Institut für Chemie Anorganischer Materialien der Technischen Universität München

Superhard nc-TiN/a-BN/a-TiB₂ and nc-M_nN/a-metal nanocrystalline composite coatings

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1. Introduction

The development of the civilization is connected with the use of new materials and new technologies for their preparation. In the 20th century the materials science and engineering developed very fast and new alloys, ceramic, plastic and composite materials appeared which were prepared by new technologies and characterized by new analytic methods. A large part of this research was focused on the preparation and utilization of materials in a form of thin films, which improve for example wear and corrosion resistance, electric, magnetic or optical properties of the basic material.

An improvement of the wear protection of machining tools incites nowadays the search for hard and superhard materials. In most of the machining applications, hardness is only one of many properties, such as high hot hardness and fracture toughness, oxidation resistance, chemical stability and low coefficient of friction, high adherence and compatibility with the substrate and low thermal conductivity, which such a material has to meet [Ve99a].

Today, more than half of all cutting tools in industry are coated by wear resistant coatings and the market is growing fast. Wear resistant coatings for high speed dry machining will allow the industry to increase the productivity of expensive automated machines and to save the high costs presently needed for environmentally hazardous coolants. Over 60 % of all coated tools on the market are still titanium nitride coated. Due to the increasing universality of TiAIN and TiCN coatings a wider use of these coatings can be expected on the market [Cs95] [Pre01].

A new class of superhard materials for wear protection has been suggested and experimentally confirmed by Vepřek et al. [Ve95a-Ve95c] [Ve96a-Ve96f]. The design concept of these novel superhard materials is based on combination of a nanocrystalline phase (typically transition metal nitride, such as TiN, W_2N , VN, TiAIN) imbedded in a very thin amorphous matrix, such as Si₃N₄ or BN. These so called nanocomposite coatings have very high hardness and resistance against cracks formation, thermal and oxidation stability and are very suitable for industrial application as wear protective coatings. Because of the large variety of possible material combinations that yield superhardness, superhard nanocomposite coatings hold the best promise of meeting all the complex demands on technically applicable superhard materials [Ve99a].

2. Goal of the work

This work describes the preparation of a new type of superhard nanocomposite coatings consisting of a nanocrystalline titanium nitride imbedded in amorphous boron nitride matrix by plasma chemical vapor deposition process. The titanium - boron - nitrogen system was chosen in order to confirm or disprove the concept for design of the superhard nanocomposite coatings [Ve95b] [Ve99a] when the boron nitride matrix instead of silicon nitride is used. By analogy with the earlier systems nc-TiN/a-Si₃N₄ [Ve95a] [Ve95b] [Chr98] [Rei95] [Pr03], studied nc-W₂N/a-Si₃N₄ [Ve96b], nc-VN/a-Si₃N₄ [Ve96a] [Ve96e], nc-TiN/a-BN [Ne00a] and nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ [Ve00a] [Ve00b] [Ne00b] [Ni00] [Mo01], the maximum hardness of the nc-TiN/a-BN/a-TiB₂¹ coatings should be obtained at the percolation threshold when there is about one monolayer of thin continuous tissue of a-BN between the TiN nanocrystals. These nc-TiN/a-BN/a-TiB₂ coatings were also compared with the same type of nanocomposite coatings deposited by vacuum-arc evaporation technique in the industrial scale equipment by the Czech company SHM Ltd.

The thermal and oxidation stability of the nc-TiN/a-BN/a-TiB₂, ZrN/Ni and Cr_2N/Ni coatings was also investigated. The ZrN/Ni coatings were prepared by author of this work as a part of her diploma work at University of West Bohemia [Ka00] [Mu01a] and provided together with Cr_2N/Ni coating [Re01] for the thermal stability measurement by Prof. J. Musil.

¹ The "Ti-B-N" coatings in this work consist of nanocrystalline TiN and amorphous BN or nanocrystalline TiN, amorphous BN and amorphous TiB₂ when the boron content in the coatings is low or high, respectively.

3. Theoretical part

3.1. Deposition techniques

The hard thin coatings can be deposited by Chemical Vapor Deposition (CVD) process at temperatures $\geq 1000^{\circ}$ C, which are not compatible with the coated steel substrates. A lowering of the deposition temperature can be obtained by utilizing very reactive feed gases or organometallic precursors, however, this can result in the increase of incorporated impurities and resultant degradation of the film properties.

For coating tool steel, Physical Vapor Deposition (PVD) or Plasma Induced Chemical Vapor Deposition (plasma CVD) processes are nowadays preferred to CVD. Plasma CVD can produce more uniform deposits on substrates with complicated shapes than the line-of-sight PVD processes, which need rotation of the working pieces in the vacuum chamber during the coating procedure. However, plasma CVD still suffers from problems such as the scaling from a small experimental reactor to large scale production units, the corrosive nature of the volatile halides precursors to the vacuum pumps and the hydrophilic nature of the deposits at the reactor walls and in the vacuum tubings. For these reasons, a combined plasma PVD and CVD technique, vacuum arc evaporation or reactive sputtering are more appropriate for industrial applications.

3.1.1. Physical plasma

A physical plasma is a partly or completely ionized gas containing charged and neutral species, including electrons, positive ions, negative ions, atoms, radicals and molecules. On average the plasma is electrically neutral. The plasma can be produced either by a thermal ionization at high temperatures of about $\geq 10000^{\circ}$ C or by a passage of electrical current (dc or hf) through the gas. The plasmas of interest for CVD here are the glow discharge plasmas (pressure range 10^{-3} to 10 mbar), which have electron densities in the range of 10^{9} to 10^{12} cm⁻³, average electron energies between 1 and 10 eV and a low degree of ionization of $10^{-6} - 10^{-3}$ [Ce90]. These plasmas are far away from thermodynamical equilibrium. The kinetic temperature of electrons (10000 to 50000 K) is much higher than the temperature of ions (\approx 500 K) and neutral particles (\approx 350 K) [Li94]. Plasmas are capable of efficiently generate chemically active species. The second feature that makes discharge plasmas so useful is their ability to generate ions and to accelerate the ions to energies of 50 - 1000 eV in the vicinity of the deposition or etching substrate [Ce90].

3.1.2. High frequency discharge

In the high frequency field (f \ge 10 MHz) the electrons move with the field frequency. However, their velocity is phase shifted compared to the field, whereby their energy remains low. Energy input to rf discharge occurs through three mechanisms. Energetic ions striking the electrode will cause the formation of secondary electrons. These electrons can be accelerated through the sheath and cause the ionization. The oscillating energetic fields in the glow can input energy directly into the electrons, much in the same way as the positive column of the dc discharge. Finally, the oscillating sheath electric field will accelerate electrons in the glow. This "surf-riding" mechanism has no direct analog in the dc discharge [Ce90].

Because of their high velocity and small mass, the diffusivity of the electrons is order of magnitude higher than that of the ions. Therefore, any surface in contact with the plasma will charge negatively with respect to the plasma in order to compensate for the different diffusivities of electron and ion and to assure equal fluxes of positively and negatively charged particles. The difference between the electric potential of the substrate and that of the surrounding unperturbed plasma - so called substrate bias - determines, together with the ratio of the mean free path to the thickness of the sheath, the impact energy of ions arriving at the surface of the growing film. This ion bombardment has important effects on the chemical and physical processes occurring during the growth and finally, on the properties of the deposited films [Ve89b].

An additional self bias of more than 100 to 1000 V can be created in high frequency discharge. Owing to the much greater mobility of the electrons compared to the ions, a given positive voltage will result in a much larger electron current than the ion current which flows for the same negative voltage. In effect, the plasma behaves like a leaking diode, showing much larger effective resistance for ion current than for electron current (Fig. 3.1). Because of the high electron mobility in the frequency range of 0.1 - 100 MHz, the resistance R_e is negligible. In the negative half-period the electrons follow the actual field and reach the electrode. In the positive half-period the ions need an additional acceleration due to the self-bias. At very high frequencies ($f \ge 40 - 80$ MHz) the impedance of the capacitor quickly decreases and the displacement current assumes the positive ions function. The self bias decreases [Kö85] [Br81] [Do85]. For the deposition parameters used in this work (industrial frequency 13.56 MHz at power 100 W and pressure 3 mbar) and without blocking capacitor the energy of ion bombarding the substrate is low.



Fig. 3.1: Equivalent diagram of the high frequency discharge space charge sheath.

Both high frequency and direct current glow discharges can yield essentially the same coatings if the ion bombardment is kept relatively low. If the discharge is operated in the abnormal glow regime the negative glow covers the whole surface of the cathode and follows the shape of a curved surface. This applies also to the hf discharge at sufficiently high power density where the high impedance of the space charge sheath near the electrode has a similar function as that in the abnormal dc glow.

3.1.3. Physical vapor deposition

PVD processes include a variety of different techniques such as vacuum evaporation, sputtering, ion plating, vacuum-arc, etc. Only the processes which are related to this work are mentioned in detail.

3.1.3.1. Conventional diode and magnetron sputtering

A low pressure plasma discharge of a type known as an abnormal negative glow diode sputtering is maintained by applying a high voltage between the cathode (target) and an anode (substrate table) at pressures in the mbar range. The current in such a discharge is carried in the vicinity of the negatively biased cathode primarily by positive ions passing out of the plasma volume and in the vicinity of the anode by electrons passing out of the plasma volume to the anode. Thus, a condition for sustaining such a discharge is that the plasma volume be a sufficient source of electrons and ions. Most of the electrical potential that is applied between the anode and cathode by the power supply is consumed in a "cathode dark space", or sheath region where strong electric fields are formed. Ions passing from the plasma volume to the cathode are accelerated by these fields and, on impact at the cathode, produce the desired sputtering. However, these ions also produce a small number of so-called "secondary electrons". These electrons are accelerated in the cathode dark space to energies approaching the applied potential, and enter the plasma volume (negative glow) where, known as "primary electrons", they collide with gas atoms and produce the volume ionization required to sustain the discharge [Th79]. The physically sputtered target atoms flow ballistically to and are deposited at the substrate. Because with argon ions the sputter yields are of the order of unity for almost all target materials, a very wide variety of pure metals, alloys, and insulators can be deposited [Li94].

For reactive sputtering, a feedstock gas whose dissociation products chemically react with the target is present in addition to the bombarding argon ions. The deposited film is a compound formed from the sputtered target materials and the reactive gas. In reactive sputtering, chemical reactions occur at both target and substrate, in addition to sputtering at the target and deposition at the substrate.

The main disadvantage of conventional diode sputtering is the direct contact of the plasma with the anode causing an uncontrollable heating of the substrates. The magnetron sputtering solves this problem. The difference of a magnetron from a conventional diode cathode is the presence of a magnetic field. The local polarity of the magnetic field is orientated such that the ExB drift paths of emitted secondary electrons form a closed loop. Due to the increase confinement of the secondary electrons in this ExB drift loop compared to a diode device, the plasma density is much higher than in conventional diode plasma. More effective ionization and confinement of the plasma causes a decrease of the total impedance of the plasma, increase of the ion current density, and therefore the discharge can be maintained at lower applied voltage and pressure with higher deposition rate without heating the substrate [Ke90] [Mu93] [Th79].

In the unbalanced magnetron, the conventional-magnetron magnetic field is modified in such a way that the magnetic field lines emanating from the edges of the magnetron target are directed towards the substrates. Therefore, a dense plasma is confined by the magnetic field between the magnetron target and the substrates.

3.1.3.2. Vacuum arc process

Arc is a discharge in a gas or vapor, that has a voltage drop at the cathode of the order of the minimum ionizing or minimum excitation potential of the gas or vapor.

It is a self-sustained discharge capable of supporting large currents by providing thermionic emission of electrons from the negative electrode [Sa90].

High densities of particles in the cathode region of the arc discharge are produced by the intense evaporation of the cathode material in cathode spots. This means that the arc itself creates the conducting medium necessary for sustaining the discharge by release of cathode material. Evaporation of material in cathode spots arises as a consequence of the high local cathode surface temperatures and the formation of small molten pools due to the very high local power density (up to 10^{10} W.m^{-2}). The evaporated material is ionized in collisions with electrons and accelerated away from the cathode because of the nonuniform potential distribution and plasma expansion. Magnetic fields can influence the arcing voltage as well as the rate and direction of motion of the cathodic spot. The disadvantage of the cathodic arc can be the emission of macroparticles.

3.1.4. Chemical vapor deposition and plasma chemical vapor deposition

CVD consists of a thermally activated gas-phase and surface reactions that produce a solid product at a surface. Usually high temperatures (700 - 1400°C) are used. In plasma CVD, the gas phase and often the surface reactions are controlled or strongly modified by the plasma. Instead of thermal activation in CVD, the critical initial step in plasma CVD is electron impact dissociation of the feedstock gas. Since $T_e \sim 2 - 5$ eV in a low-pressure discharge easily suffices for feedstock dissociation and since T_e is much greater than the substrate (and heavy particles) temperature, the deposition can be carried out at temperatures much lower than for thermal CVD. This effect of plasma can be compared to that of a catalyst [Ve89a] [Ve85] [Ve87b].

Uniformity of the deposited films is a critical issue for plasma CVD because of the high pressures, high flow rates, short mean free paths, high gas-phase reaction rates and relatively high surface sticking probabilities for molecular fragments in the gas-phase [Li94]. This combination of different factors makes it very difficult to achieve uniform flux of the fragments and ions across the substrate area.

3.2. Microstructure of thin films

The growth of thin films proceeds through consecutive steps characterized by specific processes of structure evolution: nucleation, island growth, coalescence of islands, formation of polycrystalline islands and channels, development of continuous structure and thickness growth. The final structure of the film is a result of the

creation and growth of the structural units (like grains) and their periodic reorganization during the formation of the film [Bar95] [Bar96].

The microstructure of a film strongly influences its physical and chemical properties. Microstructure is determined by a number of deposition and process parameters (substrate temperature, deposition pressure, substrate bias voltage, ion-to-atom ratio incident at the substrate) which control the energy delivered to the growing film [Ke99] [Su85] [Mu93]. This energy controls the mobility of the deposited atoms and is, therefore, the critical factor in determining the final microstructure of the coatings. The importance of microstructure on the performance of the coating has led to the development of structure zone models (SZMs) designed to describe coating structure in terms of specific deposition parameters.

Movchan and Demchishin [Mo69] showed in their classical SZM (MD model) that the structure of thick (0.3 - 2 mm) evaporated films could be describes in terms of the homologous temperature, T/T_m , (where T is the substrate temperature and T_m is the melting point of the coating material) of the coating. They identified three zones with distinct structural and physical properties (see Fig. 3.2). The low temperature zone 1 structure consists of tapered columnar grains separated by pores or voids. In this zone atomic mobility is low, incident atoms adhere where they impinge, and atomic shadowing is the dominant mechanism of the development of that structure. At higher homologous temperature atomic mobility is higher and the dense columnar zone 2 structure can form. This structure still has a distinct columnar appearance, but there are no voids between columns. In zone 3, at still higher homologous temperature.

Several attempts have been made to include the effects of ion bombardment on coating structure in a zone model. Thornton [Th77] extended the MD model to describe the structure of sputtered metal film by adding a second axis to account for the effect of argon gas pressure. He observed that the zone 1 structure persisted at higher homologous temperatures with increasing argon pressure. This is due to gas phase scattering in the plasma, which reduces the energy of the impinging ions and accentuates the atomic shadowing effect during growth. He also observed a fourth structural zone between zones 1 and 2. This was termed "zone T", as it was felt to be a transition between the two MD zones.

Messier et al. [Me84] further extended the MD model by replacing the pressure axis with a substrate bias voltage axis. Increasing bias voltage increases

the average energy of the bombarding ions, enhancing adatom mobility. Thus, at higher bias voltages, the zone 1 structure is suppressed.

Barna and Adamic [Bar95] constructed a real SZM taking into account the effect of impurities (Fig. 3.2). At low impurity level (Fig. 3.2a) the process induced segregation of impurities can be negligible at very low temperatures (zone I) and the impurity species could be incorporated into the growing lattice. In zone T the segregation of impurity species by the crystal growth increases by increasing the temperature and the impurity phase is expected to be segregated mainly at the grain boundaries. This will decrease the size of grains and can contribute to the competitive growth of crystals. In zone II a part of the first developing grain boundaries will be covered by the segregated impurity phase. Consequently the size of the developing columns will be smaller than in zone II of the ideal SZM (the SZM without impurities). In zone III the segregation of impurities by the grain boundary movement becomes effective with increasing temperature and in this way a contamination layer can develop covering completely the surface of growing crystals. This results in the development of three dimensional large grains which are separated by contamination stabilized grain boundaries. At high impurity level (Fig. 3.2c) the structure is globular in every zones with different grain sizes and the grain boundaries are covered by the impurity phase and mainly randomly oriented grains develop by repeated nucleation.

Kelly and Arnell [Kell98] described the coating structures in terms of homologous temperature, ion-to-atom ratio and substrate bias voltage. This approach allows the influence of temperature, ion energy and ion flux on the coating structure to be considered separately.



Fig. 3.2: The real structure zone models at a) low ($C_{imp} < 0.5\%$), b) medium ($C_{imp} \sim 1\%$) and c) high ($C_{imp} > 10\%$) impurities content (from [Bar95]), C_{imp} is the impurities concentration.

3.3. Properties of thin films

3.3.1. Hardness of materials and related properties

The theoretical hardness of a material H is a measure of its ability to resist deformation under isostatic pressure. The plastic indentation hardness, Eq. (3.1), is

the pressure under the indenter that causes the material to yield or "flow" (in Eq. (3.1) P is the normal load applied to the indenter and A is the area of the contact [Ta51]).

$$H = \frac{P}{A}$$
(3.1)

The theoretical hardness is proportional to the reciprocal value of the bulk modulus B. The bulk (B), Young's (E) and shear (G) moduli are connected by Eq. (3.2) and (3.3)

$$B = \frac{E}{3(1-2\nu)}$$
(3.2)

$$G = \frac{E}{2(1+\nu)}$$
(3.3)

where v is the Poisson's ratio. The "plastic" hardness depends, in addition, on the microstructure.

From Hook's law E = $d\sigma/d\epsilon$ (where σ is the applied stress and ϵ the resulting elastic strain) and the relationship between the stress (a force) and the first derivative of the binding energy E_b versus bond distance a at the equilibrium position a₀, one

obtains $E = \left(\frac{d^2 E_b}{da^2}\right)_{a(0)} \cdot a_0^2$ [He89]. Thus, a high curvature of the interatomic

potential curve at the equilibrium bond distance a_0 , i.e. a high bond energy and small bond length result in a high theoretical intrinsic hardness. A high bond energy means a high electron density between the atoms, as is found for nonpolar, covalent bond between atoms of small radii of the first period. Obviously, a high coordination number is required in order to maximize the value of the bulk modulus.

Super- and ultrahard materials are defined as those with Vickers hardness H_V of 40 - 60 GPa and \geq 70 - 80 GPa, respectively. Superhard material can be divided into intrinsic (they have high hardness due to reasons mentioned above), such as diamond ($H_V \approx$ 70 - 90 GPa), cubic boron nitride ($H_V \approx$ 48 GPa) and possibly some compounds from the B-N-C triangle [Su96] [Ve99a], and extrinsic ones, whose superhardness and other mechanical properties are determined by their microstructure. The most industrially used conventional hard coatings nowadays (TiN, CrN, TiAIN, TiCN, Al₂O₃) have hardnesses in the range of 20 - 30 GPa.

The practically achievable strength (and hardness) of engineering materials is orders of magnitude smaller than the theoretical strength $\sigma_c \cong G/2\pi$, where σ_c is the theoretical critical fracture stress and G the shear modulus [He89] [Ki71] [Ke86]. The

reason for this is that the deformation and fracture of materials occur by the multiplication and movement of dislocations in crystalline materials and growth of microcracks in glasses and ceramics, all of which require a much smaller stress than the theoretical value σ_c . Superhardness (extrinsic) can be achieved in thin coatings either by synergistic effect of energetic ion bombardment on the film microstructure (section 3.3.3.1) or by the formation of an appropriate nanostructure which hinders the growth, multiplication and propagation of flaws, such as microcracks and dislocations (section 3.3.3.2 and 3.3.3.3) [Ve02b].

3.3.2. Intrinsically hard materials

As it was already mentioned above to obtain material with a high intrinsic hardness a large coordination number, high covalent character of the bonds and short interatomic distance of the structure are required. Based on such general considerations Cohen and Sung [Li90] [Co94] [Su96] derived formula (Eq. (3.4)) which reproduced very well the bulk modulus of many materials. Based on this formula the β -C₃N₄ was predicted to exhibit extreme hardness and high modulus comparable to that of diamond.

$$B = \frac{\langle N_C \rangle}{4} \cdot (1971 - 220 \cdot \lambda) \cdot a_0^{-3.5}$$
(3.4)

Here $\langle N_c \rangle$ is the average coordination number, λ is the bond polarity, B is the bulk modulus and a_0 is the interatomic distance.

The theoretically predicted high hardness of C_3N_4 has not been experimentally documented so far [Ve99a] [Ve95c] [Ve97]. Most of the CN_x films prepared by various techniques are amorphous and substoichiometric in nitrogen, however, they find some applications such as protective, low friction coatings [Ha97] [Cu95] [Vl00] [Sj96] [Fa95]. On the other hand, polycrystalline diamond found a relatively large area of industrial applicability [Ve99a].

3.3.3. Extrinsically hard materials

As mentioned in section 3.3.1., the strength and hardness of engineering materials are orders of magnitude smaller than the theoretical one. If the microstructure of the material is designed in such a way as to efficiently hinder the multiplication and movement of dislocations or the growth of microcracks, the strength and hardness of a material can be increased by a factor of 3 - 7, i.e. superhard material should be formed when such enhancement can be achieved

starting from a hard material. This can be facilitated in various ways known from metallurgy, such as the solution, precipitation, cold work, and grain boundary hardening [He89]. The solution, precipitation and work hardening do not operate in small nanocrystals of about \leq 10 nm because solute atoms segregate to the grain boundaries and there are no dislocations in such small nanocrystals.

The grain boundary hardening is usually described by the Hall-Petch relationship (Eq. (3.5)):

$$\sigma_{\rm C} = \sigma_0 + \frac{k_{\rm gb}}{\sqrt{d}} \tag{3.5}$$

Here, σ_c is the critical fracture stress, d is the crystallite size, σ_0 describes the overall resistance of the lattice to dislocation movements and k_{gb} is a materials constant. The physics underlying the Hall-Petch relationship is the fact that the critical stress which is needed for the multiplication and movement of dislocations increases with decreasing distance of the pinning points for that dislocations, and that the energy of a dislocation pile up increases with decreasing volume of that pinning. The Hall-Petch relationship is strictly valid only when the grain size is large enough to accommodate a dislocation source since it depends on the existence of such source in its derivation [He89].

