simultaneously monitored with RHEED such that

![RHEED patterns of pure periclase MgO substrate before (a) and after (b) specific heat treatment in 100% oxygen atmosphere.](image)
10.4. FILM GROWTH MODE BY PLD AND RHEED

Structural changes due to the developing thin films were detected. The MgO substrates were prior to the film deposition thermally annealed (Fig. 7.4) to obtain optimal RHEED monitoring conditions. The patterns before (a) and after (b) the treatment are shown in Fig. 10.14. Clearly, the RHEED pattern from the treated surface (b) appears much sharper. The spotty pattern of the untreated surface (a) is changed into a sharply defined streaky pattern in the treated surface (b) and as such implying a smoothing (see Fig. 3.13) of the surface. Subsequently, the films were studied by AFM and XRD to gain information on the surface morphology and the structural composition of the deposited thin films. Additionally, FEGSEM (abbreviation for Field Emission Gun Scanning Electron Microscope\(^1\)) cross sectional imaging established the TiN layer thickness and EDX spectroscopy combined with CASINO established the TiO\(_2\) layer thickness.

### 10.4.1 TiN on MgO

A series of images in Fig. 10.15 shows the real-time RHEED patterns develop during deposition of a TiN film, where the different deposition times are noted in the individual images for a clear overview of the evolution in the growing film. The initial image shows the RHEED pattern of the annealed MgO substrate. Clearly, a development is observed as the appearance of the patterns slightly change from frame to frame. At the very initial growth stages (5 - 20 s) the intensity of the RHEED pattern decreases but with a streaky appearance of the pattern maintained. Subsequently, the streaks change (20 - 120 s) into spots and finally back into streaks again after 240 s of film deposition. The RHEED pattern is right after the initial growth stage (20 - 120 s) dominated by arrays of diffraction spots, indicating transmission (see bottom part, Fig. 3.13) due to a roughened surface. Nevertheless, the streaks reappear in the later growth stages (240 - 300 s), implying a re-smoothing of the surface morphology.

\(^{1}\)A Zeiss 1540XB cross beam field emission scanning electron microscope equipped with a focused ion beam (FIB) column and a gas injection system (GIS), where the FIB mill a trench of suitable area into the thin film sample surface such that a cross section of the involved layer is possible to inspect visibly.
Figure 10.16: AFM images recorded after 0 s (a), 120 s (b), 240 s (c), 480 s (d) and 3600 s (e) of film deposition.
10.4. FILM GROWTH MODE BY PLD AND RHEED

Figure 10.17: Surface heights evaluated from AFM images. Annotations correspond to Fig. 10.16.

A corresponding series of AFM images of the TiN film, displayed in Fig. 10.16, was recorded after deposition times of 0 s (a), 120 s (b), 240 s (c), 480 s (d) and 3600 s (e). Especially, the image obtained after 120 s of film deposition (b) is of interest, since 3D islands are distributed almost evenly across the surface. The film continues to grow with a smooth surface (c - e) as the deposition proceeds, such that the island formation is ended at this point.

The corresponding roughness development of the film surface is evaluated from the AFM images and displayed in Fig. 10.17, in which the roughness after 120 s of film deposition (red line) is increased significantly compared to the remaining measurements due to the formation of islands. The islands appear as structures of a few nm’s high and some 100 nm’s wide with a slightly pointed top. Figure 10.18 displays a distribution of the island sizes measured over an area of 5 × 5 µm². The main average island height is found to be 4.7 nm (stippled blue line), which corresponds quite well to the island heights (full red line) observed in Fig. 10.17. An additional minor fraction of islands have heights around 7.8 nm corresponding to the AFM observation (Fig. 10.16b).

Thus, the combined RHEED and AFM images reveal the initial growth mode of TiN on MgO. At first, the RHEED pattern is streaky but transforms gradually into a spotty pattern within the first 120 s, indicating transmission through the 3D islands. The initial growth with an increased roughness due to a uniform distribution of islands (see Fig. 10.16b) agrees quite well with the RHEED observations. Also, the re-appearance of streaks due to a smoother surface (after 240 s of deposition) is supported by the AFM images, since the islands have disappeared and a surface re-smoothing is observed (Fig. 10.17).

A (FEGSEM) cross section of the film deposited for 3600 s is displayed to the left in Fig. 10.19, in which the thin TiN film and MgO substrate are observed as annotated together with the protecting platinum (Pt) layer. Prior to the FEGSEM trench milling a Pt layer is deposited for protection of the thin film during the trench milling. The average film thickness is found from the SEM image by means of ImageJ to be 45 (± 5) nm, leading to an average deposition rate of ∼0.0012 nm/pulse. Also, the sample deposited for 3600 s (Fig. 10.19b) shows a surface smoothness comparable to that of the AFM image as recorded after 3600 s (Fig. 10.16e).
X-ray diffraction was measured from this thick (3600 s) film to gain a good signal as shown in Fig. 10.20, where a single peak corresponding to a (200) orientation of TiN is observed. This orientation of TiN on MgO was observed before by Wall et al. [105] in a reactive magnetron sputtering study. The crystallite size may be obtained from the broadening (at FWHM) of the XRD peak by use of Scherrer’s equation. This leads to a crystallite size of approx. 3.7 nm due to a shape factor of 0.9 and an XRD broadening at FWHM of 0.0414 rad.

Figure 10.21 shows the intensity of the specular spot (see Fig. 3.14) recorded within the masked area (see insert) and plotted as a function of deposition time. The measured RHEED intensity decreases with a distinct but minor increase after approx. 100 s of film growth and continues to decrease after the small bump but RHEED oscillations suggesting 2D layer-by-layer growth (Figs. 3.7 and A.3) are not observed. In fact, the combined RHEED patterns and AFM images indicate the initial film formation as 3D islands eventually transforming into a continuously growing film. Thus, the Volmer-Weber growth mode of Fig. 3.7 agrees with the surface morphology with islands after 120 s (Fig. 10.16b), which is supported by the corresponding RHEED pattern change from streaks to spots (Fig. 10.15) indicating transmission through the 3D islands. The final change from spots back to streaks indicates a change to a more smooth surface, which is supported both by the FEGSEM image (see Fig. 10.19) and the AFM measurements (Fig. 10.16c - e and 10.17).

The distance between diffraction spots (or streaks) and the center (specular) spot, i.e. s of Fig. 3.10, is unchanged during the film growth (see RHEED pattern development in Fig. 10.15), which indicate an epitaxial growing film. This is supported the one single peak observed in the XRD pattern (Fig. 10.20). The epitaxially growth of TiN on the MgO crystal may be a result of the small lattice mismatch (0.6%) of a-axis constants (TiN (a₀=0.4239) and MgO (a₀=0.4212)) between the growing film and the substrate.

---

2The Scherrer equation [106] correlates the broadening of an XRD peak to the size of nano-scale particles or crystallites in solids (the broadening may also be caused by other factors as e.g. instrumental effects) and is given in terms of the shape factor $K$, the X-ray wavelength $\lambda$, the line broadening of the peak (FWHM) $\beta$ and the Bragg angle $\theta_B$, where $\tau$ is the crystallite size:

$$\tau = \frac{K \lambda}{\beta \cos \theta_B}$$
10.4. FILM GROWTH MODE BY PLD AND RHEED

Figure 10.20: X-ray diffraction pattern from TiN film deposited for 3600 s on (100) MgO showing a single (200) TiN structural orientation of the film. The peak is fitted to find the FWHM.

Unfortunately, parameters as $R_s$ and $\Theta_f$ (see Fig. 3.10) were not obtained right after the RHEED experiment together with a screen-to-CCD-camera calibration such that the RHEED pattern could not be indexed. The main focus of this study was to obtain epitaxial growing thin films and study the growth mode of TiN on MgO.

This work on the TiN growth mode on MgO was a group study, where the author of this thesis personally was involved in the combined PLD thin film deposition and RHEED monitoring, the AFM recording and corresponding analysis. The SEM imaging and FEGSEM cross sectional imaging were done by Nini Pryds together with the XRD measurement.

Figure 10.21: Intensity of specular spot recorded (from a superposition of the specular spot and diffraction spots) during initial growth of the TiN film with 10 laser pulses per second. Photo insertion shows a rectangle, from which the intensity was integrated.
10.4.2 TiO$_2$ on MgO

A similar study was also carried out on TiO$_2$, in which the recorded RHEED images (displayed in the appendix in Figs. A.8 and A.9) showed a clear development from a streaky appearance to elongated spots with additional and new spots emerging. Unfortunately, the corresponding surface morphology and structural composition studies by means of AFM and XRD, respectively, did not give any information on the reasons for this development in the RHEED patterns – except from the observation of a new and different film developing on the MgO substrate surface. In addition, the RHEED intensity recorded (see Fig. A.10) during film growth displayed an almost continuous decrease – leading to no further understandings of the deposited film growth, as well.

An average deposition rate was, nevertheless, established to be approx. $10^{-4}$ nm pr laser pulse. This is low and most likely caused by the low fluence of the laser beam (see Tab. 7.1) during film growth. These results on TiO$_2$ are less strait forward compared to the TiN study above maybe caused by the fairly poor lattice mismatch of a-axis constants between TiO$_2$ and MgO, since these are considerable. The mismatch between rutile and anatase TiO$_2$ and MgO is 9.2% and 8.9%, respectively and 118% between brookite and MgO [2,107], which does not make TiO$_2$ and MgO the perfect match regarding film growth. But, MgO was chosen due to the previous experience with MgO and successful study with TiN. A more favorable substrate as e.g. SrTiO$_3$, which previously showed good results by Ong et al. [108] on film nucleation studies, may produce somewhat more accessible results.
Chapter 11

Wear on TiN and TiAlN Tribological Coatings

The response of the protective coatings to an abrasive wear process in the linear tribometer is discussed here for both the TiN and TiAlN single layer coatings and the TiAlN-on-TiN-on-Steel multi-layer system coatings. Subsequently, the simulated optical response of the two different multi-layer system to the wear process are presented together with comparisons between calculations and measurements of the simulated wear process. In addition, the proposed optical wear monitor system is proven to work as a potential warning system, where the optical reflections response from wear scars of 4 TiAlN-on-TiN-on-Steel multi-layer sample are presented together with the results of the camera and image analysis of the very same multi-layer wear scars.

11.1 Wear Quality

The wear quality of TiN and TiAlN single layer coatings (see Fig. 2.1) are discussed together with that of the TiAlN-on-TiN-on-Steel multi-layer system. The sample coatings were exposed to an abrasive reciprocating CVA wear process in the linear tribometer as described in section 8.1 and illustrated in Figs. 8.1 - 8.2. Table 8.1 displayed the fixed wear parameters for the wear tests.

Figure 11.1: Example of wear scars in TiN.

Figure 11.2: Example of wear scars in TiAlN.
11.1.1 TiN and TiAlN Single Layer Coatings

Figures 11.1 and 11.2 display a TiN and a TiAlN single layer coating, respectively, exposed to the abrasive CVA wear process. The TiN wear scars (labeled 1, 2 and 3) were worn for 30,000, 25,000 and 300,000 cycles, respectively, where the 300,000 cycles was worn with resin only, i.e. without diamond grains in the counter part coating (see Fig. 8.4). This leads only to a polishing of the coated surface as the corresponding Dektak profile (Fig. A.21) also shows. Moreover, the wear scars in the TiAlN (∼3 µm) coating (labeled 1, 2 and 3) were worn for 40,000, 40,000 and 45,000 CVA cycles, respectively.

The wear tests on these single layer coatings were performed primarily to realize the number of reciprocating cycles it takes to wear through the layer thickness of the specific coating type such that the subsequent removal of the multi-layer system top coatings could be achieved most ideally, which means that any extra knowledge as e.g. wear rates obtained on these samples are additional information. The ideal wear scar resemblance for the multi-layer systems (TiN-on-TiO$_2$-on-Steel and TiAlN-on-TiN-on-Steel) was illustrated and described above in Fig. 8.3.

Dektak Scan Profiles

One dimensional topography measurements on the wear scar surfaces were carried out with a Dektak profilometer (see section 8.1.4) to obtain cross sectional views of the scars. Figure 11.3 displays an example of a scan profile measured across the TiAlN scar 2 (Fig. 11.2). The maximum (peak) and average depth of all the wear scars were determined from such measurements together with the area from which material was removed as discussed below. The profile is characteristic for the scars introduced in the coatings with the linear tribometer in the 'sphere-on-flat' configuration (see e.g. sections 5.2.1 and 8.1). It means that the majority of the wear scars (including those of the subsequent multi-layer coatings) are very rough with many deep grooves and very sharp ridges and edges – and maybe somewhat different from what may be expected for a wear scar caused by a 'sphere-on-a-flat' wear process (see for instance section 5.3.1 above).

Single layer coatings of TiN were exposed to a number of different CVA cycles in the linear tribometer (see Tab. 8.2), where section A.3 (in the appendix) displays a complete collection the corresponding Dektak profiles together with TiN wear scar photos. Most of the TiN coating are worn completely through (the purpose of the single layer wear experiment), since the steel substrate visually appears as silvery grey areas in the bottom of the scars.

Figure 11.3: Dektak scan profile measured across the TiAlN wear scar 2 of Fig. 11.2
The TiAlN coatings were likewise exposed to the wear process and the corresponding scan profiles displayed below in section A.4 together with the wear scar photos. Only some TiAlN wear scars were worn through the coating as observed by visual inspection. Since this wear-through influences the result of the wear analysis, these scar profiles are specifically pointed out as discussed below.

Several cross sectional profiles were measured along each wear scar to probe the scar topography and find the area of maximum wear, since the final scar depth varies along the scar due to the CVA wear process. This was done by starting at the deep scar end, i.e. at the top of the scar when looking at the scar photos (e.g. Fig. 11.1) and simply measure stepwise along the scar and then select the profile with the deepest scar. The selected profiles were used in the subsequent wear analysis.

**Area of Removed Material and Scar Depths**

The area of material removed in a scar cross section was determined from the measured Dektak scan by integration of the profile from the first to the final edge. The values were plotted as a function of the number of cycles in Fig. 11.4 for the TiN (red triangles) samples and the $\sim 2 \, \mu m$ (green circles) and $\sim 3 \, \mu m$ (blue squares) TiAlN samples. Subsequently, the sample wear rates obtained below were found from these values.

Clearly, the cross section of material removed increase with the number of cycles for both TiN (red) and $\sim 3 \, \mu m$ TiAlN (blue). This is not as evident for the corresponding $\sim 2 \, \mu m$ TiAlN (green) samples, but a closer inspection of the scars (see e.g. Figs. A.25 - A.28) reveal that several (marked ** in the appendix) are worn beyond the TiAlN layer and well into the much softer steel substrate. Naturally, this wear-through causes a disturbance in the measurement such as an increased amount of removed material.

Since most of the scars have several deep grooves, the peak scar depth was defined as the dip of the deepest groove in a profile. This is plotted (empty symbols) for both the TiN (red triangles) and TiAlN samples (green circles, blue squares) in Fig. 11.5 together with the corresponding average scar depths (full symbols). The average depths of the wear scars were found by dividing the value for the area removed (Fig 11.4) with the corresponding width (from the Dektak profile) of that scar.

![Figure 11.4: Cross sectional area material removed from TiN (red triangles) and TiAlN (green circles, blue squares) single layer coatings as a function of the final number of cycles. Negative values indicate removal.](image-url)
The peak depths (empty symbols) are much more incoherent than the average depths (full symbols) with respect to the number of wear cycles. This abrupt and unclear behavior of the peak depths may indicate signs of delamination of the complete coating layer, since many wear scars reach similar depths (e.g. green empty circles) for different number of cycles. But, the average depth seems to show a connection between depth and number of wear cycles such that deeper wear scars are reached for an increasing number of cycles. This suggests that delamination mainly occurs in the bottom of the deeper grooves and not across the complete wear scar, which seems to be supported by the scan profiles. Many of these reach similar maximum depths across the scar but with many large ridges.

The specific wear rate, $k$, for the two single layer materials may be found as discussed above (see section 5.4.2) and given in Eq. (5.2) with the applied normal load, $F$, as listed in Tab. 8.1 and the number of reciprocating wear cycles, $n$, as listed in Tab. 8.2. The cross sectional areas of removed material, $A$, consist of those in Fig. 11.4 and it is thus possible to obtain values of the corresponding specific wear rates for the two single layer coating types. These are plotted for both TiN (red triangles) and TiAlN (green circles, blue squares) as a function of the final number of wear cycles in Fig. 11.6, in which those
### 11.1. WEAR QUALITY

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Wear Rate</th>
<th>$[10^{-6} \text{mm}^3/\text{Nm}]$</th>
<th>$k_{ref}$</th>
<th>Reference</th>
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<tr>
<td>TiN</td>
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<td>2.6 - 3</td>
<td>[109,110]</td>
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<td>TiAlN ($\sim$ 2 µm)</td>
<td>$k_{TiAlN}$</td>
<td>1.96 (± 0.36)</td>
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<td></td>
</tr>
<tr>
<td>TiAlN ($\sim$ 3 µm)</td>
<td>$k_{TiAlN}$</td>
<td>1.43 (± 0.39)</td>
<td>0.08 - 12</td>
<td>[109,111–113]</td>
</tr>
<tr>
<td>CrN</td>
<td>$k_{CrN}$</td>
<td>0.7 - 1.9</td>
<td></td>
<td>[114,115]</td>
</tr>
</tbody>
</table>

| Table 11.1: Specific wear rates $k_{TiN}$ and $k_{TiAlN}$ obtained by averaging the (colored) values of Fig. 11.6 together with corresponding wear rates $k_{ref}$ from the literature. $k_{CrN}$ is discussed in chapter 12 (see section 12.2.1) below. |

Worn through to the steel substrate are marked in grey, as noted. Since the values for the wear rates of the TiAlN scars worn through to steel (grey markers) deviate a lot from those not worn through, they have been omitted from the wear rate determination below such that only the colored values (green, blue) are included.

None of the TiN wear scars (red triangles) are marked with grey in the wear rate plot, since all of them were worn through to the steel substrate (see photos in section A.3) in a somewhat similar manner. Naturally, this causes an inaccuracy in the value for the obtained TiN wear rate $k_{TiN}$, since the material value from the TiN layer is mixed with the different (and higher) material value from the underlying steel.

By averaging the collection of wear rates (red triangles) of Fig. 11.6 a material dependent specific wear rate $k_{TiN}$ for TiN is obtained. Likewise, the average of the collection of TiAlN wear rates (green circles, blue squares) result in two similar material dependent specific wear rates $k_{TiAlN}$ for TiAlN – one for each sample type. $k_{TiN}$ and $k_{TiAlN}$ are listed in Tab. 11.1 together with the corresponding errors determined as one standard deviation, $\sigma$. The wear rates are given in units of $10^{-6} \text{mm}^3/\text{Nm}$.

Clearly, the two TiAlN values should not differ as they are obtained from the same material deposited under identical production parameters. In fact, they are also almost within the same order of magnitude. But, the layer thickness – or rather the interface between coating and substrate may influence the obtained values, since the $\sim$ 2 µm samples for most parts were worn exactly to the TiN-steel interface, whereas the $\sim$ 3 µm samples were far from reaching the coating-substrate interface (see the Dektak profiles). The corresponding value for TiN is a little higher, as compared to the TiAlN value(s), which could be caused either by mixing with the underlying softer steel during the wear process or simply by the fact that TiN is not as wear resistant a material as TiAlN [116].

Wear rates obtained under comparable conditions (applied normal load, sliding distance, speed etc.) but with varying counterpart materials give similar results for both materials. TiAlN wear rates obtained with a linear reciprocative tribometer setup by Mo et al. and Shum et al. [109,111] were found to be $10 \cdot 10^{-6} \text{mm}^3/\text{Nm}$ and $12 \cdot 10^{-6} \text{mm}^3/\text{Nm}$, respectively, but slightly lower values ($0.55$ and $0.084 - 0.38 \cdot 10^{-6} \text{mm}^3/\text{Nm}$) obtained with pin-on-disc setups are also seen [112,113]. Specific wear rates for TiN obtained with a reciprocative tribometer by Shum et al. [109] and in a pin-on-disc setup by Yang et al. [110] were found to be $3 \cdot 10^{-6} \text{mm}^3/\text{Nm}$ and $2.6 \cdot 10^{-6} \text{mm}^3/\text{Nm}$, respectively, which also compares very well with the values derived here (Tab. 11.1). Deviations may be caused by different test conditions (speed, applied load...) since $k$ seems to depend on these [109,110,116] but also stoichiometric variations influence the results [109], as this alters the material properties.
CHAPTER 11. WEAR ON TIN AND TIALN TRIBOLOGICAL COATINGS

Figure 11.7: Wear scars on ∼0.3 µm top TiAlN sample 41 (a) and 42 (b) with corresponding no. of cycles, n.

Figure 11.8: Wear scars on ∼1 µm top TiAlN sample 43 (a) and 44 (b) with corresponding no. of cycles, n.

Figure 11.9: Wear scars on ∼3 µm top TiAlN sample 45 (a) and 46 (b) with corresponding no. of cycles, n.
11.1. WEAR QUALITY

11.1.2 TiAlN-on-TiN-on-Steel Multi-Layer System

Six multi-layer samples of the TiAlN-on-TiN-on-Steel series (see Fig. 2.6) were also exposed to the abrasive CVA wear process, where the particular sample series consist of three top coating thicknesses of TiAlN; ~0.3 µm, ~1 µm and ~3 µm, respectively, (see Tabs. 2.7 or 10.1) with two samples of each top TiAlN layer thickness. In this case, the samples were primarily worn to remove the top TiAlN coating and allowing visible access to the embedded TiN signal layer, such that a wear scar, ideally appearing as Figs. 8.3 and 8.7 illustrated above, emerge. Additional insight achieved from a wear analysis on the multi-layer samples is, as above, merely extra information. The multi-layer samples were exposed to a number of different cycles as listed above in Tab. 8.3.

Figures 11.7 - 11.9 display all multi-layer wear scars together with the (expected) individual top TiAlN thickness noted, where the unworn multi-layer surfaces appear similar even if the top TiAlN coating thickness varies a lot (see layer thickness estimation, Tab. 10.1). This identical appearance is caused by TiAlN being non-transparent above ~0.1 µm [55, 97]. As expected, the embedded TiN coatings appear clearly in yellow in the bottom of most scars but also the steel substrate is occasionally visible – the bright shiny silvery color of steel appears in the very bottom of a few scars (Fig. 11.9). This is not ideal for the optical wear monitor, as discussed below in section 11.6, since the optical response for this steel is decreased at the red wavelength of the HeNe laser. Moreover, the sample number and scar labels of the corresponding wear scar profiles (shown in section A.4) match those of the photos.

Area of Removed Material and Scar Depths

Figure 11.10 display the area of material removed in a scar cross section as derived by integration from the first to the final edge of the measured Dektak scar profiles. The values are plotted as a function of the number of wear cycles for three TiAlN top coatings; ~0.3 µm (red triangles), ~1 µm (green circles) and ~3 µm (blue squares), where an increasing amount of material is removed for an increasing number of wear cycles. This is the impression for the individual samples considered alone, but the trend is especially evident when looking at all three sample types together where only few measurements deviates from linear. As compared to the single layer measurement (Fig. 11.4), this wear-through to the embedded TiN layer (and also the steel substrate) does not appear to influence the trend, which could be due to the more or less similar wear resistance of TiN and TiAlN as compared to the much softer steel substrate.

![Figure 11.10](image-url)

**Figure 11.10:** Cross sectional area of removed material from ~0.3 µm (red triangles), ~0.1 µm (green circles) and ~0.1 µm (blue squares) TiAlN samples of the TiAlN-on-TiN-on-Steel series. Negative values indicate removal.
The peak (maximum) scar depths, identified like before as the deepest dip of the grooves, are plotted for the TiAlN-on-TiN-on-Steel series as a function of the number of cycles in Fig. 11.11 for the ∼0.3 µm (red triangles), ∼1 µm (green circles) and ∼3 µm (blue squares) top TiAlN layer together with the corresponding average depths obtained as the area of removed material divided by the width of the scar. Both peak depths (empty symbols) and average depths (full symbols) increase with the number of wear cycles, which indicate the that previous signs of groove delamination observed for the single layer samples (Fig. 11.5) may not be present for these multi-layer samples. This is also supported by the scar profiles as the grooves of these appear to reach different depths for different number of wear cycles, even if a number of grooves in a scar reach similar (but not identical) depths.

As before, \( k \) (of Eq. (5.1)) is derived from the areas of removed material (Fig. 11.10) together with the corresponding number of wear cycles, \( n \) (see Tab. 8.3) and the applied normal load, \( F \). The derived values are plotted in Fig. 11.12 for the ∼0.3 µm (red triangles), ∼1 µm (green circles) and ∼3 µm (blue squares) top TiAlN layer samples, in which a somewhat scattered collection of wear rates is seen – as compared to the much more correlated results on the single layer samples (Fig. 11.6). But, a closer comparison of the
individual wear scar and corresponding obtained wear rate value reveals that the only connection between wear scar and wear rate of these multi-layer samples seems to be the fact that a maximal wear-through to TiN (when much TiN is visible) leads to a high value for the wear rate and vice versa for a minimal wear rate. Thus, the wear rates comparable to those of single layer TiAlN (Tab. 11.1) are obtained for wear scars barely worn through to TiN (e.g. scar 1 of sample 42, Fig. 11.7(b)). Specific wear rates (corresponding to those of Tab. 11.1) are not derived for these multi-layer samples due to the fact that all samples deliberately are worn through to TiN causing a mixing of the two materials and as a consequence of that, the much diverging wear rates.

11.2 Optical Response Simulations on Wear

The composition of the layer thickness of the two individual multi-layer systems, TiN-on-TiO$_2$-on-Steel (Fig. 2.5) and TiAlN-on-TiN-on-Steel (Fig. 2.6), are studied in order to reach the largest possible shift in the laser reflectance, $R$. Quantities such as the complex refractive indices ($\tilde{n}_{i}$) of the involved materials, the wavelength ($\lambda$) of the laser beam and the angle of incidence ($\theta$) were employed to find the right layer thicknesses ($d_{i}$) of the multi-layer systems as listed in Tab. 7.4 (see also sections 4.2 and 7.3) together with the values obtained for the refractive indices and extinction coefficients of TiO$_2$, TiN, TiAlN and 100Cr6 steel (Tab. 10.7).

