Doctoral Thesis

MOCVD and tribological properties of thin zirconium carbonitride films

Author(s):
Allenbach, Christian Peter

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MOCVD and Tribological Properties of Thin Zirconium Carbonitride Films

A dissertation submitted to the
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presented by
CHRISTIAN PETER ALLENBACH
Dipl. Werkstoff-Ing. ETH
MSc Corrosion of Engineering Materials, Imperial College, London (UK)
born on March 20, 1970
citizen of Reichenbach im Kandertal BE

accepted on the recommendation of
Prof. Dr. N.D. Spencer, examiner
Prof. Dr. L.J. Gauckler, co-examiner
Dr. M. Morstein, co-examiner

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Abstract

In this work, novel metal-organic (MO) precursors were used in a chemical vapour deposition (CVD) process to deposit zirconium-based, hard, wear-resistant coatings at moderate temperatures on HSS tool steel for low-friction tribological and cutting applications.

Initially, the suitability of the four precursors Zr(NEtMe)$_4$ (TEMAZ), Zr(pyrr)$_4$ (TPyrrZ), Zr(pip)$_4$ (TPZ), and the binuclear complex Zr$_2$(μ-N$_2$Bu)$_2$(NH$_4$Bu)$_4$ (TBUZ) for the MOCVD process was assessed based on their volatility and thermochemical stability.

These metal-organic compounds allow deposition of zirconium carbonitride films in the temperature range of 400-600°C using a system pressure of 500 Pa or lower, ammonia as reactant gas, and H$_2$ carrier gas. The coatings were characterised with respect to their chemical composition by X-ray photoelectron spectroscopy (XPS). The chemical composition and growth rates of the films were found to be largely depending on the precursor used and the deposition parameters chosen, especially the amount of ammonia reactant gas. Coating microhardness was measured using a Knoop-type indenter. A larger amount of both oxygen and adventitious carbon impurities was found to correlate with a decrease in film hardness. Smooth, predominantly columnar or domed coating microstructures were evaluated from scanning electron microscopy (SEM) cross-sectional and plan-view images. The small surface roughness was confirmed by stylus profilometry.

The dry-sliding friction behaviour of selected ZrCN coatings deposited between 450 and 500°C on polished HSS disks was evaluated versus various pin materials, such as 100Cr6 bearing steel, Hastelloy C-22, TiAl6V4, AlMg4, and a copper alloy using a pin-on-disk set-up. A range of industry-standard hard PVD and CVD coatings was commercially deposited on the same steel substrate material for comparison. These coatings, ZrN, TiN, TiCN, TiAlN, TiAlCN, TiAlCN + WC/C, WC/C, diamond-like carbon (DLC) and Al$_2$O$_3$, as well as plain polished HSS steel, were then systematically tribotested versus the various pin materials.
The friction evaluation shows that the ZrCN films prepared by our MOCVD process markedly reduce the coefficient of dry-sliding friction compared to uncoated steel, for all investigated counterbody materials. Depending on the pin material, a considerable reduction of the friction coefficient of up to 50% was also obtained relative to all commercial coatings except DLC. Under our test conditions—dry air at room temperature—the wear rates of the industrial coatings are negligible, whereas the ZrCN coatings, due to their lower hardness, exhibit noticeable wear. Profilometry of the wear track cross-section was used for the wear rate assessment. Material transfer from the pin to the coating and vice versa was determined by Imaging-XPS. SEM images were taken to document the wear tracks and debris formed.
Zusammenfassung

In dieser Arbeit wurden neuartige metallorganische (MO) Verbindungen zur chemischen Abscheidung aus der Gasphase (Chemical Vapour Deposition, CVD) eingesetzt, um bei mittleren Abscheide­temperaturen zirkonbasierte, harte und verschleissfeste Schichten auf HSS Werkzeugstahl abzuscheiden. Mögliche Anwendungsgebiete sind Systeme mit geringen Reibungskoeffizienten und spanende Bearbeitung.


Das Reibverhalten ausgewählter Zirkonkarbonitridschichten, abgeschieden zwischen 450 und 500°C auf polierten HSS-Stahlsubstraten, wurde in ungeschiemtem Zustand gegen zahlreiche Stiftwerkstoffe (100Cr6 Lagerstahl, Hastelloy C-22, TiAl6V4, AlMg4 und eine Kupferlegierung) mit einem Stift-Scheibe Tribometer untersucht. Eine Auswahl kommerzieller Schichtmaterialien wurde zu Vergleichszwecken mittels CVD- und PVD-Verfahren auf identischem Substratmaterial abgeschieden. Diese Schichten, ZrN, TiN, TiCN, TiAlN, TiAlCN, TiAlCN + WC/C, WC/C, diamantartiger Kohlenstoff (Diamond-
Like Carbon, DLC) und Al₂O₃, sowie unbeschichteter, polierter HSS Stahl wurden systematisch gegen alle Stiftwerkstoffe im Tribometer getestet.

1 Introduction

1.1 Aim of This Study

The aim of this study is to deposit and characterise a new generation of zirconium-based hard, wear-resistant and low-friction carbonitride coatings on tool steel. They are applied by metal-organic chemical vapour deposition (MOCVD) using novel tailored metal-organic precursors.

The ligands of the metal-organic precursors are chosen such that they can be cleaved by low-activation-energy routes (molecular engineering). Dedicated metal-organic (MO) compounds allow for single-source precursor processes to deposit metal carbonitrides without the need to use an external carbon source such as methane. However, such commercial precursors for the deposition of zirconium carbonitride are still lacking.

Metal-organic compounds thermochemically decompose at lower temperatures in comparison to conventional first-generation halide precursors used in high- and middle-temperature chemical vapour deposition (CVD). Thus reduction of bulk hardness for hardened steel substrates can be minimised or entirely avoided. Metal-organic precursors offer a number of fundamental benefits:

- low deposition temperature
- no corrosive or toxic byproducts
- no halide contamination of the layers
- high volatility/low evaporation temperature.

A small number of previously synthesised \(^{11}\) new, structurally related metal-organic zirconium nitride/carbonitride precursors have been evaluated for their suitability for low-temperature coating.

In an initial step, rough starting parameters for the MOCVD process were determined. In the following, the effect of deposition conditions on coating properties is investigated. Mainly the influence of deposition temperature, system reactant gas composition and feed rates are looked at. The variation of the system pressure is used mainly to adjust the precursor evaporation rate, such that film growth rates are limited up to a few hundred nm per minute. Coating properties, such as chemical composition and hardness, are determined and correlated with deposition temperature. For the most promising films,
tribological performance is tested in a pin-on-disk set-up for five different counterbody pin materials including non-ferrous alloys. Both friction coefficient and wear rate of the tribocouples are evaluated. These new tool coatings are expected to contribute towards sustainable development in several ways:

- wear reduction
- reduction of friction
- potential for lubricant-free dry or near-dry machining.

Despite the higher initial costs for MOCVD, extended tool lifecycles will be cost-effective in production. The worn tool may also be re-coated due to the low deposition temperatures applied avoiding substrate dehardening. Reducing the friction between workpiece and tool allows for dry or sparsely lubricated machining. This is beneficial as machining oils are hazardous, and expensive to dispose of. There is a possibility that through better coating, metal-machining-lubricant waste can be reduced or avoided.

1.2 Functional Surface Treatments

Many of the final physical and chemical properties of a component are related to its surface treatment—that is, performing a finishing step to an otherwise adequate product design. In general, the aim of any such treatment is to enhance properties such as wear resistance, friction, hardness, corrosion resistance, fatigue performance, biocompatibility or optical appearance. This is achieved by designing a surface and a substrate together as a system to give a cost-effective performance which neither is entirely capable of fulfilling on its own [12]. The field of surface engineering is thus multifaceted but is usually separated into two main groups of processes: surface modification and coating techniques.

**Surface modification techniques** are based on the alteration of the surface region of a material by implantation or diffusion of additional species into it, enabling the formation of a near-surface region of enhanced mechanical or chemical performance. Surface
modification techniques are beneficial if dimensional changes of the part are critical, i.e. need to be avoided or kept to a minimum.

**Coating techniques**, in contrast, are based on the deposition of a—usually thin—layer of new material on the substrate, thus enlarging the overall dimensions of the treated part.

Simply writing about coatings is actually misleading. Not only is the coating of importance, but also the system, consisting of the combination of a substrate with its adjusted properties—which have to be maintained during the coating process—and a coating deposited onto it with its properties highly depending on the deposition process. For future reference, we will use the expression "coatings" freely, bearing in mind that we mean coating systems.

While some processes, such as galvanising of steel strip for corrosion protection or the hardening of gear teeth by pack carburising have been in existence for many decades, we have recently seen the emergence of a new range of surface enhancement technologies. The predominant group among these are gas phase/vapour deposition techniques such as plasma-assisted CVD, metal-organic CVD using novel precursors, several physical vapour deposition (PVD) techniques, and plasma spraying, to name but a few. Emergent surface modification processes include plasma nitriding/carburising, ion implantation, as well as laser and electron-beam processes. Combinations of surface modification and coating techniques, often referred to as duplex treatments, benefit from the advantages of each processing step. Thereby system properties are established which neither process is capable of providing entirely on its own.

Looking at one property, hardness, Figure 1.1 outlines the achievements by various surface treatments and through coating applications. Traditional surface heat treatment gives improved hardness, whereas recent coating techniques such as CVD of hard compounds result in even higher hardness (> 2000 HV) and enhanced wear resistance.
1 Introduction

Coating thickness varies from the nm to the lower μm range for CVD and PVD coatings. This is thinner than the coating thickness or case depth of most classical thermal, thermochemical or plating processes, where the μm to mm range is aimed for.

The global market in surface engineering is large and growing, as only about 50% of the tools in metal working are currently being coated. Among the principal coating techniques, the world market breaks down in PVD 39%, CVD 26%, thermal spraying 23%, and wet processes 12%.

Vacuum and surface technologies have also made headway in the area of general machining and tooling. Tools and parts are expected to be more productive, more reliable and more durable. Hard, low-friction coatings reduce wear and yield improvement in tool productivity and part service. The coating of tools and precision components today represents a US$ 850 million market with double-digit annual growth rates. The driving force is the need for increased production rates, under conditions where uncoated tools rapidly fail.

Successful exploitation of surface engineering can provide cost benefits in at least the following ways: enhancing functional performance and reliability, higher productivity, permitting the use of cheaper substrate materials, and providing the flexibility to match substrate and surface for specific applications as well as being environmentally benign.
Chemical vapour deposition (CVD) and physical vapour deposition (PVD) are the two main groups of techniques used to deposit hard, wear-resistant coatings on cutting inserts to improve their cutting performance and lifetime. CVD has advantages over PVD such as good conformality even on complex geometries and the formation of denser films. Other benefits of CVD, such as higher growth rates and a better control of morphology, microstructure and stoichiometry of the deposited layers, and the deposition of non-stoichiometric materials have been reported. Almost half a century ago, CVD research started off with the deposition of titanium nitride (TiN) using TiCl₄ as a precursor at high temperatures of 900 to 1000°C. The first commercial products were TiN-coated cemented carbide tools. The high CVD process temperature required for the thermochemical decomposition of the precursors limits the choice of substrate materials, excluding temperature-sensitive materials and products manufactured with low size tolerances, leading to the predominant use of robust cemented carbide substrates.

The development of plasma-enhanced CVD (PECVD) and the introduction of tailored metal-organic precursors which can be decomposed at markedly lower temperatures in Metal-Organic CVD processes were found to overcome the disadvantage of conventional high-temperature CVD. Both processes allow the coating of temperature-sensitive steels. In addition, these techniques are expected to overcome the disadvantages associated with the moderate conformality of PVD coatings, while adhesion properties of MOCVD coatings may be adversely affected by reduced diffusion rates at the lower deposition temperatures chosen in comparison to conventional high- and middle-temperature CVD techniques.

Whilst some might say that TiN hard coating is now commonplace, it has to be realised that this material is far from being the solution to all wear problems. The number of hard materials with hardness values comparable to those of TiN is extensive and they differ considerably with regard to their chemical, thermal, mechanical and electrical properties. The assessment of TiN-coated inserts in milling and drilling of non-ferrous and Ti-based alloys revealed reduced performance in comparison to machining ferrous alloys. Other coatings such as zirconium nitride (ZrN), and TiₓZr₁₋ₓN prepared by PVD, have exhibited better wear resistance than TiN. Johnson et al. have reported that cathodic-arc, plasma-deposited ZrN is marginally superior to TiN in conventional metal-
cutting applications; but it outperforms TiN by a factor of two when dry-cutting titanium alloys. Experiments by Molarius et al.\textsuperscript{[13]} showed that ZrN has the best performance compared to (Ti,Al)N and TiN in dry-cutting at 30 - 60 m min\textsuperscript{-1} cutting speed and 0.25 mm rev\textsuperscript{-1} feed rate. This is in good agreement with Knöte et al.\textsuperscript{[14]} who evaluated TiZrN, TiN and ZrN in strip-turning tests, finding TiZrN, ZrN, TiN as the order of descending performance at 0.2 mm feed rate at cutting speeds of up to 150 m min\textsuperscript{-1}. At lower feed rates, TiN was almost as good as TiZrN and outperformed ZrN. Sproul\textsuperscript{[15]} noted that the workpiece material has a strong influence on the performance ranking of various transition metal nitride or carbide coatings. The inconsistency in cutting performance, however, is likely related to differences in the basic properties of the coating and its deposition process\textsuperscript{[16]}.

In addition ZrN shows better chemical stability than TiN\textsuperscript{[17]} and exhibits excellent hot hardness\textsuperscript{[18]}. Hardness is usually slightly lower than for TiN. Apart from the hard-coating applications\textsuperscript{[19]}, ZrN coatings have been widely used as diffusion barriers in integrated-circuit devices\textsuperscript{[20, 21]}, gate materials\textsuperscript{[22]}, thin-film resistors\textsuperscript{[23]}, -thermistors\textsuperscript{[24]}, Josephson junctions\textsuperscript{[25]}, decorative optical coatings\textsuperscript{[26]}, superconducting films\textsuperscript{[20, 25]}, and for cryogenic thermometers\textsuperscript{[27]}, to name but a few. Despite these promising properties of ZrN films and the related carbonitride, ZrC\textsubscript{x}N\textsubscript{1-x}, only relatively scarce data is available on the deposition by low-temperature CVD techniques. Predominantly, zirconium amides have been used as precursors. In particular, tetrakis(diethylamido)zirconium, Zr(NE\textsubscript{2})\textsubscript{4}, has successfully been used by a number of groups in a wide deposition temperature range of 200 to 650°C\textsuperscript{[16, 8, 28-32]}. Compared to early precursors such as zirconium tetrachloride\textsuperscript{[30, 33]}, Zr(NE\textsubscript{2})\textsubscript{4} offers a number of distinct advantages. Both evaporation and deposition temperatures are much lower, it is less prone to gas-phase particle formation, and halide-associated problems such as HCl formation and halide incorporation into the films are inherently avoided. However, little is known about alternatives to this substance.
References


2 Surface Engineering

The term surface engineering as a field of research and application encompasses those techniques and processes used to induce, modify and enhance the performance of surfaces with respect to wear, friction, fatigue, corrosion and biocompatibility [11]. A concise overview of the available methods and techniques is given in volume 5 of the ASM handbook [2].

Extensive surface engineering activities have been conducted in Japan, the USA, Germany, and France [3] since the mid 1980s, while efforts have been made in the UK and elsewhere in Europe to benefit from the emerging market. Companies in Switzerland and in the Principality of Liechtenstein have always been at the forefront of surface engineering, and are active in system development and manufacturing as well as in batch processing for external customers.

A common classification of surface engineering processes separates them into two groups: Surface-modification techniques and coating processes. With respect to this classification, some of the techniques used to improve tribological performance are listed in Figure 2.1 [3].

Surface-Modification Processes — These techniques are used to enhance the performance of a substrate material through changes in the near-surface region. These rely on chemical addition or heat treatment. A detailed review of available surface-modification techniques and on their applications and limits has been written by A.J. Hick [4]. Among the topics covered are thermal treatments and thermochemical diffusion treatments. The former are based on temperature-induced changes in the microstructure, also discussed for steels by Child [5]. The latter involve the diffusion of non-metallic elements, usually carbon [6] and/or nitrogen [7], from the surface into the bulk material [8]. The area of ion implantation, introduced in the 1960s and adopted for microelectronics in the 1970s, has been covered by several authors [3,9].
Fig. 2.1 Surface-modification treatments (a) and coating processes (b) to improve tribology characteristics. [3]

**Thermal treatments**
- Induction hardening
- Flame hardening
- Laser hardening
- Spark hardening
- Electron beam hardening

**Thermochemical diffusion**
- Carburizing
  - Gas
  - Liquid
  - Pack
- Carbonitriding (austenitic)
  - Gas
  - Liquid
  - Conventional<br>  - Aeration accelerated<br>  - Sulphite accelerated<br>  - Low toxicity processes
- Nitrocarburizing (ferritic)
  - Gas
  - Low pressure
- Nitriding
  - Gas
  - Conventional<br>  - Ion-nitriding
- Boriding
  - Pack
- Chromising
  - Pack
- Siliconising
  - Gas/pack
- Aluminising
  - Pack

**Surface welding**
- Oxy-acetylene<br>  - Tungsten inert gas (TIG)<br>  - Shielded metal arc<br>  - Open arc<br>  - Metal inert gas (MIG)<br>  - Submerged arc<br>  - Electro-slag<br>  - Paste fusion<br>  - Plasma arc<br>  - Laser cladding

**Electrochemical**
- Aqueous<br>  - Fused salts

**Chemical (electroless)**
- Oxy-acetylene<br>  - Tungsten inert gas (TIG)<br>  - Shielded metal arc<br>  - Open arc<br>  - Metal inert gas (MIG)<br>  - Submerged arc<br>  - Electro-slag<br>  - Paste fusion<br>  - Plasma arc<br>  - Laser cladding

**Thermal spraying**
- Flame<br>  - Powder<br>  - Wire<br>  - Electric arc metallising<br>  - Plasma<br>  - Low pressure plasma<br>  - Detonation gun

**Chemical vapour deposition (CVD)**
- Thermal CVD<br>  - Plasma-assisted CVD

**Physical vapour deposition (PVD)**
- Thermal evaporation<br>  - Ion-plating<br>  - Sputtering<br>  - Reactive ion-plating
Coating Processes — Coating processes result in enhanced system performance by depositing an additional protective layer. This layer together with the substrate chosen gives enhanced performance of the finished part. Electrochemical and electroless chemical coatings and surface welding have been extensively used for quite some time. Thermal spraying, and especially deposition from the vapour phase, were only developed in the second half of the 20th century.

The coating thickness or case depth applied can vary from less than a μm in ion implantation or chemical vapour deposition to a few mm for weld surfacing. Treatment temperatures range from ambient to the melting point of the material deposited, i.e. several hundred degrees Celsius. The use of a process is therefore limited to a range of substrate materials depending on their temperature sensitivity. Some of the older methods of surface treatment such as salt-bath nitriding or chrome plating will shortly become environmentally unacceptable and therefore will probably need to be withdrawn due to regulatory developments. Meanwhile new, high-volume markets will open-up for sustainable surface treatments.

2.1 Techniques of Vapour Deposition

Vapour-deposition techniques are broadly classified into two categories: chemical vapour deposition (CVD) and physical vapour deposition (PVD). The aim of this section is to look at the basics of CVD and PVD and to compare their respective advantages and disadvantages.

CVD — Chemical vapour deposition is a materials-synthesis process. One or more vapour-phase species are transported into a reaction chamber. They are activated thermally or by other means, such as plasma or laser stimulation in the vicinity of the substrate, to chemically react at the substrate surface. A solid film and volatile byproducts form through decomposition. The volatile products are transported away from the surface. This class of processes belongs to those vapour transfer processes that are atomistic in nature. The main features of CVD are its versatility for synthesising both simple and complex compounds with relative ease. Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition
conditions. Deposition parameters, such as temperature, pressure, input concentrations, gas-flow rates and reactor geometry determine the deposition rate and the properties of the deposited film. The reaction kinetics are important, as the deposition rate can be determined either by the substrate temperature for thermally activated processes or by the gas-flow rates in the case of concentration/diffusion-controlled processes. It is possible to deposit dense films of uniform thickness—even on substrates of complicated shape. A typical CVD reactor is shown in Figure 2.2 a). The coating envelopes the substrate wherever the gas phase has access to the substrate surface.

Thin-film materials that can be deposited by CVD cover a tremendous range of elements and compounds. Inorganic, organometallic, metal-organic, and even organic reactants are used as starting materials, commonly referred to as precursors. Only few precursors are gaseous at room temperature. Liquid precursors can be easily vaporised and introduced into the system by passing a carrier gas through a liquid reservoir. Solid reactants are more difficult to handle, especially if they cannot be liquefied, and fixed-bed evaporators need to be used.

The dissociation of the precursors takes place at elevated-to-high temperatures depending on the nature of the precursor. TiCl₄ for example, which is used for the formation of TiN, requires decomposition temperatures in excess of 850°C. Metal-organic precursors benefit from the lower energy required for their dissociation. In favourable cases, deposits can be obtained at temperatures as low as 200°C, although at these temperatures, reaction byproducts may be incorporated into the coating, affecting its functional properties.

CVD has become an important process technology in several industrial fields. Applications in solid-state microelectronics are of prime importance. Hard, wear-resistant coatings of materials such as diamond-like carbon, borides, transition metal carbides and nitrides have found important applications in tool technology. Corrosion-resistant coatings, especially oxides and nitrides, are used for metal protection in metallurgical applications. Also optical coatings have been deposited using CVD processes.
PVD — Physical vapour deposition encompasses simple atom/ion beam techniques. A wide range of techniques is available, in which the fundamental objective is to attract metal ions to the workpiece surface under the influence of an electrical bias and in the presence of a reactive gas under partial vacuum conditions \[^{15}\]. In many cases, the process involves generation and action of a plasma. The vapour is created by four main types of processes. These are evaporative deposition, sputtering, ion-plating and reactive ion-plating \[^3\]. Figure 2.3 shows the set-up of three basic PVD processes: electron beam evaporation, cathodic-arc and sputter-ion plating \[^9\].

Fig. 2.2 Basic set-up of CVD and PVD coating techniques. In CVD (a) the workpiece is surrounded by the gas phase and uniform, conformal coatings are obtained. b) PVD suffers from its line-of-sight problem with respect to conformality and thickness uniformity.

Fig. 2.3 Set-up for electron beam evaporation, cathodic-arc processes and sputter-ion plating PVD \[^9\].
PVD is, as illustrated in Figure 2.2 b), a line-of-sight process. Therefore uniform coating of parts with recessed areas is difficult. Adjusting the source location or the use of multi-source equipment in combination with sample rotation can enable the formation of rather uniform deposits on more complex geometries. However, uniform, conformal coatings, comparable to those deposited by CVD, cannot easily be obtained by PVD. Deposition temperatures are in the range of ambient to 450°C—significantly lower than for CVD. The processes therefore seldom result in substrate distortion and are also applicable to temperature-sensitive materials. Coating of architectural glass for sun blocking is just one example of a successful application of PVD technology. Of the principal commercial coating processes available, titanium nitride deposition (TiN) by plasma-assisted PVD is one of the most frequently employed \[\text{[116]}\]. The plasma activation is used to further energise the vapour phase and optimise the film density.

In general, CVD processes have the advantage over PVD processes of good conformality, while PVD processes have higher deposition rates than those in CVD processes \[\text{[113]}\]. The chemical composition of the coating and its morphology can be controlled and adjusted in both processes. The maximum acceptable deposition temperature is another criterion by which to choose one or the other process. As this doctoral work is based in the field of CVD research, PVD is not discussed in further detail but referred to as a measure for comparison of coating properties and performance.

2.2 Chemical Vapour Deposition (CVD)

Thermochemical deposition processes were first used in the 1880s for the production of incandescent lamps to improve filament strength by carbon or metal deposition \[\text{[117]}\]. In the same decade, the carbonyl nickel process was developed by Mond and others. During the next fifty years the process slowly developed and was limited mostly to pyro- and extraction metallurgy of high-purity refractory metals such as titanium, tantalum, and zirconium. It is only since the end of World War II that the process began to be used on a large scale, as researchers realised the potential of deposition and the formation of coatings and free-standing shapes in addition to metallurgical extraction \[\text{[114]}\]. The term Chemical Vapour
Deposition was first used in 1960 [18], the year when CVD was introduced in semiconductor production lines and the concept of TiC coatings on cemented carbides formed by CVD was first described [19]. Shortly after these first steps into coating-application-related research, the basis of plasma-assisted CVD in electronics was established. Towards the end of the 1960s, CVD was industrially used for the coating of cemented carbides. Metal-organic CVD was first implemented in 1968 for the deposition of GaAs [14]. Throughout the 1970s, development continued and culminated in the successful introduction of plasma-enhanced CVD and low-pressure CVD. CVD processes became more widely used during this period. It was mainly the semiconductor/microelectronic industry who made extensive use of the available processes. The development of machine-tool coatings was also important in this decade. CVD coatings are nowadays used in a variety of application fields, benefiting from their ability to be adjusted with respect to chemistry and microstructure. Commercial use ranges from semiconductor (group III-V, and II-VI) and microelectronics to tribological applications and corrosion protection. Optical films, high-Tc materials for superconductivity, photovoltaic elements and medical products are other fields where CVD is used.

Current developments in CVD focus on low-temperature forms of CVD, such as MOCVD, plasma-CVD, and photo-CVD. Applications are in the fields of semiconductor industry and microelectronics, as well as in hard coating, erosion and wear applications as lower deposition temperatures now permit the use of a broader spectrum of substrates. Advances in equipment development focus on the integration of various processes into one piece of equipment combining for example CVD, etching, ion implantation and other PVD processes. Much attention is also being drawn to enhanced control of the deposition parameters through in situ observations [14].

2.2.1 CVD Kinetics

Understanding the theory of CVD is vital for obtaining an optimal product. Critical to CVD theory are chemical kinetics, fluid mechanics, chemical engineering principles as well as an understanding of growth mechanisms. Any vapour deposition technique is based on the principles of mass transfer from one
source to another following the three fundamental steps in the formation of a deposit:

1. transfer of the precursor to the gas phase
2. transport from the source to the substrate
3. deposition onto the substrate and film growth.

These steps can either be completely separated from each other or superimposed on each other, depending upon the process under consideration [20]. In more detail, CVD can be described by the following steps:

1. diffusion of reactants towards the substrate surface
2. diffusion through the boundary layer to reach the substrate
3. adsorption of the reactants on the surface
4. surface reactions to form the deposit
5. desorption of gaseous decomposition products from the surface
6. diffusion of byproducts away from the surface.

These steps take place simultaneously and cannot be independently followed. The slowest step determines the overall deposition rate [13]. Figure 2.4 schematically illustrates the reaction sequence.

![CVD: Schematic of the reaction sequence and important reaction zones.](image-url)
The close control of these steps through the vital CVD parameters—substrate temperature, reactor pressure, gas-flow rates and gas-phase composition (precursor concentration)—determines the coating growth rate and enables the deposition of a wide variety of coatings. The selected parameters directly influence the flow regime in the reactor chamber. The velocity of gaseous reactants is reduced within the flow boundary layer formed due to drag, and reduced to zero at the substrate surface. The boundary-layer thickness in the vicinity of the substrate is important for the deposition rate, as both reactants and volatile products need to diffuse through it to reach or leave the surface.

When CVD growth rates are plotted versus reciprocal deposition temperature, the following regimes can be distinguished in Figure 2.5.

- The growth rate is controlled by surface reaction kinetics at the substrate at lower temperatures.
- At intermediate temperatures, mass-transfer-kinetics through the stagnant boundary layer limits the growth rate.
- Reduced growth rate at high temperatures due to parasitic reactions, such as increased decomposition rate on hot reactor walls or through pronounced gas-phase reactions.

The intermediate-temperature regime is also referred to as feed-rate limited deposition. It is particularly advantageous in cold-wall reactors, where it is often difficult to obtain completely uniform substrate heating. The flux of reactants to the substrate surface is proportional to the concentration of the precursor, thus allowing simple control of the magnitude of growth rate. Gas-phase reactions become progressively more important with both increasing substrate temperature and partial pressure of the reactants. At high reactant concentrations, gas-phase reactions may eventually lead to gas-phase nucleation, which is detrimental to thin-film growth.

As a general rule, the lower the deposition temperature, the lower the growth rate must be to obtain a certain level of crystal perfection, as surface mobility is reduced with decreasing substrate temperatures. The latter is needed for atomic arrangement of the deposits on the underlying surface.
2.2.2 Overview of Various CVD Techniques

Like most chemical reactions, film formation by CVD requires activation in order to proceed. Several energy sources are available for precursor activation: thermal energy, plasma, photo (laser, UV-lamps), and ion or electron beams. Thermal heating is still the major method for CVD of metals and ceramics. An overview of these techniques is given
by Pierson \cite{pierson23}. Besides this differentiation by energy input, CVD has also historically been divided into subgroups according to the nature of the precursor. Metal-organic CVD is discussed in detail in Section 2.3.

**CVD Equipment Concepts** — From an experimental point of view, any CVD system consists of a precursor evaporation and delivery system connected to a reaction chamber. A major distinction is made between hot-wall and cold-wall set-ups. A continuous gas flow through the reactor is maintained during deposition. If not depositing at atmospheric pressure, a vacuum pump is attached to the reactor to keep the deposition pressure constant. Contaminants are stripped from the exhaust gases (via a cold trap) to protect the pump system from the intake of highly reactive/corrosive species. In a *cold-wall reactor*, only the substrate is heated and the reactor walls are kept at relatively low temperature. This is beneficial, as sharp thermal gradients reduce gas phase reactions that lead to sooting. Also, improved film conformality is found \cite{pierson24}. The cold-wall design reduces the probability that competing chemical reactions at the walls will interfere with film growth. The sample can be brought to deposition temperature by inductive heating using radio frequency or by direct heating with a heating element. Resistance heating by connecting the sample to a power source and passing an electrical current through it has also been used. Unfortunately the large temperature gradient between heater and cold walls can favour the establishment of thermally driven convection in the reaction chamber. In the *hot-wall reactor*, the whole reaction chamber is brought to process temperature by an external heat source. The sample is then heated by radiation from the hot reactor wall. The major problem with hot-wall systems is that deposition can occur not only on the substrate but also on the reactor walls. These deposits can eventually spallate and contaminate the growing film during the process. Also, the correspondingly large consumption of the precursor can result in feed-rate-limited deposition at relatively low temperatures in comparison to cold-wall reactors. In addition, homogeneous gas-phase reactions in the heated gas can occur, which can lead to further reduced deposition rates through precursor scavenging.

