Cohesive & Adhesive Failure and Contact Damage of Diamond-Like Carbon (DLC) Coated Titanium Substrates

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Logic will get you from A to Z; imagination will get you everywhere

Albert Einstein
The achievements of this thesis are based on collaborations with other research groups and stimulating discussions, ideas and inputs from various people.

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Summary

Thin surface layers are utilized in many modern technological applications for optimization of surface properties such as hardness or wear. Hydrogenated diamond-like carbon (DLC) is a hard and wear resistant material and is therefore already used as a surface layer in tribological applications. However, cohesive and adhesive failure as well as contact damage often limit the lifetime of the DLC-substrate combination. Knowledge of the factors and mechanisms influencing their failure are of profound importance for industrial applications and also for the further development of protective coating systems.

DLC films on titanium substrates is, on the one hand, important for technical applications, e.g. for biomedical applications. On the other hand, from a scientific perspective, it is also an excellent model system for understanding the failure mechanisms of a hard and brittle film on a ductile metallic substrate. Thus, the cohesive and adhesive failure and the contact damage of DLC coated titanium substrates is studied in this thesis not only by analyzing the variation of the DLC film thicknesses, but also by investigating the role of the elastic-plastic deformation behavior of the titanium substrate.

The cohesive and adhesive failure is studied under uniaxial loading conditions using microtensile testing, whereas the contact damage is induced by microindentation and complemented by finite-element analysis. From the uniaxial loading experiments, the critical energy release rates for cohesive and adhesive failure as well as the fracture toughness of DLC are determined quantitatively. Additionally, it is observed that the fracture strength and the onset strain of delamination increase significantly with decreasing DLC film thickness. However, the contact damage analysis reveals that the DLC film thickness, the elastic-plastic deformation behavior of the substrate, the applied pressure and the fracture toughness affect the contact damage creation, evolution and final morphology significantly.
The combined analysis of the cohesive and adhesive failure and contact damage results in a film thickness optimization process for DLC coated ductile metallic substrates. On the one side, the DLC film thickness needs to be as thin as possible to increase fracture strength and onset strain of delamination. On the other side, in order to minimize plastic deformation of the substrate upon indentation, the DLC film should be as thick as possible.

To circumvent these opposing predictions of optimal film thicknesses, interlayers are deposited between the DLC film and the titanium substrate. The interlayer has to increase the mechanical stability of the DLC film and it also has to shield the titanium substrate from plastic deformation upon contact damage creation. To design an interlayer, which fulfills these requirements, the influence of the material structure, such as its phase, on the DLC film and titanium substrate should be known. The effect of phase can very well be studied with tantalum because it exists in the stable body-centered cubic $\alpha$-phase and in the metastable tetragonal $\beta$-phase. To deposit the desired tantalum phase on titanium substrates, a method using a reactive sputter deposited tantalum nitride seed layer is developed. $\alpha$-tantalum forms by depositing a 15 nm tantalum nitride seed layer while in its absence, $\beta$-tantalum forms. This deposition method additionally shows that, besides epitaxy, the surface chemistry of the base material substantially affects the growth of a particular phase.

With this seed layer method DLC coated titanium substrates with interlayers of $\alpha$- and $\beta$-tantalum are produced and the influence of the phase on the cohesive and adhesive failure and contact damage is examined. The analysis shows that the contact damage can be remarkably reduced with an $\alpha$-tantalum interlayer due to plastic deformation of the ductile interlayer material.
Zusammenfassung


Das kohäsive und adhäsive Versagen wird mit uniaxialen Zugversuchen untersucht, wobei Mikroindentierung ergänzend mit der Finiten-Elementen Methode zur Kontaktschadenanalyse verwendet werden. Anhand der uniaxialen Zugversuche kann die kritische Energiefreisetzungsrate für kohäsives und adhäsives Versagen sowie die Bruchzähigkeit des DLC quantitativ bestimmt werden. Dabei wird beobachtet, dass die Bruchfestigkeit und die Delaminationsdehnung mit abnehmender Schichtdicke signifikant zunehmen. Bei der Analyse der Kontaktschadenbildung zeigt sich hingegen, dass nicht nur die DLC Schichtdicke son-
dern auch die plastische Verformung des Substrates, der angelegte Druck und die Bruchzähigkeit der DLC Schicht den Kontaktschaden wesentlich mitbeeinflussen.


Um dieses Problem des DLC Schichtdickenoptimierungsprozess zu umgehen, werden zwischen dem DLC und dem Titansubstrat Zwischenschichten abgeschieden. Die Zwischenschichten müssen sowohl die mechanische Stabilität der DLC Schicht erhöhen als auch bei Kontaktschadenbildung vor plastischer Verformung des Substrates schützen. Um jedoch eine solche Zwischenschicht designen zu können, müssen die Einflüsse der Materialstruktur, z.B. der Phase, auf die DLC Schicht und das Titansubstrat bekannt sein. Der Einfluss der Phase kann mit Tantal sehr gut untersucht werden, da es sowohl in der kubisch-raumzentrierten $\alpha$-Phase als auch in der tetragonalen $\beta$-Phase existiert. Damit die gewünschte Tantalphase auf dem Titansubstrat abschichtig werden kann, wird eine Methode mit einer reaktiv hergestellten Tantalnitridkeimschicht entwickelt. Bei der Verwendung einer solchen 15 nm Tantalnitridkeimschicht wächst Tantal in der $\alpha$-Phase. Wird jedoch eine solche Tantalnitridkeimschicht nicht verwendet, formt sich die $\beta$-phase. Diese Beschichtungsmethode zeigt zudem, dass neben Epitaxie, die Oberflächenchemie des Grundmaterials das Phasenwachstum wesentlich mitbeeinflusst.

Mit dieser Keimschichtmethode werden DLC beschichtete Titansubstrate mit $\alpha$- und $\beta$-Tantal Zwischenschichten hergestellt und der Einfluss der Phase auf das kohäsive und adhäsive Versagen sowie die Kontaktschadenbildung untersucht. Es zeigt sich, dass durch die plastische Deformation einer $\alpha$-Tantal Zwischenschicht die Kontaktschadenbildung merklich reduziert werden kann.
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Introduction & Thesis Outline

In modern technology the performance and lifetime of many tools and components rely on the application of thin surface layers which provide the desired surface properties. Examples of such desired properties are multifaceted and range from a color change for esthetic reasons over passivation barriers to changes in mechanical and tribological properties.

Due to their unique combination of properties such as low wear, low friction coefficient and high scratch resistance, amorphous carbon layers are used in a wide range of applications. Amorphous carbon is a class of materials and contains a mixture of sp³ (diamond-like) and sp² (graphitic-like) hybridized carbon bonds, including the possible presence of hydrogen. The variety of amorphous carbon layers is subsumed under the term diamond-like carbon (DLC) and can be divided into the following subclasses:

- Hydrogen free amorphous carbon films (a-C)
- Hydrogen free tetrahedral amorphous carbon films (ta-C)
- Hydrogenated tetrahedral amorphous carbon films (ta-C:H)
- Hydrogenated amorphous carbon films (a-C:H)

The subclasses are often represented in a ternary phase diagram with sp³ and sp² hybridized carbon bonds and hydrogen (Fig. 1). This ternary phase diagram shows the composition range of each subclass. The most common subclass of DLC is a-C:H, and thus this subclass is often used as a synonym for DLC. For consistency and since the presented work has been performed with a-C:H the term DLC is used in this thesis for a-C:H.

In this thesis, the mechanical integrity of DLC on soft and ductile metallic substrates is investigated. In the first part the cohesive and adhesive failure and
Figure 1: Ternary phase diagram of amorphous carbon represented by $sp^2$ and $sp^3$ hybridized carbon bonds and hydrogen. Figure from [1].

Contact damage of DLC on titanium (Ti) substrates is analyzed as function of film thickness. In the second part stabilization and minimization of failure by introducing tantalum (Ta) interlayers is presented. The thesis is divided into 6 chapters and structured the following:

Chapter 1 provides the reader an overview about the concepts of amorphous carbon films and the current state of research of DLC leading to the motivation of the presented thesis. This chapter is not considered as own work and based on textbooks and peer-reviewed publications.

Chapter 2 presents the influence of the film thickness on the cohesive and adhesive failure of DLC films on Ti substrates upon uniaxial loading. This fundamental study also serves as a model system for understanding the mechanical failure mechanisms of hard and brittle films on soft and ductile metallic substrates. This chapter is, in an adapted version, published in *Acta Materialia*.

Chapter 3 provides the results of the contact damage analysis, which have been achieved by experimental and computational studies. In combination with chapter 2 a film thickness optimization process is deduced which leads
to the development of interlayer combinations for the necessary stabilization (analyzed in the subsequent chapters). This chapter is, in a slightly modified version, accepted for publication in *Journal of Materials Science*.

**Chapter 4** shows the control of the Ta-phases on Ti substrates and the correlation of phase, hardness and composition of reactively sputter deposited tantalum nitride thin films. This chapter serves as a basis for the analysis in chapter 5. A modified version is published in *Thin Solid Films*.

**Chapter 5** presents how the use of different Ta-phases affect the cohesive and adhesive failure and contact damage of DLC coated Ti substrates. The chapter wraps up and combines all knowledge gained from the previous chapters. This work is, in an adapted version, currently under review in *Surface and Coatings Technology*.

**Chapter 6** contains the conclusion and outlook. The main achievements are presented and further experiments and investigations on a theoretical and applied level are given for the remaining open questions.
Chapter 1

Diamond-Like Carbon: From the First Steps to the Current Research

1.1 Production and Growth Mechanisms of DLC

The synthesis of the first hard amorphous carbon films were published in 1953 by Schmellenmeier [2]. In 1971, the term diamond-like carbon was first used by Aisenberg and Chabot [3]. They prepared the films by ion beam deposition with an ionized carbon and argon beam, which was generated in a discharge system. In 1976, Holland and Ojha [4] reported a breakthrough work for the reproducible production of DLC by using a radio frequency glow discharge to overcome insulation problems.

One of the most common methods today for the production of DLC films is plasma-activated chemical vapor deposition (PACVD), which is based on a glow discharge process. In PACVD, a plasma disintegrates and ionizes a precursor gas, which polymerizes on the substrate surface under simultaneous ion bombardment to form a new chemical compound. For PACVD produced DLC a variety of hydrocarbons (CH$_4$, C$_2$H$_2$, C$_2$H$_4$, and C$_6$H$_6$) are typically used as precursor gas. The exact growth mechanism had been discussed in detail by Robertson [1, 5] and is schematically represented in Fig. 1.1 and Fig. 1.2.

The growth mechanisms can be divided into chemical and physical processes. The chemical processes focus on the species in the plasma and their chemical reactions at the surface of the substrate, while the physical process focuses on the penetration of high energetic ions into the already existing DLC. Through
Figure 1.1: Scheme for the formation of DLC. The precursor gas (C\textsubscript{2}H\textsubscript{2}) gets, through electron impact, disintegrated into highly reactive species which polymerize to rings, branches and chains. This forms an amorphous hydrogen containing carbon network with sp\textsuperscript{2} and sp\textsuperscript{3} bonds. DLC scheme inspired by [6].

Electron impact in the plasma the precursor gas gets disintegrated into ions (e.g. C\textsubscript{2}H\textsuperscript{+}), neutrals (undissociated precursor gas), radicals, unsaturated hydrocarbons and a significant amount of atomic hydrogen. On the surface these ions and radicals polymerize to a cross-linked network of chains, rings and branches with sp\textsuperscript{2} and sp\textsuperscript{3} hybridized carbon atoms and hydrogen (Fig. 1.1). Low energetic ions (up to \(\approx 30\) eV) stick on the topmost surface layer, forming sp\textsuperscript{2} sites, or bounce off depending on the sticking coefficient. Neutrals may also stick on the surface, however, due to the very low sticking coefficient their effect is negligible. Diradicals and unsaturated species may directly insert into C-C or C-H bonds while monoradicals have a moderate effect on the growth mechanism (Fig. 1.2).

The physical processes take place for ion energies \(>30\) eV. These ions penetrate the outer atomic layer or knock an atom on the surface deeper into the layer by elastic interaction (subplantation). The subplanted ions densify the network on a local scale and convert sp\textsuperscript{2} into sp\textsuperscript{3} sites due to the high local pressure. The higher the sp\textsuperscript{3} fraction, the more diamond-like, i.e. harder, the DLC becomes. Thus, the
subplantation process is responsible for the diamond-like behavior of the DLC. The fraction of subplanted ions reaches 100% at around 100 eV.

At higher energies the excess in subplantation energy is converted into vibrations and atomic displacement which results in local relaxation and graphitization. Hence, a competition between densification and relaxation is employed in this energy regime. The subplantation and relaxation processes are schematically shown in Fig. 1.3. Another important effect of high energetic ions is the separation of hydrogen from C-H bonds which results in increased H$_2$ recombination and desorption from the film [1].

During a PACVD deposition process several parameters can be adjusted to influence the structure and composition of the DLC. The first adjustable parameter is the precursor gas. A precursor gas with chains longer than acetylene results in a more polymeric-like DLC with a higher sp$^2$ fraction. The hydrogen concentration of the film can also be controlled by the nature of the precursor gas [1].

The second adjustable parameter is the sample self-bias voltage respectively the power which are dependent parameters. A variation of one of the parameters affects the degree of disintegration of the precursor gas and the average ion impact energy. Thus, for a low power PACVD process longer chains (mainly sp$^2$ bonds) are formed, which results in a more polymeric-like DLC. With increasing the power the sp$^3$ fraction increases, which subsequently leads to an enhanced

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**Figure 1.2:** Ion bombardment, preferential displacement and subplantation during growth of DLC. Figure adapted from [1].
Figure 1.3: Scheme of subplantation process upon direct entry and knock-on. Additionally, the relaxation of DLC upon subplantation is schematically presented. Figures from [1].

diamond-like behavior of the DLC. Beyond its highest degree (highest sp$^3$ content) of the diamond-like structure an even higher power forms a more graphitic structure due to an increased number of relaxation processes triggered by the very high impact energies of the impinging ions [1]. In addition, the hydrogen desorption also varies with the sample self-bias voltage and therefore the final hydrogen concentration can be controlled via the applied bias voltage [1].

The third adjustable parameter is the gas pressure. If the gas pressure is high an increased number of collisions and subsequent chemical reactions take place in the gas phase. Also, the average ion impact energy decreases which then also decreases the sp$^3$ fraction in the DLC film.

These growth mechanisms lead to an amorphous network of strongly cross-linked DLC containing graphitic (sp$^2$) and diamond-like (sp$^3$) carbon bonds and hydrogen. Because surface carbon atoms are terminated with hydrogen (due to its valence) DLC surfaces are hydrogenated (Fig. 1.2). Since DLC is produced with several different parameter setups and deposition techniques the composition of DLC varies. The hydrogen concentration typically ranges from 10 - 50 %, the sp$^3$ content from 20 - 60 % and the density varies between 1.5 - 2.4 g/cm$^3$. Similar to films formed using other deposition methods based on thermal quenching of energetic ions impinging a cold surface, DLC films are metastable [7].
If DLC is deposited on a carbide-forming metallic substrate such as titanium-aluminum-vanadium (TiAlV) or cobalt-chromium molybdenum (CoCrMo) an approximately 5 nm thick amorphous metal-carbide interface layer is formed as shown in Fig. 1.4 by a transmission electron microscope (TEM) image of DLC on a CoCrMo substrate \[8, 9\]. This interface layer is mainly produced by the reaction between the metal and carbon atoms.

**Figure 1.4:** Interface analysis with TEM between a DLC film and a CoCrMo substrate with numerical analysis of the contrast (a). HRTEM analysis of the 4.6 nm thick reactive interlayer (b) with selected-area electron diffractions of the CoCrMo substrate (c) and the DLC (d). The blurred halo from the DLC structure confirms the amorphous nature of the DLC. Figures from \[9\].

### 1.2 Mechanical Properties of DLC

DLC films are generally very brittle, have a high intrinsic stress and a typical hardness $< 40$ GPa. However, the mechanical properties of DLC strongly depend on the deposition procedure and precursor gas which influences the network of the DLC, the ratio of sp$^2$ and sp$^3$ hybridized carbon bonds as well as the hydrogen concentration. The polymeric DLC with a low sp$^3$ fraction and long polymeric chains is soft and ductile while with increasing sp$^3$ fraction the hardness and brittleness increases. The graphitic DLC, produced with high power, is again softer due to an increased sp$^2$ fraction. Since sp$^3$ bonds contain 50% more space than sp$^2$ bonds, the higher the fraction of sp$^3$ bonds the higher the intrinsic stress \[10\]. Multilayers or graded and alloyed structures have revealed to reduce the stress in the DLC \[5\]. The growth mechanisms in the previous subchapter have shown
FIGURE 1.5: Schematic representation of a partially di-hydrated carbon surfaces sliding against each other (a). Due to the higher electronegativity of carbon DLC surfaces are positively charged (b) which leads to a repellant force if two DLC surfaces slide against each other. This leads to a very low friction coefficient. Figures from [11].

that the DLC surface is hydrogenated and therefore partially positive charged because carbon is more electronegative than hydrogen. Thus, if two DLC coated pairs slide against each other a repelling force is exerted between the friction pairs (see Fig. 1.5) which results in an extremely low friction coefficient in vacuum or dry air [11]. Furthermore, the wear volume is much smaller for DLC-DLC friction pairs (DLC-on-DLC) compared to metal-metal friction pairs (metal-on-metal) [12] as it is shown in Fig. 1.6.