11.2.1 Layer Thicknesses for TiN-on-TiO$_2$-on-Steel Multi-Layer Samples

The optimum layer thicknesses for TiN and TiO$_2$ layers of the TiN-on-TiO$_2$-on-Steel multi-layer system is calculated to achieve the highest possible increase in the laser reflectance as the top TiN coating becomes thinner and thinner. A contour plot of the laser reflectance, $R$, is calculated (by Eqs. (4.9) - 4.12)) as a function of the TiN and TiO$_2$ layer thickness and displayed in Fig. 11.13 for TE (a) and TM (b) polarized light, where bright colors correspond to high $R$-values and dark colors corresponds to low $R$-value (see figure legend). The white areas are calculated in details in Fig. 11.14 for TE (a) and TM (b) polarized light.

![Figure 11.13: Contour plot of the calculated reflectance $R$ as a function of the top TiN coating thickness and the embedded TiO$_2$ signal layer thickness for TE (a) and TM (b) polarized laser light at an incident angle of $\theta = 45^\circ$.](image-url)
A significant decrease in $R$ is seen for TE polarized light as the TiN thickness decreases – and maximum shifts in $R$ are possible if the embedded TiO$_2$ thickness is within certain ranges. A cross section of the reflectance contour plot is plotted in Fig. 11.15 as a function of the TiO$_2$ thickness with a 5 nm top TiN coating. The cross section shows how $R$ (both TE (red lines) and TM (black dots)) drops to zero for different periodical values of the embedded TiO$_2$ thickness. In order to achieve a maximum drop in the laser reflectance a TiO$_2$ thickness of approx. 50, 200 or 300 nm etc. is necessary. Actually, the periods are spaced with approx. 135 nm and most likely caused by internal reflections within the thin and transparent TiO$_2$ layer due to the low absorption (see Tab. 10.7) in the material such that this interference pattern arise when the laser beam is scattered interlayerly between the high reflective steel substrate and the top TiN coating.

Figure 11.16 shows a cross section in the other direction of the contour plot (Figs. 11.13 or 11.14). The reflectance is calculated as a function of the decreasing TiN thickness for both an embedded TiO$_2$ layer of 50 nm (optimum thickness) and 100 nm (stippled red and black lines, not optimum thickness). A TiO$_2$ layer of 50 nm results in a possible maximum shift in $R$, while the TiN thickness decreases, of up to 0.7 (TE polarization), whereas an embedded layer of 100 nm result in a maximum possible shift of virtually nothing as seen from the stippled curves in the figure.

Angle of Incidence, $\theta$

All calculations on the laser reflectance were, so far, carried out with an incident angle of $\theta = 45^\circ$, as noted. However, this may not be the optimum angle when the goal is to achieve the largest possible shift in the reflectance, since the level of the reflectance may also depend on the angle of the incoming laser beam.

$R_{Max}$ is calculated with a 300 nm TiN thickness, since TiN is completely non-transparent above 300 nm (see Figs. 10.7 and 10.9) and $R$ has a high and unchanged level (Figs. 11.13 and 11.16) for the subsequent 200 nm’s (from 100 - 300 nm). Similarly, $R_{Min}$ is calculated with a TiN layer thickness of 5 nm, since $R$ have a minimum level between 0 and 10 nm (see Fig. 11.16 (full lines)). Table 11.2 displays the maximum and minimum reflectance values calculated with an embedded TiO$_2$ layer of 50 nm.
11.2. OPTICAL RESPONSE SIMULATIONS ON WEAR

Figure 11.15: Calculated reflectance as a function of the TiO$_2$ thickness for TE (red line) and TM (black dots) pol. light with a 5 nm top TiN coating. $\theta = 45^\circ$.

Figure 11.16: Calculated Reflectance as a function of the TiN layer thickness of 50 nm and 100 nm (stippled red and black lines) TiO$_2$ at $\theta = 45^\circ$.

nm for both the TE and TM polarization. The largest possible shift (‘Difference TE’ or ‘Difference TM’ in the table) is found for an incident angle of $\theta = 50^\circ$, where a decrease of above 0.7 is possible to achieve with a TE polarized laser beam. The shift is, nevertheless, not depending strongly on $\theta$, but very wide incident angles result in a significant drop in the possible shift, especially for TM polarized light.

From these multi-layer analysis a most ideal composition of TiN, TiO$_2$ and 100Cr6 steel may be established, such that the TiN-on-TiO$_2$-on-Steel multi-layer system, in conclusion, should be composed to have a layer thickness of the embedded TiO$_2$ signal layer of either $\sim 50$ nm, $\sim 200$ nm, $\sim 300$ nm... and the incident angle of the laser beam during measuring should be around $\theta = 50^\circ$. A TiO$_2$ layer thickness of 50 nm was based on these calculations chosen for this multi-layer system as previously listed in Tab. 2.3 and displayed in Fig. 2.7 (section 2.3.2).

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<th>$\theta$</th>
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Table 11.2: Maximum ($R_{Max}$) and minimum ($R_{Min}$) values for the laser reflectance, $R$, (both TE and TM) for different angles of incidence, $\theta$. 
CHAPTER 11. WEAR ON TIN AND TIALN TRIBOLOGICAL COATINGS

11.2.2 Layer Thicknesses for TiAlN-on-TiN-on-Steel Multi-Layer Samples

The optimal layer thicknesses of the TiAlN-on-TiN-on-Steel multi-layer system were also studied such that the highest possible shift in the reflectance as the top TiAlN coating diminishes is achieved. As before, the procedure is to initially calculate the contour plot of the laser reflectance (from Eqs. (4.9) - (4.12)) as a function of the top TiAlN coating thickness and the embedded TiN layer thickness. This is plotted in Fig. 11.17 for TE (a) and TM (b) polarized laser light, in which dark colors correspond to low \( R \) values and bright to high \( R \) values as the figure legends display. The white areas (below a TiAlN thickness of \( \sim 50 \) nm) are calculated in greater details and plotted in Fig. 11.18 for both TE (a) and TM (b) polarized light.

![Figure 11.17](image1)

Figure 11.17: Calculated reflectance as a function of the top TiAlN coating thickness and the embedded TiN signal layer thickness for TE (a) and TM (b) polarized laser light at an incident angle of \( \theta = 45^\circ \).

![Figure 11.18](image2)

Figure 11.18: Calculated reflectance as a function of the top TiAlN coating thickness and the embedded TiN signal layer thickness for TE (a) and TM (b) polarized laser light at \( \theta = 45^\circ \).
11.2. OPTICAL RESPONSE SIMULATIONS ON WEAR

As the top TiAlN coating becomes thinner, the reflectance $R$ increase almost continuously with only a few soft wiggles seen for larger TiAlN thicknesses, whereas the reflectance increases smooth and steadily for very thin TiAlN layers (below $\sim 50$ nm). This is also seen from a cross section of the laser reflectance contour plot as displayed in Fig. 11.19, in which $R$ is plotted (at $\theta = 45^\circ$) as a function of the TiAlN thickness for both TE (red line) and TM (black dots) polarizations. The largest possible shift in $R$ for this system is achieved for embedded TiN thicknesses of above approx. 40 nm, as seen from the detailed contour plots (Fig. 11.18 a and b). This means that the shift in $R$ is unaffected by the embedded TiN layer thickness providing it exceeds an approximate thickness of 40 nm. The periodically changes observed for the previous system with the embedded TiO$_2$ layer is not as clearly observed for this system and no specific TiN layer thickness should accordingly be realized. The reflectance wiggles are (as for the previous system) due to the low absorption in TiAlN (see Tab. 10.7) such that reflections internally in the TiAlN layer causes this interference-like pattern. Actually, far more heavy interference arise when the absorption in TiAlN is reduced.

Angle of Incidence, $\theta$

The reflectance was also analyzed with respect to the incident angle, since the $R$ level may also depend on $\theta$, as before. This is shown in Fig. 11.20, in which the reflectance is calculated as a function of the top TiAlN thickness for incident laser beam angles of $\theta = 0^\circ$ and $\theta = 60^\circ$. The TE (dotted red line) and TM (black crosses) reflectance calculated with an incident angle of $\theta = 0^\circ$ coincide completely, whereas $R_{TE}$ (full red line) and $R_{TM}$ (full black line) calculated at $\theta = 60^\circ$ differs somewhat and are separated in the $R$ level with quite a step. However, significant increases from the minimum $R_{Min}$ level at large TiAlN thicknesses to the maximum $R_{Max}$ at zero TiAlN thickness are seen for both polarizations and at both incident angles.

The minimum $R$ level was calculated for a TiAlN thickness of 300 nm, since the reflectance (see Figs. 11.19 and 11.20) is unchanged above this thickness. Similarly, the maximum $R$ level was calculated with no TiAlN thickness left, i.e. for 0 nm. Table 11.3 displays the obtained maximum $R_{Max}$ and minimum $R_{Min}$
### Table 11.3: Maximum ($R_{\text{Max}}$) and minimum ($R_{\text{Min}}$) values for the laser reflectance $R$ (both TE and TM) for different angles of incidence, $\theta$.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$R_{\text{TE,Max}}$</th>
<th>$R_{\text{TE,Min}}$</th>
<th>$R_{\text{TM,Max}}$</th>
<th>$R_{\text{TM,Min}}$</th>
<th>Difference TE</th>
<th>Difference TM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6529</td>
<td>0.1698</td>
<td>0.6529</td>
<td>0.1698</td>
<td>0.4831</td>
<td>0.4831</td>
</tr>
<tr>
<td>10</td>
<td>0.6576</td>
<td>0.1745</td>
<td>0.6482</td>
<td>0.1652</td>
<td>0.4832</td>
<td>0.4830</td>
</tr>
<tr>
<td>20</td>
<td>0.6717</td>
<td>0.1891</td>
<td>0.6334</td>
<td>0.1515</td>
<td>0.4826</td>
<td>0.4825</td>
</tr>
<tr>
<td>30</td>
<td>0.6948</td>
<td>0.2157</td>
<td>0.6100</td>
<td>0.1289</td>
<td>0.4792</td>
<td>0.4811</td>
</tr>
<tr>
<td>40</td>
<td>0.7267</td>
<td>0.2578</td>
<td>0.5764</td>
<td>0.0988</td>
<td>0.4690</td>
<td>0.4776</td>
</tr>
<tr>
<td>45</td>
<td>0.7458</td>
<td>0.2863</td>
<td>0.5563</td>
<td>0.0820</td>
<td>0.4595</td>
<td>0.4743</td>
</tr>
<tr>
<td>50</td>
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<td>0.3211</td>
<td>0.5344</td>
<td>0.0654</td>
<td>0.4459</td>
<td>0.4691</td>
</tr>
<tr>
<td>60</td>
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<td>0.4138</td>
<td>0.4908</td>
<td>0.0414</td>
<td>0.4012</td>
<td>0.4494</td>
</tr>
<tr>
<td>70</td>
<td>0.8702</td>
<td>0.5473</td>
<td>0.4715</td>
<td>0.0638</td>
<td>0.3229</td>
<td>0.4077</td>
</tr>
<tr>
<td>80</td>
<td>0.9322</td>
<td>0.7366</td>
<td>0.5669</td>
<td>0.2474</td>
<td>0.1955</td>
<td>0.3195</td>
</tr>
<tr>
<td>89</td>
<td>0.9930</td>
<td>0.9698</td>
<td>0.9345</td>
<td>0.8710</td>
<td>0.0232</td>
<td>0.0639</td>
</tr>
</tbody>
</table>

values (for both TE and TM polarized light) together with the largest possible change in $R$ (labeled 'Difference TE' or 'Difference TM'), which is found as the difference between the $R_{\text{Max}}$ and $R_{\text{Min}}$ for the two polarization types. The largest possible change in the reflectance level found for a normal incident angle of the laser beam such that a maximum increase in the reflectance level, for both polarizations, is achieved for $\theta = 0^\circ$. Subsequent decreases in the change are seen for all other incident angles. But, a large decrease in the reflectance level is only observed for incident angles above $\theta = 70^\circ$.

In conclusion, a very thick embedded TiN layer thickness was chosen for the TiAlN-on-TiN-on-Steel multi-layer system (see e.g. Tab. 2.4), since very deep grooves and ridges are seen in the actual wear scars (see Fig. 11.3) and a thick embedded TiN layer is preferred in order to prevent the wear process in proceeding through to the steel substrate within some of these deeper grooves. Furthermore, a thick TiN coating is far more easily produced by CemeCon as compared to very thin and precise films such as the 50 nm TiO$_2$ film of the previous case. Finally, delamination, which is poor binding between different layers such that larger pieces flake of (see e.g. section 5.2), is not as prevalent for thick coating as for very thin coatings.

### 11.3 Simulated Wear Process – Calculations Vs. Measurements

The two multi-layer sample series, TiN-on-TiO$_2$-on-Steel and TiAlN-on-TiN-on-Steel, were utilized to imitate the properties of a wear situation in the sense that the top coating becomes thinner and thinner on each of the samples (see e.g. Figs. 2.7 and 2.8). Different analyzes of the two systems lead, in the above section, to the optimum layer thickness composition and a comparison between the obtained reflectance as a function of the decreasing top coating and the reflectance measured of a series of samples with decreasing top coating is discussed here. Thus, the theoretical reflectance just derived is compared with the reflectance measured (see section 10.2) of actual samples - for the two multi-layer sample systems.
11.3.1 TiN-on-TiO$_2$-on-Steel Multi-Layer System

Figure 10.7 displayed above the laser reflectance $R(\theta)$ measured from each of the 5 samples in the TiN-on-TiO$_2$-on-Steel multi-layer series (see e.g. Fig. 2.7) for both polarizations and Fig. 11.21 displays the exact same measurement but only for $\theta = 45^\circ$ and with the reflectance now plotted for each sample as a function of the estimated top TiN layer thickness, $R(d_{TiN})$, where the error bars on the sample thicknesses arise from the independent TiO$_2$ and TiN layer thickness estimation (see Tab. 10.3). Thus, the reflectance measured (filled red squares (TE), open black squares (TM)) from the 5 samples are plotted as a function of the top TiN thickness together with the corresponding theoretical reflectance (full red line (TE), full black line (TM)), calculated as in the previous section (11.2).

The measured data sets $R(d_{TiN} = 0, 21, 41, 69$ and $107 \text{ nm})$ compares very well with the theoretically derived reflectance and show a clear decrease in $R$ as the TiN thickness decreases and especially an abrupt change in the reflectance is observed between the 41 nm layer sample and the 21 nm layer sample. The reflectance level changes from a bulk TiN level of $\sim 0.75$ and down to $\sim 0.25$ at 0 nm TiN (TE polarization) and likewise from $\sim 0.55$ for bulk TiN and down to $\sim 0.15$ for 0 nm TiN (TM polarization), which is a total decrease of roughly 0.5 in both polarizations. Moreover, the TiN coating is almost opaque at a thickness of 69 nm, since the reflectance level of this sample matches the level of the 100 nm sample, which previously was seen to be completely opaque when comparing with the thick TiN reflectance measurement (see Fig. 10.7 and 10.9).

11.3.2 TiAlN-on-TiN-on-Steel Multi-Layer System

A similar comparison of the other multi-layer series TiAlN-on-TiN-on-Steel (see e.g. Fig. 2.8) is also conducted. Figure 10.8 displayed above the laser reflectance $R(\theta)$ measured for both polarizations from each of the 5 samples and Fig. 11.22 shows precisely the same measurement but only for $\theta = 45^\circ$ and with the reflectance now plotted for each sample as a function of the estimated top TiAlN layer thickness, $R(d_{TiAlN})$, where the error bars on the sample thicknesses arise form the independent TiAlN layer thickness estimation (see Tab. 10.4). Accordingly, the reflectance measured from the 5 samples (filled red squares(TE), open black squares (TM)) is plotted as a function of the TiAlN thickness together with the theoretically derived reflectance (full red line (TE), full black line (TM)).

The measured data sets $R(d_{TiAlN} = 0, 40, 85, 101$ and $134 \text{ nm})$ of this other multi-layer series also compares well with the calculated reflectance and show a clear increase in the reflectance as the TiAlN thickness decreases. Especially, a significant increase is observed from the 40 nm layer sample to the 0 nm layer sample, which for some parts are caused by the low value of the measured reflectance as compared to the calculated. Whether this is caused by an actual thin film phenomena or maybe due to a slight production mishap is difficult to argue. The reflectance level changes, for the TE polarization, from a bulk TiAlN level of $\sim 0.3$ and up to a bulk TiN level of $\sim 0.75$ and correspondingly from $\sim 0.1$ at bulk TiAlN and up to $\sim 0.55$ at bulk TiN – for the TM polarization. In total, both polarizations show significant changes in $R$ of above 0.5, at best. Besides this, the TiAlN film is seen to become opaque for film thicknesses above 100 - 120 nm, since the reflectance levels of the two final samples are somewhat similar.
Summary on Calculations and Measurements

Clearly, the TiN-on-TiO$_2$-on-Steel multi-layer system may in principle be able to work as an optical wear monitor – the warning system previously discussed in Fig. 4.10 (see section 4.3.1) due to the fine connection between measurement and theory in Fig. 11.21. The reflectance is actually seen to decrease significantly (above 0.5) as the TiN layer becomes increasingly thinner and ultimately transparent – and the embedded TiO$_2$ layer reached, i.e. when the TiO$_2$ and TiN layers and thicknesses are arranged as described (see section 11.2). Also, the second multi-layer system, TiAlN-on-TiN-on-Steel, is proven in Fig. 11.22 to be able to work as the second warning system discussed in Fig. 4.12, since the reflectance level display a significant increase (also above 0.5) as the top TiAlN layer thickness becomes increasingly thinner and eventually transparent – and the embedded TiN signal layer reached.

Both multi-layer systems have thus proven to be able to work as part of a warning system of the optical wear monitor. Adding several alternating layers of either TiO$_2$/TiN or TiN/TiAlN to a steel tool may consequently, when combined with a red laser source and a detector in principle result in significant changes in the level of the measured laser reflectance such that warnings on the level of wear could be obtained. But, these measurements on the two sample series are only proofs, that the multi-layer systems, in theory, may work as warning systems – no actual wear processes were involved in these measurements and simulations. The subsequent sections deal with the post mortem optical response of the multi-layered samples, which have been exposed to a real abrasive wear process.

11.4 Reflection Response on Wear Scars

Wear scars on TiAlN-on-TiN-on-Steel multi-layer samples (see Figs. 11.7(a) - 11.9(b)) were studied above with Dektak profilometry (in section 11.1.2) in terms of for instance wear quality. But, these multi-layer wear scars were also studied by optical means and the results on these optical laser reflectance measurements are given here for a selected number of wear scar samples.

Wear Scar Roughness

Very rough scar surfaces with many sharp ridges and grooves were previously observed in the wear scars from the scan profiles (see e.g. Fig. 11.3). But, this extreme roughness is also seen in a micrograph example of a wear scar introduced in a TiN single layer as displayed in Fig. 11.23, in which the scar grooves and ridges are clearly visible in both the TiN coating and in the emerging steel substrate and these wear scars continues as such along the complete wear scar regardless of the material type. The extremely ridged and corrugated scar surfaces such as the micrograph example are seen for all wear scar samples in these studies. As a result, a large degree of scattering and diffraction is observed in the optical reflection response such that extremely non-collimated laser beams are reflected off the wear scars. This effect of the rough surface was discussed and illustrated above in Fig. 4.8 (see section 4.2.3), but also previously observed in reflections from tribologically worn surfaces by Le Bosse et al. [117].

A photo of the HeNe laser beam reflected of a worn surface, i.e. of a wear scar, is shown in Fig. 11.25, where a quite heavy scatter and diffraction pattern of the beam is clearly visible. This scattering effect of the reflected beam is actually observed for all wear scars and the scattered beam appearing in the photo represents more or less the reflected beam in all the reflectance measurements of wear scars studied here. Figure 11.24 displays a photo of the laser beam reflected of a corresponding (as-received) unworn sample surface, where the reflection beam is collimated and well defined, as expected. Placing a lens
11.4. REFLECTION RESPONSE ON WEAR SCARS

Figure 11.21: Measured TE (filled red squares) and TM (empty black squares) reflectance at $\theta = 45^\circ$ of the 5 samples of the TiN-on-TiO$_2$-on-Steel series (see Fig. 2.7) with top TiN layers of 0, 21, 41, 69 and 107 nm on TiO$_2$/steel together with the corresponding theoretically derived (full lines) reflectance as a function of $d_{TiN}$ the top TiN thickness.

Figure 11.22: Measured TE (filled red squares) and TM (empty black squares) reflectance at $\theta = 45^\circ$ of the 5 samples of the TiAlN-on-TiN-on-Steel series (see Fig. 2.8) with top TiAlN layers of 0, 40, 85, 101 and 134 nm on TiN/steel together with the corresponding theoretically derived (full lines) reflectance as a function of $d_{TiAlN}$ the top TiAlN thickness.
right after the sample circumvent the problem with the reflected beam scattering of the very rough wear scar. The lens collects a large fraction of the light from the scattered beam if placed sufficiently close to the sample surface and focuses the reflection beam such that most light is collected with the power meter detector head – regardless of the heavy scattering. This would otherwise be very difficult. The collecting lens is for these reasons also included in the principal drawing of the optical setup (see Fig. 8.6) above.

A full length wear scar as detected with an optical light microscope is displayed in Fig. 11.26. It was worn as Fig. 8.3 illustrated above, such that the wear process with the CVA steps on a length from 10 and down to 2 mm corresponds to the darker micrograph area to the left hand side of the scar. The final 2 mm in the CVA wear process corresponds to the brighter micrograph area to the right hand side, in which there are no CVA steps. The full length wear scar demonstrate a kind of roughness different from the previously addressed groove roughness (see Figs. 11.3 and 11.23). This other type of roughness originates specifically from the CVA wear process, in which for instance a large number of cycles leads to a large number of steps along the scar as discussed in section 8.1.1. Thus, an increased number of cycles in a wear process lead to an increased number of steps, which in turn leads to an increased roughness along the scar such that this roughness type is dependent on the number of cycles in the wear process.

**TiN-on-TiO$_2$-on-Steel Multi-Layer Samples**

The TiN-on-TiO$_2$-on-Steel multi-layer system, as it turned out was not used in the combined optics and wear studies despite the excellent result of the simulated wear in Fig. 11.21. The decision for not testing the TiN-on-TiO$_2$-on-Steel multi-layer samples was based on among other things the wear results of section 11.1, which showed extremely rough scar surfaces with the appearance of very deep grooves and ridges (see e.g. Fig. 11.3 and 11.23). The embedded TiO$_2$ signal layer of the TiN-on-TiO$_2$-on-Steel samples was constituting a thickness of a mere 50 nm, which would have completely vanished in the $\mu$m wide and deep emerging grooves. Moreover, the possibility of wearing through the very thin TiO$_2$ layer and into the steel substrate would be present for virtually all wear scars, since the wear process as it turned out was very difficult to control.

*Figure 11.23: Grooves and ridges on micrometer scale sizes detected with an optical light microscope from a wear scar introduced in a single layer of TiN on 100Cr6 steel. TiN is the bronze colored areas and steel the grey colored areas.*
11.4. REFLECTION RESPONSE ON WEAR SCARS

Figure 11.24: Photo of collimated beam spot reflected of an unworn TiN surface.

Figure 11.25: Photo of the laser beam reflected/scattered of a wear scar in a TiN surface.

Furthermore, the TiN-on-TiO$_2$-on-Steel multi-layer system was created from the concept of an initial high laser reflectance signal, which would supposedly show a dip when the TiO$_2$ signal layer was reached as discussed in section 4.3, illustrated in Fig. 4.10 and proven possible in Fig. 11.21. However, this dip or decrease in the laser reflectance would not have been possible to distinguish from a quite potential decrease caused by roughness due to the wear. Thus, it would not have been possible to decide whether a measured decrease is a result of the embedded TiO$_2$ layer being reached or if the roughness in the scar was increased. Ultimately, the TiN-on-TiO$_2$-on-Steel multi-layer system was not utilized in the combined optics and wear measurements.

11.4.1 4 TiAlN-on-TiN-on-Steel Multi-Layer Wear Scar Samples

Four different wear scars have been selected to represent the result on the laser reflectance method. Figure 11.27 displays the photos zooming in on the selected scar samples, where the scar geometry ideally corresponds to that of Fig. 8.3 such that golden yellow TiN appear in the bottom of the scar to the right hand side and the residual TiAlN thickness to the left hand side (see section 8.1.1).

The first scar example is seen in Fig. 11.27a. It is from sample 41 (scar 4, see Fig. 11.7(a)) and coated with $\sim$0.3 $\mu$m TiAlN on top of the embedded TiN. The scar emerged after 3 000 reciprocating CVA cycles with a maximum depth of 0.69 $\mu$m as derived from the Dektak scan profile of Fig. 11.28. Thus, the top TiAlN coating was worn through at the deeper scar end to the embedded TiN coating, which is quite visible with a streaky yellow appearance in the scar photo.

Figure 11.26: Roughness along wear scar caused by CVA wear process.
CHAPTER 11. WEAR ON TIN AND TIALN TRIBOLOGICAL COATINGS

Figure 11.27: Zoomed photos of selected wear scar examples studied with the laser reflectance method together with the combined camera detection and image analysis (see sections 11.5 and 11.6) below. The samples are (a) scar 4 of sample 41, (b) scar 1 of sample 44, (c) scar 1 of sample 42 and (d) scar 1 of sample 46 as seen from the complete sample collection in Figs. 11.7(a) - 11.9(b). There are no scale bars, but the scar lengths correspond ideally to those of Fig. 8.3. The corresponding number of CVA cycles are noted together with the top TiAlN layer thickness (see also Tab. 11.4 below).
11.4. REFLECTION RESPONSE ON WEAR SCARS

The second wear scar example is from sample 44 (scar 1, see Fig. 11.8(b)) and coated with $\sim 1$ $\mu$m TiAlN. It reached a maximum depth of 2.40 $\mu$m as seen from the scan profile in Fig. 11.29, which emerged after 15 000 reciprocating CVA cycles in the linear tribometer. The embedded TiN is thus visible in very pronounced yellow streaks along the bottom of the scar as the zoomed scar photo in Fig. 11.27b clearly shows.