**Thermal CVD** — In conventional thermal CVD, which mainly uses halide-containing precursors, the reaction temperature ranges from around 900 to about 2000°C, depending on the coating to be deposited. Hot- and cold-wall reactors are used.
Plasma CVD — The use of a glow-discharge plasma provides energetic species that facilitate precursor activation in the vapour phase. This enables CVD processes to take place at lower temperatures in comparison to thermal CVD. Surface temperatures are usually in the range of 100 to 700°C. Close control of the plasma properties, i.e. the collision frequency of the gaseous species, the mean free path, the electron density, and the electron-energy-distribution function, is needed to control the gas-phase chemistry and the coating properties. The process was developed to enable coating of temperature-sensitive materials, such as low-melting-point metals, materials that undergo solid-state phase transformation at high temperatures, polymers and others that cannot be coated by thermal CVD. The lower treatment temperature is also beneficial if thermal expansion mismatch between coating and substrate is critical and introduction of stresses must be minimised.

Most reactors use radio frequency (rf) in the lower MHz range (13.56 MHz) or microwave glow discharge at 2.45 GHz.

Laser CVD — The laser as a source of energy for CVD was introduced in the mid-1990s. Thermal-laser and photo-laser techniques are still in their experimental stage. A laser is used in thermal-laser CVD to heat the substrate. The wavelength of the source can be chosen such that gas molecules cause no energy loss. Because of the small heat-affected area on the substrate, deposition only takes place locally. By moving the laser spot on the surface, a full coating coverage can be achieved.

Photo-laser CVD benefits from the action of light, especially ultraviolet radiation, which provides sufficient photon energy to break the chemical bonds in the reactant molecules. While conventional UV lamps can also provide such radiation, lasers, such as eximer, provide a much higher energy density. Photo-laser CVD does not need heat as in thermal-laser CVD, as the decomposition reaction is photon-activated. This results in a treatment that takes place at room temperature on any substrate. However there is the drawback of relatively low deposition rates in comparison with the other techniques. This could be overcome by further enhancing the photon energy density of eximer lasers.

Chemical Vapour Infiltration (CVI) — CVI is a CVD process especially designed for porous substrates. Gaseous reactants penetrate a porous structure, such as a foam or an array of fibres. Deposition occurs on the foam, fibre, or preform, and the structure becomes gradually densified to form a composite. The precursor is force-fed
into the foam or fibrous weave, mat or array. CVI is a slow process, which can take up to several weeks to result in a dense product. However, full densification is nearly impossible, as closed porosity will occur by clogging of narrow channels at an early stage of the deposition cycle.

CVI is used to produce high-strength SiC fibre composites and carbon-carbon composites, as well as other reinforced metal or ceramic composites [25]. Low process temperatures are used in comparison to sintering, minimising chemical and mechanical damage to the substrate.

2.3 MOCVD

Metal-organic CVD is a variation of the conventional CVD technique. Thin layers are grown by co-pyrolysis of various combinations of metal-organic compounds and hydrides or other reactants. Metal-organic compounds show lower decomposition temperatures than purely inorganic precursors and are therefore suitable for coating at reduced temperatures, thus enabling deposition on thermally sensitive materials. MOCVD offers the possibility to form multilayer deposits with very abrupt interfaces using several precursor sources in an alternating mode. Gradient layers are deposited by gradually admixing a second precursor. Because of high equipment costs and expensive precursors, MOCVD is considered most often when high performance is essential or other processes are not suitable or available for the substrate material chosen.

A wide variety of materials can be deposited by MOCVD, either as single-crystal, polycrystalline or amorphous films. Disadvantages in comparison to traditional CVD are smaller deposition rates, increased crystal defect density, and impurity incorporation into the film. Special care must be taken in precursor handling, as many precursors are highly reactive upon exposure to air or moisture [26, 27].

Manasevit was the first to report the deposition of group III-V compounds from metal-organic and hydride sources. In that experiment, InP was deposited from trimethylindium and PH3 in a closed-tube system. But it was not until 1968 that the first deposition of crystalline gallium arsenide was obtained in an open-tube-system [14]. A vast increase in the development and use of MOCVD in the field of epitaxial deposits was observed in the mid-1980s. This is closely related to the introduction of personal computers and the resulting need for cheap mass production of large-scale-integrated
circuits. Ever since then, MOCVD for semiconductor applications has advanced rapidly, establishing itself as a unique and important technique for epitaxial crystal growth. Group III-V and II-VI compound semiconductor materials deposited by MOCVD at 600-1000°C and at pressures varying from the mbar range to atmospheric include GaAs, InAs, GaAlP, AlGaN, ZnS, ZnSe, CdS, and CdSe, to name but a few. Devices based on MOCVD coatings include lasers, solar cells, phototransistors, photocathodes, and field-effect transistors.

MOCVD has also been successfully used for the deposition of wear- and corrosion-resistant coatings. Group IV-metal nitrides, such as TiN, ZrN, HfN and equivalent carbides as well as carbonitrides, have been deposited at temperatures of 200-450°C using metal-organic precursors 128.

The fundamental processes occurring during crystal growth are commonly divided into thermodynamic and kinetic components. Thermodynamics determine the driving force behind the overall growth process, whereas kinetics define the rates at which the various processes occur. Figure 2.6 depicts the fundamental processes involved in MOCVD.

![Fundamental processes involved in metal-organic chemical vapour deposition.](image-url)
Relating the dependence of a macroscopic quantity, such as growth rate, to external parameters, such as substrate temperature, precursor flow rates and concentrations, provides insight into the overall growth mechanism. While approaches from a purely thermodynamic point of view have been made to predict MOCVD reactions, it was found that the experimentally observed growth rates were regularly less than those calculated from thermodynamic principles. Kinetic factors, either surface reaction rates or diffusion rates of species through the vapour phase and boundary layer, are what limits the growth rate. This is because they hinder the establishment of equilibrium on which thermodynamics are based. However, MOCVD is not an equilibrium process. Thus thermodynamics can to date only define certain limits for the growth process. Growth-affecting parameters, such as temperature, pressure, total gas flow, and precursor-to-reactant-gas ratio, have to be optimised empirically.

During the past few years, much of the effort has been focused on improving the quality of the material that can be grown. Much work remains to be done, especially in the areas of increasing wafer size and throughput, improving the reproducibility of some of the material properties, and understanding the basic chemical processes. 300-mm silicon-wafer technology is a result of such continuous improvement and development. While certain steps have been adapted and adjusted to the new wafer size, entire production lines for processing of 300-mm units are to be introduced in the semiconductor industry shortly.

The development of suitable precursors has been important for CVD applications ever since. Precursors were initially just taken “off the shelf”. Nowadays, the multitude of potential ligands available for MO compounds offers the possibility to design the precursor and to engineer the molecular decomposition pathway. Thus, both reduced deposition temperatures and low impurity levels can be achieved. Precursor characteristics such as volatility and thermal stability must be carefully evaluated, as they may strongly influence the deposition parameters to be chosen. More details on the evolution of MOCVD precursors for thin film coatings will be given in Chapter 4.

MOCVD can be conducted at both atmospheric pressure and under vacuum conditions. The advantage of system pressures substantially lower than 0.1 bar is that hydrodynamic effects adversely affecting the deposition process are reduced or
eliminated. Hydrodynamics, for example in a thick boundary layer, can lead to poor precursor utilisation in a diffusion-controlled growth regime. Reactants that do not diffuse through the boundary layer will be swept away to the exhaust and are lost to deposition. Vacuum MOCVD and metal-organic molecular beam epitaxy (MO-MBE) are two MOCVD processes that have been recently introduced into industrial practice. Vacuum MOCVD is used for the deposition of gallium compounds for solar-cell material \cite{29}. The operating pressure is around $5 \times 10^{-3}$ Torr, only achieved using turbomolecular pumps. MO-MBE operates using metal alkyl and hydride sources as precursors \cite{29}.

From a mechanistic point of view, two new techniques are under development using plasma and UV-light as sources of energy for the decomposition processes. Plasma-enhanced MOCVD allows the growth of coatings at even lower temperatures than conventional MOCVD. Photo-assisted MOCVD uses UV radiation to enhance the defragmentation of metal-organic compounds. This processes has been extensively used to decrease the growth temperature and to develop new selected-area deposition processes. The MO precursor should have, in addition to the general requirements, a strong adsorption band with a maximum that matches the wavelength of available UV sources. The wavelength adsorbed by a molecule depends on the nature of the chemical bonds; adsorption bands corresponding to electrons located in $\sigma$- and $\pi$-bonds/molecular orbitals occur at short and long wavelengths, respectively. Thereby the formation of free-radical species is initiated that then interact to form the desired film product. The limitations of the process to date are the unavailability of effective and economic production equipment and, in most cases, the need for photoactivation with mercury in the vapour phase to achieve acceptable film growth rates \cite{10, 30}. 
References


3 Materials for Hard Coatings

Hard, protective layers are one of the most important and versatile means of improving component performance. As tools are subject to considerable wear in milling, cutting and drilling operations, coatings play an economically important role in metal machining, world-wide. Coated inserts result in increased lifetime as well as enhanced quality of the machined surface [11]. The primary requirements for hard coatings in metal machining are: good adhesion to the tool substrate and to its adjacent coating layer in the case of multilayers, high microhardness at cutting temperature, and chemical inertness relative to the workpiece. The secondary requirements are fine-grained, crystalline microstructure, compressive residual stress, as well as crack-free and smooth surface morphology [12].

The low friction coefficient of some of these coatings already allows operation under near-dry, sparsely lubricated conditions, and under certain circumstances, the total absence of lubricant fluids. This is beneficial as the use, maintenance and especially disposal of coolant lubricants in metal machining entail enormous costs [3]. Costs for the disposal of metal-containing coolant lubricants are approximately ten times higher than the price of new fluids. In addition, health and safety requirements for workshops as well as environmental regulations must be met.

Transition metal nitrides, carbides, and carbonitrides are by far the most widely used materials for wear-resistant coatings. In the late 1960s, the introduction of chemical vapour deposition on hard, cemented-carbide cutting tool inserts was a major advancement in tooling technology. Typical performance gains of 100-300% in tool wear or 50% in cutting speed were realised [4, 5]. TiN coatings deposited by CVD are commercially available since the early 1970s, offering reduced metal-cutting friction coefficients and improved crater-wear resistance relative to TiC. Their pleasing gold colour visibly distinguishes them from TiC. From these first single-layer types, CVD technology advanced to multi-layer types, combining TiC, TiN, TiCN and alumina with the choice of layer sequence and total coating thickness being tailored to the particular metal-cutting application [12]. The fracture resistance of coatings thus is enhanced by introducing a multilayer structure with thin individual layers deposited, resulting in a high density of low-energy interfaces, suitable for energy dissipation in the layer. Transfer of
this early CVD technique to high-speed steels was not very successful because of the high process temperature involved.

With physical vapour deposition (PVD), the coating of tool steel became a practical reality [6]. Since the beginning of the 1980s, PVD ceramic coatings have been used for many applications. TiN, Ti(C,N), (Ti,Al)N and CrN are four of the most frequently used types of coatings.

(Ti,Al)N offers better oxidation resistance, Ti(C,N) is used where tough materials have to be machined, and CrN gives improved corrosion resistance [7-9]. Ti(C,N) was also reported to exhibit lower friction, which was related to the formation of a graphite layer on top of the Ti(C,N) coating, resulting in smoother chip motion [8]. However, with the introduction of difficult-to-machine materials, coating-system properties and metal-machining requirements had to be matched closely to enable economical production [10].

TiN will remain dominant for the next few years, but for particular, high-benefit situations driven by the need for increased machining productivity, some of the alternatives make more sense.

Recent improvements in Ti-based systems show that more complex composite systems containing additional elements have the potential to further improve the layer properties, such as adhesion and oxidation resistance [11, 12]. This is particularly important for dry-machining applications.

Zirconium nitride, ZrN, and its derivative zirconium carbonitride, Zr(C,N), belong to the less investigated materials. These materials, compared to titanium nitride, have a lower coefficient of friction, yet still maintain comparable hardness and chemical properties [13-15]. A number of zirconium-based layers deposited by sputtering or CVD have been investigated [16-19]. However, systematic investigations concerning the tribological properties, the substrate-coating interface, and the deposition of multi- or gradient layers—a strategy proven powerful in the homologous titanium system [11, 17]—are still lacking.

The overall perception seems to be that while ZrN would not replace TiN generally in the cutting tool marketplace, it could be a significant niche-market product. Enhanced performance has been reported for the machining of Ni-base alloys, Ti-alloys, and other non-ferrous materials [14].
There has also been a strong interest in diamond and diamond-like carbon layers, but a number of unsolved problems (oxidation resistance, adhesion, diffusion) has limited their wide technical application so far \[111, 201\].

Recently, combinations of hard coatings at the cutting edge and soft coatings applied to the entire drill bit, mainly MoS\(_2\), have been introduced to the production of metal drills \[211\]. The soft, low-friction coating does support chip flow within the helical drill flute. Thereby the use of fluids, usually the machining lubricant, for chip removal can be reduced.

### 3.1 Transition Metal Nitrides and Carbides

Transition metal nitrides and carbides are known for their extremely high melting points, excellent hardness and high wear resistance. They are frequently referred to as "refractory carbides and nitrides". Of all compounds formed between transition metal atoms and light elements H, B, C, N, and O, only nitrides and carbides are closely related in crystal structure types (face-centred-cubic: fcc), phase relationships, bonding characteristics, and electric and magnetic properties \[221\]. The reason for such a close relationship lies in the similarities of the electronic structure, size, and electronegativity of carbon and nitrogen \[231, 241\]. However, these similarities do not extend to transition-metal borides and transition-metal oxides. The latter are characteristically ionic in bonding, structure, and properties, whilst the former are more characterised by boron-boron bonds, as indicated by the proximity of the atoms in the crystal structures. Metal-C-B-N systems have also been looked at but have not been widely used as protective coatings.

Within the family of transition metal nitrides, additions of nitrogen, oxygen, and carbon can be incorporated at almost any level into the NaCl-structure without changing the crystallographic phase, but causing marked changes in the physical and chemical properties of the nitride phase.

Nitrides and carbides of titanium, zirconium, tungsten, and hafnium have been investigated in more detail for CVD. For the preparation of metal carbides and nitrides, a number of methods and reactions is available as listed in Tables 3.1 and 3.2.
### Tab. 3.1 Methods and reactions for the preparation of metal carbides. CVD and chemical vapour synthesis (CVS) methods are listed in bold. Me denotes metal, not methyl.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct reaction, either by melting or sintering of the elements or metal hydrides in a protective atmosphere or in vacuum</td>
<td>Me + C → MeC</td>
</tr>
<tr>
<td>Direct reaction of the metal oxide and excess carbon in a protective or reducing atmosphere</td>
<td>MeO + C → MeC + CO</td>
</tr>
<tr>
<td>Reaction of the metal with a carburising gas</td>
<td>Me + C₆H₆ → MeC + H₂</td>
</tr>
<tr>
<td>Precipitation from the gas phase by reacting the metal halide or metal carbonyl in hydrogen</td>
<td>MeCl₄ + C₃H₄ + H₂ → MeC + HCl + (CO, CO₂, H₂, H₂O)</td>
</tr>
</tbody>
</table>

### Tab. 3.2 Methods and reactions for the preparation of metal nitrides. CVD/CVS methods are listed in bold.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitriding the metal powders or metal hydride powders</td>
<td>Me + N₂ → MeN</td>
</tr>
<tr>
<td>Nitriding metal oxide powders in the presence of carbon</td>
<td>MeO + N₂(NH₃) + C → MeN + CO + H₂O + H₂</td>
</tr>
<tr>
<td>Reaction of metal chlorides and NH₃</td>
<td>MeCl₄ + NH₃ → MeN + HCl</td>
</tr>
<tr>
<td>Precipitation from the gas phase by reacting the metal halide in a N₂-H₂ atmosphere</td>
<td>MeCl₄ + N₂ + H₂ → MeN + HCl</td>
</tr>
</tbody>
</table>

Precipitation processes and gas-phase reactions are listed in bold. In these processes metal halides or metal carbonyl precursors are used to form deposits (CVD) or to produce powders (CVS). Frequently used precursors, their advantages and difficulties are...
described in Chapter 4. The precipitation processes resulting in the formation of sound coatings are of interest for CVD coating applications.

3.1.1 Titanium and Zirconium Nitrides, Carbides and Carbonitrides

Titanium nitride, TiN, is very stable, of high hardness, erosion and corrosion resistant and has a low coefficient of friction against ferrous alloys. TiN coatings are, for example, employed in metal machining, on gear components, or on tube- and wire-drawing dies. TiN is an ideal diffusion barrier coating between tribopartners. Microwelding is suppressed and adhesive wear strongly reduced. The reduced friction coefficient reduces thermal stress of the substrate material.

![Figure 3.1: Titanium-nitrogen phase diagram](image)

Figure 3.1 shows the phase diagram of titanium-nitrogen [25]. A wide range of stoichiometries is available, of which only TiN is of commercial importance. The stability range up to 59 at.-% Ti allows for deviations from the 1:1 Ti:N ratio. However, the properties of this NaCl-type fcc lattice strongly depend on the Ti:N ratio.

Titanium carbide, TiC, offers superior hardness and wear resistance to abrasive wear. However, it is susceptible to oxidation attack and not a good diffusion barrier coating.
Titanium carbonitride Ti(C,N) is a solid solution of TiC and TiN. A wide range of stoichiometries of TiN/TiC is accessible because both systems have fcc-type lattices and a similar lattice constant. The properties of both materials are combined, resulting in excellent protection and good friction characteristics under severe abrasive wear conditions. Gradually replacing N with C results in hardness gains. Maximum hardness values reported are 4500 HV. However, this adversely affects the toughness of the coatings, enhancing embrittlement. To avoid decreases in toughness, Ti(C,N) is often applied as multilayer structures with alternating layers having different carbon-to-nitrogen ratios. Thereby, internal stresses are reduced at the interfaces of the individual layers, offering both high ductility and increased hardness. The formation of a graphite layer on top of the Ti(C,N) coating was reported to result in smoother chip motion and a reduced mechanical load.

Zirconium-based coatings have been successfully used in microelectronics but also in engineering applications. Figure 3.2 shows the zirconium-nitrogen phase diagram.

In comparison to TiN, ZrN exhibits better chemical stability, enhanced oxidation resistance, good wear resistance, and is suitable for applications at high temperatures as in jet-engine components. The low friction coefficient allows for machining of non-
ferrous alloys at reduced lubricant usage. Wear-test results indicated that ZrN is marginally superior to TiN in machining conventional iron-base alloys but outperforms TiN by a factor of two when cutting titanium alloys \cite{11-14}. Similar results were obtained in machining tests on nickel-based alloys and Ni-containing steels \cite{6, 30, 31}. However, commercial deposition of ZrN so far has been limited to PVD and middle- to high-temperature CVD techniques. Great potential exists for the deposition on temperature-sensitive materials using MOCVD or plasma-enhanced CVD.

Recently ZrC_{0.5}N_{0.5} coatings developed by Widia Valenite have been introduced to the cemented-carbide tool market. The coatings are deposited by means of conventional CVD from ZrCl_4 at around 900°C \cite{32}.

Table 3.3 contains a ranking of nitrides, carbides and borides (borides are not looked at in detail in the present work) for a number of coating properties \cite{33}.

<table>
<thead>
<tr>
<th>Property</th>
<th>high</th>
<th>medium</th>
<th>low</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting point</td>
<td>C</td>
<td>B</td>
<td>N</td>
</tr>
<tr>
<td>stability</td>
<td>N</td>
<td>C</td>
<td>B</td>
</tr>
<tr>
<td>thermal expansion</td>
<td>N</td>
<td>C</td>
<td>B</td>
</tr>
<tr>
<td>hardness</td>
<td>B</td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>toughness</td>
<td>N</td>
<td>C</td>
<td>B</td>
</tr>
<tr>
<td>reactivity</td>
<td>B</td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>adhesion to substrate</td>
<td>B</td>
<td>C</td>
<td>N</td>
</tr>
</tbody>
</table>

From Table 3.3 it is obvious that a single coating system may not fully satisfy all needs, as properties, such as toughness and hardness, are inversely related. Multilayer or multicomponent systems are a suitable way of combining the desired properties, while minimising their disadvantages. However, deposition control is crucial for good-quality coatings, and thus not easy.

Nitride coatings benefit from the chemical stability, the toughness and the hardness as a combination of properties. The lower hardness achieved in comparison to carbides or borides is thus not a general drawback. The application of such coatings must be carefully selected to make good use of their enhanced performance.
<table>
<thead>
<tr>
<th>Coating</th>
<th>Hardness [10 N/mm²]</th>
<th>Melting Point [°C]</th>
<th>Coefficient of Thermal Expansion [10^-6 K⁻¹]</th>
<th>Maximum Temperature of Use [°C]</th>
<th>Coefficient of Friction [⁺]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>2100-2800</td>
<td>2950</td>
<td>9.35-9.40</td>
<td>500-550</td>
<td>0.1-1.15</td>
<td>5.40</td>
</tr>
<tr>
<td>TiC</td>
<td>2800-3700</td>
<td>3067</td>
<td>8.0-8.6</td>
<td>400</td>
<td>0.25-0.7</td>
<td>4.93</td>
</tr>
<tr>
<td>Ti(C,N)</td>
<td>3500-4000</td>
<td></td>
<td></td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ti,Al)N</td>
<td>2200-2400</td>
<td></td>
<td></td>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrN</td>
<td>1500-2800</td>
<td>3000</td>
<td>6.0</td>
<td></td>
<td></td>
<td>7.32</td>
</tr>
<tr>
<td>ZrC</td>
<td>2560-2900</td>
<td>3420-3445</td>
<td>7.0-7.4</td>
<td></td>
<td></td>
<td>6.63</td>
</tr>
</tbody>
</table>

*Coefficient of friction in various systems. Individual tribocouples and experimental conditions not available.

In Table 3.4, typical values are given for some of the most relevant coating properties. Data was collected from several sources [112, 13, 22, 34-39]. The data of a much wider variety of nitrides, carbides and borides is compiled in a list prepared by Friedrich et al. [39].
References


4 Precursor Development

A detailed overview of precursors used for CVD of metals has been given by Hampden-Smith and Kodas [11]. One of the aims of the development of CVD precursors is to match the need for low decomposition temperature. Precursors should be synthesised through easy routes of high yield using cheap, readily available chemicals. Precursors for CVD can be broadly classified into three types:

- inorganic precursors, which do not contain any carbon
- metal-organic precursors, which contain organic ligands, but do not possess direct metal-carbon bonds
- organometallic precursors which possess organic ligands and metal-carbon bonds.

CVD processes using metal-organic or organometallic precursors are generally referred to as metal-organic chemical vapour deposition (MOCVD). The highest potential for future materials and process development is associated with the use of the metal-organic compounds. Through molecular engineering, the selected ligands influence the precursors' properties such as thermodynamic stability, kinetic lability, solubility and volatility of the compound. The ligands have a major influence on the quality of the deposited product, as, ideally, they do control the chemical decomposition reaction taking place [12].

4.1 Inorganic Complexes

Inorganic precursors are kinetically or even thermodynamically stable compounds that need high activation energies to decompose. Decomposition takes place near the thermodynamic equilibrium and only thermodynamically stable phases can be formed. Inorganic precursors are often prone to aggregation and, as a result, exhibit low vapour pressure. Although the vapour pressure can be increased by increasing the temperature, care must be taken to avoid premature reaction of the compound in the gas phase before reaching the hot substrate surface. This can lead to irreproducible growth rates and the transport of unknown species. Clogging and the formation of powdery products may occur and interfere with the growth of clean, smooth coatings. Inorganic precursors such
as metal halides do not normally produce pure films below 600°C and generally require the presence of a reducing agent such as H₂ to avoid halide contamination. Halides incorporated in the film adversely affect the corrosion performance of any coating. Metal halides are often solids at the source temperature, which makes delivery into the reactor more difficult to control compared to liquid or gaseous precursors. Despite these drawbacks, high-purity films can be deposited at high growth rates. Deposition temperatures are in the range of about 700 to 1000°C, which limits the choice of substrate materials.

Metal halide compounds such as TiCl₄, ZrCl₄, and WCl₆ are examples of inorganic CVD precursors. They require a high input of energy for decomposition to occur due to the strong metal-halide bonds that need to be broken. In the 1920s and 1930s, the formation of TiC from the decomposition of TiCl₄ in a methane atmosphere at temperatures in excess of 1000°C was discovered. Titanium diboride was formed in a similar way. Only half a century ago, CVD research began with the deposition of titanium nitride (TiN) using TiCl₄ as a precursor and nitrogen or ammonia gas as nitrogen source. This process has been commercially used for the last three decades for the deposition of TiN on tool materials at atmospheric pressure and deposition temperatures of 900-1200°C. Typical growth rates range from 0.03 to 0.2 μm per minute, at a typical hardness of 2000-2500 HV. Equation 4.1 shows the high-temperature decomposition reaction of TiCl₄ taking place in the presence of nitrogen and ammonia at temperatures above 750°C with significant growth rates only at 900-1000°C.

\[
\text{TiCl}_4 + \frac{1}{2} \text{N}_2 + 2\text{H}_2 \rightarrow \text{TiN} + 4\text{HCl} \quad (4.1)
\]

The addition of ammonia (NH₃) enables a decomposition reaction to take place at much lower temperatures:

\[
6\text{TiCl}_4 + 8\text{NH}_3 \rightarrow 6\text{TiN} + \text{N}_2 + 24\text{HCl} \quad (4.2)
\]

This reaction is thermodynamically favourable above 300°C, but reasonable and economic film growth is obtained only above 400-450°C. To obtain usable TiN coatings, a minimum substrate temperature of 600°C is necessary. Unfortunately a side reaction leads to the formation of a Lewis acid-base adduct (see Equation 4.3), which is stable up to about 200°C.
TiCl₄ + 2NH₃ → TiCl₄2NH₃ (yellow powder-like solid)  (4.3)

In the solid state, the adduct decomposes at temperatures of 200-400°C to TiNₓClᵧ and finally to TiN above 400°C. However, the formation of these solid products is likely to occur and interfere with the main process in a cold-wall reactor only. The products formed and their yield may vary with temperature. Contamination of the coating through powder particles falling onto the substrate may occur and growth rates are adversely affected by this parasitic reaction. The powder formation can be suppressed by heating the precursor inlet tubes to above 250°C and mixing ammonia and precursor only upon entering the reactor, i.e. in the vicinity of the hot substrate.

Halide contamination in the deposit is described by almost any reference on low-temperature deposition using TiCl₄. The amount of halide contamination strongly increases with decreasing deposition temperature. Halides are not only detrimental to the coating properties such as corrosion resistance and electrical resistivity, but may already attack a steel substrate during deposition or cause etching on aluminium substrates or aluminium layers in integrated circuits.

4.2 Metal-Organic and Organometallic Precursors

There exists a wide variety of materials which could not be deposited by the conventional halide CVD process, because sufficiently reactive halides do not exist or are not volatile enough. MOCVD crosses this gap, offering a wide range of deposits including metals, transition-metal compounds as well as semiconductors and intermetallic compounds. Thermodynamically metastable phases, in particular, can be deposited by MOCVD. A large number of precursors has been looked at during fundamental studies. They offer the principal advantage of being far more reactive thermally than metal halides and related species. Stringent requirements must, however, be met for a successful MOCVD process.
Among the precursor design requirements that ideally must be satisfied are:

- good volatility to achieve high transport rates and to accommodate high growth rates by minimising intermolecular forces in the condensed state and suppression of molecular aggregation
- high purity of the precursor, to reduce contamination
- good long-term stability for storage
- liquid rather than solid for easy handling and evaporation and to ensure reproducible delivery rates
- good thermal stability during evaporation and transport in the gas phase to avoid premature decomposition
- clean decomposition on pyrolysis to give the desired material with a minimum of contamination
- non-toxic/non-pyrophoric and non-corrosive
- readily available at low cost.

Despite the progress in increasing volatility, other pathways have also been followed to enable the use of compounds of low vapour pressure—also solids—through techniques such as direct liquid injection, flash evaporation or aerosol-assisted CVD.

Having looked at the basic needs and rules to be followed in MOCVD precursor design, it is important to recognise that there are two processes: single-source and multi-source processes. If the deposition of a thin film involves more than one element, as is the case for transition metal nitrides, a single metal-organic precursor containing all these elements can be used, if it exists. In the most favourable case in nitride deposition, the centre of the metal-organic molecule contains the elements needed for the coating to be formed with direct metal-nitrogen bonds. This bond energy has to be preferably higher than the N-C bond. If this is the case, selective cleavage of the centre-ligand bonds with a kinetically controlled process is expected. If the bond to the ligand is too strong, the advantage of a single source process is lost, as one element will be partially or fully missing. Thus, coatings of the desired compound cannot form. In multi source processes, two or more precursors containing the desired elements are decomposed, supplying the elements to a reaction resulting in the formation of the desired coating.
Metal-organic precursors have the disadvantage that impurity incorporation is common. The most important contaminants are oxygen desorbed from the reactor walls or from impurities in the process gases used, and carbon. The presence of oxygen is particularly detrimental if reactive metals such as Ti, Zr, Cr are present, since they easily oxidise, and coating properties such as hardness are adversely affected thereby. Carbon-containing reaction products can be incorporated into the coating rather than leaving the deposition zone towards the exhaust due to reduced diffusion at the low deposition temperatures chosen. Carbon can be considered beneficial only if present in its carbidic form, but not if it is present as a polymeric, adventitious carbon or hydrocarbon residue.

4.3 Precursors for Ti-Based Coatings

4.3.1 Halide-Containing Precursors

Titanium tetrachloride has been used for deposition of TiN using one or more of the following carrier gases: nitrogen, hydrogen, and ammonia. Combinations looked at were TiCl₄-N₂-H₂, both at low pressure and under atmospheric conditions, at around 1000-1050°C. The addition of ammonia in atmospheric thermal CVD of TiCl₄ reduced the deposition temperature to 650-700°C when using both ammonia and hydrogen and down to 400°C when only NH₃ was added [7].

4.3.2 Metal-Organic Precursors

Many types of metal-organic compounds have been tested for their suitability to deposit clean TiN coatings by CVD. Spee et al. have given an account of the work on the development of MO precursors [4]. Part of this is listed in Table 4.1. The table also lists the CVD method with respect to operation conditions. However, from a general point of view, they are to be regarded as MOCVD due to the precursor used.
Of these precursors, only a few meet the requirements such as good thermal stability, high volatility, and low cost of precursor synthesis. The methyl and ethyl representative of the tetrakis(dialkylamido)titanium complexes are among the above-listed precursors the by far most studied metal-organic Ti-based precursors used for the deposition of TiN. They were first synthesised by Bradley in the late 1960s \([8]\) by reaction of ZrCl\(_4\) with four equivalents of a lithium dialkylamide, LiNMe\(_2\) or LiNEt\(_2\). In a more recent procedure, dialkylamidomagnesium bromides, [MgNR\(_2\)Br], were used instead of lithium amides for the metathetical reaction \([9]\).

Both in monomeric Ti(NMe\(_2\))\(_4\) and Ti(NEt\(_3\))\(_4\), the central Ti atom is exclusively bound to nitrogen by means of \(\sigma\)-bonds. Despite this favourable situation, ammonia is commonly added in the CVD process as a reactant gas. In the absence of ammonia, TiN films deposited from Ti(NR\(_2\))\(_4\) had high levels of carbon contamination. Spee et al.\([4]\) and others suggested they should rather be considered TiC.