In addition, wear products which exhibit a graphitic nature can be transferred to the partner surface and form a graphitic transfer layer [11] which reduces wear. Hence, in dry conditions a combination of low friction coefficient, low wear and high hardness can be achieved with DLC films sliding against each other. The presence of the transfer layer allows even the application of DLC in cases where lubricants cannot be used or are aimed to be replaced.

By alloying metallic elements (typically W, Ti, Nb and Ta) into the DLC a variety of properties such as hardness, Young modulus or adhesion [13] can be addi-
FIGURE 1.6: Volume loss for metal-on-metal and DLC-on-DLC (smooth and rough surfaces) sliding partners as function of the number of cycles (in million). DLC surfaces show, compared to metal-on-metal surfaces, a reduced volume loss. Figure from [12].

...tionally adjusted. Thus, DLC coated friction pairs are very interesting for many industrial applications and produced on a routinely basis with a turnover of several hundred million euros per year [14].

In contrast to the excellent tribological properties and high hardness, DLC films reveal an unsatisfactory mechanical toughness [15]. Compared to some hard ceramic coatings DLC is limited in terms of load carrying capacity [16] and overload capability [17]. This limitation is mainly attributed to a low crack resistance and a high residual compressive stress [18].

However, due to the outstanding tribological behavior of DLC, it is aimed to find appropriate countermeasures to handle these disadvantages and to finally produce long-lasting DLC friction pairs. To fulfill this aim the analysis of the cohesive and adhesive strength is a key parameter which needs to be well understood. A common method reported in the literature to evaluate the adhesive strength of DLC films is Rockwell C indentation [19] and scratch tests. For application oriented experiments of coating-substrate systems, load-scanning tests are employed in which tribological and mechanical loading can be tested simultane-
In the case of steel substrates, which are often used in industrial applications, the applicability of DLC films in high load applications was limited in the past due to the lack of adhesive strength to the steel substrate \( \text{[20]} \). To improve adhesion the usage of different adhesive interlayers have been reported \( \text{[15, 21-23]} \). Adhesion layers containing Cr and Si and an adjacent ramp layer with a chemical gradient to the final DLC composition have led to well-adhering DLC on steel substrates \( \text{[24, 25]} \).

In the case of the few nanometers thick reactively formed metal-carbide layer (see e.g. Fig. 1.4 in the previous subchapter) mechanical failure and corrosion has reported to occur within this metal-carbide layer \( \text{[9, 26]} \) as it is shown in Fig. 1.7 for DLC deposited on CoCrMo.

![Figure 1.7](image.png)

**Figure 1.7:** Crack in the reactively formed metal carbide between the DLC and a CoCrMo substrate. Figure from \[19\].

In contrast to the adhesive failure of DLC, cohesive failure is not as widely reported in in the literature. Schaufler *et al.* \[27\] compared DLC coated and uncoated thin steel foils under uniaxial loading and deduced the stress-strain behavior of DLC films. The correlation between interfacial strength and cracking behavior of DLC films was demonstrated by Jeong *et al.* \[28\]. In another study \[29\] the deformation mechanics of DLC on two different steel substrates was investigated by tensile testing and cohesive zone modeling. It was shown that the segmenta-
tion as well as delamination strongly depend on the mechanical properties of the film and substrate material. It is further reported that saturation crack spacing is either caused by localized plasticity in the substrate or by delamination of a previously cracked segment.

Besides cohesive and adhesive failure contact damage analysis is performed to investigate the effect of a high local pressure, which is applied on the surface of the DLC-substrate combination. For example, Borrero-López et al. [30] studied the contact damage of DLC films coated on brittle Si(100) as well as on softer and more compliant soda lime glass substrates. The study revealed that cracks in the DLC appear at lower pressure on soda-lime glass than on Si(100) and shows that a stiff and hard substrate reduces crack initiation in the DLC (see Fig. 1.8). The study additionally shows that the mechanical properties of the substrate material influence the failure modes in the DLC. This statement can be confirmed by a case study of DLC on CoCrMo where an imprinting of the brittle DLC film into the CoCrMo substrate was reported [31].

**Figure 1.8:** Cross-sectional contact damage analysis with a DLC film thickness of 1 µm on (A) glass and (B) Si(100) at a maximum applied load of 200 mN and the corresponding load-displacement curves. On the glass substrate the DLC reveals circumferential cracks (named as cone cracks here) whereas no damage in the DLC was observed on the Si(100) substrate. However, lateral cracks are formed in the Si(100) substrate. Figures from [30].
1.3 Motivation for PhD Thesis

The stated literature shows that the successful performance of DLC films in industrial applications is dependent on the substrate material properties. Firstly, due to the mechanical properties of the substrate and secondly, due to the chemistry at the substrate-DLC interface. Although DLC is already widely applied on harder metallic-based substrates such as steel (and most research is conducted with this substrate material) due to the excellent tribological properties it is aimed to apply DLC on softer and more compliant metallic substrates like Ti and Ti-based alloys for e.g. long-lasting biomedical applications. In such an application during processing or service mechanical loading may occur and then lead to cohesive and adhesive failure. Another factor which may lead to failure are wear or loose particles trapped between the friction pairs, which can then create a high local pressure on the DLC film and the substrate finally leading to local contact damage. Since Ti is softer and more compliant than most other tested DLC coated substrates (steel, glass, Si, and CoCrMo), the imprinting of the hard and brittle particles into the Ti substrate is even more problematic. The application of a hard and brittle DLC film on the soft and ductile Ti substrate is therefore still critical to date.

An attempt to solve this issue is to adapt the deposition parameters during the DLC growth process to obtain a desired hardness or to reduce the high intrinsic stress and brittle behavior of the DLC. This will then change the mechanical properties of the DLC which makes it more suitable for ductile metallic substrates. In most cases, such modified DLC films cannot be utilized because desirable properties (e.g. higher fracture toughness) go hand-in-hand with properties (e.g. lower hardness and higher wear), which decrease the lifetime of the DLC film. Hence, a new approach is demanded.

Size effects with improved mechanical properties have been reported in a variety of other materials [32]. Inspired by this concept, the new approach presented in this thesis is to analyze the influence of DLC film thickness on the mechanical failure mechanisms of DLC coated Ti substrates. Therefore, the influence of the DLC film thickness on the cohesive and adhesive failure (chapter 2) and on the contact damage creation, evolution and final morphology (chapter 3) of DLC coated Ti substrates was analyzed.

Another approach to make DLC coated Ti substrates more resistant to cohesive and adhesive failure and contact damage is to use a suitable interlayer combina-
tion which is deposited between the Ti substrate and the DLC film. The aim of such an interlayer combination is to avoid cohesive and adhesive failure of the DLC film as well as to shield the substrate from contact damage creation. However, not only the interlayer material but also its structure such as phase is of great importance. As such, an interlayer deposited by sputter deposition, which is a non-equilibrium process, is often not in its thermodynamic stable phase. Hence, a method is needed to trigger and to fully control the phase of the deposited interlayer material. Such a method is presented in chapter 4 for Ta. With the ability to fully control the Ta-phase the effect of the structure of Ta interlayers on the cohesive and adhesive failure and the contact damage of DLC coated Ti substrates is analyzed in chapter 5.

Besides the relevance for industrial applications of DLC coated Ti substrates, a motivation of this thesis is to contribute to the overall understanding of size effects in surface layers and failure mechanisms of hard and brittle films on ductile metallic substrates upon applying external mechanical stresses. DLC on Ti serves as an excellent model system for this analysis as the DLC is hard and brittle whereas the Ti substrate is soft and compliant. The general approach and methods from this thesis can therefore be applied to any hard material attached to a ductile metallic substrate.
Chapter 2

Cohesive and Adhesive Failure of DLC Coated Ti Substrates: A film Thickness Study

In friction pairs mechanical loading can occur during service life or processing and may lead to cohesive and adhesive failure of the film-substrate system. Adequate tools are therefore needed to study these failure mechanisms. Hence, it is necessary to develop and validate a setup capable of generating a quantitative and variable load. Uniaxial loading is a powerful tool for this analysis as uniaxial stress states can be analyzed, which makes it feasible to describe cohesive and adhesive failure quantitatively. Such a quantitative description is also necessary for further research on interface stability in terms of fracture toughness, stress corrosion cracking and fatigue. Therefore, in this chapter, the influence of DLC film thickness on the cohesive and adhesive failure of DLC coated Ti substrates is analyzed by uniaxial loading.

2.1 Uniaxial Loading

During uniaxial loading of a brittle film on a ductile substrate, the stress in the film increases until fracture occurs. The failure evolution with increasing strain $\epsilon$ can be divided into three regimes [33, 34]. In the first regime the cracking behavior is defect controlled. As soon as the local stress exceeds the fracture strength $\sigma_F$ of a defect in the film a crack will form. Since an individual fracture strength
\( \sigma_F \) can be attributed to every defect more cracks form with increasing strain \( \epsilon \). In this first regime the mean crack distance decreases rapidly with increasing strain. The transition from the first to the second regime is characterized by a significant decrease in the fragmentation rate and takes place at the crossover strain \( \epsilon_c \). In this second regime the location of newly formed cracks is determined by the stress field within existing fragments.

In a first approach, the stress distribution within a fragment can be described by a one-dimensional shear lag model \([35, 36]\), where the stress transfer from the substrate to the film is governed by the interfacial shear stress \( \tau \). The stress increase from the stress-free crack to the border of the zone in which a plateau stress exists is characterized by the stress transfer length \( \xi \). In the case of a constant stress transfer, the stress transfer length \( \xi \) is linearly proportional to the film thickness \( d \) \( (\xi \propto d) \) \([37]\) while in the case of linear elastic stress transfer, \( \xi \) is proportional to the square root of the film thickness \( d \) \( (\xi \propto d^{1/2}) \) \([35, 36]\). The stress maximum is located in the center of a fragment and therefore newly nucleated cracks form predominantly in the center of existing fragments. Once the fragment size is of the order of the stress transfer length no further cracks form even for higher strains since the stress in the fragment never exceeds the fracture stress. Hence, the number of cracks saturates and the mean crack distance \( L_{\text{sat}} \) remains constant for strains \( \epsilon_{\text{sat}} \). This crack saturation is the transition zone to the third regime, where predominantly adhesive failure occurs due to the difference in Poisson contraction between film and substrate. The three stages upon uniaxial loading and the stress distribution in a fragment upon uniaxial loading and constant shear stress transfer are schematically shown in Fig. 2.1. The cohesive and adhesive failure of the DLC film upon the uniaxial loading process is experimentally analyzed by light and electron microscopy and by atomic force microscopy (AFM).

### 2.2 Experimental Details

Laser-cut dogbone-shaped rolled Ti grade 4 substrates with a thickness of 0.4 mm were used as substrate material. The samples were polished and ground down to a roughness of \( R_{\text{rms}} \approx 3 \) nm (measured by AFM) which was polished according to the polishing procedure presented in table 2.1. Thin DLC films were deposited by PACVD using radiofrequency (RF) at 13.56 MHz in a stainless steel chamber.
Figure 2.1: Top: Schematic of the three stages which occur upon uniaxial loading. Defect controlled cracking occurs in stage I and starts at the onset strain of fragmentation $\epsilon_{on}$. The transition from stage I to stage II at the crossover strain $\epsilon_c$ and the mean crack spacing $L_c$ is characterized by a significant decrease in fragmentation rate. In this second stage fragmentation occurs predominantly in the center of existing fragments. The mean crack distance decreases until the saturation crack spacing $L_{sat}$ is reached. Stage III is characterized by adhesive failure which occurs at strains $>\epsilon_{sat}$. Bottom: Stress distribution for a constant interfacial shear stress $\tau$ in a fragment with length $L$, thickness $d$, and stress transfer length $\xi$ upon uniaxial loading.
with a base pressure of $1 \times 10^{-5}$ Pa. Prior to deposition, the Ti substrates were cleaned in situ for 60 min with an argon plasma operated at a pressure of 2.5 Pa and $-600$ V sample self-bias. Thereafter, without interruption of the plasma, the argon gas flow was stopped while acetylene ($\text{C}_2\text{H}_2$) was introduced at 1 Pa. The deposition of DLC was done at $-600$ V self-bias and a growth rate of 27 nm/min was measured. Several DLC films with thicknesses of 50 nm, 200 nm, 500 nm, 1 µm, 2 µm, and 4 µm have been deposited by adjusting the deposition time.

As this thesis is part of an ongoing project the DLC films had already been well characterized by Falub et al. [19] and Equey et al. [38]. The DLC exhibits a residual stress ($\sigma_{\text{res}}$) of $-3.8 \pm 0.3$ GPa, a hardness of 23 GPa, a Young’s modulus ($Y_{\text{DLC}}$) of 150 GPa, a Poisson’s ratio $\nu_{\text{DLC}} = 0.3$ and a hydrogen concentration of around 25%. Since the DLC films in this thesis have been produced on the same deposition machine and with identical deposition parameters as in the publications of Falub et al. [19] and Equey et al. [38] these values can be used for the further calculations and investigations.

Uniaxial loading experiments have been performed with a microtensile machine from Kammrath & Weiss GmbH (Dortmund, Germany), which had been previously mounted on the piezo controller of a confocal CRM 200 Raman microscope from Witec (Ulm, Germany) or placed in a FEI Quanta 200 FEG electron microscope (see Fig. 2.2). The Raman microscope is equipped with a light microscope and a contact AFM. The strain rate of the microtensile machine was set to $5 \times 10^{-5}$ /s and the traction distance was controlled manually. After completing each traction step, optical or electron microscope images were taken. In some distinct cases AFM scans were additionally performed. The AFM measurements were conducted with PNP-DB-20 tips from Nanoworld (Neuchâtel, Switzerland). The resolution of the AFM scan was set to 291 data points/µm². To quantify the mean crack spacing and the mean delamination spacing, the Matlab program FractureBucklingAnalysis was used [39]. This program uses optical images to classify cracks and delaminated areas. The stress transfer length $\xi$ has been determined as described by Frank [34] with $\xi = L_c/2$ where $L_c$ represents the crossover length (see Fig. 2.1). The strain was determined via the program

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<tr>
<td>1</td>
<td>#320</td>
<td>200</td>
<td>5</td>
<td>300</td>
<td>Water</td>
</tr>
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<td>#4000</td>
<td>200</td>
<td>5</td>
<td>300</td>
<td>Water</td>
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<tr>
<td>4</td>
<td>MD-Chem</td>
<td>50</td>
<td>5</td>
<td>150</td>
<td>MasterMet : $\text{H}_2\text{O}_2$ (30%) = 9:1</td>
</tr>
</tbody>
</table>
FIGURE 2.2: DLC films with variable film thickness were deposited on dogbone-shaped Ti substrates (a). Uniaxial loading was performed on a microtensile machine (b) which was mounted on a piezocontroller of a Raman microscope (c). This Raman microscope is equipped with a light microscope and an AFM.

Spotfinder [40] which is based on a cross-correlation algorithm. This program tracks a chosen point throughout a series of images. By the comparison of two tracked points, the true strain can be determined. To determine the delaminated area optical images were transformed into bicolored images and then analyzed by a customized Matlab program. This program calculates the total area of the delamination vs. the total visible area of the optical image.

2.3 Results

Upon uniaxial loading the stress in the film steadily increases and soon or later exceeds the fracture strength $\sigma_F$ of an individual defect, resulting in crack formation. For higher strains more cracks will appear followed by adhesive failure. In the first part of this section the cohesive failure is discussed while the second part focuses on the adhesive failure.
2.3.1 Cohesive Failure

The fracture pattern of the uniaxial loaded DLC films with thicknesses varying from 50 nm up to 4 µm are displayed in Fig. 2.3 and show that the crack density increases with decreasing DLC film thickness. The fracture patterns are taken at the crossover strain $\epsilon_c$ which varies with the film thickness. For a film thickness >500 µm the cracks are straight and perpendicular to the loading direction, while for a thickness of 200 nm the cracks start to deviate (waviness) from this straight cracking behavior (see boxes in the 200 nm DLC fracture pattern in Fig. 2.3). For a film thickness of 50 nm localized areas with a high crack density have been observed (see inset in the 50 nm DLC fracture pattern in Fig. 2.3).

In Fig. 2.4 an uncoated Ti substrate is shown before loading (0% strain) and shortly before rupture at a strain of 12.5%. The surface reveals to be much rougher...
at 12.5% strain than prior to loading. The increased surface roughness arises from grain rotation which is a result of the anisotropic plastic deformation of Ti grains upon uniaxial loading [41].