The embedded TiN layer barely peeps out in the third wear scar example as seen in Fig.11.27c. It is from sample 42 (scar 1, see Fig. 11.7(b)) and coated with $\sim 0.3$ $\mu$m TiAlN on top of the TiN layer. The scar emerged after 3 000 reciprocating CVA cycles and has a maximum depth of 0.38 $\mu$m (see Fig. 11.30) but most of the ridges in the scar barely reach depths of 0.2 $\mu$m, which ultimately causes the somewhat faded view of the embedded TiN layer in this scar.

Finally, the fourth example from sample 46 (scar 1, see Fig. 11.9(b)) is coated with $\sim 3$ $\mu$m TiAlN and displayed in Fig. 11.27d. The scar was worn with 40 000 cycles and has a maximum depth of 4.23 $\mu$m as seen in Fig. 11.31. Parts of this scar is worn through both the top TiAlN coating and the embedded TiN layer such that the steel substrate appear in the bottom of the scar. The emerging steel is visible in the photo as light grey areas to the right hand side of the scar.
These four scar examples (Fig. 11.27) have been studied closely by measuring the laser reflectance $R$ along the scars, from the left hand side to the right. Subsequently, the examples have also been studied with the combined camera detection and image analysis. This will be discussed further below in section 11.5. And finally, the results from the laser reflectance method and the camera detection are compared for these four examples, since they have different application possibilities (see section 11.6).

### 11.4.2 Laser Reflectance Measurements

The laser reflectance $R$ was measured with a simple optics setup (see Fig. 8.6), where the HeNe laser beam was scanning along the wear scar, i.e. along the residual top TiAlN coating as illustrated (Fig. 8.5) and described in section 8.2. The reflectance was measured at a fixed angle of incidence ($\theta = 60^\circ$) along three different path ways; an upper, a central and a lower path labeled top, center and bottom, respectively. In addition, the measured reflectance level for TiN and TiAlN is included in all displayed measurements, where $R_{\text{TiN}} = 0.78$ and $R_{\text{TiAlN}} = 0.47$ at $\theta = 60^\circ$. It should be noted that $R_{\text{TiAlN}}$ as plotted is measured from an unworn multi-layer sample, whereas the TiN level is measured from a single layer TiN coating.

Figure 11.32 shows the laser reflectance $R$ measured along scar 4 of sample 41 (Fig. 11.27a), which before the scar starts corresponds to the TiAIN level. $R$ then starts increasing steadily as the laser beam moves into the scar area of decreasing TiAIN layer thickness, continues to increase until a plateau, which corresponds fully exposed TiN, is reached and descents afterwards quickly as the laser beam moves out side the scar. The subsequent wear scar (Fig. 11.27b) measured along the scar as plotted in Fig. 11.33 has the initial $R$ level corresponding to the TiAIN level, but then starts decreasing, as the laser beam accesses the scar, until a minimum is reached between $\sim 2 - 4$ mm’s. This decrease is followed by a steady increase until a plateau, corresponding to fully exposed TiN, is reached after $\sim 8$ mm’s. Finally, $R$ drops fast to the initial TiAIN level as the beam moves outside the scar.

Clearly, the two examples demonstrate a significant increase in the measured $R$ level, while scanning along the residual top TiAIN coating and both examples show an $\sim 0.25$ increase from the TiAIN coating to the embedded TiN signal layer. This is less than what should be the experimentally feasible, i.e. the difference between the TiAIN and TiN reference levels ($R_{\text{TiAIN}} - R_{\text{TiN}} = 0.31$). But, it is a significant increase in the reflectance and only 25 - 30% below the experimental feasible maximum. A significant

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**Figure 11.32:** Reflectance measured along scar 4 of sample 41 (see Fig. 11.27a).

**Figure 11.33:** Reflectance measured along scar 1 of sample 44 (see Fig. 11.27b).
11.4. REFLECTION RESPONSE ON WEAR SCARS

decrease in the beginning of the second scan most likely arise from a roughness increase, since the first example was worn with 3,000 cycles and the latter with 15,000. The larger number of cycles result in a higher number of CVA steps along the wear scar, which in turn causes an increased roughness (see Fig. 11.26) such that a subsequent loss of light due to increased scattering appear in the beginning of the scan in the latter example (Fig. 11.33).

Figure 11.34 shows \( R \) measured along scar 1 of sample 42, where only minor and insignificant changes appear as the laser scans the wear scar. This indicates the embedded TiN has not yet been reached in the scar, but the sample photo (Fig. 11.27c) reveals TiN slightly appearing in the bottom of the scar. Apparently, TiN is not quite visible enough to result in any significant changes in \( R \) and this sample may as such visibly display the point of transition from top TiAlN to embedded TiN. The final example (Fig. 11.27d) scanned along the scar is plotted in Fig. 11.35, in which \( R \) starts decreasing for all three paths and is succeeded by an increase, which peaks around 10 mm. A subsequent fast drop and rise below and above the \( R_{TiAlN} \) level is observed as the laser beam scans past the end of the scar, which most likely is caused by an increased roughness at the scar end due to the high number of CVA steps in a fashion similar to the decrease observed in the beginning of the scan example (Fig. 11.33).

A very uneven and bumpy reflectance is measured along the final scar (Fig. 11.35) and the individual (red, green and blue) paths are quite dissimilar. The bumpy nature of the scans may be a result of the laser beam scanning across streaks of unremoved and less reflective TiAlN in the scar (dark TiAlN streaks are visible all along some scars). It could as well be a consequence of the sample being worn all the way through to the steel substrate, since steel is less reflective than TiN (see Fig. 10.9) due to different optical properties of the two materials (see Tab. 10.7). A closer view on the sample photo (Fig. 11.27d) actually reveals this and the issue will be addressed in the image analysis study.

The effect with a significant increasing change in \( R \), as the laser beam scans along scars with TiN appearing in the bottom of the scar, is seen for all successful wear scars. But, not all wear scars and corresponding reflectance measurements are as successful as the two initial measurements (Fig. 11.32 and 11.33) and the increase thus not as significant. Nevertheless, the increase in the reflectance is still quite significant for most successful wear scars. Especially when the very extreme roughness conditions and other deteriorating factors in the scars are taken into account, since these reduce the feasible change in \( R \).

**Figure 11.34:** Reflectance measured along scar 1 of sample 42 (see Fig. 11.27c).

**Figure 11.35:** Reflectance measured along scar 1 of sample 46 (see Fig. 11.27d).
11.5 Camera Detection and Image Analysis of Wear Scar

Two dimensional camera detection combined with an image analysis scheme was, as a monitoring method supplementary to the optical laser reflection response just discussed, employed to study the 4 selected TiAlN-on-TiN-on-Steel multi-layer scar samples of Fig. 11.27. The procedure with the camera detection and image analysis was previously described in section 8.3, where the idea of the rectangularly shaped mask surrounding the wear scar was illustrated in Figs. 8.7 - 8.8 and the red, green and blue pixel readout explained. Only the red and blue pixel values are included in the image analysis, due to these colors corresponding to those of TiN (red) and TiAIN (blue), as explained in section 8.3. It should be noted that the image analysis software mirrors the image, such that the surface plots are reversed compared to the scar photos.

A surface plot of the red pixel values read out from a well selected area surrounding scar 4 of sample 41 (Fig. 11.27a) is shown in Fig. 11.36a as a function of the scar width and length. Table 11.4 displays the pixel to mm gain for the photo image utilized for this scar together with the corresponding approx. size area and number of pixels. Areas of high pixel values correspond to a high amount of red in those pixels and areas of low pixel values correspond to a low amount of red, where the full scale from 0 - 255 naturally also accounts for the blue values. The corresponding blue pixel values from the same scar and mask area is shown in the surface plot in Fig. 11.36b. Areas of high red pixel values are seen, by comparing the surface plot (Fig. 11.36a) with the scar photo (Fig. 11.27a), to correspond to areas of bright TiN appearing in the bottom of the scar. Correspondingly, areas of lower blue pixel values (Fig. 11.36b) also match areas of emerging TiN. The effect is stronger for the red pixel values, where an estimated increase from red pixel values of around 100 to 200 is seen. A small effect is nevertheless also seen for the blue pixels, where the values decrease in areas corresponding to exposed TiN. This effect is a result of TiN being much more reflective in the red wavelength area than in the blue wavelength area.

Figure 11.37a shows the surface plot of red pixel values from the second example, scar 1 of sample 44 (Fig. 11.27b), and Fig. 11.37b shows the corresponding blue pixel values, both as a function of the scar length and width. The pixel to mm gain for this scar photo sample is listed in Tab. 11.4 together with corresponding approx. size area and number of pixels. This scar is seen in the photo to have a very streaky appearance, where alternating streaks of top (dark) TiAlN and embedded (bright) TiN appear all along the scar. Clearly, this striped appearance is also quite evident, especially in the red surface plot, as several tops of high pixel values appear along the scar length corresponding to areas of exposed TiN. The red pixel values rise from values just below 100 and up to around 200, whereas the blue pixel values stay at minimum values over most of the scar area. A decrease in the pixel values seems to take place for both red and blue pixels in the beginning of the scar, i.e. from ~1 to ~4 mm. The decrease in pixel values corresponds to the darker area (see scar photo) in the beginning of the scar and as mentioned above caused by the ’CVA’ roughness (see e.g Fig. 11.26 and 11.33).

The third sample, scar 1 of sample 42 (Fig. 11.27c), showed only insignificant changes in the preceding laser reflectance measurement (Fig. 11.34) due to TiN barely emerging in the bottom of the scar. However, taking a closer look on the scar with this camera detection and image analysis, alterations along the scar actually emerge. Figure 11.38a shows the surface plot of the red pixels, in which a minor increase in the pixel values appear to the end of the scar. It is not as significant as the two previous examples but a difference is clearly seen in the surface plot. A closer inspection reveals an increase in the red pixel values from around 95 to 120. The dip in pixel values at the far end of the scar (after a scar
distance of 10 mm) is most likely caused by increased roughness due to the steel ball contact reversing its movement at this position. The blue pixel surface plot seen in Fig. 11.38b shows a corresponding decrease along the scar due to poor reflection of TiN in the blue wavelength range. Furthermore, the dip appearing in the scar end of the red pixel values (after 10 mm) is also present in the blue pixel values. This means that loss of signal due to roughness in this case caused by the reciprocating motion of the contact is independent of the wavelength of detection. The (unmotivated) peak seen in both the red and blue surface plots (at a scar distance around 5 mm and scar width around 0.3 mm) corresponds to an error in the photo used for the image analysis and should as such just be disregarded. Table 11.4 displays the corresponding pixel to gain values.

Finally, the fourth example on the image analysis, scar 1 of sample 46 (see Fig. 11.27d), showed a very bumpy measurement on the laser reflectance (Fig. 11.35). Figure 11.39a displays the surface plot of the red pixel values, where the streaks of TiN along the scar appear as areas of increasing and high pixel values. The pixel values increase from around 80 to a maximum of 210. Areas of reduced pixel values are seen in the otherwise high pixel value end around scar length distances of ∼10 - 12 mm. These reduced areas emerge in some of the TiN caused streaks, where the red pixel levels are reduced with a maximum of almost 50% from 210 and down to reduced values of around 150 at the most severe areas.

The corresponding blue pixel surface plot is displayed in Fig. 11.39b, in which the reverse dark streaks equivalent to the areas of exposed TiN are observed along the scar distance. Furthermore, areas of increased blue pixel values are also seen towards the end of the wear scar such as areas of reduced red pixel values were correspondingly observed in Fig. 11.39a. The areas of reduced red pixel values and increased blue values are most likely caused by both the TiAlN and TiN sample coatings been worn through to the steel substrate such that steel emerge in these specific areas. In fact, the steel substrate does actually appear in the very bottom of this particular scar, as mentioned above (Fig. 11.27d) such that the areas of emerging steel correspond to the areas of reduced and increased red and blue pixel values, respectively. Once more, the pixel to mm gain is listed in Tab. 11.4.

It should be noted that the photos used for this image analysis of the wear scars may not be the actual photos displayed in Fig. 11.27 such that the resolution of those photos does not necessarily correspond to the referred values of gain from pixel to mm. Additionally, the sharpness or focus of the photos may not correspond to those used in the image analysis. The particular wear scar photos of Fig. 11.27 have been included since they make good visual representation of the subjects under investigation in the written text.

<table>
<thead>
<tr>
<th>Sample Photo</th>
<th>CVA cycles</th>
<th>Pixel Surface plot</th>
<th>Gain [pix/mm]</th>
<th>Mask Area [mm²]</th>
<th>Pixels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 11.27a</td>
<td>3 000</td>
<td>Fig. 11.36</td>
<td>89.28</td>
<td>0.85 × 10.76</td>
<td>76 × 961</td>
</tr>
<tr>
<td>Fig. 11.27b</td>
<td>15 000</td>
<td>Fig. 11.37</td>
<td>109.07</td>
<td>0.94 × 12.66</td>
<td>102 × 1381</td>
</tr>
<tr>
<td>Fig. 11.27c</td>
<td>3 000</td>
<td>Fig. 11.38</td>
<td>24.49</td>
<td>1.43 × 11.60</td>
<td>35 × 284</td>
</tr>
<tr>
<td>Fig. 11.27d</td>
<td>40 000</td>
<td>Fig. 11.39</td>
<td>74.63</td>
<td>1.22 × 14.37</td>
<td>91 × 1073</td>
</tr>
</tbody>
</table>

Table 11.4: Widths and lengths (in different units) of the scar examples studied by image analysis.
Figure 11.36: Surface plot of red (a) and blue (b) pixel values of scar 4 sample 41 (small insert, see Fig 11.27a).
Figure 11.37: Surface plot of red (a) and blue (b) pixel values of scar 1 sample 44 (small insert, see Fig 11.27b).
Figure 11.38: Surface plot of red (a) and blue (b) pixel values of scar 1 sample 42 (small insert, see Fig 11.27c).
Figure 11.39: Surface plot of red (a) and blue (b) pixel values of scar 1 sample 46 (small insert, see Fig. 11.27d).
CHAPTER 11. WEAR ON TIN AND TIALN TRIBOLOGICAL COATINGS

The total number of pixels and thus also the gain from pixel to mm is different for the 4 scar photos used in this study (see Tab. 11.4). The surface plots of Fig. 11.37 contains a lot of pixels, which causes the surface plots (for both red and blue pixels) to have a quite speckled appearance. The surface plots of Fig. 11.38 contains only a relative few number of pixels and as a result, the two surface plots (red and blue) are much less speckled in the appearance. The 'smoothness' of the surface plot is furthermore also influenced by the photo quality, i.e. whether or not the wear scar is in focus.

Two dimensional camera detection and subsequent image analysis have shown to be equally efficient compared to the previous laser reflectance method in the analysis of the 4 wear scar examples, such that the difference from the dark top TiAlN coating is quite clearly distinguished from the embedded bright TiN layer in the measured red pixel values. Even the rather vague scar 1 of sample 42 (Fig. 11.27c) showed visible differences in the detected red pixel values (Fig. 11.38a), when going from areas of TiAlN to areas of TiN, although the TiN was not really emerging through the TiAlN layer. Thus, the camera detection scheme may also be a quite efficient optical monitor method in observing the reflection difference from TiAlN and TiN.

11.6 Laser Reflectance Vs. Camera Detection

The two dimensional image processing analysis was done in addition to the laser reflectance measurements discussed in section 11.4.2, since a camera generally is able to detect much larger surface areas than a laser beam as Fig. 11.40 illustrates. The laser beam scanner is in the laser reflectance method setup in principle a one dimensional detection scheme (see also Fig. 8.5) since the laser beam extension is limited to \( \sim 100 \mu m \) (spot size of the laser beam), whereas the camera detects two dimensional areas of sizes depending on the resolution and optics of the specific camera.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11_40.png}
\caption{Geometrical difference between the two dimensional camera detection scheme and the (in principle) one dimensional laser reflectance method. The camera detection monitors larger areas and the laser beam monitors narrow hard-to-reach spacings.}
\end{figure}
11.6. LASER REFLECTANCE VS. CAMERA DETECTION

Figure 11.41 shows the difference between the two dimensional camera detection (white square) and the essential one dimensional laser reflectance method (stippled green line) with respect to the wear scar. The camera detects everything within the white box and the subsequent image analysis reads out the values of the red (and blue) pixel values, in which areas of high red pixel values correspond to the embedded TiN emerging through the top TiAlN coating. The laser reflectance method on the other hand, as utilized in section 11.4.2 (see also Fig. 8.5), scans the wear scar along the green line, such that a significant increase in the measured $R$ corresponds to wearing through to the embedded TiN. The size of the white mask may have been exaggerated for illustrative purposes.

The pixel values in the surface plots have been averaged across the scar width in order to compare the laser reflectance measurements (Figs. 11.32 - 11.35) with those of the camera detection and image analysis (Figs. 11.36 - 11.39). Furthermore, the average pixel values along the scar are found in percentage, where the minimum pixel value 0 naturally corresponds to 0% and the maximum pixel value of 255 to 100%, since the laser reflectance actually also is in percentage due to the reflectance expression given in Eq. 4.8 (and 4.9).

Figure 11.42 displays the laser reflectance measurement together with the averaged red and blue pixel values detected from scar 4 of sample 41. The averaged red pixel values (full red line) compared with the laser reflectance measurement (red triangles) reveals a striking similar resemblance such that both measurements initiate a steady increase after a scar length of $\sim$4 mm and both measurements reach a steady level between 8 and 10 mm’s followed by a fast drop back to the initial level. The level of the laser reflectance measurement is a little above the pixel value level outside the wear scar and the pixel value exceeds $R$ within the scar, which means a larger total increase is actually seen for the camera detection and image analysis scheme. The blue pixel level keeps an almost constant level with a minor decrease in wear scar areas of visible TiN.

The comparison of the second scar example is shown in Fig. 11.43, in which the averaged red pixel values (red line) and the measured $R$ (blue triangles) follow each other fairly well. The pixel value starts increasing slightly before $R$, however, both measurements reach a similar steady level between 8 and 11 mm, after which both drops fast to the initial level. Initially, the measured laser reflectance decreases to a minimum (around 5 mm), which is not as pronounced for the pixel value even though a minor decrease is also seen. This difference could be caused by the appearance of the wear scar, which was worn unequally.
through to TiN along the scar, i.e. the streaks of visible TiN seems longer in the topmost part of the scar as compared to the bottom part (see Fig. 11.27b). The plotted laser reflectance was measured in the bottom of the scar (see Fig. 11.33) with the shortest TiN streaks, whereas the pixel values have been averaged across the complete scar.

The third scar example, where the embedded TiN barely emerge in the bottom of the wear scar, is compared in Fig. 11.44. The measured values of $R$ (blue triangles) show very little changes, but a small increase in the averaged red pixel values (full red line) is observed, which is clearly visible in the close-up plot displayed in Fig. 11.45. The red pixel values show patterns similar to those of the previous examples with an initial decrease followed by a steady increase and a final dip at the scar end such that an increase corresponding to the embedded TiN actually is observed by the camera detection and image analysis scheme. But, only an insignificant increase of in total ~0.025 – from the initial TiAlN level (~0.385, beginning of the scar) to the embedded TiN level (~0.41, maximum pixel value) is observed. The measured reflectance $R$ does not follow the red pixel values very well. The final dip at the end of the scar (around 11 mm) is the best resemblance even if $R$ is measured from the very same scar.
Figure 11.44: Reflectance (blue triangles, Fig. 11.34) vs. averaged red and blue pixel values (full red and blue lines, respectively, Fig. 11.38) along scar 1 of sample 42 (Fig. 11.27c).

Measurements from the fourth and final scar example are compared in Fig. 11.46. The steel substrate appear beneath the embedded TiN layer in the bottom of this scar, which was clearly observed in both surface plots of the red and blue pixel values (Fig. 11.39). The steel presence is also quite visible in the averaged red and blue pixel values (full red and blue lines, respectively), since a distinct increase is seen for the averaged blue pixel values between approx. 8 and 11 mm. A corresponding minor decrease is also seen in the red pixel values. Whether the presence of the emerging steel substrate is detected in the measured $R$ (red triangles) is difficult to argue due to the very bumpy measurement. Actually, the only agreement between the two types of measurements, laser reflectance and camera detection, is the initial level and the final dip at the scar end.

Figure 11.45: Close up of the laser reflectance (triangles) and pixel values (full lines) compared in Fig. 11.44.
Summary on Laser Reflectance vs. Camera Detection

Clearly, the two optical detection methods, laser reflectance and camera detection, both demonstrate to work very well as optical wear monitor systems with the TiAlN-on-TiN-on-Steel multi-layer system. Actually, the two detection methods result in strikingly similar results on the two initial and successful examples – which makes both methods fine candidates for the detection scheme on the optical wear monitor of tribological coatings.

A laser beam in the reflectance setup would, in contrast to the large area camera detection scheme, be able to reach areas in narrow hard-to-reach spacings hidden from the camera. In addition, the camera detection scheme requires a second hand light source, such as daylight or white light from normal indoor lightning (e.g. fluorescent tube), whereas the laser reflectance scheme carries the light source (the laser beam) within the setup itself. The laser beam is more sensitive to roughness induced during the wear and the laser beam spot size could in principle by optical means (lenses etc.) be manipulated to also monitor larger areas of the sample surface. In general, the reflectance method is useful for small areas where access may be difficult to reach with camera setup, but easy to access with laser beam as illustrated in Fig 11.40, whereas the camera method may be used to monitor larger detection areas.
Chapter 12

Dynamical Wear Process Studies

The results from the dynamical wear experiments at ESRF with the TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer samples are discussed in this chapter, where it is shown how it is possible to survey the real-time development of grooves and ridges of a wear scar during an abrasive wear process by measuring the specific absorption of a CrN wear-marker layer embedded within a protective coating. It is also proven that material is moved about in the wear scar (contact zone) during the wear and that any chemical changes or oxidation processes of the Cr-layer are pure surface phenomena.

12.1 Measured Transmission and Absorption, XANES

The intensity of X-ray photons transmitted through a TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample was measured for a number of positions across the scar width prior to any wear and subsequently after selected numbers of reciprocating cycles in order to monitor the dynamical development of the wear (see sections 6.3.1 and 9.5.1). This is plotted as a function of position and number of cycles in Fig. 12.1. The transmission increases with the number of cycles as the wear process removes material from the sample surface in accordance with Fig. 6.4 and Eq. (6.1), but the increase is only between positions 30 to 60 – corresponding to the wear scar. One position corresponds approximately to 13.5 \( \mu m \) (see section 12.1.2) and the transmitted intensities are measured in region 2 (labeled \( I_{section\ 2} \)) of Fig. 9.5 corresponding to the masked area of Fig. 12.2.

![Figure 12.1: Intensity of transmitted X-ray photons measured in 80 positions across the scar width as a function of the number of reciprocating cycles. One position corresponds to ~13.5 \( \mu m \).](image-url)
The absorption, XANES, was measured in line-scans for each of the positions of Fig. 12.1 to monitor the chromium content across the full wear scar and in connection with the transmission measurement, before and after the increasing number of cycles, to monitor the wear process. Figure 12.2 shows several XANES spectra measured at two different positions for an increasing number of cycles. The red lines are measured in position 5 and the blue in position 50. Both positions corresponds to those of Fig. 12.1 such that position 50 is approximately in the center of the scar with material removed. Both red and blue XANES spectra are plotted for an increasing number of reciprocating wear cycles as noted.

All red XANES spectra are on top of each other throughout the complete wear process (from 0 - 70 000 cycles), whereas the absorption edge, of the blue XANES spectra decreases with the number of cycles as caused by the wear process wearing through the CrN sample layer, since a reduced CrN coating thickness consequently lead to less absorption (Eq. (6.1)). But, the absorption edge is only reduced as long as the wear process works its way through the embedded CrN wear marker layer, since XANES is measured on the absorption edge of this material. All CrN is removed in the scar when the absorption step is gone after approx. 60 000 cycles. Only a selection of blue spectra are included for clarity of the plot, many more spectra were in fact measured to achieve a much more detailed result.

Absorption ratios, the fraction of wearing through the embedded CrN wear-marker layer, determine how the remaining thickness is estimated (see section 12.1.1) and is obtained by relating the initial jump in absorption, \( t_0 \cdot \mu \) (before any wear) to the reduced jump, \( t_n \cdot \mu \), measured after certain numbers of cycles, \( n \). \( t \) is the sample thickness. The absorption ratios are plotted in Fig. 12.3 as a function of cycles for different selected positions across the scar width, in which position 50 (green line with grey crosses) corresponds to the blue spectra of Fig 12.2. Initially, the ratio is 1 since the embedded CrN layer is not yet reached. But as the process continues and the wear proceeds down through the top TiAlN layer and reaches the CrN layer, the absorption starts decreasing and thus also the absorption ratio. The decrease continues until an absorption ratio of 0 is reached, where all CrN is removed by the wear process, which corresponds to the principle idea of Figs. 6.6 and 6.7. The absorption decrease is very much position-dependent as the plot shows, which in turn demonstrates that the wear is very uneven across the scar. The absorption ratio decreases faster for scar center positions (45 and 50) compared to

![Image](image.png)

**Figure 12.2:** The absorption as a function of the X-ray photon energy. XANES measured around the chromium K-edge in position 5 (red lines) and in position 50 (blue lines) after certain number of cycles. The positions corresponds to those of Fig. 12.1.
outer scar positions (65 and 70), since these remain close to unity until a high number of cycles, which means the wear proceeds faster in the scar center and the ratios reveal a dynamical wearing of the CrN layer as the decrease appear bumpy in some positions. Especially, position 45 (turquoise open diamonds) show a sudden increase around 25,000 cycles (pink arrow) but also position 30 (dark blue open squares) show an uneven decrease throughout the cycles. The ratio increase indicates an CrN layer thickness increase, since the size of the absorption edge is directly linked to the thickness of the sample and the bumpy ratios indicates thus a dynamical process, where material is sometimes moved into the positions.