The mechanism for this carbon incorporation presumably involves elimination of one amine molecule and simultaneous formation of a metallocycle containing a Ti-C bond.
This intermediate species is then responsible for the occurrence of carbide carbon in the film.

\[
\begin{align*}
\text{Me}_2\text{N}^+ & \quad \text{NMe}_2 \quad \text{MeN}^+ \text{CH}_2 \\
\text{Ti} & \\
\end{align*}
\]

This mechanism accounts for the TiC found in the deposited TiN layers as described by Sugiyama et al. \cite{10} in 1975 when Ti(NMe2)4 was used as a single-source precursor. They ended up with a deposit that was reddish brown to yellowish depending on the deposition temperature. Low temperatures supported carbon incorporation leading to darker films formed. Fix et al. \cite{11} tested several metal-organic precursors, including Ti(NMe2)4 and Ti(NEt2)4. They were deposited using He or N2 carrier gas in an APCVD set-up. Chemical composition by EDX, RBS and XPS revealed large amounts of carbon and oxygen incorporation in the coatings. XPS data for Ti(NMe2)4 was 23-42 at.-% C and 12-29 at.-% O, and for Ti(NEt2)4 28-41 at.-% C and 21-31 at.-% O depending on the substrate material and deposition temperature. Fix et al. \cite{11} explained the oxygen found through traces of oxygen and/or water in the carrier gas or adsorbed to the walls of the reactor, whereas carbon undoubtedly originates from the molecular precursor. XPS studies revealed organic carbon and titanium-bound carbon.

The transamination reaction is one of the most important steps when decomposing Ti(NR2)4 (hydrogen and/or nitrogen carrier gas) in the presence of NH3 as a nitrogen source. Molecular nitrogen is not an alternative to the corrosive and toxic NH3 in the low to medium temperature CVD regime (500-800°C) because its degree of dissociation is not high enough to provide a useful nitrogen source. The transamination reaction consists of the exchange of amines as given in Equation 4.5.

\[
\text{Ti(NMe2)4} + n\text{HNR2} \rightarrow \text{Ti(NMe2)4-n(NR2)n + nHNMe2}
\] (4.5)

with \( n = 1 \) to 4. By further reaction, most prominently through \( \beta \)-elimination, the resulting compound is converted into TiN. The reaction with ammonia can reduce the carbon content to a few atomic percent. This was experimentally reported by Kurtz and Gordon \cite{15} and led to high-quality films of TiN deposited above 350°C by APCVD. Experiments by Fix. et al. \cite{12} using Ti(NMe2)4 at atmospheric pressure with ammonia
addition for deposition at 150-450°C resulted in good films only above 200°C. The carbon concentration in the coating bulk increased with increasing deposition temperature and reached a maximum of 5 at.-% at 350°C. The oxygen content was less than 1 at.-% at temperatures below 250°C. Similar experiments were performed by Prybyla et al. using Ti(NMe₂)₄, hydrogen and ammonia at temperatures near 300°C at 10⁻³ Torr, thus at much lower chamber pressure. The precursor—diluted and transported with hydrogen carrier gas—and the ammonia reactant gas were premixed in a new precursor injector operating at 50 to 300 Torr. A rapid gas-phase transamination reaction was thereby enabled, leading to the formation of a high-molecular-weight intermediate. The intermediate was found to have a high sticking coefficient and low surface mobility. Films were low in carbon contamination but oxygen was found at non-negligible amounts. This was attributed to the exposure of the coatings to air (oxygen absorption) prior to surface analysis. The presence of oxygen and its absence when investigating PVD TiN coatings using surface analytical tools also suggested that CVD coatings deposited with this method are of a lower density than the corresponding PVD films. Ruhl et al. confirmed previous research and suggested to deposit at very low pressure (0.2 mbar) using ammonia to reduce the spontaneous gas-phase transamination. Thereby incorporation of dimethylamine byproducts in the coating during deposition can be eliminated. From deposition experiments with changing ammonia-to-precursor ratio in the gas phase it was concluded to be beneficial if ammonia is present in excess, although very high concentrations had to be avoided as they reduced film growth rates markedly. The ammonia was found (by isotopic substitution experiments) to be the source of nitrogen for the TiN formed. A disadvantage of the use of ammonia is the fact that a significant part of the incorporated nitrogen remains bonded to hydrogen. Such NHₓ groups are very reactive and fast incorporation of oxygen takes place upon exposure of the coating to air. Reduced coating density also supports the formation of oxides.

Tetrakis(di)methylamido precursors were used for plasma-assisted CVD by Stock et al. Coatings were deposited at 200 to 400°C. The carbon content in the layers was reported to be 10-15 at.-% with little dependence on deposition temperature for coatings deposited from Ti(NEt₂)₄. Coatings deposited from Ti(NMe₂)₄ exhibited significantly higher carbon contamination than those from Ti(NEt₂)₄. This result was confirmed by Täschner et al. also for PACVD of tetrakisdiethylamido and tetrakisdimethylamido used in an H₂-N₂-Ar atmosphere. Stock et al. related the variation in carbon
Precursors for Ti-Based Coatings

Contamination to the two processes of deposition of the coating and ion sputtering of the coating in the plasma taking place simultaneously. Dissimilar process rates for the two precursors could lead to the discrepancy observed in chemical composition through preferential sputtering. Depth profiling revealed little change of the carbon content throughout the coating thickness. Hardness values were above 1800 HV. The loss in hardness in comparison to 3000 HV, the hardness of high temperature CVD Ti(C,N) coatings, was attributed by Stock et al.\textsuperscript{15} to organic compounds that were formed in the glow discharge, adsorbed to the surface and incorporated into the growing layer. Evidence for the presence of C-H fragments or crack products was given by Täschner et al.\textsuperscript{16}. This group found tetrakisdiethylamidotitanium and tetrakisdimethylamidotitanium precursors not to be suitable for thermally activated reaction conditions in an H\textsubscript{2}-N\textsubscript{2}-Ar atmosphere, as only black-grey porous deposits with a high content of oxygen were obtained. Experiments in an ammonia-containing atmosphere, supporting rapid transamination, were not performed.

Shin et al.\textsuperscript{17} reviewed the advantages and disadvantages of Ti(NEt\textsubscript{2})\textsubscript{4} and Ti(NMe\textsubscript{2})\textsubscript{4}. Films prepared using Ti(NEt\textsubscript{2})\textsubscript{4} have the disadvantage of relatively degraded conformality but only a negligible level of oxygen contamination, whereas Ti(NMe\textsubscript{2})\textsubscript{4} is known to produce conformal but unstable films, which are air-reactive and contain marked amounts of oxygen contamination. They also quoted relatively poor step coverage for coatings deposited in the presence of ammonia (transamination reaction), probably due to highly reactive intermediates produced in the gas phase and particle contamination. To address these problems, a pure single-source process using Ti(NEtMe\textsubscript{4}) was suggested.

Tetrakisethyimethylamidotitanium Ti(NEtMe\textsubscript{4}) was prepared to make use of the advantages only of the dialkylamido-precursors. Coatings were expected to exhibit good step coverage, high conformality and enhanced coating properties, i.e. chemical composition. Ti(NEtMe\textsubscript{4}) was then used for depositions at 250-350°C at 1 Torr chamber pressure using He carrier gas only. The activation energy of the overall reaction in the kinetic controlled regime was calculated as $E_a = 1.0$ eV. Good step coverage of 50-90% depending on the substrate temperature was found. However, the XRD pattern revealed rather broad peaks and a marked amorphous background signal. The chemical composition revealed by AES depth profiling showed high oxygen contamination of more than 20 at.-% throughout the coating\textsuperscript{17}. The explanation, that the oxygen incorporated into the film did not result from the deposition but was due to post-deposition storage and
air exposure, is questionable with regard to the given concentration depth profile. If only exposure to air were the reason, one would have to conclude that reactive species are incorporated into the coating and/or that poor coating density enables oxygen access through open pores right through the coating. Carbon contamination was still at about 18 at.-%. It was present in approximately equal amounts in its carbidic form or as polymeric, adventitious carbon. Kim et al. \textsuperscript{[18]} recently published results of MOCVD of TiN using tetrakisethylmethylamidotitanium Ti(N{\text{EtMe}}_{4}) at low pressure in a cold-wall reactor with helium or ammonia. Thermal decomposition of the precursor under helium atmosphere yielded TiN layers at deposition temperatures above 250°C. For the experiments performed at 250 to 400°C a calculated overall reaction energy in the reaction controlled kinetic regime of 70 kJ/mol was evaluated. This was compared to an activation energy of 52 kJ/mol for Ti(N{\text{Me}}_{2})_{4} and explained with the increased molecular weight of Ti(N{\text{EtMe}}_{4}). Thus Ti(N{\text{EtMe}}_{4})_{4} is considered less reactive than Ti(N{\text{Me}}_{2})_{4} but somewhat more reactive than Ti(N{\text{Et}}_{2})_{4}. A further decrease in deposition temperature down to 100°C could be achieved by using ammonia, benefiting from the transamination reaction as described analogously for Ti(N{\text{Me}}_{2})_{4} in Equation 4.2. However, deposition rates decreased markedly when using ammonia. The formation of powderlike byproducts from a parasitic reaction was described also. The reduction in growth rate was not only explained by this parasitic reaction but also by sterical hindering of ammonia access to the central Ti-atom, thus slowing down the transamination reaction favoured in the presence of ammonia. Due to the low deposition temperatures chosen, high contamination levels with carbon mainly present in its polymeric form rather than as carbide, and amorphous coating morphologies were reported.

The deposition temperatures in MOCVD can be lowered below those typical for CVD using metal halide precursors. However, the deposition process may be considerably more difficult to control and the resulting films often contain carbon and oxygen contamination \textsuperscript{[19]}.

Other MOCVD precursors which have been looked at are metal acetylacetonates M(acac)\textsubscript{n}. These substances are commercially available and have the advantage of being stable in air and readily soluble in organic solvents. Suitability for the deposition of pure metals such as iridium, scandium and rhenium and compounds such as the yttrium-barium-copper-oxide complexes used as superconductors has been shown also through
commercial applications [20]. However, they are not suitable for the deposition of transition-metal nitrides due to the preferential formation of oxides with strong Me-O bonds.

4.4 Precursors for Zr-Based Coatings
4.4.1 Halide-Containing Precursors

ZrN can be formed in conventional thermal CVD using zirconium tetrachloride, analogously to TiN [21].

4.4.2 Metal-Organic Precursors for Zr-Based Coatings

Analogous systems to the Ti-based metal-organic compounds have been synthesised in the past. However, only tetrakisdiethylamidozirconium Zr(NEt₂)₄ has been experimentally used to deposit Zr-based coatings. In 1975 Sugiyama et al. [10] tested Zr(NEt₂)₄ at 500°C and Zr(NMe₂)₄ at 400°C at atmospheric pressure, resulting in pale brownish coatings. Fix et al. [22] used Zr(NEt₂)₄ and ammonia at atmospheric pressure at temperatures of 200-400°C to deposit Zr₃N₄ with very low contamination levels of C and O. Plasma-assisted CVD using Zr(NEt₂)₄ precursor and various gas phase compositions (H₂, N₂/H₂, NH₃/H₂) have been performed by Wendel and Suhr [23]. Only the experiments with pure hydrogen were quoted to lead to films of good quality. Considerable amounts of oxygen were found in those coatings prepared with N₂/H₂ while depositions in ammonia-containing atmospheres resulted in polymeric precipitates at the electrode. Additional experiments using PACVD focussed on deposits using hydrogen as carrier/reactive gas. Good quality coatings were then deposited at temperatures as low as 300°C with best hardness values of 1900 HK. Also working with PACVD, Täschner et al. [24] deposited Zr(C,N) films in the temperature range of 280 to 580°C using Zr(NEt₂)₄ and H₂-Ar or H₂-N₂-Ar gas mixtures. The former gas mixture led to grey or dark-grey coloured coatings whilst with the latter gas mixture golden-bronze to yellow-brown coatings have been deposited. The addition of nitrogen to the gas mixture reduced the carbon content of the coatings. High oxygen contamination was found in all deposits, independent of the gases used and deposition parameters employed. Columnar grain growth was observed; and a maximum hardness of 2000 HV₀,₀₂ was measured.
A comparison of the precursors Zr(NEt₂)₄ and Zr(NEtMe)₄ with respect to their suitability for PACVD of Zr(C,N) was carried out by Berndt et al. Initial work focussed on the evaporation conditions. From this it was concluded that Zr(NEtMe)₄ can be vaporised at temperatures of 50°C. This is lower than 80°C evaporation temperature evaluated for Zr(NEt₂)₄ at 200 Pa system pressure. This makes sense with respect to the different molecular weight of these precursors, influencing the vapour pressure of the compounds. Evaluation of the chemical composition of the coatings revealed lower Zr-content and higher carbon contamination for deposits using Zr(NEtMe)₄. Because methyl ligands have a higher sticking probability than ethyl ligands, which can easily desorb as ethene by hydrogen elimination, tetrakisdiethylamido precursors lead to lower carbon content in the coating compared than those made using Zr(NEtMe)₄, if deposited under similar conditions. This result is analogous to the findings of Stock et al. presented in an earlier paper for the PACVD decomposition of similar Ti-based precursors. Contamination levels for deposits at 350°C were around 20 at.-% C and 8-12 at.-% O. Apart from the film formation, a homogenous reaction of the precursor in the gas phase occurred above 400°C, which yielded dust in the chamber or powdery layers. Kinetic data could not be obtained from the growth rates evaluated.

4.5 Conclusions for the Development of Novel Zr-Based MO Precursors

From previous research and precursor development it was concluded that tetrakis(dialkylamido)metal precursors open a successful alternative route to the formation of transition metal nitrides, avoiding the high deposition temperatures and restrictions on substrate selection related to halide-containing precursors. Much work has been performed on the preparation of TiN coatings, with or without ammonia addition. Simple single source experiments without ammonia addition to the gas phase resulted in low-quality coatings—occasionally the formation of powders only was reported. It was concluded from experimental experience that ammonia addition is beneficial by enabling a transamination reaction to take place at low temperatures. However, reaction byproducts tend to be incorporated into the coating, leading to elevated contamination levels, especially for carbon and oxygen. Precursors containing symmetrically substituted secondary amides exhibited disadvantages with respect to conformality, step coverage and
contamination levels. Thus precursors containing asymmetrically substituted amido groups have been suggested and successfully applied.
References


5 Experimental

5.1 Experimental Program: Rationale

As mentioned earlier, the deposition of hard, wear resistant transition metal nitrides on tool inserts is an effective way of enhancing tool lifetime, reducing friction between tool and workpiece, and allowing for dry or sparsely lubricated machining. Some coatings, such as TiN, are widely used in the machining of ferrous alloys. However, in the machining of new high-strength materials and non-ferrous alloys, loss of performance has been reported. The oxidation resistance of the Ti-based coatings has seen a major improvement through Al addition, resulting in the formation of a thin, protective and HT-resistant alumina layer on top of the coating. New low-friction coatings of enhanced oxidation resistance have been sought, among them Zr-based transition metal nitrides, carbides and carbonitrides. High-temperature CVD using halide-containing precursors as well as PVD were used to deposit ZrN in the past. However, in the case of CVD, a reduction of the deposition temperature was aimed for, to enable the coating of temperature sensitive substrates, such as plain HSS tool steels. Thus, precursors had to be developed allowing for decomposition and coating formation well below 600°C.

Metal-organic compounds were found suitable to match this requirement. PACVD using tetrakisdi(m)ethylamidozirconium metal-organic compounds decomposing at temperatures < 600°C has been carried out since the mid-seventies, in research laboratories. The influence of reactant gases and carrier gases present during deposition was also investigated. These coatings were not well characterised with respect to their mechanical and tribological properties. They seemed to be looked at from a semiconductor/microelectronics point of view. The metal-machining performance of Zr-based and Ti-based coatings was compared for films deposited by PVD. The promising results obtained in these tests for Zr-based coatings encouraged the development of low-temperature CVD techniques to benefit from the characteristics of CVD, such as a high degree of conformity, good adhesion and low coating roughness.

The development of Zr-containing metal-organic compounds benefited from the knowledge gained for the synthesis of Ti-based compounds. Both tetrakisdimethylamidozirconium and tetrakisdiethylamidozirconium were used for film formation. However, each of these two compounds had its advantages and drawbacks. By combining the ligands to form tetrakis(ethyl-methyl)amidozirconium (TEMAZ), a compound was
available making use mainly of the advantages of the two single-type-ligand precursors. Published work did not cover the tribological behaviour of coatings based on this precursor.

In addition, three new compounds have been synthesised for this work. Two precursors, tetrakis(pyrrolidido)zirconium (TPyrrZ) and tetrakis(piperidido)zirconium (TPZ), are similar to TEMAZ as they are based on a central Zr-atom surrounded by four ligands. The ligands are N-containing heterocycles. The third compound, bis(μ-tert-butylimido)tetrakis-(tert-butylamido)dizirconium (TBUZ), is a binuclear compound.

The experimental program for this work was set to evaluate TEMAZ, TPyrrZ, TPZ, and TBUZ and to determine the properties of coatings formed by MOCVD using these precursors. Initially the suitability of the precursors for use in MOCVD had to be assessed. Preliminary MOCVD experiments were performed to evaluate the vital process parameters, such as evaporation temperature and rates, substrate temperature, reactant and carrier gases, flow rates, and system pressure. Microhardness, growth rate and chemical composition of the deposits formed were evaluated. Based on these results, the precursors for the main experimental program were selected. Compounds found not suitable were withdrawn.

The main experimental program consisted of the formation and characterisation of coatings using several sets of deposition parameters. The parameter sets were compiled such that various aspects—the influence of deposition temperature or reactant gases used on the coating properties—could be enlightened. Depositions were mainly performed at temperatures between 400 and 600°C. Some measurements were conducted below and beyond these limits.

Coating characterisation was based on growth rate evaluation, microhardness measurements, and chemical composition. X-ray diffraction for phase analysis was performed on selected coatings only. The influence of the amount of ammonia reactant gas used during deposition on the coating properties was investigated. Furthermore, coating appearance, morphology and roughness were determined.

Tribological investigations were performed with pin-on-disk experiments on selected coatings deposited in this work and a large number of commercially coated substrates. Five different pin materials were tested on each coating. The coefficient of friction and, where applicable, the wear rate were evaluated for each tribocouple. Wear tracks were
evaluated by Imaging-XPS to determine material transfer from the pin to the coating or vice versa. SEM images were taken to document the wear tracks and debris.

5.2 Preparation of Substrates

Both steel disks and silicon wafers were used in this study. The following paragraphs describe the steps and treatments applied to the chosen substrates from the as-received samples to the polished or etched materials.

Steel Samples — Depositions under standard conditions as described in Section 5.5 were carried out on steel samples. Disks of 25 mm diameter and approximately 1.5 mm thickness were machined from rods of Böhler S390 Isomatrix steel. The chemical compositions of the steel is given in Table 5.1 \[\text{[1]}\]. S390 was heat treated and hardened to values of 65 HRC. A surface finish of N5 (Ra 0.4 μm, DIN ISO 1302 \[\text{[2]}\]) or better was achieved by subsequent machine grinding.

The roughness of the surfaces in the as-received state was found not to be suitable for the post-deposition characterisation methods chosen. The surface to be coated was therefore subjected to wet grinding using SiC emery paper of grit 500 and 1000. Diamond polishing was performed using 6- and 3-μm diamond suspensions. Ultrasonic (US) cleaning of the samples to remove debris and abrasive particles was performed in ethanol after each grinding and polishing step. Finally the samples were US-cleaned for three minutes in ethanol and dried in hot air. Alternatively, samples were purchased in industrially ground and polished condition.

The surface roughness of both manually and industrially polished surfaces was evaluated by means of profilometry (see Section 5.6.2) and atomic force microscopy (see Section 5.6.5) as Ra < 7 nm.

<table>
<thead>
<tr>
<th>Tab. 5.1</th>
<th>Composition in wt.-% of steel Böhler Isomatrix S390 according to the analysis of the manufacturers datasheet [\text{[1]}].</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>S390</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Prior to deposition, samples were degreased and US-cleaned in acetone for five minutes, blown dry with helium and finally air plasma-cleaned for one minute at maximum power (100 W) in a commercial plasma-cleaner (Harrick PDC-32G).

**Silicon Wafers** — Silicon wafers were mainly used for preliminary experiments. Single-side-polished Si <100> wafers from Virginia Semiconductor Inc. (Fredericksburg, VA 22401, USA) of 25 and 29 mm diameter and approximately 0.4 mm thickness were used in this study. They were degreased, US-cleaned in acetone and subjected to a three-step process of etching (3% HF, 5 min), oxidising (10% HNO₃, 3 min), and final etching (3% HF, 3 min) prior to deposition. After each step, the wafers were rinsed with ultra-high-purity water and finally blown dry in helium.

### 5.3 Precursors: Synthesis and Handling

The precursors used in this study are displayed in Figure 6.1—results and discussion section. The compounds are air-sensitive. Synthesis, storage, and handling, i.e. transfer to the evaporator, was therefore performed under dry nitrogen using standard Schlenk techniques.

Precursor synthesis and analysis were performed by Dr. M. Morstein [3].

#### 5.3.1 Tetrakis(ethylmethylamido)zirconium (TEMAZ), 1.

In a first step, lithium ethylmethylamide was prepared at 0°C from 145 ml 1.6 mol/l n-butyllithium hexane solution (232.0 mmol) and a slight excess of ethylmethylamine (FLUKA Chemicals, 99.7% purity; 15.21 g, 257.3 mmol) in 250 ml pentane, and the precipitated amide collected by filtration. After drying, the amide (14.63 g, 224.9 mmol) was re-suspended in 500 ml ether and, over a period of 1 1/2 hours, dropwise added to a stirred suspension of 1/4 eq. (13.09 g, 56.13 mmol) anhydrous zirconium tetrachloride in 300 ml ether, kept at -60°C. The suspension soon transformed to a thick slurry, but became well stirrable again towards the end of the addition. Stirring was maintained, and the reaction mixture allowed to warm up overnight, being subsequently filtered to remove the LiCl and washed with 50 ml of pentane. Removal of solvent from the filtrate at room temperature left the crude product, which was purified by short-path distillation at 70°C
bath temperature and $10^{-3}$ mbar (coldfinger at -15°C). Pure TEMAZ was obtained as a pale yellow, mobile liquid in 13.77 g (42.55 mmol, 76.0%) yield.

**Elemental analysis:**

$C_{12}H_{32}N_4Zr$, $M = 323.64$ g/mol

calc.: C 44.54%  H 9.97%  N 17.31%  Zr 28.19%

found:  C 40.33%  H 8.87%  N 15.52%  Zr 27.94%

$^1H$-NMR (400 MHz, $C_6D_6$, $\delta$ in ppm): 3.25 (q, 2 H, CH$_2$, $^3J_{HH} = 6.76$ Hz), 2.98 (s, 3 H, CH$_3$ [Me]), 1.15 (s, 3 H, CH$_3$ [Et]);

$^{13}$C-{$^1H$}-NMR: 49.2 (s, CH$_2$), 37.5 (s, CH$_3$ [Me]), 16.0 (s, CH$_3$ [Et]).

5.3.2 Tetrakis(pyrrolidido)zirconium (TPyrZ), 2.

At 0°C, a solution of 15.41 g Li(pyrr) (200.12 mmol) in 225 ml THF was slowly added to 1/4 eq. (11.66 g, 50.03 mmol) ZrCl$_4$ in 130 ml ether. Precipitation of LiCl was observed; the solution was kept stirring overnight. After filtration and washing with 60 ml pentane, the combined filtrates were dried and the semi-solid residue was sublimed from the melt at 120-130°C at 5 $10^{-2}$ mbar to give 4.87 g (13.10 mmol, 26.2%) pure product $C_{16}H_{32}N_4Zr$ (371.7 g/mol).

5.3.3 Tetrakis(piperidido)zirconium (TPZ), 3.

This compound was prepared analogously to 1. by reacting 12.23 g (134.27 mmol) Li(pip) and 7.82 g (33.57 mmol) ZrCl$_4$ in a total of 675 ml ether at -30°C. After sublimation from the melt at 130°C/$10^{-2}$ mbar to a -20°C cold finger, pure TPZ ($C_{20}H_{40}N_4Zr$, 427.8 g/mol) was obtained as a pale yellow, crystalline solid in 7.71 g (18.02 mmol, 56.7%) yield.

$^1H$-NMR (400 MHz, $C_6D_6$, $\delta$ in ppm): 3.48 (s, 4 H, $\alpha$-CH$_2$), 1.49 (m, 6 H, $\beta$-CH$_2$ + $\gamma$-CH$_2$); $^{13}$C-{$^1H$}-NMR: 50.9 (s, $\alpha$-CH$_2$), 29.6 (s, $\beta$-CH$_2$), 26.2 (s, $\gamma$-CH$_2$).

5.3.4 Bis($\mu$-tertbutylimido)tetrakis(tert-butyramidoo)dizirconium (TBUZ), 4.

By reacting LiNHrBu (14.73 g, 186.3 mmol) and ZrCl$_4$ (10.79 g, 46.30 mmol) in 600 ml ether at -40°C analogous to the above-described procedures, we did not obtain the homoleptic primary amido complex Zr(NHrBu)$_4$. Instead, by elimination of NH$_2$rBu
from this intermediate, the binuclear, imido-bridged complex \((\text{NHrBu})_2\text{Zr}(\mu-\text{N}7\text{Bu})\text{Zr}(\text{NHrBu})_2\) formed, in 14.13 g (23.04 mmol, 99.5%) crude yield. After sublimation at 155°C/10⁻³ mbar, pure TBUZ \([\text{NHrBu}]_2\text{Zr}(\mu-\text{N}7\text{Bu})\text{Zr}(\text{NHrBu})_2\] was obtained as a sulphur-yellow, crystalline powder in 7.68 g (12.52 mmol, 63.6%) yield. The compound exhibits fluorescence both in daylight and, very intense, if irradiated with 365 nm UV light. M.p.: >166°C dec.

**Elemental analysis:**

\[
\text{C}_2\text{H}_{58}\text{N}_6\text{Zr}_2, M = 613.21 \text{ g/mol}
\]

Calc.: \(\text{C} 47.01\% \quad \text{H} 9.53\% \quad \text{N} 13.70\% \quad \text{Zr} 29.75\%\)

Found: \(\text{C} 46.79\% \quad \text{H} 9.55\% \quad \text{N} 13.52\% \quad \text{Zr} 28.80\%\)

**NMR** (400 MHz, \(\text{C}_6\text{D}_6\), \(\delta\) in ppm, all singlets): \(^1\text{H}\) 4.08 (4 H, NH), 1.46 (18 H, NC\((\text{CH}_3)_3\)), 1.41 (36 H, NHC\((\text{CH}_3)_3\)); \(^{13}\text{C}\{^1\text{H}\} 61.7 \quad \text{(NC\((\text{CH}_3)_3\))}, \quad 53.5 \quad \text{(NHC\((\text{CH}_3)_3\))}, \quad 36.4 \quad \text{(NHC\((\text{CH}_3)_3\))}, \quad 35.4 \quad \text{(NHC\((\text{CH}_3)_3\)).}\]

### 5.4 CVD-Reactor

The self-built CVD experimental apparatus, schematically illustrated in Figure 5.2, consisted of a hydrogen carrier gas delivery assembly, an ammonia/nitrogen reactant gas delivery line, a helium backfill line (not drawn), a precursor handling and evaporation system, and a cold-wall reactor connected to a pump stand and a vacuum control unit.

#### 5.4.1 Carrier Gas, Backfill, and Reactant Gas Delivery Assembly

All gas lines were made of 6x4 mm diameter stainless steel AISI 316L (DIN 1.4435) tubing with Swagelock® fittings. The number of connector fittings was kept to a minimum.

For precursor evaporation and transportation into the reactor, hydrogen carrier gas of purity 99.9999% was used. After passing through a Merck Oxisorb® purifier, specified by the manufacturer to remove oxygen to below 100 ppb, the gas stream divided in two, such that one branch, regulated by mass-flow controller 1 (MFC 1), led into the evaporator. The other branch was used to dilute and transport the vaporised precursor into the reactor (MFC 2).

The ammonia/nitrogen reactant gas mixture contained 9.86 vol.-% NH₃. It was made from nitrogen of a total purity of 99.999% and UHP NH₃. This line was regulated by
MFC 3 after purification of the gas mixture with a Millipore Waferpure Micro® purifier, specified to remove oxygen to less than 1 ppb.

A helium backfill line (He 99.9999) was connected to the bottom of the reactor (not displayed in Figure 5.2). It was used to bring the reactor chamber quickly back to atmospheric pressure before sample introduction, for connection of the bubbler, or at the end of each deposition cycle.

The mass-flow controllers (Brooks 5850S) were calibrated for helium flows (MFC 1, MFC 2) and nitrogen (MFC 3) and operated by a Brooks Model 0154 control
and read-out unit. Full-scale values for the real gases flowing through the MFC were adjusted in the control-unit settings using gas-conversion factors \[4\]. For single gases, Equation 5.1 was used to determine the full-scale value for the gas used:

\[
FS_2 = \frac{FS_1 \cdot CF_2}{CF_1}
\]  

(5.1)

- \(FS_1\) full-scale value of calibration gas
- \(CF_1\) conversion factor of calibration gas vs. \(N_2\)
- \(FS_2\) full-scale value for gas used
- \(CF_2\) conversion factor for gas used vs. \(N_2\).

For gas mixtures of gases A and B in the ratios \(M_A\) and \(M_B\) (\(M_A + M_B = 1\)), Equation 5.2 was used to determine the conversion factor of the mixture \(CF_{AB}\):

\[
CF_{AB} = \frac{1}{M_A + M_B} CF_A + CF_B
\]

(5.2)

Using the result from Equation 5.2 in 5.1 the full-scale value for gas mixtures \(FS_{AB}\) can be calculated for any given calibration gas as:

\[
FS_{AB} = \frac{FS_1 \cdot CF_{AB}}{CF_1} = \frac{FS_1}{CF_1 \left(\frac{M_A + M_B}{CF_A + CF_B}\right)}
\]

(5.3)

Conversion factors used for the calculations of \(FS_{AB}\) are given in Table 5.2.

**Tab. 5.2** Conversion factors of a few selected gases vs. nitrogen. Nitrogen equals 1.000 for conversion factors.

<table>
<thead>
<tr>
<th>gas</th>
<th>symbol</th>
<th>sensor conversion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>NH₃</td>
<td>0.788</td>
</tr>
<tr>
<td>helium</td>
<td>He</td>
<td>1.389</td>
</tr>
<tr>
<td>hydrogen</td>
<td>H₂</td>
<td>1.010</td>
</tr>
<tr>
<td>nitrogen / ammonia 9:1</td>
<td>N₂/NH₃ 9:1</td>
<td>0.974</td>
</tr>
</tbody>
</table>
Table 5.3 lists the calibration gases used for the mass-flow controllers, the full scale tested with the calibration gas and the calculated full-scale values for the process gases employed.

### 5.4.2 Metal-Organic Precursor Evaporator

The precursors TEMAZ, TPyrrZ, and TPZ, all liquid at evaporation temperature, were evaporated in a temperature-controlled double-walled glass bubbler. A stream of hydrogen was passed through a capillary immersed in the precursor. By adding glass beads, heavy bubbling, splashing and thereby flash evaporation of the precursor on the hot evaporator glass surface above the liquid reservoir could be minimised.