The Griffith theory of crack growth [Gr21], which applies to brittle glasses and ceramics, may yield a similar dependence of the critical fracture (crack growth) stress on the grain size. Accordingly, the critical stress σ_c for the growth of a microcrack of a size a_0 (a flaw usually originating from the sample preparation) is given by Eq. (3.6):

$$\sigma_{\rm C} = k_{\rm crack} \cdot \sqrt{\frac{2 {\rm E} \gamma_{\rm S}}{\pi a_0}} \propto \frac{1}{\sqrt{d}}$$
(3.6)

Here, E is the Young's modulus, γ_s the surface cohesive energy, and k_{crack} is a constant which depends on the nature and shape of the microcrack and the geometry of the applied load [He89]. In a well-compacted sample, the maximum size of the microcracks scales with the grains. For these reasons, the Hall-Petch relationship, Eq. (3.5), should be consider as a semiempirical formula which is valid down to a crystallite size of 20 - 50 nm. With the crystallite size decreasing below this limit, the strength and hardness decrease again (reverse Hall-Petch relationship) [Ca95]. This softening can be associated with the grain boundary sliding due to the increasing fraction of the relatively soft material within the grain boundaries [Si95].

A further increase of the strength and hardness with decreasing crystallite size can be achieved only if grain boundary sliding can be blocked by an appropriate design of the material structure. This is the basis of the concept for the design of superhard nanocomposites (section 3.3.3.3.).

Another possible way to strengthen a material is based on the formation of either multilayers consisting of two different materials with large differences in elastic moduli, sharp interface, and small thickness (lattice period) of about 10 nm [Ko70] (section 3.3.3.2) or coatings deposited under energetic ion bombardment with a high defect density ("work hardening") and high biaxial compressive stress [Ve02b] (section 3.3.3.1).

3.3.3.1. Hardening by energetic ion bombardment

The measured hardness of a material decreases with applied tensile stress and increases with applied compressive stress. When the stress is predominantly uniaxial, the influence of the stress is greater for specimens loaded in tension than those loaded in compression [Ts96] [Sw01]. The hardness enhancement in a bulk material due to the compressive stress is approximately equal to the value of the compressive stress [Sw01]. From this reason the maximum compressive stress in the range of 5 - 8 GPa in thin films can not enhance the value of measured hardness to 60 - 70 GPa (such a high hardness is often reported for PVD deposited thin films [Mu88] [Va88] [He97a] [Mi99]). Such a drastic enhancement of the hardness is caused by the synergistic effect of the energetic ion bombardment on the growing film [Mis99b] [Mis99a] [Ho80] [Sa82] [Ve87a]. The high energetic ion bombardment promotes simultaneously the increase of the compressive stress, decrease of the crystallite size, densification of grain boundaries and displacement damage (i.e. formation of point and extended defects) which all alone and even more together results in such a strong increase of hardness up to 70 - 100 GPa.

The hardening due to the synergistic effect of the ion bombardment can be easily distinguished from the superhardness originates from the film nanostructure. The substantial evidence of hardening mode gives the annealing experiment. During the annealing (or during the deposition at higher temperatures) the compressive stress and damaged structure are relaxed and the hardness decreases to the value of bulk material [He97a] [Ka01] [Mu99a].

Obviously, the enhancement of the hardness due to high energetic ion bombardment is of little interest for applications, such as cutting tools for dry

machining where the coatings reach a high temperature of 600 - 800°C. In contrast to that, the superhardness of the nanocomposites (section 3.3.3.3.) remains stable after annealing to high temperatures of up to 1100°C, because the superhardness originates from the nanostructure that is stable up to the high temperature [Ve02b].

3.3.3.2. Heterostructures

The strengthening of materials in heterostructures (superlattices) of a few nanometer thickness, consisting of multilayers made of alternating materials with different elastic moduli was suggested by Koehler [Ko70] and, later on, experimentally confirmed and extended by a number of workers [Le78] [Ba98] [Chu95] [An95].

Originally Koehler suggested depositing epitaxial multilayers of two different metals, M(1) and M(2), having as different elastic moduli as possible, $E_{M(2)} > E_{M(1)}$, but a similar thermal expansion and strong bonds. The thickness of the layers should be so small that no dislocation source could operate within the layers. If under applied stress a dislocation, which would form in the softer layer M(1), would move towards the M(1)/M(2) interface, elastic strain induced in the second layer M(2) with the higher elastic modulus would cause a repulsing force that would hinder the dislocation from crossing that interface. Thus, the strength of such multilayers would be larger than that expected from the rule of mixture. If such heterostructures are made of hard transition metal nitrides or carbides, their hardness can exceed 40 GPa and more [Yo01] [Li95] [Wu97] [Sp96a] [Chu93] [He87].

Generally the hardness of different type of heterostructures reaches a maximum at certain value of the lattice period, λ (less than 10 nm, in the most cases 5 - 7 nm). For a large period, where the dislocation multiplication source can still operate, the increase of the hardness and the tensile strength with decreasing layer thickness is due to the increase of the critical stress needed to multiplicate dislocations. Usually one finds strengthening dependence similar to the Hall-Petch relationship. The decrease of the hardness at small lattice periods can be caused either by the roughness of the interface due to interdiffusion during the preparation or by the opposing forces on a dislocation at the interface [Ba98]. As soon as the layers interdiffuse, they will lose the chemical modulation of the layers and difference in elastic modulus between the layers. When the two layers have similar elastic moduli, there is no enhancement in the hardness for a polycrystalline or epitaxial superlattice films [Sp96a] [Chu95] [Ba98] [Sp96b].

The application of the multilayers coatings for cutting tools has been fairly well developed [Ve99a] [Ho03]. However, the maximum hardness of the superlattice coating is very strongly dependent on the superlattice period. The strong dependence of H on λ may cause large variations in the coating hardness, when deposited in industrial machines because it is difficult to assure the same thickness of all superlattice layers on all coated objects, particularly when they have a complex shape. Similar variations of H can also be caused by the interdiffusion of elements in neighboring layers at high service temperatures. These problems can be avoided in nanocrystalline composite coatings.

3.3.3.3. Nanocrystalline composite coatings

Grain boundary hardening could in principle yield superhard materials if the grain boundary sliding could be avoided in hard polycrystalline materials with grain sizes in the range of few nanometers. The appropriate design of nanocomposites (Fig. 3.3) with strong grain boundaries such as nanocrystalline/ amorphous (nc-/a-) [Ve96b] [Ve95a] [Ve95b] [Ve96a] [Ve96e] [Chr98] or nanocrystalline biphase (nc-/nc-) [Ho99] composites can avoid grain boundary sliding [Ve98a]. The hardness of such a material should continue to increase even for grain sizes below 6 - 10 nm. When designed of strong materials, essentially all such nanocomposites should reach a superhardness of \geq 40 GPa [Ve98a] [Ve95a] [Ve95b] [Ve96a-Ve96c].

The concept for the design of the superhard nanocomposites [Ve98a] [Ve01] is based on a thermodynamically driven segregation in binary (and ternary) systems which display immiscibility and undergo spinodal decomposition even at high temperatures. The condition for spinodal decomposition in a binary system $A_{1-x}B_x$ to occur is a negative second derivative of the free energy of formation of the mixed phase $A_{1-x}B_x$ with an infinitesimal change of the composition $A_{1-(x\pm\delta)}B_{x\pm\delta}$, (Eq. (3.7))

$$\frac{\partial^2 \Delta G_f^0(A_{1-x}B_x)}{\partial x^2} < 0$$
(3.7)

Therefore, any infinitesimally small local compositional fluctuation decreases the free energy of the system thus leading to a spontaneous segregation. The segregation occurs spontaneously without any kinetically hindered nucleation, resulting in a fine nanostructure with a characteristic length scale which is determined by the balance between the change in free energy due to decomposition, concentration gradients and the elastic strain energy due to the incoherence of the interface between the two segregated phases [Mä01] [Sch95]. As a result, a nanocomposite with a low concentration of flaws due to "self-organization" forms which remains stable against coarsening (Ostwald ripening) as long as the condition $\partial^2 \Delta G_f^0 / \partial x^2 < 0$ remains valid [Ve01] [Ve99a] [Ar01] [Ni01] [Ve99b] [Ve98c].



Fig. 3.3: Nanostructure of the superhard nc-M_eN/a-Si₃N₄ nanocomposites (from [Ve95a] [Ve95b]).

The condition of strong segregation between the phases is satisfied for all thermodynamically stable transition metal nitrides provided the nitrogen activity is sufficiently high and the preparation occurs at temperatures below about 600°C [Ve96c] [Pro03]. Under conditions of an intense low pressure plasma and neutral gas temperature of about 500°C, there is enough activation energy available to kinetically catalyze such a segregation, but the temperature is still low enough to avoid the entropy driven mixing [Ve96b]. The latter is fulfilled for plasma CVD of binary nanocomposites deposited at a relatively high pressure of \geq 1 mbar and high plasma density. In the case of plasma PVD at much lower pressure and temperature, formation of the nanostructure is not fully completed during deposition [Pro03]. Upon annealing, such nanocomposites show a complex structural relaxation, accompanied by an increase of the hardness, after which they remain stable up to a high temperature of \geq 1000°C [Mä01] [An91].

The nanostructured superhard nanocomposites can sustain a much larger strain than the conventional hard materials [Ve01]. The 3 – 10 nm size nanocrystals cannot accommodate any crystal plasticity nor any other form of flaw [Li02] because

the elastic strain, which would be induced by a dislocation in the nanocrystal, would push it out into the grain boundary. The most probable fracture mechanism of the nanocomposite materials should be initiation and growth of intergranular cracks propagating within the interfacial component [Ve96a] [Ve96b] [Ni01]. But in the randomly oriented nanocomposites the size of such cracks can be only a fraction of the crystallite size, so the stress concentration factor of an atomically sharp crack is very low and the critical stress for the crack growth approaches extremely high values [Ve00b]. Because only the stress component perpendicular to the crack plane causes the crack growth, the first nano-sized cracks to be considered as operating under an applied load are those within the interfaces perpendicular to the direction of the applied tensile stress. After the opening, the nanocrack can grow within that plane only up to the nearest obstacle, such as the neighbor nanocrystal, where it has to undergo deflection and branching which further decreases of the stress concentration factor. Thus, for a nanocomposite with grain size of a few nanometers and the thickness of the interface phase of about 1 monolayer the deflected and branched crack will stop within a small distance of the order of 1 nm unless the applied stress will be significantly increased which would lead to catastrophic fracture. For these reasons, contained fracture of the nanocomposites due to a formation and stable growth of nanocracks is unlikely and other mechanisms of plastic deformation should be responsible for the high hardness and elastic recovery found in these materials. The high elastic recovery of the nanocomposites can be explained by a reversible non-linear flexing (a "partial opening and closure") of interplanar spacing between nanocrystallites [Ve02c] [Ve01] [Ve00b].

A variety of nanocomposites suitable for protection of cutting tools or for tribological applications was prepared [Ve99a] [Vo00]. In the appropriately synthesized binary systems the hardness of the nanocomposites exceeds significantly that given by the rule of mixtures in bulk. For example, the hardness of nc- M_nN/a -Si₃N₄ (M = Ti, W, V) binary nanocomposites with the optimum content of Si₃N₄ close to the percolation threshold reaches 50 GPa [Shi92] [Ve95a] [Ve95b] [Ve96a] [Ve96a] [Ve96b] [Chr98] [Ve96e] [Ve98a] [Ve98b] [Ve99b] [Ni99] although that of the individual nitrides does not exceed 21 GPa in bulk [Ho86]. The ultrahardness of ≥ 80 GPa was achieved for nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ nanocomposites when the surface of the TiN nanocrystals was covered with approximately one monolayer of Si₃N₄ [Ni01] [Ve00a] [Ve00b] [Ne00b] [Mo01]. Thus the percolation of Si₃N₄ is much more important for achieving superhardness than the small crystallite size [Ni01]. In

contrast, a binary solid solution, such as $TiN_{1-x}C_x$, shows a monotonous increase of the hardness with x increasing from 0 (H_V \approx 22 GPa for TiN) to 1 (H_V \approx 40 GPa for TiC) [Ve96b], thus following the rule of mixtures.

3.4. Literature overview

3.4.1. TiN coatings

TiN overlay coatings find numerous applications on cutting tools, as a decorative coating or as diffusion barriers in electronic microcircuits [Yo89] [Yo91]. TiN is a hard material and is very stable except that it oxidizes readily at temperatures above 550°C [Ku86]. TiN coatings can be deposited by a high temperature ($\geq 1000^{\circ}$ C) CVD process [Ka75] [Kas00]. The lowering of the deposition temperature to 400 - 700°C is obtained by utilizing TiCl₄ and NH₃ gases [Ku86] [Yo89] [Bu92] [Yo91] [He93] [Bu91] or organometallic compounds [We93] [Ru93], but it can lead to an increase of incorporated impurities such as chlorine, oxygen and carbon and to a degradation of the film properties [Be90] [Su90].

Thus the better way for the deposition of TiN coatings is to used PVD or plasma CVD processes. Either PVD techniques such as reactive sputtering [Mu88] [Va88] [Mü82] [Mi95] [Su98] [Mi97] [Bä95] [Ke99] [He97a] [Lo97b] [Ma02], arc evaporation [Wul97] [Eg97] [Kar00a], ion plating [Bu81] [Mi95] or plasma CVD at high frequency [Hi86a] [Hi87] [Hi86b] [Hi88] [La90] [La89] [Ja89a] [Ja89b] [Ma86] [Sa88] [Ia89] [Ki99b] [Ki96] or direct current [Pa96] [May86] [Sh84] [Ar88] [Ar81] discharge can give good quality TiN films.

TiN of stoichiometric composition has NaCl structure and a lattice parameter of 4.24 Å. However, for thin films the lattice parameter deviating from the abovementioned bulk values is frequently reported [Su85]. These deviations can be caused by different phenomena such as stresses cause by the difference in thermal expansion coefficient between the film and the substrate, substitutional impurities such oxygen and carbon, high compressive stresses due to incorporation of argon or interstitial nitrogen or by the non-stoichiometry of the film [Lo97b] [Su85] [Na75] [Oe98]. The color of the TiN coatings is also dependent on the film stoichiometry. The color of substoichiometric TiN_{1-x} film is metallic gray to pale yellow, stoichiometric film has golden like color and the TiN_{1+x} films are brownish [Pa96] [La90] [La89] [Ja89a] [Ja89b] [Sh84] [Sa88] [May86] [Ia89].

The mechanical properties of the plasma CVD deposited TiN coatings strongly depend on the chlorine content in the coatings [Rei95], which can be decreased by

decreasing TiCl₄ flow, increasing temperature and discharge current density or increasing H_2 inlet fraction [La89] [Ja89a] [Sa88] [Pa96] [Hi86b] [Ar81] [Hi86a] [Hi87] [Ja89b]. The residual chlorine content in the film generally originates from the incomplete dissociations of the used chlorine source materials.

The grain size in TiN films is generally below 100 nm if the films are grown at temperatures below approximately 600°C [Hi86a] [Hi87] [La89] [Pa96] [Ja89a] [Mu88]. At the substrate temperature of 300 - 550°C the TiN films have a structure typical of a zone T according to the classification by Thornton [Th77] [Th86] and normally grow with a (111) and (200) preferred orientation for PVD and plasma CVD, respectively [Su85] [Hi86a] [Ja89b] [Ma86] [Ja89a] [Sa88] [Ia89] [Ki96]. Upon energetic ion bombardment, reduced porosity, changes in the preferred growth orientation and increased hardness are found [Ke99] [Oe98] [La89] [Pa96] [Ma02].

For dense stoichiometric TiN films hardness values between 20 and 30 GPa [Hi86a] [Hi87] [Hi86b] [Ar88] [La89] [La90] [Ma86] [May86] [Pa96] [Sh97] [Ki96] [Bu81] [Mü82] [Ke99] and resistivities between 20 and 30 μ Ω.cm [Su85] are reported. Due to the synergistic effect of the ion bombardment the hardness of the TiN coatings can achieve a range of 70 - 80 GPa [Mu88] [Va88].

In order to improve the adhesion properties of the PVD coatings a Ti interlayer which reduces the thermal stress can be deposited between the substrate and the film [Mi97] [Sh92] [Shi97] [Hu88].

Improved wear behavior compared to TiN coatings has been stated with (Ti,AI)N [Mü86] [Ki96] [Tan92], (Ti,Zr)N and (Ti,AI,V)N [Kn86] [Mü86] or TiCN [Kar00b] coatings. Aluminum was chosen because it forms a stable aluminum oxide layers on the top of the Ti_{1-x}Al_xN coatings, when exposed to air at elevated temperatures. This oxide layer protects the remaining Ti_{1-x}Al_xN coatings from further oxidation [Ki96] [In97] [Ki97] [Ki99a] [Pr00] [Mü86] and improves the oxidation resistance as compared to TiN coatings [Kn86] [Hei98] [Tan92] [Mü86].

The lattice parameter of the Ti_{1-x}Al_xN is smaller than that of TiN because the titanium atoms in the TiN lattice are replaced by smaller aluminum atoms [An99] [Pr00]. The structure of the Ti_{1-x}Al_xN film depends on the amount of Al added [Mu00b]. The Ti_{1-x}Al_xN coatings prepared by plasma CVD [Ja98] [Le94] [Pr00] show the fcc structure up to an aluminum content of x = 0.77 - 0.9. For sputtered Ti_{1-x}Al_xN films it was found that the film has fcc structure for x ≤ 0.65 [Wa93]. Depending on the aluminum content, the hardness of Ti_{1-x}Al_xN coatings is in the range of 22 - 30 GPa [Kn86] [Ki96] [An99] [Tan92] [Le94] [Mü86].

During annealing at 900°C the phase separation of the metastable $Ti_{1-x}AI_xN$ structure can be detected [Mü86] [Hö02]. Hultman and co-workers [Hu91] reported on the formation of nanocomposites due to spinodal decomposition of $Ti_{1-x}AI_xN$ ($0 \le x \le 0.4$) at elevated temperatures during deposition.

The chemically most stable coatings used in the commercial production so far are AI_2O_3 prepared by thermal CVD, and $Ti_{1-x}AI_xN$, prepared by PVD [Ho99].

3.4.2. Ti-B-N system

The potential disadvantage of the nc- M_nN/a -Si₃N₄ system might be the solubility of silicon in some metals including aluminum alloys, superalloys and others. An even better choice of the amorphous (or nanocrystalline) phase in combination with a nanocrystalline transition metal nitride would be boron nitride because boron atoms can be three- and fourfold coordinated, the B-N bond is stronger than the Si-N one and Ti-B-N coatings are compatible with the majority of engineerings materials [Pf99a] [Ta92]. The problem in the preparation of the nc-TiN/BN nanocomposite is associated with formation of the soft hexagonal phase h-BN which results in a strong decrease of the hardness of the composite when the nitrogen content is increased from the composition of TiN/TiB₂ towards that of TiN/BN_x. The deposition conditions which promote both the phase segregation and the formation of cubic c-BN are a high plasma density, high deposition temperature and high ion bombardment [Ve98a] [Ve99a].

The thermal stability of the fully segregated, binary TiN + BN system depends on the nitrogen pressure. The decomposition TiN + 2BN \rightarrow TiB₂ + 3/2N₂ commences about 1350°C at nitrogen pressure of 1 mbar and the decomposition temperature increases to 1600°C at P(N₂) = 500 mbar. At a lower nitrogen pressure the decomposition temperature decreases and a complex multiphase diagram applies including a variety of Ti_xB_y, Ti_nN_m and further mixed phases Ti_xB_yN_z [Ro92]. This explains the complexity of phases found in coatings deposited by the PVD techniques under a low nitrogen pressure or even without nitrogen. Under conditions of plasma CVD, when the nitrogen pressure of several mbar is sufficiently high, the binary system of stoichiometric TiN and BN should be stable. Therefore, only under these conditions the spontaneous formation of the nc-TiN/a-BN nanocomposite should occur.

A large number of "Ti-B-N" coatings with different composition and structure prepared by a variety of methods have been reported, such as the formation of a

homogeneous phase TiB_xN_y [Wo99] [De95] [Mo96] [Mi90] [He99] [Gi93], amorphous Ti-B-N coatings [Wi99] [Ot00] [Pf99a] [Ma93] [Kn90], mixture of phases TiN, TiB₂ and BN or TiB [Cha97] [Ba97] [Re98] [Ao02] [So02] or TiN, TiB, BN and Ti-B-N [Ya95] [Ya96a] [Qi97] [Ya96b]. The increase of the lattice parameter of TiN due to an incorporation of boron during the formation of fcc Ti-B-N phase was also reported [Mi89] [Mi98] [Lo97a] [Ka89] [Pf99a] [Pf99b].

Other authors have found phase segregation with the formation of binary phases TiN and TiB₂ [Ha94] [Mo95] [Gi97] [Ma00] [Mi99] [He97a] [He98] [Oh97]. At a lower boron content a nanocrystalline TiN and a quasi-amorphous TiB₂ phase are formed whereas a higher boron content leads to a structure consisting of quasi-amorphous TiN and nanocrystalline TiB₂ [Ma00] [Mi99] [Pi02a] [Kn91] [Gi97].

Some papers also reported on formation of nanocomposites consisting of nc-TiN (or nc-TiB₂) phase imbedded in a BN matrix which can be hexagonal, amorphous or cubic [Pi01] [Pi02a] [May97] [He98] [Ho99] [He01] [Pi02b], but in most cases these coatings were relatively soft \leq 20 GPa [Pi01] [Pi02a] [He01] [May97]. Héau and Terrat [He98] reported a hardness of 80 GPa in Ti-B-N coatings deposited by magnetron co-sputtering from Ti and TiB₂ targets and having the composition 13 at.% B, 37 at.% Ti and 50 at.% N, but the hardness was unstable and decreased to about 46 GPa after several days indicating that it was enhanced by energetic ion bombardment.

Hardness of 40 - 70 GPa was reported in many papers [Ha94] [Gi97] [Lo97a] [Wo99] [De95] [Mo96] [He99] [Mi99] [Cha97] [Ho99] [Ya95] [Ya96a] [Qi97] [Ya96b] [Mi90] [Re98] [Hea97] [Pf99a] [Pf99b] [Gi93] [Mi98] [He98] [He97a] [Ho95] [Ve98a] [Ao02] [So02] [Fr91] [Kn90], but for majority of the Ti-B-N coatings it probably resulted from the energetic ion bombardment during the deposition [Mi99] [Mi98] [Qi97] [Ke98] [Mi90] [Lo97b] [Wi97].

In general, the hardness as a function of composition did not follow the rule of mixture but displayed a maximum at a given composition, where the microstructure of the films was very uniform (no columnar growth) and the crystallite size was a few nm. With increasing nitrogen content, when the h-BN phase was formed, the hardness of the film strongly decreased [Gi97] [Mo96] [Ot00] [He01] [Mi90] [Re98] [Mi89] [Kn91] [Cha97] [Ba95] [Kn90] [Re99c]. If, however, much higher temperature, high plasma density, and negative bias were used, the formation of the h-BN was suppressed and superhard nc-TiN/c-BN nanocomposites were obtained by a combined plasma PVD and CVD [Ho99]. These coatings showed the best

performance at low cutting speed of 150 - 210 m/min where abrasive wear dominates [Ho99] [Ho00].

Several researches have also reported an increase of the hardness of various Ti-B-N coatings if they were, after deposition at a relatively low temperature, postannealed and the segregation was completed [Wi99] [Mo95] [Ha94] [Re99c] [Se98].