Real-time absorption ratios are is shown in Fig. 12.4 across the entire scar width, in which the ratios are plotted from 1 to 0. Most CrN is removed in a wide range around the scar center after the final cycle and the bumpy appearance of the absorption fractions with the uneven decrease is observed in different positions. Some absorption ratios increase beyond 1 right before CrN starts being removed. This increase above 1 should indicate an increase in the CrN layer thickness in the sample column. Whether the CrN thickness increase in some area columns is caused by some kind of plastic deformation of the

Figure 12.3: Absorption ratios in different position of the wear scar as a function of cycles. A ratio of 1 corresponds to the CrN layer being untouched and 0 to all CrN being removed.

Figure 12.4: Real-time development of absorption ratios across the scar width. A ratios of 1 corresponds to the embedded CrN layer be untouched and 0 to all CrN being removed.
sample layers or just by calculation or detector issues is difficult to argue. This increase is observed for several positions but the effect is most noticeable in the scar center in positions 40 - 50.

12.1.1 Thickness from Absorption and Transmission

The remaining thickness \( t \) of the sample during the dynamical wear was derived from the standard absorption expression by conversion of the intensity transmitted through the unworn multi-layer sample

\[
T = \frac{I}{I_0} = e^{-\mu_{VC}t_{VC}} e^{-\mu_{TiAlN}t_{TiAlN2}} e^{-\mu_{CrN}t_{CrN}} e^{-\mu_{TiAlN}t_{TiAlN1}},
\]

where \( t_{TiAlN2} \) is the thickness of the embedded TiAlN layer and \( t_{TiAlN1} \) of the top TiAlN layer. The remaining thickness in the different layers is thus

\[
t_{TiAlN1} = \frac{\ln(I_{Sample,n}/I_0) + \mu_{VC}t_{VC} + \mu_{TiAlN}t_{TiAlN2} + \mu_{CrN}t_{CrN}}{\mu_{TiAlN}} \tag{12.2}
\]

\[
t_{CrN} = \frac{\ln(I_{Sample,n}/I_0) + \mu_{VC}t_{VC} + \mu_{TiAlN}t_{TiAlN2}}{\mu_{CrN}} \tag{12.3}
\]

\[
t_{TiAlN2} = \frac{\ln(I_{Sample,n}/I_0) + \mu_{VC}t_{VC}}{\mu_{TiAlN}} \tag{12.4}
\]

where \( I_{Sample,n} \) is the measured intensities of transmitted photons shown in Fig. 12.1 (n is the number of cycles), \( I_0 \) is found from the initial measured intensity \( I_{Sample, 0} \) (from an unworn sample part, e.g. at position 5) and from the absorption coefficients, \( \mu_{layer} \), and thicknesses \( t_{layer} \) of the different layers via the relation \( I_0 = I_{Sample, 0}/e^{-\sum \mu_{layer}t_{layer}} \). The specific absorption coefficients found within the energy range of the masked area of Fig. 12.2 and thicknesses of the different layers are listed in Tab. 12.1, in which the transmission through the individual layers are included as well. It should be noted that only 22% of the initial photons transmit through the supporting vitreous carbon substrate and that a mere \( \sim 15\% \) of the initial photons pass through the complete multi-layer sample, which leaves \( \sim 7\% \) of maximum change in the total transmission such that a small signal with a large background is left to monitor the wear of the layers. The limited transmission is caused by the thickness of the supporting carbon disc, which necessarily has to be thick enough to sustain the wear without breaking or bending.

The regimes for using either of Eqs. (12.2) - (12.4) is determined by the absorption ratios of Figs. 12.3 such that Eq. (12.2) is used in areas with an absorption ratio of 1 (when the \( CrN \) not yet have been reached) and Eq. (12.3) is used in areas of ratios between 1 and 0 (when the \( CrN \) layer is wearing away). Finally, Eq. (12.4) is used in areas with absorption ratios of 0, as all \( CrN \) have been removed at this point\(^1\).

Figure 12.5 shows a visual expression for the real-time development of the sample thickness as the wear process works its way through the surface and into the depth of sample \( I^2 \) where the remaining thickness (by Eqs. (12.2) - (12.4)) is plotted as a function of the scar width and the number of reciprocating cycles. Initially, the surface is still intact, however, after some thousand cycles a decrease around the scar

\(^1\)Actually, the regimes was set a little more loose such that Eq. (12.3) was used when \( 0.1 < t_n\mu/I_0\mu < 0.9 \) and correspondingly for the the other two regimes, due to the uneven nature of the ratios as discussed above.

\(^2\)See settings for the wear experiment in Tab. 9.2.
center (approximately between positions 30 - 60) emerges, which corresponds to surface material being removed. An increasing amount of material is worn away during the process until termination (at 70000 cycles). The scar itself is about 800 $\mu$m wide and monitored at 80 positions across the scar width including unworn parts to either of the sides leaving the scar itself within 25-30 positions. Each position corresponds to approx. 13.5 $\mu$m, which means that only major features are possible to identify. The initial sample thickness is defined as the sum of the thickness of the individual layers (see Tab. 12.1), which means that the initial (and unworn) sample surface in the plot is at 1003.34 $\mu$m. Some material appears to gather on the left hand side of the scar center (between positions 70 and 80) half way through the complete experiment (after approx. 40000 cycles), since the reconstructed surface height increases in this area. This could indicate wear debris, i.e. sample material worn away, assembling at one side of the wear scar during the process. A cross section of the corresponding wear scar shows in Fig. 12.6 the

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**Figure 12.5:** Real-time development of the layer thickness across the scar width of sample I as derived by the combined Eqs. (12.1)-(12.4) and absorption ratios (Fig. 12.4).

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**Figure 12.6:** Thickness as a function of the position across the scar width for a selected number of cycles.
Figure 12.7: Real-time development of the layer thickness across the scar width for Sample II (a) and Sample III (b) with altered applied normal load. (see Tab. 9.2). One position correspond in Sample II (a) to ∼7.5 µm and in Sample III (b) to ∼8.2 µm.
12.1. MEASURED TRANSMISSION AND ABSORPTION, XANES

<table>
<thead>
<tr>
<th>Material</th>
<th>( \mu ) [1/( \mu \text{m} )]</th>
<th>Thickness, ( t ) [( \mu \text{m} )]</th>
<th>Transmission</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAlN (top coating)</td>
<td>0.1058</td>
<td>1.508</td>
<td>0.85</td>
</tr>
<tr>
<td>CrN</td>
<td>0.2417</td>
<td>0.567</td>
<td>0.87</td>
</tr>
<tr>
<td>TiAlN (embedded)</td>
<td>0.1058</td>
<td>1.266</td>
<td>0.87</td>
</tr>
<tr>
<td>C (vitreous carbon)</td>
<td>0.0015</td>
<td>1000</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 12.1: Absorption coefficient \( \mu \), layer thickness and transmission through each separate layer determined in region 2 (masked area of Fig. 12.2). Layer thicknesses were found in section 10.1.1 (see Tab. 10.2), the transmission and absorption coefficient by use of [35,118].

increasing depth during the wear via selected lines constituting the surface plot (Fig. 12.5). Clearly, from this view it is a case of abrasive wear without the previous (see section 11.1) signs of delamination, since the wear proceeds relatively consistent through the different layers without entire layers being stripped off between two measurements. The remaining thickness evaluated in the supporting carbon substrate layer was found by Eq. (12.4), which means that the values plotted in this region are approximated in thickness equivalence of TiAlN, since it is not possible to determine the interface between the embedded TiAlN layer and the carbon substrate spectroscopically (from XANES and Eqs. (12.2) - (12.4)).

Other samples, labeled sample \( II \), \( III \) and \( IV \), were also exposed to the wear process in the NOMAD tribometer while the dynamic wear was studied. The normal load of samples \( II \) and \( III \) were changed after an initial number of cycles (see Tab. 9.2) to obtain a less severe wear process as this was considered to enhanced oxidation of the chromium layer as discussed below.

The remaining thicknesses of sample \( II \) and \( III \) were estimated as before. Figures 12.7a and 12.7b show the real-time development of the thickness found across the scar width for sample \( II \) and \( III \), respectively, where the initial 25 000 cycles have been omitted in both plots. The corresponding wear cross sections are displayed in Figs. 12.8 and 12.9, in which the instantaneous wear during the process can be followed through the layers. Both experiments show increased wear for increased number of cycles but it is not clear if these two wear scars exhibit pure abrasive wear, since wear caused by delamination could take place in the grooves as they develop very fast for these two samples. The much larger ridges and deeper grooves developed compared to sample \( I \) could be caused by the reduced load applied on these two samples, since it somehow seems to cause more rough scars (see e.g. section 12.2.2).

![Figure 12.8: Sample II. Wear cross section.](image1)

![Figure 12.9: Sample III. Wear cross section.](image2)
These three examples I, II and III prove it to be possible to survey the development of a wear process in real-time measurements – during the actual wear experiment. In fact, dynamical properties of the wear are discovered as discussed below.

12.1.2 Thickness from Dektak Profilometer

A cross section of the wear scar measured with the profilometer (a) and the corresponding final cross section (b) based on the absorption and transmission measurement (Fig. 12.6) for sample I are plotted together in Fig. 12.10, where the final plot (c) is discussed in section 12.1.3. The two profiles demonstrate that the major features in the wear scar are reproduced by the transmission method to a large extent, especially when it is kept in mind that the two cross sections have not been measured in the same longitudinal position of the scar. Furthermore, the resolution across the scar width in the transmission and absorption based profile (b) is limited by the relatively large step size (∼13.5 µm/position) of this measurement such that minor details in the scar are not reproduced.

Figure 12.11 compares the Dektak scan profile (a) of sample II with the final profile (b) from the transmission and absorption measurements (of Fig. 12.8), where a good resemblance between the two profiles is observed. Many features from the scan profile (a) are quite clearly reproduced in the transmission and absorption based profile (b), even if the resolution of the latter is limited by the beam step size, which is ∼7.5 µm/position for this sample. The resolution is much better than for the previous sample though, which the fine correspondence between the two profiles also shows. The profilometer measurement of sample III is also compared with the final cross section profile from the thickness estimation (see Fig. 12.9) as Fig. 12.12 shows, where several features of the scan profile (a) are reproduced in the profile based on the transmission and absorption measurement (b). The resolution of this latter sample is ∼8.2 µm/position, which is comparable to that of sample II.

The comparison of the transmission and absorption based thickness profiles to those of the Dektak profiles supports the reliability of the method for in-situ determination of the wear depth, since several major characteristics are reproduced by X-ray monitoring method in especially samples II and III. Also minor details in these two latter samples, where the spatial resolution was increased, are actually reproduced.

At this level of accuracy, dynamical measurements of the average scar depth and detailed structures in the scar with profilometry are not possible. Detailed structures in a scar, including ridges and grooves cannot be measured before and after a certain wear sequence in view of the fact that it is very hard to reposition a profilometer on a dynamically changing surface with sufficient accuracy. The profilometer measurements delivers a precise scan profile after the end of a wear sequence, but it does not give any information on the dynamics of the features and characteristics during the wear process.

The resolution of the profiles is estimated by a calibration between the Dektak scan profile (a) and the corresponding transmission and absorption based profile (b) such that the width of the scar in the two measurements was compared and a conversion factor estimated. These numbers found for the resolution should thus be taken as approximate values, since the scan profile and absorption based profile was not located on the exact same longitudinal position in the scar. As a result, the scar width measured with the Dektak may not be the exact same as that of the absorption based profile.

The Dektak profile was measured ex-situ such that the cross section was not located exactly on the same position on the longitudinal direction of the scar as that of the absorption profile. This also applies to the Dektak measurements of the samples II and III.
12.1. MEASURED TRANSMISSION AND ABSORPTION, XANES

Figure 12.10: End profile of wear scar from Dektak profilometer (a), thickness (b) and absorption measurements by mapping (c). Sample I.
Figure 12.11: End profile of wear scar from Dektak profilometer (a), thickness (b) and absorption measurements by mapping (c). Sample II.
Figure 12.12: End profile of wear scar from Dektak profilometer (a), thickness (b) and absorption measurements by mapping (c). Sample III.
Furthermore, the spatial extension of the X-ray beam is limited to $5 \times 8 \, \mu m^2$ (full width at half maximum) as previously mentioned in Tab. 9.1 in chapter 9. This makes the spatial resolution of the two latter samples (II and III) very close to best possible with current beam dimensions.

12.1.3 Mapping Wear Scars

A final XANES map of the wear scars was measured after termination of each wear experiment, where the area of measured XANES spectra covers a significant fraction of the scars (see section 9.2). Both sample I and II were mapped with XANES spectroscopy, whereas sample III was not since this sample was the very final and the synchrotron ring current dumped 5 min after the final XANES measurement!

Figure 12.13a shows the relative absorption over part of the wear scar of sample I, where ratios of $t_n/\mu$ (see e.g. Fig. 12.3 and 12.4) are plotted in a longitudinal length of the scar for an area covering the complete scar width. Thus, areas of untouched CrN are seen to both sides of the scar, where the scar itself is within approximately positions 20 - 40 (y direction). A corresponding XANES map of the wear scar of sample II is displayed in Fig. 12.13b. Both surface plots reveal absorption fractions above 0 in the bottom of the scars, where especially sample II shows quite large fractions of CrN remaining in the scar. This means that ridges of CrN are preserved in the bottom of the scars after the wear process has passed beyond the CrN layer and well into the embedded TiAlN layer – according to the profilometry (Dektak) measurements (Figs. 12.10 and 12.11). Figure. 12.10c, 12.11c and 12.12c for sample I, II and III, respectively, also display these ridges of CrN in greater details, where the mean of absorption ratios along the (longitudinal) scar length is plotted$^4$.

With CrN ridges are present in the wear scar of sample I (Fig. 12.10c and Fig. 12.13a) as observed in position 20 towards the scar edge. Very little CrN is, however, seen in the scar center (position ~30) indicating CrN practically being removed here. This is also supported by the SEM image of the wear scar displayed in Fig. 12.14a, where black corresponds to the carbon substrate, dark grey to TiAlN (both the top layer and the embedded layer) and bright grey to the wear-marker layer, CrN. In contrast, substantial CrN ridges are observed in the scar center of sample II (Fig 12.11c and Fig. 12.13b). These CrN ridges correspond furthermore to those measured with profilometry (Fig. 12.11a) such that a clear presence of CrN is seen on top of the ridges in the scar, which the SEM image in Fig. 12.14b also supports, where streaky areas of bright CrN are seen within the scar center. Thus, these measurements show that quite a large fraction of CrN is left in the scar center of this sample even if the scar was actually worn way beyond the CrN layer and into the embedded TiAlN layer as measured with profilometry. The final sample (III) also demonstrates how CrN is present in the bottom of this scar as seen from the absorption measurement in Fig. 12.12c, where several minor CrN ridges are detected. These small CrN ridges are also seen in the SEM image displayed in Fig. 12.14c and especially in the detailed SEM of Fig. 12.15. The CrN ridges are, nevertheless, present even if the wear process again has worn below the CrN layer according to the profilometry measurement (Fig. 12.12a).

The comparison of the three samples shows that ridges of CrN are actually preserved in the wear scar of samples II and III even if the profilometry demonstrated scar depths beyond the CrN layer. This could be caused by CrN being moved about in the scar such that the topmost ridges consist of CrN. Alternatively, a plastic deformation of the supporting vitreous carbon substrate as a consequence of a slight substrate compression could also result in the preservation of CrN below the originally layer height.

$^4$The resolution of the CrN mean (Figs. 12.10c, 12.11c and 12.12c) is much lower than those of the thickness plots (Figs. 12.10b, 12.11b and 12.12b) since e.g. the 50 positions of Fig. 12.10c corresponds to the 80 positions of Figs. 12.10b.
Figure 12.13: Mapping of absorption ratio for scar area of a) sample I (70 000 cycles, 3 N) and b) sample II (60 000 cycles, 3 and 1.5 N). Absorption ratio of 1 corresponds to untouched CrN layer and 0 to all CrN being removed. Both scar show large ridges of CrN in the scar bottom.
Figure 12.14: SEM (TM1000) images of sample I (a), sample II (b) and sample III (c). Black corresponds to the carbon substrate, dark grey to TiAlN (both top and embedded layer) and bright grey to CrN.
12.1. MEASURED TRANSMISSION AND ABSORPTION, XANES

An additional sample (IV) mapped with XANES spectra, was worn with a normal load of 3 N during the complete experiment (0 - 36 000 cycles, see Tab. 9.2). All CrN is completely removed in the scar center as Fig. 12.16 shows. The surface plot is entirely flat in the bottom of the scar, which just demonstrates that ridges of CrN may not necessarily be left in the scar after wear process termination and all CrN may eventually be completely removed – also after a mere 36 000 wear cycles as this measurement shows. Naturally, this fast wear could be a result of wear by delamination. The differences observed in the maps (Figs. 12.13 and 12.16) corresponds to the uncorrelated and much diverging wear depths previously observed in section 11.1 for single layer coatings.

Figure 12.15: Detailed SEM image of sample III (see SEM image in Fig. 12.14c).

Figure 12.16: Mapping of absorption ratios across scar area of sample IV (36 000 cycles, 3 N), where all CrN is removed in the scar center leaving no CrN ridges as compared to samples I and II (Fig. 12.13). Absorption ratio of 1 corresponds to untouched CrN layer and 0 to all CrN being removed.
12.2 Wear Scar Development

Figure 12.17 shows a detailed cross section of the instantaneous depth development in the wear scar of the three layers of sample I, TiAlN, CrN and TiAlN, where different ridges and grooves are possible to follow during the wear process. The remaining sample thickness is plotted only for the tribological coatings on the multi-layer sample and only the central parts of the scar has been included and is thus a close up of Fig. 12.6, but with focus on the dynamical development in the tribological layers.

Two specific ridges are pointed out (red arrow) and two specific grooves are pointed out (blue arrow), since these give interesting information on some of the dynamics of this specific wear process. The first ridge labeled A (position 36) is preserved during the process, compared to the neighboring grooves, just as a major groove labeled B (position 42) is maintained practically from the beginning of the wear. A third feature, labeled C in the figure (position 39) is initially a sharp major ridge (red arrow), which is sustained during a large part of the wear process. Suddenly, the ridge, nevertheless, starts wearing down after 38 000 cycles and is converted into a groove (blue arrow) as the wear process proceeds, which may indicate wear by delamination in this specific position. The reverse situation, i.e. a groove turning into a ridge is actually also seen, however, not very clearly. This is in position 38, where a groove (next to C) changes into a minor ridge as the ridge in position 39 (C) changes into a groove. In this case the groove-ridge transformation and vice versa in the two positions seem connected.

The stochastic nature of the wear process is shown in details in Fig. 12.18, where the instantaneous depths of the A, B and C features (Fig. 12.17) are displayed together. Initially, the wear sets in after approx. 10 000 cycles, where the behavior in each of the individual positions A (red discs), B (green squares) and C (blue triangles) is very irregular and none of them seem to show linear dependencies. The thickness is sometimes seen to increase locally most likely a result of the counterpart (wear sphere, see Fig. 9.9) carrying wear debris into the local position. The CrN layer is reached after approx. 20 000 cycles of wear for the three positions displayed. The wear-marker layer is, nevertheless, worn through at very differently. The green squares (position 42) are seen to wear through the CrN layer within a few thousand cycles, whereas the red discs (position 36) do not pass the CrN-to-TiAlN interface until after 40 000 cycles as a consequence of the wear process pausing for almost 15 000 cycles at that specific position, which indicates slow wear and/or a possible supply of material from neighboring grooves evolving. The blue triangles (position 39) display a quite jumpy wear process in the CrN layer with material constantly moving in and out of the position especially at the top TiAlN-CrN interface. The CrN layer, nevertheless, wears out within 15 000 cycles in that position.

Once the wear reaches the CrN-TiAlN interface and proceeds through the bottom TiAlN layer, the wear continues quite regularly for the red discs and for the blue triangles (positions 36 and 39). However, the green squares (B of Fig. 12.17) are seen to display a quite significant increase half way through the bottom TiAlN layer most likely as a result of material being removed into that position for instance via material delaminated elsewhere (e.g. position 39) Subsequently, the wear proceeds regularly until the carbon substrate is reached. The wear increases fast for all three positions as the carbon substrate is reached, since vitreous carbon is not a tribological material and thus not able to withstand the extreme wear conditions.

A very dynamical stochastic process is observed in the wear scar. Material is possibly moved in and out of the positions such that ridges and grooves are constantly emerging and disappearing. This dynamical nature may also possibly explain the diverging results on scar depths of the TiN and TiAlN single-layers coatings (see section 11.1). The uncertainty of these measurements on the dynamical wear is ~ 6 - 200 nm estimated from the initial (and unworn sample) measure.
12.2. WEAR SCAR DEVELOPMENT

Figure 12.17: Wear scar cross section of the instantaneous depth after a number of cycles. The carbon substrate surface is at 1000 μm and the hard coatings have been noted. Sample I.

Figure 12.18: Instantaneous depth for three positions corresponding to those (A, B and C) of Fig. 12.17 in the scar. Sample I.
12.2.1 Dynamical Development of Wear Rates

The real-time development of a wear scar during the wear process is monitored with these combined X-ray transmission and absorption measurements and as a result, the development of the wear rate during the wear process can be studied. The previous specific wear rate, \( k \), is derived from the cross sectional area of material removed in a scar, \( A \), (see sections 5.4.2 and 11.1) and may be obtained from the remaining sample thickness evaluated above for both samples I, II and III.

Area of Removed Material

Real-time monitoring of the sample thickness (see Fig. 12.5) is as such used to find the development of the area of material removed in the scar cross section by integration over the scar width of sample I. These are plotted (red triangles) as a function of the number of wear cycles in Fig. 12.19 together with the approximate positions (grey areas) of the different interfaces in the multi-layered sample. Naturally, these interface markings are unprecise to the point that the interface is not reached simultaneously across the complete wear scar (see e.g. Fig. 12.17 or Fig. 12.3) and it is as such difficult to state precisely at which number of cycles an interface is reached.

Clearly, an increasing amount of material is removed for an increasing number of cycles with a stagnating 'running in' period in the beginning of the wear, which corresponds well with the initial stagnating depths observed in Fig. 12.18. A minor bump appear in the descent right after approx. 20 000 cycles, which from the instantaneous scar depth of Fig. 12.17 is identified (yellow line) as the wear process reaching of the interface between top TiAlN and CrN for the first time. Comparable signs, in the removed material plot (Fig. 12.19), of the wear process reaching the subsequent interface, between CrN and embedded TiAlN, at approx. 30 000 cycles (grey line) and the final interface (TiAlN - carbon) at approx. 45 000 cycles (dark grey line), are not that easily identified. But, the material removal seemingly descents faster after the final (TiAlN - carbon) interface most likely due to the much much softer vitreous carbon substrate.

\( k \) (of Eq. (5.1)) is derived for sample I from the removed material (Fig. 12.19) together with the corresponding number of cycles, \( n \), and normal load, \( F \), (see Tab. 9.2) and plotted (blue squares) as a function of the number of wear cycles in Fig. 12.20 with the different multi-layer interfaces (marked light grey, dark grey, grey and light grey areas) as noted. Sample I.

![Figure 12.19](image-url)
grey and dark grey) as noted. The figure displays the development of the wear rate during the wear process, in which it should be noted that a pure material dependent wear rate is obtained only for the top TiAlN layer, i.e. prior to the top TiAlN - CrN interface (light grey), since the material of the different layers is mixed accumulatively as the wear process proceeds beyond the initial interface and through the different layers.

Variations in the development of the specific wear rate are clearly visible such that a ‘running in’ with initial increasing values is observed for the top TiAlN layer most likely as a result of an increased number of wear particles entering the contact as illustrated above in Fig. 5.3, part 3. As the wear process reaches the initial interface (light grey), the wear rate decreases slightly and subsequently levels out between the initial (light grey) and final interface (dark grey), i.e. between the embedded TiAlN and the carbon substrate, probably due to slightly different wear properties of CrN and TiAlN combined with a steady-state condition between wear particles leaving and entering the contact (see Fig. 5.3, part 4). After the final interface (dark grey), towards the end of the sample wear, the wear rate increase again, probably caused by the much softer and much less wear resistant carbon substrate. The obtained wear rates develop within the range of values of the previous wear rates obtained for TiAlN (see Tab. 11.1 and e.g. [109, 111–113]). Since these wear rates were derived under somewhat different experimental conditions with altered parameters such as slightly higher load, longer sliding distance (both in one stroke and in total) and slightly different counterpart (resin-diamond reinforced steel ball vs. spherically molded resin-diamond) different values may be expected.

Previous CrN wear rates obtained under similar conditions (in pin-on-disc setups with varying counterpart materials) is found by Cai et al. to be $1.89 \times 10^{-6}$ mm$^3$/Nm and by Polcar et al. to be $\sim 0.7 \times 10^{-6}$ mm$^3$/Nm [114, 115], which is comparable with the (TiAlN and) CrN mixture wear rate as the wear process moves through the the layer. Since the TiAlN and CrN wear rates (see Tab. 11.1) are comparable [112, 114] the layers are difficult to distinguish in the wear rate development plot such that no distinct variations are seen with respect to the embedded CrN marker layer. Naturally, this is also accompanied by the accumulatively mixing of the different layer materials in the wear scar, which tends to cause perturbed results.

Figure 12.20: Development of the specific wear rate of sample I while the wear process proceeds through the multi-layer sample as a function of the number of wear cycles. Approximate interface positions are marked (light grey, grey and dark grey areas) as noted.
12.2.2 Roughness Development in Wear Scar

The development of the scars as the wear process proceeds through the different layers of the three samples I, II and III is displayed above in Figs. 12.6, 12.8 and 12.9, respectively. The three instantaneous wear scar cross sections indicate an increased roughness in the appearance of the scar such that the grooves become increasingly deeper as the wear process proceeds through the sample layers.

A very crude estimation of the development in the grooves and ridges is found for the samples, where only the bottom and center part of the scars, corresponding to e.g. the masked area of Fig. 12.21, are studied. The figure shows a selection of scar cross sections of sample III (Fig. 12.9), where the masked area is defined such that the scar edges are excluded from the estimation leaving only the grooves and ridges of the scar bottom to be investigated. The development in the roughness is found by initially define the masked area of the scar bottom. Subsequently, the mean value (dashed lines) of the scar cross section (full lines) is found for each measured cross section within the masked area together with a maximum value of the cross section (also within the masked area) such that the difference between the mean value and the maximum value results in a crude expression for the development of the roughness in the scar as the number of wear cycles increases.