The solid precursor TBUZ was mixed with ground glass at a ratio of 1:2, and filled into a double-walled, fixed-bed type glass evaporator. Hydrogen was passed through this bed and fed into the reactor.

The evaporation rate was in all cases determined by weight-loss measurements. A higher flow rate was needed for the fixed-bed solid precursor evaporator to achieve comparable evaporation rates as used with liquid bubblers.

### 5.4.3 CVD Cold-Wall Reactor Chamber

The cold-wall reactor, see Section 2.2.2, consisted of a vertical cylindrically shaped fused silica tube of 56 mm inner diameter ending in stainless steel fittings and flanges on either side (Figure 5.2). The substrate was placed on an Advanced Ceramics Boralectric® pyrolytic boron-nitride coated graphite resistive heater. A shielded K-type thermocouple (0.5 mm outer diameter), was used both for direct surface-temperature measurement and to hold the sample in place during the experiment. The accuracy of all high-temperature
measurements using K-type thermocouples is ±2°C. The reproducibility is ±0.5°C. Constant temperatures and temperature profiles could be run by means of a PID temperature controller.

The saturated gas exiting from the evaporator, for precursors 1., 2., and 3. additionally diluted with hydrogen carrier gas (MFC 2), entered the reactor through the main gas inlet tube, which was equipped with a Philips Thermocoax heating coil. By means of heating tape and Thermocoax coil, all feed lines and the main inlet tube were kept at least 15°C above the evaporator temperature in order to prevent condensation of the precursor.

The ammonia/nitrogen reactant gas mixture (MFC 3) entered the reactor through a 6 mm outer diameter stainless steel tube, visually aligned at the centre of the main inlet tube and ending 10 mm above the end of the latter. Here the precursor-carrier gas mixture was combined with the ammonia/nitrogen reactant gas. The inlet position was adjusted such that gas-phase reactions far above the hot substrate activated by radiative heating, could be minimised.

The samples were mounted at a distance of 15 mm from the end of the main inlet gas tube, thus avoiding eddies in the stagnant-flow streamlines. This was confirmed by Dauelsberg et al. by numerical modelling of flow and heat transfer for this reactor geometry and substrate position [15]. Two process gas mixtures were looked at. Mixture 1 (50% He, 45% O₂, 5% H₂O), mainly used for work on zirconium dioxides and mixture 2 (95% H₂, 5% NH₃) to represent experimental conditions close to the ones used in this work, simplified by using H₂ as an approximation for H₂ and N₂ present in the reactor.

The temperature distribution along the reactor wall was measured with a thermocouple specially designed for surface temperature measurements and compared with the computed data. Figure 5.3 shows fairly good agreement between experimental and computational results for the wall-temperature profiles. The peak temperature observed represents the location of the sample and heating element.

The different transport properties of gas mixtures 1 and 2 have a significant impact on flow characteristics and heat transfer. The temperature distribution and the reactor operating parameters were used to calculate streamlines and isotherms for the two mixtures under identical conditions in the reactor. The results are displayed in Figure 5.4.
Fig. 5.3 Experimental and calculated temperature distribution along the reactor wall. Gas 2 (95% H₂, 5% NH₃), total flow 45 scem, P = 500 Pa, T_{substrate} = 550°C, T_{inlet} = 150°C [5].

Fig. 5.4 Isotherms and streamlines for gas 1 (50% He, 45% O₂, 5% H₂O) and gas 2 (95% H₂, 5% NH₃). Total flow 45 scem, P = 500 Pa, T_{substrate} = 550°C, T_{inlet} = 150°C [5].
The Reynolds number of gas 1 is larger than that of gas 2 by a factor of approximately 2.5 for the same process conditions, resulting in a more pronounced formation of vortices due to separation at the opening of the inlet tube and downstream of the substrate. The use of gas 2 results in a more uniform temperature distribution on the surface of the heated substrate than gas 1. Changes of pressure at a constant flow rate were found to have only little effect on the flow structure in the investigated pressure range of 100-1000 Pa. However, the temperature gradients above the substrate are steeper and flow velocities are increased when the pressure is decreased at a constant flow rate. This corresponds to reduced residence times of the reacting gas mixtures in the hot zone.

Changes in the total flow rate influence the temperature distribution at the substrate surface, the intensity of the vortices upstream and downstream of the substrate, and the steepness of the temperature gradient.

In another set of measurements and calculations, the power input of the heating element was kept constant. The surface temperature in the centre of the sample was measured at three different flow rates. The temperature distribution on the sample surface as displayed in Figure 5.5 was then calculated using the flow-dependent surface temperatures measured together with the flow and temperature regime calculated for this reactor geometry and operating parameters.

**Fig. 5.5** Calculated temperature distribution on the substrate surface for various flow rates at constant power supply to the ceramic heating element. Flow rates of 15, 45, and 100 sccm, \( P = 500 \text{ Pa} \) \(^{15}\).
The temperature level at the surface of the substrate is lowered with increasing flow rates and the temperature profiles are changed from a convex to a concave shape. This is partially related to the increased cooling rate by the impinging flow, partially to a small recirculation downstream of the substrate that becomes more intense at larger flow rates and increases the cooling from below. However, for the flow rates used in this study for thin film deposition, the temperature distribution for 45 scem in Figure 5.5 would apply giving a rather uniform temperature distribution over the sample surface which is considered beneficial for uniform growth rates and coating thickness.

The deposition reactor is completed by a cold trap used to strip ammonia and reaction byproducts from the exhaust. A rotary pump, a computer-controlled downstream throttle valve, and a capacitive pressure gauge were used to maintain a constant deposition pressure.

5.5 Deposition

The range of deposition parameters chosen for MOCVD using the precursors TEMAZ, 1., TPyrrZ, 2., TPZ, 3., and TBUZ, 4. is given in Table 6.2 (Chapter 6 - Results and Discussion).

The reactor was conditioned for 24 hours prior to sample loading. The chamber and all lines downstream from the MFCs were evacuated. Heating tapes and a hot-air fan were used to bake the feed lines and the fused silica tube to remove adsorbed water. After final preparation as described in Section 5.2, the sample was placed on the heating element and held in place by the thermocouple used for direct sample-surface-temperature measurement during the experiment. The sample loading into the reactor was carried out under a permanent countercflow of helium through the backfill line. The reactor was pumped down and the substrate heated to 200°C, where it was kept for three minutes upon reaching this temperature to displace moisture on the sample and hot plate. Thereafter, the system was left to cool down under vacuum. The evaporator was connected to the thermostat bath. The throttle valve was closed and the reactor backfilled with helium to atmospheric pressure. The evaporator was connected to the reactor under a steady countercflow of helium. The throttle valve was slowly opened and the system left to be pumped down. Upon reaching full opening of the valve, i.e. maximum pumping rate, the chosen deposition pressure was set at the valve control unit.
A flow of 20 sccm hydrogen through MFC 2 was regulated and the chosen pressure established by the control unit, which adjusted the valve opening position accordingly. The thermostat was set to the evaporation temperature and the precursor left to be heated up. The sample was brought to deposition temperature prior to the evaporator reaching a steady-state temperature. The cold trap was filled with liquid nitrogen and the reactant gas flow was set to the chosen value. One minute after the evaporation temperature was reached, the hydrogen-carrier flow-rate was set to the deposition parameter, the capillary was lowered into the precursor reservoir (precursors TEMAZ, TPyrrZ, and TPZ) and hydrogen passed through it. For depositions using the fixed-bed evaporator, the hydrogen flow through the evaporator was regulated to the deposition value. The deposition-time measurement was started. The surface of the sample was visually observed during the experiment. Generally the formation of a visible deposit started shortly after introduction of the saturated gas into the reactor. At the end of the deposition, the capillary was removed from the liquid reservoir when using precursors TEMAZ, TPyrrZ, and TPZ, and the bubbler quickly cooled to stop further precursor evaporation. For the solid precursor TBUZ, the flow through the evaporator was bypassed and the evaporator quickly cooled. All other parameters were kept constant for another 10 minutes. The sample was then left to cool down at a controlled rate of 20°C min⁻¹, and the reactor backfilled with He to ambient pressure. Coated samples were stored in vacuum in a desiccator charged with silica gel.

5.6 Coating Characterisation Methods

The deposits have been characterised by elemental and structural analysis using the following methods: optical light microscopy, scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and atomic force microscopy (AFM). Furthermore, coating thickness and hardness were investigated. Surface roughness was evaluated by means of stylus profilometry and AFM. Tribological evaluations were performed using a pin-on-disk set-up under controlled atmosphere.
5.6.1 Hardness

Hardness is defined as the mechanical resistance that one material presents to the indentation of a second, harder material. Thus, hardness measurements can be of qualitative to quantitative nature, depending on the test used \[^6\]. The results depend not only on the elastic and plastic properties of the material to be evaluated but also on the shape and properties of the test body and the test conditions.

**Principle** — The classical methods for hardness evaluation are Vickers (HV), Knoop (HK), Brinell (HB), and Rockwell. Rockwell is further divided in HRC, which is the most frequently used Rockwell test, HRA, HRB, and HRF \[^2\]. An indenter, of a specified geometry, is placed on the sample surface. A load is applied for a certain time, allowing plastic deformation of the sample to take place. After retracting the indenter the indent size of the remaining plastic indentation deformation is measured directly through the eyepiece of an optical microscope. Alternatively a video image is analysed using imaging analysis software for the indent size evaluation. The hardness is calculated from the dimensions evaluated \[^7\].

For thin functional coatings, it must be ensured that the deformation of the substrate under the indenter will not occur \[^8\]. Therefore the indent depth must be much smaller than the coating thickness. Microhardness measurements use low loads for indentation. Thus only small and shallow indents are formed. The Knoop diamond cut has the advantage of smaller indent depth compared to Vickers hardness testing at the same load. It is therefore often used for microhardness measurements. Figure 5.6 \[^9\] shows the geometries of the Vickers and Knoop indenter.
The Vickers indenter is of pyramidal shape with equal diagonal length and a face-to-face apex angle of 136°. For hardness evaluation, both diagonals of the indent are measured. The average value is used for the hardness calculation \[^{[9]}\].

The Knoop diamond has two diagonals \(d\) and \(D\) of different length. This is caused by the different major and minor apex angles of 172.5° and 130° of the cut resulting in a rhombohedral cross-section. Only the longer diagonal \(D\) of the indent is used for the hardness evaluation \[^{[10]}\].

\[
HK_p = \frac{C_K P}{D^2} \quad (5.4)
\]

\(P\)  applied force in units of grams-force

\(C_K\)  proportionality constant.
This increases the susceptibility of the measurement to anisotropy in surface mechanical properties. The penetration depth is 0.635 that of the Vickers indenter, assuming equal test force and hardness number. Knoop numbers HK are usually higher than Vickers hardness values HV. This is because HK is calculated as force per unit of projected area of indentation, whereas HV is defined as force per unit facet area. The facet area of the Vickers pyramid is larger than the projection area of the Knoop indent.

Instrument — Microhardness values were evaluated using a Leitz Durimet hardness tester with a load of 25 gf and a Knoop pyramidal indenter. The total time for approach and indentation was 30 seconds. A minimum of five indents was measured on each sample to evaluate mean hardness and standard deviation. The penetration depth calculated from the indenter geometry and the diagonal D is approximately 0.62 \( \mu m \) for 1000 HK and 0.78 \( \mu m \) for 600 HK.

5.6.2 Roughness (Stylus Method)

The contact stylus method is, in industry, the most widely used non-destructive method for surface roughness determination. The technique is well established and described in a number of textbooks and review papers \[11-14\].

Principle — A stylus is traversed across a surface at a given, constant velocity. To ensure contact with the surface, a load in the mg-range is applied to the tip. The tip is usually a diamond with defined geometry (conical or pyramidal with flat or rounded tip) and fixed to a lever. While moving the stylus along the surface, the tip-movement in z-direction of the lever is converted into an electrical signal through a transducer. This signal describes the surface profile \( h(x) \) if plotted on a chart versus the location \( x \) of the tip at each time during the measurement. Roughness average, \( R_\alpha \), is defined as in Equation 5.7 as the arithmetical average of the departures of the profile above and below the reference line throughout the prescribed sampling length. Surface roughness values are normally assessed as mean results of several sampling lengths taken consecutively along the surface.
For a discrete number of points \( n \) measured along the length \( l \), Equation 5.7 can be written as:

\[
R_n = \frac{1}{n} \sum_{i=0}^{n} |h_i| \tag{5.8}
\]

\( h_i \) difference of real value and mean value profile.

The lateral resolution depends on the velocity at which the stylus is moved over the surface. The lower this speed, the higher the resolution\(^{[15]}\).

As the tip is not of a mathematical point but of finite dimensions, a so-called effective profile is actually recorded. This effect gains importance and affects the accuracy of the method if very narrow but deep features of peaks and valleys must be followed by the tip.

Instrument — Profilometry measurements were performed on a Tencor Instruments alpha-step 200 with a diamond tip of 0.2 \( \mu \text{m} \) tip radius at 4 mg load. Sampling lengths were 2000 \( \mu \text{m} \) with 1 \( \mu \text{m} \) horizontal resolution when evaluating wear tracks and average surface roughness and 400 \( \mu \text{m} \) with 0.2 \( \mu \text{m} \) horizontal resolution when evaluating surface roughness only. The time for one measurement was 40 s.

5.6.3 X-ray Photoelectron Spectroscopy (XPS) for Chemical Analysis and Imaging

Principle — X-ray photoelectron spectroscopy (XPS) uses soft X-rays to determine the binding energy of electrons escaping from the inner atomic shells of the elements present at the surface. The X-rays commonly used are Mg-K\( \alpha \) (1253.6 eV) and Al-K\( \alpha \) (1486.6 eV) which are characterised by their relatively low intensity of bremsstrahlung. Measurements are performed under ultra-high vacuum (UHV).

XPS is intensively used in surface science\(^{[16]}\) because of its high surface sensitivity. Sampling depth is typically in the range of 20-30 Å. XPS offers the ability to determine the elements present in the surface region, their oxidation state and their number. Thereby quantitative analysis of the surface composition to a sensitivity of \( 10^{-1} \) at.-\% is possible.
The basic effect in XPS is the absorption of a quantum of energy or photon, $h\nu$, and the ejection of an electron, the photoelectron as displayed in Figure 5.7 a) \cite{117}. In addition, and subsequent to the photoelectron removal, the excited atom can relax with the production of an Auger electron as described in Figure 5.7 b) or by emission of a photon. As a photon interacts with atoms in a material, the photon is absorbed with a probability proportional to the photoelectric cross-section. The entire photon energy is absorbed by electrons bound to the atom. If the photon energy $h\nu$ is greater than the electron binding energy $E_B$, then the electron will be emitted from the atom with a kinetic energy $E_{\text{kin}}$ given by Equation 5.9 as:

$$E_{\text{kin}} = h\nu - E_B - \Phi,$$

(5.9)

The binding energy is defined as the electron orbital energy level with respect to the Fermi level, or the energy with which the electron is bound to the atom. Since the kinetic energy of photoelectrons is typically $\leq 1200$ eV, the mean free path of electrons in this kinetic range is in the nm-range for solid materials, thus they can only escape from shallow depths ($\leq 30$ Å). To determine the binding energy $E_B$, the kinetic energy must be accurately measured with an electrostatic electron energy analyser. The photon energy must be known and closely controlled. The spectrometer work function $\Phi_s$ is dealt with as a calibration parameter. Its value is frequently checked using standard specimens such as Au, Cu, or Ag.
The binding energy is sensitive to the oxidation state of the atom looked at. For atoms present in a compound in comparison to the pure element, a chemical shift is determined, which is directly related to the oxidation state in which the element is found in the compound. Thereby identification of an unknown compound and of the binding properties and chemical state is possible through comparison with standard specimen of known composition.

Standard X-ray sources do not produce monochromatic radiation. Besides $K\alpha_{1,2}$ a series of side lines $K\alpha_{3,4}$ and $K\beta$ are emitted. These photons are capable of producing photoelectrons which then interact and lead to satellite signals in the binding energy spectrum in the vicinity of the peaks caused by the $K\alpha_{1,2}$ irradiation at known energy difference and relative intensity to the main signals.

Imaging-XPS, an addition to standard XPS investigation, enables the chemical mapping of investigated surfaces. The sample is irradiated by an X-ray beam as in conventional XPS but the photoelectrons are not only collected according to their binding energy but analysed with respect to their location of origin on the surface by rastering the photoelectron beam upon entering the analyser.

**Instrument** — XPS experiments were performed using a Physical Electronics PHI Model 5700 instrument, equipped with a Mg/Al twin anode, using Al-K$\alpha$ irradiation at 350 W and a take-off angle of 45°. The chamber pressure was $6 \times 10^{-9}$ Torr or better during analysis. The binding energy scale of the instrument was calibrated using the Au 4f (84.0 eV), the Cu 2p (932.7 eV), and the Ag 3d (368.3 eV) peak obtained by irradiating pure Au, Cu and Ag with Al-K$\alpha$. Low-resolution survey scans (0-1000 eV) were collected at a pass energy of 187.85 eV, with 0.4 eV and 100 ms per step. High-resolution detail spectra in the energy ranges of the O 1s, C 1s, N 1s and Zr 3d states were collected at a pass energy of 23.50 eV, 0.05 eV step width and 100 ms time per step. Electron binding energies were calibrated with respect to the C 1s line at 284.6 eV. Acquisition times were kept short, to avoid X-ray induced damage. Ar$^+$-sputtering was accomplished with a rasterised (5x5 mm area), differentially pumped ion gun operating at 3 keV. The chemical composition was evaluated at a sputter depth equivalent to 220 nm SiO$_2$. Depth profiles were calibrated against a SiO$_2$ standard.
Elemental analysis was carried out using the PHI PC-Access ESCA V6.0 software. The atomic concentration was obtained from the integrated peak areas (integrated background) employing Physical Electronics' sensitivity factors. Detail spectra were deconvoluted by a nonlinear least-square method with a mixed Gaussian/Lorentzian peak shape after subtraction of the integrated background.

In Imaging-XPS, photoelectrons within a window of 2 by 2 mm (on the sample surface 2 x 2.8 mm due to the 45° take-off angle) were analysed. The data was acquired in the unscanned mode at a pass energy of 187.85 eV, with 1.6 eV and 100 ms per step. The scan window was divided in 64 x 64 cells for collection. The area of the track on the sample surface to be looked at was always placed in a similar way with the track running from the upper left-hand corner to the lower right-hand corner as shown in Figure 5.8. Maps were collected and displayed for the elements of interest. Information of the elements present in the wear track and its vicinity were derived from these maps.

Fig. 5.8 Location of the wear track in Imaging-XPS maps collected for evaluation of the elements present and their location within the mapped area. The dimensions, 2 by 2.8 mm, state the real size looked at on the sample surface whereas the analyser window is 2 by 2 mm at a take-off angle of 45°.

5.6.4 Growth Rate Evaluation Based on Coating Thickness

The coating thickness is accessible via several methods: cross-sectioning and direct measurement of the thickness (optical or by SEM), through weight-gain measurements, by scratch profilometry using the stylus method, and through dimple-grinding.
Principle — Coating thickness determination by using sample weight-change, surface area and coating material density is a method which has been used for a long time, especially in the field of corrosion, to determine oxidation process rates. The thickness accuracy highly depends on the precision of the balance used and the coating density. Calculating thickness for dense materials, when examining porous coatings will result in a discrepancy between optically evaluated and calculated thickness. Cross-sectioning of coating systems using standard metallographical techniques and optical microscopy or SEM for investigation are widely used characterisation methods offering direct imaging. Scratch profilometry uses a classical stylus to evaluate the depth of scratches applied to a coating. This method relies on the coating to fail in the scratch region and to expose the underlying substrate surface. If the coating is not scratched through entirely or, if the substrate is damaged by the scratch, false thickness values will be evaluated. Coating thickness is also accessible using a micro-scale abrasive test as shown in Figure 5.9. This is a destructive method which leaves a dimple in the coating and substrate material. It was designed to evaluate wear performance but also provides information on the coating thickness. The method has been developed and applied to hard coatings by Hutchings and Rutherford [19-21]. By measuring the dimensions $x$ and $y$ of a pair of concentrical circles, the coating thickness or individual layer thickness $D$ can be approximated as:

$$D = \frac{xy}{d}$$

(5.10)

where $d$ is the diameter of the sphere.
Fig 5.9 Micro-abrasion tester: a), b), and c) show the test equipment set-up consisting of sample holder, steel ball, slurry delivery, ball drive shaft, and load measurement cell. d) image of a dimple: cross-sectional view revealing coating and substrate and the relevant dimensions measured for coating thickness evaluation. a) and b): 19]. c): courtesy of CSEM.

**Instrument** — Coating thickness was measured using a CSEM Calowear dimple grinder or, alternatively, determined from cross-sectional images taken using field-emission scanning electron microscopy (FESEM).
The micro-abrasive wear test gives an accuracy for the coating thickness evaluation of 250 nm. CSEM's own SiC slurry was used. Easy sample fixation is combined with short measurement time. The only disadvantage is that the sample surface is exposed to the slurry used, thus Calowear must be performed as the last test in a series, as XPS and tribotesting results might be adversely affected by the slurry abrasive particles.

FESEM results in better accuracy but only if the sample is properly aligned in the sample holder. The sample size is restricted to 5x10 mm to fit the holder. Thus a piece of material must be carefully cut from the sample, which is easy for silicon wafer substrates but more challenging for coated steel samples. Excessive heat due to cutting must be avoided. The coating must be broken to reveal the cross-section and not cut through, as cutting would likely cause delamination, flaking off, or smearing of material along the flank.

Scratch profilometry using the stylus method (see Section 5.6.2) on scratches applied by hand with a hardened metal stylus was found not suitable, as selective scratching of the coating without cutting the substrate material was difficult.

Thickness calculation from weight-gain measurements was predominantly used for coatings deposited on Si-wafers. The layers were assumed to have a density of 7.35 g cm\(^{-3}\) as quoted for cubic ZrN\(^{[22]}\).

5.6.5 Atomic Force Microscopy (AFM)

As a complementary technique atomic force microscopy (AFM) was used to characterise plain steel surfaces and coated surfaces with respect to surface roughness. Data was compared with profilometry data.

Principle — The AFM system allows the determination of three-dimensional surface topography in the nanometer range and, due to the mechanical set-up, friction force measurements. The AFM technique can be understood as a nano-size stylus method. Principally it is based on the measurement of the location of an ultra-sharp tip, typically of < 100 nm radius, in x-y-z coordinates. The tip is fixed on a cantilever of known spring constant. The motion of the tip is followed by a laser beam. The beam is deflected if the tip changes its position. Measurements can be performed setting a fixed tip position and moving the sample table in x-y for scanning and in z direction to keep the tip steady or by moving the table with the sample in x-y for scanning the area and tracing the z-changes of the tip position for height. Thus by processing x-, y-, and z-signal, a three-
dimensional image of the surface topography can be obtained. The data collected can be used to extract various roughness values and histograms. Permanent contact of the tip is used in contact mode measurements while the tip is oscillating at high frequency in tapping mode, just touching the surface before being retracted. The mode selected depends on the sample and the properties to be investigated.

**Instrument** — Atomic force microscopy was used together with profilometry to evaluate the surface quality of both plain substrates and coated surfaces. A DI Nanoscope III AFM (Digital Instruments, Santa Barbara, CA 93117, USA) was used to investigate scanning areas of 100 by 100 μm (512 by 512 pixels) and to calculate the average surface roughness Rₐ of that area. For surface roughness evaluation, the maximum difference between the highest and the lowest point on the surface should not exceed 5 μm, otherwise the z-displacement limit of the scanner is reached.

### 5.6.6 Scanning Electron Microscopy

Scanning electron microscopes (SEM) are most suitable to acquire topographic images of sample surfaces at high depth of focus (0.01 – 100 μm). In SEM systems a focussed, relatively high-energy primary electron beam is used for sample illumination and rastered over the area of interest. The lateral resolution is determined by the focussed beam spot size (1-10 nm). Backscattered electrons (BSE), secondary electrons (SE) and characteristic X-rays are emitted from the surface, collected and analyzed. SE are caused by electron cascade processes and are of low energy (several eV), also leading to characteristic X-ray emission of the elements present. This radiation can be used for quantitative analysis by an energy dispersive X-ray spectrometer (EDX). The SE detected can only leave the material from the topmost 1-10 nm thick near-surface volume. BSE can escape from a higher depth and are of the same energy as the initial electrons in the primary beam.

**Principle** — The illumination system consists of an electron gun using a heated filament or a field-emission tip as electron emitter. Field-emission electron guns give better source stability, narrower electron energy spread, enhanced brightness, improved resolution and analytical capabilities. The field-emission tips also have a longer operational life compared to hot-filament SEM but field emission SEM systems (FESEM) are more
difficult to maintain, as vacuum requirements are critical. The electrons are accelerated by a high voltage applied between filament or tip and anode, typically of 5-30 kV, and passed through subsequent electromagnetic lenses where the beam is focussed and/or collimated. Suitably located mechanical apertures are used to define the beam, along with coils for beam alignment, astigmatism correction, and beam scanning. A vacuum environment is required to limit scattering of the electrons by gas molecules. The topographic contrast is the most widely used operation mode of SEM. It is obtained from SE analysis. The SE yield strongly depends on the local tilt of the sample surface. Sharp edges and small particles cause higher SE emission than flat areas. Further detail of the surface topography is revealed by the shadowing contrast, which is superimposed on the surface-tilt contrast. SE can therefore be useful for the visualisation of rough surfaces with high slope angles, but are practically useless for ultrasmooth surfaces where BSE are used for material- and orientation contrast. In materials contrast, bright areas are associated with heavy elements and vice versa. Large depth of focus, high lateral resolution, affordable equipment and easy operation make SEM an excellent tool for surface visualisation and analysis.

**Instrument** — Coating morphology in cross-sectional and plan view was imaged on a Hitachi S-900 in-lens field-emission scanning electron microscope. The system was operated at low acceleration voltages of 5 keV or less to achieve both acceptable clarity of the images and high magnifications. Wear tracks were looked at using a JEOL JSM 6400 scanning electron microscope at 20 kV. SE signal was used. The aim was to find areas of coating deterioration and to check for wear particles and debris and their location.

### 5.6.7 X-Ray Diffraction Analysis (XRD)

**Principle** — X-ray diffraction analysis is used to identify the crystallographic structure of a material. If more than one crystallographic phase is present, then each will give a distinct diffraction pattern. The analysis is, if not looking at an entirely new structure, based on the comparison of an experimentally collected diffraction pattern with patterns of substances, the structures of which are already known. This comparison is made considerably easier if the chemical composition of the coating can be determined, for example by XPS, because the number of possible structures is then limited. In a
A typical XRD experiment, a beam of X-rays—monochromated or not, depending on the diffractometer type used—hits the coated surface from which it is diffracted. The intensity of the diffracted beam is recorded as a function of the diffraction angle, $\theta$. The intensity of the beam will be nonzero only at those diffraction angles at which the Bragg condition is satisfied $^{[23]}$. The intensity of the diffracted beam depends on several factors such as the structure of the material, the volume irradiated, the diffraction geometry and the sample alignment.

**Instrument** — X-ray diffraction spectra using Cu-K\(\alpha\) irradiation were collected on a Scintag Inc. XDS 2000 (source: 30 mA at 40 kV; angle: 2-70° 2$\theta$, PT 1.8-3.6, step 0.03; sample rotation: off) or on a Siemens D5000 (source: 35 mA at 45 kV; angle: 15-70° 2$\theta$, PT 6-10, step 0.02; sample rotation: on). Further data treatment and comparison with JCPDS record 35-753 (ZrN) was done using the MacDiff software package $^{[24]}$.

### 5.6.8 Tribology and Wear

In this section, the pin-on-disk tribometer and the evaluation of wear rates are explained. Pins and coatings tested against each other by this method are listed.

**Principle** — A pin is placed on a sample and subjected to a normal load. The sample moves at a constant velocity relative to the pin. The friction force is measured continuously with the friction force cell fixed to the pin holder. The quotient of friction force measured and normal load applied is the coefficient of friction $\mu$. The motion of the pin can be reciprocal or continuous in a straight or circular direction. The circular set-up as given in Figure 5.10 is predominant.

After each full revolution the pin re-passes the track from the previous revolution. The wear scar caused thereby can be evaluated chemically by XPS, Imaging-XPS and geometrically through profilometry to give an account of the wear rate.
The wear rate evaluation is based on the evaluation of the cross-section of the wear track by means of profilometry. Profiles were collected at three different positions along the wear track with the profile sampling length perpendicular to the wear track. The cross-section of the wear scar was evaluated for each profile. Figure 5.11 shows the worn area in a cross-section view used for wear rate evaluation.

The average cross-section area of the wear track of the three measurements was multiplied by the circumference of the wear track middle line to give the volume worn. This volume was then divided by the total sliding distance and by the load to calculate the normalised wear rate. Thus direct comparison of the wear data evaluated, independent of the parameters chosen for the tribomeasurements is possible.

Instrument — Pin-on-disk tribotests were performed on a CSEM tribometer (CSEM S.A., Neuchâtel, Switzerland) in controlled atmosphere. Relative humidity was
reduced to 5-7% r.h. during the experiment by passing dry air through the measurement compartment. The equipment was placed in an air-conditioned room. Temperatures were 22-24°C. Temperature and humidity within the compartment were monitored with a combined thermometer and hygrometer (temperature: ± 1°C, humidity: ± 4% r.h.).

The tribometer consists of a motor-driven, rotating sample holder, a pin holder fixed to the load arm, a load arm to apply a static load to the pin, and a strain-gauge fixed to the arm for friction-force evaluation. The load on the arm and thus on the pin can be adjusted by placing defined weights on the arm. A maximum load of 10 N is specified to ensure the integrity and accuracy of the tribometer used.

Friction-force readings were plotted on a chart recorder and simultaneously passed to a computer. Electronical data acquisition at various sampling rates and mathematical operations performed on the data sets allowed a fast way of post-experimental data processing and visualisation of friction-coefficient-vs.-time-diagrams.

The friction-force cell was calibrated by applying a known lateral force and recording the strain-gauge output. This reading was converted from voltage into load. These steps were repeated at different lateral forces. The settings at the tribometer for the load calibration were adjusted to equalise load reading and lateral force. A high correlation coefficient between lateral force and measured load was aimed for to guarantee linearity over the full load range.

Individual measurements consisted of pin preparation, compartment conditioning and finally tribotesting. The pin was subjected to dry grinding at 2 N load with SiC emery paper of grit 1000 while fixed in the holder attached to the load arm. Thereafter, the pin was US-cleaned in acetone for two minutes, blown dry with helium and fixed to the arm. The arm was moved to the chosen radius on the sample surface. The load was applied and the arm put in the horizontal position. The friction-force reading was checked and set to zero if necessary. The sample and holder were fixed and the height of the turning table was adjusted. The compartment was then flooded with dry air. Upon reaching relative humidity readings of less than 10%, the measurement was started. Friction-force data was collected on a chart recorder and with a computer connected to the force-cell signal output. The relative sliding velocity between pin and disk was set to 1 m min⁻¹ for all measurements. The sampling rate for the data collection with the PC was set to 29 Hz. This was found to reduce signal noise and artefacts in the readings. See Section 6.5.1 for details on the sampling rate.
Pin Materials — Five different pins were tested against the various coatings. Pin materials chosen are listed in Table 5.4 with details of chemical composition and hardness.