The onset strain of fragmentation and the stress transfer length $\xi$ have been plotted as function of the film thickness and are displayed in Fig. 2.5. For film thicknesses $>1\,\mu m$, the onset strain of fragmentation changes only marginally, whereas for films $<1\,\mu m$ a significant increased onset strain of fragmentation with decreasing film thickness has been observed. The increased onset strain of fragmentation for films $<1\,\mu m$ reveals that a higher fracture strength is present in this thickness regime while the fracture strength for film thicknesses $>1\,\mu m$ changes only marginally. In addition, the stress transfer length $\xi$ increases for an increasing film thickness, which implies that at strains $>\epsilon_{sat}$ the saturation crack spacing is bigger for thicker DLC films.

To monitor the growth of cracks an AFM measurement of a 4\,\mu m DLC film at a strain of 3.3% was taken and is displayed in Fig. 2.6. The cracks in Fig. 2.6 are numbered according to their appearance and show a clear trend that the earlier the cracks appear, the wider they are. The limiting factor to enter the crack is hence the AFM tip convolution. Thus, in contrast to the crack width, the crack depth is not represented well.

**Figure 2.4:** Optical images of a polished Ti substrate (a) before loading and (b) at 12.5% strain. The surface is much rougher shortly before failure than at its initial state due to the anisotropic deformation of the Ti grains upon uniaxial loading.
**Figure 2.5**: Onset strain of fragmentation $\epsilon_{\text{on}}$ and stress transfer length $\xi$ as function of the DLC film thickness $d$. The stress transfer length has been determined by $\xi = L_c/2$, where $L_c$ represents the crossover length.

**Figure 2.6**: Broad AFM scan of a 4 μm DLC coated Ti substrate at a strain of 3.3%. The cracks are numbered according to their first appearance. The earlier the cracks form the wider they are.
2.3.2 Adhesive Failure

Upon uniaxial loading, the Poisson effect leads to compressive stresses perpendicular to the loading direction and may result in adhesive failure. If adhesive failure occurs, the film starts to buckle or spalls from the substrate, which leads to delaminated areas (patches). In this study, only the presence of patches has been observed. For film thicknesses >1 µm, the patches are constrained by the crack spacing and the area of a single patch increases with increasing film thickness as shown in Fig. 2.7 where DLC films with thicknesses of 200 nm, 500 nm, 1 µm and 2 µm are presented at a strain of 8%.

\[
\text{delamination area ratio (DAR)} = \frac{\text{delaminated area}}{\text{total area of optical image}} \quad (2.1)
\]

**Figure 2.7:** Optical images of DLC films with thicknesses of 2 µm, 1 µm, 500 nm, and 200 nm at a strain of 8%. The arrows indicate patches and reveal that the area of a single patch increases with increasing DLC film thickness. For a DLC film thickness of 500 nm and 200 nm, pronounced delamination along the Ti grain boundaries is observed. For a DLC film thickness of 200 nm, pronounced delamination along the Ti grain boundaries has been observed (see 200 nm and 500 nm DLC film thickness in Fig. 2.7). While for a 50 nm DLC film substrate fracture occurred prior to patch formation. In order to quantify the area of the patches as function of the strain, the delamination area ratio (DAR) (equation 2.1) has been defined. The DAR determines the area of the patches vs. the total area of an optical image.
The DAR as function of the strain is plotted in Fig. 2.8 and shows a thickness and strain dependency: for film thicknesses >1 μm the DAR reveals a strong dependency on the strain while for films 500 nm and 200 nm thick, the DAR changes only marginally with increasing strain. In addition, the onset strain of delamination decreases with increasing film thickness.

**Figure 2.8:** Top: Bicolored transformation for the determination of the DAR. Bottom: DAR as function of the strain for various film thicknesses. The onset strain of delamination decreases with increasing DLC film thickness. For film thicknesses >1 μm the DAR reveals to be film thickness and strain dependent while for film thicknesses of 500 nm and 200 nm the effect of the strain is only secondary.
2.4 Discussion

Upon uniaxial loading elastic-plastic deformation of the Ti substrate affects the stress generation in the DLC film. In the elastic region the substrate deforms homogeneously and the stress transfer takes place as it is described in the shear lag model. If, however, the Ti yields, two cases need to be distinguished:

- Prior to grain rotation the Ti substrate still deforms homogeneously and the stress transfer is as in the elastic part. The difference from the elastic region to the homogeneously deformed yielding zone is the rate of shear stress increase at the interface upon traction. The yielding effectively reduces the stress increase and therefore the increase in stress transfer is reduced per unit increment traction compared to the elastic region.

- At a later stage the Ti substrate deforms inhomogeneously due to grain rotation. This grain rotation significantly affects the stress in the DLC film on a local scale and creates zones with higher stresses and zones with lower stresses.

Those effects are independent of the film thickness since the DLC film thicknesses are much smaller compared to the thickness of the Ti substrate. Thus, the deformations in the Ti substrate such as grain rotation are an inherent behavior of the Ti and not caused by the DLC film.

If, upon uniaxial loading, the fracture strength is exceeded, brittle films form a straight crack pattern as it has been shown in other studies (e.g. [42]). This observation can be confirmed by DLC on Ti for film thicknesses >500 nm. However, for a DLC film thickness of 200 nm the crack pattern is affected by the anisotropic deformation of Ti grains and is revealed to be wavy in localized areas. This waviness reduces the stress generation in the film from Poisson contraction. Because the angle of the deviation from the straight cracking behavior is rather small the differences in stress reduction from Poisson contraction are small too. This statement can be confirmed by Fig. 2.7 where patch formation is present even in the area where deviation from the straight crack pattern was observed. If the stress reduction would be sufficiently effective no patches would form in this zone.

In the extreme case of a 50 nm DLC film the anisotropic deformation of the Ti grains creates high local strains which result in localized fragmentation in this area. The localized fragmentation is an indication that in this thickness regime
the DLC fracture pattern is mainly governed by the anisotropic deformation of the Ti grains. Fig. 2.6 shows that after the formation of a crack the elastic and plastic deformation of the substrate widens the crack spacing. Since the crack depth measurement by AFM is constrained by the tip convolution, the more appropriate measure to quantify crack growth is the width and not the depth as described in Ref. [43]. Thus, the crack spacing is a measure to quantify the age of already existing cracks as shown in Fig. 2.6.

The onset strain of fragmentation analysis has shown that the fracture strength undergoes a film thickness size effect behavior. In the literature an increased fracture strength for DLC films is often achieved by applying a bias voltage during the deposition procedure [44]. This study shows an alternative way to control the DLC fracture strength is by controlling the film thickness. The fracture strength is significantly increased by keeping the DLC film thickness < 1\,\mu m.

According to Hutchinson and Suo [45] the energy release rate for crack channeling \( G_{ss} \) is given by \( G_{ss} = \sigma^2 \cdot d \cdot z / Y \), where \( \sigma \) is the applied stress, \( d \) the film thickness, \( Y \) the effective Young’s modulus of the film which is given by \( Y = Y/(1-\nu^2) \) with \( \nu \) the Poisson’s ratio, and \( z \) is a geometry factor which depends on the ratio of the film thickness \( d \) and the mean crack spacing at crack saturation \( L_{sat} \) \((d/L_{sat})\). In addition, the ratio of the film thickness \( d \) and the mean crack spacing at crack saturation \( L_{sat} \) was much smaller than 1 \((d/L_{sat} \ll 1)\). By following Hutchinson and Suo [45], this leads to a \( z \)-value equal to 2. Since the strain at crack saturation is known for various film thicknesses the energy release rate \( G_{ss} \) at the front of a growing crack can be determined and is displayed in table 2.2.

The residual stress of \(-3.8 \, \text{GPa}\) has been taken into consideration for the stress calculation. Based on the values of the energy release rate the fracture toughness \( K_{IC} \), given by \( K_{IC} = (Y \cdot G_{ss})^{1/2} \), is straightforward to calculate and is also shown in table 2.2. With the values in table 2.2 and the effective Young’s modulus of DLC an average energy release rate for cohesive failure of \( G_{ss} = 63.5 \pm 2.6 \, \text{J/m}^2 \) and an average fracture toughness of \( K_{IC} = 3.2 \pm 0.1 \, \text{MPa m}^{1/2} \) have been determined.

**Table 2.2:** Energy release rate and fracture toughness for various DLC film thicknesses.

<table>
<thead>
<tr>
<th>Film thickness [nm]</th>
<th>Energy release rate ( G_{ss} ) [J/m(^2)]</th>
<th>Fracture toughness ( K_{IC} ) [MPa m(^{1/2})]</th>
</tr>
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<tbody>
<tr>
<td>200</td>
<td>59.1</td>
<td>3.1</td>
</tr>
<tr>
<td>500</td>
<td>65.5</td>
<td>3.3</td>
</tr>
<tr>
<td>1000</td>
<td>64.1</td>
<td>3.2</td>
</tr>
<tr>
<td>2000</td>
<td>65.2</td>
<td>3.3</td>
</tr>
<tr>
<td>4000</td>
<td>63.5</td>
<td>3.2</td>
</tr>
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</table>
The fracture toughness of $3.2 \pm 0.1 \text{ MPa m}^{1/2}$ is slightly higher than the values of $1.7 - 2 \text{ MPa m}^{1/2}$ found in the literature [46, 47]. The differences could arise from a lower Young’s modulus of the DLC [46] or because the fracture toughness was determined via an indentation method [47]. Furthermore, DLC describes a class of material in which, depending on the deposition conditions, a certain variation in film properties is obtained [7]. A factor of two deviation of the measured values compared to the literature can therefore be considered acceptable, since the DLC films in Refs. [46, 47] were deposited by magnetron sputtering [46] or by PACVD using a constant power setting of 200 W. In addition, in Ref. [47] the fracture toughness was determined via an indentation method. Since the techniques for the determination of the fracture toughness in Ref. [47] and in this study differ, a certain difference in both values is to be expected.

Upon further loading the formation of patches has been observed. Such patch formation occurs if the driving force for delamination is stronger than the adhesion between the DLC and the Ti substrate. The threshold limit for delamination is described by the critical energy release rate $G_{IC}$ for delamination.

In the case presented here an orthogonal system is considered. The $x$-axis is along the loading direction where tensile stresses are applied and the $y$-axis is perpendicular to the loading direction (see Fig. 2.2 where, due to Poisson contraction, compressive stresses are generated. For the formation of a single patch the critical energy release rate $G_{IC}$ is given by equation 2.2 where $\Delta E$ is the energy difference upon patch formation, while $L_{sat}$, $d$, $\gamma$, and $A$ represent the saturated crack spacing, the film thickness, surface tension and the area of a single patch, respectively. The surface tension term is significantly smaller and can therefore be neglected.

$$G_{IC} = \frac{\Delta E - 2 \cdot d \cdot L_{sat} \cdot \gamma}{A} \approx \frac{\Delta E}{A} \quad (2.2)$$

By considering a single patch with area $A$, prior to patch formation the energy in the film is given by the strain energy $E_\epsilon$, the patch area and the film thickness, while after patch formation the energy is equal to zero since the strain energy is equal to zero. Therefore, the energy difference $\Delta E$ is equal to the energy prior to patch formation and can be calculated as the product of film thickness and the integrated strain energy over the patch area $A$. Since the area $A$ of a single patch can be described by a component along the $x$- and $y$-axis with $x_A$ and $y_A$ the energy difference is equal to:
\[ \Delta E = d \cdot \int_A E_\epsilon \, dA = d \cdot \int_{x_A \, y_A} E_\epsilon \, dx \, dy \] (2.3)

In the present case of a biaxial stress state the local strain energy \( E_\epsilon \) is given by \( E_\epsilon = \frac{1}{2} \cdot \sigma^2(x,y) \). Due to the orientation of the coordinate system all components of the stress tensor, except \( \sigma_{xx} \) and \( \sigma_{yy} \), are considered to be equal to 0 (i.e. \( \sigma^2(x,y) \approx \sigma_{xx}^2 + \sigma_{yy}^2 \)), with

\[
\sigma_{xx} = (\sigma_{res} + \epsilon \cdot Y) \cdot f(x) = \overline{\sigma_{xx}} \cdot f(x) \quad \text{and} \quad (2.4)
\]

\[
\sigma_{yy} = (\sigma_{res} - \nu \cdot \epsilon \cdot Y \cdot (1 - f(x)) = \overline{\sigma_{yy}} \cdot (1 - f(x)) \] (2.5)

The function \( f(x) \) depends on the mode of the stress transfer (constant or linear) from the substrate to the film. By combining equations 2.3 - 2.5 the total energy integrated over the patch area is equal to:

\[
\Delta E = d \cdot \int_{x_A \, y_A} E_\epsilon \, dx \, dy = d \cdot y_A \cdot \int_0^{x_A} \frac{\sigma_{xx}^2 + \sigma_{yy}^2}{2} \, dx \] (2.6)

Assuming a constant shear stress transfer and no plateau stress (since patch formation occurs at strains \( >\epsilon_{sat} \) and therefore it is assumed that \( x_A \) is equal to twice the stress transfer length \( \xi \) \( (x_A = 2 \cdot \xi) \)), integration over the patch area \( A \) leads to the following analytical expression:

\[
\Delta E = \frac{d \cdot y_A \cdot \xi}{3 \cdot Y} (\overline{\sigma_{xx}} + \overline{\sigma_{yy}}) \] (2.7)

Since the stress transfer lengths could also overlap, the calculated value needs to be treated as an upper bound limit. With the known energy difference the critical energy release rate \( G_{IC} \) in equation 2.2 can be calculated. The input parameters (shear transfer length \( \xi \), the patch area and the crack spacing \( L_{sat} \), onset strain of delamination) can be extracted from previous experiments as well as from Ref. [19] for the Young’s modulus of the DLC. For 4\,\mu m, 2\,\mu m and 1\,\mu m DLC films (due to grain rotation thinner DLC films show pronounced delamination along the Ti grain boundaries which leads to a different stress state and therefore the presented calculation cannot be applied) the critical energy release rates are equal.
to 593 J/m², 587 J/m² and 556 J/m², respectively, which gives an average value of 579 ± 20 J/m².

Falub et al. [19] determined on Ti substrates that a 16 µm DLC film, produced with the same deposition parameters as the DLC used in this study, reveals an energy release rate of ≈ 500 J/m². Since in the study of Falub et al. the DLC did not spall from the Ti substrates it can be concluded that the critical energy release rate is >500 J/m² which is in accordance with the calculated values in this work. Note the big difference in value between $G_{ss}$ and $G_{IC}$. Two reasons may explain this difference. Firstly, for $G_{ss}$ tensile stresses are considered, whereas for $G_{IC}$ compressive stresses trigger the patch formation. Secondly, the stress intensity at the crack tip is responsible for the crack propagation. Upon crack propagation along the interface of DLC and Ti the plastic deformation of the Ti substrate blunts the crack tip and reduces the stress intensity at the crack tip [48]. This leads to an increased resistance to crack propagation which is not the case for the cohesive failure in the brittle DLC. Thus, the plastic deformation of the Ti substrate leads to an apparent increased value of the critical energy release rate $G_{IC}$ necessary to generate the stress intensity required for crack propagation at the interface crack tip. In addition, the crack opening for $G_{ss}$ is perpendicular to the loading direction, while for $G_{IC}$ the crack opening is parallel to the direction of the Poisson contraction. Hence, the crack opening for $G_{ss}$ is facilitated.

The analysis of the onset strain of delamination has shown a film thickness size effect for adhesive failure. To increase the onset strain of delamination adhesion promoters have been described in the literature [47]. This study shows an alternative way to increase the onset strain of delamination by decreasing the film thickness. However, during the analysis of the delamination process buckling of the DLC film has never been observed. Three different assumptions are posed to elucidate the reason for the lack of observation of such buckles.

- The first assumption is that the stress is too small to buckle a stiff film like DLC. The buckling stress $\sigma_B$ can be calculated by the Euler criterion for a free-standing film [49] which is given by $\sigma_B = \frac{\pi^2 \Sigma}{12 \left( \frac{2d}{y_{buckle}} \right)^2}$ with $d$ the film thickness, $\Sigma$ the effective Young’s modulus, and $y_{buckle}$ the buckle width. With the calculated buckling stress an energy release rate between 32 J/m² and 260 J/m² for film thicknesses from 1 µm up to 4 µm is present. In this study, the critical energy release rate $G_{IC}$ is much higher (and has been exceeded) which proves that enough stress is present to trigger the buckling process, respectively to generate a force tending to separate the DLC film.
from the substrate.

- The second assumption for the lack of observation of buckling is due to the brittleness of the film which leads to cohesive failure at the edges of the buckles shortly after the buckling process has started. Since Tsubone [50] observed buckles on DLC films with a much lower Young’s modulus this assumption can be confirmed and shows that the brittleness of the film influences the formation of buckles.

