# Summary and outlook

## 1. Introduction

This thesis describes research on the deposition of polycrystalline diamond films onto steel substrates by means of the hot-filament chemical vapour deposition (HFCVD) method. Using this technique, thin layers consisting of randomly oriented diamond crystallites can easily be produced on substrate materials such as graphite, molybdenum, silicon and tungsten carbide [6, 2]. As steels are one of the most applied materials in today's industry, the use of steel substrate materials for the deposition of diamond coatings might find a wide application market. Till date, however, the direct deposition of diamond films onto steel substrate materials has been reported less frequently, because the diamond deposition process is complicated by a number of severe problems [7]. It has been reported by Ong and Chang that the nucleation of diamond particles is extremely difficult due to the catalytic effect of iron on gas precursors, such as methane, to form graphitic soot. Moreover, the mismatch in thermal expansion coefficients of the grown diamond layers and the steel substrate will result in poor adhesion properties. In addition, the rapid diffusion of atomic carbon into the steel substrate reduces the amount of surface carbon species available for diamond growth. To solve these problems, several studies are reported on the application of interlayer systems or steel surface pretreatments [4, 8]. An overview of the different interlayer systems and pretreatment procedures reported so far is given in section 2.5.

As the number of different steels is extremely large, two types of steel, which are commonly used for various industrial applications, are selected in the present work, *i.e.* AISI type 316 austenitic stainless steel and ferritic high-speed steel (toolbit, Quality-No. 1.3207). Three types of interlayer systems have been investigated, *i.e.* thin silicon layers (35-150 nm), about 2-μm thick physical vapour deposited (PVD) CrN coatings and diffusion modified borided steels. The adhesion and corrosion pitting behaviour of the various diamond/interlayer/steel systems have been examined by means of indentation/scratch adhesion testing and electrochemical polarization measurements, respectively. In the following paragraphs, the main outcomes of the work described in this thesis are summarized and discussed. In section 9.5, recommendations for future research are given.

## 2. Direct deposition of diamond onto steel

Upon direct deposition, large amounts of graphitic soot are observed in the case of high-speed steel substrates, followed by the growth of diamond polycrystallites on top of a thick graphite layer. On the stainless steel the formation of a thick graphitic layer is not observed, as a composite structure of diamond and iron carbides is formed directly on the exposed surface. Based on cross-sectional analysis of the coated AISI type 316 stainless and high-speed steel substrates, it is seen that the in-diffusion of atomic carbon results in a highly different carburization process for both types of steel. At the surface of the austenitic stainless steel, a homogeneous iron carbide layer is formed, while a less uniform carbide case is observed for the high-speed steel. The difference in iron carbide formation and thus in the volume fraction of free iron at the exposed surfaces might explain the formation of large amounts of graphite in the case of the high-speed steel and that of diamond and iron carbides in the case of the stainless steel. As the growth of diamond directly onto steel substrate materials results in low quality and non-continuous diamond films, the use of interlayer systems to block the diffusion of both atomic carbon and iron are found necessary.

In order to gain more understanding of the effect of a surface pretreatment on the nucleation and growth of diamond onto strongly carbide forming materials, a substrate pretreatment based on gas nitriding of pure chromium substrates is studied and described in Chapter 3 as well. It is well known that the use of pure chromium substrates generally results in the growth of individual diamond grains only [5]. From the present work, it can be concluded that the gas nitriding pretreatment, which leads to the formation of a surface layer consisting of the more resistant CrN and $Cr_2N$ phases, favours the formation of continuous diamond films. In the case of steel substrates, the application of the gas nitriding pretreatment would result in the formation of iron nitrides. Therefore, an interlayer system consisting of a homogeneous PVD CrN coating is chosen and described in Chapter 4.

# 3. Use of interlayer systems

Using PVD CrN interlayers and applying similar diamond growth conditions, continuous and adherent diamond films are obtained on the high-speed steel, whereas only individual crystallites are observed on the stainless steel due to partial delamination of the initially grown films. Micro-Raman spectroscopy measurements on the grown diamond layers show residual stress values of about 4 GPa for the high-speed steel and values of even 11-14 GPa are derived for the stainless steel, which explains the difference in adhesion. The results described in Chapter 4 clearly reveal different carburization of the CrN interlayer during the diamond CVD process for both types of steel. X-ray diffraction and EDAX analysis indicate the presence of mainly $Cr_7C_3$ on the high-speed steel, whereas $Cr_3C_2$ is the dominant carbide phase on the stainless steel. The present study also shows that the effect of the tool steel surface roughness on the nucleation and adhesion is very large. In Chapter 5 it is shown that Si interlayers of about 35 nm are efficient diffusion barriers for Fe but not for C during diamond growth onto steel. Despite the high diffusion rate of elemental Fe in the bulk Si phase [9], the diffusion of Fe from the steel matrix is most probably blocked by the formation of FeSiC phases at the surface. Because of the formed diffusion barrier, good quality diamond crystallites with a low fraction of graphite phases are deposited. However, the high carburization rate reduces the nucleation kinetics for diamond and a diamond/carbide composite structure is formed.

The third type of interlayer system, which has been studied in the present work and which is described in Chapter 6, comprises a diffusion modified boride surface layer. By means of pack boriding, thick boride cases containing FeB and/or $Fe_2B$ phases are produced on both stainless and tool steel substrates. These boride layers show a very high surface hardness (>3000 VHN), which gradually decreases on approaching the bulk. The presence of FeB at the surface results in very high thermal stresses and delamination of the diamond films on both types of steel. If only a $Fe_2B$ phase is present, continuous diamond films with low residual stresses are grown on both borided stainless and tool steel.