Table 5.4 Chemical composition and hardness of pin material used for tribotesting.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Hardness [HK_{0.025/30}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6 steel</td>
<td>C 0.98, Cr 1.50, Si 0.25, Mn 0.35, Ni 0.15, balance Fe 585</td>
</tr>
<tr>
<td>Hastelloy C22</td>
<td>Ni 56, Cr 22, Mo 13, W 3, Co 2.5, Fe 3 297</td>
</tr>
<tr>
<td>TiAl6V4</td>
<td>Al 6, V 4, Fe &lt; 0.25, O &lt; 0.2, balance Ti 234</td>
</tr>
<tr>
<td>SM451C Cu-alloy</td>
<td>Ni 1.0, Pb 1.0, P 0.2, balance Cu 121</td>
</tr>
<tr>
<td>AlMg4</td>
<td>Mg 4.0, Si &lt; 0.4, Cu &lt; 0.1, Mn 0.45, Cr 0.15, Fe &lt; 0.5, Zn &lt; 0.25, balance Al 80</td>
</tr>
</tbody>
</table>

100Cr6 is a typical bearing material used for balls or needles. It exhibited the highest hardness of all pins used. The Ni-based alloy Hastelloy C-22 consists mainly of Ni, Cr, and Mo. Especially Cr is known for forming dense surface oxide layers upon exposure to air, protecting the underlying material. TiAl6V4 is an alloy widely used for human-body implants due to its excellent biocompatibility. However, difficulties in machining need to be overcome. SM451C is a Cu-based alloy in hardened condition. AlMg4 is used in aerospace industry as a lightweight alloy. It will protect its surface by a naturally grown film of alumina upon exposure to air. Oxide formation takes place very rapidly. Also wear debris of such an alloy will oxidise quickly.

Industrially Coated Samples — Table 5.5 lists the coatings that were commercially coated and tested for comparison with the deposits formed in this work. As processes and equipment were proprietary, only little detailed information could be obtained from the manufacturers.
### Industrially deposited coatings. Processes used and properties.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Commercial deposition process and properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrN I (PVD)</td>
<td>Decorative coating, cathodic-arc, low ion energy, 300-500 nm thickness</td>
</tr>
<tr>
<td>ZrN II (PVD)</td>
<td>Tribocoating, cathodic-arc, 2.5 μm thickness, HV = 2800</td>
</tr>
<tr>
<td>TiN (CVD)</td>
<td>High-temperature process, TiCl₄/H₂, HV 1900-2400</td>
</tr>
<tr>
<td>TiN (PVD)</td>
<td>Cathodic-arc</td>
</tr>
<tr>
<td>TiCN (CVD)</td>
<td>Ti₃C₀.₃N₀.₇, medium-temperature process (720-900°C), TiCl₄/H₂/CH₃CN, HV 2500-2800</td>
</tr>
<tr>
<td>TiCN (PVD)</td>
<td>Cathodic-arc deposited, TiC₀.₃N₀.₅, HV = 2650</td>
</tr>
<tr>
<td>TiAlCN (PVD)</td>
<td>Cathodic-arc deposited, Ti₆Al₁₂C₀.₂₅N₀.₇₅, HV = 3300</td>
</tr>
<tr>
<td>TiAlN + WC/C (PVD)</td>
<td>Hybrid process: cathodic-arc + sputtering, multiple layered, lamellar structure, HV₀.₀₅ ≈ 3000</td>
</tr>
<tr>
<td>Balinit Hardlube</td>
<td>Hybrid process, cathodic-arc + sputtering, lamellar structure, HV₀.₀₅ = 1000</td>
</tr>
<tr>
<td>WC/C (PVD)</td>
<td>Hybrid process: cathodic-arc + sputtering, lamellar structure, HV₀.₀₅ ≈ 4200</td>
</tr>
<tr>
<td>Balinit C</td>
<td>DLC, HV₀.₀₅ 2000-3000</td>
</tr>
<tr>
<td>DLC I (PECVD)</td>
<td>Amorphous diamond-like carbon, HV₀.₀₅ ≈ 4200</td>
</tr>
<tr>
<td>DLC II (PECVD)</td>
<td>DLC, HV₀.₀₅ 2000-3000</td>
</tr>
<tr>
<td>Al₂O₃ (CVD)</td>
<td>κ-Al₂O₃, AlCl₃, high-temperature process, TiCN intermediate precoating</td>
</tr>
</tbody>
</table>

The coatings chosen represent the wide range of hard, wear resistant coatings available on the market formed by vapour deposition processes. They were applied to the steel S390 disks used in this work.

Two ZrN coatings deposited by PVD were available for tribotesting. The decorative coating ZrN I was of low thickness. The deposition process was optimised to obtain a very shiny, lustre surface finish. ZrN II represents a tribocoating of 2.5 μm thickness. TiN and TiCN coatings were deposited by PVD and CVD. Ti-based aluminium nitrides and aluminium carbonitrides for enhanced oxidation resistance were deposited by PVD. The multilayer/lamellar structures Balinit Hardlube and Balinit C were deposited by combined cathodic-arc deposition and sputtering. Diamond-like carbon (DLC) coatings were tested for comparison because of their excellent friction performance. They are very hard, chemically inert but usually highly stressed in thicknesses greater than one μm. Alumina coatings were chosen to represent the wide range of oxide coatings. They perform very well in harsh environment even at elevated temperatures due to excellent stability and oxidation resistance [25].
References


6 Results and Discussion

6.1 New Metal-Organic Precursors for Zirconium Nitride CVD

To deposit zirconium nitride or -carbonitride at moderate temperatures, the predominantly used precursor is Zr(NEt₂)₄, a representative of the tetravalent tetrakis-(dialkylamido)zirconium complexes. Surprisingly, with the exception of individual reports on Zr(NMe₂)₄ [¹, ²], Zr[N(Me)CH₂CHeczy (cp = η⁴-cyclopentadienyl) [²] and Zr(NEtMe)₄ [³], alternatives to this simple but efficient compound have not been considered. Our goal was therefore to study the impact of related precursors containing different amido ligands on the CVD film quality.

![Chemical structures](image)

**Fig. 6.1** Structure of alternative zirconium(carbonitride) precursors: TEMAZ (tetrakis(ethylmethylamido)zirconium) 1., TPyrrZ (tetrakis(pyrdidido)zirconium) 2., TPZ (tetrakis(piperidido)zirconium) 3., and TBUZ (tetrakis(tert-butylamido)bis(tert-butylimido)zirconium) 4.

Figure 6.1 shows the four selected compounds. One aliphatic, two alicyclic secondary amido derivatives as well as a binuclear mixed amido/imido complex were used for MOCVD. From the molecular set-up, these precursors were expected to exhibit different volatility, thermal stability and deposition behaviour. The properties of the coatings deposited were evaluated and compared for various sets of deposition parameters chosen.

6.2 Surface Temperature — A Function of the Internal Temperature and the Reactor Pressure

The influence of the selected method of surface temperature measurement on the steel substrate bulk hardness was looked at. The degree of substrate dehardening due to annealing taking place at elevated temperatures was evaluated under experimental conditions for various temperatures and pressures.
Initial annealing tests on S390 steel disks at surface temperatures of up to 700°C confirmed the loss of bulk hardness. This made further investigations necessary to determine the maximum acceptable internal temperature of the sample disk to maintain bulk hardness or to minimise dehardening at a given system pressure.

A steel disk was prepared such that a thermocouple could be inserted into a hole, drilled into the side of the steel disk. The sample was placed on the heating element and, as for the deposition experiments, a thermocouple was placed on its top surface. This thermocouple was used for surface-temperature measurement and control. Setting the PID controller to the chosen temperature, the surface temperature was kept constant. Meanwhile, the internal temperature was monitored by the thermocouple introduced into the sample. A series of surface temperatures was tested at both 50 and 500 Pa reactor pressure with 58 sccm He flow and an inlet tube temperature of 100°C to simulate deposition conditions in the reactor. The data is displayed in Figure 6.2.

As can be seen from the data, the internal temperature is always higher than the surface temperature. This is explained by the set-up with the sample placed on the heating element. Convection and radiation towards the reactor space occur at the sample surface. Additional cooling of the sample surface is caused by the gases flowing past it. Thus for a chosen surface temperature, a higher internal temperature must always be maintained to counterbalance the cooling effects. The difference between the two temperatures is pressure dependent. Lower internal temperatures are required at 500 Pa in comparison to 50 Pa system pressure. This is contradictory to expectations, as convection cooling would benefit from the elevated pressure, resulting in higher internal temperatures required at higher system pressure to maintain identical surface temperature as at 50 Pa. However, not only convection but also flow rates must be accounted for. As flows are measured at atmospheric pressure in the MFC, the flow-rate equivalent due to gas expansion at system pressure has been calculated. As an example, 1 sccm at atmospheric pressure expanded at room temperature equals to 1993 sccm at 50 Pa and to 199 sccm at 500 Pa. Thus a factor of 10 is determined between flow rates at 50 and 500 Pa. This causes additional cooling at 50 Pa, which seems to be much more pronounced in comparison to the changes in convection cooling.
Fig. 6.2 Influence of the reactor pressure on the internal sample temperature at a given surface temperature. The surface temperature was controlled by means of PID. The internal temperature of the steel sample was measured by a thermocouple inserted into a hole from the side. The gas flow was 58 sccm He. The inlet tube was kept at 100°C.

It was concluded that the higher deposition pressure of 500 Pa is beneficial to maintain the bulk hardness because lower internal temperatures are required to achieve the same surface temperature as for 50 Pa. There is an almost linear correlation between internal and surface temperature at 500 Pa. The linear regression is given in Equation 6.1.

$$T_{\text{internal}} = 1.271 T_{\text{surface}} - 48.944$$  \hspace{1cm} (6.1)

with all temperatures in °C.

Additional tempering tests were performed at surface temperatures of 463, 483 and 511°C to see if the bulk hardness can be predicted accurately. The internal temperature was calculated from the set surface temperature according to Equation 6.1. The expected bulk hardness value after annealing at the calculated internal temperature was taken from the tempering chart of steel S390 (Figure 6.3) [4]. The bulk hardness was compared with the sample hardness evaluated after annealing on the upper and lower surface of the disk.
using a Rockwell C tester. This hardness test is bulk-sensitive, involving large-size indents and plastic deformation.

Fig. 6.3 Tempering chart of steel S390. Holding time 3 x 2 hours; specimen size: square 25 mm; austenizing in salt bath. Hardening temperatures: 1150°C—solid line, 1210°C—dashed line. 600°C is the maximum internal temperature acceptable to maintain bulk hardness. This results in slightly more than 500°C surface temperature at 500 Pa under standard gas flow rates. Adapted from [14].

The results of this comparison are listed in Table 6.1 and do confirm the suitability of Equation 6.1. The maximum hardness according to the tempering chart of above 67 HRC could not be reached anymore. The samples used already had a lower initial hardness of approximately 65.4 HRC in the as-delivered condition, prior to annealing under simulated deposition conditions.

Good quantitative agreement between expected and measured hardness is found. At 600°C internal temperature, the experimentally evaluated hardness of 61.0/61.5 HRC is somewhere in the middle between 59 and 63 HRC, the hardness values attributed to initial hardening temperatures of 1150°C (solid line) and 1210°C (dashed line) respectively. It is therefore concluded that the initial hardening temperature chosen—unknown due to samples being commercially hardened in a proprietary process—was likely to be somewhere between 1150 and 1250°C.
The hardness values measured on the lower and upper side of the sample do not differ much. Bearing in mind that the sample is heated from the lower side, we conclude that the temperature distribution throughout the sample must be uniform at deposition temperature.

Tab. 6.1 Influence of deposition temperature on substrate dehardening. The internal temperature is used to determine the expected hardness from the tempering chart. Reactor pressure: 500 Pa.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>463</td>
<td>540</td>
<td>67</td>
<td>65.3</td>
<td>65.3</td>
</tr>
<tr>
<td>483</td>
<td>565</td>
<td>65</td>
<td>64.4</td>
<td>64.9</td>
</tr>
<tr>
<td>511</td>
<td>600</td>
<td>59</td>
<td>61.0</td>
<td>61.5</td>
</tr>
</tbody>
</table>

Fig. 6.4 Surface temperature as a function of the reactor pressure at various constant internal temperatures. The internal temperature of the steel sample was measured by a thermocouple inserted into a hole from the side. The gas flow was 58 sccm He. The inlet tube was kept at 100°C.
The influence of the reactor pressure was looked at over a wider range of pressures. In Figure 6.4 the surface temperature is plotted vs. the reactor pressure at a chosen internal temperature. To collect these data, the thermocouple measuring the internal temperature was connected to the PID controller to regulate the heating element. In this way a constant internal temperature can be maintained. Meanwhile, the thermocouple placed on the sample was used to monitor the surface temperature. This confirms that the difference between internal and surface temperature is reduced with increasing total pressure.

For the MOCVD experiments we conclude both from the tempering chart and the experimentally observed hardness degradation, that the internal temperature should not exceed 600°C. This translates—for the steel samples used—into a maximum applicable surface temperature of 550°C. Figure 6.4 was used subsequently for all experiments to estimate the internal temperature and thus the bulk hardness after deposition at a given substrate temperature and pressure.

6.3 MOCVD

As quoted earlier, the coating properties can be closely controlled and adjusted in MOCVD by carefully selecting and controlling the deposition parameters, i.e. substrate temperature, reactor pressure, evaporator temperature, and gas-flow rates.

Table 6.2 contains the parameter sets used for the four different precursors. In most cases NH₃ was used as reactant gas. Si-wafers were used with the parameter sets A0 (Ø 29 mm), A3 and B0 (Ø 25 mm). Steel disks of material S390 were used for all other sets and depositions. The effect of precursor, system pressure, deposition temperature, and NH₃ addition on coating growth rates and properties was studied in detail using parameter sets A2, A3, B1 and C1.
Tab. 6.2 Deposition parameters used for TEMAZ, TPyrZ, TPZ, and TBUZ metal-organic precursors. Parameter sets for preliminary experiments are printed in italics.

<table>
<thead>
<tr>
<th>precursor</th>
<th>P</th>
<th>T_{sub}</th>
<th>T_{evap}</th>
<th>H_{2} (MFC 1)</th>
<th>H_{2} (MFC 2)</th>
<th>N_{2}/NH_{3} (MFC 3)</th>
<th>parameter set #</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMAZ</td>
<td>50</td>
<td>500-700</td>
<td>75.0</td>
<td>5</td>
<td>25</td>
<td>30</td>
<td>A0</td>
</tr>
<tr>
<td>Zr(NEtMe)_{4}</td>
<td>500</td>
<td>450-600</td>
<td>100.0</td>
<td>3</td>
<td>60</td>
<td>10, 7.5, 10, 20</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>400-550</td>
<td>87.5</td>
<td>3</td>
<td>60</td>
<td>0</td>
<td>A2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>325-550</td>
<td>60.0</td>
<td>3</td>
<td>60</td>
<td>0</td>
<td>A3</td>
</tr>
<tr>
<td>TPyrZ</td>
<td>50</td>
<td>550</td>
<td>134</td>
<td>5</td>
<td>25</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>Zr(pyr)_{4}</td>
<td>50</td>
<td>550</td>
<td>134</td>
<td>5 He</td>
<td>25 He</td>
<td>30</td>
<td>-</td>
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<tr>
<td></td>
<td>500</td>
<td>500</td>
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<td>-</td>
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<tr>
<td></td>
<td>500</td>
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6.3.1 Preliminary Experiments

Preliminary experiments were performed to learn more about the characteristics of the reactor in its present set-up and to identify the best range of deposition parameters for each precursor.

TEMAZ — This compound was first used in 1995 by Berndt et al. \[3\] for plasma-enhanced CVD of ZrCN. The authors describe it as an air-sensitive liquid, which is more volatile than Zr(NEt_{2})_{4}. In contrast, the solid dimethylamido complex is less volatile, because it forms associated [Zr(NMe_{2})_{4}]_{n}, both in the solid state \[5\] (n = 2) and in solution \[6\] (n = 1.2). TEMAZ is considered an attractive choice for zirconium nitride and -carbonitride MOCVD, since it is the lowest molecular weight liquid of the series of tetravalent amides. It is easily accessible by standard synthetic routes and has a high volatility. However, neither synthesis nor characterisation were previously reported. The synthetic route as described in Section 5.3.1 results in a yield of 76% of pure, pale yellow
liquid of low viscosity. The distillation bath temperature of 70°C at 0.1 Pa was taken as an indicator for the evaporator temperature.

Coatings deposited using TEMAZ at parameters listed as set A0 on Si-wafers of 29 mm diameter were sound and well adhering. Their hardness was higher than the steel substrate hardness (575 HK) only for deposits formed at 550°C or below (Figure 6.5, filled squares). However, these parameters would not be suitable for steel substrates, since bulk dehardening would occur over the entire temperature range of 500 to 700°C tested. At internal sample temperature of beyond 700°C for any surface temperature of 500°C and higher (Figure 6.4), dehardening would occur according to the tempering chart (Figure 6.3).

![Fig. 6.5 TEMAZ: Influence of the system pressure and the evaporator temperature on the coating hardness. The plain steel S390 had a hardness of 575 HK in the pre-deposition condition. Parameter sets and substrates used are given in brackets.](image)

Growth rates were as high as 1 μm per minute as displayed in Figure 6.6. High levels of oxygen contamination were found, as illustrated in Figure 6.7. They increased towards higher substrate temperatures while hardness values dropped.

In a first attempt to improve coating quality, the amount of precursor in the gas phase had to be reduced. This was expected to reduce the growth rate, thus positively reflecting on the chemical composition, e.g. the levels of contamination, and the hardness of the coatings. The system pressure was therefore increased to 500 Pa. Thereby the expansion of the carrier gas with respect to atmospheric pressure was reduced by one order of
magnitude from 1:2370 at 50 Pa to 1:237 at 500 Pa, leading to a correspondingly reduced evaporation rate. In addition, coatings can now be deposited on steel substrates as dehardening is minimised at 500 Pa.

![Fig. 6.6 TEMAZ: Influence of the system pressure and the evaporator temperature on the coating growth rate. High growth rates caused internal stress leading to delamination, cracking and/or flaking of coatings. Parameter sets and substrates used are given in brackets.](image)

At an evaporation temperature of 75°C, no visible deposits formed. The evaporation temperature was raised to 100°C to re-establish saturation of the gas phase with the precursor. Gas flow rates were changed, such that the amount of ammonia was reduced to prevent parasitic decomposition in the gas phase. These parameters are listed as set A1. Coatings were deposited on steel disks. However, the growth rate was only slightly reduced which may be associated to the increased evaporator temperature. Thus a similar amount of precursor was available for deposition per time unit as with set A0. In addition, lowering the reactant gas flow reduces the detrimental parasitic precursor consumption in the gas phase, leading to higher amounts of precursor available for deposition. Deposits were found to form at substrate temperatures below 500°C. Film hardness was increased in comparison to experiments using parameter set A0, for the first time going beyond the plain steel substrate hardness. At substrate temperatures of above 550°C, the dehardening of the S390 steel substrates affects the microhardness readings and may well be more pronounced than the reduction in hardness caused by carbon and oxygen contamination of the
the coating. The underlying substrate cannot support the hard coating against the indenting diamond tip as in the initial hard condition. Thus, in total, a reduced hardness is measured. The oxygen contamination was markedly reduced, and the chemical composition did not change significantly with deposition temperature. Growth rates were still high and did not vary much with temperature.

Reducing the TEMAZ evaporation temperature to 87.5°C at 500 Pa (set A2, deposited on S390), growth rates of around 100 nm per minute were obtained using 10 sccm N₂/NH₃. Thereby the gas expansion factor in the bubbler was changed to 245.
Further depositions using TEMAZ to study the influence of ammonia addition on the film formation were based on set A2 at 500 and 550°C. The amount of \( \text{N}_2/\text{NH}_3 \) mixture was varied from 0 to 7.5, 10 and 20 sccm \( \text{N}_2/\text{NH}_3 \). Additional experiments using parameter set A3 and Si-wafers of 25 mm diameter were carried out without ammonia addition at various substrate temperatures. Growth rates dropped well below 100 nm min\(^{-1} \) whilst hardness values for coatings deposited above 400°C were found similar to deposits using parameter set A2.

The deposition parameter sets A2 and A3 as listed in Table 6.2 were found promising for detailed MOCVD experiments using the precursor TEMAZ. The results of the characterisation of the coatings formed are discussed in detail in Section 6.4.

The two alicyclic secondary amido derivatives TPyrrZ and TPZ have not been synthesised before. The stress in the cyclic structure of TPyrrZ, albeit low in comparison to a 3- or 4-membered ring, may additionally support decomposition at lower temperatures, in comparison to TEMAZ. For TPZ, due to the chair conformation, almost ideal tetrahedral binding angles are obtained.

The purified precursors (synthetic routes: see Sections 5.3.2 and 5.3.3) were pale yellow, crystalline solids. This made their use for MOCVD more difficult as powders are not as easy to handle as liquids, which can be measured and transported without exposure to air using syringes. The yield of TPZ was 57%, whereas only 26% were achieved for the production of TPyrrZ. From an economical point of view this certainly is an intrinsic drawback for the latter substance.

The distillation bath temperatures of 130°C at 1 Pa for TPZ and 120-130°C at 5 Pa for TPyrrZ indicate that these two compounds are significantly less volatile than TEMAZ (70°C at 0.1 Pa). It must be noted that these precursors are heated above the melting point for the deposition experiments. The standard liquid evaporator can therefore be used.

**TPyrrZ** — Deposits using TPyrrZ were initially formed at 50 Pa reactor pressure, using hydrogen as carrier gas and \( \text{NH}_3/\text{N}_2 \) addition. The optimum evaporator temperature was found to be 134°C. An experiment using He as carrier gas showed little changes in chemical composition but slightly reduced coating hardness as listed in Table 6.3. High
growth rates of 280 and 570 nm per minute were obtained in both cases. To reduce the
growth rate, the system pressure was increased to 500 Pa, as described earlier for
TEMAZ. Hardness values for deposits at 500 Pa were below the steel substrate hardness.
The microhardness was not measurable due to low coating thickness in the case of the
coating formed using He as carrier gas. The constraints to be observed for accurate
Knoop hardness measurements could not be matched.

The oxygen levels detected were lower than in TEMAZ-based coatings. This is due to the
higher stability of the TPyrrZ precursor, preventing reaction with residual oxygen present
in the reactor. However, this increased stability bears a drawback with respect to carbon
incorporation, as incomplete decomposition of the precursor will result in increased
carbon incorporation into the coating. Deconvolution of the C-1s XPS peaks for the
above samples was used to evaluate the percentage of carbodic and adventitious or
polymeric carbon present. Of the carbon content listed in Table 6.3, only 30-43% was
carbodic in nature. The majority of carbon present is of the undesirable adventitious form
which reduces the hardness of the coating.

Based on these results and in combination with the difficulties in precursor
synthesis, it was decided not to further investigate the metal-organic compound TPyrrZ.
TPZ — Preliminary experiments using the heterocyclic amido complex TPZ showed that a much higher evaporation temperature of 160°C was needed for this precursor at 50 Pa system pressure (parameter set B0, Si-wafers). This is due to the lower volatility in comparison to TEMAZ, also caused by the increase in molecular weight of the ligands. Experiments using set B0 resulted in coatings of higher hardness (HK 870-1040, Figure 6.8) than deposits formed using TEMAZ as precursor. Growth rates in the range of 70 to 200 nm per minute, as displayed in Figure 6.9, were much lower compared to initial depositions using TEMAZ.

Fig. 6.8 TPZ: Influence of the system pressure and the evaporator temperature on the hardness. Parameter sets and substrates used are given in brackets.
Fig. 6.9  
TPZ: Influence of the system pressure and the evaporator temperature on the coating growth rate. High growth rates cause internal stress leading to delamination, cracking and/or flaking of coatings. Parameter sets and substrates used are given in brackets.

Fig. 6.10  
TPZ: Chemical composition for coatings deposited on Si-wafers using parameter set B0 and on S390 steel disks using set B1. Comparable amounts of Zr are found. Overall contamination levels vary little; a minimum is found at 475°C for set B1. Parameter sets and substrates used are given in brackets.
The XPS chemical compositions of the coatings are plotted in Figure 6.10. They were almost independent of the deposition parameters for coatings made with set B0 on Si-wafers. The oxygen contamination was below 11 at.-%. A tendency of coating deterioration through cracking, partial delamination and flaking-off was observed towards higher deposition temperatures. Furthermore, precursor consumption through evaporation at 160°C was found to be too high, resulting in the re-sublimation of unused precursor in the lower, colder areas of the reactor and the formation of yellow-brownish, powdery deposits on both the quartz tube and the inlet tube in the vicinity of the hot plate. Precursor consumption rate and powder formation were addressed by increasing the system pressure to 200 Pa, slightly reducing the evaporator temperature to 155°C and changing the gas flow rates to values given in parameter set B1. The elevated pressure is also beneficial with respect to reducing sample dehardening due to annealing as discussed in Section 6.2. First tests at 500 and 550°C substrate temperature showed that hardness, growth rates and chemical composition were similar to deposits formed at the same temperatures using set B0.

The first results obtained from coatings formed at 500 and 550°C using parameter set B1 were promising with respect to hardness, growth rates and oxygen content observed. The deposition temperature interval was therefore extended to 400-575°C. The characterisation of the coatings deposited in this range using parameter set B1 is given in Section 6.4.

**TBUZ** — The binuclear primary amido/imido complex TBUZ can be synthesised as described in Section 5.3.4 at a yield of 64%. The compound was solid, both at room temperature and at the evaporation temperature of 155°C. Therefore, the fixed bed solid evaporator was used for this compound. Precursor and ground glass were mixed and placed on a glass frit within a tube, through which a controlled amount of carrier gas was passed. A similar set of parameters as for the deposition using TPZ was found suitable.
6.4 Coating Characterisation

6.4.1 X-Ray Diffraction

The steel substrate XRD spectra as displayed in Figure 6.11 was evaluated on plain material in pre-deposition condition. The distinct peaks also show-up in the spectra collected on coated disks. The effect is more pronounced for the coating deposited using TPZ in comparison to the one made from TEMAZ. This is related to the coating thickness which is lower in the case of the TPZ-based deposit allowing for higher intensity from the underlying substrate.

Phase analysis confirmed the formation of a cubic phase. Through comparison of the peak positions and intensities of cubic ZrN according to powder diffraction file (PDF) 35-753, ZrC (PDF 35-784), and our coatings we conclude that both ZrN and ZrC are present in our coatings. This is supported by the fact that carbon in the coating deposited using TEMAZ is at 58% present in the carbide form as determined by XPS.
Oxygen incorporation resulting in oxide phases, such as ZrO$_2$, did not result in distinct peaks. The peak positions of monoclinic ZrO$_2$ (PDF 37-1484), given in Figure 6.11 for comparison, were not identified in the spectra collected on coated samples. This may be due to the fact that the oxides formed are X-ray amorphous. The films have little crystallinity and are not significantly textured. The broadness of the diffraction peaks corresponds to nanosized crystallites.

### 6.4.2 Growth Rates

Figure 6.12 shows the influence of the deposition temperature on the growth rates for experiments using the precursors TEMAZ, TPZ, and TBUZ at parameter sets A2, B1, and C1 respectively. Detailed data are listed in Table 6.4.

**TEMAZ** — For coatings deposited on S390 steel disks using precursor TEMAZ and NH$_3$ addition (set A2) the precursor partial pressure was calculated from the precursor evaporation rate as an average of $p_{\text{TEMAZ}} = 4.94 \pm 0.18$ Pa. The amount of precursor entering the reactor per time unit was calculated as $2.98 \pm 0.11 \times 10^{-5}$ mol min$^{-1}$. The deposits formed at growth rates of 120 to 215 nm min$^{-1}$. A decrease of the growth rate was found with increasing substrate temperature. This is probably related to thermally activated gas-phase reactions resulting in a partial depletion of precursor at the substrate surface.

The formation of coatings on steel substrates using TEMAZ without the addition of NH$_3$ (set A2, 0 sccm N$_2$/NH$_3$, T 500/550°C) resulted in thick coatings deposited at high growth rates of 590 to 670 nm min$^{-1}$. The coating quality was rather poor. Cracks and flaking-off were observed, occasionally resulting in the complete delamination and destruction of the coating through internal stress caused by both too high a deposition rate and coating thickness. This indicates that without ammonia addition, the delivery of the precursor is not challenged by a parasitic reaction, therefore yielding higher growth rates. This condition should be avoided in deposition of quality coatings.

Coatings of good quality could only be deposited without NH$_3$ if the evaporation temperature was lowered to 60°C (parameter set A3). The amount of precursor evaporated per time is then reduced and the growth rate shifted to lower values of roughly 20 to 35 nm min$^{-1}$. Two kinetic regions were established. Up to 375°C an overall activation energy of 30 kJ mol$^{-1}$ was calculated. But above 375°C deposition temperature the curve
transforms into a straight line of negative slope at an overall activation energy of 7 kJ mol⁻¹. This might be due to the fact that the end of the inlet tube above the hot plate is heated through radiation. Therefore, deposition may also take place on the inlet tube. The temperature at the end of the inlet tube was measured under process conditions to be as high as 260°C for a substrate temperature of 500°C and a nominal inlet temperature of 150°C, measured outside on the upper part of the tube. This is high enough to cause precipitation from the gas phase at the inlet tube. Higher substrate temperatures will give rise to even higher temperatures at the exit of the inlet tube, thus enhancing the effect and resulting in lower deposition rates due to pronounced precursor consumption above the substrate.

Growth rates of a few 100 nm min⁻¹ are acceptable if parameter set A2 is used, resulting in well-adhering, smooth coatings. The reaction seems to be mass-transfer controlled and is superimposed by a parasitic gas phase reaction. When no ammonia reactant gas is added during deposition, high, detrimental growth rates are observed due to the lack of the parasitic, precursor-consuming reaction in the gas phase. Thus the evaporation temperature must be lowered from 87.5°C to 60°C to obtain dense, smooth and crack-free coatings. Both the kinetically controlled and the mass-transfer controlled regimes are found in the log growth rate vs. reciprocal temperature plot for coatings deposited using parameter set A3.

**TPZ** — For coatings deposited using precursor TPZ at parameter set B1 the precursor partial pressure was $p_{TPZ} = 1.54 \pm 0.12$ Pa. The amount of precursor entering the reactor per time unit was evaluated as $2.39 \pm 0.19 \times 10^{-5}$ mol min⁻¹.