- The third assumption for the absence of buckles is an adhesion-based phenomenon of the film on the substrate. To elucidate this phenomenon three different cases of adhesion (poor adhesion, moderate adhesion and best adhesion) are distinguished. In the case of poor adhesion crack propagation between the film and the substrate occurs at relatively low compressive stresses. This will then result in a relatively wide buckle width. Due to the relatively wide width the stresses at the edges and on the top of the buckle are small and therefore no cracking of the film occurs. In the case of moderate adhesion buckling and mid-point cracking is observed, which has already reported in other systems (see for example [43, 51] among others). In the case of best adhesion no buckling occurs which then results in the formation of patches. The three cases are schematically shown in Fig. 2.9 and can be used for the qualitative determination of adhesion of film-substrate combinations. However, the brittleness of the film plays an important role irrespective of whether buckling, mid-point cracking or patch formation is observed. If the adhesion of very brittle films on substrates is poor or moderate cracks at the edges of the buckles, as presented in assumption 2, appear, which results in patch formation of the film. This patch formation would lead to the incorrect conclusion that best adhesion had been achieved. Hence, to qualitatively analyze the adhesion Fig. 2.9 is restricted to ductile and moderately brittle films.

Since Ti is a carbide-forming material in the case presented here of DLC on Ti an approximately 5 nm thick titanium carbide layer is formed as it has been shown by X-ray photoelectron spectroscopy (XPS) for DLC on other metal-carbide forming substrates such as CoCrMo [9, 52] and TiAlV [8] as reported in chapter 1. The composition of the reactively formed interface, its mechanical strength as well as its corrosion properties then decides the adhesion behavior of the DLC film on the Ti substrate [9]. Although such carbide bonds are generally strong the adhesive strength of DLC on Ti cannot be qualitatively determined from the film.
buckling geometry, depicted in Fig. 2.9, as the DLC film is very brittle and cracking at the edges of the buckles, as reported in assumption 2, cannot be excluded. Nevertheless, it is assumed that the lack of observation of DLC buckles is due to a combination of strong adhesion and cracking at the edges of the buckle because of the brittle nature of DLC.

![Diagram showing delamination process, buckle width, and cracking behavior depending on adhesion.]

**Figure 2.9:** Schematic representation of the delamination process, buckle width and cracking behavior depending on the adhesion of a film on a substrate.

The analyzed DAR has been shown to be strain and film thickness dependent for films > 1 µm while for films < 500 nm the effect of the strain is secondary. To ex-
plain this different behavior, the two quantities (area of a single patch and number of patches) which determine the DAR are considered separately:

- Fig. 2.7 shows that the area of a single patch increases with increasing film thickness. Hence, the area of a single delamination increases with increasing film thickness.

- In a regime where Poisson contraction triggers the delamination (>1 µm) the number of patches can be estimated by the following argument: Since the delamination process is a stress relaxation process (as is the cracking process) the minimum distance between two adjacent patches along the axis perpendicular to the loading direction can be expressed by a modified stress transfer length $\xi^*$. In the case of a constant stress transfer, $\xi^*$ scales with the film thickness $d$.

Since the area of a single patch as well as the number of patches increase with the film thickness $d$, the DAR increases with increasing film thickness, which is in agreement with Fig. 2.8. However, this argumentation is only valid as long as the patches do not form along the Ti grain boundaries as it is has been observed for film thicknesses of 500 nm and 200 nm where grain rotation occurs. This rotation may result in high compressive stresses along the Ti grain boundaries, causing pronounced delamination in this area. As soon as the rotation has finalized, only a minor additional number of patches will form.

Therefore, in the thickness regime where grain rotation is the main trigger for delamination the strain dependency on the DAR shows only a secondary effect.

### 2.5 Conclusion

- The correlation of film thickness with the cohesive and adhesive failure of hard and brittle films on ductile metallic substrates has been analyzed with the model system DLC on Ti and by uniaxial loading. The fracture strength and onset strain of delamination of the film have shown a film thickness size effect.

- The cohesive and adhesive failure of DLC coated Ti substrates have been described quantitatively. The energy release rate for cohesive failure $G_{ss}$ and the fracture toughness $K_{IC}$ of DLC have been determined to be 63.5 ±
2.6 J/m$^2$ and 3.2 ± 0.1 MPa m$^{1/2}$ while the critical energy release rate for adhesive failure $G_{IC}$ is equal to 579 ± 20 J/m$^2$.

- The anisotropic deformation of the Ti substrate affects the cohesive and adhesive failure of DLC if the film thickness is <1 µm.

- A schematic is presented to qualitatively determine the adhesion of ductile and moderately brittle films on any kind of substrates.
Chapter 3

Contact Damage of DLC Coated Ti Substrates

In addition to cohesive and adhesive failure, another factor limiting the applicability of DLC coated Ti substrates is damage created by wear or loose particles that are trapped between the friction pairs. These particles may get pressed into the DLC and Ti substrate and can create contact damage in the DLC film and the substrate. Thus, the contact damage needs to be studied, like the cohesive and adhesive failure by uniaxial loading, by an appropriate experimental setup.

Since microindentation allows application of a variable and quantitative load this experimental setup is used in this chapter to describe and understand the contact damage creation, evolution and final morphology.

3.1 Contact Damage Analysis

The stress distribution upon indentation attracted many researches in the past two centuries. The first analytical solution was developed by Hertz (1857-1894) for homogenous and isotropic materials using a spherical indenter tip [53]. The stress distribution can, due to the axial symmetry, be described by radial, hoop and out of plane stresses. However, Hertz’s theory is only applicable on isotropic and homogenous bodies and is therefore not suitable for a coated system like DLC on Ti. Although several attempts had been made in the past for finding an analytical solution for the stress distribution of coated systems (by e.g. calculating the effective contact area and indentation depth as function of the indenter
geometric and applied load \cite{54,55}) the breakthrough in solving contact damage problems of coated systems was the emerging computer power technology in the 1960's. This allows, by using methods like finite-element analysis (FEA), to solve highly non-linear problems where no analytical solutions exist. Hence, to fully understand and describe contact damage complementary investigations of experimental and computational methods are needed. Therefore, in this chapter contact damage is induced by instrumented microindentation and is additionally complemented with indentation simulated by static FEA. Such an approach is also needed for any hard layer attached on a ductile metallic substrate which undergo contact damage. Thus, this study serves also as model system for the general understanding of the contact damage creation, evolution and final morphology of a hard layer deposited on a ductile metallic substrate.

3.2 Experimental Details

To generate the input data for the static FEA uniaxial loading is needed. The procedure of the FEA, uniaxial loading and microindentation to analyze contact damage creation, evolution and final morphology is presented hereafter.

3.2.1 Uniaxial Loading & FEA

Static FEA was performed with the commercially available FE software Comsol\textsuperscript{®} (version 4.3). A spherical indenter with radius of 10 µm was pressed into the DLC-Ti structure with a maximum load of 500 mN acting normal to the surface with DLC film thicknesses varying from 50 nm up to 10 µm. In the FEA an axially symmetric contact pair model was used. The meshing was optimized for processing time without information loss in the output quality. Fixed constraints were used on the side and bottom of the system. Since the contact area and indentation depth of the DLC-Ti system changes with load, a continuation solver was used with a steadily increasing normal load. The DLC was considered as fully elastic while the Ti substrate deformation was considered as elastic-plastic. The output data of the FEA are radial stresses for the DLC and von Mises principal stresses for the Ti substrate.

Since the Ti substrate deforms elastic-plastically the input data for the FEA were determined by uniaxial loading as reported in chapter 2 with a microtensile ma-
chine, a 0.4 mm thick dogbone-shaped Ti grade 4 substrate which was tested with a strain rate of $5 \times 10^{-5}$ /s to fracture. The load-displacement curves were recorded and due the known geometry converted into an engineering stress-strain curve. The engineering stress-strain curve was then modeled by two linear fits: the first fit covered the elastic part and results to the Young’s modulus of Ti ($Y_{Ti}$) while the second fit describes the plastic part with the isotropic tangent modulus ($Y_{Tiso}$).

### 3.2.2 Microindentation

DLC films with thicknesses of 50 nm, 500 nm, 1 µm, and 1.5 µm were deposited by PACVD with acetylene ($C_2H_2$) as precursor gas and a self-bias of $-600$ V on previously grinded and polished Ti grade 4 substrates as described in chapter 2. Contact damage was induced with a MTS Nanoindenter XP from Agilent Technologies (Santa Clara, CA, USA) equipped with a 10 µm spherical diamond indenter from Synton (Nidau, Switzerland). The loading and unloading rate was set at 1 mN/s and a peak holding time of 5 s was used. Loads from 80 - 500 mN were applied and load-displacement curves were recorded. Surface damage was analyzed by a LEO scanning electron microscope (Carl Zeiss, Germany) with a Gemini field emission column, operating at 5 keV acceleration voltage, a base pressure of $10^{-6}$ mbar and a working distances of 3 mm. The secondary electrons were detected with an in-lens detector. Cross sectional analysis was carried out with a Helios Nanolab 600i focus ion beam (FIB) using a 30 kV gallium ion beam for material removal. Prior to cross sectioning platinum cover layers were deposited on the imprints.

### 3.3 Results

#### 3.3.1 Uniaxial Loading & FEA

The Ti substrate was tested by uniaxial loading to derive the stress-strain curve as input data for the FEA analysis. Two linear fits were applied to describe the elastic and the plastic part in the engineering stress-strain curve (Fig. 3.1). With the first linear fit for the elastic part and an offset yield strength of 0.2% ($R_{p0.2}$) a yield stress $\sigma_y$ of 648 MPa and a Young’s modulus $Y_{Ti}$ of 115 GPa were determined.
for the Ti. The second linear fit for the plastic part revealed an isotropic tangent modulus $Y_{Ti,iso}$ of 2.0 GPa. These values and the Young’s modulus of the DLC film (175 GPa used in this simulation) were implemented in the FEA model.

![Graph showing stress-strain curve for Ti](image)

**Figure 3.1:** Experimental and fitted stress-strain curve of Ti with linear fits for the elastic and plastic part. A 0.2% offset yield ($R_{p0.2}$) was used for the yield point determination. The Ti substrate shows a yield strength $\sigma_y$ of 648 MPa while the elastic modulus $Y_{Ti}$ and the isotropic tangent modulus $Y_{Ti,iso}$ are equal to 115 GPa and 2.0 GPa respectively.

Upon simulated indentation with FEA three different locations in the DLC exhibiting high tensile stresses were observed as shown for a 500 nm DLC film at 150 mN in Fig. 3.2. The first location, indicated by zone 1 in Fig. 3.2 (called *interface center*) is at the interface of the DLC film and Ti substrate. The second location is at the contact zone of indenter and surface (zone 2 in Fig. 3.2, called *surface center*) where the indenter contacts the DLC and the third location (zone 3 in Fig. 3.2, called *edge*) where failure is prone to happen is at the edge of the indent where radial tensile stresses are generated. Plots as shown in Fig. 3.2 were performed for film thicknesses varying between 50 nm and 10 µm and with steadily increasing load up to 500 mN. From these plots the following trends were observed:

- The stresses at the *surface center* are compressive for low loads and turn into tensile stresses by increasing the load.

- With increasing film thickness the load which needs to be applied to turn the *surface center* stresses from compressive into tensile increases.
- Above a film thickness of 1 µm the stresses at the surface center are still compressive even at the highest applied load of 500 mN.

- At the interface center and the edge zones tensile stresses are observed regardless of the indentation depth.

![Diagram](image)

**Figure 3.2:** Simulated stress distribution at a film thickness of 500 nm and a load of 150 mN with the three numbered stress intense locations. Location 1 is underneath the center of the indenter at the interface DLC-Ti and called interface center; location 2 (called surface center) is in the center of the indent at the surface of the DLC film and location 3 (called edge) is at the edge of the indent.

### 3.3.2 Microindentation

Experimental contact damage as induced by loads ranging from 80 mN to 500 mN in DLC of film thicknesses varying from 50 nm up to 1.5 µm is shown in Fig. 3.3. Fig. 3.3 reveals that the final contact damage morphology changes significantly with applied load and film thickness. At loads of 80 mN and 150 mN the diameter of the indent increases with decreasing film thickness which is not anymore the case for higher loads, indicating that in this high load regime most of the deformation is localized in the substrate which cannot be shielded by the DLC film. At a load of 150 mN and DLC film thicknesses of 500 nm, 1 µm and 1.5 µm the first circumferential cracks (which are from now on called edge cracks) are clearly visible and their number is increased with increasing load and DLC film thickness. Such a behavior was, however, not observed for the 50 nm DLC film where only
few edge cracks are visible. The dominant failure mode in this thickness regime is cracks in the inner zone of the indent. Such cracks are also observed in thicker films but appear to be less dominant as their number scales inversely with the stress transfer length [35-37]. A spiral-like morphology was observed at a load of 300 mN and a DLC film thickness of 1.5 µm.

**Figure 3.3:** Top view of the final contact damage morphology for various loads and film thicknesses taken by secondary electron microscope images.

The evolution of the contact damage was analyzed by load-displacement curves and cross sections of the indents (Fig. 3.4). At a load of 150 mN the load-displacement curves of the 500 nm and 1 µm DLC films show pop-ins which are indicated in Fig. 3.4 and characterized by a discontinuity (at loads >150 mN more than one pop-in was present in the load-displacement curves which is not shown here). To investigate the origin of the first pop-in cross sections of the 500 nm and 1 µm DLC film indented with 150 mN were examined. At a DLC film thickness of 50 nm no pop-in was observed even at the highest load of 500 mN and therefore the cross
section was acquired at the contact damage created with a load of 500 mN. Additionally, the comparison of the load-displacement curves shows that an increased DLC film thickness reduces the total indentation depth into the DLC-Ti structure.

The taken cross sections in Fig. 3.4 reveal that edge and interface center cracks are present for the shown cases. From the cross sections of the 500 nm and 1 µm DLC films it can be concluded that the interface center crack nucleated at the Ti-DLC interface. Lateral cracks in the center of the DLC film were only observed at a film thickness of 1 µm. Such lateral cracks are initiated by an uniaxial stress perpendicular to the crack direction which is in the present case the out of plane direction and is parallel to the loading direction. This out of plane stress is assumed to occur during the unloading process.

3.4 Discussion

The observation from FEA that with increasing DLC film thickness an increasing load is needed to turn the surface center stress from compressive to tensile can be understood by considering the two extreme cases of very thick films and film thicknesses tending towards zero. For very thick films the stress distribution in the film can be considered as a plate-like deformation. Thus, the stresses are compressive at the surface center and tensile at the interface center. In the other extreme case of very thin films the plastic deformation of the Ti substrate increases the strain in the DLC film which consequently leads to overall tensile stresses in the DLC. Hence, for very thin DLC films a membrane-like behavior [56] is present with tensile stresses at the surface center and interface center. Using the stress values extracted from FEA in the DLC film at the three defined locations from Fig. 3.2 (edge, interface center and surface center) a failure plot is generated and presented in Fig. 3.5 (note the logarithmic scale) for DLC and Ti.

For the curves Edge [d], Interface Center and Surface Center (they correspond to the locations edge, interface center and surface center) the following failure criterion was applied: Up to a film thickness of 200 nm[1] the stress at fracture $\sigma_F$ of the DLC was calculated by the Griffith criterion (equation 3.1) [57] where $d$ is the critical flaw size and assumed to be equal to the film thickness $d$ while $K_{IC}$ represents the

---

[1] The determination of the stress at fracture, calculated with the Griffith criterion up to a film thickness of 200 nm, appears to be reasonable since crack patterns of DLC films in this thickness regime have shown to be influenced by the anisotropic deformation of the Ti substrate (see chapter 2).
Figure 3.4: Load-displacement curves and the corresponding cross sections for a 1 µm and 500 nm DLC film at 150 mN and for a 50 nm film at 500 mN. For film thicknesses of 1 µm and 500 nm pop-ins in the load-displacement curves are present. Cracks at the edge and at the DLC-Ti interface are present in all three cases. Lateral cracks are only present in the 1 µm DLC film.

Fracture toughness of the DLC film. Thus, the maximum flaw size is comparable to the film thickness. For the fracture toughness $K_{IC}$ a value of 3.2 MPa m$^{1/2}$ was taken as reported in table 2.2 in chapter 2. For DLC films >200 nm the stress at fracture is determined by the onset strain of fragmentation with the values reported in chapter 2.

$$\sigma_F = \frac{K_{IC}}{\sqrt{\pi \cdot d}}$$

(3.1)
If the load exceeds the fracture stress at one of the locations failure in the DLC occurs. Hence, from the failure plot the location of first failure (as function of the film thickness) can be deduced by considering the absolute film thickness \(d\) and the load \(P\) (consider bottom and left axis in Fig. 3.5). Since the curves Edge \([d]\), Interface Center and Surface Center are determined with the absolute values of the film thickness they follow a film thickness size effect behavior for very thin films (see chapter 2).

Furthermore, the Ti substrate yields if the von Mises stress from FEA exceeds the yield stress of the Ti (648 MPa) which is represented by the curve Yield. The curve Yield shows that an increasing DLC film thickness increases the resistance to plastic deformation of the substrate upon contact damage creation. This observation is in accordance with Fig. 3.4 where, upon microindentation, a decreasing penetration depth was observed with increasing DLC film thickness.

In FEA the plastic deformation of the substrate is modeled with the isotropic tangent modulus \(Y_{\text{Tiso}}\), fitted on the engineering stress-strain curve, which leads to an underestimation of the true stress-strain curve. Thus, the deformation modeled in the plastic zone of the Ti substrate is overestimated which results in an overestimation of the stresses in the DLC.