Figure 12.22 shows the development in the ridges and grooves of the wear scar of sample I (blue triangles), sample II (red squares) and sample III (green circles) as the wear process proceeds through the sample material, where the roughness values were found between positions 34 and 52 (sample I), positions 64 and 101 (sample II) and between positions 75 and 110 (sample III) all of which are in the bottom of the respective wear scars as Fig. 12.21 illustrates. Initially, the roughness of sample I (blue triangles) is rather low corresponding to the initial sample surface roughness and a small steady increase is observed.
12.3 Phase Change Studies

Chromium of the tribological wear-marker material CrN is known as a strongly oxidizing metal and oxygen actually bind to the exposed CrN layer, which is observed when studying the wear scar by combined EDX element surface detection and SEM imaging. Figure 12.23 displays a SEM image of a wear scar sample (not previously described), on which the different layers, identified as in Fig. 12.14, are exposed around the edges of the scar.

It is possible to distinguish between the individual elements in the different layers by combining SEM imaging of the wear scar with EDX element surface detection as seen in Fig. 12.24, where carbon atoms (in pink (a)) are detected solely in the very scar bottom and nitrogen atoms (in cyan (b)) are detected everywhere but at the very scar bottom, since all three protective coatings are nitrides. Aluminum and titanium atoms (in green (c) and in red (d), respectively) are only detected in areas of exposed TiAlN, i.e. on top of the unworn sample surface and in areas of exposed embedded TiAlN. Chromium atoms (in blue (e)) are only detected in areas of exposed CrN and finally, oxygen atoms (in yellow (f)) are also only detected in corresponding areas, i.e. in areas of exposed CrN, which means that the chromium nitride...
layer is oxidized. Actually, the only coating material oxidized is CrN as Fig. 12.24 clearly demonstrates. This phase change from the nitride binding in CrN to an oxide binding, may be studied by X-ray absorption – XANES, since the position of the absorption edge (in photon energy) and the wiggles in the spectrum depend on the chemical binding of the material as discussed in section 6.2.1.

Line-scans of XANES spectra measured for each transmission measurements (see Fig. 12.2) were studied closely for possible changes in the absorption edge during the wear process. Initially, the XANES spectra measured from CrN in the multi-layer sample were compared to a reference XANES measurement from a CrN sample as grown by MBE (molecular beam epitaxy). This is seen in Fig. 12.25, where the measured XANES spectra (green lines) are plotted for different increasing number of cycles, causing the decrease in absorption as before, and compared with a reference CrN measurement (black lines) of Kimura et al. [119]. The reference measurement have been scaled to match the XANES measurement, since only the relative differences in wiggles position (in photon energy) are of interest. The measured XANES spectra are compared to three different common oxide phases of chromium; CrO$_2$, CrO$_3$ and Cr$_2$O$_3$, which were all previously measured by Pantelouris et al. [120].

12.3.1 Chromium Oxide Phases

Initially, the measured XANES (green lines) are plotted in Fig. 12.26a together with XANES spectroscopy on CrO$_2$, where the edge of the reference spectra (blue lines) are shifted down in energies as a consequence of the oxygen binding. Subsequently, the CrN Kimura et. al reference spectrum (black lines of Fig. 12.25) was subtracted from the measured XANES spectra (green lines of Fig. 12.25) to exclude all absorption signals from CrN in the measured XANES leaving only possible signals from other chemical

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Figure 12.23: SEM image of additional wear scar sample. Black is the carbon substrate, dark grey is TiAlN and bright grey is CrN. Measured at Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, France.

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5The analysis was performed on XANES spectra measured as a function of the number of cycles in position 50 as seen in Fig. 12.2 of the scar induced in sample I.
Figure 12.24: Combined SEM imaging and EDX elements detection of carbon (a), nitrogen (b), aluminum (c), titanium (d), chromium (e) and oxygen (f) in the wear scar shown in Fig. 12.23. Measured at Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, France.
CHAPTER 12. DYNAMICAL WEAR PROCESS STUDIES

Figure 12.25: XANES measured from sample I (green lines) compared with XANES measured of CrN reference sample grown by MBE (black line, [119]) for different number of cycles (i.e. sample thicknesses).

bindings of chromium. Thus, these subtraction spectra reveal if any shifts in edges or peaks, caused by other chemical bindings of chromium, are present or arise during the measurement. The subtracted spectra (green lines) are plotted in Fig. 12.26b together with the reference CrO\textsubscript{2} spectra (blue lines) to compare possible peaks arising due to oxidation of the chromium layer. All subtraction spectra pass through 0 at the position of the main CrN peak (pointed out), due the CrN ref. spectrum (black lines) being fitted to the measured XANES (green lines of Fig. 12.25) at this position.

Similar plots are displayed for CrO\textsubscript{3} in Figs. 12.26c and 12.26d, in which the XANES reference spectra on CrO\textsubscript{3} are shown in red lines, where parts of the pre-edge peak of CrO\textsubscript{3} is observed around photon energies of 5980 eV. (Actually, a small pre-edge peak is also seen in the XANES spectrum of CrO\textsubscript{2} (in blue), just above 5980 eV in Fig. 12.26a.) Finally, the corresponding XANES reference plots for Cr\textsubscript{3}O\textsubscript{3} are displayed in purple lines in Figs. 12.26e and 12.26f. The subtraction plots, i.e. the green lines of Figs. 12.26b, 12.26d, and 12.26f, are all identical. They have been plotted repeatedly to compare them individually with the different oxide phases of chromium.

The difference between the reference CrN spectra (black lines, Fig. 12.25) and the XANES spectra are seen from the subtractions plots (green line), where a particular divergence is observed right after the position of the main CrN peak at photon energies of 6010 eV. This difference is actually also clearly visible in Fig. 12.25 as the black curves of the reference spectra decrease below the measured spectra around these energies. Several other minor differences also appear for energies below the main CrN absorption peak. Four such minor divergence peaks appear to arise as a consequence of the pre-peak wiggles seen in the reference spectrum. These wiggles are more clearly visible in the close up plot displayed in Fig. 12.27 and actually not seen in the measured XANES, except from the initial and minor peak around 5990 eV.

The appearance of the subtraction spectra does not resemblance any of the three chromium oxide phases and the most striking feature at 6010 eV does, furthermore, not correspond to the absorption edge of any of the oxide phases. The structure of the subtraction curves could either arise as a result of signals from oxide phases of chromium or it could also just be caused by our CrN film being of a less good quality compared to the MBE grown reference sample. The CrN film of the reference measurement
12.3. PHASE CHANGE STUDIES

Figure 12.26: Measured XANES (green lines) compared to reference spectrum on CrO$_2$ (blue (a)), CrO$_3$ (red (c)) and Cr$_2$O$_3$ (purple (e)) by Pantelouris et.al. [120]. CrN reference spectrum by Kimura et.al. [119] subtracted from measured XANES (green lines) and compared to reference spectrum on CrO$_2$ (blue (b)), CrO$_3$ (red (d)) and Cr$_2$O$_3$ (purple (f)).
was produced by MBE, which is good method to produce films of really high quality, whereas the CrN films in the multi-layer samples were produced in an industrial production facility, which may not lead to such high quality films. The best argument for not being able to detect any of the three phases is that the main divergence peak (at 6010 eV) is much larger than any of the other minor pre-edge peaks (between 5895 - 6005 eV) – if there really was any oxidation signals the initial absorption peak should be the major feature as seen in the blue, red and purple reference spectra.

Oxygen bind especially to chromium as the SEM and EDX detection schemes of Fig. 12.24f clearly demonstrates. But the oxygen was not possible to detect by X-ray absorption spectroscopy, i.e. XANES measurements. This means the oxidation of chromium nitride must either be a pure surface phenomenon or the effect is too small to detect with the transmission method applied at this dynamical wear study. The CrN layer does not seem to be particularly oxidized during the wear process, since no new peaks, indicating formation of new chemical bonds, arise during the process. Actually, all subtraction curves diminish more or less at equal rates during the wear process such that whatever oxide phases of chromium being present in the CrN layer or on the surface of the CrN layer (as seen in Fig. 12.24f) may be impossible to detect with this transmission method, where a mere ∼3% of the complete transmission signal (see Tab. 12.1) is from the chromium layer. Furthermore, the oxidation may also have formed during the CrN film deposition. This is possible since oxygen in small and uncontrolled amounts may have been present in the PVD chamber during deposition of the CrN film, which means that the CrN film used here may just not be a 100% uncontaminated material sample.
Part V

SUMMARY
Chapter 13

Conclusion and Future Developments

13.1 Conclusion

A variety of thick and thin films and coatings ranging from relatively simple single-layer coatings to rather advanced multi-layer sample systems of coatings with embedded signal or marker layers, i.e. TiN-on-TiO$_2$-on-Steel, TiAlN-on-TiN-on-Steel and TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon, were studied in the work presented in this thesis.

Various films and coatings have been studied in many different ways, where locally produced PLD films of TiN and TiO$_2$ were studied with respect to the initial film nucleation by in-situ RHEED monitoring. Commercially PVD and e-beam evaporation produced films and coatings of TiO$_2$, TiN, TiAlN and CrN were studied by combined tribo-optical means in order to verify the proposed optical wear monitor with the embedded optical signal layer, but also for pure optical and pure tribological purposes. And the dynamical wear process of the wear multi-layer system with the embedded wear-marker layer was studied in real-time XAS and transmission experiments by means of specific synchrotron radiation.

The results on the numerous different measurements and experiments proved for a large part to be very successful such as the determination of the initial growth mode of TiN as deposited by PLD. But also the proposed optical wear monitor with embedded signal layers was demonstrated to be a potential candidate for wear monitoring of protectively coated industrial steel tools. TiO$_2$ thin films for the optical wear monitor system TiN-on-TiO$_2$-on-Steel were replaced by commercially electron-beam evaporation produced films due to the complexity of TiO$_2$ film production by PLD, which was discovered not to be simple. Moreover, it also proved possible to follow the dynamical development of the wear process through several interfaces by the real-time XAS and transmission monitoring.

Estimation of Refractive Indices and Extinction Coefficients

The refractive index, $n$, and the extinction coefficient, $k$, of the complex refractive index $\tilde{n}$ were estimated for different coatings and materials by use of the laser reflectance method and the very simple reflectance setup as discussed in chapter 10. Moreover, the complex refractive index was estimated for a thin transparent TiO$_2$ coating, which is possible as long as the accurate coating thickness together with the complex refractive index of the underlying substrate is known in advance.
The method proved to show quite trustworthy results as the values obtained were remarkably similar to those of the literature, where any deviations could be a result of variations in the stoichiometric composition of the coating material studied as this effects the refractive index. It is a very simple technique and requires only a minor optical setup (see Fig. 7.11) to measure the reflectance as a function of the incident angle, $R(\theta)$, where subsequent calculations reveal $n$ and $k$ of the complex refractive index.

**Film Growth Studies by PLD, RHEED and AFM**

The initial film nucleation of TiN grown with pulsed laser deposition on single crystals of MgO was studied by RHEED, AFM surface characterization and X-ray diffraction as discussed in section 10.4. A comparison of the recorded RHEED images with the corresponding AFM micrographs revealed a preliminary Volmer-Weber growth mode, where the initial nucleation of 3D islands of TiN was followed by a continuously growing film of relatively smooth surface. Furthermore, a single structural crystal orientation of the deposited TiN film was determined by use of XRD and epitaxial growth of the film was established. Unfortunately, an analogous growth mode studies of TiO$_2$ deposited also on MgO did not demonstrate similar clear results.

**Combined Optics and Wear Studies**

Theoretical and simulated wear process by multi-layer sample series of TiAlN-on-TiN-on-Steel showed a very good resemblance and the warning systems with the embedded optical TiN signal layer proved to be a reliable solution for optical monitoring of wear. In addition, the warning system proved to work very well as the test samples of TiAlN-on-TiN-on-Steel multi-layers were exposed to an actual wear process. Both the laser reflectance method and the camera detection combined with the image analysis proved to be valid solutions for optical monitoring of abrasive wear of coatings.

The other multi-layer system TiN-on-TiO$_2$-on-Steel did also prove to work excellent as an optical wear monitor – *in theory*, where the simulated wear process with the sample series demonstrated fine possibilities as a warning system with a thin embedded optical signal layer of TiO$_2$ as shown in chapter 11. However, the TiN-on-TiO$_2$-on-Steel multi-layer system was never tested in any actual wear process as a consequence of two motives previously mentioned;

1) The signal from the ultra thin TiO$_2$ coating (50 nm) would have absolutely vanished in the extreme rough and ridgy wear scar surface produced by the harsh wear conditions of the linear tribometer, where ridges and grooves of micrometer sizes were observed in almost every measurement.

2) The system was, furthermore, composed such that the reflectance should decrease as the wear reaches the embedded signal layer but the wear process itself will also cause a decrease in the reflection as a consequence of an increased roughness in the scar surface. Thus, it would not be possible to distinguish any decrease caused by the wear process reaching the embedded signal layer from a decrease caused by induced roughness.
13.2. **FUTURE DEVELOPMENTS**

**Combined X-ray and Wear Studies**

Real-time experiments of abrasive wear measurements in the portable linear tribometer, the NOMAD, together with X-rays by synchrotron radiation and subsequent analyses of the wear process revealed the dynamical development of the wear scars induced in TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer samples with the embedded CrN wear-marker layer.

Combined transmission and XANES measurements on the chromium K-edge (absorption edge) lead to knowledge of the dynamical development in the wear scar during the wear process as discussed in chapter 12, where the wear rate development from the multi-layer sample was studied as well together with a very rude graphical expression of the development of ridges and grooves in the scar center. Moreover, possible phase changes of the chromium layer were studied with XANES, as initial SEM and EDX surface element detection (Fig. 12.24) did demonstrate signs of oxidations. This was unfortunately not really observed with XANES when subtraction spectra were compared to XANES spectra of different oxide phases of chromium.

**Single Layer Wear Results**

It was possible to establish values for the specific wear rates of both TiN and TiAlN single layers with results remarkably similar to those of the literature, in which divergencies are otherwise often seen due to slight differences in experimental parameters. Multi-layer wear rates were derived with wear rates similar those of the single layer coatings, which indicate the wear properties of multi-layered coatings correspond to those of the single layers even if wear due to delamination was observed occasionally.

**13.2 Future Developments**

This study of different tribological and optical coatings revealed many very different results, which to a great extent all turned out to be very successful with many informative and constructive results. Naturally, there is room for improvements within the themes of this project and various future prospects or development possibilities are discussed here for the different topics of this study.

**Film Growth Studies by PLD and RHEED**

The initial film growth and nucleation study of TiO$_2$ by RHEED did not reach satisfactory results on establishing film growth mode as discussed in section 10.4.2 due to lack of correspondence between the RHEED pattern and intensity measurements, AFM images and XRD measurements. The film growth of TiO$_2$ could favorably be studied by use of a different substrate material such as e.g. LaAlO$_3$ or SrTiO$_3$, which both previously have shown fine results as substrate for TiO$_2$ film growth and RHEED studies [108, 121]. At least a better film and substrate match should be chosen for a subsequent TiO$_2$ film growth study.

**Combined Wear and Optics Studies**

The fine results on the combined wear and optics experiments discussed in section 11.4 and shown in Figs. 11.32 and 11.33 may be improved by elaboration of the linear tribometer setup (Fig. 8.1) to also include a HeNe laser source and a detector such that real in-situ monitoring of the wear scar during the actual wear is achieved. This is realized by practically merging the reflectance setup (Fig. 8.6) together with the tribometer as Fig. 13.1 illustrates in principle.
The laser beam should preferably be incident on the sample in the smallest possible angle as discussed in section 11.2.2, since this will give the largest possible shift in the detected reflectance (see e.g. Tab. 11.3). This is, nevertheless, very difficult due to the composition of the tribometer, where the arm (with the steel ball contact) blocks the line of sight between a high angle laser beam and the sample surface. Thus, a lower angle of the incident laser beam may be chosen (e.g. $\theta = 60^\circ$) such that the laser may reach the contact zone on the sample surface without the tribometer arm blocking the line of sight during the wear experiment. Parenthetically, this is also the main reason why the laser reflectance, $R$, of section 11.4 was measured at the fairly low angle, $\theta = 60^\circ$. Consequently, it should be possible to monitor the wear of TiAlN-on-TiN-on-Steel multi-layer samples as the wear process proceeds through the top TiAlN tribological coating and reaches the embedded TiN signal layer by measuring the increasing level of reflectance during the wear process.

Additionally, a camera detector observing larger sample areas in-situ while being exposed to the abrasive wear process in the linear tribometer combined with image processing to automatically monitor areas may also be a possible improvement of the experiments discussed in section 11.5. This most likely requires larger samples as the current tribometer setup will not allow the camera direct visible access to the sample surface, since the top part of the tribometer (the arm, see e.g. Figs. 8.1 and 8.2) blocks the line of sight as before. It should otherwise be possible to install in the linear tribometer setup.

**Combined Wear and X-ray Studies**

In order to achieve better statistics on development dynamics a more systematic measurement series with respect to normal load, number of cycles vs measuring (steps) etc. should be prepared and performed with a high brilliance synchrotron radiation source such as e.g. ESRF, since the experiments and analyses presented in chapter 12 showed quite fragmented results. This would require a large amount of work as all ESRF measurements would have to be repeated, but the analysis software is of course readily present.

The oxidation of the embedded CrN layer in the TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample appears to be a pure surface phenomenon, since it was not possible to measure any real changes in the CrN absorption edge (see discussed in section 12.3), where any possible oxidation signals

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**Figure 13.1:** *In-situ monitoring of wear process in linear tribometer. A fusion of Figs. 8.1 and 8.6.*
most likely ‘drowned’ in the comparatively large background signal from the supporting carbon substrate and additional tribological TiAlN layers.

A re-design of the samples and setup such that a possible phase change (oxidation) of CrN during wear is detected would require a re-think of the complete experiment. At least only the topmost parts of the contact zone of this multi-layer sample system should be studied, if the oxidation is a pure surface incident. XANES is otherwise a fine way to reveal chemical phase changes in materials due to the shift in absorption edge position.

The combined wear and X-ray experiment performed at the ESRF was not a real in-situ experiment in the true sense of the word, but rather a real-time experiment as the wear process was paused during transmission and XANES measuring. A real in-situ experiment should be measured during the process. True in-situ measurement would require to measure the wear during the process, which means to pass the X-ray beam through both the wear sphere and the contact zone (see Fig. 9.9) such that the development may be measured while it happens. The wear sphere should in this case be placed on the stationary part and the sample on the moving part. However, two problems complicate this in-situ setup;

1) The wear sphere consists of resin mixed with powdered diamonds. The resin consists of a polymer composed essentially of carbon and hydrogen, which both are low Z elements. Thus, the X-ray beam should pass through the resin relatively easy. But, the powdered diamonds consists of diamond grains, i.e. thousands of small more or less perfect crystals oriented in different directions, which all scatter the X-ray photons. This leaves the detected transmission and XANES signals practically useless and makes this measurement method quite difficult.

2) The sample and contact zone move during measurement of the real in-situ experiment and the integration time for measuring XANES is 50 ms and twice the time, 0.1 s, for the transmission measurement (see Tab. 9.1). Furthermore, the repetition frequency in this experiment was set to 5 Hz and the scar length to 1.5 mm (see Tab. 9.2), which causes the sample to have covered a distance of 375 $\mu$m during a single point XANES measurement and 700 $\mu$m during a transmission measurement. This is naturally not suitable and probably makes this suggested in-situ detection scheme non-feasible.
Appendix A

Additionals

Comparisons of the measured and calculated laser reflectance $R$ (see section 10.2) are included in the appendix together with additional scar sample photos and Dektak scan profiles of the induced wear scars (see section 11.1). Initially, a drawing of the ESRF BM29 beamline (see section 9.1.1) is displayed here together with a Cr-foil absorption measurement for the EXAFS calibration at the ESRF. In addition, photos of a resin-diamond reinforced steel ball (see section 8.1.2) before and after a wear experiment are also included.

Figure A.1: Beamline setup at BM29, which was used in the EXAFS measurement described in chapter 9. The figure is from [94].
APPENDIX A. ADDITIONALS

A.1 Reflectance – Measured vs. Theory

The measured laser reflectance is plotted (triangles) together with the calculated reflectance (full lines) for the two multi-layer series, $\text{TiN-on-TiO}_2\text{-on-Steel}$ and $\text{TiAlN-on-TiN-on-Steel}$, in Figs. A.5 and A.6, respectively, for the 5 individual samples in each series. The reflectance $R$ (of Eqs. (4.9 - 4.12)) as a function of the incident angle, $\theta$, was applied in the calculations together with the obtained complex refractive indices, $\tilde{n}$ (Tab. 10.7), where deviations may be caused by errors in the estimations of the layer thicknesses and refractive indices together with possible limitations in the Mathematica’s performance on the large expression for $R$ in the multi-layer systems.

In addition, the laser reflectance measured of bulky material samples is plotted (triangles) together with the calculated reflectance (full line) for TiN (a), 100Cr6 steel (b) and TiAlN (c), respectively, in Fig. A.7. The errors (light cyan) on the calculated reflectance arise from the errors on the derived complex refractive indices (Tab. 10.7), where the measured values mostly are within the errors range.

Figure A.2: The absorption from a chromium foil measured around the Cr K-edge was used for energy calibration of the multi-layer EXAFS measurement (chapter 9).

Figure A.3: Specular RHEED intensity during homoepitaxial growth of SrTiO$_3$ [122]. A fluctuating intensity in the specular RHEED spot cause the oscillations as the film coverage changes during the two dimensional layer-by-layer growth (see Fig. 3.14).

Figure A.4: Photos of resin-diamond coating (see Fig. 8.4) reinforcing steel ball counterpart prior to (a) and after (b) wear process.
Figure A.5: $R(\theta)$ (of Eq. (4.9)) measured (triangles) vs. calculated (full lines) for 0 nm (a), 21 nm (b), 41 nm (c), 69 nm (d) and 107 nm (e) TiN on 47 nm TiO$_2$. Derived complex refractive indices, $\tilde{n}$, for TiN and TiO$_2$ (Tab. 10.7) were employed in the calculation.
Figure A.6: $R(\theta)$ (of Eq. (4.9)) measured (triangles) vs. calculated (full lines) for 0 nm (a), 40 nm (b), 85 nm (c), 101 nm (d) and 134 nm (e) TiAlN on thick TiN. Derived complex refractive indices, $\tilde{n}$, for TiN and TiAlN (Tab. 10.7) were employed in the calculation.
Figure A.7: Measured (triangles) vs. calculated (full lines) laser reflectance, $R(\theta)$, (of Eq. (4.9)) for thick TiN (a), 100Cr6 bearing ball steel (b) and thick TiAlN (c). The errors (cyan) arise from the errors of the derived complex refractive indices, $\tilde{n}$, for TiN, steel and TiAlN (Tab. 10.7).
Figure A.8: Real-time RHEED patterns showing the development of TiO$_2$ deposited by PLD at 700 °C after 0 s, 40 s, 80 s, 120 s, 160 s, 200 s, 240 s, 280 s and 300 s of deposition with 1 laser pulse per second.
A.2 \textit{TiO}_2 \textit{RHEED} images

The series of \textit{in-situ} RHEED images shows in Fig. A.8 the initial real-time development (from 0 s to 300 s) of the diffracted patterns during growth of TiO\textsubscript{2} on MgO with deposition at 1 laser pulse pr second. The subsequent development as the growth continues is shown for deposition times of 600 s (a) and 1200 s (b) in Fig. A.9 together with a RHEED image recorded after 1200 s (c) of deposition with 40 pulses pr second to achieve a thicker film for thickness estimation.

Clearly, the streaky appearance gradually changes into elongated spots after 160 s of film deposition and after 200 s new spots in between the existing spots emerge. The new spots are clear and distinct after 300 s and also clearly observed (Fig. A.9) after both 600 s and 1200 s of film deposition. But, corresponding AFM images together with XRD film studies (neither included here) revealed no indications to what may cause this change from streaks to spots in the RHEED patterns such that e.g. a growth mode for the TiO\textsubscript{2} film could be established. The recorded intensity of the specular spot (see Fig. A.10) didn’t either lead to further growth mode results, since it e.g. showed no signs of oscillations, associated with 2 dimensional layer-by-layer growth.

The film thickness was estimated of the thicker (1200 s, 1 Hz) film with CASINO and measured EDX signals (see sections 7.2.2 and 10.1.2) to be \( \sim 25 \) nm, which led to a rather low average deposition rate of \( \sim 10^{-4} \) nm pr laser pulse, most likely because of the low laser fluence (see. Tab. 7.1) in this experiment. The film thickness was also attempted estimated with the FEGSEM cross sectional imaging, initially with the 1200 s (1 Hz) film and subsequently with the much thicker 1200 s (40 Hz) film. But either of the two deposited films were possible to distinguish from the MgO substrate in the sample cross section, due to the rather thin extension of the film.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{RHEED_Intensity.png}
\caption{Intensity of specular spot during growth of the TiO\textsubscript{2} film for 1200 s with 1 laser pulse pr second.}
\end{figure}
A.3 TiN Samples

Photos of all the single-layer TiN wear scar samples (see e.g. Tabs. 2.6 and 8.2) are displayed here. All the wear scars included in the wear quality analysis (see section 11.1) are worn through to the steel substrate. These are marked with * in the Dektak profiles shown below.

Sample 17 scar 3 (Fig. A.11) shows a pure TiN-steel contact, in which the reinforcing resin-diamond coating detached from the steel ball during the wear process, such that the steel ball was severely worn and not the TiN coating. Thus, the grey stuff is steel ball residue left on the TiN coating. Moreover, sample 19 scar 3 and sample 20 scar 1 were worn with resin only, causing a polished ‘wear scar’ only.