Coefficient of friction of Ti-B-N films was reported between 0.05 - 1 [Ya96a] [Re98] [Wo99] [Ho95] [Ta92] [Ro01] [Pf99a] [He97a] [He01] [Pf01] [Ot00] [Qi97] [Mo96]. The abrasive wear tests carried out in water have shown that some chemical interactions occur when coatings with high B content were tested [He98] [Hea97]. The friction coefficient and abrasive wear behavior of TiAIN coatings were improved by boron addition [Zh02] [Pa03].

TiAlBN coatings deposited by PVD exhibited excellent wear resistance, with optimized coating compositions demonstrating a 150 % increase in lifetime compared to standard TiAlN coatings in wet-cutting drill test [Ba02a] [Ba02b]. These coatings exhibited a three-phase composition of (Ti,Al)N + BN + TiB₂ and maximum hardness of 37 GPa. Optimum drilling performance was obtained for a coating with a phase fraction of approximately 90 % (Ti,Al)N and 10 % BN. The microstructure was described as nanocrystalline (Ti,Al)N grains separated by an intergranular amorphous BN phase, in which the average (Ti,Al)N grain size and grain separation was determined to be 26 and 3 nm, respectively. The improved performance was attributed to the compliant a-BN phase allowing some (Ti,Al)N grain displacement under load, reducing the elastic modulus, increasing the toughness and ultimately enhancing wear resistance [Ba02a].

3.4.3. nc-M_nN/a-metal coatings

By analogy with the well known cemented carbide WC-Co, idea behind the preparation of nc- M_nN/a - M_e coatings consisting of a hard transition metal nitride M_nN and a soft metal M_e which does not form any stable nitrides (e.g. $M = Cr, Zr, ..., M_e = Ni, Cu$) is based on a combination of a hard, but relatively brittle nitride with a soft metal which should provide the coatings with a better fracture toughness [Mu98a] [Mu00a] [V000]. This approach is different from the principle for design of superhard nanocomposite coatings consisting of a hard transition metal nitride and a covalent nitride which show a thermodynamically driven, strong spinodal segregation [Ve95a] [Ve99a] [Ka03].

According to Musil [Mu00a] there are two groups of superhard nanocomposite coatings: nc-M_nN/nitride and nc-M_nN/metal. Unfortunately, the results in the section 5.5.2. show that the hardness enhancement in nc-M_eN/a-metal coatings is most probably due to a synergistic effect of energetic ion bombardment during the deposition and the annealing to a relatively low temperature of \geq 400°C results in the stress relaxation and decrease of the hardness to the ordinary bulk values [Ve02b] [Ka01].

4. Experimental

4.1. Deposition of the coatings

4.1.1. TiN and nc-TiN/a-BN/a-TiB₂ coatings deposited by plasma CVD

The deposition of TiN and nc-TiN/a-BN/a-TiB₂ coatings was carried out in a reactor made of silica glass (volume 1.2 I) inserted into an electrical oven (Fig. 4.1).



Fig. 4.1: Schema of the HF plasma CVD apparatus (MFC = mass flow controller).

Initially the substrate was mounted on the stainless steel substrate holder by only one connection between the substrate holder and the substrate which led to inhomogeneous depositions due to non-uniform distribution of a current density on the substrate. In the second stage, the substrate was mounted on the substrate holder by two connections. This arrangement produced very homogeneous films. In the third stage the substrate was held by steel ring with four screws and pressed to the holder to insure good contact between the holder and the substrate. In this arrangement the deposition on different type of substrates was possible. The substrate holder was connected to the output from transmitter-amplifiermatchbox assembly as a driven electrode of a high frequency discharge. Three quartz glass tubes around the holder hindered the deposition of the film on the lateral faces of the holder. The second electrode was a 70 mm wide grounded nickel sheet around the silica tube. During the deposition, the reactor was heated by means of an 1.5 kW external furnace. The temperature of the furnace was controlled by means of a NiCr/Ni thermocouple inserted into the oven and *Omega Micromega CN 77340* controller. Because of the strong r.f. interference during deposition, the temperature measurements were carried out only at the beginning and the end of the deposition process.

The reactor was evacuated with rotary pump *Pfeiffer DUO 008 B* which allowed us to evacuate the chamber to 2.10^{-2} mbar. The pressure was measured by means of a capacitance manometer *MKS BAX 122 Baratron* in the range of 10^{-3} - 10 mbar supplied with *MKS PDR-C-IB* readout unit.

The reactant gases (nitrogen, hydrogen, boron trichloride and titanium tetrachloride) were introduced through the gas manifold as shown in Fig. 4.1. The TiCl₄ line was heated to prevent gas condensation. No carrier gas was used for TiCl₄ or BCl₃ gases. The flow of nitrogen and hydrogen was controlled by means of *MKS 1179 MASS-FLO* mass flow controllers with *MKS 247C* control unit whereas the flow of BCl₃ and TiCl₄ was adjusted by means of a needle valve *NUPRO BMG (SS-6BMG-MM)*. The TiCl₄ bubbler was immersed into a thermostat *HUBER T 301* in order to keep the TiCl₄ pressure constant. The stability of the thermostat setting of $\pm 0.005^{\circ}$ C assured a TiCl₄ vapor pressure accuracy of ± 0.008 mbar. Before entering the reactor, the gases were mixed within a mixing chamber. The typical temperature of thermostat was 24.1°C which corresponded to TiCl₄ saturation pressure of 16 mbar. The pressure of BCl₃ in cylinder was about 1.5 atm [Gm86].

The plasma ignition and maintenance were provided by means of a high frequency transmitter *Kenwood TS-440 S* fed by *Kenwood PS 50* power supply. The signal from the sender was amplified by *Kenwood TL 922* amplifier. The maximum power output was 700 W.

Because the HF plasma has a complex impedance (capacitive, inductive, and resistive components) and the majority of power supplies are designed to be most efficient when powering a simple 50 Ω load, the matching network must be inserted between the amplifier output and plasma. The role of the matching network is to

transform the high impedance of the plasma to the 50 Ω output of the amplifier and in such a way to maximize the power that can be delivered to the plasma.

The matchbox *MFJ Versa Tuner 989 C* was used in this work. The coupling between the matchbox and the substrate holder was done by means of 40 mm wide and 0.1 mm thick copper sheet. All high frequency parts were shielded by copper sheath.

The films were deposited on stainless steel substrates (0.5 mm thick, 20 mm diameter), silicon wafers with (111) orientation, molybdenum substrates (1 mm thick) and steel strips (0.3 mm thick). The stainless steel substrates were washed with aceton and than etched for 30 minutes with stainless-steel-etching-paste *ANTOX 71E*. Then the paste was washed out with water and the substrates were kept for 120 minutes at 60°C in 10 % solution of *Deconex* (alkaline labor-cleaner). After removing from *Deconex* the substrates were cleaned with water and dried at 120°C in oven. Before each deposition the substrate was cleaned in isopropanol ultrasonic bath for 5 minutes, dried and weighed by using an ultra-micro balance *Sartorius Supermikro S4* with an accuracy of $\pm 0.1 \mu g$.

After mounting the substrate in the reactor, the reactor was evacuated to a pressure below 2.10⁻² mbar with a simultaneous heating to 570°C. Afterwards, the leak rate was checked. For the determination of the leak rate, the reactor was completely evacuated to the basic pressure, than the pump was closed for a given time interval t and the pressure increase Δp was measured. The leak rate was calculated as $L = (\Delta p \cdot V)/t$, where L is the real and virtual leak rate (i.e. real leaks and outgassing from the reactor walls) and V is the volume of the reactor and tubings. The leak rate was below 5.10⁻⁴ mbar.l/s in all deposition experiments which, at given total gas flow rate of 55 sccm (0.92 mbar.l/s), assured a sufficient purity during the deposition.

The nitrogen flow of 5 sccm and hydrogen flow of 50 sccm was adjusted and the total pressure in the reactor was set to 3 mbar by means of a throttle valve which reduced the effective pumping speed. Afterwards, the pure $H_2 + N_2$ discharge was ignited and maintained for 15 minutes in order to clean the reactor walls and substrates. Afterwards, the TiCl₄ line was opened and approximately 0.8 µm thin TiN interlayer was deposited between substrate and nc-TiN/a-BN/a-TiB₂ coating in order to improve the adhesion.

The deposition time of several hours was chosen depending on the desired thickness of the film. After the end of deposition, all gases except of nitrogen were

closed, the oven was switched off and the reactor was allowed to cool down to room temperature under nitrogen flow. After each deposition the reactor was cleaned with H_2O_2 - NH_3 solution. The film thickness was determined from the weight increase assuming a constant density of bulk TiN (5.4 g/cm³). This value was confirmed on several samples by measuring the film thickness in scanning electron microscope.

After each deposition the leak rate of the reactor was again checked and the flows of TiCl₄ and BCl₃ were measured and adjusted for the next experiment. For the measurement of the TiCl₄ and BCl₃ flow the reactor was evacuated to the basic pressure p_{basic} and than the pressure was adjusted to 5 mbar with 100 sccm of hydrogen and 25 sccm of nitrogen. This was done to always reach an approximately same effective pumping speed $S_{\text{eff}} = \frac{125}{(5 - p_{\text{basic}}) \cdot 60}$ [I/s]. Using this effective pumping speed the reactor was let to evacuate to the basic pressure p_{basic} again and afterwards the TiCl₄ bubbler or BCl₃ line were opened, the pressure increase was measured and the flow f in sccm was calculated as $f = S_{\text{eff}} \cdot (p_{\text{TiCl}_4} - p_{\text{basic}}) \cdot 60$. The optimization of the parameters for the deposition of TiN coatings and the used deposition parameters for nc-TiN/a-BN/a-TiB₂ coatings are listed section 5.1.

4.1.2. nc-TiN/a-TiB₂ coatings deposited by arc evaporation

The nc-TiN/a-TiB₂ coatings were deposited on a production scale plasma PVD & CVD equipment consisting of vacuum arc evaporation from a central cylindrical titanium cathode in combination with plasma CVD of boron from borazine ($B_3N_3H_6$) (Fig. 4.2) in the Czech company SHM Ltd.

The cooling of the cathode was provided by water flowing in the axial direction inside of the cathode. The movement of the cathode spot of the arc was controlled by magnetic field which was induced by a combination of permanent magnets and electric coils. The axial component of the field drove the motion of the spot around the axis of symmetry whereas the axial shift of the magnetic field, which was controlled by the coils, controlled the axial movement of the cathodic spot. The spot was moved at a time scale of several tens of millisecond up and down. The substrates were mounted on several holders which were placed symmetrically around the cathode and rotating [Ho00].

A typical deposition parameters used at deposition of nc-TiN/a-TiB₂ coatings are listed in the Table 4.1.



Fig. 4.2: Schematics of the industrial coating equipment based on vacuum arc evaporation from central titanium cathode for the deposition of nc-TiN/a-TiB₂ coatings (from [Ve02d]).

Table	4.1:	Deposition	parameters	used	for	the	deposition	of	nc-TiN/a-TiB ₂	by
vacuur	m-arc	evaporation	system.							

Deposition parameter				
substrate temperature [°C]	536 - 700			
negative substrate bias [V]	100 - 200			
total pressure [Pa]	1.17 - 1.29			
arc voltage [V]	41 - 53			
arc current [A]	2 - 4.3			
substrate current [A]	43 - 76			
electrode current [A]	80 - 100			
B ₃ N ₃ H ₆ flow [sccm]	230 - 340			
film thickness [µm]	1.5 - 6.6			
substrate	WC-Co			

4.1.3. ZrN/Ni and Cr₂N/Ni coatings deposited by magnetron sputtering

The ZrN/Ni and Cr₂N/Ni coatings were prepared by d.c. reactive magnetron sputtering of a ZrNi (90:10 at.%) alloyed target (Fig. 4.3) and a Cr target fixed to the magnetron cathode with a Ni ring in a mixture of Ar and N₂ (both of 99.999% purity)

onto steel substrates (a disc 25 mm in diameter and 5 mm thick). A planar circular unbalanced magnetron with a diameter of 100 mm (internal diameter of the Ni ring $\emptyset_i = 84$ mm) was used for deposition of the coatings at a substrate temperature of 300 and 200°C, respectively, and a negative bias between -30 and -200 V for the ZrN/Ni and -200 V for Cr₂N/Ni. The target was directly cooled with water. The distance between the target and substrate holder was 60 mm and the area of the substrate holder was 70 cm². The composition of the target was adjusted to the required composition of the deposit for the given system. In addition, the ratio of the metals (e. g. Zr:Ni or Cr:Ni) could be also varied by an appropriate choice of the substrate bias between -30 and -200 V and ion current density to the surface of the growing film during the deposition.



Fig. 4.3: Schema of the d.c. unbalanced magnetron system used for deposition of *ZrN/Ni* coatings.

The total deposition pressure was 0.7 Pa for ZrN/Ni coatings and 0.5 Pa for Cr_2N/Ni coatings. The substrate was placed on a movable and heatable substrate holder electrically insulated from the grounded chamber. A shutter placed between the magnetron and the substrate holder allowed the magnetron cathode surface to

be precleaned before the film deposition. More details about the deposition of ZrN/Ni and Cr₂N/Ni coatings are in [Mu01a] [Re00] [Ka00] [Re01].

4.2. Thin film characterization

4.2.1. Hardness measurement

At least three categories of practically measured type of hardness can be distinguished: scratch hardness (Mohs scale in mineralogy), static indentation hardness (Brinell, Vickers or Knoop indenters), and dynamic hardness. The static indentation measurements are the only ones that can be relatively simply applied to the measurement of superhard materials. During the measurement, the diamond pyramid is pressed into the tested material under a defined load L (kg) and, after unloading, the average value of the two diagonals d (mm) of the remaining plastic deformation is measured under a microscope. The Vickers hardness H is then calculated as

$$H = c \cdot \frac{L}{A_{p}}$$
(4.1)

where A_p is the projected area of indentation. The constant value c depends on the type of the indenter [Ta51].

Modern indentometers for the measurement of the hardness of thin films use a computer controlled stepwise increase of the load up to a chosen maximum L_{max} followed by stepwise unloading [Do86] [Be93] [Ph98]. Instead of measuring the diagonal of the plastic deformation, the indentation depth h is measured electronically and the indentation curve is evaluated.

The value of elastic modulus can be also obtained from indentation technique, but this value can be affected by a high pressure induced under the indenter during the measurement [Ve01] [Ve02a] [Ve03c] [Ve02c]. The researchers verified that, for conventional relatively soft materials, the indentation technique yields correct values of Young's modulus [Do86] [Be93]. However, it was shown recently that the values of the elastic modulus obtained from the unloading part of the indentation curve measured on superhard materials that display a large elastic recovery are close to the zero-pressure shear modulus of the coatings as measured by means of vibrating reed, surface Brillouin scattering and high-pressure X-Ray diffraction [Ve03a].

The hardness of the films in this work was measured by means of the automated load-depth sensing indentation technique using a computer controlled indentometer *Fischerscope H100* equipped with a Vickers diamond indenter. The
Vickers indenter is a regular pyramid with an angle of 136° between the opposite faces. Figure 4.4. shows the loading and unloading curve as recorded by the sensing indentation technique. The area between the loading curve and the axis of the indentation depth is the total energy of the deformation, the area between the unloading curve and that axis is the energy of the elastic deformation and the area between the loading and unloading curve is the dissipated energy of the plastic deformation which is a measure of the hardness. The smaller the ratio of the dissipated energy of plastic deformation to that of the total energy of deformation the higher the elastic recovery.



Fig. 4.4: The loading and unloading curve as a result of the indentation technique measurement. The elastic modulus can be calculated form the segment h_{max} - h'_r . The indentation depth h'_r is crucial for the determination of the plastic hardness. W_e is the elastic and W_p the plastic part of the deformation energy.

At the beginning of the measurement the diamond tip approaches the surface of a sample. Then the tip is step-wise pushed into a tested material by increasing the applied load up to a chosen maximum and the indentation depth is measured at each step. The applied load is increased by square law to provide more or less constant increase of the indentation depth through the whole loading. Increase of indentation depth is also constant for each step and shows a typical delay. Therefore it is necessary to increase the load after the depth reaches some equilibrium stage. A maximum delay of 1 s is sufficient for the majority of materials. At the maximum load the creep can be measured as a change of the indentation depth with time. Finally the load decreases again in the same way as upon loading and the indentation depth is recorded. The loading and unloading time of typically 60 s and the creep time of 10 s were chosen in this work.

The hardness and elastic modulus are determined from the measured indentation curve by extrapolating the unloading curve from the maximum applied load L_{max} to load zero. The linear part of unloading curve corresponds to pure elastic recovery of material at constant contact area corresponding to Hook's law [Ve99a] [Ph98] [Ph93] [Be93] [Do86]. There are different ways of the extrapolation giving different values of hardness and elastic modulus [He03]. Doerner and Nix method [Do86] uses a linear extrapolation of the unloading curve between 70 and 100 % of L_{max} , the *Fischerscope* equipment [Be93] uses 80 to 100 % of L_{max} and Oliver and Pharr [Ph93] developed a power-law fitting of the unloading curve to determine the "corrected indentation depth" h_{cor} . The plastic hardness H_{pl} obtained from the *Fischerscope H100* corresponds to classical Vickers hardness H_V calculated according to Eq. (4.1).

The area A can be calculated from the corrected indentation depth h'_r and the geometry of the Vickers indenter ($\alpha = 136^{\circ}$) according to Eq. (4.2.), from which Eq. (4.3.) between the plastic hardness H_{pl} and the indentation corrected depth h'_r follows.

$$A = 4 \cdot \frac{\sin\left(\frac{\alpha}{2}\right)}{\cos^2\left(\frac{\alpha}{2}\right)} \cdot h'_r = 26.43 \cdot h'_r^2$$
(4.2)

$$H_{pl} = \frac{L_{max}}{26.43 \cdot h'_{r}^{2}}$$
(4.3)

Here, L_{max} is the maximal applied load.

The universal hardness H_u is calculated using Eq. (4.3.) if the corrected indentation depth h'_r is replaced by the maximal indentation depth h_{max} . The universal hardness describes the combined effect of the plastic and elastic deformation, the latter including also the elastic deformation of the indenter.

The "effective modulus" measured by the load-depth sensing indentation technique is calculated from the linear part of the unloading curve according to Eq. (4.4) [Sn65] and corrected for the elastic deformation of the diamond indenter [Ph98] [Ph93] [Be93] [Do86].

$$\frac{E}{(1-v^{2})} = \frac{L_{max}}{2(h_{max} - h'_{r})} \sqrt{\frac{\pi}{A}}$$
(4.4)

Here, E is the "effective elastic modulus", v is the Poisson's ratio, A is the contact area, L_{max} is the maximal load, h_{max} is the maximal indentation depth and h'_r is the corrected indentation depth (linear extrapolation of the unloading curve). More recent work has, however, shown that the original formula used for the evaluation of the elastic modulus is too simplified in real indentation measurements. Thus, the "effective elastic modulus" measured by the indentation is a complex function of the compression, shear and tensile components of the elastic tensor and the corresponding moduli [Ve02c].

The toughness of thin films is usually determined from the dependence of the length of radial cracks extending from the "diagonals" of the indentation on the applied load. However, no diagonal cracks were found for a series of indentations into a large number of the nanocomposite coatings with applied load increasing up to 1000 mN. This may be due either to a high fracture toughness or to a high threshold for the initiation of the crack by the Vickers indenter [Ne00b] [Ph98].

Because of the deviation of the indenter from the ideal form, different corrections have to be done. Most important is the correction for a tip blunting. This correction is done by calibration of the indentometer on materials with constant and depth independent hardness and elastic modulus, such as silicon and Sapphire. The correction factors are obtained by fitting of universal hardness as function of indentation depth for constant H_u value for indentation depth higher than normally 0.1 μ m.

Before each measurement the hardness of Si(111) ($H_{pl} = 10.3$ GPa) and Sapphire ($H_{pl} = 21$ GPa) was checked to assure the correct hardness of the coatings. The measurement was then done in a load range between 5 and 1000 mN (typically 30 - 200 mN) and only the load independent values of the hardness which do not show any creep were consider as reliable. At each load several indentation measurements at different locations on the film were made and the average value for that load was taken. The hardness from indentometer was also periodically compared with the classical Vickers hardness calculated from the remaining plastic deformation obtained by scanning electron microscope whose magnification was calibrated by means of a photomask provided to us by company Infineon.

The measurement of elastic properties of superhard nanocomposite coatings by indentation techniques can be subject to a number of possible errors such as:

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1) indentation size effect (the increase of the hardness with decreasing applied maximum load). The reason can be indenter tip blunting, non-representatively small volume of the material to be tested, a too small stress under the indenter which does not reach the yield stress of that material, surface layers with different mechanical properties, surface roughness, work hardening of surface due to cutting and polishing of the sample, finite separation of the deformation bands and others [Ve02a] [Ve03c] [Bu01] [Sa86] [Ve99a],

2) the composite effect of the system of superhard coating on a softer substrate. In order to exclude the effects of the deformation of the substrate, the indentation depth should not exceed 5 % of the film thickness [He03] [Bu01] [Ve99a],

3) high compressive or tensile stress in the coatings [Sw01] [Ts96],

4) severe elastic deformation of the diamond indenter which falsifies the measured indentation depth obtained from the extrapolation of the unloading curve [Ve02a] [Ve03c] [He03],

5) time delayed anelastic response [Ve02a],

6) the effect of pile-up or sink-in on the projected area [Li99] [Ts96].

Even if one takes into account all these problems one should keep in mind that the Vickers technique, which was originally developed for conventional alloys and materials with hardnesses \leq 20 GPa, is up to its limit when measuring materials whose hardness approaches that of diamond.

The Hertzian analysis of the non-linear elastic response upon unloading provides analytical solutions which can be used to verify if the hardness values measured on the super- and ultrahard coatings are self-consistent and to estimate the tensile strength of the super- and ultrahard nanocomposite coatings [Ar01] [Ve01] [Ve02c]. The tensile strength of the superhard nanocomposites reaches an appreciable fraction of the ideal cohesive strength that is predicted on the basis of the Universal Binding Energy Relation [Ro84] [Ve02a] [Ve03c].

4.2.2. Stress measurement

Residual stress can be measured by a X-ray diffraction or a mechanical bending plate method. Usually a good agreement is found between the results obtained from these two methods [Vi95] [Va00]. The XRD method is based on a measurement of the change in the lattice plane distance of a certain hkl plane set for different orientations of the specimen. With the bending plate method the change in

curvature of a substrate is measured which is a result of the present residual stress in the deposited coating.

The residual stress in a thin coating consists of extrinsic and intrinsic components $\sigma_{res} = \sigma_{ext} + \sigma_{int}$. The extrinsic (thermal stress) component arises as a result of differences between the thermal expansion coefficients $\Delta \alpha$ of the coating and the substrate, $\sigma_{ext} = E_s \cdot \Delta \alpha \cdot \Delta T$, where E_s is the Young's modulus of the substrate, and ΔT the difference between the deposition temperature and room temperature.

In deflection technique a thin coating on a much thicker substrate, where the lateral dimensions of the coating and substrate are much greater than their total thicknesses, is considered [Vi95]. After thin film deposition a shear stresses at the coating/substrate interface are created. These forces cause the substrate to bend elastically, and this flexure can be measured.