The failure plot shows that the location of first failure in the DLC is predominately at the edge. For very thin films, however, the three curves Edge \([d]\), Surface Center and Interface Center are within a very small load range and therefore first failure cannot be predicted. This observation confirms the membrane-like behavior of thin DLC films and additionally shows that in this film thickness regime failure is defect controlled (i.e. the film cracks at one of three locations depending on the size of a local defect).

This defect controlled cracking can also be illustrated for DLC film thicknesses between 900 nm - 1.6 \(\mu\)m where the load to initiate first failure in the DLC is nearly identical at the edge and at the interface center. Thus, the location of first failure is either at the edge or interface center depending on the size and location of a defect. This statement can be rationalized by the comparison of the contact damage morphologies of 1 \(\mu\)m and 1.5 \(\mu\)m DLC at 300 mN in Fig. 3.3. Although both film thicknesses are in the regime where the appearance of edge and interface cracks is equally probable at the DLC film thickness of 1.5 \(\mu\)m a spiral-like shape was observed while for a 1 \(\mu\)m DLC film edge cracks are present. The spiral-like shape arises from a propagating stress front starting from the center of the indentation,
Figure 3.5: Simulated failure plot shown with the absolute loads and film thicknesses as well as with the pressure and the \(d/R\) ratio. The curves represent the critical load (pressure) and film thickness \((d/R)\) upon the substrate yields respectively the location where first failure in the DLC occurs. Four zones are marked where yielding and cracking occur (or are absent) as well as exemplary micrographs are given at 80 mN and 300 mN for a 50 nm DLC film and at 150 mN and 500 mN for a 500 nm (indicated by \(x^a\), \(x^b\), \(x^c\), \(x^d\) in the failure plot). The extracted values from FEA are represented by data points while the corresponding fits are shown as curves.

as also reported by \cite{58}, and shows that an interface center crack nucleated first, in contrast to the 1 \(\mu\)m DLC film where an edge crack nucleated first. From the examination of first failure and the micrographs in Fig. 3.3 it can be concluded that the first pop-in in Fig. 3.4 were formed by edge cracks which is in accordance with \cite{59, 60}. The absence of pop-ins for the 50 nm DLC film is probably due to a lack of force and/or displacement resolution.

Additionally, in the failure plot in Fig. 3.5 the following four distinct zones could be identified:

- Elastic zone (green zone): No yielding in the Ti substrate and no cracking in the DLC film.
- Plastic zone (white zone): Yielding in the Ti substrate and no cracking in the DLC film. An exemplary micrograph is presented and denoted with a (50 nm DLC at 80 mN). The crack in the micrograph is probably induced by a local defect. The corresponding location in the failure plot is indicated by a cross ($x^a$).

- Plastic-cracking zone (bright yellow zone): Yielding in the Ti substrate and cracking in DLC film: Exemplary micrographs are given and denoted with b (50 nm DLC at 300 mN), c (500 nm DLC at 150 mN), and d (500 nm at 500 mN). The corresponding locations in the failure plot are indicated by crosses ($x^b$, $x^c$, $x^d$).

- Elastic-cracking zone (dark yellow zone): No yielding in the Ti substrate but cracking in the DLC film for thick DLC films.

The elastic and the plastic-cracking zones (green and bright yellow zones) approach each other with increasing film thickness and finally overlap at a film thickness of around 5 µm and form then the elastic-cracking zone (dark yellow zone) where cracking of the DLC occurs prior to substrate yielding. To design a contact damage resistant system the film and substrate should deform elastically up to the highest load possible (elastic limit). From the failure plot in Fig. 3.5 it can be deduced that this will be the case at a film thickness of 5 µm, which is indicated by a circle. An alternative way to design a crack resistant coating system, is to protect the DLC film as much as possible from fracture. This corresponds to the highest load which is not in the bright or dark yellow zone in Fig. 3.5 and the case at a film thickness of 60 nm (indicated by a star in the failure plot).

So far, the failure plot is presented with absolute loads and film thicknesses which have been determined with an indenter radius of 10 µm. However, upon indentation the stress distribution in a film-substrate combination depends on the ratio of film thickness and the indenter radius [56]. To generalize the failure plot the curves are additionally represented by the normalized film thickness and the applied pressure. To normalize the film thickness and to determine the applied pressure the procedure of Michler et al. [56] can be followed which shows that the film thickness $d$ and the applied load $P$ are divided by the radius $R$ of the indenter resulting to a normalized film thickness $d/R$ and an applied pressure $P/R^2$ (consider top and right axis in Fig. 3.5). With this generalization the failure plot can be adapted to any film thickness and indenter radius.
However, since the curves Edge [d], Surface Center and Interface Center obey a film thickness size effect, a macroscopic failure criterion needs to be determined for the normalized film thickness (d/R ratio). For this macroscopic failure criterion the stress at fracture of a 10 µm DLC film was taken. Since failure occurs in most cases at the edge the influence of a variable d/R ratio is only shown for this location and is represented by the curve Edge [d/R]. The curve Edge [d/R] also affects the design of a contact damage resistant DLC system as the highest pressure of the elastic zone and highest pressure prior to DLC cracking coincide at a d/R ratio of 0.5.

The current industry standard with DLC film thicknesses varying from 1 - 5 µm is also shown in the failure plot in Fig. 3.5. Although this industry standard is within the range of the highest load of the elastic zone (circle in the failure plot in Fig. 3.5) if very thin DLC films would be used almost double the load could be applied prior to DLC film cracking (consider the logarithmic scale).

Since DLC is a material class with variable properties [7] to produce long lasting DLC films on ductile metallic substrates understanding the effect of e.g. a changing fracture toughness and its influence on the failure plot is a valuable input. In Fig. 3.6 this effect is shown with a fracture toughness variation from 1.7 MPa m$^{1/2}$ over 4.5 MPa m$^{1/2}$ to 6.0 MPa m$^{1/2}$ and their influence on the curves Edge [d], Interface Center and Surface Center. The values are within a range of reported values in the literature [46, 47, 61, 62]. The fracture toughness of DLC can be varied by a different deposition procedure or by using a different precursor gas than acetylene which then forms a more polymeric-like DLC [5] (see chapter 1).

The analysis reveals that with increasing fracture toughness the highest load of the elastic zone (green zone) increases as well to higher film thicknesses (see position change of circles in Fig. 3.6 upon increasing fracture toughness). In addition, the highest load which is not in the bright or dark yellow zone (no DLC cracking), can be found at very thin DLC film thicknesses for a fracture toughness of 1.7 MPa m$^{1/2}$ (indicated by the star in Fig. 3.6 top).

However, at a fracture toughness of 4.5 MPa m$^{1/2}$ the highest load to avoid DLC cracking (dark and bright yellow zones) is identical for very thin DLC films (around 50 nm) and at a film thickness of around 4.5 µm (indicated by the two stars in Fig. 3.6 center). For an even higher fracture toughness of 6.0 MPa m$^{1/2}$ the highest load prior to DLC film cracking (highest load of green and white zones) shifts to a film thickness of 5 µm (d/R ratio of 0.5) which is indicated in
**Figure 3.6:** The effect of the DLC fracture toughness, varying from 1.7 MPa m$^{1/2}$ (top) over 4.5 MPa m$^{1/2}$ (center) to 6.0 MPa m$^{1/2}$ (bottom), on the zones in the failure plot (same coloring used as in Fig. 3.5). With increasing fracture toughness the maximum load to retain in the elastic zone increases and also shifts to a higher DLC film thicknesses (see circles). Similarly, the maximum load (pressure) which can be applied prior to DLC film cracking, can be found, at a very low film thickness (50 nm) for a fracture toughness of 1.7 MPa m$^{1/2}$, and shifts to higher values with increasing fracture toughness (see stars).
Fig. 3.6 on the bottom. In this fracture toughness regime the highest elastic limit (green zone) is reached at a film thickness of around 9 µm (indicated by the star in Fig. 3.6 bottom). Hence, the fracture toughness affects the design of a contact damage resistant system.

From the presented analysis it can be concluded that the contact damage creation, evolution and final morphology is strongly dependent on the load, the particle (indenter) size, the DLC film thickness, the elastic-plastic behavior of the substrate (which is necessary to predict contact damage on soft and ductile metallic substrates), and the mechanical properties such as fracture toughness of the DLC. By knowing these parameters the contact damage can be minimized by controlling the DLC film thickness.

In combination with chapter 2 the presented results lead to a film thickness optimization process for applications of DLC films on ductile metallic substrates: On the one hand thin DLC films have an increased fracture strength (as shown in chapter 2) and show no lateral cracks upon contact damage creation (see Fig. 3.4) whereas on the other hand thicker DLC films reveal an increased resistance to plastic deformation of the substrate upon contact damage creation. Hence, to get a high fracture strength the DLC film thickness needs to be as thin as possible while to avoid plastic deformation of the substrate upon contact damage creation the DLC film needs to be as thick as possible. Since in most tribological applications a high fracture strength of the film and a high resistance to plastic deformation upon contact damage creation is aimed a compromise in DLC film thickness needs to be made in order to avoid the disadvantageous properties of a too thin or too thick DLC film. This compromise requires a film thickness optimization process.

### 3.5 Conclusion

- Contact damage in DLC on Ti substrates was analyzed by instrumented microindentation and FEA. The DLC film thickness as well as the elastic-plastic deformation of the Ti substrate were found to significantly affect the contact damage creation, evolution and its final morphology. A transition from a membrane-like to a plate-like deformation was observed upon increasing the DLC film thickness.

- A failure plot is presented with the location of first failure in the DLC and
yielding of the substrate as function of the film thickness. Four distinct zones were identified where failure in DLC and Ti is present respectively where it is absent. A change in fracture toughness significantly affects the failure plot.

- A film thickness optimization process was presented for DLC films on ductile metallic substrates since thicker films shield plastic deformation of the substrate while thinner films show an increased fracture strength.
Chapter 4

Sputter Deposited Tantalum & Tantalum Nitride Thin Films

The sliding partners in most tribological applications are aimed for possessing high fracture strengths, high onset strains of delamination and a high resistance to contact damage. These requirements are also employed for the DLC-Ti system and should be achieved with an ideal DLC film thickness. However, the previous two chapters about the cohesive and adhesive failure and contact damage have revealed a film thickness dependence for these three failure mechanisms. They have shown that the fracture strength and onset strain of delamination can be increased by decreasing the film thickness whereas thicker films shield the substrate from plastic deformation upon indentation.

Due to this opposing behavior a film thickness optimization process is required. However, to combine a high fracture strength of the DLC film and a high resistance to plastic deformation of the substrate upon contact damage, an alternative is to strengthen the DLC coated Ti system with a suitable interlayer combination. The choice of the interlayer combination depends on the adhesive strength between the Ti substrate and the DLC film, the mechanical performance as well as on the ability to deposit it by a vacuum deposition method.

Ta and tantalum nitride are excellent candidates as they have already been used as adhesion promoters in the microelectronics industry [63, 64] and can be deposited by sputter deposition. Since sputter deposition is a non-equilibrium process the phase of the deposited interlayer material can also be present in a metastable form. The control and prediction of the deposited phases is essential to de-
scribe the mechanical deformation behavior of the interlayer material as well as its influence on the DLC film and Ti substrate. Thus, in this chapter a method is presented to trigger and to fully control the phases of Ta and tantalum nitride on Ti substrates upon sputter deposition. Additionally, the mechanical properties of the Ta and tantalum nitride layers are analyzed.

4.1 Tantalum & Tantalum Nitride

Ta and tantalum nitride thin films are known for their high temperature stability and are chemically inert. Besides their application as adhesion promoters they are used as diffusion barriers [63, 64] and in biomedical applications [65]. Tantalum nitride thin films have also become technologically important as wear resistant [66], and functionalized optical coatings [67].

Since pure Ta exists in the thermodynamically stable body-centered cubic (bcc) \( \alpha \)-phase and in the metastable tetragonal \( \beta \)-phase \( \alpha \)-Ta is less brittle than \( \beta \)-Ta.

The growth of \( \alpha \)-Ta is promoted by increasing the substrate temperature which results in an increased mobility of freshly adsorbed atoms. These atoms then have a higher probability of finding a lower energy adsorption site and hence form a more stable structure [68]. A low lattice mismatch of the underlying substrate and the \( \alpha \)-phase promotes epitaxial growth and forms \( \alpha \)-Ta. Such \( \alpha \)-Ta promoting substrates are Nb [69], W [70], Cu [71], Al [72], and Cr [73]. Thin tantalum nitride layers are used in the microelectronics industry [74] and for protective coatings on steel [68] to promote the growth of \( \alpha \)-Ta. The presence of oxygen containing impurities is an important factor for the growth and nucleation of \( \beta \)-Ta during sputter deposition [75]. The phase transformation from \( \beta \) to \( \alpha \)-Ta occurs at a temperature between 300 °C and 400 °C, however, oxygen impurities within the Ta layer or the presence of oxygen can result in a significantly higher transition temperature [76].

Furthermore, the production of tantalum nitride by reactive sputter deposition with a mixture of nitrogen and argon gas is a well-established method. The following tantalum nitride structures have been discovered experimentally: Heating the substrate to 300 °C and a \( \text{N}_2/\text{Ar} \) flow ratio of 4% - 30% leads to an orthorhombic Ta\(_4\)N phase [77]. Tetragonal \( \beta \)-Ta (330) and hexagonal stoichiometric TaN were observed at lower (10% - 20%) flow ratios, whereas orthorhombic TaN and orthorhombic Ta\(_3\)N\(_5\) were present at higher (40%) flow ratios [78]. Other re-
searchers report a change in structure upon increasing the N$_2$/Ar flow ratio from $\alpha$- or $\beta$-Ta to Ta$_2$N, and finally to TaN [79–81].

4.2 Experimental Details

DC magnetron sputtering (PVD Products, Inc. USA) with a Ta target (99.95 % purity) was performed for the deposition of Ta and tantalum nitride thin films. Ar gas (99.998 % purity) has been used as working gas for the deposition of pure Ta, while a mixture of Ar and N$_2$ gas (99.9999 % purity) has been used for the reactive formation of tantalum nitride films. The total working pressure and the total gas flow were kept constant at 0.67 Pa and 10 sccm, respectively. For the deposition of tantalum nitride the N$_2$/Ar flow ratio has been varied from 10 % to 70 %. The investigated film thicknesses were 400 nm for all Ta and tantalum nitride films. The sputtering time has been adapted according to the deposition rates, which are shown in table 4.1.

Ta and tantalum nitride were deposited on bare Si(100) wafers and polished Ti. To keep the natural oxide layers on Si(100) and Ti no RF sputter cleaning has been performed prior to the deposition of Ta. In addition, pure Ta has been sputtered on 1 µm amorphous DLC previously deposited on Si(100), and on tantalum nitride seed layers previously deposited on Si(100) and Ti substrates. The DLC film was deposited as described in chapter 2. The tantalum nitride seed layer has been deposited for 75 s with a N$_2$/Ar flow ratio of 25 %. After 15 nm (75 s) sputtering the N$_2$ gas flow has been turned off and the Ta has then been deposited without interruption of the sputtering process. The nitrogen concentration in the tantalum nitride thin films has been analyzed by XPS and Rutherford backscattering spectrometry (RBS). XPS has been used for tantalum nitride films produced at N$_2$/Ar flow ratios varying from 10 % to 70 % and RBS for tantalum nitride films produced at flow ratios of 20 %, 25 % and 30 %. XPS spectra were acquired on a Physical Electronics (PHI) Quantum 2000 photoelectron spectrometer using monochromatic Al-K$_\alpha$ radiation ($h\nu = 1486.6$ eV) and a hemispherical capacitor electron-energy analyzer equipped with a channel plate and a position-sensitive table.

<table>
<thead>
<tr>
<th>N$_2$/Ar flow ratio [%]</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate [nm/min]</td>
<td>15.5</td>
<td>14.3</td>
<td>13.0</td>
<td>12.1</td>
<td>11.4</td>
<td>10.7</td>
<td>9.9</td>
<td>9.6</td>
<td>8.6</td>
<td>8.3</td>
</tr>
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</table>

Table 4.1: Flow ratio and the corresponding growth rates of the sputter deposited Ta and tantalum nitride thin films.
detector. The electron take-off angle was 45° and the analyzer was operated in the constant pass energy (23.5 eV) mode for all measurements. The beam diameter was typically 150 µm. Sputter cleaning was performed with Ar ions and the sputter rate was determined on Ta₂O₅ to 6 nm/min at an acceleration energy of 2 kV and 19 nm/min at 4 kV. The nitrogen concentrations measured by XPS have been calculated based on the peak splitting of the N1s/Ta4p3 overlapping peaks. Measurements were taken after 20 s Ar sputtering at 2 kV plus an additional Ar sputtering process at 4 kV for 60 s. The RBS measurements have been performed using a 2 MeV ⁴He beam with a silicon PIN diode detector under 168°. The collected data has been evaluated by the RUMP program [82]. Mechanical hardness measurements have been made with a Triboindenter from Hysitron Inc., Minneapolis, MN, USA, using a Berkovich indenter with radius of curvature R = 150 nm. The indentation depth was kept below 10% of the film thickness to eliminate substrate effects. Indentation tests at each load were repeated at least 16 times and then averaged. Nanoindentation data has been analyzed by the Oliver-Pharr method [83]. Phase analysis was performed by X-ray diffraction (XRD) with an X’Pert Pro diffractometer from PANalytical using Cu-Kα radiation (λ = 1.54 × 10⁻¹⁰ m). Θ-2Θ scans were acquired within a range of 20° to 100°, a 5° offset angle and a step size of 0.0167°. The use of such a 5° offset angle does not lead to diffraction peaks of the Si(100) substrate and facilitates the interpretation of the data.