A transition between kinetically and feed-rate-limited growth regimes is observed at approximately 500°C. Below 500°C, the calculated overall activation energy for precursor decomposition is about 80 kJ mol⁻¹. At higher temperatures, a temperature-independent growth rate plateau of around 160 nm min⁻¹ is found. This is attributed to the mass-transfer-controlled regime. However, at temperatures above 550°C, the growth rate was found to decrease due to more pronounced gas-phase reactions resulting in powder-like, yellow-brownish deposits on inlet tube and reactor walls.
The deposition parameters chosen result in smooth, glossy and well-adhering coatings.

![Graph showing growth rates of coatings deposited under standard conditions using TEMAZ, TPZ, and TBUZ on steel S390 with ammonia reactant gas. TEMAZ was also deposited without ammonia addition on Si-wafers. Parameter sets and substrates used are given in brackets.](image)

**Fig. 6.12** Growth rates of coatings deposited under standard conditions using TEMAZ, TPZ, and TBUZ on steel S390 with ammonia reactant gas. TEMAZ was also deposited without ammonia addition on Si-wafers. Parameter sets and substrates used are given in brackets.

**TBUZ** — TBUZ was deposited in a somewhat narrower temperature range of 450 to 550°C (parameter set C1). The precursor partial pressure was 0.86±0.16 Pa and the amount of precursor entering the reactor was evaluated as 1.26±0.48 $10^{-5}$ mol min$^{-1}$. The growth rate scatters in the range of 30-110 nm min$^{-1}$; no linearity or plateau region was found. This scattering is related to the fixed-bed precursor evaporator used. The solid precursor is mixed with glass powder. This mixture, filled into the evaporator, forms the bed. During evaporation, the precursor powder grain size will be gradually reduced, changing the surface-to-volume ratio, thus changing the evaporation rate. In addition to this effect, the agglomeration of powder grains upon exposure to the evaporation temperature was observed. In addition, the bed was compacted by the carrier gas passed through. It is difficult to maintain constant evaporation rates.
During deposition, only very little brownish deposit on the reactor and inlet tube walls was observed. This is an indication that the precursor was not heavily consumed by gas phase reactions, but available for the deposition reaction.

**Tab. 6.4** Survey of growth rates, hardness and XPS chemical compositions of films deposited from TEMAZ, TPZ, and TBUZ.

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*: porous coating—thickness and hardness could not be evaluated, rapid growth, individual needles grow at sample border

**: partial delamination, cracked, no XPS measurement possible

***: XPS measurement could not be carried out.

### 6.4.3 Hardness

Figure 6.13 contains an overview of the measured film microhardness values. Parameters used are identical to those of the series displayed in Figure 6.12 for growth rates. For all coatings, we found, to some extent, an influence of the oxygen contamination on the hardness. This is discussed in greater detail in Sections 6.4.5 and 6.4.6.
Fig. 6.13 Impact of deposition temperature on Knoop microhardness. S.390 steel samples were coated using the precursors TEMAZ, TPZ, and TBUZ at parameter sets A2, B1, and C1 respectively. TEMAZ was also used in experiments without NH₃-addition to the gas phase to form deposits on Si-wafers. The hardness of plain steel S390 in pre-deposition condition is 575 HK. Parameter sets and substrates used are given in brackets.

TEMAZ — For coatings deposited on steel S390 using TEMAZ with ammonia addition (parameter set A2), hardness values of 670 to 837 HK are measured. This is higher than the hardness of the plain uncoated steel substrate. A hardness maximum of 837 HK is found at 500°C substrate temperature. The decrease of the hardness of coatings formed at above 500°C may only partly be explained by loss of bulk hardness of the underlying steel disk. The amount of impurities and their effect on the coating microhardness must also be considered.

Slightly greater hardness of roughly 700 to 900 HK was achieved when depositing without the addition of NH₃ (set A3) at substrate temperatures of 425 to 525°C. A hardness plateau is found in this temperature interval. Up to 425°C, hardness increases with increasing substrate temperature. But coating hardness is only higher than the plain steel hardness at deposition temperatures of 375°C and beyond.
TPZ — Coatings using TPZ and parameter set B1 with 10 sccm reactant gas were deposited on S390 steel disks. At substrate temperatures of 450°C and higher, the hardness went beyond the hardness of the uncoated substrate. Values of 850 to 1030 HK were measured. The maximum hardness of 1030 HK was obtained on a coating formed at 475°C. A slight decrease of the coating microhardness is found towards higher temperatures. This may be related to the accuracy of the microhardness measurement technique used. The variation in hardness at T > 475°C is within the scatter band of the hardness test (±27 HK at 500°C to ±79 HK at 550°C). In addition, the chemical composition of the coating and the effect of the deposition temperature on the substrate hardness should be considered.

TBUZ — Coatings based on the precursor TBUZ are generally soft; the hardness values decrease with increasing temperature starting from around 614 HK at 450°C and going down to 225 HK at 550°C. Thus, coating the substrate is actually reducing the product hardness, as the initial steel hardness is 575 HK. These coatings were deposited on Si-wafers. The loss of coating hardness can therefore not be explained by the loss of substrate hardness due to annealing as it would be in the case of steel substrates. The hardness reduction may be due to the generally high oxygen content of the coatings, further increasing with increasing deposition temperature. The low hardness evaluated can also be an indicator for low crystallinity of the coating.

6.4.4 Chemical Composition

The chemical composition was evaluated from XPS measurements for coatings deposited using the precursors TEMAZ, TPZ, and TBUZ at parameter sets A2, B1, and C1 respectively. Coatings were also formed without ammonia addition using TEMAZ at operating parameters A3. An overview of the results is given in Figure 6.14.
Fig. 6.14 Overview of chemical compositions as a function of deposition temperature: Coatings were deposited on steel S390 using TEMAZ, TPZ, and TBUZ under operating conditions A2, B1, and C1 respectively. TEMAZ was also used in experiments without ammonia addition to the gas phase. The coatings were deposited on Si-wafers employing parameter set A3. Parameter sets and substrates used are given in brackets.

TEMAZ — For deposition experiments on steel S390 using TEMAZ with NH₃ addition (set A2), both the zirconium and the nitrogen content decrease with increasing temperature. Zr varies in the range of 29-42 at.-%. N is found at 14-24 at.-%. The Zr:N ratio varies from 1.6 to 2.3. The carbon content is in the range of 30-38 at.-%. The carbon is present as carbide and adventitious carbon at approximately equal amounts (1:1). The carbide carbon is the preferred form, as carbides will support the overall hardness of the coating while adventitious carbon will reduce the hardness. The oxygen content increases towards higher deposition temperatures from 4 at.-% to a
maximum of 26 at.-% at 525°C. The total amount of the contaminants C and O present increases with increasing temperature.

Si-wafers were also coated using TEMAZ without NH₃ addition at parameter set A3. The carbon content did not vary much with changing deposition temperature. Levels were around 29 to 34 at.-% C. The oxygen content increased from non-detectable at 340°C to 27 at.-% at 550°C deposition temperature. Similar contents of oxygen were found in comparison to the deposits formed with ammonia addition. Both zirconium and nitrogen contents decreased when going for higher deposition temperatures. The ratio of Zr:N was around 1.8 to 2.1 at temperatures from 340 to 450°C.

TPZ — Deposits on steel S390 were formed using the precursor TPZ and deposition parameters B1. A substantial oxygen contamination of 24 to 41 at.-% is found at deposition temperatures below 475°C. A minimum of 2 at.-% O is reached at 475°C and values below 10 at.-% are maintained up to 525°C. The Zr content of 26 to 32 at.-% is lower than for the coatings made from TEMAZ. The Zr:N ratio is 1.7 to 1.9 for deposits formed at 450 to 575 °C. Looking at the carbon content, we found higher C-levels of 28 to 52 at.-% for the coatings formed using TPZ in comparison to TEMAZ. The carbon incorporated was present at 40 at.-% only in the carbidic form. The rest was adventitious carbon.

This can be explained by the difference in the ligands. For TEMAZ, each hydrocarbon group can be cleaved individually and will then leave the boundary layer or, in the worst case, be incorporated into the coating. For the cyclic ligands in TPZ, two bonds need to be broken to release the hydrocarbon chain. Since these two bonds will be cleaved consecutively, the residence time of the metal-organic compound at the surface will be longer. Thus, the probability for incorporation of shorter fragments of CₓHᵧ is high. The overall number of short fragments is likely to be higher than the number of ligands released for TEMAZ. Thus, the probability for their incorporation is higher, resulting in larger amounts of incorporated carbon. The type of carbon, carbidic or adventitious, and the amount at which each is present, can also be influenced by the ligands. For TPZ it is expected that a larger amount of adventitious carbon will be incorporated in comparison to TEMAZ due to the greater number of carbon atoms in the precursor present for an identical number of N-C bonds (also see Section 6.4.5).
TBUZ — The binuclear precursor was used in experiments for deposits formed on steel S390 at deposition parameters C1. The amount of zirconium is almost constant in the range of 31 to 35 at.-%. The nitrogen content decreases with increasing temperature from 16 to 3 at.-%. Thus the Zr:N ratio increases from 2:1 up to 10:1 with increasing temperature. The carbon content of 13-19 at.-% is rather stable over the entire deposition temperature interval. The oxygen content increases from 32 to 51 at.-% at the highest deposition temperature. This is the highest oxygen content for any coating deposited under standard conditions. Thus, oxide formation is predominant; the nitride formation is challenged. This may be explained with the higher affinity of zirconium to oxygen than to nitrogen and carbon as reflected in the standard enthalpy of formation \[ \Delta H \]

\[
\Delta H_{\text{ZrO}_2(m)} = -1100.6 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{\text{ZrN}} = -365.3 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{\text{ZrC}} = -196.7 \text{ kJ mol}^{-1}
\]

The coating integrity and hardness will be adversely affected. The high content of oxygen may also be an indicator that only partly decomposed hydrocarbon residues have been incorporated. Upon exposure of the sample to air, these hydrocarbons will quickly oxidise, leading to an increased overall oxygen content in the coating. The stability of the TBUZ compound seems to be too high for proper decomposition in low-temperature MOCVD applications at the chosen parameters.

6.4.5 Carbon and Oxygen Incorporation

The influence of carbon and oxygen incorporation on the coating hardness has been mentioned in the previous sections. The following paragraphs look at this issue in more detail using XPS peak fitting for C-1s signal deconvolution and sputter-depth profiling.

Carbon — The peak deconvolution of carbon 1s XPS signals for four coatings is displayed in Figure 6.15.

For the coatings formed using TEMAZ, carbon was present in the carbide form (binding energy of \(=282\) eV) at 60% for 50 Pa and at 52% for 500 Pa system pressure.
For coatings made using TPZ as precursor, higher amounts of adventitious carbon were found in comparison to coatings made using TEMAZ. 52% carbidic carbon were measured at 50 Pa and only 40% at 200 Pa reactor pressure.

As carbon incorporation cannot be avoided with the present precursors [81], it must be mentioned that it should preferentially be present in its (hard) carbidic form, rather than the soft, amorphous, adventitious form.

![Graph showing XPS C-1s detail spectra](image)

**Fig. 6.15** XPS C-1s detail spectra. Coatings using the precursor TEMAZ were deposited at 500°C at 50 or 500 Pa system pressure using parameter sets A0 or A1 to deposit on Si-wafers or steel S390 respectively. Coatings using TPZ were deposited at 550°C at 50 or 200 Pa system pressure using parameter sets B0 and B1 to coat Si-wafers and steel disks respectively. The signal of carbidic carbon is expected at binding energies of around 282 eV. Adventitious carbon is found at binding energies of 284.5 eV. At higher binding energies, carbon is present in the oxidised form [91]. Parameter sets and substrates used are given in brackets. The binding energy scale was not shifted for charging compensation.

To display the influence of the amount of hard-phase-forming carbon and nitrogen on the hardness, XPS curve fitting was performed on a series of coatings deposited using TEMAZ and parameter set A1 in the temperature range of 485 to 600°C. For each deposition temperature, the coating chemical composition was evaluated and the C-1s peak fitted to determine the amount of carbidic carbon. The amounts of nitrogen and
carbidic carbon were added. Hardness measured was plotted against this sum as shown in Figure 6.16. High hardness corresponds to low deposition temperature and \textit{vice versa}. The beneficial influence of nitrides and carbides on the coating hardness has been confirmed.

![Graph showing the influence of nitrogen and carbidic carbon on hardness](image)

Fig. 6.16 Influence of the amount of nitrogen and carbidic carbon present in the coating on the hardness evaluated for coatings deposited at substrate temperatures in the range of 485 to 600°C using TEMAZ and parameter set A1. Substrate: steel S390.

**Oxygen** — As mentioned by Zilko \textsuperscript{10}, room air can readily contaminate the reactants and the deposition system. It is also known that oxygen and water adsorbed on the reactor walls and inside the tubing are difficult to remove \textsuperscript{8}. Variable amounts of oxygen impurities depending on deposition parameters and gas purity used have been reported by Täschner et al.\textsuperscript{111} for PECVD and Kim et al.\textsuperscript{112} for LPCVD of TiN using metal-organic precursors. Oxygen contamination was also attributed to the density of the coatings, influencing the access and inward diffusion of oxygen to the coating upon air exposure. He et al.\textsuperscript{13} quoted the surface adsorption of oxygen and the existence of oxygen in the films as consistent with the high affinity of Zr for this element and the fact, that oxygen diffuses into the surface layer of thin coatings upon exposure to ambient...
atmosphere, as described by Smith et al.\textsuperscript{[1-4]}. Ruhl et al.\textsuperscript{[15]} showed that films of TiNC deposited by LPCVD had a fairly low oxygen concentration of about 0.6 at.-% as-deposited. However, after a few days of storage in air, the oxygen contamination increased to about 13 at.-%.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig617.png}
\caption{XPS sputter depth profile of a coating deposited on steel S390 according to parameter set C1 at 475°C using TBUZ precursor. The sputter rate for SiO\textsubscript{2}-standard used for sputter depth calibration is 7.8 nm/min.}
\end{figure}

As can be seen from Figure 6.17, the oxygen is not only present at the surface but is incorporated throughout the entire coating thickness. Thus oxygen must have been present during the deposition process, probably resulting from sources described by Fix et al.\textsuperscript{[8]} or from virtual leaks. The latter serve as traps for residual gases and are difficult to flush\textsuperscript{[10]}. Inward diffusion due to open porosity is unlikely to yield such marked amounts of oxygen incorporation at a rather uniform level of contamination over the entire coating thickness.
6.4.6 Combined Discussion — Growth Rates, Hardness and Chemical Composition

TEMAZ — For coatings deposited using the precursor TEMAZ at parameter set A2, the microhardness values measured—670-837 HK—do not vary much with deposition temperature. A steady increase of oxygen contamination is registered with increasing temperature, whereas the carbon content remains around 30 to 38 at.-%. The carbon is present at approximately equal amounts in the carbidic and in the adventitious, polymeric form. ZrCN coatings, deposited by PACVD in H\textsubscript{2}-N\textsubscript{2} plasma using the metal-organic precursor Zr(NEt\textsubscript{2})\textsubscript{4}, were reported to have similar hardness values of 510 to 1400 HK\textsubscript{0.01} \textsuperscript{16}, \textsuperscript{17}. From their chemical composition—the carbon was found at equal amounts as carbidic and adventitious carbon—it was concluded, as by others \textsuperscript{18}, \textsuperscript{81}, that the hardness is influenced by the carbon content.

C-levels do not vary much in our coatings. The variation of the oxygen contamination with deposition temperature is more pronounced. Highest hardness is found at 500\textdegree C, where the chemical composition shows oxygen contamination at an average value for this series of experiments. Surprisingly, the hardness does not drop markedly on coatings deposited at 500 and 550\textdegree C, where higher contamination levels were measured. The coating formed at 450\textdegree C, although containing the lowest amount of oxygen incorporated in this series, does not stand out with high hardness values.

The increase in contaminant levels, especially oxygen, does not directly translate into a loss of coating hardness. Therefore the oxygen concentration—and to a minor issue the carbon concentration—cannot be the only factors influencing the hardness of the coating. Coating density and crystallinity are also important and may compensate to a certain extent the influence oxygen incorporation has on the coating properties. The columnar morphology found (see Section 6.4.8) always contains a certain amount of porosity. XRD confirmed that both oxygen and adventitious carbon are present as amorphous impurities, which adversely affect the hardness properties.

Microhardness values of 700 to 900 HK are measured on coatings deposited on Si-wafers at substrate temperatures of 425\textdegree C and higher using TEMAZ and parameter set A3 without NH\textsubscript{3} addition. In this deposition temperature range, the chemical composition of coatings made without ammonia addition was very similar to those formed using parameter set A2 and 10 sccm flow of reactant gas mixture. The increase in oxygen-levels
observed does not translate into a loss of hardness at temperatures above 425°C as a hardness plateau is observed. Coatings formed at temperatures below 425°C are porous and of low crystallinity. The coating hardness drops below the initial substrate hardness of 575 HK.

TPZ — Coatings deposited on S390 steel substrates using the precursor TPZ at parameters given in set B1 were generally of higher hardness than the coatings formed using TEMAZ at parameters A2. The oxygen level of the former is lower in comparison to the latter coatings. The change in the oxygen content of TPZ-based coatings closely follows the changes in hardness with an inverse law; the higher the oxygen content, the lower the hardness. This can be explained by the difference in hardness between oxides, nitrides, carbonitrides and carbides. Friedrich et al. [19] quote hardness values for oxides to be approximately two thirds of the hardness of the corresponding nitrides and carbides. From the XPS C-1s deconvolution, it was found that the carbon is present in its adventitious form at a higher ratio of up to 60% in TPZ-based coatings than in TEMAZ-based film. However, due to the fact that carbon is the predominant contaminant in TPZ-based deposits, more carbidic carbon and much less oxide phase are present in total in comparison to TEMAZ-based deposits. Thus, the overall hardness is higher for the TPZ-based films.

TBUZ — S390 steel substrates were coated by MOCVD using the precursor TBUZ at parameter set C1. These coatings revealed the highest oxygen contents of all coatings deposited and investigated in this work. The Zr-content remained around 31 to 35 at.-%. The Zr:N ratio increased from 2:1 to 10:1. Carbon levels remain below 20 at.-%. Thus, with respect to the chemical composition, it would be more appropriate to talk of zirconium oxynitrides with carbon impurities. In comparison to TPZ-based films, a similar influence of the oxygen content on the hardness is found: The hardness decreases with increasing oxygen contamination. The oxygen content—and the loss of hardness associated to it—is so high that the beneficial effect of any hard nitride formed is more than counterbalanced. The coating hardness evaluated drops well below the initial substrate hardness almost over the entire
deposition temperature range tested. There is no benefit in applying TBUZ-based coatings.
The precursor does not meet the expectations both with respect to coating properties and the viewpoint of precursor handling as it is solid at evaporation temperature, resulting in non-steady evaporation rates.

6.4.7 Influence of Ammonia

The addition of ammonia to the gas phase was expected to influence the precursor decomposition pathway. Changes in the precursor decomposition might also affect the coating properties. Therefore a detailed investigation of the influence of the ammonia content in the gas phase during deposition on the final coating properties was carried out for the precursors TEMAZ and TPZ.

Coatings were deposited on steel S390 using parameter set A2 for TEMAZ and set B1 for TPZ. But in addition to 10 sccm ammonia/nitrogen mixture, also 0, 7.5, and 20 sccm were fed into the reactor. This is equal to ammonia-to-precursor ratios of approximately 0, 1, 1.3, and 2.5 for experiments using TEMAZ and 0, 1.2, 1.4 and 3.2 for TPZ. Substrate temperatures chosen were 500°C and 550°C—the deposition temperatures at which best combined coating properties were obtained when applying sets A2 and B1 with 10 sccm N₂/NH₃. Growth rate, hardness and chemical composition were looked at. The experimental data are listed in Table 6.5 and visually displayed in Figure 6.18.
### Tab. 6.5 Influence of ammonia addition on growth rates and film properties of films deposited from TEMAZ and TPZ.

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<th>growth rate [nm min^{-1}]</th>
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<th>N [at.-%]</th>
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Fig. 6.18 Influence of ammonia addition to the gas phase on coating growth rate, hardness and chemical composition. Coatings were deposited on S390 steel disks at 500 and 550°C substrate temperature using parameter set A2 for TEMAZ and set B1 for TPZ.

TEMAZ — The diagrams for growth rate and hardness show changes of the properties with increasing N2/NH3 flow to be similar for both deposition temperatures. High growth rates of 669 nm min⁻¹ were measured at 500°C substrate temperature and
591 nm min$^{-1}$ at 550°C without NH$_3$ addition. Adding ammonia greatly reduced the growth rate down to 100-200 nm min$^{-1}$ at 10 and 20 sccm N$_2$/NH$_3$ (NH$_3$/prec = 1.3 and 2.5). This is attributed to the influence of ammonia present in the gas phase on the reaction pathway. Parasitic reactions in the gas phase reduce the amount of precursor available for decomposition and coating formation at the hot substrate surface. During the deposition experiments, yellow-brown, smeary to powdery material precipitated at the hot surfaces close to the substrate, i.e. the end of the inlet tube and the reactor walls near the hot zone. The amount of deposit increased with increasing ammonia partial pressure. Similar observations have also been reported by both Kim$^{12}$ during the deposition of TiN from tetrakis(ethylmethylamido)titanium, and Wendel and Suhr$^{20}$ for PECVD of ZrN using tetrakis(diethylamido)zirconium.

At the various amounts of ammonia addition chosen for these experiments, we found 12 to 17 at.-% oxygen at 500°C deposition temperature. At 550°C, the oxygen content varies more strongly with increasing flow of reactant gas mixture, starting at 26 at.-% for no NH$_3$ addition, increasing to 35 at.-% at 7.5 sccm (NH$_3$/prec = 1). Slightly lower amounts of 19 and 16 at.-% O were determined at 10 and 20 sccm N$_2$/NH$_3$ (NH$_3$/prec = 1.3 and 2.5) respectively. It is unclear if the increased oxygen content at 7.5 sccm N$_2$/NH$_3$ (NH$_3$/prec = 1) is a genuine effect, as lower oxygen contamination is expected for higher growth rates. This is due to the reduced possibility of incorporation into the coating caused by the reduced residual time of O at the surface. The variation in oxygen contamination could also be related to the sample history. Storage conditions are known to greatly affect the chemical composition of the coating$^{15, 21}$. When coatings are deposited using NH$_3$, a transamination decomposition pathway is followed, leading to reactive NH$_X$ compounds at the surface. They are likely to be incorporated into the film during deposition, as found for TiN$^{15}$. NH$_X$ easily reacts with oxygen present. Thus fast oxidation was observed even under high vacuum conditions. As our samples were stored in an evacuated vessel, oxygen will still be present at any time during storage. The total storage duration in addition may influence the degree of oxidation. Clearly the hardness is adversely affected thereby as shown in Figure 6.18.

Comparing the oxygen contamination for coatings deposited at 500°C and 550°C at aforementioned amounts of NH$_3$, we found higher oxygen contamination at 550°C. The hardness evaluated on coatings deposited at 550°C is lower than for those made at 500°C. This supports the previous conclusion, that higher oxygen content means more oxide
formation, leading to an overall reduction in hardness in comparison to coatings made at 500°C. It is interesting to see that for 20 sccm N₂/NH₃ (NH₃/prec = 2.5), almost identical concentrations of oxygen are found for deposition at 500 and 550°C, and that hardness values are equally low. Hardness values of 722-851 HK—above the plain steel hardness of 575 HK—were measured for coatings deposited at 500°C substrate temperature and reactant gas flows of up to 10 sccm N₂/NH₃. Coatings deposited at 550°C substrate temperature were only harder than the plain steel at 0 and 10 sccm N₂/NH₃.

A favourable combination of growth rate, hardness and chemical composition was achieved at both 500 and 550°C deposition temperature using 10 sccm N₂/NH₃ flow.

**TPZ** — For coatings formed at 500°C substrate temperature using TPZ, high hardness values of 929 and 850 HK were found at 7.5 and 10 sccm NH₃/N₂ (NH₃/prec = 1.2 and 1.4) respectively. At 550°C deposition temperature, 850 and 934 HK were measured at 7.5 and 10 sccm NH₃/N₂ (NH₃/prec = 1.2 and 1.4). Higher and lower values of NH₃ were detrimental to the coating hardness.

Looking at the coating growth rate we found that at a substrate temperature of 550°C, the growth rate almost linearly decreases with increasing the amount of ammonia gas flow to the reactor during deposition. But at 500°C deposition temperature, a change in the slope of the curve is found at 10 sccm N₂/NH₃ (NH₃/prec = 1.4). At flow rates of 10 sccm and higher, the curves are almost identical. Without the addition of ammonia, we find that increasing the substrate temperature increases the growth rate. This is in good agreement with a surface kinetically controlled reaction and decomposition pathway. Adding ammonia likely changes the pathway of decomposition from a kinetically controlled pyrolysis to a concentration-controlled transamination reaction that is only possible in the presence of NH₃. The reaction rate of a concentration-controlled reaction depends on the number of species available for deposition, which depends on the evaporation temperature and system pressure but not on the substrate temperature. Gas-phase reactions between ammonia and the precursor molecules taking place at the same time as the main decomposition reaction at the hot surface act as a parasitic reaction to the deposition process. Therefore, lower deposition rates are established upon increasing ammonia flow.
The chemical composition shows a high carbon content at flows of up to 10 sccm NH$_3$/N$_2$ (NH$_3$/prec ≈ 1.4) and a decrease in carbon but increase in oxygen at 20 sccm (NH$_3$/prec ≈ 3.2). In the latter case, the hardness is reduced due to the presence of oxides. The amount of Zr present does not significantly depend on deposition temperature and reactant gas flow. When no NH$_3$ is added to the gas phase, the high growth rate of 176 nm/min at 500°C and 258 nm/min at 550°C resulted in smooth, glossy and well-adherent coatings of 5.3 μm (500°C) and 7.7 μm (550°C) thickness. Despite the fact that low contamination levels of oxygen and high levels of carbon were found, hardness was low without ammonia addition. The deconvolution of the carbon signal revealed that a comparable amount of carbon was present in its carbidic form as well as in the adventitious form. The hardness is increased when ammonia is added to a NH$_3$/precursor ratio of 1 and 1.3 (flow rates of 7.5 and 10 sccm reactant gas). The XPS spectra for the C-1s region did not change significantly. Only at 20 sccm N$_2$/NH$_3$ (NH$_3$/prec = 3.2) we found markedly more carbon incorporated in its carbidic rather than the adventitious form. Nevertheless, hardness values dropped due to higher oxygen contamination. Coating morphology was not investigated by SEM but might well have an effect on the hardness as irregular, columnar coatings deposited at elevated temperatures are known to improve hardness in comparison to deposits formed at lower temperatures as quoted for TiN [22].

Coatings deposited using TPZ yield the best coating properties with respect to hardness, growth rates and chemical composition at both 500 and 550°C at flow rates 7.5 and 10 sccm reactant gas mixture. The smallest amounts of oxygen contamination were found at 7.5 sccm reactant gas flow.

6.4.8 Appearance, Morphology, and Roughness

Good conformality and uniform coverage were generally achieved. Figure 6.19 shows a cross-sectional view of a coating deposited on a SiC-grit-1000-ground steel disk. The coating surface closely follows the topography of the substrate. Columnar growth was observed. The film adhesion on steel substrates was also found to be good, as coatings were observed to fail internally rather than at the interface during cleavage for FESEM sample preparation.
Results and Discussion

Fig. 6.19 Cross-sectional FESEM image revealing good conformity of a coating deposited at 500°C using the precursor TEMAZ. Parameter set A1. Substrate: steel S390 substrate, manually ground to SiC grit 1000.

**TEMAZ** — Coatings deposited on Si-wafers using TEMAZ precursor and parameter set A0 were of blue-grey colour, smooth and had a glossy, mirror-like appearance. Wide cracks were observed in plan view at 500°C only. At 600 to 700°C, the surface was still shiny with a domed appearance observed at higher magnification. Cone growth and columnar morphology — considered responsible for the cracks observed — were found at 500°C (Figure 6.20), changing to a columnar morphology at 600°C and above. The surface appearance was cauliflower-like.

A similar coating morphology of domed surface appearance with columnar and occasional cone growth was described by Rie et al.\cite{16,17} for ZrCN deposited by PACVD using the precursor Zr(NEt₂)₄ in a H₂-N₂ plasma. Bales et al. relate this coating morphology to coatings grown in the kinetically controlled regime at slow surface kinetics\cite{23}. Under these conditions, initially local topography maxima flatten out and local minima become more cusplike. At intermediate times, the interface evolves towards a morphology that resembles a collection of parabolic fronts with larger parabolic sections growing at the expense of smaller sections.
Coatings made using parameter set A1 were prone to cracking. Delamination of the deposits occurred at temperatures of 475°C and higher. This is related to the high growth rates of several 100 nm min⁻¹ at which the coatings formed, resulting in residual internal stress. Columnar morphology with occasional cone growth was found at all deposition temperatures higher than 425°C. Coatings deposited at 425°C and lower were porous, poorly adherent and sooty. Higher surface roughness was visually evaluated.

After changing the deposition parameters to achieve lower growth rates—parameter set A2—smooth, well-adherent coatings of bronze to blue-grey colour were deposited on steel disks using TEMAZ. Apart from the 400°C deposition temperature, where a fine crack-network was observed, only few, rather straight and long cracks were seen on the coatings. Figure 6.21 shows three coatings deposited at 475, 500, and 550°C substrate temperature. Cross-sectional images revealed a columnar morphology in the submicron range with an increasing column width when going to higher temperatures. The fracture line is not a straight line and the fracture surface—deliberately caused to reveal the cross section—is not flat. This is caused by the columnar structure which does not break like a solid bulk material along lattice planes but rather along defects (not lattice defects!) or points of low mechanical strength in the microstructure, such as boundaries of individual columns. The presence of an amorphous, non-textured phase as concluded from XRD measurements can also be considered to be detrimental to obtaining flat fracture surfaces. Plan-view images at 500 and 550°C deposition temperature represent the domed to
cauliflower-like surface appearance and the increase in column width for the higher temperature. Also, agglomeration of columns to larger bundles is seen. Boundaries and gaps between such bundles are larger for coatings deposited at high temperatures due to mismatch of the coefficients of thermal expansion between the coating and the substrate. This can be seen in the plan-view images in Figure 6.21.

Fig. 6.21 Cross-sectional and plan view FESEM images of coatings deposited on S390 steel disks using TEMAZ under conditions given in parameter set A2 and 10 sccm reactant gas mixture.

Varying the amount of ammonia addition to the gas phase from 0 to 20 sccm N₂/NH₃ but keeping other parameters as in set A2, smooth and glossy coatings were deposited on steel substrates. No remarkable changes in visual appearance and by optical microscopy were found as a function of the ammonia addition. No cracking was observed at 10 or more sccm N₂/NH₃.

Coatings deposited on Si-wafers according to parameter set A3 in the range of 325 to 550°C at reduced growth rates without NH₃ were not mirror-like. They were
yellow-brown to grey-black in appearance, depending on the deposition temperature. Cracking and delamination occurred at temperatures of 400°C and below. Increased deposition temperature resulted in generally smoother coatings.