# 4. Adhesion and corrosion resistance of diamond coated steel

From the indentation and scratch adhesion tests, which are described in Chapter 7, critical load values for coating failure are obtained from the acoustic emission signals combined with surface analysis of the tested regions. The adhesion tests performed on diamond coated molybdenum and AISI type 316 stainless steel substrates with PVD CrN and boride interlayers show critical loads of 135, 100 and 69 N, respectively. A direct comparison made with the strongly adhering diamond layers on the molybdenum substrates indicates only a slightly inferior adhesion for the diamond coated stainless steel with the CrN interlayer. The scratch test performed on the diamond/borided steel system shows no significant coating failure up to 80 N. Applying both Rockwell C and steel ball indenters, kinetic friction coefficients in the range of 0.10-0.35 are derived. As the critical load values determined by both indentation and scratch adhesion tests are very sensitive to intrinsic and extrinsic factors such as indenter tip radius and testing environment, a direct comparison with other work is very difficult. In addition, the very few adhesion tests, which are described in literature, are performed on diamond coated tool steel and/or carbon steel substrates. Nevertheless, the present work shows that the use of boride and PVD CrN interlayers is highly promising for the growth of diamond films onto stainless steel substrates as well.

The corrosion resistance of the diamond coated tool steels with the three types of interlayer systems is evaluated by means of electrochemical polarization studies (Chapter 8). The corrosion resistance of blank tool steel in sodium chloride solutions is very low, but is significantly increased by the deposition of protective diamond layers. The present study shows that the effect of the applied interlayer systems on the shift of the corrosion potential is very strong. This can be explained by the seeping of electrolyte solution through the diamond films via pores and junctions between the individual grains, thereby attacking the underlying interlayer system.

# 5. Future work

From the three types of interlayer systems studied in this work, the thin Si layers show minor results. It can be concluded that single Si interlayers are not very useful for the deposition of continuous diamond coatings on steels because of the inferior diffusion barrier properties for atomic iron and carbon. Despite the formation of good quality diamond crystallites, the production of continuous and well-adhering diamond films will be extremely difficult. Therefore, the use of Si interlayers for tribological applications of diamond coated steels can be ruled out and will not be studied in planned future work. The adhesion tests of the diamond coated stainless steels with the two other interlayer systems, which have been produced by pack boriding and CrN coating, show promising results. Optimization of these interlayers including layer thickness and chemical composition as well as the optimization of suitable substrate pretreatments is considered necessary in subsequent studies. As the thermal stresses acting on the grown diamond films are high and will have a negative effect on the tribological performance of the diamond coated steels, a detailed study of the effect of an increased CrN layer thickness on the accommodation of the thermal stresses will be rewarding. Also, the application of different PVD methods to produce these CrN interlayers might lead to still better accommodation of the residual stresses and/or adhesion of the grown diamond films. Similarly, the effect of the iron boride layer thickness on the accommodation of the thermal stresses needs to be investigated into more detail.

In Chapters 4 and 6 it has been shown that the substrate pretreatments prior to diamond growth have a strong effect on the nucleation and adhesion of the diamond layers. For example, a detailed study of the effect of applying different sand blasting and ultrasonic scratching procedures might further improve the nucleation and adhesion of the diamond films. In this respect, optimization of the diamond CVD process for each of the interlayer systems individually will also contribute to better results. The application of a two-step deposition process based on a relatively short nucleation step and a subsequent growth step has been proven to be very efficient for the growth of high quality and good performance diamond films on various substrates [1, 3]. The introduction of a bias-enhanced nucleation (BEN) step has to be considered in future work as well, as the applied bias leads to ion bombardment of the steel substrate, thereby resulting in better nucleation kinetics and adhesion of the diamond coatings.

Apart from the optimization of the substrate pretreatment and CVD process steps, additional work has to be done on the production and characterization of (ultra-) nanocrystalline diamond films. Using methane/argon as well as methane/hydrogen gas mixtures, fine-grained and high quality diamond films can be produced. Changing the gas mixture composition, the structure, composition and properties of the formed carbon films can easily be tuned. As nanocrystalline films show hardness values close to pure diamond, surface roughness values in the nanometer range and a thermal stability comparable to microcrystalline diamond films, these are very promising as protective coatings on steels as well. For the boride and PVD CrN interlayer systems, the fabrication of nanocrystalline diamond films and the characterization of the mechanical and electrochemical properties of these films will be explored in future work.

The indentation and scratch adhesion tests described in the present work indicate good adhesion of the diamond coatings on borided and CrN coated stainless steel. In future work, also the adhesion of diamond coatings on tool steel substrates has to be investigated. In order to evaluate the applicability of diamond coated steels with boride and CrN interlayers, the tribological properties such as the wear resistance and friction behaviour under sliding contact need to be studied. This can be done by applying the pin-on-disk tribometer and/or the rubber wheel test. In addition, the use of complex shaped steel substrates is the next, non-trivial step in evaluating the applicability of steel substrate materials for industrial purposes. The presence of convex and concave substrate shapes will have a strong effect on the adhesion of the grown diamond layers. The residual, thermal stresses acting on curved surfaces will have components both parallel and perpendicular to the diamond layer, whereas the stresses acting on diamond films grown on flat substrates are considered biaxial. This will complicate the bonding properties of the diamond/interlayer/steel systems significantly.

The present work has led to a better understanding of the use of various interlayer systems for the deposition of diamond onto steels. Though the diffusion modified boride and PVD CrN interlayers show highly promising results, the search for new interlayer systems has to be continued in the future. The most promising interlayers are based on diffusion modified systems, as these can accommodate the residual stresses more easily [10]. From the present work as well as from earlier studies [4, 8], it can be concluded that the application of Cr(-N) based interlayer systems results in superior adhesion of the grown diamond films and therefore in superior tribological properties of the diamond coated steels as well.

# 6. References

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