4.3 Results

4.3.1 Tantalum

Ta has been deposited on DLC, tantalum nitride seed layers, and on Ti and Si(100) substrates which still contained their natural oxide layers. The deposited Ta films have been characterized by XRD and nanoindentation. The XRD data reveals that β-Ta is formed on the amorphous DLC, and on the natural oxide layers of Ti and Si(100) substrates. The diffraction peaks (002) and (004) at 33.6° and 71.0° respectively were present in all β-Ta films (Fig. 4.1a)-(c)). A 15 nm tantalum nitride seed layer, previously deposited on Si(100) and Ti, leads however to the formation of α-Ta, which is indicated by the diffraction peaks (110), (200), (211) and (220) at 38.5°, 55.6°, 69.6° and 82.5° (Fig. 4.1d)-(e)). All diffraction peaks are at slightly lower diffraction angles than the literature values and indicate that the Ta
films are under compressive stress. In all β-Ta films, the (002) and (004) diffraction peaks have been observed and show that this phase is, regardless of the substrate, textured along (002). This observation is in accordance with other investigations performed on β-Ta [84, 85]. The reason for the preferential formation of (002) textured β-Ta is controversially discussed in the literature. Some researchers claim that β-Ta is formed since the stress is lower in β-Ta films than in α-Ta films for film thicknesses smaller than 5 µm [73]. Other theories conclude that the β-Ta is formed because the stable α-Ta requires additional energy to form [86]. The hardness of α- and β-Ta was measured to be $7 \pm 0.8$ GPa and $14.0 \pm 0.6$ GPa respectively. The hardness measurements of β-Ta is in agreement with [87] while the hardness of α-Ta is smaller than the value of 11.6 GPa reported in the literature [88].

**Figure 4.1:** XRD patterns of deposited Ta on (a) Ti, (b) Si(100), (c) DLC, (d) fcc-TaN seed layer on Ti, and (e) fcc-TaN seed layer on Si(100). β-Ta is formed on the natural oxide layers of Ti and Si(100) substrates and on the amorphous DLC. A 15 nm fcc-TaN seed layer on Ti and Si(100) results in the formation of α-Ta. The peaks indicated by s originate from the Ti substrate.
4.3.2 Tantalum Nitride

The reactive sputtered tantalum nitride films, which have been deposited on Ti and Si(100) substrates have been analyzed by XRD, RBS and XPS, and nanoindentation. For a N$_2$/Ar flow ratio of 20% and 30%, the XRD analysis of the reactively formed tantalum nitride reveals face-centered cubic tantalum nitride (fcc-TaN) on Ti as it is indicated by the diffraction peaks (111), (200) and (220) at 35.8°, 41.6° and 60.3° (Fig. 4.2).

![XRD patterns reveal stoichiometric fcc-TaN upon reactive sputtering on Ti for N$_2$/Ar flow ratios of (a) 20% and (b) 30%. The diffraction peaks of (110), (200) and (220) are at lower angles than the literature value and reveal that the fcc-TaN is under compressive stress. The peaks indicated by s originate from the Ti substrate.](image)

**Figure 4.2:** XRD patterns reveal stoichiometric fcc-TaN upon reactive sputtering on Ti for N$_2$/Ar flow ratios of (a) 20% and (b) 30%. The diffraction peaks of (110), (200) and (220) are at lower angles than the literature value and reveal that the fcc-TaN is under compressive stress. The peaks indicated by s originate from the Ti substrate.

For N$_2$/Ar flow ratios of 20% - 70% the same diffraction peaks have been observed on Si(100) (Fig. 4.3b-i)). The diffraction angles for flow ratios >10% are at slightly smaller diffraction angles than the literature values and indicate, as for the pure Ta, that the films are under compressive stress. Above flow ratios of 45%, the relative intensity of the (200) peak becomes stronger than the (110) peak, leading to the conclusion that the fcc-TaN is textured along (100) for flow ratios >45%. Furthermore, for a flow ratio of 10% the diffraction peak is broader and at a higher diffraction angle than for flow ratios >10%. This broadness of the diffraction peak indicates that the tantalum nitride is x-ray amorphous, however, local ordering cannot be excluded.
Figure 4.3: XRD analysis of the reactively formed tantalum nitride on Si(100) reveals (a) amorphous Ta-rich tantalum nitride for a flow ratio of 10%. For flow ratios of 20% - 45% (b-g), stoichiometric fcc-TaN is formed, followed by (100) textured fcc-TaN for flow ratios above 45% (g-i). The diffraction peaks are at lower angles than the literature value and indicate that the films are under compressive stress.

The hardness of the fcc-TaN film increases up to a N₂/Ar flow ratio of 45% to its maximum value of 20.6 ± 0.6 GPa, followed by a decrease in hardness for further increasing flow ratios (Fig. 4.4). For flow ratios from 0% to 20% a linear increase in nitrogen concentration has been measured by XPS. Above a 20% flow ratio, the nitrogen concentration changes only marginally. For flow ratios of 20%, 25% and 30% the RBS measurements indicate a nitrogen concentration of 50 at.%, 52 at.% and 51 at.%, which is a mean factor of 1.95 above the nitrogen concentration measured by XPS. The hardness plotted as function of the nitrogen concentration measured by XPS (inset in Fig. 4.4) reveals a change in hardness although the nitrogen concentration changes only marginally.
4.4 Discussion

4.4.1 Tantalum

$\beta$-Ta was observed on the amorphous DLC, and on the natural oxide layers of Ti and Si(100) substrates, whereas a 15 nm fcc-TaN seed layer leads to the formation of $\alpha$-Ta. The formation of $\alpha$- or $\beta$-Ta on a particular substrate is in the literature often described by epitaxial growth [69–73]. However, the substrates which have been used in this study exhibit amorphous surfaces since DLC is an amorphous network composed of strongly cross-linked carbon atoms, and the natural oxide layers of Ti and Si(100) exhibit an amorphous nature as reported in [89, 90]. Hence, no epitaxial growth can occur due to the absence of long-range order in the amorphous layers.

This work shows therefore that the formation of $\alpha$- and $\beta$-Ta on Ti is sensitive to the existence of a natural oxide layer, since $\alpha$-Ta has been reported on sputter deposited Ti [91] where no oxide layer is present while in this study on Ti with...
a natural oxide layer $\beta$-Ta has been observed. Similar work has been performed by Feinstein on Mo [92]. Feinstein reported $\alpha$-Ta on Mo and $\beta$-Ta on Mo with an oxidized surface. The work of Feinstein [92] and this study on Ti lead to the conclusion that the chemical composition of the topmost layers of the substrate influences the formation of $\alpha$- and $\beta$-Ta.

However, it is possible, by a simple method, to form $\alpha$-Ta on an oxidized surface. The deposition of 15 nm fcc-TaN, as already reported by Gladczuk [93] on steel, leads to the growth of $\alpha$-Ta on Ti and Si(100). The advantage of the deposition of such a seed layer is the simplicity of the process, and it ensures no oxidation at the interface between fcc-TaN and Ta since the transition from fcc-TaN to Ta has been conducted without interrupting the sputtering process.

### 4.4.2 Tantalum Nitride

The formation of fcc-TaN has been observed on Ti for flow ratios of 20\% and 30\% (higher flow ratios have not been tested) and on Si(100) substrates for flow ratios varying from 20\% - 70\%. The nitrogen concentration measured by XPS was lower than measured by RBS, by a factor of 1.95. This may be explained by preferential nitrogen sputtering during the sputter cleaning process prior to the XPS measurement. Preferential sputtering of nitrogen atoms is hence resulting in a nitrogen depletion at the surface. This preferential sputtering of tantalum nitride was also described by Palacio [94] causing a nitrogen depletion which depends on the Ar ion energy. Palacio measured the surface concentrations by Auger electron spectroscopy, however, no quantitative values are given. Analogously to this work, a nitrogen depletion at the surface of tantalum nitrides caused by preferential sputtering is qualitatively reported in [95]. In this work, the XRD data reveal stoichiometric fcc-TaN, which implies a nitrogen concentration of around 50 at.\%

The nitrogen concentration measured by RBS is hence in accordance with the XRD measurements and lead to the conclusion that the nitrogen concentrations determined by XPS measurements is too low by a factor of 0.51.

At a flow ratio of 20\% the XPS measurement reveals a nitrogen concentration of 13.4\%. This value is lower than the nitrogen concentration measured for stoichiometric TaN and indicates that the tantalum nitride is Ta-rich at a flow ratio of 10\%. In addition, the nitrogen concentration increases linearly for flow ratios between 0\% and 20\%. The linearity leads to the assumption that the correction factor is constant for all flow ratios in this regime. Since the correction factor is
1.96 at a flow ratio of 20% this would lead to a nitrogen concentration of 26.1 at.% at a flow ratio of 10%. This value is well below the stoichiometric TaN and leads also to the conclusion that the tantalum nitride is Ta-rich at a flow ratio of 10%. The first stoichiometric fcc-TaN seems then to be reached at a flow ratio of 20%. Upon increasing the N$_2$/Ar flow ratio the following evolution in phase and composition have therefore been observed: Amorphous Ta-rich tantalum nitride at a flow ratio of 10%, followed by fcc-TaN for flow ratios varying from 20% to 45%. Above flow ratios of 45% (100) textured fcc-TaN is formed.

The hardness analysis shows an increase up to a flow ratio of 45% followed by a decrease in hardness for higher flow ratios. This change in hardness can be induced by changes in grain size, stoichiometry, phase, residual stress or the appearance of texture. For flow ratios above 10%, the stoichiometry changes are only marginally and the fcc-TaN phase is present. The drastic changes in hardness are hence not associated by a change in stoichiometry or phase.

The residual stress is influenced by the stoichiometry, phase, film thickness and the deposition conditions. Due to only marginal changes of the stoichiometry and the monophasic behavior for flow ratios >10%, the influence of stoichiometry and phase on the residual stress is assumed to be constant for flow ratios >10%. The same argument holds for the film thickness and the deposition conditions since these parameters have been kept constant for all flow ratios.

In the regime of flow ratios from 20% to 45%, stoichiometry, phase and residual stress and texture do not change significantly and thus, unlike grain size, only have a secondary effect on hardness. The grain size is determined by the broadness of the diffraction peaks and determined by the Debye-Scherrer formula in equation 4.1 with the wavelength $\lambda$, the full width half maximum intensity (FWHM) $\beta$ and the Bragg-angle $\theta$.

$$\text{mean crystal size} = \frac{0.9 \cdot \lambda}{\beta \cdot \cos(\theta)}$$ (4.1)

However, the non-uniform stress in the films influences the broadness of the peaks as well. But since the influence of the residual stress is considered as constant for flow ratios >10% a change in peak broadening is associated with a change in grain size. Such a grain size dependent increase in hardness is often described by the Hall-Petch [96, 97] effect. However, the Hall-Petch relationship is not free of controversy since a substantial deviation from the Hall-Petch relation-
ship has been observed for Fe and Ni over a broad range of grain sizes \cite{98,99}. These findings indicate that the inverse square-root behavior is only applicable over a limited range of grain sizes. The effect of the deviation of inverse square-root behavior in the Hall-Petch effect is described by Meyers and Ashworth, and Fu \cite{100,101}. Meyers and Ashworth consider the material as a composite of continuous grain boundaries and islands of bulk grains with a grain size diameter of \( D \) and a thickness \( t \) of the grain boundary layer. The plasticity within the grains plays a crucial role in the theory of Meyers and Ashworth (see composite system in Fig. 4.5).

![Figure 4.5: Polycrystalline model system with grain diameter \( D \) and grain boundary thickness \( t \). Figure inspired by \cite{101.}

In a ceramic compound such as tantalum nitride, plastic deformation only occurs under high pressure as it is the case during the nanoindentation process. Localized plasticity (micro yielding) occurs by deformation bands and at stresses much lower than the conventional macro yield stress. These deformation bands create stress concentrations at the grain boundaries \cite{102} and form a hardened grain boundary layer with thickness \( t \). At the macro yield stress the bulk of the grains undergo plastic deformation. For the case under investigation Meyers and Ashworth consider the grain boundary layer with yield stress \( \sigma_{GB} \) and the grains with yield stress \( \sigma_{Grain} \). By taking into consideration the composite formed by grain boundaries and island of bulk grains, the flow stress is then given by equation \ref{eq:4.2} where \( A \) and \( B \) represent the area fractions of the grains and the grain boundary network. The fcc-TaN is formed by such a composite since it is a polycrystalline aggregate with grain boundaries and island of bulk grains.

\[
\sigma_{Yield} = A \cdot \sigma_{Grain} + B \cdot \sigma_{GB}
\] (4.2)
If the area fractions $A$ and $B$ are substituted by the grain diameter $D$ and the thickness $t$ of the grain boundary layer, the yield stress is given by equation 4.3, where $\alpha$ and $\beta$ are constants given by the geometry of the grains.

$$\sigma_{\text{Yield}} = \sigma_{\text{Grain}} + \alpha \cdot t \cdot D^{-1} \cdot [\sigma_{\text{Grain}} - \sigma_{\text{GB}}] - \beta \cdot t^2 \cdot D^{-2} \cdot [\sigma_{\text{Grain}} - \sigma_{\text{GB}}] \quad (4.3)$$

For spherical grains, this equation predicts $\sigma_{\text{Yield}} = \sigma_{\text{Grain}}$ for very large grains (since $D^{-2}$ is much smaller than $D^{-1}$) and $\sigma_{\text{Yield}} = \sigma_{\text{GB}}$ if $D = 2 \cdot t$ (e.g. the whole material is grain boundary layer). However, when the grain size decreases the $D^{-2}$ term becomes more important and the equation deviates from the classical Hall-Petch relationship and approaches finally $\sigma_{\text{GB}}$.

Meyers and Ashworth consider the grain boundary layer $t$ as function of $D$ ($t = k \cdot D^{1/2}$), meaning that at small grain sizes, the grain boundary layer $t$ increases rapidly with grain diameter and at large grain sizes this dependency becomes smaller. Substituting $t$ as function of $D$ in equation 4.3 one arrives at the following relationship:

$$\sigma_{\text{Yield}} = \sigma_{\text{Grain}} + \alpha \cdot k \cdot D^{-1/2} \cdot [\sigma_{\text{Grain}} - \sigma_{\text{GB}}] - \beta \cdot k^2 \cdot D^{-1} \cdot [\sigma_{\text{Grain}} - \sigma_{\text{GB}}] \quad (4.4)$$

This equation predicts a $D^{-1/2}$ (Hall-Petch) relationship for large grain sizes. For decreasing grain sizes the $D^{-1}$ term becomes more and more dominant. In order to verify the correlation of the Hall-Petch relationship and the Meyers and Ashworth relationship the increase in hardness $H$, which has been observed for flow ratios varying from 20% to 45%, have been plotted as function of the grain size $D$ (Fig. 4.6). The data set has then been fitted by a Hall-Petch relationship $H = H_0 + a \cdot D^{-1/2}$ and a Meyers and Ashworth relationship $H = H_0 + b \cdot D^{-1/2} + c \cdot D^{-1}$ with $H_0 = 3.6$ GPa as it has been determined for TaN grain sizes >250 µm [103]. The fit of the Hall-Petch relationship correlates with $R^2 = 0.76$ and the fit of the Meyers and Ashworth relationship correlates with $R^2 = 0.98$.

The strong correlation of the Meyers and Ashworth relationship supports this theory and leads to the conclusion that the hardening behavior for nanocrystalline materials can no longer be explained by the Hall-Petch relationship.
For flow ratios >45%, the fcc-TaN films are (100) textured. The hardness of a textured material is usually higher compared to a non-textured material [104]. However, this study reveals a contradictory behavior. Since the grain sizes are below 10 nm for flow ratios >45%, the hardness evolution seems to follow an inverse Hall-Petch behavior, where the deformation process is dominated by grain boundary sliding [105].

4.5 Conclusion

- The effect of the underlying substrate on the Ta phase and the influence of a changing N₂/Ar flow ratio on hardness, phase and composition of reactively formed tantalum nitride have been investigated. The study on Ta has shown that the chemical composition of the topmost layers needs to be considered to explain the formation of α- or β-Ta on a particular substrate. By the deposition of a 15 nm fcc-TaN seed layer, a simple process is presented to form α-Ta on the natural oxide layers of Ti and Si(100).
• For the reactively formed tantalum nitride thin films amorphous Ta rich tantalum nitride has been observed at a flow ratio of 10%, followed by fcc-TaN for flow ratios varying from 20% to 45%.