TPZ — MOCVD experiments using TPZ as precursor at parameters listed in set B0 led to smooth, glossy, grey-black coatings deposited on Si-wafers. No cracks were observed, but some flaking-off at 550 and 600°C deposition temperature was found. The coating morphology was predominantly fine grained, except for the deposit obtained at 600°C where a fine columnar structure was found.

Using the parameters listed as parameter set B1, smooth and glossy coatings were deposited on steel disks using TPZ precursor. Cross-sectional images of coatings deposited at 400, 500 and 525°C are printed in Figure 6.22. A columnar morphology was found at all deposition temperatures, changing from coarse columns and some cone growth at 400°C—as seen in the middle to left part of the left image—to finer columnar structure at higher temperatures as in the right image for 525°C. However, in comparison to coatings deposited using TEMAZ, coarser columns were grown using the TPZ precursor. Apart from the deposition temperature needed to decompose the precursor, the mobility of the species adsorbed at the surface and the nucleation sites and growth mechanism are of importance in determining the growth conditions and coating morphology. However, since these steps are partly taking place in parallel, they cannot be individually scrutinised for MOCVD. Thus, only the final morphology can be commented on.

A plan-view image taken of a coating deposited at 450°C shows similar surface morphology as found for coatings using TEMAZ precursor. Cracks were only observed at temperatures of 525°C and higher. Interestingly these cracks were mainly unidirectionally oriented. A preferential orientation of the substrate material caused by grinding and polishing steps applied during the sample preparation prior to deposition cannot be excluded and might be the reason for this behaviour.
The influence of ammonia on the deposition process was also evaluated for coatings formed on steel substrates using TPZ and parameter set B1. Reactant gas flow rates of \( \text{N}_2/\text{NH}_3 \) 9:1 of 0, 7.5, 10 and 20 sccm were employed. All coatings were optically smooth and glossy. At 550°C no cracks were observed in the coatings but addition of 10 sccm ammonia mixture resulted in some minor delamination and flaking-off of particles.

From the similarities in cross-sectional and surface morphology, comparable coating hardness—at least at certain deposition temperatures—and little difference in chemical composition, it is expected that similar results in tribotesting for coatings formed using TEMAZ and TPZ will be obtained.

**TBUZ** — Deposits based on TBUZ using the parameters listed in set C1 were mostly smooth and of blue-black colour. Cracks were observed at 450–475, 525 and 550°C. At 550°C deposition temperature, the coating was slightly rough but still mirror-
like for the eye. The deposits were slightly opaque at deposition temperatures of 475°C and higher. Together with the XPS compositional analysis—revealing up to 51 at.% oxygen present in the coating—this could be an indicator for the formation and presence of zirconium oxide.

### 6.4.9 Substrate and Coating Roughness

Plain steel substrate and coating roughness were characterised by means of profilometry. The steel substrates were investigated after machine grinding and polishing. Alternatively, manual grinding using SiC emery paper to grit 1000 followed an initial machine grinding step, to which all samples were subjected during sample preparation in the workshop. Hand-polishing using diamond suspensions to 6 or 3 μm, was subsequently carried out. AFM images of two surfaces prepared accordingly are shown in Figures 6.23 and 6.24.

![AFM image of a hand-polished surface.](image)

**Fig. 6.23** AFM image of a hand-polished surface. Manual grinding was performed using SiC emery paper to grit 1000, followed by manual diamond polishing to 1 μm. R₉ 6.89 nm, 2.062 fractal dimension.

![Machine-polished steel surface.](image)

**Fig. 6.24** Machine-polished steel surface. Some scratches remain visible. R₉ 3.453 nm, 2.152 fractal dimension.
The manually finished surface in Figure 6.23 is visually smooth. The AFM image reveals small humps and a rather uniform appearance. The average roughness ($R_a$) is less than 7 nm. No scratches or scars from the grinding or polishing steps are visible. The fractal dimension, a measure of the self-similarity of the surface structure, was calculated as 2.062.

The machine-finished sample surface, given in Figure 6.24, exhibits an average roughness of 3.5 nm. This is lower than the surface roughness of the hand-finished sample. The fractal dimension is 2.152. This is an indicator that this surface, in comparison to the manually polished sample shown in Figure 6.23 has more long-range order left on the surface. This is also obvious from the AFM image, as the surface still does contain remains of scratches and scars from the machining and polishing steps.

A comparison of the two surfaces shows that manual preparation results in smearing of the material and a certain waviness rather than roughness. The machine-prepared surface is more uniform with respect to the feature height. Thus it was concluded that machine-grinding and -polishing result in a controlled, reproducible quality whereas manual preparation allows for a marked influence by the operator.

Surface roughness, appearance and morphology of commercially available deposits and the influence of the deposition method on these properties were to be compared to Zr-based deposits formed by MOCVD using novel precursors.

The plan-view image of TiCN commercially deposited by means of PVD is shown in Figure 6.25. The droplets found on the surface are typical for the cathodic arc-PVD process. Droplets of sizes up to 10 μm were found. There are also spots where droplets had been sticking to the surface but later debonded, leaving a small crater behind. Due to these droplets and the craters as well as the reduced smoothness, the average roughness was around 100 nm, thus much higher than that of the plain, polished substrate.

With respect to surface roughness, similar results were obtained from a TiCN coating deposited by medium-temperature CVD. The surface shown in Figure 6.26 exhibits sharp-edged, pyramidal shaped crystallites which might act as micro cutting edges. The pyramidal shape—in comparison to smooth coatings as deposited in this work—may initially reduce the area of contact during the run-in phase of a pin-on-disk tribology experiment. However, during the experiment, the valleys between the asperities in contact may gradually be filled with wear debris from either pin and/or coating, thus resulting in a larger apparent area of contact with longer measurement time.
Although these two coatings have a totally different surface appearance, their average roughness is similar. This clearly shows the limits of the $R_3$-value, where the average is formed, thus small numbers of large deviations from an otherwise smooth surface are balanced against the remaining surface area.

**Fig. 6.25** TiCN coating commercially deposited by PVD. Droplets on the surface, typical for this vacuum-arc process, are clearly visible. Some are still sticking to the surface, others left behind small craters.

$R_3$ is approximately 100 nm.

**Fig. 6.26** TiCN coating deposited by high-temperature CVD. Sharp-edged, pyramidal-shaped crystallites formed that might act as micro-cutting edges.

$R_3$ is approximately 100 nm.

The surface roughness of a number of coatings deposited in this work and some of the commercially formed deposits was evaluated. Profilometry scans were taken over a total length of 2000 and 400 $\mu$m, with a five times higher resolution of 0.2 $\mu$m in the scan direction for measurements over 400 $\mu$m. The results are displayed in Figure 6.27.
Fig. 6.27 Roughness values evaluated by profilometry for various coatings deposited on steel S390 and for uncoated, polished steel S390. The profilometer was operated at two scan ranges: 2000 μm and 400 μm. Scan time was 40 s.

All coatings prepared in this work exhibited Ra of less than 30 nm. Of the commercial coatings, only the surface roughness of DLC I was as low. The changes in surface roughness measured when changing the scan length are dependent on the technique used. In profilometry, the surface height is traced along a track on the surface followed by the moving stylus. If the track runs over a surface area with many deviations from the average surface, the reading of the average roughness will clearly be influenced. Certainly the track length will have an influence on the likelihood to hit such a "bad" spot. From Figures 6.25 and 6.26 one would expect this to happen more often for PVD coatings at 2000 μm scan range. Looking at the data we find higher Ra values for the longer tracks, apart from TiCN (PVD). However, one must bear in mind that the data given in Figure 6.27 always corresponds to the average of four independent readings on scan tracks randomly placed on the surface to be investigated.
6.5 Tribology

Dry-sliding pin-on-disk tribotests were performed in controlled atmosphere to evaluate and compare the frictional properties and wear behaviour of coatings prepared in this work. Five different pin materials—100Cr6, TiAl6V4, Hastelloy C-22, Cu-alloy SM451C, and AlMg4—were chosen as tribopartners. The combinations of pin materials and new coatings tested represent a wide range of future applications for the coatings deposited. The aim was to compare and rank the coatings with respect to their suitability for both the machining of ferrous alloys, titanium- and nickel-based materials, and copper and aluminium alloys or low-friction applications.

Furthermore, commercially available hard, wear-resistant coatings were tribotested against the same pin materials. Thereby the performance of the new coatings can be directly compared to the coating systems used at present in metal machining and for frictional applications.

6.5.1 Sampling Rates and Noise Reduction

Initially, the operating parameters of the CSEM tribometer, especially the sampling rate at which the data was collected by the PC, were varied to minimise noise from the main power supply and to restrict the amount of data collected to a manageable size. The sampling rate of the data collection card could be adjusted over a wide interval up to the kHz range. However, such high sampling rates would result in oversized data files that could not be imported into spreadsheets and graphics software.

To evaluate the influence of load, sliding speed, and sampling frequency on signal noise, a series of measurements was performed. The friction force vs. time data was then subjected to Fourier transformation and interpreted as intensity vs. frequency plots. These plots were used to identify eigenfrequencies in the spectrum. It was found that the table-driving motor did not cause characteristic eigenfrequencies, but generally resulted in higher noise levels. Similar results were obtained when investigating the influence of the load applied to the pin. At multiples of 10 Hz, strong peaks were found in the Fourier spectra. They were likely caused by the main a.c. power supply and insufficient filtering of the feed at the a.c./d.c.-converter. Further tests showed that eigenfrequencies could be avoided or strongly reduced if odd, or prime numbers were chosen as the sampling rate.
Figure 6.28 shows that the sampling rate does not influence the mean coefficient of friction and the standard deviation. With increasing coefficient of friction the scatter band broadens as signal and friction force scatter level are increased.

![Graph showing independence of the average coefficient of friction from the sampling rate.](image)

**Fig 6.28** Independence of the average coefficient of friction from the sampling rate. Coatings were deposited on steel disks by MOCVD at 500°C using the precursor TEMAZ at parameter set A2 and by PVD to form TiCN. Tests were performed in dry air at ambient temperature using a 100Cr6 steel pin. Sliding velocity 1 m/min; data collection sampling rates of 29, 293, 397, and 491 Hz.

In Figure 6.29, the coefficient of friction evaluated at 29 and 491 Hz is displayed in a time window of eight seconds width only. The signal repeats approximately every 2.26 seconds, which corresponds to one complete revolution of the sample under the pin. The scatter is primarily caused by periodic fluctuations. They are an indicator for geometrical misalignment within the tribometer, which could not be adjusted. Another source of signal fluctuation lies in chaotic movement of wear particles and debris in the gap between the two adjacent, moving surfaces. Tumbling, sliding or rolling can occur. These different modes affect the friction force signal.
As concluded from Figure 6.28, the mean value of the coefficient of friction was not affected by the sampling rate. But can the true friction curve be accurately represented if data is collected at 29 Hz sampling rate? As can be seen from Figure 6.29, there is a great similarity between the curves evaluated at 29 and 491 Hz. Obviously the data collected at 491 Hz represents the fluctuations in the friction force reading vs. time in greater detail. The third curve represents the data collected at 491 Hz, but smoothed by subjecting the raw data to a moving average calculation over a period of 17 points. The data collected at 29 Hz and the smoothed one show a great similarity. However, the standard deviation benefits from the smoothing and is reduced from $1.9 \times 10^{-2}$ to $1.5 \times 10^{-2}$. The aim of this work is to look at the overall, general tribological performance of a pin-coating tribocouple and not at localised events with high resolution.
Thus it was concluded that the friction force vs. time and thereby the average coefficient of friction could be measured with sufficient accuracy using a sampling rate of 29 Hz.

6.5.2 Tribocouples

The tribocouples listed in Table 6.6 consisting of a pin from Table 5.4 and a coating prepared in this study or an industrially coated sample from Table 5.5 were tested using the CSEM tribometer. Typical data, collected with the PC connected, are displayed in Figure 6.30 as friction coefficient vs. time curves. Within such a set of data, the run-in period, as well as the part of the curve indicating that the coating was worn through (usually characterised by a marked increase in friction force), were not included in the calculation of the mean value of the coefficient of friction and the standard deviation.
**Tab. 6.6** Coefficient of friction for various tribocouples tested at ambient temperature in dry air at a sliding velocity of 1m/min and a total sliding distance of 15 m. Data was collected during one measurement for each tribocouple. Average coefficient of friction and standard deviation were calculated for a steady state region in the friction force vs. time plot.

<table>
<thead>
<tr>
<th>coating</th>
<th>pin material / load</th>
<th>100Cr6 / 2N</th>
<th>TiAl6V4 / 2N</th>
<th>C-22 / 2.6N</th>
<th>SM451C / 2N</th>
<th>AlMg4 / 2N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;(\mu)&gt;</td>
<td>(\sigma)</td>
<td>&lt;(\mu)&gt;</td>
<td>(\sigma)</td>
<td>&lt;(\mu)&gt;</td>
<td>(\sigma)</td>
</tr>
<tr>
<td>TMAZ, 500°C</td>
<td>0.36 ±0.07</td>
<td>0.34 ±0.01</td>
<td>0.31 ±0.02</td>
<td>0.38 ±0.05</td>
<td>0.41 ±0.02</td>
<td></td>
</tr>
<tr>
<td>TMAZ, 550°C</td>
<td>0.31 ±0.03</td>
<td>0.26 ±0.03</td>
<td>0.30 ±0.04</td>
<td>0.41 ±0.03</td>
<td>0.41 ±0.02</td>
<td></td>
</tr>
<tr>
<td>TPZ, 450/475°C</td>
<td>0.31 ±0.03</td>
<td>0.34 ±0.02</td>
<td>0.37 ±0.03</td>
<td>0.39 ±0.04</td>
<td>0.42 ±0.05</td>
<td></td>
</tr>
<tr>
<td>TBUZ, 463°C</td>
<td>0.27 ±0.03</td>
<td>0.30 ±0.03</td>
<td>0.31 ±0.03</td>
<td>0.32 ±0.03</td>
<td>0.29 ±0.02</td>
<td></td>
</tr>
<tr>
<td>ZrN I (PVD)</td>
<td>0.79 ±0.32</td>
<td>0.31 ±0.06</td>
<td>0.65 ±0.20</td>
<td>0.63 ±0.18</td>
<td>0.29 ±0.09</td>
<td></td>
</tr>
<tr>
<td>ZrN II (PVD)</td>
<td>0.83 ±0.22</td>
<td>0.41 ±0.12</td>
<td>0.72 ±0.14</td>
<td>0.72 ±0.12</td>
<td>0.60 ±0.11</td>
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</tr>
<tr>
<td>TiN (CVD)</td>
<td>0.92 ±0.13</td>
<td>0.58 ±0.17</td>
<td>0.76 ±0.17</td>
<td>0.72 ±0.19</td>
<td>0.47 ±0.12</td>
<td></td>
</tr>
<tr>
<td>TiN (PVD)</td>
<td>0.73 ±0.21</td>
<td>0.63 ±0.12</td>
<td>0.74 ±0.13</td>
<td>0.70 ±0.10</td>
<td>0.63 ±0.21</td>
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<tr>
<td>TiCN (CVD)</td>
<td>0.78 ±0.12</td>
<td>0.62 ±0.21</td>
<td>0.74 ±0.16</td>
<td>0.68 ±0.12</td>
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<tr>
<td>TiCN (PVD)</td>
<td>0.89 ±0.09</td>
<td>0.63 ±0.16</td>
<td>0.78 ±0.09</td>
<td>0.69 ±0.09</td>
<td>0.72 ±0.17</td>
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<tr>
<td>TiAlN (PVD)</td>
<td>0.77 ±0.18</td>
<td>0.54 ±0.16</td>
<td>0.80 ±0.08</td>
<td>0.63 ±0.12</td>
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<tr>
<td>TiAlCN (PVD)</td>
<td>0.71 ±0.09</td>
<td>0.61 ±0.17</td>
<td>0.73 ±0.09</td>
<td>0.58 ±0.17</td>
<td>0.74 ±0.12</td>
<td></td>
</tr>
<tr>
<td>TiAIN + WC/C</td>
<td>0.64 ±0.15</td>
<td>0.33 ±0.07</td>
<td>0.26 ±0.04</td>
<td>0.31 ±0.05</td>
<td>0.36 ±0.11</td>
<td></td>
</tr>
<tr>
<td>Balinit Hardlube (PVD)</td>
<td>0.47 ±0.04</td>
<td>0.16 ±0.01</td>
<td>0.15 ±0.02</td>
<td>0.41 ±0.05</td>
<td>0.13 ±0.02</td>
<td></td>
</tr>
<tr>
<td>WC/C, Balinit C (PVD)</td>
<td>0.22 ±0.05</td>
<td>0.09 ±0.02</td>
<td>0.14 ±0.01</td>
<td>0.43 ±0.03</td>
<td>0.09 ±0.03</td>
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</tr>
<tr>
<td>DLC I (PECVD)</td>
<td>0.29 ±0.04</td>
<td>0.09 ±0.02</td>
<td>0.26 ±0.12</td>
<td>0.45 ±0.04</td>
<td>0.10 ±0.02</td>
<td></td>
</tr>
<tr>
<td>DLC II (PECVD)</td>
<td>0.85 ±0.26</td>
<td>0.58 ±0.20</td>
<td>0.65 ±0.18</td>
<td>0.65 ±0.08</td>
<td>0.54 ±0.18</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3) (CVD)</td>
<td>0.78 ±0.15</td>
<td>0.78 ±0.11</td>
<td>0.88 ±0.11</td>
<td>0.62 ±0.17</td>
<td>0.62 ±0.23</td>
<td></td>
</tr>
</tbody>
</table>
The run-in period is usually, but not in the case of DLC, characterised by an increase of the coefficient of friction to reach steady-state conditions. The very thin oxide film naturally formed on coating surfaces and clearly detected by XPS depth profiling causes low friction values, but is quickly worn through and removed, thus exposing the underlying coating to the pin material against which a higher coefficient of friction is measured. Similar results were obtained in an AFM-investigation on VC and surface-oxidised VC by Merrill and Perry [24]. For DLC, an increase is typically followed by a decrease towards the steady-state coefficient of friction. This is associated with the formation of carbon wear products that subsequently act as solid lubricants, thus reducing the overall friction coefficient observed.
6.5.3 Coefficient of Friction

Prior to the tribological screening of the tribocouples mentioned above, the influence of the load on the friction force and the obeyance of Amontons' first law of friction needed to be investigated. Figure 6.31 shows the results of these experiments as friction force evaluated vs. applied load. The coefficient of friction $\mu$ is the slope of the linear regression of the data points. As can be seen in the plot and concluded from the high correlation coefficient, the first law of friction is well followed.

For the following experiments a load of 2N (2.6 N for Hastelloy C-22 due to 1.14 mm pin diameter) was chosen as a result of this investigation. Using this intermediate load it was expected not to create too much wear and thereby to avoid reaching the substrate during the experimental duration and sliding distance. 4 N load were also applied on a 100Cr6 pin on selected coatings to confirm compliance with Amontons' first law of friction at two different loads for these coatings.

![Graph](image)

**Fig. 6.31** Evaluation of the compliance with Amontons' first law of friction for a coating deposited on steel S390 at 500°C using the TEFMAZ precursor and parameter set A2 (839 HK). Friction measurements were performed in dry air (< 10% r.h.) on the CSEM pin-on-disk tribometer in the load range 0.5-5 N using a 100Cr6 steel pin (ø 1 mm) sliding on a coating.
A comparison of the dry-sliding coefficient of friction evaluated for tribocouples involving the five pin materials and the coatings prepared in this work as well as commercially available ZrN (by PVD) and TiN (by CVD and PVD) coatings, is given in Figure 6.32. In Table 6.6, the data is listed in detail with mean value and standard deviation.

As a first result we found that the coatings prepared using the novel metal-organic precursors exhibit significantly lower dry-sliding friction coefficients in the range of 0.26 to 0.41 in comparison to the commercially available products. Rie et al. [16] reported slightly lower coefficients of friction of 0.20-0.27 for 100Cr6 sliding against ZrCN. The
test load applied and the environmental conditions are not given. For the coatings prepared in this work, only little influence of the pin material on the coefficient of friction was found.

There is a tendency towards higher friction coefficients in dry-sliding against the copper- and aluminium-based alloys. Of all pin materials used these are the softest (most ductile) ones. The oxidation resistance of the Ti- and Al-alloy is reduced in comparison to the other materials tested. Thus wear and wear debris formation are expected at higher rates than for the other pin materials. Mohrbacher et al. evaluated the influence of moisture present on the oxide film formation on TiN coatings during tribotesting. They concluded that moisture present in the tribotest chamber accelerates the formation of a highly defective, probably substoichiometric modification of rutile (TiO$_2$), for which a lubricating effect has been postulated. At reduced humidity, it can be assumed that the adsorption of moisture from the test atmosphere to the TiN surface becomes rate controlling for the formation of lubricious debris. This does not only apply to the coatings but, as in our case, also to the least noble pin materials tested.

In contrast to our ZrCN coatings, we found higher friction coefficients for most commercially coated samples. This can be explained by the findings of Mohrbacher et al. as mentioned above. This group reported high coefficients of friction of around 0.8—very similar to our results—for fretting experiments performed with 100Cr6 on TiN in dry air. Tests in moist air resulted in lower friction coefficients of around 0.2. These results were obtained on three TiN coatings, all formed applying different coating techniques. Thus, changes in the coefficient of friction due to various surface morphologies of the differently processed TiN coatings are negligible compared to those induced by the variations in relative humidity. Boring et al. and Severin et al. also reported an increase in the coefficient of friction with decreasing humidity in the test chamber.

Only ZrN I sliding against TiAl6V4 and AlMg4 deviated from this trend. Friction coefficients of these tribocouples were comparable to those evaluated for coatings prepared in this work. However, it could not be clarified if similar or different wear mechanisms take place when rubbing TiAl6V4 and SM451C against ZrN I or against our Zr-based coatings. The integrity of the ZrN I coating over the entire measurement time is questionable and may result in friction coefficient readings for the tribocouple pin on substrate instead of pin on coating. ZrN II in comparison to ZrN I does not show as
significant a reduction in friction against the AlMg4 pin. The friction coefficients evaluated against the other pins are similar to those evaluated for ZrN I.

The results of the friction measurements were not correlated with the surface roughness values. For example, plain S390 steel has a low roughness but friction coefficients are as high as for the ZrN and TiN coatings.

A larger number of commercially coated samples was tested under identical conditions. The coefficients of friction for the individual tribocouples are given in Figure 6.33 and Table 6.6. Looking at a broader selection of Ti-based CVD and/or PVD coatings, namely TiCN, TiAIN and TiAICN, we found little influence of the coating composition and deposition technique used on the coefficient of friction. For a specific film, the friction force rather depends on the pin material. The ranking within the alloy counterbodies is similar for the transition metal nitrides and carbonitrides, resulting in a typical fingerprint. In most cases, we find 100Cr6, Hastelloy C-22 and AlMg4 causing highest friction against the chosen substrates. The explanations given earlier for these high friction values also do apply to these coatings. The chosen dry-sliding experimental condition is especially challenging as friction conditions are severe, certainly influencing the wear behaviour of the coatings tested.

We also measured specially designed low-friction coatings, such as Balinit Hardlube, Balinit C, amorphous diamond-like carbon coatings DLC I and DLC II, as well as a ceramic alumina coating formed by CVD. Both DLC I and DLC II exhibited low coefficients of friction. For dry-sliding of DLC vs. steel friction coefficients quoted in literature are around 0.1-0.3, covering a wide range of steel qualities and humidity \[128\]. Our results are consistent with this statement apart from higher friction coefficients evaluated in tribotests against the copper alloy SM451C. Profilometry investigation of the wear track did not confirm material transfer from the pin to the coating surface. However, Imaging-XPS clearly revealed Cu to be present in the wear track on the coated surface. Therefore metal-metal contact between the Cu-alloy pin and transferred Cu smeared along the wear track seems to dominate in this experiment. Copper-copper tribopairs usually yield friction coefficients of 0.7-1.4 \[29\]. Balinit Hardlube, a lamellar multilayer coating consisting of TiAlN and WC/C, was closer to the frictional behaviour of the novel coatings than to the other commercially coated layers, only going below \( \mu = 0.4 \) for tribotests of 100Cr6 against the coating.
Balinit C (lamellar multilayer coating of WC/C deposited by PVD) performed almost as well in the tribotests as DLC. It also displayed markedly higher friction coefficients when tested against SM451C. Only testing against the hard 100Cr6 pin resulted in a higher friction coefficient.

As shown in Figure 6.33, little difference between alumina and other commercial coatings was found with respect to the friction behaviour, despite the fact that the alumina coating exhibited the highest surface roughness of all commercial layers investigated.

Fig. 6.33 Coefficient of friction: Comparison of novel coatings prepared in-house and commercially available deposits. Tribocouples were tested at 2 N load in dry air at ambient temperature. Five pin materials—100Cr6, TiAl6V4, Hastelloy C-22 (2.6 N load), SM451C, and AlMg4—were used. Diamond-like-carbon coatings are labeled I and II to differentiate between two manufacturers.
Reviewing the above-discussed data for all commercial Ti- or Zr-based coatings, the absence of a clear influence of the coating material on the coefficient of friction was unexpected. We also conclude from the data collected, that the deposition process (PVD vs. CVD) has no significant influence on the friction behaviour. This is interesting, as the surface morphology of TiCN by PVD and by CVD is very different, even if similar average surface roughness was evaluated.

To confirm Amontons' first law of friction under the given experimental conditions for a series of coatings, their coefficient of friction against 100Cr6 was evaluated at 2 and 4 N load. The friction coefficients evaluated are listed in Table 6.7 and plotted in Figure 6.34.

**Tab. 6.7** Influence of load on coefficient of friction (mean value $\mu$ and standard deviation $\sigma$) for various tribocouples tested at ambient temperature in dry air at a sliding velocity of 1 m/min and a total sliding distance of 15 m.

<table>
<thead>
<tr>
<th>coating</th>
<th>load</th>
<th>$&lt;\mu&gt;$</th>
<th>$\sigma$</th>
<th>$&lt;\mu&gt;$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMAZ, 500°C</td>
<td>2 N</td>
<td>0.36</td>
<td>±0.07</td>
<td>0.34</td>
<td>±0.04</td>
</tr>
<tr>
<td>TEMAZ, 550°C</td>
<td>4 N</td>
<td>0.31</td>
<td>±0.03</td>
<td>0.27</td>
<td>±0.03</td>
</tr>
<tr>
<td>TiP, 475°C</td>
<td>2 N</td>
<td>0.31</td>
<td>±0.03</td>
<td>0.32</td>
<td>±0.02</td>
</tr>
<tr>
<td>TiN (CVD)</td>
<td>4 N</td>
<td>0.92</td>
<td>±0.13</td>
<td>0.89</td>
<td>±0.17</td>
</tr>
<tr>
<td>TiN (PVD)</td>
<td>2 N</td>
<td>0.73</td>
<td>±0.21</td>
<td>0.69</td>
<td>±0.13</td>
</tr>
<tr>
<td>TiCN (CVD)</td>
<td>4 N</td>
<td>0.78</td>
<td>±0.12</td>
<td>0.81</td>
<td>±0.15</td>
</tr>
<tr>
<td>TiCN (PVD)</td>
<td>2 N</td>
<td>0.89</td>
<td>±0.09</td>
<td>0.80</td>
<td>±0.08</td>
</tr>
<tr>
<td>TiAlCN (PVD)</td>
<td>4 N</td>
<td>0.71</td>
<td>±0.09</td>
<td>0.63</td>
<td>±0.07</td>
</tr>
<tr>
<td>Al₂O₃ (CVD)</td>
<td>2 N</td>
<td>0.85</td>
<td>±0.26</td>
<td>0.82</td>
<td>±0.11</td>
</tr>
<tr>
<td>DLC (PECVD)</td>
<td>4 N</td>
<td>0.22</td>
<td>±0.05</td>
<td>0.20</td>
<td>±0.01</td>
</tr>
<tr>
<td>steel S390</td>
<td>2 N</td>
<td>0.78</td>
<td>±0.15</td>
<td>0.85</td>
<td>±0.15</td>
</tr>
</tbody>
</table>
Fig. 6.34 Load-independent friction behaviour of a variety of coatings sliding against 100Cr6 pin in dry air at 2 and 4 N load.

Calculating the mean value of the coefficient of friction evaluated both at 2 and at 4 N load, the deviation of the values from this mean value was in most cases less than 5%, thus in the range of the scatter band evaluated in Figure 6.31. There was no trend to higher friction with either one of the loads. Only TEMAZ at 550°C was with 7.4% beyond this limit.

It is therefore concluded that Amontons' first law of friction can be applied to a wide range of commercially available Ti-based or DLC coatings. The friction coefficient measured for any individual load tested experimentally is representative for the load range of 0.5-5 N.
6.6 Wear

Both visual inspection by optical microscopy and profilometry of the track region were applied to determine the occurrence of wear on the coating surface. If wear was detected, more detailed profilometry of the wear track, as described in Section 5.6.8, was used to determine normalised wear rates—defined as wear volume per total sliding distance and applied load.

6.6.1 Wear Rates

Wear was primarily observed on the coatings prepared in this work. For the commercial coatings, wear could not be detected, either by profilometry or by optical microscopy. This is also partially due to the high intrinsic roughness of the commercially coated surfaces, which makes it difficult to detect small topographical changes.

Wear rates evaluated for the coatings prepared in this work are given in Table 6.8. The data are also shown in Figure 6.35. It must be noted that there have been cases where the pin did wear through the coating and reached the steel substrate material despite the intermediate load chosen. These tests are marked with an asterisk (*) in Figure 6.35. There clearly is a difference in the wear performance of the coatings against steel 100Cr6, Hastelloy C-22, and the Ti-based alloy in comparison to the Cu- and Al-based alloys. The latter two pin materials caused much higher wear rates than the former materials.

<table>
<thead>
<tr>
<th>pin hardness</th>
<th>wear rate $[10^{-7} \text{ mm}^3 (\text{mm N})^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TBUZ 463°C (540 HK)</td>
</tr>
<tr>
<td>100Cr6</td>
<td>585</td>
</tr>
<tr>
<td>TiAl6V4</td>
<td>234</td>
</tr>
<tr>
<td>Hastelloy C-22</td>
<td>297</td>
</tr>
<tr>
<td>Cu SM451C</td>
<td>121</td>
</tr>
<tr>
<td>AlMg4</td>
<td>80</td>
</tr>
</tbody>
</table>
Within the group consisting of pins 100Cr6, TiAl6V4, and Hastelloy C-22, a clear influence of the coating hardness on the wear rate observed was found. Highest wear rates were determined on the softest coating deposited using TBUZ (540 HK). For the tribotest against Hastelloy-C22 the pin wore through the coating and reached the substrate. Thus the wear rate would likely be higher if the coating had been thicker, allowing for wear to take place between coating and pin for the entire measurement time and not only for part of it until reaching the substrate. In this case the substrate is harder than the coating.

From Figure 6.35, comparing the data obtained for tests against one pin material only, we conclude that increasing coating hardness is beneficial for obtaining reduced wear rates. As coating hardness is affected by the chemical composition of the deposit as given in Figure 6.14, the precursor selection does indirectly influence the tribological...
performance. Combining results from chemical composition determination and coating hardness measurements with the wear rates it is clear that oxygen incorporation has a major, detrimental influence on the overall triboperformance.