Stoney [St09] has derived a mathematical expression between the radius of curvature and the stress, σ_{res} :

$$\sigma_{\rm res} = \frac{E_{\rm s}}{1 - v_{\rm s}} \cdot \frac{t_{\rm s}^2}{6t_{\rm f}} \cdot \left(\frac{1}{r_{\rm a}} - \frac{1}{r_{\rm b}}\right)$$
(4.5)

where $E_s/(1-v_S)$ is the biaxial modulus of the substrate, t_S and t_f are the substrate and coating thicknesses, r_a is the radius of curvature after deposition and r_b is the radius of curvature for uncoated substrate.

In this work a stainless steel strips (30 x 3 x 0.3 mm) were coated by approximately 6 μ m thick coatings, the radius of the curvature was optically measured, and the stress was calculated according to Stoney equation (Eq. (4.5)) [Ne00a] [Pr03].

The sin² ψ method was also used in this work to determine the biaxial stress in the coatings [No87]. The average values obtained from the dependence of the lattice parameter of TiN (331), (420) and (422) reflections on sin² ψ were taken. The details of this method and the calculation algorithm are in the thesis of Prochazka [Pr03].

4.2.3. X-ray Diffraction (XRD)

The X-ray diffraction is an important non-destructive material testing method which can yield the information about a crystallite structure of the material including a grain size, preferential orientation and lattice dilatation. The XRD analysis is based on the constructive interference of X-ray of a wave length λ on crystal lattice planes

(hkl) with spacing d_{hkl}, which is described by the Bragg's law, Eq. (4.6). It gives the permitted angles of reflection, θ , in terms of λ and the spacing of the reflecting planes d [KI74].

$$2d_{hkl} \cdot \sin \theta = n \cdot \lambda \tag{4.6}$$

Here n is the diffraction order. The intensity of the diffracted X-ray is given by the structure factor proportional to the electron density.

The width of the diffraction peaks is an integral convolution mainly of the instrumental broadening, broadening due to finite crystallite size and random strain of the lattice. The instrumental broadening can be minimized by the appropriate adjustment of the instrument and is determined by the measurement of the reference sample.

The dependence of the crystallite size on the broadening of the peak is described by Scherrer formula (Eq. (4.7))

$$\beta_{k} = \frac{k \cdot \lambda}{d_{hkl} \cdot \cos \theta}$$
(4.7)

Here β_k is the broadening of the peak due to small crystallite size, the constant k depends on the shape of the crystals (for the cubic ones k = 0.94), λ is a wave length of used X-ray, d_{hkl} is the crystallite size in the direction hkl and θ is the Bragg's angle. For the calculation of the peak width the Full Width at Half Maximum (FWHM) is often used. However, this is correct only for Gauss shape of the peak and uniform crystallite sizes which influences the shape of the Bragg diffraction peaks. In such a case the Scherrer formula (Eq. (4.7)) yields incorrect results. Stokes and Wilson have shown that Eq. (4.7) can give correct value of the average crystallite size if the integral width of the peak instead of FWHM is used [KI74].

The lattice strain ε is the ratio of the deformed and relaxed crystal lattice planes distance, $\varepsilon = \Delta \delta / \delta_0$. Random strain arises due to microstresses e.g. as a result of a thermal mismatch or incoherency of the interfaces between different phases in the sample. When integrated over the whole volume the random strains cancel out. The random distortion of the lattice spacing due to these strains results in shifts of the corresponding Bragg reflection peaks which, integrated over the sample, yields a broadening β_e due to the random strain ε given by Eq. (4.8) [KI74]

$$\beta_{\rm e} = 4\varepsilon \cdot \tan \theta \tag{4.8}$$

Because the measured peak shape is the convolution of the Gauss and Cauchy function, the peaks were fitted by Pearson VII function [Ne00a]. In order to distinguish between the broadening contribution of the diffraction peaks due to the finite crystallite size and to random strain the Fourier transform method of Warren and Averbach was used [KI74] [Ne00a]. The computer software WAXARD for the Warren-Averbach analysis developed by Nesladek [Ne00a] was used in this work.

X-ray diffractometer *Siemens D5000* with Cu-K_{$\alpha 1$} (λ = 1.54056 Å) radiation was used for XRD measurements. The X-rays from Cu-tube passed a nickel-foil-filter behind the divergent lens before reaching the sample. The diffracted X-rays passed through the 2 mm wide scattered-ray-lens, 0.6 mm wide detector lens, the secondary monochromator and finally were recorded by a scintillation tube. The Cu-tube was operated at voltage of 40 kV and current of 30 mA. The measuring time was 15 s at each step with step size 0.05° in 20 range between 20 and 100° which gives the optimum signal-to-noise ratio and angle resolution.

All coatings were measured in the Bragg-Brentano parafocusing geometry where the normal to the film surface is in the middle of the angle between the X-ray source and the detector. This geometry allowed us to determine the preferential orientation of the crystallites. The "glancing incidence" geometry, where the angle between the X-ray beam and the surface of the film is kept constant and small while the X-ray detector is scanned along 20, was used whenever it was necessary to avoid the strong reflections from the substrate. The diffraction pattern were fitted by using profile fitting computer software *Siemens Diffrac AT* version 3.0 in order to obtain the exact peak position, integral width, FWHM and the exponent factor of the Pearson VII function.

4.2.4. Scanning electron microscopy (SEM) and Energy dispersive analysis of X-ray (EDX)

For the determination of the film morphology and optical evaluation of the hardness Scanning Electron Microscope *JEOL 5900L* was used. Elemental analysis of the coatings was done by means of *JEOL JSM-35C* analyser which was attached to that SEM.

The primary electrons emitted from the thermionic tungsten cathode and accelerated by high voltage (typically 25 kV) to the sample surface produce secondary electrons and X-rays fluorescence in the sample which are detected by appropriate detectors. The secondary electrons are used for the SEM image. The

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resolution depends on the depth from which the secondary electrons are emitted and on the diameter of the primary electron beam. The characteristic X-ray fluorescence is used for the EDX analysis according to Eq. (4.9)

$$\sqrt{v} = a(Z - b) \tag{4.9}$$

where v is the wave number, Z is the atomic number, a and b are constants. The intensity of the X-rays for any element in the films depends on the kinetic energy of the primary electrons, incident angle, atomic number of the element Z, its concentration and on the "matrix effect" which depends on the average Z of the sample. In order to obtain correct analytical results, all these effects have to be accounted for together with the subtraction of the bremsstrahlung. This is done by a routine computer procedure which is available at the instrument.

Because of the low sensitivity of EDX to low-Z elements and of the cut-off due to the beryllium window at the energy corresponding to the B line, the elemental analysis was compared and calibrated using the elastic recoil detection spectroscopy [Ve00b] [Be98].

4.2.5. Elastic recoil detection (ERD)

In the ERD measurements, heavy ions of a mass M_p , such as Ar, Ni, Kr, Xe or CI, with high kinetic energy in the range of MeV are used as projectiles to collide with the lighter target atoms in the sample knocking them out of the sample. If an atom of a mass M_t in the sample at a depth of x is knocked out by the primary projectile ion of energy ($E_0 - \Delta E_p(x)$), this atom will gain an energy E_r given by Eq. (4.10)

$$E_{r} = k(E_{0} - \Delta E_{p}(\mathbf{x}))$$
(4.10)

where $k = 4 \cdot (M_p M_t / (M_p + M_t)^2) \cdot \cos^2 \theta$ and θ is the scattering angle between the primary ion beam and the direction where the atom is knocked-off from the sample. E_0 is the energy of the primary beam and $\Delta E_p(x)$ are the energy losses of the primary ion due to ionization of the atoms of the sample when it penetrates into the depth x. In order to obtain a high sensitivity $M_p > M_t$ is used. The atom knocked-off from the sample in the depth x also looses a part of its energy of ΔE_r during escaping from the sample, so that it reaches the detector with the energy of $E_r(x)$, Eq. (4.11)

$$E_{r}(x) = k(E_{0} - \Delta E_{p}(x)) - \Delta E_{r}(x)$$
(4.11)

During the knock-off and escape out of the sample the atoms are ionized which enables one to focus them on a detector. The ERD detectors measure the energy, mass and charge of the atom from the target which reaches it. In such a way it is possible to obtain the composition of the sample as a function of its depth.

ERD does not need any calibration because the values of the Rutherford cross-sections are available [Do95] [Do96].

4.2.6. X-ray photoelectron spectroscopy (XPS)

The XPS is based on the external photoelectric effect. When an atom absorbs a photon with sufficient energy hv, it is ionized and escaping electron has a kinetic energy E_{kin} given by Eq. (4.12)

$$E_{kin} = h\nu - (E_B + \delta E)$$
(4.12)

Here, E_B is the binding energy of electron in the atom and δE is a discrete energy loss, such as the chemical shift. The binding energy E_B is characteristic of the given atom and orbital and the chemical shift δE depends on the chemical environment of that atom. Thus, XPS can be used for quantitative analysis of a solid and for determination of the binding states, i.e. the phase composition.

When an atom A is bonded to an atom B with a different electronegativity the total electron charge on atom A changes by δq_A and the binding energy changes by $\delta E = k \cdot \delta q_A$. In a solid, the charge on the neighboring atoms which are at a distance r_{AB} also influences the chemical shift thus giving Eq. (4.13)

$$\delta E = \mathbf{k} \cdot \delta \mathbf{q}_{\mathrm{A}} + \sum_{\mathrm{A} \neq \mathrm{B}} \frac{\delta \mathbf{q}_{\mathrm{B}}}{\mathbf{r}_{\mathrm{A}\mathrm{B}}}$$
(4.13)

where the sum is over all neighbors B.

The Leybold LHS 10 ESCA surface analytic system with a hemispherical energy analyzer was used with the AIK_{α} source and recorded in ΔE = const. mode that provided a constant sensitivity which was needed for quantitative analysis. Repetitive scans of selected spectral regions and signal averaging were used in order to obtain a sufficient signal-to-noise ratio. Before each measurement the film surface was sputtered by Ar ions to remove the surface contamination. The background subtraction was done using the Shirley non-linear background subtraction method. The ERD results were used to calibrate the XPS spectra.

5. Result and discussion

5.1. TiN films deposited by plasma CVD and optimization of the deposition parameters

The kinetics and reaction mechanisms under conditions of plasma CVD are complex. Often, intermediates are formed that play a crucial role in the mechanism of the overall reaction leading to the deposition of the film. In spite of the effort that was conducted at our institute in order to obtain insight into the reaction mechanism of the TiN deposition from $TiCl_4 + H_2 + N_2$, kinetic and mechanistic data, which would enable us to optimize the deposition conditions by means of computer-aided numerical modeling, are not available. Therefore the optimum conditions, such as high and uniform deposition rate over the whole substrate area, low concentration of chlorine impurity, high hardness and adhesion had to be found experimentally.

Following the work of Nesladek [Ne00a], the given deposition parameters (flow rate (H₂) = 150 sccm, flow rate (N₂) = 25 sccm, flow rate (TiCl₄) = 1.5 - 2.3 sccm, HF power P_{hf} = 150 W, temperature T = 650°C, pressure p = 2 mbar and 80 mm distance between the substrate holder and gas inlet) were taken as starting parameters for the optimization of the TiN film depositions. An appropriate combination of the parameters giving a sufficiently high deposition rate (> 3 Å/s), stoichiometric composition of the film, good adhesion of the film to the substrate, low chlorine content and hardness of the coating comparable with the bulk TiN hardness had to be found. There are some important parameters that could be adjusted for this purpose: the flow rate of each gas and their ratio, the dwell time, the deposition pressure, HF power and temperature.

It was impossible to obtain a deposition of the TiN coating on the substrate using 80 mm distance between the substrate holder and the gas inlet. The deposition of the good quality film was observed only on the reactor wall close to the gas input. When the substrate holder was moved 20 mm under the gas inlet the film on the substrate appeared, but the deposition rate was not sufficient. The significant increase of the deposition rate was observed with decreasing total flow rate of H₂ and N₂ keeping the ratio of H₂:N₂ = 10 (see Fig. 5.1). The deposition rate > 3 Å/s was achieved for the total flow rate smaller than 80 sccm. The decrease of the total flow rate smaller than 80 sccm. The decrease of the total flow rate smaller than gases. Under these conditions, when the partial pressure of nitrogen was still sufficiently high, the stoichiometric TiN film

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should be produced. Because the deposition rate was acceptable at low flow of nitrogen (3 - 5 sccm), no carrier gas was used for TiCl₄ [Rei95].

According to work of Nesladek [Ne00a], the chlorine content in the film must be below 0.5 at.% to have no influence on the coating properties, adhesion and long time stability. In the work of Reiprich [Rei95] the concentration of chlorine is much higher (around 2 at.%) and it agrees with the later mentioned results in this work. Usually low chlorine content in the coatings is required. However, the extremely low friction coefficients against ball-bearing steel of 0.17 - 0.22 have been obtained for TiN coatings with chlorine content in the range of 3.2 - 6.3 at.% [St03] [Mi03a], but the thermal stability of the low-friction effect was essentially limited up to 70°C [Bad03]. It was assumed that an interfacial chlorine-containing film of low shear strength was formed between the two friction partners in combination with humidity, where the chlorine within the grain boundaries serves as chlorine reservoir.



Fig. 5.1: The dependence of the TiN deposition rate on the total flow rate of H_2 and N_2 , ($T = 535^{\circ}C$, p = 3 mbar, $P_{hf} = 150$ W, $H_2/N_2 = 10$, flow rate (TiCl₄) = 2.3 sccm).

The dependence of the chlorine content of the film on the total flow rate of H_2 and N_2 is shown in Fig. 5.2. The increase of the chlorine content with decreasing total flow rate of H_2 and N_2 is due to the decrease of the partial pressure of hydrogen than removes CI by the formation of HCI which avoids its incorporation into the growing

film. The chlorine incorporated in the TiN films is mainly present at the grain boundaries as titanium subchlorides [Bu92]. Crystalline TiNCI or NH_4CI phases were observed in the coatings with chlorine content higher than 8.5 -10 at.% [He93] [Ar88]. This was never the case in the present work.



Fig. 5.2: The dependence of the chlorine content in the TiN films on the total flow rate of H_2 and N_2 , ($T = 535^{\circ}C$, p = 3 mbar, $P_{hf} = 150$ W, $H_2/N_2 = 10$, flow rate (TiCl₄) = 2.3 sccm).

One can see in Fig. 5.2 that at a high deposition rate of \geq 6 Å/s (see Fig. 5.1) chlorine content in the TiN film is low and has no influence on its properties, such as the hardness and adhesion. This is shown in Fig. 5.3, where the dependence of the hardness and the crystallite size on the total gas flow is plotted. The hardness and the crystallite size remain constant over the whole range. The hardness in the range of 25 - 27 GPa agrees very well with data reported for TiN coatings deposited by plasma CVD [Ar88] [La89] [La90] [May86] [Pa96] [Sh97]. The indentation elastic modulus of TiN coatings was around 250 GPa in agreement with the work of Reiprich [Rei95]. TiN films in this work show strong TiN (200) preferential orientation except of very thick coatings where the preferential orientation is (111). This effect has been interpreted in terms of a competition between surface energy, strain energy, and stopping energy [Ma99].



Fig. 5.3: The dependence of the hardness and the crystallite size on the total flow rate of H_2 and N_2 , ($T = 535^{\circ}C$, p = 3 mbar, $P_{hf} = 150$ W, $H_2/N_2 = 10$, flow rate (TiCl₄) = 2.3 sccm).

As the next step of the optimization of the deposition parameters we studied the influence of the total pressure, flow rate of TiCl₄ and HF power on the deposition rate and the coating properties. These studies were done at a constant total flow rate of $H_2 = 55$ sccm, $N_2 = 5$ sccm and the H_2/N_2 ratio of 10.

The change of the total pressure from 3 to 8 mbar (T = 502° C, P_{hf} = 100 W, flow rate (TiCl₄) = 2.5 sccm were kept constant) had no influence on the deposition rate, hardness, crystallite size and the chlorine content in the coatings. However, the most homogeneous coatings were obtained at the lowest pressure of 3 mbar.

With increasing TiCl₄ flow rate from 1.0 to 2.5 sccm and other parameters constant (T = 499°C, p = 3 mbar, P_{hf} = 100 W) only a small increase of the deposition rate was found (from 3.7 Å/s to 5.7 Å/s). No change in the hardness, crystallite size and chlorine content was detected. The increase of the deposition rate with increasing TiCl₄ flow rate can be explained by the increasing amount of TiCl₄ which is available for the decomposition in the plasma.

The dependences of the deposition rate and chlorine content on the HF power are shown in Fig. 5.4 and 5.5., respectively. The reaction rate is proportional to the

electron density and thereby to the power density. With increasing power the reaction rate increases which leads to the increase of the deposition rate (see Fig. 5.4). Reiprich [Rei95] observed a maximum of the deposition rate at a power of 100 W. A further increase of the power led to a decrease of the deposition rate. This decrease was explained by the deposition of the TiN film on the reactor wall, which led to the depletion of the reactive species in the gas phase.



Fig. 5.4: Dependence of the TiN deposition rate on the power, $(T = 550^{\circ}C, p = 3 \text{ mbar, flow rate } (H_2) = 50 \text{ sccm, flow rate } (N_2) = 5 \text{ sccm, flow rate } (TiCl_4) = 1.7 \text{ sccm}$.

The chlorine content in the coating increases with decreasing power (see Fig. 5.5). At the low power the concentration of the electrons is low, resulting in a low fragmentation of the TiCl₄ molecules. When the thermal energy and the ion bombardment are also low for a complete cleavage of the chlorine from the growing film, the enhanced incorporation of the TiCl_x fragments into the growing film occurs. The decreasing temperature and decreasing power density can also result in the deterioration of the film crystallinity [Ja89b] [Hi86a] [Sa88], because chlorine atoms induce lattice defects in TiN [Ja89b].

Increasing power has no influence on the hardness of the coatings. The hardness remains around 22 - 25 GPa even at the smallest power of 50 W, when the

chlorine content in the coatings reaches 2.3 at.%. The crystallite size around 30 - 35 nm is larger then in the pervious series (see Fig. 5.3).

A SEM micrograph of a typical TiN coating is shown in Fig. 5.6. According to the classification of Thornton [Th77] [Th86] the TiN coating has a fibrous structure typical of zone T.



Fig. 5.5: Dependence of the chlorine content in the TiN films on the hf power, (T= 550°C, p = 3 mbar, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm).



Fig. 5.6: SEM micrograph of the TiN coating, ($T = 569^{\circ}C$, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.68 sccm).

Based on these results the optimum deposition conditions shown in Table 5.1 were chosen for the deposition of Ti-B-N coatings.

Table 5.1: The deposition parameters used for the deposition of nc-TiN/a-BN/a-TiB₂ coatings by means of plasma CVD.

13.56 MHz
50 sccm
5 sccm
1.7 - 1.9 sccm
0 - 1.8 sccm
3 mbar
100 - 110 W
550 - 600°C
5 - 10 µm
0.65 - 1.0 nm/s
stainless steel, silicon (111), α-Fe, molybdenum

The goal of the next section was to prepare films with different boron content in order to study the effect of the BN and TiB_2 phases on the properties of the deposited film. Nesladek [Ne00a] has found, that the use of B_2H_6 as a source of boron led to blockage of the inlet tubings due to its too high reactivity. Thus the BCl₃ was used in this work.

5.2. Ti-B-N films deposited by plasma CVD

5.2.1. Deposition rate

The deposition rate of nc-TiN/a-BN/a-TiB₂ coatings shown in Fig. 5.7 remains constant with BCI_3 flow rate increasing from 0 to 1.7 sccm. The content of boron in the coatings at highest flow rate of BCI_3 used in this work is around 15 at.% (see Fig. 5.11a).





Fig. 5.7: Dependence of the deposition rate on the BCl₃/TiCl₄-flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (see Fig. 4.1, different substrates as indicated in the insert), ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

5.2.2. Composition of the coatings

In the deposition series with one point connection (Fig. 5.8a) the chlorine content in the coatings increases above the $BCI_3/TiCI_4$ -flow rate ratio of 0.6 to 2.5 - 4.5 at.% and deteriorates their properties. In the series with two points connection the chlorine content is less than 1.5 at.% even at the highest total flow rates of chlorides. A similar, low content of chlorine is found also for the "full contact" holder and stainless steel substrates (Fig. 5.8b). In coatings deposited on silicon substrates and a $BCI_3/TiCI_4$ -flow ratio of more than 0.35 the chlorine content strongly increases due probably to a bad electric contact and higher h.f. impedance (i.e. lower ion bombardment) of those substrates.



Fig. 5.8: Dependence of the chlorine content in the coatings on the BCl₃/TiCl₄-flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (different substrates), ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

The color of the TiN coatings or nc-TiN/a-BN/a-TiB₂ coatings with low boron content is golden yellow indicating a composition close to the stoichiometric δ -TiN. With increasing boron content the color changes from golden yellow film to silver like film, that is typical for substoichiometric TiN_{1-x}. A too high chlorine content causes the appearance of a black powder-like deposit.

The elemental analysis of all coatings was done by means of EDX and for several selected ones also by means of the much time consuming ERD. Figure 5.9 shows the Ti/N ratio determined by EDX vs. the ratio of the flow rate of BCl₃ to TiCl₄ and Fig. 5.10 shows the comparison of the EDX and ERD analyses. Obviously, EDX overestimates the Ti/N ratio because of its low sensitivity for light elements (here nitrogen) and impossibility to measure and include boron. Nevertheless, from the comparison in Fig. 5.10 and the EDX-data in Fig. 5.9 one can conclude that the composition of the coatings with a low boron content (deposited at BCl₃/TiCl₄-ratio of ≤ 0.4) is close to the stoichiometric δ -TiN (nitrogen substoichiometry of about 4 to 8 at.%).





Fig. 5.9: Dependence of the Ti/N ratio obtained by the EDX analysis on the $BCl_3/TiCl_4$ -flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (different substrates), ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCl_4$) = 1.7 sccm, flow rate (BCl_3) = 0 - 1.8 sccm).

The chlorine content obtained from ERD and EDX analyses agrees reasonably well. The content of oxygen, hydrogen and carbon impurities is relatively high in comparison with nc-TiN/a-Si₃N₄ [Ve95a] [Ve95b] [Chr98] [Rei95] (see Table 5.2). The preliminary results of Prochazka and Veprek [Pro03] suggest that oxygen impurity of the order of 1 at.% noticeably deteriorates the hardness of the coatings.

Table 5.2: Comparison of the average value of impurities amount in the nc-TiN/ a-BN/a-TiB₂ and nc-TiN/a-Si₃N₄ coatings [Ni00] [Ve00b].

system	H ₂ [at.%]	O ₂ [at.%]	C [at.%]
nc-TiN/a-BN/a-TiB ₂	0.52	0.85	0.05
nc-TiN/a-Si₃N₄	0.1	0.07	-



Fig. 5.10: Comparison of the Ti/N ratio obtained by means of EDX and ERD analyses, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCI_4$) = 1.7 sccm, flow rate (BCI_3) = 0.05 - 1.6 sccm).