![Figure A.11: Wear scars on sample 17.](image1)

![Figure A.12: Wear scars on sample 18.](image2)

![Figure A.13: Wear scars on sample 19.](image3)

![Figure A.14: Wear scars on sample 20.](image4)

**Dektak Profiles**

The Dektak scan profiles measured from the above TiN wear scars and leading to the results on the wear quality are displayed below.
A.3. TIN SAMPLES

Figure A.15: Wear tracks on sample 17 scar 1.

Figure A.16: Wear tracks on sample 17 scar 2.

Figure A.17: Wear tracks on sample 18 scar 2.

Figure A.18: Wear tracks on sample 18 scar 3.

Figure A.19: Wear tracks on sample 19 scar 1.

Figure A.20: Wear tracks on sample 19 scar 2.
Figure A.21: Wear tracks on sample 19 scar 3.

Figure A.22: Wear tracks on sample 20 scar 1.

Figure A.23: Wear tracks on sample 20 scar 2'.

Figure A.24: Wear tracks on sample 20 scar 3'.
A.4 TIALN SAMPLES

A.4 TiAlN Samples

Photos of all the wear scar examples of the TiAlN single layer coatings are displayed here, where the initial four (Figs. A.25 - A.28) are coated with $\sim 2 \, \mu\text{m}$ TiAlN and the final two (Figs. A.29 - A.30) with $\sim 3 \, \mu\text{m}$ (see Tab. 2.6). All samples and wear scars have been labeled in order possibly relate a scar to the right Dektak profile displayed in the subsequent pages.

All TiAlN wear scar samples were included in the wear quality analysis (see section 11.1), but some scars were worn beyond the film-substrate interface and through to steel (seen as bright grey appearing in the bottom of the scar in question). These are important in the results of the analysis and thus marked with ** in the Dektak scan profiles below.
Figure A.25: *Wear scars on sample 12.*

Figure A.26: *Wear scars on sample 13.*

Figure A.27: *Wear scars on sample 14.*

Figure A.28: *Wear scars on sample 15.*

Figure A.29: *Wear scars on sample 53.*

Figure A.30: *Wear scars on sample 55.*
Dektak Scan Profiles – 2 µm TiAlN

Figure A.31: Scan profile of sample 12 track 1.

Figure A.32: Scan profile of sample 12 track 2.

Figure A.33: Scan profile of sample 12 track 3.

Figure A.34: Scan profile of sample 13 track 1.

Figure A.35: Scan profile of sample 13 track 2.

Figure A.36: Scan profile of sample 13 track 3.
Figure A.37: Scan profile of sample 14 track 1.

Figure A.38: Scan profile of sample 14 track 2.

Figure A.39: Scan profile of sample 14 track 3.

Figure A.40: Scan profile of sample 15 track 1.

Figure A.41: Scan profile of sample 15 track 2.

Figure A.42: Scan profile of sample 15 track 3.
A.4. TIALN SAMPLES

Dektak Scan Profiles – 3 μm TiAlN

Figure A.43: Scan profile of sample 53 track 1.

Figure A.44: Scan profile of sample 53 track 2.

Figure A.45: Scan profile of sample 53 track 3.

Figure A.46: Scan profile of sample 55 track 1.

Figure A.47: Scan profile of sample 55 track 2.

Figure A.48: Scan profile of sample 55 track 3*.
Figure A.49: EXAFS measured of TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample at the BM29 beamline around the chromium K-edge.

A.5 Pixel to Energy Calibration, EXAFS

EXAFS was measured from a TiAlN-on-CrN-on-TiAlN-on-Vitreous Carbon multi-layer sample (Fig. 2.9) in order to convert the pixel numbers of the position sensitive detector array at the ID24 beamline into the X-ray photon energies of the beam (see sections 9.2 - 9.4). Figure A.49 displays EXAFS measured (at BM29) as a function of the X-ray photon energy from 5.908 - 6.849 keV, where the beamline initially was calibrated to the Cr K-edge of a Cr standard metal foil through a subsequent comparison with table values [35]. The discrete jump in the absorption as the X-ray photon energies are scanned across the CrN absorption edge is clearly visible. As a result of the nitride binding of CrN the edge is located about 10 eV higher than the edge of free chromium (Fig. A.2), which was also observed by Kimura et al. [119]. A number of EXAFS-wiggles over quite a range of the spectrum are also visible in the spectrum but not be studied further.

Figure 9.5 displayed above the absorption spectrum (XANES) measured with the 2048 pixels of the position sensitive detector around the absorption edge. The wiggles in that XANES spectrum are identical to those of the EXAFS spectrum (Fig. A.49) since they come from identical samples. The linear correspondence between the pixel number and the X-ray photon energy is plotted in Fig. A.50, in which the position of the 5 XANES wiggles and the corresponding initial 5 EXAFS wiggles (red triangles) were used in the calibration. The calibration result in a complete XANES energy range of 163.7 eV, from 5.955 to 6.119 keV. A single pixel corresponds thus to an energy range of 0.08 eV.
Appendix B

Reviewed Papers
Design of optical reflectance signals for wear control by varying the thickness of thin films of Ti-compounds

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Received 14 February 2008, in final form 18 April 2008
Published 12 June 2008
Online at stacks.iop.org/JPhysD/41/135307

Abstract
We have optimized two Ti-compound systems for the largest possible shift in reflectance of visible laser light over a film thickness range of 100 nm on the basis of Fresnel’s reflection law and experimental measurements. With a model system consisting of a tribological TiN layer on top of a 50 nm TiO₂ signal layer on bearing steel the largest possible shift of the reflectance can be obtained. For a second model system of tribological TiAlN layer on top of a 3 µm thick layer of TiN we have also demonstrated that the reflectance changes significantly with decreasing thickness of the TiAlN films. The precise thickness of the thin films was determined with a combination of energy-dispersive x-ray analysis and Monte Carlo simulations. These results show that optical monitoring with the reflectance is a potential technique for determining the residual thickness of thin tribological films prior to complete wear.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Tribological hard coatings of materials such as titanium nitride (TiN), titanium aluminium nitride (TiAlN) and chromium nitride are being increasingly used in industrial production lines, due to their high wear resistance [1, 2] and decorative appearance [3]. However, even tribological coatings will eventually wear out and there is thus a growing demand for monitoring equipment, which warns the industrial production operator before the tribological layer is removed.

In this work we thus investigated two systems: (i) thin TiN layers deposited on a thin titanium dioxide (TiO₂) layer with bearing steel as a substrate and (ii) thin layers of TiAlN deposited on a 3 µm thick film of TiN with bearing steel as an underlying substrate as well. TiO₂ is usually not employed as a tribological coating, but the refractive index is significantly different from that of TiN. This means that the thickness of a residual layer of TiN after a wear process can be determined optically, provided that the refractive indices of all materials are well known. The second system consists of two tribological coatings, but many of the physical properties, e.g. the mass density, of TiAlN are not known accurately. Also for this system the thickness of the residual top-layer of TiAlN can be determined optically. Thus, the well-known material TiN is a constituent of both systems: a tribological coating in system (i) and an ‘upper’ substrate-layer for TiAlN in system (ii). This is possible because the optical properties as shown below are substantially different from those of both TiO₂ and TiAlN. The measured reflectance, R, of the combined TiN–TiO₂–steel multi-layer model system (i) is found to be substantially reduced from 0.75 down to 0.2 as the TiN layer thickness decreases from 100 to 0 nm. The reflectance for the TiAlN system was found to increase from the bulk value of TiAlN of
about 0.15–0.35 up to 0.5–0.7 for the substrate-layer of TiN dependent on the polarization.

2. Film production

The films that have been studied in this work have been produced by two different (thin) film production methods. TiN and the TiAlN films of 4–5 different thicknesses have been produced in an industrial physical vapour deposition (PVD) setup [5]. The layer of TiO₂ has been produced commercially by electron beam evaporation on polished steel substrates in an argon gas [6].

The thin TiN and TiAlN films of increasing thickness of 0, 20, 40, 70 and 100 nm have been produced with PVD by CemeCon Scandinavia A/S with identical process parameters but with increasing deposition times after a preliminary thickness calibration for TiN based on the optical method described below. The films for this work (table 2) were deposited on the bearing steel substrates (100C6) from titanium and aluminium targets mounted in a discharge chamber with a mixture of argon and nitrogen. We have determined the precise film thickness optically and with a standard method in thin film production, based on the scanning electron microscopy (SEM) technique as described below, since the PVD process can be difficult to control for films of thicknesses below 100 nm.

A schematic drawing of one of these multi-layer structures is shown in figure 1, where the TiN layer is deposited on top of a 50 nm TiO₂ layer, which in turn is deposited on top of a polished bearing steel sample. The steel substrates have initially been polished to have a roughness of around 1 μm in order to obtain a well-defined optical surface. The wear takes place from the TiN layer side, where the laser beam (λ = 633 nm) also is irradiating the sample, and thus the laser reflectance R is measured as indicated in the figure.

3. Optical method

The reflectance R of a laser beam from a multi-layer structure, such as the one displayed in figure 1, can be described theoretically by Fresnel’s reflection law [7, 8] as

\[ R = \left| \frac{r_{12} + r_{234} \exp[i2k_{z, 2}d_2]}{1 + r_{12}r_{234} \exp[i2k_{z, 2}d_2]} \right|^2, \tag{1} \]

where the amplitude reflection coefficients \( r_{12} \) and \( r_{234} \) are given by

\[ r_{12} = \frac{n_2^n k_{z, 1} - n_2^n k_{z, 2}}{n_2^n k_{z, 1} + n_2^n k_{z, 2}} \]

and

\[ r_{234} = \frac{n_3^n k_{z, 3} + n_2^n k_{z, 3}}{n_3^n k_{z, 3} - n_2^n k_{z, 3}} \]

and the normal wave vector component \( k_{z,i} \) by

\[ k_{z,i} = \frac{2\pi}{\lambda} \sqrt{n_i^2 - N^2}. \]

\( n_i = n + ik \) is the complex refractive index of medium i depending on the refractive index n and the extinction coefficient k. \( \rho = 0 \) (or \( \rho = 1 \)) corresponds to the TE (or TM) polarization of the light, \( d_i \) is the layer thickness of layer i and \( \lambda \) is the wavelength of the laser beam. \( N = n_i \sin \theta_i \) is the normalized tangential component of the wave vector and seen to be independent of the medium due to Snell’s law. This means that the normal wave vector component is dependent on both the refractive index \( n_i \) and the angle of incidence \( \theta_i \).

The laser reflectance is measured as shown in figure 1, where the 633 nm TE (s) polarized or TM (p) polarized laser beam is reflected from the films. The intensity of the reflected TE or TM polarized beam is measured for increasing angles of incidence, \( \theta_i \). The measured reflectance shown in figure 2 for TiN illustrates the difference between the TE and the TM reflectance. The TE reflectance (red) curve increases with the angle of incidence and the TM (blue) reflectance curve decreases until the Brewster angle (the angle of minimum laser reflectance for the TM polarized beam), above which it increases again [7].

An optimum TiO₂ layer thickness of 50 nm in the model system (i) has been deduced from the theoretical calculations of the reflectance given in equation (1). This TiO₂ thickness is seen from the calculations to give the largest possible change of reflectance of 0.5 when going from 100 to 0 nm TiN in the TiN–TiO₂–steel model system. In contrast, for model system (ii) TiAlN–TiN–steel the thickness of the underlying ‘signal’ layer of TiN turned out be unimportant, and we have, therefore, used a standard thickness of 3 μm for all layers of TiN on bearing steel.

4. Results: reflectance from bulk TiN, TiAlN and bearing steel

In order to determine the index of refraction of the TiN tribolayer, the laser reflectance for both TE and TM polarized light was measured for a TiN sample. The sample is different from the multi-layer samples described in figure 1, but produced in an identical process on polished bearing steel substrates. If films of TiN (or other materials) are not produced after exactly the same process parameters, the stoichiometry and thereby also the index of refraction may change [9–11].

The reflectance measurement shown in figure 2 demonstrates how the reflectance depends on the TiN layer thickness. The figure shows the measured TE (red) and TM (blue) reflectance versus the angle of incidence of the laser beam for two different samples—a sample with approximately 20 nm TiN (triangles) and a sample with approximately 3 μm TiN (squares) deposited on transparent glass substrates. In order to see the difference of the multilayer samples described in figure 1, but produced in an identical process on polished bearing steel substrates. If films of TiN (or other materials) are not produced after exactly the same process parameters, the stoichiometry and thereby also the index of refraction may change [9–11].

The reflectance measurement shown in figure 2 demonstrates how the reflectance depends on the TiN layer thickness. The figure shows the measured TE (red) and TM (blue) reflectance versus the angle of incidence of the laser beam for two different samples—a sample with approximately 20 nm TiN (triangles) and a sample with approximately 3 μm TiN (squares) deposited on transparent glass substrates. In order to see the difference of the reflectance level for thin and thick TiN layers, respectively, the TiN have been deposited on glass substrates in figure 2, since the optical properties of TiN and steel are similar (see below). The similar optical properties of TiN and steel would not display such an increase in the reflectance level as seen in figure 2. Nevertheless, it is clear from the measurements displayed in the figure that a large TiN layer thickness leads to a high reflectance and a thin layer thickness may lead to a low reflectance.

3 μm TiN is completely non-transparent to the laser light, which makes it comparatively simple to estimate the refractive index of the TiN layer, as there are no reflections arising
Figure 1. The TiN–TiO₂–steel model system of thin films of tribological TiN of 0, 20, 40, 70 and 100 nm has been produced on top of a 50 nm TiO₂ layer on a series of steel (100C6) samples. The reflectance is measured from the TiN layer side of the samples as indicated.

Figure 2. The laser reflectance measured for a 20 nm (triangles) and a 3 µm (squares) TiN layer thickness on a glass substrate for increasing incident angles, θ, of the laser beam on the sample surface. Red (filled) symbols are for TE (s) polarized light and blue (empty) symbols are for TM (p) polarized light at 633 nm.

from the underlyng layers or interfaces, such that the type of substrate has no significance at all. The complex refractive index is found by initially measuring the reflectance of the non-transparent layer for increasing incident angles (see figure 2). Subsequently, the reflectance contour curves calculated from equation (1) for specific sets of measured reflectance and corresponding angle of incidence (R, θ) have been plotted in figure 3 as a function of the refractive index n and the extinction coefficient k of the complex refractive index. The reflectance contour curves were calculated for a specific incident angle θ and a TiN layer thickness of 3 µm. Each set of contour curves (each colour) comprises a centre curve, calculated directly from the measured reflectance and corresponding angle, and two ‘flanking curves’ corresponding to the error arising when measuring the reflectance.

Contour curves corresponding to particular (R, θ) sets displayed in different colours are seen in figure 3 to cross each other within a small area. The curves plotted in the figure are measured around the lowest reflection value with TM polarized light, e.g. around the Brewster angle at 65°. The (R, θ) sets for which the contour curves have been plotted in figure 3 have been listed in table 1.

A small inset in figure 3 shows all the TM reflectance contour curves in order to demonstrate that not only the selected contour lines of the main figure, but all lines cross each other within a small area, from which n and k can be determined. For simplicity only the selected reflectance contour lines around the Brewster angle of the main figure have been used in the evaluation of n and k. The TE contour curves have for clarity been left out, but they do follow the green shaded contour curves of the small inset and thus also cross the other curves within the area.

Thus the analysis of figure 3 shows how it is possible to estimate the refractive index n and the extinction coefficient k of the TiN layer, simply by measuring the laser reflectance for increasing angles of incidence for a completely opaque TiN layer. The complex refractive index at 633 nm was estimated from the crossing of the reflectance contour lines, displayed in figure 3, to be

\[ n_{\text{TIN}} = 0.92(\pm0.04) + i2.63(\pm0.12). \] (2)

The refractive index has been found as the centre point of the area spanned by the crossing of the selected reflectance contour lines. The errors are given by the outermost boundaries of the crossing area, where measuring errors are included.

The index of refraction found for TiN agrees with the expected ones for this type of material [7, 12]. It is similar to
that of metallic compounds with a relatively strong absorption due to the high value of the extinction coefficient $k$, and with a high reflectivity due to the comparatively small refractive index $n$.

The complex index of refraction for TiAlN has been evaluated in a similar way to that for the thick TiN samples:

$$n_{\text{TiAlN}} = 1.76(\pm0.07) + i0.929(\pm0.068).$$

Within the uncertainty this value agrees with that from the literature [9].

Finally, the index of refraction has also been estimated for the polished steel substrate, which is also needed in order to calculate the reflectance coefficient of thin layers deposited on top of the steel samples. The complex refractive index for the 100C6 steel substrate has been estimated to be

$$n_{\text{100C6}} = 2.21(\pm0.56) + i3.07(\pm0.59).$$

The complex refractive index of any type of steel is highly dependent on the composition and manufacturing process, since the production is different from one manufacturer to another, and occasionally with a varying composition. The type of steel used here is seen to display a very high absorption and a very high reflectivity, since both the refractive index and the extinction coefficient are relatively high.

5. Results: reflectance from thin film multi-layer systems of TiN and TiAlN

The laser reflectance at an angle of incidence of 45° for the five multi-layer structure samples of the TiN/TiO$_2$ model system (i) with increasing TiN layer thicknesses is shown in figure 4, where all five TE (full symbols) and TM (empty symbols) reflectance measurements are plotted together with the calculated reflectance (solid curves). The data sets show a clear increase in the reflectance as the TiN layer thickness increases and especially an abrupt change in the reflectance is seen from the 20 nm layer to the 40 nm layer. Furthermore, the data show that TiN is almost opaque for a layer thickness of 70 nm, since the reflectance for the 70 nm sample and the 100 nm sample is seen to be quite similar. This is supported by the measurement of the full reflectance of these two multi-layer samples for a large range of angles similar to that shown in figure 2 and from the work of Roquiny et al [3].

The TiO$_2$ layer and the TiN layer thickness of the five samples of figure 4 have also been estimated independently of the optical method with a combination of SEM and the program CASINO [13]. The energy dispersive x-ray (EDX) signals from Ti in the deposited TiN and TiO$_2$ layers and Fe of the steel substrate in the samples were measured and compared with CASINO’s Monte Carlo simulations of electron trajectories in both the TiN and the TiO$_2$ layers and the steel substrate, such that the total TiN layer thickness could be deduced. The estimated TiN thicknesses have been listed in table 2. The TiO$_2$ layers of the five samples can be assumed to have the same thickness and stoichiometry, since all the TiO$_2$ layers have been produced in the same batch. The TiO$_2$ film thickness could be estimated independently from a sample without any TiN deposition with the combined EDX and CASINO method. This method has previously been used to estimate the film thickness for other deposition techniques as well [14]. The errors in the TiN layer thickness arise from the comparison of EDX measurements and CASINO simulations.

The TiO$_2$ layer thickness was also determined with the combined EDX and CASINO method. The TiO$_2$ layer thickness was estimated from the ‘0 nm’ TiN sample, i.e. the sample without any TiN deposition but with a ‘pre-etching’ included, to be 47 nm. This value is obtained under the assumption that the TiO$_2$ film is predominantly the anatase phase with a density of 3.89 g cm$^{-3}$ [15]. If the film contains the rutile phase with a density of 4.26 g cm$^{-3}$ the layer thickness is estimated by EDX and CASINO to be 43 nm. It has not been established which phase the TiO$_2$ layer has, due to the small difference in the estimated layer thickness between the two phases. In fact, the layer is most likely in the anatase phase with the production method at low temperature [16].

Also the thicknesses of the TiAlN films deposited on 3 µm thick layers of TiN of system (ii) were determined by the combined EDX and CASINO method. In this case the Ti and Al signals were compared. For the TiAlN the same deposition time as that for TiN was used which results in a slightly larger thickness for TiAlN. The thickness of the TiAlN films is listed in table 2. The TE and the TM reflectance at 45° from the TiAlN films with increasing film thickness is shown in figure 5 together with the theoretical calculations (solid curves). The value of the reflectance changes from the bulk TiAlN value (~0.1 for TM and ~0.3 for the TE polarization) up to the bulk value (>0.5) for TiN at 0 nm TiAlN thickness. In contrast to TiN the TiAlN films become opaque for a film thickness above 100–120 nm.

It is possible to derive the refractive index of the TiO$_2$ layer deposited on the polished steel substrates with the same method as for the 3 µm TiN layer, even though the layer is transparent and not very thick. Once the layer thickness is known explicitly from the combined EDX and CASINO method, the reflectance
and therefore the wear of TiN on TiO2 can be monitored with TiN layer thickness of 70 nm [12], the residual layer thickness measurements show that the TiN layer is almost opaque at a thickness dependent on the TiN layer thickness, as the value increases with TiN layer thickness for our model system (i). Since the refractive index may change with different deposition parameters.

The behaviour of the reflectance for thin films of TiAlN on TiN for our model system (ii) is somewhat more complex. As seen in figure 5 the reflectance decreases with decreasing film thickness, before it increases drastically at a film thickness below 40 nm. The theoretical curve based on equation (1) exhibits a minimum at a thickness of about 60–70 nm depending on the polarization. It also means that monitoring of residual thickness can be carried out solely for a thickness below 40 nm.

Nevertheless, the results show that the reflectance changes with more than 0.5 for both model systems. Under the assumption that the wear is homogenous and the residual surfaces have a limited roughness, the thickness of the residual layers can be determined from the reflectance. Roughness and wear debris induced by wear are clearly issues to be considered and will be investigated in future work, where also the adhesion between different layers, i.e. the substrate, the signal layer and the tribological layer, will be considered.

6. Discussion

Figures 2 and 4 illustrate directly that the reflectance is dependent on the TiN layer thickness, as the value increases with TiN layer thickness for our model system (i). Since the measurements show that the TiN layer is almost opaque at a TiN level thickness of 70 nm [12], the residual layer thickness and therefore the wear of TiN on TiO2 can be monitored unambiguously with the reflectance from thicknesses below 70–100 nm.

The behaviour of the reflectance for thin films of TiAlN on TiN for our model system (ii) is somewhat more complex. As seen in figure 5 the reflectance decreases with decreasing film thickness, before it increases drastically at a film thickness below 40 nm. The theoretical curve based on equation (1) and full refractive index from this work.

n_{TiO2} = 2.795(±0.045) + i0.018(±0.009),

which is similar to values found by others, e.g. [17, 18]. The numbers have been found by averaging the n and k values found for TiO2 layer thicknesses of 42 nm, 45 nm and 47 nm, corresponding to the thickness derived for the three phases of TiO2, anatase, rutile and brookite. Thus deviations from the expected anatase phase lead only to a slight difference in the index of refraction.

7. Conclusion

We have in this work designed a multi-layer system suitable for optical monitoring of wear. We have demonstrated the principles and reported the feasibility for tribological hard coatings, where an optical signal layer of 50 nm TiO2 embedded within a tribological TiN coating will lead to a shift of 0.5 in the laser reflectance as the tribological layer is worn out. Similarly we have demonstrated that also a system of a signal layer of TiN embedded in a tribological coating of TiAlN will lead to a similar shift of the reflectance, but in the opposite direction. The signal layer of TiO2 has an optimum thickness of 50 nm on bearing steel, whereas the thickness of the signal layer of TiN in TiAlN plays a minor role in the shift of reflectance.

We have furthermore demonstrated how it is possible to estimate both the refractive index n and the extinction coefficient k of a thick layer, simply by measuring the reflectance as a function of the incident angle θ. In addition, we have determined both the refractive index and the extinction coefficient of TiN, TiAlN and TiO2, if the layer thickness was determined in advance from EDX measurements and CASINO simulations. For the application of optical monitoring it is important to have a relatively precise knowledge of the optical properties of thin films, produced by e.g. PVD, since the stoichiometric composition of elements and thereby the refractive index may change with different deposition parameters.

Acknowledgments

This work has been supported by the Danish Strategic Research Council with the NABIIT grant 2106-05-0035.

References


| Table 2. TiN and TiAlN layer thicknesses as estimated by the combined EDX and CASINO method. The first row gives the planned layer thickness. |
| Expected layer thickness [nm] | 20 | 40 | 70 | 100 |
| TiN layer thickness [nm] | 21 (±1.5) | 40.7 (±1.5) | 69.6 (±1.5) | 107.3 (±2.9) |
| TiAlN layer thickness [nm] | 40 (±6.3) | 85 (±10.2) | 101 (±10.3) | 133.7 (±11.9) |
Growth of thin films of TiN on MgO(100) monitored by high-pressure RHEED

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Received: 12 October 2007 / Accepted: 4 March 2008 / Published online: 16 June 2008
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Abstract Reflection high-energy electron diffraction (RHEED) operated at high pressure has been used to monitor the initial growth of titanium nitride (TiN) thin films on single-crystal (100) MgO substrates by pulsed laser deposition (PLD). This is the first RHEED study where the growth of TiN films is produced by PLD directly from a TiN target. At the initial stage of the growth (average thickness ∼2.4 nm) the formation of islands is observed. During the continuous growth the islands merge into a smooth surface as indicated by the RHEED, atomic force microscopy and field emission scanning electron microscopy. These observations are in good agreement with the three-dimensional Volmer–Weber growth type, by which three-dimensional crystallites are formed and later cause a continuous surface roughening. This leads to an exponential decrease in the intensity of the specular spot in the RHEED pattern as well.

PACS 68.37Ps · 68.55.A- · 61.14.Hg · 61.16.Nz

1 Introduction

Titanium nitride (TiN) coating has been utilized widely for improving cutting performance and wear resistance of tools owing to the high hardness and chemical stability at elevated temperature. Coating of TiN is usually carried out by chemical vapor deposition (CVD) but, because of the high deposition temperature, i.e. 900–1000 °C, which is around the softening temperature of many materials, e.g. high-speed steels, such a technique is often replaced by other techniques which require moderate substrate temperature to form oriented crystalline films, e.g. plasma CVD or physical vapor deposition (PVD) [1, 2].

The major obstacle to low-temperature growth is the difficulty to achieve high surface mobility required for the nucleation and growth of crystalline or epitaxial films at low substrate temperature. This limitation can be overcome by delivering the material to the substrate with sufficiently high kinetic energy and can be accomplished by the use of pulsed laser deposition (PLD) [3, 4]. The strong laser–target interaction results in heating of the solid target, followed by ablation of some of the target material as a plasma. With a little loss of energy in a moderate background gas pressure, the plasma is transported to and the atoms deposited onto the substrate [5]. Several groups have reported the formation of TiN by PLD using either metallic targets in a nitriding atmosphere [6] or stoichiometric TiN targets [7].