The wear rate is not significantly influenced by the pin hardness as can be seen from Figure 6.35. When testing 100Cr6 (585 HK), TiAl6V4 (234 HK), and Hastelloy C-22 (297 HK) against the coatings of highest hardness (830 HK, 1030 HK), similar low wear rates were evaluated and no effect of the pin material on the wear rate was observed. This may be explained by the fact that all of these three pins are of lower hardness than their countersurface (coating) in the pin-on-disk tests. Thus wear performance is dominated by the coating properties rather than by the pin; the softer material is expected to be subjected to heavier abrasive wear than the harder counterbody as already covered in the early work by Bowden and Tabor [30]. However, the hardness difference is not sufficient to protect the coating from being worn by the pin. As the wear rate of the pin was not determined it is not possible to draw further conclusions with respect to the ratio of coating wear to pin wear.

For the softer two coatings formed at 550°C using TBUZ and TEMAZ (540 and 570 HK) the wear rate is affected by the pin material involved in the tribotest. Highest wear rates are found when testing against 100Cr6. A lower wear rate is evaluated for the harder coating. In this case the pin is only slightly harder than the coating. Lower wear rates are found in tests against Hastelloy C-22 and TiAl6V4. These pins are of similar hardness which is reflected by the fact, that their wear rate against the TEMAZ-based coating deposited at 550°C (570 HK) is quite similar, around $2 \times 10^{-7} \text{ mm}^2 \text{ N}^{-1}$.

Generally higher wear rates were found in tribotests involving the Cu- and Al-based alloys as pin materials in comparison to the experiments with 100Cr6, TiAl6V4, and Hastelloy C-22. Similar wear rates around $5.4 \times 10^{-7}$ to $5.5 \times 10^{-7} \text{ mm}^2 \text{ N}^{-1}$ were found only for SM451C and AlMg4 against TEMAZ deposited at 550°C (570 HK). An influence of the coating and pin hardness on the wear behaviour, as described earlier for 100Cr6, TiAl6V4, and Hastelloy C-22, could not be found. As a tendency, one can say that AlMg4 results in high wear rates, despite the fact that this pin material is softer than the Cu-alloy. An explanation for this effect is the rapid formation of aluminium oxide upon exposure of clean surface material to ambient air. The AlMg4-pin and any wear debris will quickly oxidise at their surface and a thin layer of alumina will form. As alumina is of higher hardness (1800-3000 HV [19]) than the bulk pin material and also
harder than the Cu-alloy SM451C, it will, if present as wear debris and at the rubbing contacts, raise the wear rate. Alumina may be embedded into the soft pin and then act like a cutting or ploughing edge as described by Bowden and Tabor \cite{30}. The high wear rate against the coating formed using TPZ is explained by the fact that the coating tested in this experiment is only of 914 HK and, looking at its chemical composition, consists of almost 24 at.-% O and 40 at.-% C while the N-content dropped from 18 to 10 at.-%. Thus the phase content of zirconium nitrides and -carbides is reduced in comparison to the deposit formed at 475°C used with the first three pin materials. Nevertheless it is still harder than any of the other coatings deposited using TEMAZ and TBUZ. Despite the enhanced hardness, the trend towards increased wear rates is clear in dry-sliding against AIMg4 and SM451C and backed up by the data collected on TEMAZ- and TBUZ-based coatings.

For both pin materials, micro cold welding between asperities present at either pin or coating surface may also be taken into consideration. The formation, usually depending on contact pressure and sliding velocity, and breaking of such microjoints, will change the surface morphology and roughness. Broken-up weld joints may reduce the flattening and smearing commonly observed on rubbing surfaces and cause continuous renewal of sharp edges and formation of novel asperities of contact thus causing continuous wear resulting in elevated wear rates. The breaking-out of larger bits of coating material can be induced, thereby further increasing the wear rate by having such chunks of material embedded into the pin surface where they will act against the coating, causing local events of material rubbing against identical counterpart—a combination known to cause higher wear rates. The coefficients of friction were also raised.

6.6.2 Imaging-XPS and XPS Evaluation of Wear Tracks and Pins

To evaluate the material transfer during tribotests from the pin to the coating and/or vice versa, a coating deposited at 550°C using the precursor TEMAZ and parameter set A2 and a TiN coating deposited by PVD were each tribotested against all pin materials involved in this study. Tests were performed in dry air at loads of 4 N for 100Cr6 and TiAl6V4, at 2 N for the copper and aluminium alloy, and at 2.6 N for the Hastelloy C-22.

The wear tracks were looked at by means of profilometry, optical microscopy and Imaging-XPS. To check if coating material was transferred to the pin surface, visual
inspection by light microscopy as well as XPS investigation of the pin surface were undertaken. While no wear could be found by means of light microscopy and profilometry on the TiN (PVD) coating, severe wear of $1.8 \times 10^{-7}$ to $5.5 \times 10^{-7} \text{ mm}^2 \text{ N}^{-1}$ was detected after tribotests performed on the coating deposited using the precursor TEMAZ. For the industrially coated samples, no transfer of coating material or wear debris to the pin could be found by XPS. However, for tribotests involving the coatings prepared in this study, material transfer or pick-up of wear debris particles by the pin could be confirmed by XPS measurements.

**Imaging-XPS of Wear Tracks on a Coating Made from TEMAZ**

Figure 6.36 shows the Imaging-XPS maps collected in the wear-track region of a coating formed at 550°C on steel S390 using TEMAZ as precursor at parameter conditions A2.

**100Cr6** — After tribotesting against 100Cr6, neither Fe nor Cr from the pin could be detected within the track. The clear manifestation of the track in the Zr image can be explained by the fact that the thin oxide layer naturally formed on top of the coating is removed in the track region. In addition, the coating is partly worn. XPS is highly surface sensitive and allows for a clear distinction between the various chemical states of an element. The contrast in the Zr-image clearly represents the different chemical states of Zr in the track region and the surrounding surface area. XPS evaluation of the pin after tribotesting confirmed that Zr was transferred to the pin. Only one third of the pin surface was determined to be worn, and the remaining surface area looked unchanged by light microscopy. The track width was smaller than the pin diameter.

**TiAl6V4** — After the pin-on-disk experiment with the TiAl6V4 pin, wear of the pin was detected. The coating was also heavily worn. As can be seen in the Ti-scan image of the wear track on the coating, material transfer from the TiAl6V4 pin to the coating occurred. The minor elements of the alloy are not detectable in the wear track region at the XPS operating parameters chosen due to the low sensitivity factor of Al and the low content of V present in the pin material. No signals corresponding to Fe were detected which indicates that the coating has not been worn through to the underlying substrate.
Fig. 6.36 Imaging-XPS analysis of wear tracks on coatings deposited on steel disks at 550°C using TEMAZ at parameter set A2. Test load: 4 N for 100Cr6 and TiAl6V4, 2.6 N for Hastelloy C-22, 2 N for SM451C and AlMg4. For all tribocouples, wear of the coating was detected by means of profilometry. Binding energy regions analysed: Zr 3d, N 1s, Fe 2p, Cr 2p, Ti 2p, Al 2p, Ni 2p, Cu 2p, O 1s.
The Zr-image shows a dark track region. This is explained by the coating being worn by each revolution of the pin on the disk. More importantly, material is transferred from the pin to the substrate at the same time, leaving behind a thin spread of pin material covering the underlying coating. The composition information from this region is thereby shielded, resulting in reduced intensity in the Zr-image but enhanced intensity in the Ti-image. On the pin, Zr and N were detected, as wear particles were sticking to the pin surface. One third of the pin surface is heavily worn. Optical evaluation showed a number of small pits. Such material tear-out can also be observed in cases of cold-welding and subsequent breaking of the bond associated with adhesive wear. Under the given conditions, especially the dry air environment, this might seem like a plausible explanation.

**Hastelloy C-22** — Using the Hastelloy C-22 pin, neither Ni nor Cr could be detected in the wear track region. Thus no significant material transfer from the pin to the coating is detected. The contrast in the Zr-image is caused by the different chemical states of Zr—oxidised on the surface and present as a nitride and/or carbide in the track region. The number of counts is also influenced by the compositional difference in at.-% if present in ZrN (50 at.-% N) or in ZrO₂ (33 at.-% N).

**SM451C** — Testing against the Cu-alloy SM451C, the Cu intensity is not very pronounced but in the O-image, the track is clearly visible. The oxygen map was collected because one would imagine any Cu transferred to the coating being quickly oxidised as samples were exposed to air during and after testing. The oxygen signal intensity might also be enhanced by the oxidation of zirconium due to tribooxidation or oxidised abrasive wear debris present in the wear track region. Looking at the Zr- and N-images, one can easily identify the track region as the brighter area present.

**AIMg4** — Using the AIMg4 pin, similar observations were made and conclusions drawn as for the Cu-pin. However, Al was very difficult to detect. Bearing in mind that XPS is a surface sensitive analytical tool, the absence of a clearly visible track in the Al-image may be explained by the fact that only little pin material was transferred to the coating. The sensitivity of XPS strongly depends on the element to be detected. Unfortunately Al is one of the elements with a low sensitivity. The strong oxygen signal in the track region could be attributed to tribooxidation of the coating during the experiment.
Imaging-XPS of Wear Tracks on TiN (PVD)

Imaging-XPS maps collected on a commercially deposited TiN PVD-coating are shown in Figure 6.37.

100Cr6 — The transfer of Fe from the pin to the track is confirmed by the Fe-elemental map. Thereby, all other signals were to some extent attenuated, resulting in reduced intensities in the wear-track region of the Ti- and N-images collected. Visual inspection of the pin surface showed a thin red line running through the centre of the pin. The pin was not further investigated but it is assumed that this line consists of iron oxide.

TiAl6V4 — The majority of the Ti-signal intensity collected represents Ti in its oxidised state. This is caused by the natural oxidation of the coating surface upon exposure to air. For tribotesting against TiAl6V4, pin material is transferred from the pin to the track and very likely to be oxidised. This is concluded from the fact that the track region on the coating is not as distinct in the Ti-map as it is the N-map. If the track is covered by TiAlV4, metallic Ti or tribooxidation products, the N-intensity in XPS-images will be partly blocked. Al and V were difficult to detect for reasons explained earlier. However, the XPS images taken show higher intensities for these elements in the track region. The pin surface was uniformly worn. N has been detected on the pin by XPS. From the optical evaluation of the pin surface and from profilometry of the coating, it was concluded that the wear of the pin was more pronounced than the wear of the coating; material transfer thus occurred mainly from the pin to the coating supporting the conclusions made on shielding-off the XPS-information of the coating by a film of transferred material.

Hastelloy C-22 — The track region was analysed for Ni and Cr apart from the coating elements. Both Ni and Cr were well detectable. No wear could be determined by means of profilometry. Optical microscopy on the pin surface showed wear scars, indicating that this surface was worn rather than the coating counterpart in the tribosystem. Thus it was concluded that the pin was worn during the tribotests by abrasive wear, resulting in a thin layer containing Ni and Cr on the coating. However, this material build-up was too small to be detectable and distinguishable from the initial surface topography by profilometry measurements.

SM451C — Looking at the XPS images collected on the surface tested vs. the Cu-alloy SM451C, the Cu transfer from the pin to the substrate due to abrasive wear is very pronounced. Both the Ti and N-signal are reduced in intensity in the track region due to this transfer layer. Material build-up was detected by profilometry.
Fig. 6.37 Imaging-XPS analysis of wear tracks on a TiN coating commercially deposited on steel S390. Test load: 4N for 100Cr6 and TiAl6V4, 2.6N for Hastelloy C-22, 2N for SM451C and AlMg4. No wear of the coating was detected by profilometry. Material transfer from the pin to the coating has been confirmed. Binding energy regions analysed: Ti 2p, N 1s, Fe 2p, Cr 2p, Al 2p, V 2p, Ni 2p, Cu 2p, O 1s.
AlMg4 — Similar results were obtained in a test with AlMg4 on TiN (PVD). Here the Al signal intensity is higher in the wear track region of the surface, indicating material transfer from the pin to the substrate.

From the above observations it can be concluded that mainly material transfer from the pin to the coating is observed. No wear of the coating could be found by means of profilometry but material build-up was occasionally detected. This means that the pin material is more prone to wear, which is due to its lower hardness compared to the hard coatings. The soft pin materials like the Cu- and Al-based alloys exhibited severe wear. These alloys, together with TiAl6V4 were also expected to strongly oxidise at the surface. This is also valid for any wear particles formed during tribotesting.

6.6.3 SEM Images of Wear Tracks

SEM images of the wear tracks caused by the pin materials AlMg4 or SM451C on alumina, DLC I, and on a coating deposited using TEMAZ were taken to find out more about the wear process and wear particles/debris.

Figure 6.38 shows the track region after tribotesting with AlMg4 at 2 N load on a coating deposited at 550°C on steel S390 using TEMAZ at parameter set A2. The full width of the track is shown in the left image. In the centre of the track there are several distinct white lines visible which run parallel to the sliding direction. These lines, brighter because of charging during SEM, represent the border between coated areas and surface areas where the coating has been worn through, fully revealing the underlying substrate. In the right image such a border is enlarged. The band, running through the centre of the image from bottom right to top left, shows the underlying substrate. The border of the remaining coating is not a straight line. It contains sections where bits of the coating had broken off, leaving behind pockets which subsequently filled-up with wear debris. The debris is almost entirely located in these pockets. Only very little is present in the band of the substrate surface exposed. As the formation and shape of the pockets develops with time, it is imagined that occasionally larger bits of the coating break off. Such material will be broken down into wear particles, which roll between pin and coating, unless they are small enough to be entrapped within the pockets. In the centre of the image there is some coating material left, forming a barrier, behind which the wear debris piles up. This
ridge would have likely failed and debonded, had the tribotest been continued. A new pocket would form, supporting the on-going deterioration process in a similar way to macroscopic coastline degradation.

Fig. 6.38 SEM images of the wear track caused by an AlMg4 pin (2 N load) sliding on a coating deposited on steel S390 at 500°C using TEMA on parameter set A2.

Left: The entire track width is visible. The black lines indicate the track location. The coating has been worn through to the substrate in some areas.

Right: Enlarged section of the centre of the wear track. The coating has been worn through in the centre of image. The "coastline" of the adjacent coating is not straight but contains pockets which are filled with wear debris. The debris is slightly darker in contrast or shines bright due to charging of the poorly conducting oxide film.

Similar wear behaviour was found when sliding a SM451C pin on the coating made using TEMA. The image shown in Figure 6.39, right, explains how the worn material is collected in the pockets of the borderline between coating and substrate. Particles enter the pocket from the lower right-hand corner, where they are compacted by the sliding movement of the pin passing the area. At the other end of the pocket, some material is torn out of the pocket again. Shadows at the upper right border of the coating indicate that the coating locally debonded from the substrate. In this image, looking at the coating surface, we find distinct, parallel running lines. They represent hill-valley formations, which are caused by the pin gradually wearing the surface each time the pin passes.
Fig. 6.39 Left SEM image: wear track caused by a Cu-alloy SM-451C pin (2 N load) sliding on DLC 1. The entire track width is visible. The black lines identify the track location. Build-up of wear particles along the edge of the track. Centre not worn.

Right SEM image: wear track caused by a Cu-alloy SM-451C pin (2 N load) sliding on a coating deposited at 500°C using TEMAZ. The image centre reveals the substrate surface. Formation of wear-debris pile-up in the pockets of the coastline-shaped border of the remaining coating. The shadow between border and substrate may be interpreted as delamination failure of the coating in this area.

In Figure 6.39, left, a SEM image of the tribotrack of SM-451C on DLC 1 is printed. Two distinct white bands represent the borders of the track region. They consists of fine particles which have been moved outwards from the central track region during tribotesting. The central track region also does contain wear particles but not as high an amount as along the border. It is concluded that this debris must have been worn off from the pin because no wear of the coating could be detected by means of profilometry and also due to the hardness difference between pin and coating.
Fig. 6.40 SEM images of the wear track caused by an AlMg4 pin (2 N load) sliding on an alumina (Al$_2$O$_3$) coating.

Left: The entire track width is visible. The black lines indicate the track location. Brighter spots in the track region are enlarged in the right image.

Right: Enlarged section shows platelets of worn material deposited or smeared over the initial coating surface. The lower right-hand corner represents the initial surface state. Loose debris fills the gaps between the platelets. The sliding direction is clearly visible. The edges of the platelets are shining bright in SEM due to charging.

Figures 6.40 and 6.41 contain images taken after tribotesting on alumina coatings. In Figure 6.40, left, the wear track caused by sliding an AlMg4 pin at 2 N load on the alumina coating is clearly visible by the bright spots on the surface. They only partially cover the surface. An enlarged view of such a spot is given in Figure 6.40, right. Platelets of material cover the coating surface. The initial alumina surface appearance is represented in the lower right-hand corner. Sliding scars are visible on the top surface of these platelets and wear debris is trapped between them and at the borders located opposite to the sliding direction. The wear particles present may reduce friction as rolling particles between pin and counterbody may positively affect friction values. The platelets indicate material transfer from the pin to the coating, which was confirmed by Imaging-XPS. The small debris particles are very bright in the SEM images. This is caused by charging, which is attributed to the particles being enveloped by a sound oxide film. Stronger oxygen signals were also found by Imaging-XPS in the track region, which does support the explanation that tribooxidation takes place during the experiment to which the pin
material is more susceptible to than the coating as alumina is already present in a stable oxidised form.

![SEM images of the wear track caused by a Cu-alloy SM451C pin (2 N load) sliding on an alumina (Al₂O₃) coating.](image)

**Fig. 6.41** SEM images of the wear track caused by a Cu-alloy SM451C pin (2 N load) sliding on an alumina (Al₂O₃) coating.

Left: The entire track width is visible. The black lines indicate the track location. The spotted surface is a result of the deposition process causing the formation of small humps.

Right: Enlarged top section of such a hump showing platelets of worn material deposited or smeared over the initial coating surface. Apart from the platelets there is not much loose debris visible.

When using a Cu-pin instead of the AlMg₄ on alumina, a similar appearance of the wear track was found by SEM as shown in Figure 6.41. The wear track shows brighter areas usually located on top or in the vicinity of the humps found on the coating surface. These hump are due to the high compressive stresses caused in the coating during deposition and cooling. An enlarged section of such a bright spot is given in Figure 6.41, right. The platelets are found spread out on the surface, not only in one surface plane but occasionally overlapping. Imaging-XPS revealed Cu to be present in the wear track thus material transfer and/or wear debris should be observed. From the SEM image one can conclude that mainly material transfer is observed as particles found in Figure 6.40, right, for AlMg₄ on alumina are not present in this case. Thus material transfer and subsequent sliding on this is predominant.
Reference


7 Summary and Conclusions

In this work, four alternative metal-organic zirconium precursors, TEMAZ, TPyrrZ, TPZ, and TBUZ, have been evaluated for low-temperature MOCVD of zirconium carbonitride coatings on HSS tool steel. All precursors belong to the same structural group, containing Zr ligated by four secondary amido groups.

TEMAZ is liquid at room temperature; all other precursors are solid. At the chosen evaporation temperature, TBUZ remains solid while all other precursors liquefy. The volatility strongly depends on the ligand size. Bulky ligands and the binuclear structure resulted in elevated evaporation temperatures above 150°C in order to obtain a similar precursor concentration in the gas phase as for the precursor TEMAZ which was evaporated between 60 and 100°C.

The ligand size does not only affect the evaporation temperature. Higher chemical and thermal stability were found for large, bulky ligands due to shielding of the central Me-atom or binucleus. Addition of ammonia was expected to support the attack of the centre of the compound, resulting in reduced decomposition temperatures due to a transamination pathway.

Coatings were deposited at temperatures compatible to the chosen HSS tool steel substrate material. A maximum applicable surface temperature of 550°C was chosen to avoid substrate dehardening during MOCVD.

Initial experiments revealed that TPyrrZ is difficult to decompose. The thermal stability of the compound resulted in high carbon contamination of 45 to 60 at.-%, of which up to 70% was present in the adventitious form. The mechanical and chemical coating properties evaluated did not meet expectations. Based on these results and because of the low yield and difficulties in the synthesis of the precursor, it was decided not to further investigate TPyrrZ.

The compound was not found suitable for low-temperature MOCVD and the experimental program was discontinued after the preliminary tests.
The other three metal-organic compounds TEMAZ, TPZ, and TBUZ were found to be suitable for use in the MOCVD process. They are prone to parasitic gas-phase reactions if ammonia is added. This is an effective way to control and reduce the coating growth rate and allowed for operation in the mass-transfer-controlled regime of the overall reaction kinetics.

The coatings formed using the precursor TBUZ at 450 to 550°C deposition temperature grew at very low rates of 30 to 110 nm min\(^{-1}\). This solid compound can only be brought into the gas phase using the fixed bed glass evaporator. However, our results show that this evaporator in combination with TBUZ does not give steady, reproducible evaporation rates due to bed compaction and changes in the powder size and the surface-to-volume ratio. The Zr:N ratio increased from 2:1 to 10:1 with increasing deposition temperature. The coatings showed high amounts of oxygen incorporation of up to 50 at.-%. Therefore this is no longer considered a carbonitride but, from the chemical composition, a zirconium oxide coating. As an effect of the high amount of oxygen incorporated, the hardness values drop well below that of the initial steel substrate.

The hardness and chemical composition of the coatings deposited using TBUZ do not match expectations. The precursor seems to be too stable for clean decomposition. Low growth rates may additionally support the incorporation of contaminants.

For TEMAZ we found that the precursor evaporation rate and thus the growth rate strongly depend on the system operating pressure. The precursor is of higher volatility than the other compounds, thus the evaporation temperature was lower and had to be adjusted to the reactor pressure. Internal stress builds up in fast-grown, thick coatings often resulting in cracking and delamination. A combination of 500 Pa pressure and 87.5 or 60°C evaporation temperature, the latter if no ammonia is added, resulted in smooth, conformal, sound, and well-adhering coatings of predominantly columnar morphology. The deposition process is mass-transfer controlled in the temperature range of 400 to 550°C for coatings deposited at a reactor pressure of 500 Pa and 87.5°C evaporator temperature adding 10 sccm reactant gas mixture. Coating hardness yielded values of 670 to 837 HK, thus well beyond the initial steel substrate hardness of 575 HK. The
carbon incorporated was mainly present in the carbidic form. Oxygen contamination increased with increasing deposition temperature. This is an indicator that TEMAZ is of reduced stability, thus easy to decompose but at the same time prone to strong reactions with oxygen, especially if reactive byproducts are incorporated into the coating which will strongly oxidise upon sample exposure to air. The columnar coating morphology found allows oxygen access through open porosity and inwards diffusion.

If no ammonia was added, the evaporation temperature was set to 60°C to reduce the evaporation rate and the amount of precursor available for reaction at the hot surface, as no parasitic gas-phase reaction will partially consume the precursor. Slightly higher hardness values of 830 to 900 HK were achieved in comparison to the experiments with 10 sccm reactant gas addition. Dense, smooth films were obtained only at 450°C deposition temperature and beyond. The growth rates evaluated in experiments at 325 to 550°C deposition temperature allowed for the clear distinction between a kinetically controlled regime at low temperatures and a mass-transfer controlled decomposition path at 375°C and higher. In the mass-transfer-controlled regime, an activation energy of 7 kJ mol\(^{-1}\) was calculated from the Arrhenius plot.

Experiments using TEMAZ were performed at various amounts of ammonia addition to the reactor gas phase at 500 and 550°C. The influence of the deposition temperature on the properties evaluated is not marked. A favourable combination of growth rate, chemical composition and hardness was achieved at both 500 and 550°C deposition temperature using 10 sccm N\(_2\)/NH\(_3\) mixture. No ammonia addition resulted in high growth rates, whereas 20 sccm N\(_2\)/NH\(_3\) resulted in reduced growth rates in comparison and lower hardness.

We conclude that the precursor TEMAZ is well suitable for the MOCVD process. Best combined properties, e.g. hardness, growth rates, and chemical composition are achieved at 475 to 500°C deposition temperature and 500 Pa pressure using 10 sccm N\(_2\)/NH\(_3\) reactant gas.

Coatings deposited using TPZ yielded hardness values of 850 to 1030 HK in the temperature range above 450°C at 200 Pa reactor pressure and 10 sccm reactant gas addition. The hardness did not vary much with deposition temperature if coated at 450°C.
and higher. These are the highest hardness values of all coatings deposited by MOCVD in this work.

At temperatures below 500°C the overall reaction is kinetically controlled. The activation energy is 80 kJ mol\(^{-1}\). At higher temperatures, the mass-transfer-controlled regime caused a growth-rate plateau around 160 nm/min with increasing deposition temperature. The parasitic gas-phase reaction was more pronounced at temperatures of 550° and higher, leading to a reduction in growth rate and powder-like deposits on the inlet tube and reactor walls.

Larger amounts of oxygen contamination (24-41 at.-\%) were found at 450°C and below. These coatings were not dense and their properties did not match expectations. At higher temperatures, oxygen was incorporated at amounts of up to 11 at.-\% only. This is much less in comparison to the oxygen incorporation determined in TEMAZ-based films deposited at the same temperatures.

No significant increase in hardness was observed in comparison to TEMAZ-based deposits. The carbon contents evaluated in TPZ-based coatings were higher than in TEMAZ-based films. Carbon was to a lesser percentage present in the carbidic form in comparison to TEMAZ-based deposits where carbidic carbon is the predominant form; the increase in carbon incorporation does not translate into an increase of hard, carbidic phase.

Varying the ammonia addition from 0 to 20 sccm N\(_2\)/NH\(_3\) we found highest hardness and lowest contamination levels at both 7.5 and 10 sccm N\(_2\)/NH\(_3\). Due to ammonia addition, the reaction is mass-transfer controlled.

We conclude for the precursor TPZ, suitable for MOCVD, that best combined coating properties are found at 475°C deposition temperature, adding 10 sccm ammonia-containing reactant gas to the gas phase.

One main goal of this work was to investigate if ZrCN films are suitable for friction coatings. Therefore tribological investigations involved the coatings with the best combined properties deposited using TEMAZ and TPZ, and one TBUZ-based deposit formed at 463°C. They were compared to commercially available Ti-based coatings, ZrN, alumina, DLC, and the plain, uncoated steel substrate.
The coatings prepared using TEMAZ, TPZ, and TBUZ considerably lower the dry-sliding coefficient of friction against all pin materials used to a range of 0.26-0.41, in comparison to roughly 0.6-0.8 for sliding on the commercially coated samples and the plain steel. The coatings made from different precursors did not yield marked variations in their tribological behaviour—the friction coefficients were very similar. Thus, the pin material is more important for the friction values evaluated than the precursor used. The soft pins made from Cu-alloy SM451C and the aluminium alloy AlMg4 caused the highest dry-sliding friction coefficients against coatings prepared in this work. This is due to oxidation of wear debris as these are the least noble pin materials used.

For commercially coated samples, except DLC, higher friction coefficients of around 0.6 to 0.8 are found. Comparing the tribological performance for example for TiCN by PVD and CVD, we found that the deposition technique used does not dominate the frictional properties. The coating surface roughness, affected by the coating technique used, does not correlate with the friction-force readings. The pin material yields much stronger variations in friction coefficients.

From the friction coefficient measurements at different loads we conclude that Amontons' first law of friction can be applied in the load range of 0.5-5 N to a wide range of commercially available Ti-based, DLC and alumina coatings as well as the deposits formed in this work using metal-organic compounds.

For the commercially coated samples, wear could not be detected. Apart from the high hardness this may also be due to the fact that these coatings are of higher initial surface roughness, and thus wear is difficult to detect. Significant film wear rates were determined for coatings deposited by MOCVD in dry-sliding tribotests against the five pin materials. The tribocouples involving the Cu- and Al-alloys yielded the highest wear rates. For experiments using pins made of 100Cr6, TiAl6V4 and Hastelloy C-22 the wear rates were lower. Here we found a significant correlation between coating hardness and the wear performance evaluated. The harder the coating, the lower the wear-rate. The best coating of those deposited in this study with respect to wear is made from TPZ at 475°C. For this coating we do not find an influence of the pin materials 100Cr6, TiAl6V4 and Hastelloy-C22 on the wear rate. For the TEMAZ-based coating deposited at 500°C the wear rates showed a threefold increase.
(0.37 \times 10^{-7} \text{ to } 0.55 \times 10^{-7} \text{ mm}^2 \text{ N}^{-1}) \text{ in comparison to the TPZ-based deposit for which wear rates of maximum } 0.15 \times 10^{-7} \text{ mm}^2 \text{ N}^{-1} \text{ were evaluated. Nevertheless, the influence of the pin material on the wear rate detected is negligible. These two coatings yield the best overall performance of the deposits formed in this study.}

Imaging-XPS and SEM investigations lead to the conclusion that in tribocouples involving the commercially coated materials, the pin is predominantly worn and material is transferred to the coating resulting in unfavourable metal-metal tribopairs. The coatings are of higher hardness than the pins. Depending on the pin material, the debris or transferred material will quickly oxidise.

For the coatings deposited by MOCVD, both pin and coating are worn. No pin material is transferred to the coating causing metal-metal tribocouples. On the coatings we find locations where wear debris from pin and coating is collected in pockets. If the wear continues they disappear and new pockets form. Thus, fluctuations in the friction-force reading are expected as the wear debris will, upon opening of a pocket, act as a third body, rolling or tumbling between the two sliding surfaces. This debris is generally strongly oxidised. Thus its surface is hard and it may plough into the pin surface, especially in the case of the soft pin materials SM451C and AlMg4.

The coatings deposited by MOCVD using TEMAZ, TPZ and TBUZ can markedly reduce friction against a variety of materials in dry-sliding applications in comparison to conventional coatings. However, only TEMAZ and TPZ are found suitable with respect to the coating hardness achieved.

Their hardness needs to be further enhanced through reduction of the amount of contaminants, mainly adventitious carbon and oxygen. This will also reduce the wear rates, which currently do not compare to commercial coatings.
Curriculum Vitae

Personal

Name               Christian Peter Allenbach
Date of Birth      March 20, 1970
Nationality        Swiss, Citizen of Reichenbach im Kandertal BE
Marital Status     Single

Education

10/1996 – date    PhD Student, Laboratory for Surface Science and Technology, Swiss Federal Institute of Technology, Zurich
                  Dept. Materials. Imperial College, London, Great Britain
10/1989 – 02/1995 Diploma in Materials Science "Dipl. Werkstoff-Ing. ETH"
                  Dept. Materials. Swiss Federal Institute of Technology, Zurich
09/1989           Maturität, Typus C
04/1985 – 09/1989 Kantonsschule Hardwald, Olten
04/1977 – 04/1985 Primarschule and Bezirksschule, Olten

Work Experience

from 06/2000       Rothrist Tube (Switzerland) Inc., Rothrist
10/1996 – 05/2000  Laboratory for Surface Science and Technology, Swiss Federal Institute of Technology, Zurich
03/1995 – 08/1995  Corporate Research and Development Centre, Hilti AG, Schaan, Principality of Liechtenstein
03/1993 – 04/1993  Dept. Turbo Generators, ABB Power Generation Ltd., Birr