The boron content in all coatings was calculated from the linear fit between the boron content obtained by ERD analysis and the flow rate ratio of chlorides (Fig. 5.11a). Because only 2 coatings with [B] > 8 at.% were measured by ERD, the boron scale in next figures (for example in Fig. 5.12) is only an approximation based on the linear fit. Figure 5.11b shows the titanium and nitrogen content obtained by means of ERD as function of the BCl₃/TiCl₄-flow ratio.



Fig. 5.11: Composition of the nc-TiN/a-BN/a-TiB₂ coatings measured by ERD vs. the $BCI_3/TiCI_4$ -flow rate ratio: **a**) boron content and linear fit, **b**) titanium and nitrogen content, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCI_4$) = 1.7 sccm, flow rate (BCI_3) = 0.05 - 1.6 sccm).

5.2.3. Hardness and elastic modulus

Figure 5.12 shows that with increasing ratio of the flow rate of BCI_3 to $TiCI_4$ the hardness of the coatings increases up to 50 GPa and, at even higher flow rate ratio, it slightly decreases still being in the range of about 40 GPa. This is different from the results of Nesladek [Ne00a], where the nc-TiN/BN coatings showed the hardness maximum at ca. 6 - 9 at.% of boron in the film. In present work, the coatings can be superhard in very broad range of the boron content (see the boron scale on the top of the Fig. 5.12). This behavior is explained below by the percolation threshold.

The vertical line in Fig. 5.12a separates the region where the fraction of TiB_2 phase measured by XPS is small and can be neglected as compared to BN phase (left hand site) and that where the content of this phase increases and becomes comparable with BN phase (right hand site).

The relatively large scattering of hardness values in Fig. 5.12a for one point connection holder is caused by the inhomogeneity of these films due to non-uniform distribution of the current density on the substrate. The coatings from series with two points connection or full contact holder are homogeneous.





Fig. 5.12: Dependence of the hardness on the BCl₃/TiCl₄-flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (different substrates as indicated in the insert), ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} =$ 100 - 110 W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

The lower hardness of some coatings in Fig. 5.12b as compared to Fig. 5.12a is probably due to the deposition on a variety of different substrates with different thermal expansion coefficients. The values of the thermal expansion coefficient for different type of substrates and films are listed in Table 5.3. Due to the low thermal expansion coefficient of silicon and molybdenum as compared with the TiN, these coatings are under tensile stress and crack patterns are formed [Mi00] [Mi01] [Ne00a]. Figure 5.13 shows a tensile stress crack pattern of nc-TiN/a-BN/a-TiB₂ coating deposited on molybdenum substrate. This problem can be solved by predeposition of ca. 4 μ m thick layer of TiN on silicon or molybdenum substrate before the deposition of the nc-TiN/a-BN/a-TiB₂ film [Ve98a]. The thermal stress of TiN film on high speed steel or stainless steel substrate does not exceed 0.5 GPa [Oe95a] [Ne00a]. The compressive stress in the nc-TiN/a-BN/a-TiB₂ coatings deposited on stainless steel strips is below 2 GPa and similar stresses were obtained

from $\sin^2 \Psi$ method of coatings deposited on stainless steel substrates (see Fig. 5.14). The biaxial stress calculated according to $\sin^2 \Psi$ method was obtained from the dependence of the lattice parameter of (422), (420) and (331) TiN reflections on the $\sin^2 \Psi$. This small compressive stress has no influence on the hardness of the coatings, which remains stable during annealing to very high temperatures (see section 5.5.1).

Table 5.3: Thermal expansion coefficient of substrate and coating materials used in the present work (from [Mu93]).

Material	Thermal expansion coefficient [10 ⁻⁶ K ⁻¹]
WC + 5.5 % Co	5.5
WC + 12.2 % Co	6.1
low alloy steel	15
high speed steel	12
Silicon	4 (3.25)
Molybdenum	5.5
TiN	9.4 (9.35)
TiB ₂	7.8
ZrN	7.2
CrN	2.3



Fig. 5.13: Typical example of the tensile crack pattern in nc-TiN/a-BN/a-TiB₂ coating deposited on molybdenum substrate, the tensile stress in the coating calculated by means of the $\sin^2 \Psi$ method is 2.4 GPa, (T = 596°C, p = 3 mbar, P_{hf} = 110 W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.92 sccm, flow rate (BCl₃) = 0.65 sccm).



Fig. 5.14: Compressive stress of TiN and nc-TiN/a-BN/a-TiB₂ coatings deposited on stainless steel substrates calculated from the bending of the steel strip and from the $\sin^2 \psi$ method, ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.4 sccm).

The chlorine content in the films has significant effect on the hardness of the coatings. Figure 5.15 shows the dependence of the hardness on the chlorine content. From this figure it is clear, that the chlorine content higher than ca. 2 at.% causes a decrease of the hardness. In addition, also the adhesion of the coatings deteriorates. The low hardness of some coatings (especially on silicon substrate) at higher BCl₃/TiCl₄-flow rate ratio in Fig. 5.12 is caused by a too high chlorine content (see Fig. 5.8).



Fig. 5.15: Dependence of the hardness on the chlorine content for coatings with flow rate ratio $BCl_3/TiCl_4 > 0.1$, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCl_4$) = 1.7 sccm, flow rate (BCl_3) = 0.17 - 1.8 sccm).

The hardness of the coatings measured by means of load-depth sensing indentation technique was verified by the hardness calculation from the size of the remaining plastic deformations obtained from calibrated SEM. The comparison of hardnesses in Fig. 5.16 shows the correctness of the hardness measurement. The indentation depth should not exceed 10 % (or even 5 % [He03]) of the film thickness in order to avoid the influence of the soft substrate. Whenever the indentation depth exceeds 10 % the Fischerscope yields lower values of hardness than SEM because, during the indentation, it is sensing also the deformation of the substrate (see Fig. 5.16). An example of typical SEM micrograph of the remaining plastic deformation in nc-TiN/a-BN/a-TiB₂ coating is shown in Fig. 5.17. An example of the calibration control of SEM magnification is shown in Fig. 5.18. A photolithographic mask with an exact spacing of metallic lines was used for the calibration of the SEM.



Fig. 5.16: Comparison of the hardness from load-depth sensing indentation technique and from the SEM micrographs of the remaining plastic deformation, $h_{corr.}$ is the corrected indentation depth, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCl_4$) = 1.7 sccm, flow rate (BCl_3) = 0.25 - 1.0 sccm).



Fig. 5.17: Example of a SEM micrograph showing the remaining plastic deformation of nc-TiN/a-BN/a-TiB₂ coating. Load = 150 mN, H_{SEM} = 40.8 GPa, H_{Fisch} = 41.1 GPa, $(T = 588^{\circ}C, p = 3 \text{ mbar}, P_{hf} = 110 \text{ W}$, flow rate $(H_2) = 50 \text{ sccm}$, flow rate $(N_2) = 5 \text{ sccm}$, flow rate $(TiCI_4) = 2.16 \text{ sccm}$, flow rate $(BCI_3) = 1.26 \text{ sccm}$).



Fig. 5.18: Example of the magnification control of SEM. A photolithographic mask with an exact spacing of metallic lines was used for the calibration.

Figure 5.19 shows the relationship between the hardness and elastic modulus measured by means of the load-depth sensing indentation technique. This relationship is usually linear for superhard nanocomposite coatings and represents the behavior of brittle material [Ne00a] [Rei95] [Ni00] [Mo01]. The elastic strain to failure, which is related to the ratio of hardness (H) and Young's modulus (E), has been shown to be a suitable parameter for predicting wear resistance [Le00]. However, the elastic modulus from indentation technique does not correspond to the Young's modulus of the material [Ve03a].

The slope of the unloading curve at the maximum load is used to calculate the composite Young's modulus of the indenter and material being tested from which the modulus of the material is determined [Do86] [Be93]. It is based on Sneddon's analysis of the indentation of a rigid flat punch into an elastic half space [Sn65]. This analysis was shown to apply for any axially symmetric indenter [Ph98] and also when plastic deformation of the indenter material occurs [Che97]. The researchers also carefully verified that, for conventional relatively soft materials, this procedure yields correct values of Young's modulus [Do86] [Be93]. In the case of superhard coatings when the pressure under indenter reaches \geq 40 GPa the pressure enhancement of the moduli has to be taken into account [Ve02c].

The Young's and shear moduli measurements of nc-TiN/a-Si₃N₄ and nc-TiN/a-BN/a-TiB₂ nanocomposite coatings were carried out by means of Surface Brillouin Scattering (SBS) [Ma03]. The moduli were close to 450 GPa and 220 GPa for the Young's and shear modulus, respectively [Ma03]. These results agree with the measurement of the Young's modulus of nc-TiN/a-Si₃N₄ nanocomposite coatings by

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means of Vibrating Reed technique [Li03] and of bulk modulus by means of High Pressure X-Ray Diffraction [Pri03]. This value is also close to the reported experimental [Re98] and calculated one [Ah96].



Fig. 5.19: Relationship between the hardness and the indentation elastic modulus for nc-TiN/a-BN/a-TiB₂ nanocomposite coatings, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

The elastic moduli obtained by the standard evaluation procedure from the unloading curve of the load-depth sensing indentation technique for the coatings measured by SBS were around 270 GPa [Ve03a] [Ve03b]. Thus it can be concluded that the elastic modulus measured by indentation at superhard coatings is close to the value of shear modulus of these materials and not to the Young's modulus as usually assumed [Ve03a] [Ve03b]. The elastic deformation of the diamond indenter is probably one of the reason of this discrepancy. Another possibility is the very complex, non-uniform distribution of the stress under and around the indenter that includes a large fraction of shear. The most important reason of this discrepancy is the change of the contact area with the load upon unloading from L_{max} [Ve03a].

The elastic recovery of nc-TiN/a-BN/a-TiB₂ coatings is in the range of 60 % for pure TiN to 80 % for the nc-TiN/a-BN/a-TiB₂ coatings with the highest hardness of

45 - 50 GPa. An attempt to measure the stress intensity factor of the nc-TiN/a-BN/ a-TiB₂ coatings was not successful because radial cracks were not found even at very high loads of 1000 mN as it was also in the case of superhard and ultrahard nc-TiN/a-Si₃N₄ and nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ coatings [Ve00a]. Because the Vickers indenter has very high threshold for the crack initiation [Ha95] and the nanocomposite coatings have generally high elasticity and toughness the radial cracks are usually not observed [Ve99a].

Hertzian analysis of the non-linear elastic deformation during the contact of a spherical indenter with a flat, semi-infinite body upon unloading provides analytical solutions that can be used in order to check the self-consistency of the measured mechanical properties, verification of true elastic unloading upon indentation and effect of cracking. Because of these reasons the Hertzian analysis of a number of indentations was done. For the comparison of the indentation measurements with Hertzian theory one should ideally use a spherical indenter with a small radius of $\leq 20 \ \mu m$ in order to reach the yield stress in the coating under the indenter at loads of $\leq 150 - 200 \ m$ compatible with several μm thick coatings on a softer substrate. However, because of difficulties of the fabrication of such small spherical indenters with the desirable precision, Vickers indenter was used that, because of its geometry, assures a fairly good approximation to a spherical Brinell one [Ve02a].

It was found [Ar01] [Ve02c] for ultrahard nc-TiN/a-Si₃N₄/a- & nc- TiSi₂ coatings which showed a high elastic recovery of > 90 % that the unloading curve meets very well the Hertzian relationship (Eq. (5.1)) between the indentation depth h(L) and the load L.

$$\ln h(L) = \frac{1}{3} \left[-\ln \left(\frac{E^2 \cdot R}{1.861} \right) \right] + \frac{2}{3} \ln L$$
(5.1)

This analysis was extended to a series of other super- and ultrahard coatings in order to assess to what extent the behavior of the material with a high elastic recovery of 80 to 94 % upon unloading can be consider as true elastic response [Ve02a]. Furthermore, it was shown that crack formation in the coating under a very high load corresponding to a strain of 5 - 20 % can be clearly observed as steps on the loading curve and as a deviation of the unloading curve from the Hertzian log(h)-log(L) behavior as given by Eq. (5.1).



Fig. 5.20: The nc-TiN/a-BN/a-TiB₂ coating indented at 150 mN load: <u>a)</u> the indentation curve (SEM micrograph is in Fig. 5.17), <u>b)</u> the corresponding Hertzian log(h) - log(L) plot, ($T = 588^{\circ}C$, p = 3 mbar, $P_{hf} = 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 2.16 sccm, flow rate (BCl₃) = 1.26 sccm).

Figure 5.20a shows a loading-unloading curve for indentation into a 4.9 μ m thick nc-TiN/a-BN/a-TiB₂ coating (SEM micrograph in Fig. 5.17) and Fig. 5.20b shows the corresponding Hertzian plot (Eq. (5.1)) of the unloading curve. One notices that the unloading curve gives a fairly good log(h) – log(L) dependence according to Eq. (5.1). Whenever no cracks were seen neither on the loading indentation curve nor on the SEM micrographs, the unloading curve obeyed the Hertzian log(h) – log(L) dependence.

If one crack appears at the periphery of the contact upon a larger load and indentation depth, it can be detected as a step on the loading curve while the unloading curve shows only a slight deviation from the log (h) - log (L) behavior. This is illustrated by Fig. 5.21.

The penetration of an indenter into a sample leads to the accumulation of deformation energy in the vicinity of the indenter. The resulting stress distribution in the sample originates from the interaction of the deformation energy with the sample material. Critical local ranges of the stress field are considered as sources for crack formation. Crack formation itself is related to stress relaxation and to a decrease in the elastic energy accumulated in the system, which also holds for coating-substrate systems where coating, substrate and/or interface cracks can occur. Indentation crack patterns of such samples are thus at least qualitative indicator for critical stress field ranges. Cracks both parallel and perpendicular to the surface forming at any location in a coating-substrate system can be detected in the depth sensing indentation experiments, but only cracks perpendicular to the surface can be observed by SEM top-view investigation [Ka98].





Fig. 5.21: The nc-TiN/a-BN/a-TiB₂ coating which has been indented at a relatively large load and indentation depth of about 17 % of the film thickness: <u>a)</u> SEM micrograph, <u>b)</u> the indentation curve, <u>c)</u> the log(h) – log(L) plot, ($T = 575^{\circ}C$, p = 3 mbar, $P_{hf} = 100 \text{ W}$, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.6 sccm, flow rate (BCl₃) = 0.1 sccm).

Bull et al. [Bu89] have shown for hard brittle materials that, when the contact area extends under increasing load, cracking occurs at the outer edges where the tensile stresses of the surrounding elastic field combine with stretching imposed by the sloping faces of indenter. They observed that cracking occurs at intervals, forming visible lines at an average spacing characteristic of the material, the grain size and the surface finish. When cracking occurs, it will partly relieve this local tension and the next advance of the contact area is then supported elastically. After some critical build-up of stress, further cracking will occur.

However, when cracks were formed upon indentation at very high loads the log(h) - log(L) plot of the unloading curve deviated from linear. Figure 5.22 shows such an example for the nc-TiN/a-BN/a-TiB₂ superhard nanocomposite. The cracks can be counted on both the loading curve as well as on the SEM micrograph. If more cracks are formed they can be identified on both the loading curve and in the SEM micrograph and the Hertzian plot is even more non-linear.

These results show that the unloading curves of sufficiently thick and strong coatings which do not show any sign of crack formation display a very good Hertzian log (h)-log (L) linear dependence according to Eq. (5.1).




Fig. 5.22: Example of an indentation into nc-TiN/a-BN/a-TiB₂ coating at a high load of 500 mN with the formation of two cracks upon loading and distorted Hertzian log(h) - log(L) dependence, <u>a)</u> SEM micrograph, <u>b)</u> the indentation curve, <u>c)</u> the log(h) - log(L) plot, ($T = 566^{\circ}C$, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0.25 sccm).

It was shown [Ve02c] [Ar01] that the ideal cohesive strength σ_{IC} of materials such as nitride ceramics can reach a value of about 46 GPa. The tensile strength of the superhard coatings approaches this value [Ve02a] [Ve03c]. Upon the indentation, the maximum tensile stress develops at the periphery of the contact between the indenter and the material under test. Within the framework of the Hertzian theory for a spherical indenter this "radial stress" σ_R is given by equation (5.2).

$$\sigma_{\rm R} = \frac{(1-2\nu)}{2.46\pi} \left(\frac{{\rm L} \cdot {\rm E}^2}{{\rm R}^2}\right)^{1/3}$$
(5.2)

Here v is the Poisson's ratio of the material being tested, L the load and R the radius of the spherical indenter. The geometry of the Vickers indenter with the angle of 136° was chosen in order to match closely the Brinell spherical one [Ta51]. However, for microindentation at indentation depth h of 0.3 - 2 µm used in these measurements the effective tip radius changes with h. At low loads and indentation depths it approaches the radius of the tip of about 0.5 µm [Ar01] [Ve03c] and increases with increasing h. Therefore the experimental data can be used to estimate the radial stress at the maximum load upon indentation only at low loads where the value of the radius calculated from the Hertzian analysis is close to 0.5 µm. The radius R of the indenter is estimated from equation (5.3):

$$h = 1.23 \left(\frac{L^2}{E^2 \cdot R}\right)^{1/3}$$
(5.3)

For the quaternary ultrahard nc-TiN/a-Si $_3N_4/a$ - & nc-TiSi $_2$ coatings the estimated tensile radial stress (Eq. (5.3)) was about 33 GPa closely approaching the ideal cohesive strength [Jh01].

Figure 5.23 shows the radial stress calculated for a number of different coatings from the measured indentation data and FEM calculation [Ve02a]. These results show that the superhard nanocomposites prepared according to the generic design principle are indeed extraordinary strong material.



Fig. 5.23: Radial stress vs. hardness for indentations where the log(h) - log(L) was linear. Calculation of the radial stress of nc-TiN/a-BN/a-TiB₂ coatings was done by author of this work, FEM of the radial stress of nc-TiN/a-Si₃N₄/a- & nc- TiSi₂ coatings was done by He et. al [He03] and calculation of the radial stress of nc-TiN/a-Si₃N₄/a- & nc- TiSi₂ coatings was done by author of this work from indentation curves provided by Männling [Mä03].

5.2.4. Crystallite size

The crystallite size of the nc-TiN/a-BN/a-TiB₂ nanocomposites (Fig. 5.24) of 10 - 40 nm for flow rate ratio ≤ 0.6 , is much larger than that of the nc-TiN/a-Si₃N₄ [Ve95a] [Ve95b] [Chr98] [Rei95] [Pr03], nc-W₂N/a-Si₃N₄ [Ve96b], nc-VN/a-Si₃N₄ [Ve96a] [Ve96e] and nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ [Ve00a] [Ve00b] [Ne00b] [Ni00] [Mo01] ones. It decreases to 3 - 7 nm at higher BCl₃ flow when the a-TiB₂ phase is formed in addition to a-BN (XPS data). This decrease is in agreement with the work of Nesladek [Ne00a]. The crystallite size of nanocomposite coatings formed by spinodal decomposition is determined by the balance between the change in free energy due to decomposition, concentration gradients and the elastic strain energy due to the incoherence of the interface between the segregated phases [Sch95].

The increasing content of chlorine in the coatings with increasing ratio of the flow of BCl₃ to TiCl₄ can also have an influence on the crystallite size. The decrease

of the crystallite size with increasing chlorine content in the coatings was observed for plasma CVD deposited TiN films [St03]. The chlorine atoms were assumed to act as active impurities, which might segregate onto the growing crystal faces if the solubility limit of the TiN phase is exceeded. In this case, a change of the structure forming mechanisms leads to a much smaller grain size because of a higher number of nucleation sites resulting in a more pronounced nanocrystalline structure.





Fig. 5.24: Dependence of the crystallite size on the BCl₃/TiCl₄-flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (different substrates), ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

5.2.5. Preferential orientation

Typical examples of XRD pattern of TiN and nc-TiN/a-BN/a-TiB₂ coatings with different boron content are shown in Fig. 5.25. The only crystalline phase which was detected by means of XRD in all coatings discussed here was the fcc TiN showing a preferential (200) orientation in agreement with the results of other authors [Mi00] [Re99a] [Ka89] [Pf99a] [Hei99]. At low content of boron the (200) orientation is strong and it slightly decreases with increasing BCl₃/TiCl₄-flow rate ratio. Figure 5.26 shows the dependence of the preferential orientation on the BCl₃/TiCl₄-flow rate ratio.



Fig. 5.25: XRD patterns of TiN and nc-TiN/a-BN/a-TiB₂ coatings with different boron content deposited on stainless steel substrates, ($T = 550 - 600^{\circ}C$, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

The nc-TiN/a-Si₃N₄ coatings typically show (200) texture which changes to random orientation of the crystallites when the silicon content reaches about 10 at.% [Ni99] [Ne00a] [Pr03] [Le02]. The probably reason of this difference is the much larger incoherence strain between TiN and BN as compared to nc-TiN/a-Si₃N₄. According to the thermodynamics of spinodal decomposition a larger incoherency strain results in a larger periodicity (i.e. crystallite size) of the segregated nanostructure [Sch95]. This is indeed observed experimentally in this work. For a boron content of about 7 - 8 at.% the crystallite size is still around 10 nm whereas in the case of nc-TiN/a-Si₃N₄ it decreased to 3 - 4 nm.

The random strain is the average value of the heterogeneous strains that is acting in different directions on the individual crystals. It causes no macroscopic stress. The origin of this strain is the disorder within the grain boundaries and a mismatch between the different phases. For example, for crystalline Si films deposited at a floating potential, a lattice expansion is observed which increases with decreasing crystallite size and reaches a value of $\sim 1 - 1.2\%$ for a critical crystallite size of \sim 30 Å [Sa82] [Ve87a]. The dilatation is due to the tendency of the system to minimize the structural disorder within the grain boundaries combined with the anharmonicity of the interatomic potential [Ve96f]. Dilatation ($\Delta a/a_0$) can decrease with increasing negative bias due to the compressive stress built into the deposited films [Sa82] [Ve87a]. The observable influence of the random strain on the peaks position in the XRD pattern for small crystallite size < 5 nm can be overlapped by the compressive stress peak shift [Ve87a] [Re95] [Ve95a] [Ne00a]. In the case of nc-TiN/a-BN/a-TiB₂ coatings the random strain calculated from the Warren-Averbach analysis increases with decreasing crystallite size in agreement with the nc-TiN/ a-Si₃N₄ coatings [Ni99] (see Fig. 5.27). There is no correlation between the measured hardness and the random lattice strain in agreement with [Ni99] [Ne00b].





Fig. 5.26: Dependence of the preferential orientation on the BCl₃/TiCl₄-flow rate ratio for <u>a</u>) one and two connections holder (stainless steel substrates), <u>b</u>) full contact holder (different substrates), ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0 - 1.8 sccm).