Eventually, even good tribological coatings will wear in the long run and there is thus a growing demand for monitoring equipment, which is warning the industrial production operator before the tribological layer is wearing out and the coated tool severely damaged [8, 9]. The present study is a part of a work which aims at investigating the possibility to monitor optically a system of thin TiN layers deposited on a thin titanium dioxide (TiO2) layer, and as the first step we have studied the growth of TiN on a well-known substrate.

In this study we are trying to explore the initial stage of the nucleation and growth of TiN on a single MgO substrate in nitrogen background gas. High-pressure reflection high-energy electron diffraction (RHEED) was used to study in
situ the nucleation and growth of the film. Due to the sensitivity of the RHEED it is possible to study the development during the earliest stage of film growth.

2 Experiments

The TiN films have been deposited in the large-area PLD facility at Risø National Laboratory [10]. The film deposition took place in an ultra-high-vacuum chamber with a base pressure of $10^{-9}$ mbar. A target of TiN was irradiated with 20-ns laser pulses from an excimer laser at 248 nm with a fluence of 4 J/cm² and a frequency of 10 Hz.

The ablated material was collected on substrates located at a distance of 88 mm from the target. The films were grown on a circular substrate with 25.4 mm in diameter of MgO (100) single crystal. Prior to the deposition the substrates were annealed at 1000 °C for 40 h in oxygen atmosphere to clean the substrate surface. During the deposition the temperature was kept constant at a selected value of 700 °C, and nitrogen background gas was introduced into the chamber providing a background pressure of 0.02 mbar. The TiN target used for the investigation is a commercial target from Williams Advanced Materials.

The nucleation and growth of the TiN was observed in situ using a high-pressure RHEED system. The typical parameters were 35 keV for the electron energy and 1.5 µA for the beam current. The diffraction pattern was observed using a CCD camera and the recorded videos were then analyzed with commercial software KSA 400 [11].

After the deposition, the films were analyzed by X-ray diffraction (XRD) using a Bragg–Brentano geometry with a STOE & CIE θ/θ powder diffractometer equipped with an energy-dispersive Kevex detector. The radiation used was Cu–Kα.

The morphology of the films and the roughness were investigated with atomic force microscopy (AFM). Cross sectioning of the sample surface was performed on a Zeiss 1540XB cross beam field emission scanning electron microscope (FEGSEM) equipped with a focused ion beam (FIB) column and a gas injection system (GIS). To observe the cross section of the deposited layer, a 3–4 µm deep $3 \times 10$ µm² trench was milled into the sample surface using the FIB system. To protect the thin deposited layer during the milling process, a platinum layer with an area of $1 \times 10$ µm² was initially deposited on top of the sample surface. The trench was milled slightly into the Pt layer using a beam current of 200 pA for the initial, rough milling, while 10–20 pA was used for the final surface polishing of the cross sections.

3 Results

As indicated above, the MgO(100) single-crystal substrate was heat treated in oxygen atmosphere at 1000 °C and then immediately introduced into the vacuum chamber. Figure 1 shows the RHEED pattern from MgO(100) before and after the surface cleaning taken at room temperature. It is obvious from this figure that it is crucial to treat the substrate before the film deposition. As seen from the images, before the annealing, MgO has a spotty pattern which indicates a rough surface, while after the heat treatment sharp streaks were observed indicating a smooth surface. Moreover, after the heat treatment of the surface, the sharpness of the streaks increases, which means that a superior surface crystallographic quality is achieved compared with the surface before the annealing.

Figure 2 shows a series of RHEED patterns obtained from (a) an as-annealed MgO surface at 700 °C, and the same substrate deposited at (b) 5 s, (c) 10 s, (d) 20 s, (e) 30 s, (f) 40 s, (g) 60 s, (h) 120 s, (i) 240 and (j) 300 s. At the very initial stage of the growth, i.e. up to 10 s, the intensity of the RHEED pattern seems to decrease but still maintains the streaky appearance. Above this deposition time, the pattern changes from being streaky to spotty ($t = 20–120$ s) and

![Fig. 1 RHEED pattern of the MgO surface taken at room temperature (a) before heat treatment and (b) after heat treatment at 1000 °C for 40 h](image-url)
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Figure 2: Real-time RHEED pattern showing the development of the TiN deposited by PLD at 700 °C during the growth at times (a) 0 s, (b) 5 s, (c) 10 s, (d) 20 s, (e) 30 s, (f) 40 s, (g) 60 s, (h) 120 s, (i) 240 s, (j) 300 s and (k) 3600 s.

Finally, after a sufficiently long deposition time, the RHEED patterns show streaky features again. This indicates a transition from rougher to smoother surface morphology.

Figure 3 shows a series of AFM images corresponding to Fig. 2 and taken at deposition times of (a) 0 s, (b) 120 s, (c) 240 s, (d) 480 s and (e) 3600 s. The results obtained with the AFM are consistent with the RHEED results described above. As described above, the RHEED patterns are predominantly streaky. However, the RHEED patterns are found to gradually transform into spotty patterns within the first minute, thus indicating the formation of 3D islands. The initial growth as seen in Fig. 3b agrees well with the RHEED observations and exhibits islands, all of which are distributed homogeneously over the surface. Figure 4 shows the shape and the size distribution of the islands. From this figure, the average height of the islands measured over an area of $5 \times 5 \mu m^2$ is found to be 4.7 nm. By counting the number of the islands, the density after 120 s of deposition is calculated to be $6 \times 10^9$ islands/cm$^2$.

As the deposition time proceeds, i.e. above 240 s (corresponding to an average thickness of ~ 4.8 nm of a complete layer), the films continue to grow with a smooth surface covering the substrate area. At this stage there is no evidence for the formation of islands neither by RHEED nor by AFM. In order to verify our observations, we have investigated the surface and the cross section of the film with FEGSEM and FIB. Figure 5 shows the micrographs of the surfaces for samples deposited in 480 s (a) and 3600 s (b) as well as a cross section for the film deposited for 3600 s. As one can see from Fig. 5a and b, the surfaces of the film are relatively smooth, as also indicated from Fig. 3. The cross section revealed that the film grows as a dense film with a columnar appearance and a thickness of about 42 nm. The reduced surface roughness evaluated from AFM images confirmed the improvement of surface smoothness as the deposition time increases (see Fig. 6). These results also agree well with the RHEED observations, in which the appearance of streaks rather than arrays of spots above 240 s indicates a smoother surface morphology.

Figure 7 shows an X-ray diffraction pattern from the TiN film deposited for 3600 s. The average thickness of the film was found to be 42 nm, which gives a deposition rate of 0.012 nm/s. A single reflection of the (200) TiN orientation was observed, indicating that the columnar grains are oriented normal to the substrate. Observations of the growth orientation (200) of TiN were also previously reported in [11–13]. From the measurements of the full width at half maximum (FWHM) of the (200) peak the crystallite size was estimated using Scherrer’s equation. The peak FWHM is estimated by fitting the peaks to a Voigt function. The FWHM was found to be 0.0414 radian, which corresponds to a crystallite size of about 3.7 nm.

Figure 8 shows the RHEED intensity vs. time. Analysis of the recorded intensity of the RHEED patterns shows that the
intensity of the specular spot decreases with increasing film thickness up to about 50 s, from which a distinct increase of the spot intensity is observed. Note that the RHEED intensity as a function of time in Fig. 8 was obtained from the diffraction spot marked in Fig. 8, which is a superposition of reflection and diffraction spots.

4 Discussion

Based on the RHEED, AFM and FEGSEM observations the nucleation and growth of the TiN can be interpreted as a Volmer–Weber (VW) growth mode, consisting of an initial 3D growth of islands which in a later stage merge into a continuous columnar film. This growth mode agrees with the behavior of the RHEED pattern which changes from being streaks to spots, thereby indicating the formation of islands. The corresponding surface morphology is presented in Fig. 3b, which obviously reveals the formation of islands. At a time above approx. 240 s these islands seem to have merged into a dense, smooth film as indicated from both RHEED and AFM (Fig. 2b, c). The cross section of the film deposited for 3600 s supported our interpretation and revealed that the film indeed after the initial growth stage continues to grow as a dense, columnar film with a relatively smooth surface (Fig. 5).

The observations of the RHEED intensity evolution (Fig. 8) agree well with our AFM images and the RHEED
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Fig. 4 The size distribution of the islands taken from an area of 5 x 5 µm² for sample deposited for 120 s at 700 °C. The inserted figure shows an AFM micrograph of one of the islands.

Fig. 5 Micrographs of the surfaces for samples deposited for (a) 480 s and (b) 3600 s taken by FEGSEM. The film cross section is taken from the film deposited for 3600 s.

diffraction pattern (Fig. 2d–h and Fig. 3a, b) and indicate the formation of 3D islands during this period of time. After this time, the spot intensity monotonically decreases and then becomes almost constant within about 360 s, which corresponds to the change from initially point-like diffraction spots to streaks (Fig. 2i, j) with a relatively smooth surface (Figs. 3 and 5). It should be noted that the interpretation of the RHEED intensity evolution is rather difficult to assign to the surface roughness only, because the ‘reflected spot’ combines features that come from the superposition of reflection and diffraction under our experimental conditions. However, qualitatively these observations are in good agreement with our hypothesis that the growth of the TiN is dominated by the three-dimensional Volmer–Weber (VW) growth, and produces three-dimensional crystallites that lead to a continuous surface roughening and exponential decrease in the intensity of the specular spot.

The texture of the initial layers is affected by two important energy parameters: the film/substrate interfacial energy, \( \gamma_{if/s} \), and the film surface energy, \( \gamma_{s/f} \). The minimization of both \( \gamma_{if/s} \) and \( \gamma_{s/f} \) is the primary driver for texture development in the initial stage. For epitaxial growth, lattice matching causes a large decrease in \( \gamma_{if/s} \), and the deposited film orientation is determined by the orientation of the substrate. The competing planes in the TiN film are (200) with the lowest surface energy and (111) with the lowest strain energy [10]. The RHEED pattern reveals that the TiN grows epitaxially with sharper diffraction spots corresponding to the TiN orientation.
cubic structure (Fig. 2d–h). These results are not surprising and are expected because of the small mismatch (0.6%) between TiN \((a_0 = 0.4239 \text{ nm})\) and MgO \((a_0 = 0.4212 \text{ nm})\). Thus, the structure similarity favors epitaxy. X-ray diffraction measurements on the deposited film show a single (200) orientation (see Fig. 7). There is no obvious explanation for the formation of crystal orientation (200) in thin films of TiN. However, it was proposed in the case of TiN films that the atoms would be arranged into the plane with the lowest surface energy, i.e. (200) in the TiN crystal, with the NaCl-type structure [14].

5 Summary

In situ RHEED experiments in combination with AFM and FEGSEM have provided insights into the growth of TiN on MgO during PLD after optimization of the pre-annealing condition for the MgO substrates. The films were found to grow in a well-oriented single (200) plane. A good agreement is obtained between the recorded RHEED pattern during the initial growth and the morphology of the film observed by AFM and FEGSEM. For this growth-time range, we find that the behavior of the TiN is dominated by the three-dimensional Volmer–Weber growth, and three-dimensional crystallites are produced. After the initial growth stage a continuous and dense columnar film with a relatively smooth surface was observed.

Acknowledgements The authors would like to thank Dr. Karin Vels Hansen for the help with the AFM measurements. Furthermore, we would like to thank Mr. Finn Saxild for valuable help with the deposition using PLD. This work has been supported by the Danish Strategic Research Council with the NABIIT grant 2106-05-0035.

References

1. Introduction

Titanium dioxide has been studied considerably due to both physical and chemical properties of the material. The material has a wide range of technological application possibilities owing to its dielectric, electrochemical, photocatalytic and optical properties [1]. The three TiO2 phases; anatase, rutile and brookite, also give a scientific interest, since they exhibit different properties, stabilities and growth modes [2].

Investigations of TiO2 growth modes by combined RHEED and PLD setups have been conducted prior to this work [3,4], but with substrates other than MgO, i.e. with SrTiO3 and TiO2 substrates. Other groups have studied deposition of TiO2 on MgO [5,6], but not by the combined use of PLD and RHEED. To our knowledge no previous RHEED investigations of the TiO2 growth mode on MgO deposited by PLD have been conducted so far.

Another titanium compound, titanium nitride (TiN), is often utilized as industrial tribological coatings for improving the cutting performance and wear resistance of tools. This industrialized deployment of TiN is due to the very high hardness and chemical stability of the material [7]. The present growth study of TiO2 is part of a work, which is investigating the possibility of an optically monitoring system consisting of tribological TiN on top of an optical TiO2 layer. TiO2 is usually not utilized as a tribological coating, but the refractive index is significantly different from that of TiN. This means that the thickness of a thin, residual layer of tribological TiN (on top of an optical TiO2 layer) exposed to a wear process can be determined optically, if the refractive index of all materials is known in advance [8].

The lattice mismatch of a-axis constants between MgO and rutile or anatase TiO2 is considerable. The mismatch between rutile and anatase TiO2 and the substrate is 9.2 and 9.9%, respectively. The lattice mismatch between brookite and MgO is 11.9%. This does not make TiO2 and MgO a good match regarding film growth. Our previous studies of TiN on MgO [9] and our optical monitoring system with TiN and TiO2 [8] lead us, nevertheless, to choose MgO as a substrate in this TiO2 study.

Here we present a study of the initial growth stages of TiO2 on single crystal MgO deposited by PLD from a TiO2 target. The change in surface structure during the complete growth process was monitored with \textit{in situ} high pressure RHEED [10].
A high pressure RHEED system was applied to observe the film growth in situ. Typical parameters for the RHEED system were electron energy of 35 keV and a beam current of 1 μA. The diffracted RHEED patterns were collected on a fluorescent screen and observed with a CCD camera. The recorded movies were subsequently analyzed by the use of the commercial software KSA 400. A combination of SEM and the program CASINO [13] was used to estimate the film thickness. The energy dispersive X-ray (EDX) signals from Ti in the deposited film and Mg of the substrate were measured and compared with Monte Carlo simulations of electron trajectories from CASINO in both the film and substrate, such that a layer thickness could be obtained, and thereby the film growth rate. The morphology and surface structure of the deposited films were investigated with a DIVIE SPM atomic force microscope after film deposition. Analysis of the AFM images gave additional information on the height and roughness of the film surfaces.

3. Results

A RHEED pattern from an MgO (1 0 0) single-crystalline substrate recorded prior to film deposition (see Fig. 1a) is slightly asymmetric and shows long vertical streaks, which is characteristics of a smooth surface. The corresponding AFM scan from the MgO (1 0 0) substrate surface is shown in Fig. 1b, where the substrate sample prior to deposition and AFM measurement was thermally annealed and directly measured afterwards. The root mean square deviation roughness (RMS) of the substrate surface was found by the DualScope (tm) software to be ~7 nm, which is higher than expected, although we have used an identical heat treatment procedure as described in [12]. The relative high surface roughness could be due to the comparatively short annealing time, e.g. see [9]. This means that the surface as observed by AFM is not as smooth, as we would have expected from the observation of the RHEED image (Fig. 1a), which indicates a smooth surface.

A series of in situ RHEED patterns taken from the film surface at different times (a) 300 s, (b) 400 s, (c) 500 s and (d) 600 s is shown in Fig. 2a–d. The vertical sharp streaky pattern from the substrate observed in the RHEED image (Fig. 1a) disappeared gradually until the average film thickness exceeds around 0.03 nm (after 300 s). After 300 s the diffraction streaks from the substrate shift into an elongated spotty-shaped appearance (see Fig. 2a–b). New spots also started appearing after ~450 s and turned clearly visible after 600 s (Fig. 2d). The appearance of these diffraction spots are round and almost but not regular streaks.

A gradual transformation from the streaky patterns into elongated spotty-shaped patterns is seen within the first few hundred seconds of deposition. This indicates that the film growth proceeds through a three-dimensional island-like growth mode with a relatively rough surface. It is well known that a 2D growth regime is associated with streaky RHEED patterns, due to reflection diffraction on a smooth surface. A 3D growth is characterized by spotty patterns, due to transmission diffraction through 3D islands [14]. A transition from 2D to 3D growth could, nevertheless, not be observed from the intensity of the specular spot. An analysis of the recorded RHEED pattern showed an overall decrease in the intensity of the specular spot (see Fig. 2e). The decrease is occurring fast during the first 100 s. This is followed by almost stagnation during the subsequent 500 s, after which a more rapid decrease is seen. The intensity of the specular spot shows no sign of oscillations associated with layer-by-layer (2D) growth. The deposition of a 0.1 nm film (1200 s) gave rise to the RHEED diffraction pattern presented in Fig. 3a, where the appearance is similar to that of Fig. 2d (600 s). The pattern possesses typical 3D diffraction features indicating the growth of 3D islands. The interpretation given in the RHEED schematics (Fig. 3b) for a TiO2 film corresponds to the following orientation relationships: rutile TiO2(1 0 0) || MgO(1 0 0).

The topography of the film surfaces has been investigated with AFM for different deposition times (see Fig. 1b and 4). These images correspond to the thin films leading to the RHEED patterns of Fig. 2d and 3a. The AFM images of Fig. 4 have been obtained after (a) 600 s and (b) 1200 s. The images give the impression of an almost uniform film growth, where valleys and gorges of the substrate are filled during the PLD, since the MgO substrate contour (Fig. 1b) is seen to get more blurred for longer deposition periods and since the surfaces (Fig. 4) appear to get smoother for longer deposition periods. The surface height (see Fig. 5a) has been evaluated directly from the AFM images (Fig. 1b and 4), i.e. at the initial stage of the deposition (0 s, blue diamonds) and after 600 s (red triangles) and 1200 s (green squares). The roughness of the surface is changing during the deposition. The evaluated surface is initially rather rough (0 s), then smoothing out (600 s) and finally getting slightly rougher again after 1200 s. It should be noted that the surface after 1200 s of deposition is not even as rough or structured as the naked MgO substrate.

A combination of the program CASINO and measured EDX signals from both film and substrate has been used to deduce the layer thickness of a film deposited for 7200 s with a 40 Hz repetition rate of the laser. The EDX signals were obtained during 120 s of measuring at 15 different positions across the film surface to get good statistics on the film thickness evaluation. The average film thickness was estimated to be ~25 nm. This leads to a fairly
low average deposition rate, $10^{-4}$ nm per laser pulse, primarily because of the low fluence.

4. Discussion

A new structure growing on top of the substrate surface is clearly distinguished as seen from the RHEED observations during the film growth, i.e. the patterns change significantly during the film deposition from a RHEED pattern corresponding to the naked surface (Fig. 1a) to a RHEED pattern (Fig. 3a) corresponding to a thin film deposited on the initial surface. This new structure (as observed from the RHEED pattern) is visible already in the initial stage of the film growth and it is seen to keep the same appearance during longer deposition periods, even if the intensity decreases towards the end of the deposition. Furthermore, the streaks of the initial RHEED image (Fig. 1a) evolve during the initial stage until a RHEED pattern with modulated streaks appears after, a few hundred laser pulses (Fig. 2). Subsequently, the initial streaks are transformed into elongated diffraction spots corresponding to the TiO$_2$ rutile structure, which could be a result of transmission diffraction pattern, where the electrons pass through the rutile crystallites. This implies a growth of three-dimensional islands and an orientation relationship between the substrate and the supposed TiO$_2$ film is interpreted in Fig. 3b as rutile TiO$_2$(1 0 0) || MgO(1 0 0).

The film growth mode was furthermore investigated by analysis of the RHEED intensity of the specular spot, which in this measurement is the same position as the diffracted spot. The
intensity of the specular spot (Fig. 2e) descends continuously without oscillations, which thus gives us no conclusions regarding the growth mode of the film. The interpretation of the RHEED intensity evolution is rather difficult to assign to the surface roughness only, since the specular spot in this case also is the diffracted spot and since the “reflected spot” thus combines features, which come from the superposition of reflection and diffraction. The AFM images of the surfaces, on the other hand, exhibited no signs of island nucleation in the initial stages of the film growth either. The AFM images revealed a relatively uniform growth of the deposited film (Fig. 4), i.e. island growth is not observed. An explanation of this could be that the film seems to grow in a mode, where it is initially filling up the valleys in the rough substrate surface leaving the new film surface more and more uniform with the original contour from the substrate more and more blurred. In this way we would not see any oscillations in the intensity of the specular spot due to a layer-by-layer growth mode and we would not see signs of island growth in the AFM images. This growth mode is suggested in the schematic drawing in Fig. 5b with an initially quite rough substrate surface ($t = 0$ s, MgO) followed by a less rough surface layer ($t = 600$ s, TiO$_2$). The final surface layer ($t = 1200$ s, TiO$_2$) is getting slightly rougher again as indicated in the figure. This is seen to correspond quite well to the measured surface roughness (Fig. 5a).

A previous RHEED study of TiN growth mode on (1 0 0) MgO [9], showed more distinct results compared with this work. The thin TiN films were found to grow in a well oriented single plane (2 0 0) and the initial evolution stage was dominated by 3D crystallites of Volmer–Weber growth. This could also be case for TiO$_2$, since the RHEED pattern turned from a streaky appearance to a spotty appearance and the RHEED intensity showed no oscillations indicating layer-by-layer growth. Nevertheless, no formation of island nucleation was observed. Thus within the characterization conditions, the present work on TiO$_2$ growth mode does not show any direct indication of either island or layer-by-layer growth.

5. Conclusion

In situ high-energy RHEED experiments combined with AFM have provided some insight into the growth of TiO$_2$ on MgO by PLD with typical deposition conditions. The RHEED experiment showed a clear evidence of a new structure forming as the initial RHEED pattern of the naked MgO substrate (Fig. 1a) changed into a RHEED pattern with a different appearance and with new spots emerging (Fig. 2). Unfortunately, no obvious layer-by-layer growth, due to lack of RHEED oscillations, was seen and there seemed to be no obvious island nucleation in the initial stage of the growth. This may indicate a uniform filling of the initial gorges and ravines of the substrate surface during the film deposition (Fig. 5b) leaving the initial surface contours smoother and smoother during the film growth, rather than for instance layer-by-layer growth. Further investigations are thus necessary in order to have a completely clear picture of the TiO$_2$ growth on MgO.

Acknowledgements

The authors would like to thank J. W. Andreasen, F. Saxild and J. Geyti. This work is supported by the Danish Strategic Research Council with the NABIIT grant 2106-05-0035.

References


Optical Detections From Worn and Unworn Titanium Compound Surfaces

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Received: 21 January 2009 / Accepted: 8 July 2009
© Springer Science+Business Media, LLC 2009

Abstract Wear-induced roughness in terms of grooves, sharp ridges, and edges leads to scattering of the reflected light and leads unavoidably to a reduction of the optical signals in a standard specular geometry. However, by using a double-layer system consisting of titanium aluminum nitride (TiAlN) on top of a titanium nitride (TiN) layer we obtain an increase in the reflected light as a result of wear. The relative change of reflectance of light from the tribological TiAlN coated surface to the underlying layer of TiN is similar for non-worn surfaces and for surfaces exposed to an abrasive wear process. The induced roughness reduces the signals from worn samples, in a standard specular geometry, by up to 30% compared with unworn samples. Our model system of TiAlN coatings on top of ‘optical’ signal layers of TiN deposited on a 100Cr6 steel substrate, was exposed to a reciprocating wear process with up to $10^5$ repetitive cycles in a linear tribometer. The worn TiAlN layers of thicknesses up to 3 μm, with strongly developed grooves and ridges, were subsequently used for the reflectance measurements. The results show that optical reflectance monitoring is a potential technique for intelligent determination of a residual thickness of realistic tribological coatings prior to complete wear.

Keywords Coatings wear-resistant · Aluminum ·
Titanium · Nitrides · Abrasive wear · Monitoring ·
Optics · Dynamic light scattering

1 Introduction

Roughness, such as micrometer-size grooves and ridges by means of tribological wear, often leads to strong scattering of light [1]. For a specific laser beam geometry the reflectance measured in the specular direction can be strongly reduced by such grooves and ridges. Therefore, it is important to relate the signals for all optical measurements on worn surfaces to those from unworn surfaces. In the present study, we have investigated the behavior of the reflectance from a model system of a titanium aluminum nitride, TiAlN, coating on top of an ‘optical’ signal layer of titanium nitride, TiN, deposited on a steel substrate.

Tribological coatings or thin layers of TiAlN and TiN are being used increasingly in industrial production lines and in cutting tools due to the distinct wear resistant properties of these ceramic materials [2–5]. Tools and other mechanical components in the production lines are often tribologically coated to prevent the parts from wearing out by the constant movements. Hard ceramic coatings do, however, eventually also wear out, and a recoating of the surface is necessary before severe damage is caused on the production line tools. Consequently, we have suggested a remote optical monitoring system for the tribologically coated surface. The monitoring system was modeled and previously tested to show a strong
relative change in the measured laser reflectance signal as the tribological top coating is wearing out [6]. It is thus possible to stop the production prior to any product or tool damages.

The model system, consisting of a multi-layer structure with a tribological TiAlN layer on top of an 'optical' TiN signal layer on a steel substrate, has been demonstrated to show features that can be used for an intelligent warning system in combination with a laser reflectance setup [6]. The developed model system is based on calculations with Fresnel's reflection law, in which the laser reflectance signal, $R$, from the multi-layer structure is seen to depend on the wavelength, $\lambda$, and angle of incidence, $\theta$, of the laser beam upon the multi-layer surface, the complex refractive index, $n = n + ik$, and the thickness, $d$, of the individual material layers involved [7, 8]. This means that if the layer thickness of the top layer starts decreasing, a change in the laser reflectance is seen, when the layer is sufficiently thin such that it is becoming transparent for the laser beam—and if the refractive indices of the involved materials differ significantly from each other. We have utilized this principle to compose test samples with multi-layer structure materials, which give a strong signal change in the laser reflectance when the top layer is sufficiently thin. The two ceramics TiAlN and TiN are both well-known and already applied as tribological hard coatings. Additionally, they are seen to have refractive indices [6, 9, 10], which lead to a strong change in the laser reflectance. The two materials are thus very well suited for this combined wear and optics study.