• Above a flow ratio of 45% (100) textured fcc-TaN is formed. The increase in hardness for flow ratios between 20% and 45% is associated with the decrease in grain size and shows a stronger correlation for the Meyers and Ashworth relationship than for the Hall-Petch relationship. It can hence be concluded that the hardening effect for nanocrystalline materials can no longer be explained by the Hall-Petch relationship.
Chapter 5

Controlling Cohesive & Adhesive Failure and Contact Damage of DLC Coated Ti Substrates by the Ta Interlayer Phase

During service life and processing DLC sliding partners are subject to contact damage and cohesive and adhesive failure which may limit their lifetime. From the results in chapter 2 (cohesive and adhesive failure) and 3 (contact damage) a DLC film thickness optimization process was deduced and showed that a high fracture strength of the DLC film and a high resistance to plastic deformation of the substrate upon indentation cannot be achieved simultaneously with an ideal DLC film thickness.

To combine these properties, the approach in this chapter, is the use of a suitable interlayer combination which is deposited between the Ti substrate and the DLC film. However, not only the interlayer material but also its structure (e.g. phase) can influence the mechanical properties of the interlayer combination and can thereby affect the cohesive and adhesive failure and contact damage. Hence, the effect of the phase of the interlayer material on these failure mechanisms requires a systematic investigation and a qualitative description. With the method presented in chapter 4 to trigger and to fully control the Ta phase on Ti substrates and the experimental setups from chapters 2 and 3 such an investigation is now feasible and presented hereafter.
With this analysis the thesis provides a solid basis about the influence of film thickness and interlayer structure on the cohesive and adhesive failure and contact damage of DLC coated Ti substrates. It will then be possible to further develop long-lasting DLC coated Ti substrates with a suitable interlayer combination which is resistant to these failure mechanisms.

5.1 Interlayers in DLC Coated Systems

The reduction of the high intrinsic stress of DLC films as well as the use of adhesion promoters have drawn the attention of several researchers in the past. A common direction is to use interlayers deposited between the substrate and the DLC film to reduce stress concentrations. The inclusion of ductile metals in the DLC to form a nanocomposite (acting as crack blunting centers) or multi- or graded layers have shown to reduce stress in the DLC [106–109].

To increase the adhesive strength Cr and Si containing adhesion layers and an adjacent ramp layer have led to well-adhering DLC on steel substrates [24, 25] as it was reported in chapter 1.

Although stress-reduction and adhesion-promoting interlayers are already applied in industrial applications, knowledge on the effect of the interlayer material structure (e.g. phase) and its consequences on the failure behavior of DLC coated substrates is lacking. Ta as interlayer material is perfectly suited for this study as \(\alpha\)-Ta is more ductile and softer compared to the hard and brittle \(\beta\)-Ta. Hence, in this study DLC coated Ti substrates with \(\alpha\)- or \(\beta\)-Ta interlayers were investigated (from now on called \(\alpha\)-Ta/DLC and \(\beta\)-Ta/DLC).

5.2 Experimental Details

The \(\alpha\)-Ta/DLC and \(\beta\)-Ta/DLC samples consist of 500 nm Ta interlayer and a 500 nm DLC film deposited on the interlayer. Additionally, a 1 \(\mu\)m thick DLC film was deposited on a Ti substrate without a Ta interlayer and is used as a reference sample for contact damage analysis.

The sample preparation as well as the experimental setups for the cohesive and adhesive failure and contact damage is based on chapters 2-4. Prior to the depo-
sition process the Ti substrates (for the analysis of the cohesive and adhesive fail-
ure, the Ti substrates were laser-cut dogbone-shaped) were ground and polished
to a surface roughness of 3 nm according to the polishing procedure in table 2.1
in chapter 2. To deposit $\alpha$-Ta and $\beta$-Ta two different routines were performed:
For $\alpha$-Ta a 15 nm stoichiometric TaN seed layer was deposited with a $N_2/Ar$ flow
ratio of 25% on the previously sputter cleaned Ti surface as described in chapter
4. Without interrupting the sputtering process the $N_2$ flow was turned off which
then results in $\alpha$-Ta. Since $\beta$-Ta grows on a natural Ti surface comprising of a thin
surface oxide layer, the Ti was sputter cleaned for only a few minutes and the Ta
was deposited without a seed layer according to the procedure in the previous
chapter and reported in [110]. After growing the Ta layer the DLC was deposited
on top without interrupting the sputtering process to ensure well-defined and
contamination-free interfaces. The DLC was deposited by PACVD with an RF
self-bias of $-600$ V and acetylene ($C_2H_2$) as precursor gas (see chapter 2 for more
details). For the reference sample the procedure of the Ta-interlayer deposition
was omitted.

To analyze cohesive and adhesive failure of $\alpha$-Ta/DLC and $\beta$-Ta/DLC the coated
dogbone-shaped Ti substrates were tested by uniaxial loading with a microtensile
machine and an applied strain rate of $5 \times 10^{-5}$/s until fracture of the Ti substrate.

By using the program Spotfinder [40] the onset strains of fragmentation and de-
lamination were determined. Contact damage was induced by microindentation
with a 10 $\mu$m spherical diamond indenter, a loading and unloading rate of 1 mN/s
and a peak holding time of 5 s. The surface damage and cross sections from the
indents were then analyzed by a Helios Nanolab 600i FIB. For the cross sectional
analysis a 30 kV gallium ion beam was used for milling.

Composition measurement and energy dispersive X-ray spectroscopy (EDX) mapp-
ings were carried out using a Zeiss LEO 1530 with a Thermo Scientific UltraDry
II EDX detector. The SEM was operated at 5 kV in high-current mode and the
sample was positioned at 10 mm working distance (take-off angle 35°). Image ac-
quision was done using the in-lens (SE) detector. The 60 $\mu$m aperture was used
for the mappings, for which 50 frames of 256 x 192 pixels were collected with 10 s
acquisition time per frame. The image pixel size in the mappings was 0.2 - 1.2 $\mu$m.
The Ta-M, Ti-L, O-K and C-K lines were selected for the mappings. Quantifica-
tion of the spectra was carried out in the NSS 3 software (Thermo Scientific) using
Gaussian peak fits and PROZA (Phi-Rho-Z) correction.
5.3 Results

5.3.1 Cohesive and Adhesive Failure

The onset strains of fragmentation (cohesive failure in the DLC film) and delamination (adhesive failure) were determined from the uniaxial loading experiments and are shown in Fig. 5.1. The data points for the 500 nm and 1 µm DLC on Ti, where no interlayer was applied, are taken from Fig. 2.5 in chapter 2 and are shown only for comparison. The onset strain of fragmentation of α-Ta/DLC is very similar to the onset strain of fragmentation of a 500 nm DLC on Ti. The adhesive failure analysis reveals that the application of a Ta interlayer results in a decreased onset strain of delamination compared to DLC on Ti. For β-Ta/DLC an even lower onset strain of delamination is observed than for α-Ta/DLC.

![Onset strain of fragmentation (cohesive failure) and delamination (adhesive failure) for α-Ta/DLC and β-Ta/DLC. The values for 500 nm DLC and 1 µm DLC (DLC is deposited on Ti without interlayer) are taken from Fig. 2.5 in chapter 2. The total deposited thickness of α-Ta/DLC and β-Ta/DLC is 1 µm.](image)

The EDX distribution presented in Fig. 5.2 (obtained after fracture of the Ti substrate), shows a high Ti content at the patches as well as a strong carbon signal at the location where the DLC film is still adhering for α-Ta/DLC and β-Ta/DLC.
**Figure 5.2:** Secondary electron microscope (SEM) images (top) and EDX spectra (denoted as Carbon, Tantalum and Titanium) for the systems $\alpha$-Ta/DLC and $\beta$-Ta/DLC. For both systems the Ti and carbon distribution is strong at the area of the patches respectively at the location where the DLC film is still adhering. For $\beta$-Ta/DLC an increased Ta distribution was measured at the patches which was no the case for $\alpha$-Ta/DLC. Bottom: Schematic of a patch for $\alpha$-Ta/DLC and $\beta$-Ta/DLC (not in scale model).
However, at the patches of the $\beta$-Ta/DLC film a weak Ta signal was measured, while for $\alpha$-Ta/DLC the Ta signal showed no increase at the patches. It can therefore be concluded that in $\alpha$-Ta/DLC the delamination occurs along the Ti-TaN interface while in $\beta$-Ta/DLC delamination occurs within the $\beta$-Ta layer so that $\beta$-Ta is still present after delamination. The schematics of the expected morphology after patch formation of $\alpha$-Ta/DLC and $\beta$-Ta/DLC are additionally shown in Fig. 5.2 on the bottom.

5.3.2 Contact Damage

The top view of the created contact damage in the systems $\alpha$-Ta/DLC, $\beta$-Ta/DLC and 1 $\mu$m DLC at loads of 300 mN and 500 mN are shown in Fig. 5.3. The overall damage is reduced in $\alpha$-Ta/DLC compared to $\beta$-Ta/DLC and 1 $\mu$m DLC on Ti. In particular, the number of circumferential cracks is lower and the cracks are smoother which is visible at a load of 500 mN. The damage in the inner zone of the indent is much more pronounced for the systems $\beta$-Ta interlayer and 1 $\mu$m DLC compared to the $\alpha$-Ta/DLC.

![Figure 5.3: Contact damage top view of the systems 1 $\mu$m DLC, $\alpha$-Ta/DLC and $\beta$-Ta/DLC at loads of 300 mN and 500 mN. For $\alpha$-Ta/DLC the contact damage is smoother and the number of circumferential cracks is lower compared to $\beta$-Ta/DLC and 1 $\mu$m DLC.](image)

The corresponding FIB cross sections from the top views are displayed in Fig. 5.4 (taken from the center of the indents). The cross section analysis reveals that the cracks in $\beta$-Ta/DLC nucleated at the Ti-Ta interface and propagate through the $\beta$-Ta layer into the DLC while for $\alpha$-Ta/DLC crack nucleation occurs at the Ta-DLC interface as it is visible at a load of 300 mN. For the 1 $\mu$m DLC film the
cracks were initiated at the Ti-DLC interface. In the α-Ta/DLC system, the DLC film gets additionally pressed into the plastically deformable α-Ta layer. Such an imprinting was, however, not observed in the other two systems.

![Cross-sectional analysis of the indents in Fig. 5.3 (taken from the center of the indent). In β-Ta/DLC and 1 μm DLC the cracks nucleate at the interface Ti-Ta respectively Ti-DLC while for α-Ta/DLC the cracks are initiated at the interface Ta-DLC. With increasing load crack growth occurs.](image)

### 5.4 Discussion

The weakest layer determines the cohesive failure, which is the layer where the fracture strength is exceeded first. Since the β-Ta/DLC system, which also consists of a 500 nm DLC film fails at a lower onset strain of fragmentation than 500 nm DLC on Ti, it can be concluded that the weakest part in the β-Ta/DLC system is the β-Ta interlayer. If, however, the onset strain of fragmentation of α-Ta/DLC is compared with 500 nm DLC on Ti it appears that the values are very close. Thus, in the α-Ta/DLC system the DLC film fails first and is therefore the limiting factor for the onset strain of fragmentation. From this observation, it can be deduced that the onset strain of fragmentation respectively the fracture strength of a β-Ta layer is lower compared to a α-Ta layer at equivalent film thicknesses. This observation is in accordance with [34]. The reason behind this phenomenon is the difference in crystallographic unit cells of α- and β-Ta: α-Ta, which is present in the ductile bcc unit cell deforms plastically prior to crack formation while the tetragonal β-Ta is brittle and has therefore only limited ability for plastic deformation.
As the weakest layer determines the cohesive failure, adhesive failure is governed by the weakest interface. To understand the difference in onset strain of delamination in Fig. 5.1 the following four interfaces need to be distinguished:

- Ti-DLC (for 500 nm/1 µm DLC on Ti)
- Ta-DLC (for α-Ta/DLC and β-Ta/DLC)
- Ti-TaN and TaN-Ta (for α-Ta/DLC)
- Ti-Ta respectively Ti oxide-Ta (for β-Ta/DLC)

Upon depositing DLC on a carbide-forming metallic substrate an approximately 5 nm thick metal-carbide is formed, as it was shown for TiAlV and CoCrMo substrates [8, 9, 52] (see chapter 1). Thus, at the Ti-DLC interface a Ti carbide is present. Since Ta is also a carbide-forming metal a thin Ta carbide layer is likely to be formed at the Ta-DLC interface. At the Ti-TaN and Ti-Ta interfaces, a few nanometer thick diffusion zone is present as Ti and Ta are miscible [111]. The interface TaN-Ta is formed upon epitaxial growth [70, 71, 73].

In β-Ta/DLC, the weakest interface is the Ti-Ta diffusion zone as Ta carbides are very strong. Hence, crack nucleation is expected to occur at the Ti-Ta interface. Due to the ductile behavior of the Ti substrate the crack tip gets blunted (i.e. reduction of stress intensity at the crack tip because of the plastic deformation of materials nearby [48]). This crack tip blunting results in an increased resistance to crack propagation. However, a deviation of the crack tip into the brittle β-Ta layer decreases this resistance and facilitates crack propagation. Hence, cracking is initiated at the Ti-Ta interface and due to deviation of the crack tip the crack will then propagate in the β-Ta layer. A remaining Ta layer is therefore present after patch formation and measurable by EDX in the β-Ta/DLC system as shown in Fig. 5.2. Since the crack tip propagates along the direction where the lowest stress intensity is needed for crack growth it is expected that a hillock formation occurs, and island of Ta remain on the Ti substrate after delamination (Fig. 5.2 β-Ta/DLC scheme).

From EDX analysis of the α-Ta/DLC system, it can be concluded that patch formation occurs along the few nanometer thick Ti-TaN diffusion zone, as no Ta is measured at the patches. Hence, in the α-Ta/DLC system the Ti-TaN interface is the weakest. However, as described in the β-Ta/DLC system, a deviation of the crack tip, is assumed to be unfeasible as any deviation into the ductile Ti or
$\alpha$-Ta layer would effectively blunt the crack tip and consumes energy by plastic deformation. Subsequently it increases the effective fracture toughness.

Note that the presence of the Ti as well as the close vicinity of the ductile $\alpha$-Ta layer also blunts the crack tip at the Ti-TaN interface and reduces the stress intensity at the crack tip (see e.g. [48]). This effect effectively increases the onset strain of delamination of $\alpha$-Ta/DLC.

It can therefore be concluded that the reason for the difference in onset strain of delamination of the $\alpha$-Ta/DLC and $\beta$-Ta/DLC systems is because of the energy absorption of the plastically deformable $\alpha$-Ta layer as well as due crack tip blunting and the resulting reduction of the stress intensity at the crack tip. Thus, the stress intensity required to separate the interfaces is higher in the $\alpha$-Ta/DLC system compared to the $\beta$-Ta/DLC system which then results in a difference in the onset strain of delamination.

The influence of the ductility can also be observed in the contact damage analysis. Due to the plastically deformed $\alpha$-Ta, unlike the $\beta$-Ta/DLC system, cracks were initiated at the Ta-DLC interface, which significantly increases the resistance to crack nucleation and contact damage. Thus, not only the composition of the interlayer, but also its structure is key to understand and control cohesive and adhesive failure and contact damage.

5.5 Conclusion

- The influence of $\alpha$-Ta and $\beta$-Ta interlayers on the contact damage and the cohesive and adhesive failure of DLC coated Ti substrates is investigated. The more ductile $\alpha$-interlayer showed improved results in all investigated cases compared to the brittle $\beta$-Ta. Due to plastic deformation of the $\alpha$-Ta interlayer the resistance to contact damage is significantly enhanced.

- In $\alpha$-Ta/DLC delamination occurs along the Ti-TaN interface (as the $\alpha$-Ta is produced with a TaN seed layer) while in $\beta$-Ta/DLC the crack propagates through the $\beta$-Ta interlayer. Thus, in the $\beta$-Ta/DLC system $\beta$-Ta remains on the Ti after patch formation.
5.6 Appendix: Influence of the Interlayer Elastic Modulus on the Stress Distribution during Indentation

In chapter 3 the influence of the DLC film thickness on the stress distribution upon contact damage is shown. By using interlayers between the Ti substrate and the DLC film the maximum stress state and stress distribution can change. Hence, it is necessary to determine the influence of the interlayer elastic modulus ($Y_{int}$) on the stress distribution upon contact damage creation. The stress distribution was determined by FEA with the modeling software Comsol® (version 4.3). Interlayer and DLC film thicknesses of 500 nm and 1 µm respectively were used for the FEA-simulation. The Young’s moduli of the interlayers were chosen to be 80 GPa (lower than the Young’s moduli of Ti and DLC), 150 GPa (of the order of the Young’s modulus of DLC), and 220 GPa (higher than the Young’s moduli of Ti and DLC). On applying loads of 200 mN the substrate, interlayer and DLC deformed elastically and radial stresses were extracted by the procedure outlined in chapter 3. The corresponding radial stress distribution (Fig. 5.5) shows that the location of stress concentrations varies depending on the value of $Y_{int}$ (indicated by arrows): In the case of $Y_{int} = 80$ GPa, the stress concentration occurred at the interlayer-DLC interface. If, however, the Young’s modulus of the interlayer has a value of 220 GPa the stress concentration is at the substrate-interlayer interface. For $Y_{int} = 150$ GPa the stress is distributed over the two interfaces.