Figure 5.28 shows the dependence of the TiN lattice dilatation on the crystallite size of nc-TiN/a-BN/a-TiB₂ coatings deposited with "two points" and "full holder" connection, where the coatings are homogeneous, on stainless steel substrates. The lattice dilatation of nc-Si [Ve81] and nc-TiN/a-Si₃N₄ [Ve95b] coatings are included for comparison. The increase of the lattice dilatation for nc-Si was explained by the increasing effect of the tensile stress within the grain boundaries that is pulling apart the crystallites, this effect being larger for smaller crystallites [Ve81]. Similar explanation applies also for the nc-TiN/a-Si₃N₄ system because the Si₃N₄ matches fairly well on the surface of TiN. However, in the nc-TiN/a-BN the mismatch is much larger because of the small size of the boron atoms (see Fig. 5.31). Therefore, the tensile stress within the grain boundaries is much larger in the latter case. This can explain why the lattice dilatation is relatively larger also for larger crystallite sizes of TiN as shown in Fig. 5.28 for nc-TiN/a-BN/a-TiB₂.



Fig. 5.27: Dependence of the random strain calculated from the Warren-Averbach analysis on the crystallite size, the random strain of nc-TiN/a-Si₃N₄ coatings [Ni99] was included for comparison.



Fig. 5.28. Dependence of the lattice dilatation ($\Delta a/a_0$) on the crystallite size of nc-TiN/a-BN/a-TiB₂, nc-Si [Ve81] and nc-TiN/a-Si₃N₄ [Ve95b] coatings.

5.2.6. Phase composition

Generally, the Ti-Si-N nanocomposite films are composed of TiN nanocrystallites imbedded in an amorphous SiN_x matrix [Ve95b] [Chr98].

The Ti-B-N nanocomposite films in this work are composted of TiN nanocrystallites imbedded in an amorphous BN or BN and TiB₂ matrix. From Fig. 5.29a and 5.29b one can see that in the nanocomposites prepared by means of plasma CVD at a relatively high partial pressure of nitrogen of about 0.3 mbar as compared with the PVD techniques BN is the dominant boron containing phase when the total boron content does not exceed about 8 at.%. The TiB₂ fraction can be neglected in these coatings. In agreement with [Ne00a] the coatings with 3 at.% of boron contain about 75% of BN phase. The minor contribution of the signal from TiB₂ is within the accuracy of the fitting of the measured curve by Gaussian peak. The experimental XPS peaks are asymmetrically broaden due to electrons shake-ups at the Fermi level and inelastically scattered electrons of the given line. In the case of coatings with higher boron content (Fig. 5.29c) the TiB₂ phase becomes dominant.





Fig. 5.29: B 1s region of the XPS spectra of nc-TiN/a-BN/a-TiB₂ nanocomposites prepared by plasma CVD for sample with approximately <u>a</u>) 2 at.%, <u>b</u>) 8 at.% and <u>c</u>) 15 at.% of boron.

The assignment of the peaks to BN and TiB₂ is in agreement with the data of other authors [Mo95] [Ca78] [Br90]. The peak at a binding energy of about 186 eV was assigned to the boron atoms incorporated either in the TiN grains or localized at the grain boundaries [Ba02b]. However, the results in Fig. 5.30 support the assignment of this peak to boron atoms at the TiN surface being bonded simultaneously to Ti and N. In Fig. 5.30 the fraction of the three phases vs. the crystallite size is shown. It is well known that less than about 10 – 20 nm small nanocrystals are free of any defects because of a relatively high, destabilizing contribution of such defect to the total free energy of such nanocrystal combined with a short diffusion length to the grain boundaries. In Fig. 5.30 any dependence of the fraction of the phases on the crystallite size can not be seen although the latter changes between about 5 and 35 nm. Therefore the peak at $E_b \approx 186$ eV was attributed to boron atoms located at the surfaces of the TiN nanocrystals.



Fig. 5.30: Fraction of the BN, TiB and TiB₂ phases vs. crystallite size.

In the case of nc-TiN/a-Si₃N₄ coatings the lattice matching of the TiN grains with Si₃N₄ phase is much better than with BN phase in the nc-TiN/a-BN coatings because of the difference between the silicon and boron atoms size. Large strain energy (lattice mismatch) can hinder the segregation. Because of the larger strain

energy the nc-TiN/a-BN coatings are expected to have larger crystallite size in comparison with nc-TiN/a-Si $_3N_4$ coatings.

In Fig. 5.31 one can see that a certain amount of boron atoms has to be connected to titanium atoms. This can explain appearance of the TiB peak in XPS spectra for nc-TiN/a-BN/a-TiB₂ coatings.



Fig. 5.31: Example of a nc-TiN/a-BN coating structure. Large filled yellow circles are titanium atoms, smaller perforated red circles are nitrogen atoms on top of the TiN (111) surface and the smallest perforated green circles are boron atoms connected to nitrogen. The smallest filled gray atoms are boron atoms connected to titanium. Boron atoms are much smaller that titanium atoms and some fraction of them has to be connected to titanium atoms. (This "modeling" was done by Dr. D. Azinovic; with permission).

5.2.7. Coverage of TiN nanocrystals with BN

One can see from Fig. 5.24 and 5.12 that although the crystallite size and the boron content significantly change between the BCl₃/TiCl₄-flow ratio of 0.2 and 1.1 the hardness of films deposited on stainless steel substrates does not show any significant change in that range. The only clear change is the increase of the hardness from the usual value of 23 - 25 GPa for pure TiN to 40 - 50 GPa with the addition of boron for the BCl₃/TiCl₄ gas flow ratio between 0 and 0.15. This is further emphasized by Fig. 5.32 which shows the hardness vs. crystallite size for coatings which were so far completely analyzed (i. e. also by ERD and XPS).



Fig. 5.32: Hardness vs. crystallite size for nc-TiN/a-BN/a-TiB₂ coatings, ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100 - 110$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0.05 - 1.6 sccm).

If the specific surface area is calculated from the measured crystallite size and the coverage of the TiN nanocrystals surfaces is calculated from the boron nitride content determined by ERD and XPS, it is seen in Fig. 5.33 that maximum hardness is achieved at about one monolayer coverage. The numbers next to the points in Fig. 5.33 indicate the crystallite size. One can see that for achievement of the high hardness in the case of nc-TiN/a-BN/a-TiB₂ nanocomposite coatings the coverage is

more important that the small crystallite size. One notices that the points with a large crystallite size in Fig. 5.33 correspond to nc-TiN/a-BN with low TiB₂ fraction whereas those with a low crystallite size contain TiB₂ as the dominant phase. Nevertheless, regardless of the TiB₂ fraction the coverage of the TiN nanocrystals with about 1 monolayer of BN is necessary in order to achieve the highest hardness.



Fig. 5.33: Dependence of the hardness on the surface coverage of TiN nanocrystals by BN. The numbers next to the points indicate the crystallite size, $(T = 550 - 600^{\circ}C, p = 3 \text{ mbar}, P_{hf} = 100 - 110 \text{ W}$, flow rate $(H_2) = 50 \text{ sccm}$, flow rate $(N_2) = 5 \text{ sccm}$, flow rate $(TiCl_4) = 1.7 \text{ sccm}$, flow rate $(BCl_3) = 0 - 1.6 \text{ sccm}$).

The specific surface area of the TiN nanocrystals was calculated assuming a cubic shape. This is based on earlier investigations of the nc-TiN/a-Si₃N₄ [Chr98] and nc-TiN/a-Si₃N₄/a-TiSi₂ coatings by means of high resolution transmission electron microscopy which reveals a fairly regular shape and uniform size of the TiN nanocrystals. The results shown in Fig. 5.33 agree surprisingly well with those obtained earlier for the binary nc-TiN/a-Si₃N₄ [Ve95b] [Ni01] [Pr03], nc-W₂N/a-Si₃N₄ [Ve96a] and ternary nc-TiN/a-Si₃N₄/a-TiSi₂ [Ni01] coatings. In spite of the limited accuracy of such calculations due to unavoidable errors of the analyses and lack of knowledge of the exact shape of the TiN nanocrystals, this agreement is very

encouraging because it lends a strong support to the generic concept for design of superhard nanocomposite coatings [Ve95b].

5.2.8. Microstructure and morphology

The typical columnar structure of plasma deposited TiN vanishes with increasing content of $a-Si_3N_4$ [Ve95c] [Ve96a] and an isotropic finely grained nanostructure develops when the concentration of silicon in the film is around 5 - 10 at.% [Ve95b] [Ve95c] [Ve96a] [Chr98] [Va00] [Va98] [Shi92]. Further increase of the silicon content causes again the coarsening of the structure [Ve95c] [Rei95]. Increasing boron content in Ti-B-N coatings leads to a less columnar, more dense and featureless coating structure [Ba99] [We90].

The nc-TiN/a-BN/a-TiB₂ nanocomposite coatings show similar morphology development (see Fig. 5.34). The addition of boron nitride into the coatings leads to a change of their morphology from the columnar to more dense and isotropic one. However, the columnar morphology is still apparent on all SEM cross-sections in Fig. 5.34, regardless of the content of boron and the coverage. This can be caused by too short distance between the gas inlet and the substrate holder. The BCl₃ does not have enough time to form the BN phase only and as a consequence the formation of TiB₂ phase appears. The columnar morphology results in a formation of shear bands during the indentation into the nc-TiN/a-BN/a-TiB₂ coatings at high loads of 500 - 1000 mN (see Fig. 5.35). The nc-TiN/a-Si₃N₄ coatings with optimum silicon content have dense and non-columnar structure [Pr03] and show only Hertzian circular cracks when indented at high loads [Ne00a].



a) [B]_{ERD}=0.9 at.%, C=0.52, H=34.4 GPa d=30.8 nm, fraction (TiB₂)=0



b) [B]_{ERD}=2 at.%, C=1.26, H=47 GPa d=34.7 nm, fraction (TiB₂)=0.05



c) [B]_{ERD}=2.25 at.%, C=1.45, H=35 GPa d=35.4 nm, fraction (TiB₂)=0.05



d) [B]_{ERD}=3.7 at.%, C=1.8, H=28.1 GPa d=26.2 nm, fraction (TiB₂)=0.06



e) [B]_{ERD}=5.25 at.%, C=0.87, H=48.4 GPa d=8.6 nm, fraction (TiB₂)=0.09



f) [B]_{ERD}=6.4 at.%, C=1.61, H=34.6 GPa d=17.7 nm, fraction (TiB₂)=0.22





g) [*B*]_{CAL}=12.9 at.%, C=n.m., H=39.7 GPa h) [*B*]_{XPS}=15.5 at.%, C=1.12, H=39.7 GPa d=6.4 nm, fraction (TiB₂)=n.m. d=4.8 nm, fraction (TiB₂)=0.12

Fig. 5.34: The development of the morphology of the nc-TiN/a-BN/a-TiB₂ coatings with increasing content of boron in the coatings. $[B]_{ERD}$ and $[B]_{XPS}$ are the boron content obtained by means of ERD or XPS, respectively, $[B]_{CAL}$ is the boron content calculated from linear fit (see Fig. 5.11a), C is the coverage of TiN nanocrystals by BN (see Fig. 5.33), H and d are the hardness and crystallite size, respectively, and "fraction (TiB₂)" means the amount of TiB₂ phase obtained by XPS analysis (see Fig. 5.30), (n.m. = not measured).



Fig. 5.35. Formation of the radial cracks (Fig. 5.35b) and/or shear bands (Fig. 5.35a) during the indentation into nc-TiN/a-BN/a-TiB₂ coatings at load of 1000 mN: <u>a)</u> sample HF121201, ($T = 535^{\circ}C$, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCI_4$) = 1.75 sccm, flow rate (BCI_3) = 0.25 sccm), <u>b)</u> sample HF191101, ($T = 575^{\circ}C$, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCI_4$) = 1.6 sccm, flow rate (BCI_3) = 0.1 sccm).

5.3. Ti-B-N films deposited by means of vacuum arc PVD

Superhard coatings of the composition of nc-TiN_{1-x}/a-TiB₂ with a minor contribution of the amorphous BN phase were deposited by means of vacuum arc evaporation of titanium in borazine (B₃N₃H₆) atmosphere at a pressure of about 1.17 - 1.29 Pa and deposition temperature of 536 - 700°C on cemented carbide substrates. Because the only source of nitrogen was the borazine, the fcc TiN_{1-x} crystalline phase was substoichiometric with crystallite size of about 3 - 7 nm. Figure 5.36 shows an example of the XRD pattern. These coatings had a metallic gray color which changed to gold-like upon annealing in N₂. Because of a low emission of macroparticles the surface of the coatings was fairly smooth with R_m \approx 0.15 µm [Zi02] (see Fig. 5.37).

ERD analysis revealed a composition of about 22 - 24 at.% of boron and 23 - 26 at.% of nitrogen, the balance to 100 % being titanium. In spite of this relatively high boron content, no crystalline boron-containing phase was detected by XRD. The B 1s region of the XPS spectra shown in Fig. 5.38 reveals TiB_2 as the dominant phase with a minor contribution of BN.



Fig. 5.36: XRD pattern of nc-TiN_{1-x}/a-TiB₂ coating deposited on WC-Co substrate, the TiN reflections are indicated in the figure, other peaks are from the substrate (for deposition parameters see Table 4.1).



Fig. 5.37: SEM micrograph of the surface of the nc-TiN/a-TiB₂ coating deposited by vacuum arc evaporation, (for deposition parameters see Table 4.1).



Fig. 5.38: B 1s region of the XPS spectra of the nc-TiN/a-TiB₂ coating, (for deposition parameters see Table 4.1).

The load independent hardness varied between about 45 and 65 GPa as a function of the deposition parameters (substrate current density and bias) for an indentation depth of \geq 0.3 µm. The correlation of the elastic modulus with the hardness is shown in Fig. 5.39. As mentioned above, the elastic modulus from the indentation technique does not correspond to the Young's modulus of the coatings [Ve03a]. The elastic recovery of these coatings is in the range of 70 - 85 %.

Because these coatings were deposited at large negative bias of -100 - 200 V they have a relatively high biaxial compressive stress of ≥ 5 GPa as measured from bending of the steel strips [Zi02]. Nevertheless, they show a much better thermal stability than the ZrN/Ni and Cr₂N/Ni samples (see below).



Fig. 5.39: Correlation between the hardness and the indentation elastic modulus for arc evaporated nc-TiN/a-TiB₂ coatings, (for deposition parameters see Table 4.1).

5.4. nc-M_nN /a-metal coatings

ZrN/Ni and Cr₂N/Ni coatings were deposited by magnetron sputtering at a deposition temperature of 200 - 300°C, Ar + N₂ pressure of 0.5 - 0.7 Pa and deposition rate about 0.5 nm/s with a thickness of 2 – 3.7 μ m [Mu01a] [Re00] [Ka00] [Re01]. ZrN/Ni films consisted of a slightly overstoichiometric nanocrystalline ZrN with nickel content between about 0.5 and 4 at.%. The nickel content and the preferential orientation of as-deposited ZrN/Ni films depended on the applied bias voltage and ion current density to the surface of the growing films. The coatings with higher nickel content (~ 4 at.%) deposited at low bias and low ion current density showed the preferential orientation ZrN (200), whereas the coatings with lower nickel content (~ 0.5 at.%) deposited at high bias and high ion current density had the preferential orientation (111). The nickel content in the coatings decreased with increasing negative bias due to its preferential resputtering from the growing film.

During a magnetron sputtering the surface of the growing film is bombarded by energetic ions. This can cause an incorporation of ions into the film mainly at low deposition temperature and generation of compressive stress in the coatings due to overstoichiometric nitrogen content and inert gas incorporation [Wi67] [Th77] [Oe95a] [Oe95b] [Ra97]. Annealing drives the excess N to empty lattice sites or, as a competing process, to precipitate at grain boundaries as gas bubbles [Hu89a] [Hu89b] [Hu00]. The high energetic ion bombardment promotes simultaneously the increase of the compressive stress, decrease of the crystallite size, densification of grain boundaries and displacement damage (see section 3.3.3.1).

Figure 5.40 shows the dependence of the composition of the ZrN/Ni coatings on the applied negative bias during the deposition. With increasing negative bias the kinetic energy of ions increases. Consequently, the amount of incorporated argon in the coatings increases [Mi98] and it can also cause surface blisters in subsequent annealing [Th77]. In the case of ZrN/Ni coatings the amount of incorporated argon increases from 1.3 at.% to 2.6 at.% with increasing negative bias from -30 V to -250 V at total pressure 0.7 Pa and substrate current density 1.2 mA/cm². The substrate current density was kept constant by changing the current through the electromagnets behind the target. Magnetron sputtering of ZrN have shown, that the overstoichiometry of nitrogen can reach about 15 at.% [Oe95b]. Correspondingly the compressive stresses can be high.

The morphology of the ZrN/Ni coating deposited by magnetron sputtering shown in Fig. 5.41 has the typical columnar feature of zone T of the Thornton's diagram [Th77] [Th86].



Fig. 5.40: Dependence of the chemical composition (EDX) of ZrN/Ni coatings on the applied negative bias during the depositions, ($T = 300^{\circ}$ C, $i_s = 1.2 \text{ mA/cm}^2$, $p_{N2} = 0.05 \text{ Pa}$, $p_{tot} = 0.7 \text{ Pa}$).

The second type of coating studied here had chemical composition of Cr_2N with 8 at.% of nickel. The reflections on XRD pattern could not be assigned to neither Cr_2N nor CrN (see Fig. 5.68 for as deposited coating). This corresponds to results of Musil et. al [Re01] [Mu98b] for the same type of coatings.

The hardness of ZrN/Ni and Cr_2N/Ni coatings obtained by the load-depth sensing technique agrees with the hardness calculated from the remaining indentations observed by means of calibrated SEM (see Fig. 5.42). When the indentation depth exceeds more than 10 % of the film thickness, the effect of the soft substrate appears.

The hardnesses and the crystallite sizes of the as deposited ZrN/Ni coatings are shown in Fig. 5.61 and Fig. 5.63, respectively. The hardness and the crystallite size of the as deposited Cr_2N/Ni coating are shown in Fig. 5.67.



Fig. 5.41: SEM micrograph of the ZrN/Ni coating, (Ni = 4.1 at.%, U_b = -50 V, T = 300° C, i_s = 1.2 mA/cm², p_{N2} = 0.05 Pa, p_{tot} = 0.7 Pa).



Fig. 5.42: Comparison of the hardness of ZrN/Ni coatings measured by the loaddepth sensing technique and calculated from the size of the remaining plastic deformation (SEM). Loads from 30 mN to 1000 mN, $h_{corr.}$ means indentation depth corrected for the blunt tip, (T = 300°C, $i_s = 0.6 - 1.2 \text{ mA/cm}^2$, $U_b = -30 - -200 \text{ V}$, $p_{tot} = 0.7 \text{ Pa}$, $p_{N2} = 0.05 \text{ Pa}$).

Figure 5.43 shows a SEM micrograph of the remaining plastic indentation of ZrN/Ni coating. The surface of ZrN/Ni coatings as deposited or after annealing to

600°C is smooth without blisters and there is no sign of pile-up around the indentation.

Several researches have shown in the past that, upon indentation, some ceramic coatings undergo plastic deformation via the formation of shear bands or cracks. These can be seen in SEM micrographs as a crack-like pattern parallel to the edges of the indented area as seen in Fig. 5.44a. The number of the "cracks" seen in the micrograph corresponds to the number of steps on the loading curve (Fig. 5.44b). The first crack is observed when the maximum indentation depth reaches 25 % of the film thickness, the second crack is at 33 % of the film thickness and the third one at 45 % etc. Such a behavior was fairly reproducible for this type of the coatings [Ve02a] [Ve03c].



Fig. 5.43: SEM micrograph of remaining plastic deformation of ZrN/Ni coating. The sample was tilted (40°) to get a better contrast, the hardness H_{SEM} was calculated from the untilted picture, load 70 mN, H_{SEM} = 27.5 GPa, H_{FISCH} = 23.4 GPa, h_{ind}/t_{layer} = 11.4 %, (T = 300°C, i_s = 1.2 mA/cm², U_b = -100 V, p_{tot} = 0.7 Pa, p_{N2} = 0.05 Pa).





Fig. 5.44: <u>a)</u> SEM micrograph of remaining plastic deformation of 2.8 μ m thick ZrN/Ni coating (crystallite size 5.3 nm) indented at 500 mN load and <u>b</u>) the corresponding loading-unloading curve. The sample was tilted (40°) to get a better contrast. The arrows on the loading curve indicate the cracks, (T = 300°C, *i*_s = 1.2 mA/cm², U_b = -100 V, *p*_{tot} = 0.7 Pa, *p*_{N2} = 0.05 Pa).

5.5. Thermal stability

Figure 5.45 shows the dependence of the recrystallization temperature of nc-TiN/a-Si₃N₄ and other nanocomposite coatings on their crystallite size [Ve99b] [Ve99a]. The crystallite size was controlled by the composition of the films and/or by the ion bombardment. The films in Fig. 5.45 were annealed under 5 - 10 mbar of forming gas (95 % N₂ / 5 % H₂) for 30 min. The hardness of the films did not change up to their recrystallization temperature. Upon recrystallization the hardness decreased.



Fig. 5.45: Recrystallization temperature vs. crystallite size of as deposited coatings for different type of nanocomposite coatings. The hardness of the coatings remains unchanged up to the recrystallization (from [Ve99a]).

This clearly shows that the stability of the hardness of these nanocomposite coatings is controlled by the stability of the nanostructure and it is not influenced by the small biaxial compressive stress of $\leq 0.4 - 2$ GPa [Ve99b] [Ni99]. The recrystallization temperature increases with decreasing crystallite size, thus the stability of the nanostructure in these coatings is determined by the crystallite size irrespective of the hardness [Ve99a] [Ni99] [Ni01]. The increasing recrystallization

temperature with decreasing crystallite size was observed also for TiB_xN_y coatings [Ma00].

5.5.1. Thermal stability of Ti-B-N coatings

The annealing of Ti-B-N coatings in this work was done in 1 atm. of pure nitrogen to avoid the surface oxidation which occurred during annealing at 10 mbar of forming gas. The temperature was reached with a controlled heating rate of 3 K/min and the samples were kept at the given temperature for 30 minutes.

The following effects can be responsible for the softening of the Ti-B-N coatings during annealing: the relaxation of the compressive stress, the recrystallization, the loss of boron from the film and the diffusion of elements from the substrates to the coatings. As it is shown below, the loss of boron from the coating together with the diffusion of substrate elements into the coating during annealing are crucial for the thermal stability of nc-TiN/a-BN/a-TiB₂ and nc-TiN/a-TiB₂ coatings. Summary of all data about the annealed nc-TiN/a-BN/a-TiB₂ samples deposited by plasma CVD is listed in Table 5.4. The overview of all annealed coatings deposited by plasma CVD is shown in Fig. 5.59a-m at the end of section 5.5.1 (page 107). Summary of all data about the annealed nc-TiN/a-TiB₂ coatings deposited by vacuum arc PVD is listed in Table 5.5. The overview of all these coatings is shown in Fig. 5.60a-c at the end of section 5.5.1 (page 113).