The idea of including a signal layer in a coating has also been reported by Muratore et al. [11] and Eldridge and Bencic [12]. Muratore et al. [11] used the luminescence from an embedded layer of yttria-stabilized zirconia (YSZ) in a molybdenum disulfide layer to monitor the wear of a thermal barrier coating. A similar approach based on reflectance-enhanced luminescence was used by Eldridge and Bencic [12] also for thermal barrier coatings. However, in our case we have focused our study on the hard titanium compounds with an embedded 'optical' signal layers monitored with a simple measurement of the optical reflectance from the worn samples.

The previously tested theoretical model system [6] did not involve actual wear of the samples, but consisted of several multi-layer samples with decreasing TiAlN layer thicknesses to simulate a wear process with TiAlN being removed during the wear. Here we present the succeeding experiment, where multi-layer test samples of TiAlN and TiN on steel have been exposed to an abrasive wear process to remove the TiAlN top coating making the underlying TiN layer visible. Subsequent laser scanning along the introduced wear scars revealed a significant change of the measured laser reflectance.

2 Experiments

Test samples of 100Cr6 steel substrates $(15 \times 15 \times 2 \text{ mm}^3)$ with layers of TiAlN and TiN have all been produced in a similar way. Initially, a steel substrate is coated with $\sim 2.5 \mu\text{m TiN}$, which in turn is coated with up to $3 \mu\text{m TiAlN}$. This sample sandwich of steel, TiN and TiAlN is seen in the graphical drawing in Fig. 1, where the steel substrate is gray, TiN is the bright golden yellow layer, and TiAlN the darker bluish gray layer. Three different sample series with TiAlN layer thicknesses of $\sim 0.3$, $\sim 1$, and $\sim 3 \mu\text{m}$, respectively, have been exposed to a linear reciprocating wear process with a sliding contact in a highly controlled tribometer. This was done in order to strip off the tribological top coating leaving the embedded signal layer of TiN naked, as indicated in the figure.

Both types of coatings, TiAlN and TiN, have been produced in an industrial physical vapor deposition (PVD) setup by CemeCon Scandinavia A/S [13]. Before all depositions the sample surfaces were ion etched as a part of the PVD process to achieve a better adhesion between the substrate and the different layers. The steel substrates have initially been polished to a roughness of $\sim 1 \mu\text{m}$ prior to the TiN depositions.

The dry sliding friction of the TiAlN coatings at room temperature $(T = 20 \degree\text{C})$ was performed on a state of the art linear tribometer. The reciprocating linear tribometer consists essentially of a base, where the test sample is mounted, a long arm, where the contact part, in this case a 100Cr6 bearing steel ball (diameter $= 12.7 \text{ mm}$), is attached, an oscillator, which is controlling the horizontal sliding movement of the contact, and a sensor, which is placed between the arm and the oscillator and is detecting various test information such as normal load, speed of the motion. The specific linear tribometer has previously been described [14]. The sample is placed on the base right beneath the steel ball contact, where a normal load is applied to the sample surface via the base and the steel ball as seen in the schematics of Fig. 2. A feedback loop is

![Fig. 1](image.png)
keeping the applied normal load on a constant level by controlling the deflection of the sensor (e.g., normal load) combined with a vertical movement of the base toward or away from the contact. The highly controlled reciprocating movement of the contact is executed by the oscillator, a linear servo drive, which also controls the continuously varying amplitude (CVA) of the steel ball. This is a special linear reciprocative wear process, in which the amplitude is slightly reduced for each cycle, i.e., the contact amplitude is continuously reduced along the scar. The continuous variation of the amplitude of the contact motion ensures a right-angled trapezoid shaped wear scar as depicted in Fig. 1. Here the tribological TiAlN top-coating is removed such that the TiAlN thickness is decreasing along the scar and the embedded TiN signal layer is reached and appearing in the bottom of the scar. The CVA maximum (initial) and minimum (final) amplitudes of the contact motion used in this experiment are noted in the figure. It should be noted that a small number of cycles leads to a small number of steps along the residual TiAlN layer thickness and vice versa for a large number of cycles, i.e., a larger number of cycles in the CVA process gives more steps, which in turn may result in an increased roughness along the scar.

An improved wear resistance of the contact (the steel ball surface) has been employed by introducing a coating on the steel ball surface. This was done since the hardness and wear resistance of the TiAlN and TiN coatings is much higher than the steel ball [2, 15, 16], i.e., without any surface hardening the steel ball will be worn instead of the tribological coatings. This improved coating consists of a mixture of powdered resin (MECAPREX KM-EM), powdered diamonds (DIPROTEX MSY 0–0.2 μm), and a solvent (MECAPREX KMR (methyl–methacrylate)), which is mixed into a viscous paste and fixed on the steel ball contact zone. The paste covers the contact zone, dries fast and hardens within some hours, which results in a uniform coverage nearly matching the surface of the steel ball contact. The powdered diamond grain size diameter is up to a maximum of 200 nm and the ratio between the resin powder and the diamond powder was 4:1; as listed in Table 1. The wear of all the tested samples was induced with a number of fixed parameters, e.g., the applied normal load, the repetition frequency, the amplitudes, and the resin diamond powder ratio (Table 1). Only the number of cycles, i.e., the wear distance, in the tests was changed for the different samples (Table 2). A normal load of 5 N was chosen to induce a convenient wear rate such that a complete wear run could be carried out within some hours.

A Dektak scan profilometer (Veeco 200VI) was used to measure the maximum scar depth introduced in the sample coatings. After the scan profile was obtained the laser reflectance of the induced wear scar was measured at a wavelength of 633 nm. The principle of the reflectance measurement is seen in Fig. 3a, where the laser beam is scanning the surface along the wear scar to record the decreasing residual TiAlN layer thickness and finally beyond the end of the scar. The incident angle \( \theta \) of the laser beam is kept fixed at \( \theta = 60^\circ \) during the complete reflectance measurement as noted in the figure. This means that the sample position, and not the laser beam path, was actually translated during the reflectance detection.

The optical setup for measuring the laser reflectance, \( R \), consists basically of a HeNe laser source (HRP050 from Thorlabs) with a wavelength of 633 nm and a few optical parts as seen in Fig. 3b. A TE/TM polarizer is transmitting either the TE (s) or the TM (p) polarization of the initially linearly polarized laser beam. The polarization (TE) was used in the present measurements since it gave a larger enhancement of the signal for the two Ti-components and has thus also been used here even if the signal difference is

![Fig. 2 Schematics of the linear tribometer with a 12.7 mm 100Cr6 bearing steel ball contact](image)

Table 1 Fixed settings for the linear wear, where the ratio is between the resin powder and the powered diamond grains

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (N)</td>
<td>5</td>
</tr>
<tr>
<td>( A_{\text{max}} ) (mm)</td>
<td>10</td>
</tr>
<tr>
<td>( A_{\text{min}} ) (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Grain size (μm)</td>
<td>0–0.2</td>
</tr>
<tr>
<td>Ratio</td>
<td>4:1</td>
</tr>
</tbody>
</table>

Table 2 Variable wear parameters; the number of cycles in a test for the sample types 0.3, 1, or 3 μm TiAlN on TiN and steel

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Cycles</th>
<th>Sample type</th>
<th>Cycles</th>
<th>Sample type</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 μm</td>
<td>3000</td>
<td>1 μm</td>
<td>12000</td>
<td>3 μm</td>
<td>35000</td>
</tr>
<tr>
<td>–</td>
<td>3000</td>
<td>–</td>
<td>15000</td>
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<td>40000</td>
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<tr>
<td>–</td>
<td>5000</td>
<td>–</td>
<td>17500</td>
<td>–</td>
<td>45000</td>
</tr>
<tr>
<td>–</td>
<td>10000</td>
<td>–</td>
<td>20000</td>
<td>–</td>
<td>100000</td>
</tr>
<tr>
<td>–</td>
<td>12000</td>
<td></td>
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</tbody>
</table>

The samples scanned for the laser reflectance is marked in italic.
within the uncertainty of the reflectance measured on the worn surface parts. The two lenses focus the laser beam initially on the wear scar to a diameter of $\sim 100\ \mu m$ and subsequently on the power meter detector head as the beam is reflected on the sample surface. The samples, for which the reflectance measurements are shown in the present study, are indicated in italic in Table 2.

### 3 Results

All scar depths measured with the Dektak profilometer have been plotted in Fig. 4 as a function of the number of cycles for 0.3 μm (red triangles), 1 μm (green squares), and 3 μm (blue diamonds) TiAlN on TiN and steel. In general, the depths are seen to increase with the number of cycles, i.e., more material is removed during longer wear processes. Furthermore, the dependence of the maximum track depth on the number of cycles can clearly be approximated by a linear function, even though the scattering of the data points is pronounced for the individual sample types, i.e., 0.3, 1, and 3 μm TiAlN. The estimated cross sections (calculated from the profile line scans), corresponding to removed material, can be approximated by a similar linearly decreasing function, which means that more material actually has been removed during longer wear processes.

Almost all samples are seen to be worn beyond the TiAlN/TiN interface, i.e., the maximum track depths measured for each wear scan is below either a depth level of 0.3, 1, or 3 μm, corresponding to the possible TiAlN layer thicknesses. This means that the embedded TiN layer should be visible in the bottom of almost all tracks measured, which actually also is the case as seen from wear scars. Additionally, one sample worn for 100000 cycles is seen (Fig. 4) to have a scar, which is going through both the tribological TiAlN top coating and the TiN signal layer, and well into the steel substrate. A track depth of $\sim 6.5\ \mu m$ is reached by this high number of cycles, where most of both the TiAlN and TiN coatings have been removed over the complete scar. This wear is not an ideal situation for measuring the laser reflectance of the wear scar, since also the TiN layer has been removed. If there is no TiN layer left, no difference in reflectance from the unworn to the bottom of the scar will be seen from TiAlN to steel, since the refractive index of this specific steel substrate is similar to that of TiAlN [6]. Obviously, a loss due to roughness in this wear scar is also seen. Successful wear cases are shown in the inserted photos of Figs. 5 and 6. No trace of the steel substrate is visible in the two wear scars and all TiAlN has been removed at the right end of the scars. The scar begins on the left hand side and ends on the right hand side of the photos, where the yellow TiN is clearly emerging in the bottom of both wear tracks. These two types of wear cases will lead to the highest possible increase of the measured reflectance.

Two different wear scars were measured optically. Figures 5 and 6 show the measured laser reflectance from the samples, where reference reflectance levels for unworn TiN and TiAlN (measured at $\theta = 60^\circ$) also have been included. Both laser reflectance measurements display a significant reflectance enhancement, when the laser beam is scanned along the wear scar, i.e., when the laser beam...
meets the residual TiAlN layer and subsequently the exposed TiN layer (Fig. 3a). Figure 5 shows the reflectance from a sample with 0.3 μm TiAlN on TiN and steel, where the scar was produced by moving the steel ball across the sample surface 3000 times leading to a maximum depth in the surface of 0.69 μm (see red triangle pointed out in Fig. 4). This means that the scar is reaching well beyond the TiAlN/TiN interface at the deep end of the scar and the yellowish TiN signal layer is thus visible in the bottom of the scar. The specific scar is excellent for laser reflectance measurements.

The measured reflectance (Fig. 5) keeps a constant level of 0.5 (matching to the unworn TiAlN level) until ~4 mm, where a steady, almost linear increase up to 0.65–0.75 is seen (~8 mm). Here the reflectance level is constant as well and after ~10 mm it decreases rapidly down to the initial level of 0.5. The reflectance is measured at three different lateral laser beam positions (red triangles, green crosses, and blue squares) along the same scar, leading to only slightly different responses in the reflectance. At the constant high level (between 7 and 10 mm) the reflectance varies slightly from one track to another. This is probably due to the grooves and sharp edges in the wear scar, which is not uniform as in the ideal situation (Figs. 1, 3a). Nevertheless, all three reflectance scans of this sample are really quite similar with a total distinct shift of reflectance of 0.2–0.25 from the unworn to the worn surface, where the loss due to roughness thus also is included.

Figure 5 shows as well how the laser reflectance increases abruptly half way across the scan. This abrupt increase occurs just when the embedded TiN layer is becoming visible beneath the TiAlN top-coating, i.e., when the residual TiAlN layer is thin enough for the laser beam to interact with the embedded TiN layer. According to our previous results [6] the reflectance starts to increase for a residual layer below 80–100 nm TiAlN on top of TiN. The wear of the 300-nm thick TiAlN layer is non-uniform over the track, which means that there must be sufficiently many grooves with a depth that exceeds 200–220 nm between ~4 and ~8 mm, since the measured reflectance suddenly starts increasing at this point. Furthermore, the reflectance increase is seen to be almost perfectly linear, which is caused by a strong raise of the reflectance due to the decreasing thickness of the TiAlN layer combined with a low degree of roughness in the scar caused by the relatively few number of cycles (3000) in this specific test. Between 7 and 9 mm a constant reflectance level, corresponding to the reflectance value of a worn TiN surface, is obtained. A rough estimate gives that the 3000 cycles remove on the average of 80 nm across the complete wear track (calculated by the scar width at the maximum depth), which leads to an average wear rate of 0.03 nm/cycle. The small average thickness removed (80 nm compared to the measured maximum depth of 670 nm) is due to a very uneven wear track with several deep grooves and ridges as discussed below. The measurement displayed here demonstrates that the wear of a thin layer certainly does not change the optical properties of the material, since an increase in reflectance is obtained, as expected.

The reflectance measured from a sample with a 1 μm TiAlN top coating is shown in Fig. 6. The scar is produced by the steel ball sliding across the surface 17500 times, leading to a maximum depth in the track of 2.32 μm (green square pointed out in Fig. 4). The scar is thus reaching far beyond the TiAlN/TiN interface and into the embedded optical TiN layer. The embedded TiN layer is appearing in
the bottom of the scar, which is clearly visible in the small wear scar photo (see inset of Fig. 6). The laser reflectance, measured as for the previous sample (see Fig. 3a), is seen to initially start decreasing from a reflectance level of \( \sim 0.4 \) down to \( \sim 0.3 \). Between 2 and 6 mm the reflectance level starts to increase from \( \sim 0.3 \) to up to \( \sim 0.65 \), where it keeps almost constant between 6 and 9 mm. The laser reflectance drops subsequently very fast down to \( \sim 0.4 \) after which a slight increase up to the initial level is seen at the end of the wear scar. Again the reflectance is measured three times (red diamonds, green crosses, and blue squares) at slightly different lateral positions of the laser beam, causing the small difference in the measured laser reflectance. A total increase, including the roughness effect, of the reflectance of 0.15–0.2 is seen in this sample from the unworn to the worn surface. A rough estimate gives that 17500 cycles removed on the average of 700 nm across the complete wear track (found by the scar width at the max depth). This leads to an average wear rate of 0.04 nm/cycle. Again the rather small average thickness removed (700 nm compared with the 2320 nm at maximum depth) is caused by the several deep grooves and ridges in the wear scar.

A large decrease in the measured reflectance level (Fig. 6) is seen in the beginning of the laser scan (from 0 to 2 mm) and a smaller dip is seen at the end of the scan (from 10 to 11 mm). These reflectance dips are most likely arising from loss of light due to an increased roughness in the wear scar caused by the increased number of reduction steps in the CVA procedure as compared to the relative small number of cycles (3000) in the previous reflectance measurement (Fig. 5). This is causing an increased accumulation of removed material along the residual TiAlN layer thickness, which is absorbing the light, since removed material is deposited at the end of each amplitude movement. Furthermore, the higher number of steps (17500) along the residual TiAlN layer thickness results in additional edges and oblique areas, which then again leads to increased scattering of the light. A higher degree of scattering of the incident laser beam due to diffraction on the accumulated sharp edges in the wear scar and reflection on oblique areas in the scar is thus also seen. Actually, the two inserted photos reveal some dark lines in the horizontal direction of the scars. These dark lines are sharp ridges and edges developed during the wear process, which lead to a strong diffraction scattering of the light, where the ridges and edges are seen from the Dektak profiles to be deeper and more severe for a higher number of cycles. This leads to a higher degree of diffraction and thus to a larger loss in the measured laser reflectance for the sample with the highest number of cycles; 17500 (Fig. 6). The large diffraction scattering of the laser light means that a considerable fraction of the otherwise collimated laser beam never reaches the power meter detector head, also when a large focusing lens is placed as close to the sample surface as possible. Eventually, a drop in the reflectance is seen. This unexpected and relatively large drop is not seen for the sample worn for 3000 cycles, but is distinct for the sample worn for 17500 cycles. This is probably caused by an increased accumulation of roughness during the long wear process as mentioned. It should be noted that the width of the ridges and edges are of a much larger order of magnitude (above micrometer size) compared to the diamond grain size diameter (\( \geq 200 \) nm, see Table 1), which means that the grooves and ridges are not caused by individual diamond grains. An estimated loss due to diffraction of the laser beam is around 0.3 which is comparable to the unworn TiN level at \( \theta = 60^\circ \).

It is important to realize that if the multi-layer sandwich model system was composed oppositely, i.e., with a tribological TiN coating on top of optical TiAlN on a steel substrate, a decrease, instead of an increase, in the measured reflectance would be expected due to the nature of the refractive indices of the respective materials. In such a case the decrease could be caused either by the roughness induced during the wear process or by the change of the optical properties of the two materials, since both effects would lead to a reduction of the reflectance. It would thus not be possible to decide whether the change in signal was caused by the optical signal layer (i.e., here TiAlN) or by the roughness induced by the wear. By composing the test samples as presented here, i.e., with a TiAlN tribo-coating on top of an optical signal layer of TiN, it is possible to determine the wearing out of the TiAlN top-coating by a remote optical system.

4 Conclusion

We have shown how it is possible to measure the laser beam reflection of both worn and unworn surfaces of multilayer TiAlN and TiN on steel. We have furthermore shown that we obtain the expected, significant increase in the measured laser reflectance from the embedded TiN layer, when it is being exposed to laser light after the linear reciprocative CVA wear process.

For the thick films the increase of the laser reflectance signal is about one-half of the value expected from theoretical calculations [6], in which a maximum reflectance increase of 0.5 was predicted without any real wear issues, such as debris and roughness, considered. A considerable change in the laser reflectance level is thus obtained regardless of a major loss of light due to a high scattering by diffraction and specular reflection from oblique surface areas. This surface modification leads to an estimated loss of 0.3 of the total light reflection from the sample surface. From the laser beam scanning along the residual TiAlN...
layer one measures an almost linear increase in the reflectance because of the gradual removal of the TiAlN layer. It supports the prediction from our previous investigation on unworn samples that the reflectance signal will increase when the TiAlN top-coating is worn such that it is becoming transparent for the laser beam.

Acknowledgment This study has been supported by the Danish Strategic Research Council with the NABIT grant 2106-05-0035.

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Wear monitoring of protective nitride coatings using image processing

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1. Introduction

Hard coatings of tribological materials such as titanium nitride (TiN), titanium aluminium nitride (TiAlN) and chromium nitride are used frequently for tools in industrial production lines because of their high wear resistance [1–5]. However, tribological coatings exposed to wear will eventually be removed. Thus there is a growing demand for monitoring equipment, which warns an industrial production operator before the tribological layer is worn out and the coated tool and the produced items are severely damaged [6]. We have, therefore, modeled and tested a nitride system, where the tribological layer is deposited on an optical layer such that the color changes strongly when the tribological layer is removed. The inclusion of a signal layer in a tribological coating during wear has also been used for wear of thermal barrier coatings [7,8].

We have designed a model system consisting of a multi-layer structure with a tribological TiAlN layer on top of an optical TiN layer on a bearing steel substrate [9]. Initially, a steel substrate is coated with ~2.5 µm gold-like, shiny TiN, which in turn is coated with up to 0.3 µm dark bluish-grey TiAlN. Since the color of the TiN layer differs strongly from that of the TiAlN, the color of the sample surface is expected to change from dark bluish-grey to bright golden yellow during wear. The principle of the monitoring is based on image analysis of the pixels of red, green and blue (RGB) from a worn area.

Once the pixel values correspond to TiN, the TiAlN has been worn out. Recent results from similar samples have demonstrated that the reflected laser light can be used for monitoring as well. Since the reflectance for laser light at 633 nm is strongly dependent on the surface materials, the magnitude of the signal from the samples was used as an indicator of the instantaneous thickness of the upper layer. The reflectance from the TiAlN layer and the TiN layer is not only different for unworn surfaces, but also from strongly worn surfaces of a top-layer of TiAlN and the bottom-layer of TiN with grooves and ridges [9]. In contrast to the analysis of the wear track in Ref. [9], we show in the present work that the same sample system can be used for a simple image analysis based on the three colors (RGB) red, green and blue over the full wear scar and not only along a line scan as in Ref. [9]. The full image does also allow us to recognize wear patterns, once the top coating layer is partly worn out. To our knowledge very few attempts have been carried out to apply color image analysis during wear [10]. It may not work for all industrial cases, but could be a good option for tools used for injection moulding of plastics, where cavity surfaces are subjected mainly to abrasive wear.

2. Experimental method

Test samples of 100Cr6 steel substrates 15 × 15 × 2 mm³ with layers of 0.3 µm TiAlN on top of 2.5 µm TiN were produced in an industrial physical vapor deposition (PVD) setup by CemeCon Scandinavia as described earlier [5,9]. The sample used in the present analysis is shown in Fig. 1. Four yellow wear tracks are seen on the bluish, grey coating of TiAlN. In the right-hand bottom corner the underlying steel substrate (covered by a holder arm during deposition) is seen.

The wear was performed at a reciprocating linear tribo-meter at the Laboratory of Tribology and System Dynamics as a dry sliding friction at room temperature (T = 20 °C) [9,11]. The tribo-meter...
consists of a base, on which the test sample is mounted, and a long arm, on which the contact part, a 100 Cr6 bearing steel ball with a diameter of 12.7 mm, is mounted. The sliding movement of the ball and the attached load sensor is controlled by an oscillator and is carried out with a cycle frequency of 10 Hz. As shown in Fig. 2 the sample is placed on the base right below the steel ball contact, such that a normal load is applied on the sample surface. A feed-back loop is maintaining a constant load on the sample of 5 N by controlling the deflection of the normal load sensor. The highly controlled wear track is worn with the contact part moving with continuously varying amplitude (CVA), by which the amplitude is slightly reduced for each cycle. It means that a high cycle number leads to a high number of steps along the residual TiAlN top coating and vice versa for a small number of cycles. Eventually, the track will end up as a trapezoidally shaped wear scar as seen in Fig. 2. The tribological layer of TiAlN becomes gradually thinner and the embedded TiN layer appears in the bottom of the track.

In order to obtain a feasible wear rate the steel ball surface was coated with a mixture (1:4) of powdered resin and diamond grains up to 200 nm. With this coating a wear scar in a hard coating as TiAlN could be produced in a few hours.

The wear scar exposed to 12,000 cycles within the white frame in Fig. 1 (labeled 2) was selected for image analysis. The other wear scars (1,3,4) have not been used in this image analysis. The image taken with the camera was loaded into the LabView program, where a pixel to mm calibration was initially performed by use of a ruler. The image photo for analysis was taken with a Canon 350D Digital camera and the software was created in the programming language LabView from National Instruments. The selected area for the image analysis is approx. 12.25 × 1.35 mm² (or 485 × 54 pixels) as found by the pixel to mm calibration.

The RGB (red–green–blue) values of each pixel in the selected image area were then examined by the image analysis LabView program. This means that the program, for each pixel in the rectangle, reads out a number for the red pixel value, a number for the green pixel value and a number for the blue pixel value, i.e. three numbers for the RGB value are assigned to each pixel. It should be noted that only the red and blue values have been used for the two specific components TiN and TiAlN and their colors in this investigation.

The RGB values, i.e. the red, green and blue values are counted within specific wavelength ranges. The red values are roughly detected from 550 to 700 nm with a peak around 600 nm, the green values from 450 to 600 nm with a peak around 525 nm and finally the blue values from 400 to 525 nm with a peak around 450 nm. The overlap between the red and blue values is at a minimum [12].

3. Results

The red pixel values of the wear scar are depicted in a contour plot (Fig. 3) in the geometry indicated in Figs. 1 and 2. The pixel value of the red color is high except in the beginning of the wear track, where only the TiAlN layer is seen. The yellow, golden TiN layer has a strong red component which, wherever it is visible, leads to a high value for the red pixels. A similar contour plot of the blue pixels is shown in Fig. 4. In contrast to the red pixel plot, there is only a slight decrease from the beginning of the wear track to the fully worn area. The blue component originates from both layers with a stronger contribution from the darker, bluish TiAlN, since the area with the visible TiN shows slightly decreased values for the blue pixels. From the two contour plots, obviously the R-plot gives the strongest change from the TiAlN to the TiN, and will clearly be more suitable for automatic RGB image processing than the B-plot for this tribological coating combination.
The average values of the red and blue pixel values across the track (i.e. the pixel values have been averaged row by row) have been plotted as a function of wear distance in Fig. 5. The measured reflectance of TE-polarized light from a HeNe laser at 633 nm in the middle of the wear scar is shown as well [9]. The two “red” curves, the average of the red pixel values and the reflectance of the red laser light, show a similar appearance along the wear scar. The initial, stronger increase of the red pixel curve is possibly due to the averaging of pixel values over the full width of the track compared with the reflectance from a small laser spot along a single line of the reflectance [9]. Obviously, the averaged red pixel curve and the reflectance increase as the residual layer of TiAlN is becoming thinner, until the level of TiN has been reached. In contrast, the blue pixel curve decreases continuously along the track and reaches a minimum at the TiN level due to the low content of blue color in the material.

4. Conclusion

We have shown that RGB image analysis can be used for monitoring of wear of hard coatings such as TiAlN. The basic idea is that a thin “warning” layer of a tribological material of a different color, e.g. in our case the golden, yellow TiN, is embedded in the main coating or deposited directly on the underlying steel. Once the color of a pre-selected area changes because of the appearance of the “warning” layer, the top coating has been partly or fully worn out. The analysis can be made fully computerized such that any change of color is automatically recorded. This work can be a starting point for the development of scientific and industrial techniques for remote wear control in real time.

Acknowledgements

This work has been supported by the Danish Strategic Research Council with the NABIIT grant 2106-05-0035.

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