The stress distribution with FEA shows that the Young’s modulus of the interlayer material can remarkably reduce stress concentrations if $Y_{int}$ is of the order of $Y_{DLC}$. Multilayers could therefore be a suitable way to further reduce stress concentrations and increase the resistance to contact damage creation.
FIGURE 5.5: Radial stress distribution simulated by static FEA for 500 nm thick interlayers with Young’s moduli of 80 GPa (top), 150 GPa (center) and 220 GPa (bottom) and a 1 µm DLC film at a load of 200 mN. For a Young’s modulus of 80 GPa the stress concentration is at the interlayer-DLC interface whereas for a Young’s modulus of 220 GPa the stress concentration is at the substrate-interlayer interface. For a Young’s modulus of 150 GPa the stress is distributed over the two interfaces.
Chapter 6

General Conclusion and Outlook

Throughout this thesis a variety of different methods and techniques were used to understand the cohesive and adhesive failure and contact damage of DLC coated Ti substrates. The major achievements are presented in the General Conclusion and for the remaining open questions further investigations necessary are provided in the Outlook.

6.1 General Conclusion

In this thesis, the cohesive and adhesive failure and contact damage of DLC coated Ti substrates was analyzed by varying the thickness of the DLC film and incorporating the substrate and interlayer plasticity. The cohesive and adhesive failure of the film-substrate system was studied by uniaxial loading while the contact damage investigation was studied using microindentation and static FEA.

From the uniaxial loading experiments the energy release rates for cohesive and adhesive failure were quantitatively determined to be $63.5 \pm 2.6 \text{ J/m}^2$ and $579 \pm 20 \text{ J/m}^2$ respectively. The fracture toughness $K_{IC}$ of the DLC film was determined to be $3.2 \pm 0.1 \text{ MPa m}^{1/2}$. A significant increase in fracture strength and onset strain of delamination was observed for DLC films $<1 \mu\text{m}$. This shows that in this thickness regime the mechanical properties of the DLC films undergo a transition (i.e. a film thickness size effect).

The contact damage analysis provided a failure plot. By using this failure plot
the location of first failure in the DLC film can be deduced. First failure occurs predominately at the edge of the indentation, however, for very thin DLC films the location of first failure is defect controlled due to their membrane-like deformation behavior.

Based on this failure plot four distinct zones were identified where failure in DLC and Ti is present respectively where it is absent. The distribution of these zones depends on the elastic-plastic deformation behavior of the substrate, as well as on the film thickness and the fracture toughness of the DLC film.

The presented work on the cohesive and adhesive failure and contact damage analysis reveals that the fracture strength and onset strain of delamination increases with decreasing film thickness while the substrate yielding is prevented by an increasing DLC film thickness. To combine a high DLC fracture strength with the absence of plastic deformation of the substrate upon indentation a compromise in DLC film thickness needs to be made. This compromise results in a film thickness optimization process for applications of DLC coated ductile metallic substrates.

An option to combine high fracture strength of the DLC and the absence of plastic deformation of the substrate upon contact damage creation is the use of suitable interlayers which are deposited between the DLC film and the Ti substrate. The influence of material structure such as the phase of the interlayer on the cohesive and adhesive failure and the contact damage was analyzed with Ta interlayers in its ductile bcc $\alpha$-phase and in its brittle tetragonal $\beta$-phase. To deposit Ta in its desired phase on Ti substrates a deposition method using a reactively sputter deposited TaN seed layer was developed. With the application of such a 15 nm TaN seed layer on Ti substrates Ta always grows in its $\alpha$-phase. If, however, no TaN seed layer is applied $\beta$-Ta is formed on the natural oxide layer of Ti. The underlying study showed that, besides epitaxy, the surface chemistry of the base material influences the growth of Ta phases.

With this deposition method DLC coated Ti substrates with $\alpha$ and $\beta$-Ta interlayers were produced and the effect of the Ta phase on the adhesive and cohesive failure and contact damage was analyzed by uniaxial loading and microindentation. It was shown that the ductile $\alpha$-Ta interlayer significantly increases the resistance to contact damage. However, the introduction of Ta interlayers does not increase the fracture strength and onset strain of delamination.

The presented work of this thesis is not exclusively related to DLC films on Ti
substrates. The concepts, investigations, and methods presented in this thesis can be adapted to any other hard layer deposited on soft and ductile metallic substrates. Hence, profound insights into the mechanical failure behavior of a system comprising a hard single layer on a ductile metallic substrate can be deduced from this thesis. In addition, the thesis shows the implications of film thickness and interlayer material structures in the coating technology where high fracture strengths, high onset strains of delamination and a high resistance to deformation of the substrate is needed simultaneously. Such requirements are typically the case in frictional contacts and therefore applicable to moving implants, engines components, bearings, and even tools.

With the knowledge gained in this thesis a solid basis is provided to develop in the future a more damage tolerant and long-lasting system consisting of a ductile metallic substrate, a suitable interlayer combination and an ideal DLC film thickness. To achieve this goal further research is needed and is presented in the Outlook.

6.2 Outlook

To achieve the goal of long-lasting and damage tolerant DLC coated ductile metallic substrates fundamental research on mechanics and materials as well as research on the development of suitable interlayer combinations is needed. The first part of this outlook focuses on mechanics and materials, while the second part focuses on the development of interlayer combinations.

6.2.1 Mechanics and Materials

To increase the lifetime of a system the prediction of failure is essential. This requires a detailed understanding of the deformation mechanisms and the mechanical integrity of the system, of each individual layer and of the interaction of the layers. Further knowledge in the mechanical stability of the DLC and the materials used in an interlayer combination is needed. To acquire this detailed understanding the following 4 research topics are proposed:

Dynamic FEA: Static FEA, which was used in this thesis, revealed the location of first failure in the DLC upon contact damage creation. With the use of dynamic
FEA, where crack formation and crack growing is implemented, a detailed understanding of the final stress distribution, crack pattern and crack morphology would be provided. Furthermore, areas with high and low stress can be modeled on an applied level and would deliver information for the development of suitable interlayer combinations.

**Stress intensity:** To determine crack propagation within a layer or at the interface of two layers the stress intensity is a key parameter which needs to be known. The determination is of particular interest if ductile phases or ductile materials are present because they may alter the geometry at the crack tip which affects the stress intensity and the resulting crack growth. The expected crack blunting behavior through a ductile phase is a very complex phenomenon and needs to be modeled by FEA as it was shown by Lane [48].

**Stress distribution:** The stress distribution and stress evolution in the interlayer material and the DLC upon uniaxial loading is currently not known. The stress distribution in the interlayer material can be analyzed by an in-situ uniaxial loading experiment with a high power x-ray source which would be accessible at a synchrotron facility. To analyze the stress depth profile in the interlayer and substrate material a 2 dimensional parallel x-ray beam [112] would provide knowledge of the location where high stresses could be expected and failure is prone to happen and areas where low stresses are present. An option to analyze the stress evolution upon deformation in the DLC film is Raman spectroscopy since DLC is a Raman active material. A peak shift of the Raman spectrum can then be correlated to the strain in the DLC film as it has been performed for other materials like Si [113] and for the determination of the residual stress of DLC [114].

**Materials:** To gain further knowledge into the failure mechanisms of DLC films the effect of shear stress, shock absorption, fatigue and aging also need to be investigated. Such an aging effect was reported by Bull [115] with a decreased Young’s modulus over time for a slightly different DLC than the one used in this study. The phase of the interlayer material has shown an effect on the cohesive and adhesive failure and contact damage. To get a full understanding of interlayer material parameters which affect failure the influence of texture, hardness, Young’s modulus, grain size and residual stress needs to be analyzed.

An important analysis is the stress field in the Ti substrate and interlayer material upon repeated frictional sliding on the surface. If a single sliding event creates a dislocation, repeated frictional sliding will result in dislocation pile-ups. These
dislocation pile-ups will create a stress field (backstress) which hinders sooner or later the nucleation and movement of newly formed dislocations. It is assumed that the backstress increases with an increasing number of sliding events and may lead to failure of the DLC film upon repeated frictional sliding. The evolution of the backstress as function of the applied pressure, sliding numbers, DLC film thickness, materials combination and material structures is hence essential to know.

### 6.2.2 Interlayer Combinations

In all industrial applications the occurrence of cracks and other defects are inevitable over time and therefore the system consisting of substrate, interlayer and DLC film needs to be optimized towards damage tolerance. An important task towards this goal is to design a system with a suitable interlayer combination to minimize crack nucleation and crack growth. The following 5 interlayer combinations are promising:

**Phase transformation:** Tolerance against crack propagation can be achieved by phase transformation as it has been shown by CrN/AlN multilayers [116]. The metastable cubic-AlN undergoes a strain induced phase transformation to the stable wurtzite-AlN which goes along with a volume increase. The volume increase at the crack tip hinders the propagation of the crack effectively by absorbing energy, or by deflecting or even stopping the crack [116]. Other examples of such strain-induced phase transformation are polycrystalline yttrium-stabilized tetragonal zirconia (Y-TZP) which exhibits excellent flexural strength and a high fracture toughness [117].

**Gradient structure:** Interfaces between the individual layers have shown to be critical for crack nucleation and crack propagation (i.e. delamination). These failure mechanisms are due to abrupt changes in mechanical properties or poor adhesion between the layers. An interlayer combination which does not show such an abrupt change at the interface is a gradient structure where a gradual transition from the substrate to the film material is deposited (e.g. in the case of Ti substrates a co-sputtering process of Ti and DLC where the Ti deposition rate is gradually decreased and the DLC deposition rate is gradually increased). Such a gradient structure does not create strain misfits. The gradual variation also ensures no abrupt change in chemistry. Furthermore, the absence of boundaries effectively reduces stress concentrations. These three effects reduce the risk for
cohesive and adhesive failure.

**Multilayers:** To achieve an interlayer which is hard and ductile, multilayers made out of alternating structure of ductile and hard layers is promising. Ductile materials such as face-centered cubic (fcc) metals show pronounced ability to stop crack growing as the crack tip gets blunted, while the hard layers protect the substrate from yielding upon contact damage creation.

**Nanocrystalline metals:** The beneficial properties of nanocrystalline metals are high yield and high fracture strength. However, they show a reduced elongation and toughness. Therefore a combination of nanocrystalline and microcrystalline layers could be a suitable interlayer combination. Due to their higher yield and fracture strength the nanocrystalline layers should be located at areas where failure is prone to happen, while the microcrystalline layers increase the toughness and reduce crack growth [118].

**Surface treatment:** The thesis has shown that contact damage is prone to happen if the substrate is ductile. An option to get rid of this ductility issue is to harden the topmost microns of the substrate material by a surface treatment (e.g. shot-peening). With this surface treatment a harder substrate surface is employed which should diminish contact damage creation significantly. The advantage of this method is that no interlayer needs to be deposited. In addition, if the substrate material is harder the dilemma of a too thick or too thin DLC film as presented in chapter 3 does not exist anymore and as consequence the DLC film thickness could be reduced to increase the fracture strength of the DLC film.

### 6.3 Final Remarks

To justify whether the proposed interlayer combinations are suitable candidates for future applications, their effect on mechanical failure needs to be tested individually. Gradient structures and multilayers can be deposited by magnetron sputtering which allows processing in the same deposition chamber as the PACVD produced DLC film. Hence, with this deposition process, well-defined and contamination-free interfaces can be ensured. As compared to multilayers, gradient structures would be advantageous as discontinuous interfaces, which are prone to crack nucleation, can be eliminated. However, if a crack nucleates in a gradient structure, catastrophic failure may occur as crack growth cannot be stopped (i.e. low damage tolerance).
Multilayers can solve this problem as they intrinsically allow for the combination of different materials and material structures. This makes it possible to adapt and design the properties of the interlayer combination for the specific needs of an application. With this unique flexibility in design several requirements demanded of the film and the substrate system (e.g. high strength, high resistance to plastic deformation upon contact damage creation, high adhesive strength between the individual layers, damage tolerance) can be met.

Due to this enormous potential multilayers seem to be the most promising interlayer combination for applications. Thus, in the case presented in this thesis where long-lasting DLC coated Ti substrates simultaneously exhibiting high resistance to cohesive and adhesive failure as well as contact damage, a sandwich-like structure composed of a combination of crack-stopping and energy absorbing layers (e.g. by phase transformation or fcc metals) which are embedded in hard and stiff layers are a suitable option. In such an interlayer combination, the hard layers shield the substrate from plastic deformation upon contact damage creation while the ductile layers hinder crack propagation and therefore increase the resistance to cohesive and adhesive failure.
Bibliography


Declaration

The outcome of this thesis was accomplished by collaborations between several people. In this section, each person who has contributed is listed in alphabetic order.

**Best James** is Post-Doc at EMPA Thun. He performed the microindentation in chapter 5.

**Döbeli Max** is a research associate in the laboratory for Ion Beam Physics at ETH Zurich. He conducted the RBS measurements in chapter 4.

**Gerberich William** is a professor at the University of Minnesota (MN, USA). He contributed to the quantitative determination of the cohesive and adhesive failure in chapter 2.

**Hauert Roland** is a senior scientist at EMPA Dübendorf and was the principal investigator of the project. His ideas and inputs contributed to the chapters 2-6.

**Häfliger Kathrin** is a former student at Materials Science Department at ETH Zurich and conducted a Master-project under my supervision. She contributed to chapter 2.

**Jäger Dominik** is a former PhD student at EMPA Dübendorf. He assisted with the deposition of the DLC films during the maternity leave of Kerstin Thorwarth.

**Muff Daniel** is a PhD student in the Laboratory for Nanometallurgy. He designed the dogbone-shaped Ti substrates which were used in chapter 2 and 5.
Müller Ulrich is senior scientist at EMPA Dübendorf. He conducted the XPS analysis in chapter 4.

Müller Claudia is a former PhD student in the Laboratory for Nanometallurgy. She performed EDX measurements for chapter 5.

Raghavan Rejin is a former scientist at EMPA Thun. He performed the microindentation in chapter 3.

Rico Adrian is student at the Materials Science Department at ETH Zurich and performed his Bachelor-Thesis under my supervision. He contributed to chapter 5.

Schwarzenberger Michael is a former student at the Materials Science Department at ETH Zurich and carried out his Bachelor-Thesis under my supervision. His work contributed to chapter 4.

Spolenak Ralph is the head of the Laboratory for Nanometallurgy at ETH Zurich and supervised the PhD thesis. His ideas and inputs contributed to the chapters 2-6.

Süess Martin is a former PhD student in the Laboratory for Nanometallurgy at ETH Zurich. He carried out FIB cross sections for chapter 3 and 5.

Thorwarth Götz is a former senior development engineer at DePuy Synthes. His ideas and inputs contributed to the chapters 2-6.

Thorwarth Kerstin is a research associate at EMPA Dübendorf. She assisted with the deposition of the DLC films. Additionally, her ideas and inputs contributed to the chapters 2-6.
Vüllers Franz is a PhD student in the Laboratory for Nanometallurgy. He performed EDX measurements for chapter 5.

Wyss Andreas is a PhD student in the Laboratory for Nanometallurgy. He performed a Master-project and his Master-thesis under my supervision and contributed to the chapters 3, 5 and 6. He developed and carried out the FEA simulation in chapter 3 and 5.

Zou Yu is a PhD student in the Laboratory for Nanometallurgy. He carried out FIB cross sections for chapter 5.
Curriculum Vitae

Personal

Name               Daniel Bernoulli
Date of Birth      March 14th 1986
Nationality        Swiss

Education


10/2010            MSc EPF in Materials Science and Engineering

09/2008–02/2010    Joint master in Materials Science and Engineering at ETH Zurich and EPF Lausanne, Switzerland.


09/2008            BSc EPFL in Materials Science and Engineering

09/2005–08/2008    Bachelor in Materials Science and Engineering at EPF Lausanne, Switzerland.
08/2007–05/2008 Exchange year at the National University of Singapore (NUS), Singapore.

08/2005 Matura at the Mathematisch-Naturwissenschaftliches Gymnasium Rämibühl Zürich (MNG), Switzerland.

Scientific work

Publications

Pending


2015


2013


### Talks

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<td>2014</td>
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<td>2013</td>
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### Posters

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<tr>
<td>2012</td>
<td>7th Materials Research Graduate Symposium, Zurich, Switzerland. CCMX annual meeting, Bern, Switzerland. 13th International Conference on Plasma Surface Engineering (PSE), Garmisch-Partenkirchen, Germany.</td>
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### Awards & Fellowships

Best poster in 2012 and 2013 (as co-author) at the CCMX annual meeting.

Early-Postdoc Fellowship from the Swiss National Science Foundation (SNSF), 2014.