Table 5.4: Deposition parameters and properties of the nc-TiN/a-BN/a-TiB₂ coatings deposited by plasma CVD which were used in annealing experiments, (flow rate $(H_2) = 50$ sccm, flow rate $(N_2) = 5$ sccm, flow rate $(TiCI_4) = 1.7$ sccm, $P_{hf} = 100 - 110$ W, p = 3 mbar).

sample		[B] _{CAL.}	T _{dep} [°C]	thick.	dep. r. [Å/s]	H _{AD} [GPa]	Cr. Size	[CI] [at %]	sub- strate
			[0]	[biii]	[740]		[nm]	[41.70]	Strate
HF191101	0.06	0.8/-	575	4.8	6.6	36.8	28.3	0.68	SS
HF161002	0.13	1.7/-	587	6.0	5.6	37.1	16.4	1.06	Si
HF121201	0.14	1.8/-	535	6.0	8.9	40.7	20.9	1.23	SS
HF100402	0.14	1.8/-	583	3.5	4.9	43.1	12.8	1.72	SS
HF190601	0.15	1.9/-	562	5.9	8.2	39.0	10.1	0.68	SS
HF120601	0.24	3.1/4	567	6.0	8.4	39.2	30.4	1.03	SS
HF141002	0.32	4.1/-	572	6.0	5.6	41.9	12.9	1.17	Si
HF040702	0.33	4.3/-	599	6.5	6.0	35.6	9.9	1.04	Si
HF190602	0.36	4.6/-	593	8.4	5.9	45.2	13.1	1.47	α-Fe
HF240701	0.38	4.9/-	588	6.6	9.2	51.6	5.7	1.4	SS
HF100701	0.48	6.2/5.25	587	6.1	8.3	47.2	9.3	1.22	SS
HF181201	0.92	11.9/15	538	7.9	11.0	36.6	6.3	1.49	SS
HF150102	1.0	12.9/-	566	6.4	8.8	39.7	7.4	1.64	SS

Table 5.5: Deposition parameters and properties of the nc-TiN/a-TiB₂ coatings deposited by vacuum arc PVD which were used in the annealing experiments.

sample	0210/2	0810/2	0502/1-3
temperature	700°C	600°C	597°C
electrode current	100 A	100 A	80 A
substrate bias	-100 V	-100 V	-200 V
arc voltage	46 V	53 V	45 V
pressure	1.21 Pa	1.17 Pa	1.285 Pa
B ₃ N ₃ H ₆ flow	230 sccm	230 sccm	340 sccm
thickness TiN+TiBN	3.1 μm	1.5 μm	3.8 μm
thickness TiN	0.8 μm	0.7 μm	0.2 μm
crystallite size	7.2 nm	5.9 nm	3.3 nm
boron content	~ 23 at.%	~ 23 at.%	-
nitrogen content	23-26 at.%	23-26 at.%	-
hardness as dep.	48.8 GPa	48.8 GPa	46.7 GPa

5.5.1.1. Stress relaxation

Because of the relatively small value of the biaxial compressive stress of about 2 GPa in the coatings deposited by plasma CVD on stainless steel substrates (see Fig. 5.14) its relaxation upon annealing might decrease the measured hardness only

by that amount. Such changes are within the errors of the hardness measurements. Figure 5.46 shows the dependence of the lattice parameter measured in the direction perpendicular to the surface of the coatings on the annealing temperature. There is either no change of the lattice parameter at all or if there is some decrease, it has no effect on the hardness of the coatings (see for example sample HF190602 in Fig. 5.46 and Fig. 5.59i). Figure 5.47 shows one example of the changes of the lattice parameter and biaxial stress in the coating vs. the annealing temperature. The hardness and the crystallite size of this coating remained stable up to annealing temperature of 1100°C (see Fig. 5.59a).



Fig. 5.46: Change of the lattice parameter vs. annealing temperature of nc-TiN/ a-BN/a-TiB₂ coatings deposited by plasma CVD, (SS = stainless steel substrate, Si = silicon substrate, α Fe = α -Fe substrate).



Fig. 5.47: Change of the lattice parameter and the biaxial stress calculated from $\sin^2 \psi$ method vs. annealing temperature, (nc-TiN/a-BN coating deposited by plasma CVD on stainless steel substrate, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate ($TiCl_4$) = 1.6 sccm, flow rate (BCl₃) = 0.1, P_{hf} = 100 W, p = 3 mbar).

The nc-TiN/a-TiB₂ coatings deposited by vacuum arc PVD have high compressive stress of > 5 GPa [Zi02]. For small crystallite size \leq 5 nm the shift of the XRD peaks due to the compressive stress can be influenced by grain boundary dilatation. The lattice parameter of TiN in these coatings after annealing to the given temperature is plotted in Fig. 5.48. Although these coatings have high compressive stress, no decrease of the hardness during annealing as a consequence of the stress relaxation was found.

5.5.1.2. Recrystallization

There is no unambiguous correlation between the changes of the crystallite size and hardness upon annealing for both types of the coatings. In almost all annealing experiments there is no change of crystallite size even when the hardness decreases at a certain annealing temperature (see Fig. 5.59 and 5.60).



Fig. 5.48: Changes of the lattice parameter vs. annealing temperature of nc-TiN/ a-TiB₂ coatings deposited by arc evaporation, (substrate cemented carbide).

5.5.1.3. Loss of boron

The decrease of the hardness of the nc-TiN/a-BN/a-TiB₂ and nc-TiN/a-TiB₂ coatings during annealing is probably due to oxidation of TiB₂ phase by the residual oxygen impurities in the N₂ atmosphere, evaporation of BO_x and resultant loss of boron from the coating. In the annealed samples, the boron content decreases and oxygen content increases significantly from the bulk of the coating towards the surface. This is documented by the ERD data in Fig. 5.49 and by XPS spectra in Fig. 5.50, 5.51 and 5.52. One sees that the boron content strongly decreases towards the surface (Fig. 5.49), the TiB₂ phase completely vanishes and only a small peak of boron oxide and boron nitride remains (Fig. 5.50, 5.51 and 5.52) after the annealing. Table 5.6 summarizes the results for these samples for which the ERD analysis could be done. Considering the saturation pressure of boron oxide at the given annealing temperature one can easily estimate the evaporation rate. This estimate shows that the boron is lost via the oxidation by residual oxygen at a level of \geq 10 ppm and sublimation of the boron oxide.

Table 5.6: Comparison of the film composition (ERD) for as deposited and annealed nc-TiN/a-BN/a-TiB₂ and nc-TiN/a-TiB₂ coatings.

sample	boron [at.%] bulk→surface	oxygen [at.%]	chlorine [at.%]	hydrogen [at.%]	titanium [at.%]	nitrogen [at.%]
HF181201 as deposited	15	0.9	1.5	0	48	35
HF181201 ann. at 1000°C	15 → 1.8	10	1	4	48	28
HF100701 as deposited	6	0.4	1.7	0.3	51	44
HF100701 ann. at 950°C	7 → 2	5	1.5	0.4	50	40
HF120601 as deposited	4	0.4	1.5	2.0	56	37
HF120601 ann. at 900°C	5.5 → 3.3	2.2	1.5	1.25	53	35
SHM0502/1-3 ann. at 1000°C	12 → 0	15	-	3	44	33



Fig. 5.49: Comparison of the boron content (ERD) in the as deposited and annealed sample HF181201 deposited by plasma CVD.



Fig. 5.50: XPS spectra of the B 1s region of sample HF181201 (plasma CVD) as deposited ([B] = 15 at.%) and after annealing at 1000° C.



Fig. 5.51: XPS spectra of the B 1s region of the sample SHM0810/2 (arc PVD) as deposited ([B] = 22 at.%) and after annealing at 1000° C.



Fig. 5.52: XPS spectra of the B 1s region of the sample SHM0502/1-3 (arc PVD) as deposited, after annealing at 800° and after annealing at 1000°C.

Héau et al. [He99] reported the stability of hardness under annealing in vacuum up to 827° C for Ti-B-N coatings deposited by sputtering. The decrease of hardness observed above 827° C was caused by the disappearance of TiB₂ phase, which completely disappeared above 1027° C.

Even in 1 atm. of high purity nitrogen the pressure of the residual oxygen in the annealing oven is of orders of more than 10^{-3} mbar. This is obviously sufficient to remove the boron from the coatings by oxidation of TiB₂ phase and evaporation of BO_x (see above). This example shows the limitation of the thermal stability of the coatings with a phase which is susceptible to the oxidation like TiB₂.

After each annealing step, an oxide layer on the top of the surface of the nc-TiN/a-TiB₂ coating deposited by vacuum arc PVD was formed even though the annealing experiments were carried out at atmospheric pressure of nitrogen. This oxide layer was always mechanically polished away before the next annealing step. The hardness measured on the sample with oxide layer was much lower than the hardness measured on the polished surface. A comparison of the appearance of the unpolished surface of the nc-TiN/a-TiB₂ coating deposited by vacuum arc PVD after deposition and after annealing at 1000°C is shown in Fig. 5.53. The nc-TiN/a-BN/ a-TiB₂ coatings deposited by plasma CVD are much stable against oxidation of the surface in comparison with nc-TiN/a-TiB₂ coatings. A comparison of the appearance of the unpolished surface of the nc-TiN/a-BN/a-TiB₂ coating after deposition and after annealing at 1000° C is shown in Fig. 5.54.





Fig. 5.53: The nc-TiN/a-TiB₂ coating surface (sample SHM0810/2, arc PVD) <u>**a**</u>) as deposited without polishing and <u>**b**</u>) after annealing at 1000°C without polishing.



Fig. 5.54: The nc-TiN/a-BN/a-TiB₂ coating surface (sample HF121201, plasma CVD) <u>**a**</u>) as deposited without polishing and <u>**b**</u>) after annealing at 1000°C without polishing.

5.5.1.4. Diffusion of elements from the substrate into the coatings

For coatings deposited by plasma CVD on stainless steel substrates the diffusion of Cr and Fe was observed by EDX at temperature of $\geq 900^{\circ}$ C (see Fig. 5.55). Figure 5.55 shows the chromium content in pure TiN and nc-TiN/a-BN/a-TiB₂ ([B] = 12.9 at.%) coating after annealing at 1050°C. The nc-TiN/a-BN/a-TiB₂ coating is more resistant against the diffusion of chromium in comparison with TiN. Procházka [Pr03] has found that the diffusion of molybdenum from the substrate into the nc-TiN/a-Si₃N₄ coatings started at much higher annealing temperature compared to TiN. The diffusion of substrate elements into the coating together with loss of
boron from the coating are the decisive factors for thermal stability of nc-TiN/a-BN /a-TiB₂ nanocomposites. SEM micrographs of the cross-section of the coating as deposited and after annealing at 900°C are shown in Fig. 5.56. A formation of layered-like structure in the annealed sample is clearly visible (Fig. 5.56b). The thermal stability of coatings deposited on silicon substrates is higher compared with the coatings on stainless steel substrates because silicon from that substrate does not diffuse noticeably into the coating during the annealing.

The nc-TiN/a-TiB₂ coatings prepared by vacuum arc PVD were deposited on cemented carbide substrates. Männling [Mä03] [Mä01] reported a diffusion of Co from the cemented carbide substrate into the nc-Ti_{1-x}Al_xN/a-Si₃N₄ coatings which started at a temperature of T \geq 1000°C. The diffusion of cobalt into the 3 µm thick Ti_{1-x}Al_xN coating was observed at 1250°C [Hö02]. The same behavior of WC-Co substrates and nc-TiN/a-TiB₂ films can be expected.



Fig. 5.55: Chromium content in TiN and nc-TiN/a-BN/a-TiB₂ coating deposited by plasma CVD after annealing at 1050° C.

The diffusion of Fe from substrate into the $(Ti_{1-x}AI_x)N$ coatings was found at 900°C [Ki99a] [Sm98]. Also the diffusion of boron from TiB₂ coatings into the steel substrate during annealing at 800°C and diffusion of molybdenum from substrate into the TiB_{2-x}N_y coating at 1200°C were observed [Wi97] [Wi99] [Mi90].





Fig. 5.56: SEM micrographs of the cross-section of the sample HF190601 ([B] = 1.9 at.%) <u>a</u>) as deposited and <u>b</u>) after annealing at 900°C.

5.5.1.5. Thermal stability vs. coating properties

The thermal stability of nc-TiN/a-BN/a-TiB₂ and nc-TiN_{1-x}/a-TiB₂ nanocomposite coatings is somewhat lower that of the nc-TiN/a-Si₃N₄ and nc-TiN/ a-Si₃N₄/a-TiSi₂ reported earlier (see Fig. 5.45). The thermal stability of Ti-B-N coatings shows no dependence on neither the crystallite size (see Fig. 5.57) nor the boron content in the coatings (see Fig. 5.58). Balzer et al. [Ba99] have shown that for arc evaporated Ti-B-N coatings the thermal stability increases with increasing boron content. Mitterer et al. [Mi03b] reported thermal stability of TiN/TiB₂ nanocomposites up to 1000° C, but this result was based only on the observing of grain coarsening.

In spite of these extensive studies, several questions regarding the effect of the composition and nanostructure on the thermal stability of the "Ti-B-N" coatings remain open. For example, the effect of the relative ratio of the BN and TiB₂ phases in coatings with the same crystallite size and overall composition as well as the effect of the coverage of the TiN nanocrystals with BN could not be studied in details because the analyses of the overall composition by ERD, of the phases by XPS and of the crystallite size by XRD are time consuming. The problem is further complicated by the coexistence of the BN and TiB₂ phases and of the N-B-Ti surface groups. Nevertheless the available data show that the behavior of this system is similar to the nc-TiN/a-Si₃N₄ but the boron containing phases, in particular the TiB₂-one, are less stable against oxidation than Si₃N₄.



Fig. 5.57: Thermal stability of nc-TiN/a-BN/a-TiB₂ and nc-TiN/a-TiB₂ coatings vs. the initial crystallite size.



Fig. 5.58: Dependence of the thermal stability of $nc-TiN/a-BN/a-TiB_2$ coatings deposited by plasma CVD on boron content.

The results presented in this section show that the high hardness of 45 - 55 GPa in nc-TiN/a-BN/a-TiB₂ coatings is due to the formation of nanostructure and not to the enhancement caused by energetic ion bombardment during the deposition as in the case of the ZrN/Ni and Cr₂N/Ni coatings prepared by magnetron sputtering at a low pressure (see next chapter 5.5.2).















Fig. 5.59: Dependence of the hardness and the crystallite size on the annealing temperature for coatings deposited by plasma CVD, (for deposition parameters see Table 5.4).





Fig. 5.60. Dependence of the hardness and the crystallite size on the annealing temperature for nc-TiN/a-TiB₂ coatings deposited by vacuum arc PVD, (for deposition parameters see Table 5.5), n.m.= not measured.

5.5.2. Thermal stability of nc-M_nN/a-metal coatings

Because the high thermal stability is one of many requirements for industrial applications of hard and superhard coatings [Ve99a], it was important to investigate also the thermal stability of the nc- M_nN/a -metal coatings deposited by means of reactive sputtering with unbalanced magnetron at a low pressure of 0.5 - 0.7 Pa. The annealing of these coatings was carried out in forming gas at a total pressure of 10 mbar under a fast gas flow of ca. 30 sccm for a period of 30 minutes at maximum temperature, i.e. under the same conditions as done for the nc-TiN/a-Si₃N₄ and other nacomposites in Fig. 5.45 (see p. 94).

5.5.2.1. nc-ZrN/a-Ni coatings

Figure 5.61 shows the dependence of the hardness, measured by the loaddepth sensing indentation technique, on the annealing temperature for the ZrN/Ni coatings with a higher (Fig. 5.61a) and lower (Fig. 5.61b) content of nickel. From Fig. 5.61 one can see that, regardless of the content of nickel and applied bias, the hardness of the films decreases upon annealing at a temperature of \geq 450°C and at T \geq 600°C it is approaching the value typical of bulk ZrN of 16 GPa [Ho86]. ZrN films with a lower content of nickel of 0.46 – 0.57 at.% (Fig. 5.61b) seem to be slightly more stable whereas for those with Ni content between 3.2 and 4.1 at.% the hardness decrease is clearly seen already at an annealing temperature of 450°C for all three samples (Fig. 5.61a).

The lower thermal stability of ZrN/Ni coatings with higher Ni content can be caused by larger amount of the soft metallic matrix in the coatings. Usually, a detrimental effect of the increasing amount of the soft metallic phase accumulated on the grain boundaries on hardness was observed for the nc-M_nN/a-metal coatings [Ba03] [My03] [Ze00] [Mu99a] [Mi98] [Mu01b] [Mu98b] [Mu99b].

Herr and Broszeit [He97a] [He97b] have shown that the hardness of sputterdeposited HfB₂ decreases from 72 GPa to 17 GPa upon annealing at 650°C. This was accompanied by a decrease of the compressive biaxial stress from 7 GPa in asdeposited films to about \leq 2 GPa after the annealing. Similar decrease of the hardness due to decrease of the compressive stress during isothermal annealing was observed for the arc evaporated TiC_xN_{1-x} [Kar02] and a variety of other coatings. For these reasons XRD measurements on the ZrN/Ni coatings were done in order to determine the changes of the lattice parameter perpendicular to the surface upon annealing.

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A biaxial compressive stress causes a lateral compressive (negative) strain $\varepsilon_{par.}$ within the plane of the coatings which, in turn, leads to a dilatation $\varepsilon_{perp.} = -\varepsilon_{par.} v$ (v is the Poisson's ratio) in the direction normal to that plane [Pe88]. The lattice parameter of ZrN reported in JCPDS tables is 0.457756 nm and the thermal expansion coefficient is according to Holleck [Ho86] 7.2·10⁻⁶ K⁻¹.

Because the thermal dilatation coefficient of ZrN is slightly smaller than that of the steel substrate (see Table 5.3, page 57) and due to the relatively low deposition temperature ($\sigma_{thermal} \sim 0.5$ GPa), the appreciable increase of the lattice parameter in the direction perpendicular to the film surface as seen in Fig. 5.62 is due predominantly to a biaxial compressive stress induced in the films by energetic ion bombardment during their deposition. This is well known and documented in the literature for plasma PVD films, mainly those deposited by sputtering at low pressure [Ho80] because the surface of the growing films is bombarded by energetic primary ions which were reflected from the target. In the case of magnetron sputtering, the highest stress values can be observed at high substrate bias voltages, low pressures and low substrate temperatures [Oe95a]. The expanded lattice parameter of ZrN samples in the as-received conditions was found to contract upon the tempering [Pe88] and the contraction is generally completed after 1 h at 800°C.





Fig. 5.61: Dependence of hardness of the ZrN/Ni coatings on the temperature of isochronal annealing in forming gas for 30 min per each step, (U_b is the substrate bias and i_s is the current density to the substrate during the deposition).

From the data in Fig. 5.62 and the elastic modulus of ZrN reported by Holleck [Ho86] of 510 GPa one can estimate the biaxial compressive stress in the as-deposited ZrN/Ni coatings to be in a range of about \geq 5 GPa. This is supported by fact that the hardness of pure ZrN deposited in the same deposition apparatus using the same deposition conditions is around 40 - 45 GPa (see Fig. 6 in [Mu01b]). This hardness is obviously higher then the hardness of 16 GPa reported for bulk ZrN by Holleck [Ho86]. Let us emphasize again, that the hardness enhancement is due to a complex synergistic effect of the energetic ion bombardment and not to the biaxial compressive stress only. The latter is, however, convenient to measure.

Figure 5.63 shows the dependence of the crystallite size on the annealing temperature for the same series of coatings as shown in Fig. 5.61. One can see that the main deposition parameter controlling the crystallite size of as-deposited ZrN/Ni films at a constant deposition temperature of 300°C is the substrate bias. The

crystallite size decreases with negative bias increasing from -30 V to -100 V and remains nearly constant upon a further increase of that bias.

As seen in the Fig. 5.63, the crystallite size does not show any significant change with the annealing temperature. The crystallite size calculated by the Scherrer formula was verified by the Warren-Averbach Fourier transform analysis [Ne00a].

Musil et al. [Mu01b] reported very high thermal stability of ZrN/Cu coatings up to 900°C. This thermal stability was however determined only by observing the intensity changes of the ZrN (111) Bragg reflections during the annealing of the coatings. The almost constant intensity up to 900°C was claimed to be the factor showing high thermal stability of this coating. Unfortunately the hardness of the coating during the annealing was not measured. As shown here the hardness of the ZrN/Ni coatings decreases rapidly upon annealing at a temperature of \geq 500°C but there is no change of the intensity of Bragg reflections up to the maximum annealing temperature of 700°C used.



Fig. 5.62: Dependence of the average value of shift of the lattice parameter of ZrN on the annealing temperature.

The relatively high stability of nanometer-sized ZrN/Ni coatings against recrystallization is due to the oxidation of grain boundaries that hinders the diffusion-controlled Ostwald's ripening. Figure 5.64 shows two examples of XRD pattern where the Bragg reflection of ZrO₂ (111) appears after the annealing to 650°C. The first sign of this peak is observed already after annealing at 500°C where the relaxation of the compressive stress commences (Fig. 5.62). Besides the oxidation of the grain boundaries, oxide-rich surface layer forms after each annealing steps whose hardness is significantly lower (up to 10 GPa) than that of the coatings. Therefore, this layer was removed by polishing prior to each measurement shown in Fig. 5.61.



Fig. 5.63: Crystallite size of as deposited ZrN/Ni films and its dependence on the annealing temperature for the same series of ZrN/Ni coatings as shown above, (i_s is the current density to the substrate, U_b is the bias voltage).



Fig. 5.64: The comparison of XRD patterns of ZrN/Ni coatings as-deposited and after annealing at $T = 650^{\circ}$ C, <u>a)</u> sample 04/08/02 with higher Ni content (4.1 at.%), <u>b)</u> sample 04/08/07 with lower Ni content (0.57 at.%). After annealing at 550°C, ZrO₂ (111) reflection appears, (S = substrate).

After annealing at temperatures $T \ge 650^{\circ}C$ also the formation of blisters on the surface can be seen in Fig. 5.65a and 5.65b. The SEM micrographs of the indentations into the coating annealed at 650°C show "pile-up" at higher loads (Fig. 5.65c). The blistering was explained by an oversaturation of the coatings by nitrogen or inert gas atoms situated on interstitial sites. Annealing drives the excess

of nitrogen to precipitate at grain boundaries forming gas bubbles [Hu89a] [Hu89b] [Hu00].

The content of incorporated argon in the ZrN/Ni coatings decreases slightly and the nitrogen amount decreases rapidly during the annealing. This is accompanied by the strong increase of oxygen content (see Fig. 5.66).







Fig. 5.65: SEM micrograph of the surface of the ZrN/Ni (04/08/02) coating after annealing at 650°C, <u>a)</u> oxidation of the surface, <u>b)</u> remaining plastic deformation, load 50 mN, tilted 60°, $HV_{SEM} = 17.1$ GPa, $HV_{FISCH} = 11.8$ GPa, $h_{ind}/t_{layer} = 13.6$ %, <u>c)</u> remaining plastic deformation, load 70 mN, tilted 50°, $HV_{SEM} = 7.5$ GPa, $HV_{FISCH} =$ 9.8 GPa, $h_{ind}/t_{layer} = 15.8$ %.

The decrease of the hardness and of the lattice parameter of crystal planes parallel to the substrate upon isochronal annealing between 400 and 700°C for 30 min shows that the hardness enhancement in these coatings is due to the energetic ion bombardment during the deposition. No hardness enhancement which could be attributed to the formation of a nanocomposite structure was found.



Fig. 5.66: Chemical composition (EDX) of ZrN/Ni film as deposited and after annealing at 600, 650 and 700°C.

5.5.2.2. nc-Cr₂N/a-Ni coatings

For the Cr₂N/Ni coating, similar results were found as for the ZrN/Ni coatings reported above. The Cr₂N/Ni sample was divided into four parts and one part was annealed by Männling [Mä03]. The results shown in Fig. 5.67 and 5.68 were measured by author of this work on other three parts of the Cr₂N/Ni sample and are in agreement with the work of Männling [Mä03]. Figure 5.67 shows one example of the annealing behavior of the Cr₂N/Ni coating with nickel content of 8 at.% which was deposited at a substrate temperature of 200°C and a bias of –200 V. One notices that as-deposited film has a hardness of about 36 GPa and a crystallite size of 4.4 nm (similar to the ZrN/Ni deposited at the same bias). Upon annealing to a temperature of 500 and 600°C the hardness decreased to about 22 and 15 GPa, respectively. The crystallite size showed a small continuous decrease during the annealing. After annealing at 600°C the Bragg reflections of Cr₂N vanished and new ones appeared which may be due to a formation of a Cr-Ni-Fe alloy (see Fig. 5.68). The disappearance of the Bragg reflections of Cr₂N is due to its low thermal stability which is typical for all metals of the VI d group (Cr, Mo, W).



Fig. 5.67: Dependence of the hardness and crystallite size of Cr_2N/Ni coating with 8 at.% of Ni on the annealing temperature.



Fig. 5.68: Comparison of XRD patterns of Cr₂N/Ni coating as deposited and after annealing.

5.6. Oxidation resistance of nc-TiN/a-BN/a-TiB₂ coatings

The nc-TiN/a-Si₃N₄ [Ve95b] [Ve96b] [Va00] [Di99] and nc-(Ti_{1-x}Al_xN)/a-Si₃N₄ [Ho99] [Ho00] nanocomposite coatings show oxidation resistance in air up to $T \ge 800^{\circ}C$ like the Ti_{1-x}Al_xN coatings. Even a small amount of Al or Si addition to TiN has a large effects on the improvement in both micro-hardness and oxidation resistance of TiN film [Mü86] [Kn86] [Shi92] [Ve95b]. Münz et. al [Mc90] [Do97] have shown that a further improvement can be achieved by alloying small amount of yttrium to (Ti_{1-x}Al_x)N or (Ti_{1-x-y}Al_xCr_y)N that segregates at grain boundaries and hinders the oxidation by blocking the diffusion along the grain boundaries. Amorphous aluminum oxide and silicon oxide formed at the initial oxidation stage on Ti-Al-N and Ti-Si-N, respectively, are retarding further oxidation [Mü86] [Ho86]. However, the well known protection effect of a dense oxide layer does not work for single-phase nanocrystalline materials, such as nc-Si [Cu86] and TiN [GI97] because of a fast diffusion of oxygen through the grain boundaries and oxidation taking place therein. The protection of the diffusion within the grain boundaries and their oxidation are therefore more important for nano-sized coatings than the frequently quoted and studied formation of surface "protecting" layer [Pro03]. The a-Si₃N₄ in the grain boundaries hinders strongly the diffusion of molybdenum into the coatings as compared with pure TiN and it also hinders the diffusion of oxygen and thus the oxidation rate of the nc-TiN/a-Si₃N₄ coatings (see Fig. 5.70) [Pro03]. The oxidation resistance of nc-TiN/a-Si₃N₄/a- & nc- TiSi₂ coatings decreases with decreasing amount of Si₃N₄ phase and increasing amount of TiSi₂ phase [Mo01].

Héau et al. [He99] reported a strong increase of the oxidation above a critical temperature of 627° C for the TiN_x(B)_y coatings heated in oxygen. The onset for rapid oxidation and rutile TiO₂ formation for Ti(B,N) prepared by plasma CVD was observed at 760 - 770°C [Mi01].

In the present work we studied the oxidation resistance of the nc-TiN/a-BN/ a-TiB₂ coatings prepared by plasma CVD. Because the TiB₂ phase oxidizes faster than the BN one the present measurements focused on coatings with a low boron content of < 6 at.% in which the TiB₂ fraction is small. The weight gain due to the oxidation of the coatings at the given temperature is shown in Fig. 5.69. One can see that the oxidation resistance of the nc-TiN/a-BN coatings is better than that of pure TiN, but it is worse than that of nc-TiN/a-Si₃N₄ or nc-(Ti_{1-x}Al_xN)/a-Si₃N₄ coatings [Ve95b] [Ve96b] [Va00] [Ve98a] [Ho99] [Ho00] [Pr003]. A comparison of the oxidation resistance of nc-TiN/a-Si₃N₄ coatings deposited by magnetron sputtering [Pr03] [Pro03] with nc-TiN/a-BN coatings deposited by plasma CVD is shown in Fig. 5.70. The measurement of the oxidation resistance of nc-TiN/a-Si₃N₄ coatings was done by author of this work on coatings kindly provided by Procházka [Pr03]. The nc-TiN/ a-Si₃N₄ coatings show much better oxidation resistance than nc-TiN/a-BN coatings.



Fig. 5.69: Dependence of the weight increase due to the oxidation of nc-TiN/a-BN coatings at the given temperature for 2 hrs. The numbers within the insert indicate the boron content in the coatings.

The SEM cross-sections of the nc-TiN/a-Si₃N₄ coatings after annealing in air at 900° C for 2 hrs are shown in Fig. 5.71. The SEM mirographs of the surface of the nc-TiN/a-Si₃N₄ coatings after annealing in air at 1000° C for 2 hrs are shown in Fig. 5.72. The TiO₂ rutile formation was observed on the surface of the coatings. It was confirmed by XRD measurements shown in Fig. 5.73. Obviously the high oxidation resistance of nc-TiN/a-Si₃N₄ coatings is rather due to the silicon nitride in the grain boundaries which blocks the diffusion of oxygen than due to the formation of protective silicon oxide layer on the top of the coatings.

XRD patterns of as deposited nc-TiN/a-BN coating and after its annealing in air at 800°C for 2 hrs are shown in Fig. 5.74. After the annealing at 600°C rutile TiO₂ formation was observed. In the case of nc-TiN/a-Si₃N₄ coatings, the crystallite size remained constant after annealing in air up to 1000°C (see Fig. 5.73), whereas that of

the nc-TiN/a-BN ones increased from the initial value of 4 - 12 nm to 30 nm (see Fig. 5.74). The increase of the crystallite size is related to the boron disappearance from the coatings due to evaporation of B_2O_3 .



Fig. 5.70: Dependence of the weight increase due to the oxidation of nc-TiN/a-BN (plasma CVD) and nc-TiN/a-Si₃N₄ (PVD) coatings at the given temperature for 2 hrs. The data about annealing of the nc-TiN/a-Si₃N₄ coating deposited by plasma CVD by Reiprich [Rei95] [Ve95b] are also included, although this coating was kept at the given temperature only for 15 minutes. The numbers within the insert indicate the boron and silicon content in the coatings.



Fig. 5.71: SEM cross-sections of nc-TiN/a-Si₃N₄ coatings with <u>a)</u> 10.5 at.% Si and <u>b)</u> 5.3 at.% Si after annealing in air at 900°C for 2 hrs.



Fig. 5.72: SEM micrographs of the surface of nc-TiN/a-Si₃N₄ coatings with <u>a)</u> 10.5 at.% Si and <u>b)</u> 5.3 at.% Si after annealing in air at 1000°C for 2 hrs.



Bragg Angle 2 θ [°]

Fig. 5.73: Comparison of XRD patterns of as deposited nc-TiN/a-Si₃N₄ coating and after annealing in air at 900 and 1000° C for 2 hrs.

The oxidation resistance of nc-TiN/a-BN coatings can be improved by addition of AI as shown for nc-TiAIN/a-BN [Ba02a] [Ba02b] and nc-TiAIN/a-TiB₂/h-BN [Re99b] [Sh01].



Fig. 5.74: Comparison of XRD patterns of as deposited nc-TiN/a-BN coating and after annealing in air at 800°C for 2 hrs.

5.7. Long-term stability of the coatings

The binary nc-TiN/a-Si₃N₄ coatings with the chlorine content higher than 1 at.% showed a decrease of the hardness with time [Ne00a] whereas those with chlorine content below 0.5 at.% remained stable for the whole period of measurements of 3 years [Ne00a].

The superhard nanocomposites consisting of phases with polar bonds (e. g. $TiSi_x$, TiB_x) are expected to display a decrease of the hardness during a long term exposure to air. This is particularly the case for the ternary and quaternary nanocomposites nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ which keep the original hardness for a period of several months to one year but show a decrease of the hardness afterwards [Mo01]. For these reasons we investigated the long-term behavior of the hardness of the coatings prepared and studied in course of this work.



Fig. 5.75: The long-term hardness stability of the nc-TiN/a-BN coatings, ($T = 550 - 600^{\circ}$ C, p = 3 mbar, $P_{hf} = 100$ W, flow rate (H_2) = 50 sccm, flow rate (N_2) = 5 sccm, flow rate (TiCl₄) = 1.7 sccm, flow rate (BCl₃) = 0.1 - 1.0 sccm).

Figure 5.75 shows the long-term stability of the hardness of the nc-TiN/a-BN coatings. In spite of the relatively high content of chlorine (> 0.5 at.%), the coatings are stable for years.

By analogy with the degradation of the nc-TiN/a-Si₃N₄/a- & nc- TiSi₂ coatings we expected that also the nc-TiN/a-TiB₂ coatings prepared by vacuum arc PVD at the company SHM Ltd. may undergo a similar degradation. In order to speed-up this study the coatings were exposed to 100 % humid air at a temperature of 60 - 70°C. However, in spite of these harsh conditions, these coatings remained stable (see Fig. 5.76).



Fig. 5.76: The long time hardness stability of the nc-TiN/a-TiB₂ coatings (deposited by arc PVD) in 100 % humid air at 60 - 70° C, (for deposition parameters see Table 4.1).

The ZrN/Ni coatings deposited by magnetron sputtering, whose hardness was enhanced by energetic ion bombardment during their deposition, showed a decrease of the hardness on the time scale of months (see Fig. 5.77).

The decrease of the hardness with time can be caused by the relaxation of biaxial and/or random stress, oxygen impurities and/or surface oxidation and incomplete phase transformation [Mo01].



Fig. 5.77: Dependence of the hardness of ZrN/Ni coatings on the time from deposition, (for deposition parameters see section 4.1.3).

5.8. Possible artefacts of the hardness measurement on superhard coatings

Measurements of hardness by means of automated load-depth-sensing technique can be subjected to many artefacts when applied to superhard materials [Ve99a] [Ve02b] [Ve03a] [Ve03b] [He03]. We refer to these publications for further details. In this section only the effects of anelastic response of the steel substrate will be shown. All measurements presented in this section were done by author of this work on either nc-TiN/a-BN/a-TiB₂ coatings or nc-TiN/a-Si₃N₄ coatings kindly provided by Moto [Mo01], who found out the effect of the "dwell" time on the value of measured hardness (see below).

Modern indentometers allow one to select under a microscope the desirable positions on the surface of the sample where the measurements should be done and perform the chosen series of measurements automatically. In the case of the indentometer Fischerscope 100 that was used in this work the selected number of measurements is done one by one with a "dwell" time of about 30 - 40 seconds between individual measurements, when there is no contact between the indenter and the coating. The possible effect of both the "dwell" and the loading/unloading time on the measured value of hardness was investigated. Whereas there was no significant effect of the loading/unloading time above the chosen value of 60 s, the dwell time between the subsequent measurements has a significant effect as seen in Fig. 5.78. With the dwell time increasing from the shortest one of 30 - 40 s the measured hardness increases by 50 to 100 %. No such effect was found for bulk and softer materials, such as the steel substrate (H \approx 2 GPa), glass (H \approx 6 GPa) and single crystal Sapphire wafer ($H \approx 21$ GPa) [Ve02a]. One can see that the measured hardness of the coatings increases with increasing "dwell" time between the measurements.

Figure 5.79 shows the measured hardness for a series of consecutive measurements with dwell time of 40 s. The conditions were chosen so that the first measurement in the series was done 300 s after the previous series, i. e. the first points correspond to the dwell time of 300 s whereas the later ones to 40 s as in Fig. 5.78. One can see the reproducibility of the effect which increases with decreasing applied load. To complete the picture, two representative examples of the indentation curves are shown in Fig. 5.80 emphasizing that this effect was reproduced on several samples of nc-TiN/a-Si₃N₄ and nc-TiN/a-BN superhard nanocomposite coatings deposited on steel substrates. In order to find which of these measurements (short or long dwell time) are correct the obtained values of

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"indentation" hardness were compared with those calculated from the projected area of the remaining indentation using a calibrated SEM.



Fig. 5.78: Dependence of the hardness (average value of 5 indentations) measured by the indentometer at two different loads vs. the dwell time between the individual measurements: <u>a)</u> nc-TiN/a-BN and <u>b)</u> nc-TiN/a-Si₃N₄ coating deposited at 0.5 mm thick steel substrate. The time for the loading and unloading was chosen to be 60 s for each with a delay at the maximum load ("creep time") of 10 s.



Fig. 5.79: Hardness values in a series of subsequent measurements with dwell time of about 40 s; first measurement was done with dwell time 300 s; <u>**a**</u>) nc-TiN/a-Si₃N₄ and <u>**b**</u>) nc-TiN/a-BN coating.



Fig. 5.80: Representative example of indentation curves for a short (40 s) and long (300 s) dwell time for two nc-TiN/a-Si₃N₄ coatings.

Figure 5.81 shows such a comparison for a long dwell time of 300 s. One can clearly see that the values obtained from the indentometer at long dwell time are too high and incorrect.



Fig. 5.81: Comparison of the hardness measured by the load-depth sensing technique at a load of 50 mN and long dwell time of 300 s with that determined from the projected area of the remaining plastic deformation which was measured by means of a calibrated SEM, <u>a)</u> nc-TiN/a-BN and <u>b)</u> nc-TiN/a-Si₃N₄ coating.

This effect can be explained by anelastic deformation of the coating/substrate pair during the measurement [Ve02a]. In order to fix the position of the sample, the Fischerscope 100 first presses a thick ring made of strong steel to the surface of the sample with a load of 50 N and only afterwards the indenter in the center of that ring begins to approach and contact the surface. The high load on the ring causes a slight "lift-up" deformation of the sample within and around the ring which consists of an instantaneous elastic and a small, time delayed anelastic deformation of the substrate. Because the anelastic deformation upon applying the large load to the ring and recovery upon unloading needs a time of several hundred seconds, the anelastic part of the lift-up remains fairly constant during the measurements at the short dwell time but it becomes significant for the measurements on superhard coatings with a long dwell time. In Fig. 5.82 the "lift-up" is shown as a the negative creep on the loading-unloading curve during the measurement with long dwell time of 300 s.

From Fig. 5.80 one can estimate that a lift-up of $0.04 - 0.07 \mu m$ (i.e. a total strain of the substrate/coating system of only 10^{-4}) is sufficient to cause the observed differences in the measured hardness of superhard coatings when the corrected indentation depth at the high loads is 0.3 to 0.4 μm . Because the indentation depth decreases with decreasing applied load, this effect is more pronounced at low applied loads as shown by the present results. This effect is difficult to find on the soft steel substrate because of a larger indentation depth of the order of 2 μm where anelastic lift-up results in an error of the measured hardness of < 7 %. The absence of this effect in Sapphire is due to the absence of anelasticity in this material.

In order to emphasize the necessity of a careful verification of the hardness values measured by the indentometer, a comparison of the results from indentation measurements with the Vickers hardness calculated form the projected area of the permanent deformation is shown in Fig. 5.83. The indentation depth was 1.7 % and 10 % of the coatings thickness for the smallest (5 mN) and largest (100 mN) load, respectively. One can see that the load-depth sensing technique at small loads of < 30 mN strongly overestimates the hardness of the coatings whereas at loads 50 - 100 mN the difference between the values from the indentometer and from the projected area of the remaining indentation determined by a calibrated SEM agrees within the usual accuracy of such measurements of $\leq \pm 10$ %. It is important to notice that no enhancement of the hardness is observed for the SEM data thus confirming that the pressure under the indenter reaches the yield stress of that material and the correct, load independent hardness is found.



Fig. 5.82: Creep vs. dwell time for 3 different samples (1 sample nc-TiN/a-Si₃N₄, 2 samples nc-TiN/a-BN), load 30 - 100 mN.

Figure 5.84 shows the values of hardness measured on Si (111) wafer and Sapphire (001) by the indentation technique. Because the hardness remains constant up to the lowest load of 5 mN we conclude that the calibration of the indentometer and the correction for the finite tip radius were done correctly. Thus, the strong enhancement of the hardness found at low loads in Fig. 5.81 cannot be explained by the "Indentation Size Effect" due to blunt tip. The most probable reason for the observed effect is elastic deformation of the indenter [He03].



Fig. 5.83: Values of hardness obtained by the automated indentation technique and by calibrated SEM vs. applied load.



Fig. 5.84: Dependence of the hardness and the indentation depth of silicon and Sapphire standards on the applied load. It shows that the calibration of the indentometer and correction for the finite radius of the indenter tip were done correctly (see text).
The results presented in this subsection show that reliable measurements of the hardness by load-depth sensing technique can be done only within the load independent regime when the indentation depth exceeds 0.2 µm, in agreement with the results of Bull [Bu01]. According to the generally accepted "rule-of-thumb" criterion for ordinary hard coatings the maximum indentation depth should not exceed 10 % of the film thickness. He and Veprek [He03] [Ve02a] [Ve03c] have shown that for super- and ultrahard nanocomposites this criterion is not valid and the indentation depth should be less than 10 % of the film thickness. With increasing yield stress (i.e. hardness) of the coatings the minimum thickness that is needed to avoid plastic deformation of the substrate increases [Ve02a] [Chu00].

6. Summary and conclusions

Using high frequency plasma CVD at a total pressure of several mbar with TiCl₄, BCl₃, N₂ and H₂ as reactants, superhard nanocomposite coatings with hardness of 40 - 50 GPa (see Fig. 5.33) were successfully and reproducibly deposited and characterized in terms of mechanical properties, phase composition and nanostructure. Several authors reported about the preparation of superhard TiN/TiB₂ coatings prepared by reactive sputtering with only a small fraction of BN. Efforts to increase the fraction of the BN phase resulted in soft films. In contrast, plasma CVD yielded superhard nc-TiN/a-BN and nc-TiN/a-BN/a-TiB₂ coatings in a wide range of the fractions of BN and TiB₂ phases. This was attributed to the high chemical activity of nitrogen under the conditions of plasma CVD [Pro03].

The concept for the design of the superhard nanocomposites [Ve98a] [Ve01] is based on a thermodynamically driven segregation in binary (and ternary) systems which display immiscibility and undergo spinodal decomposition even at high temperatures. The "Ti-B-N" coatings in this work were composed of TiN nanocrystallites imbedded in amorphous BN matrix (boron content less than 8 at.%) or in amorphous BN and TiB₂ matrix (boron content higher than approximately 8 at.%) (Fig. 5.29). Because of the larger strain energy the nc-TiN/a-BN coatings had larger crystallite size in comparison with nc-TiN/a-Si₃N₄ coatings [Sch95]. By analogy with the earlier studied systems nc-TiN/a-Si₃N₄ [Ve95a] [Ve95b] [Chr98] [Rei95] [Pr03], nc-W₂N/a-Si₃N₄ [Ve96b], nc-VN/a-Si₃N₄ [Ve96a] [Ve96e], and nc-TiN/a-Si₃N₄/a-&nc-TiSi₂ [Ve00a] [Ve00b] [Ne00b] [Ni00] [Mo01], the maximum hardness of the nc-TiN/a-BN/a-TiB₂ coatings was obtained at the percolation threshold when there is about one monolayer of thin continuous tissue of a-BN between the TiN nanocrystals (Fig. 5.33). The percolation of Si₃N₄ [Ni01] or BN phase was found to be much more important for achieving superhardness than the small crystallite size as originally believed [Ve95b].

The typical columnar structure of plasma deposited TiN almost vanished with increasing content of a-BN and a more isotropic nanostructure developed when the concentration of boron in the film is ≥ 4 at.% (see Fig. 5.34). However, because of a persistence of the columnar structure the nc-TiN/a-BN/a-TiB₂ coatings showed a shear bands when indented at high loads of 500 - 1000 mN (see Fig. 5.35) in contrast to nc-TiN/a-Si₃N₄ coatings where circular ("Hertzian") cracks were formed [Ne00a] [Pr03].

The compressive stress in the nc-TiN/a-BN/a-TiB₂ coatings was below 2 GPa (Fig. 5.14) and had no influence on the hardness of the coatings, which remained stable during annealing to very high temperatures (Fig. 5.57). Hardness measured by load depth sensing indentation technique agreed with the hardness calculated from the projected area of the remaining plastic deformation obtained by calibrated SEM (Fig. 5.16). The elastic modulus measured by indentation at superhard coatings was close to value of shear modulus of these materials and not to the Young's modulus as usually assumed [Ma03] [Ve03a] [Ve03b].

The "Ti-B-N" superhard coatings (H = 45 - 65 GPa) prepared by vacuum arc evaporation were substoichiometric nc-TiN_{1-x}/a-TiB₂ with a minor contribution of the BN phase (Fig. 5.38) and a relatively high compressive stress of \geq 5 GPa. Nevertheless, they showed a much better thermal stability than the ZrN/Ni and Cr₂N/Ni coatings (see below).

It was verified that the high hardness of 40 - 50 GPa for nc-TiN/a-BN/a-TiB₂ coatings is due to the formation of nanostructure and not to the enhancement caused by energetic ion bombardment during the deposition as in the case of ZrN/Ni and Cr_2N/Ni coatings prepared by magnetron sputtering at a low pressure. No hardness enhancement in ZrN/Ni and Cr_2N/Ni coatings which could be attributed to the formation of a nanocomposite structure was found (Fig. 5.61 and 5.67). The loss of boron from the coating together with the diffusion of substrate elements into the coating during annealing had crucial influence on the thermal stability of nc-TiN/a-BN/a-TiB₂ and nc-TiN/a-TiB₂ coatings. This showed the limitation of the thermal stability of the coatings containing a phase like TiB₂ which is susceptible to the oxidation.

An improvement of the stability of the coatings against oxidation at higher temperature of 600° C was found for nc-TiN/a-BN coatings as compared to TiN (Fig. 5.69). This improvement was, however, smaller than for the nc-TiN/a-Si₃N₄ nanocomposites (Fig. 5.70) in which case the silicon nitride in the grain boundaries blocks the diffusion of oxygen [Pro03].

Measurements of hardness by means of automated load-depth-sensing technique can be subjected to many artefacts when applied to superhard materials [Ve99a] [Ve02b] [Ve03a] [Ve03b] [He03]. The effect of anelastic response of the steel substrate was shown (Fig. 5.78) and explained by anelastic deformation of the coating/substrate pair during the measurement [Ve02a].

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