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TiAlN-based Coatings at High Pressures and Temperatures

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Abstract

TiAlN and TiAlN-based coatings that are used of relevance as protection of cutting tool inserts used in metal machining have been studied. All coatings were deposited by reactive cathodic arc evaporation using industrial scale deposition systems. The metal content of the coatings was varied by using different combinations of compound cathodes. The as-deposited coatings were temperature annealed at ambient pressure and in some cases also at high pressure. The resulting microstructure was first evaluated through a combination of x-ray diffraction and transmission electron microscopy. In addition, mechanical properties such as hardness by nanoindentation were also reported.

TiAlN coatings with two different compositions were deposited on polycrystalline boron nitride substrates and then high pressure high temperature treated in a BELT press at constant 5.35 GPa and at 1050 and 1300 °C for different times.

For high pressure high temperature treated TiAlN it has been shown that the decomposition is slower at higher pressure compared to ambient pressure and that no chemical interaction takes place between TiAlN and polycrystalline cubic boron nitride during the experiments. It is concluded that this film has the potential to protect a polycrystalline cubic boron nitride substrate during metal machining due to a high chemical integrity.

TiZrAlN coatings with different predicted driving forces for spinodal decomposition were furthermore annealed at different temperatures. For this material system it has been shown that for Zr-poor compositions the tendency for phase separation between ZrN and AlN is strong at elevated temperatures and that after spinodal decomposition stable TiZrN is formed.

Preface

This licentiate thesis is the result of my work between January 2011 and November 2014 in the research group of Nanostructured Materials, a part of the Department of Physics, Chemistry and Biology (IFM) at Linköping University in Sweden. My research has been conducted in collaboration with Dalarna University, SECO Tools, Sandvik, Element Six, Uddeholms and SKF. The work has been funded by the Swedish Knowledge Foundation (KK-stiftelsen) and the Swedish Foundation for Strategic Research (SSF) through the program Designed Multicomponent Coatings (Mulifilms).

Included Papers

Paper I

High pressure and high temperature behavior of TiAlN coatings deposited on c-BN based substrates

R. Pilemalm, J. Zhu, A. Sjögren, J. M. Andersson and M. Odén

In Manuscript

Paper II

High temperature phase decomposition in $Ti_xZr_yAl_2N$

H. Lind, **R. Pilemalm**, L. Rogström, N. Ghafoor, R. Forsén, L. Johnson, M. Jöesaar, M. Odén and I. A. Abrikosov

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The Creator of the laws of Physics: יהוה

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1. Introduction

Nowadays, coatings and thin films are widely used and people encounter them daily in life often without even considering their importance. However, the materials science of coatings and thin films is today a well-established line of research, where a distinction between thin films and bulk materials has been made. The use of thin films has the purpose of tuning or adding properties to an item consisting of another material. Examples of where thin films are used include applications where decorative, optical, resistive, mechanical or thermal properties are of importance. In order to scientifically describe the behavior of thin films, solid state physics, physical metallurgy, quantum mechanics and thermodynamics are required and both theoretical and experimental considerations are needed to understand their micro- and nanostructure.

The focus of this thesis is coatings that are deposited on cuttings tools used for machining i.e. milling or turning of metals. By depositing the inserts with hard ceramic coatings properties as wear resistance, increased hardness and oxidation resistance can be improved. In turn, this leads to a more efficient cutting process in the sense of higher cutting speeds and a longer use of every single cutting insert [1]. There has been an evolution of hard coatings on cutting inserts since the late 1960's. In 1980's TiN was introduced and it led to a protection of the surface of the inserts and thus a better wear resistance. The next step was to add Al to TiN and it resulted in

better oxidation resistance and in addition age hardening was observed as temperature was elevated. Today TiAlN is one of the most used coatings for cutting inserts [2,3]. The effects of temperature have been reported in numerous of studies. However, because the area of contact between a cutting insert and the work material is small, there is a need to also understand pressure effects and recently attention has also started to be paid to pressure in combination with temperature effects [4,5]. In the first paper of this thesis the influence of pressure on the microstructure evolution in TiAlN is discussed and it is shown that it is beneficial for the stability of the coating. In addition, the interaction between the coating and the substrate, which in this case is polycrystalline cubic boron nitride (PCBN) is discussed.

Cutting inserts made of PCBN contains a large fraction of cubic boron nitride (*c*-BN), which has the advantage of being the hardest material known next to diamond. Additionally, it has high thermal stability, high thermal conductivity and in cuttings operations chemically relatively inert [9]. The composite material PCBN consists of *c*-BN grains in a matrix of different carbides, oxides and nitrides. In spite of its high hardness, tests to coat PCBN inserts with softer coatings are of interest, when considering additional wear mechanisms to abrasion such as oxidation. In such cases TiAlN is a natural candidate.

A natural third step in the evolution of hard coatings is to introduce a fourth element to TiAlN. Several successful attempts have been reported where for example Cr or Y has been used [6-8]. The introduction of a fourth element may drastically change the driving force for decomposition at elevated temperature and thereby the thermal stability. In fact, the introduction of a fourth element can be used in order to tune the stability. In

the second paper the influence of adding Zr to TiAlN is discussed. Zr is an element already in use in industry for other coatings and the paper shows that it is potential as an alloying element.

In conclusion, this thesis pushes the evolution of hard coatings by first contribute to the understanding on how of high pressure and high temperature (HPHT) affects the microstructure evolution of TiAlN and in particular when deposited on PCBN and secondly reports the effects and thermal stability of TiAlN alloyed with Zr.

2. Aim of the Thesis

The aim of this thesis is from a materials scientific point of view to increase the fundamental understanding of the decomposition of TiAlN at HPHT conditions and especially when it is deposited on PCBN. Furthermore, this work aims to increase the understanding of the decomposition of TiZrAlN at elevated temperatures.

3. Thin Films and Coatings

Thin films have a thickness in the range nanometers to micrometers and by that the meaning becomes narrower than coating. Thin films or multilayer of thin films are deposited on bulk materials that are referred to as substrates and this implies that the properties of bulk materials can be combined with the properties of thin films. This thesis pays attention to ceramic hard coatings that except high hardness also can give other benefits such as wear resistance, heat resistance, inertness, thermal shock resistance and this means that these can protect cutting tools against wear, corrosion and oxidation. Metal-cutting tools are mainly coated by either chemical vapor deposition (CVD) or by physical vapor deposition (PVD) [1].

The CVD technique makes use of chemical reactions between molecules referred to as precursors that preferably only contain the atoms that finally are to compose the thin film. The precursors are carried in to a reactor with a carrier gas and there the chemical reactions take place. One way of controlling the process is by changing temperature and some chemical reactions require high temperatures and in some cases up to 2000°C. One advantage of CVD is that complex geometries can be deposited [10].

Concerning PVD, it is based on physical processes and there are many different kinds of PVD techniques. All coatings in this thesis are deposited by cathodic arc evaporation, why the next chapter deals with this in particular. Evaporation based deposition methods together with sputtering

based methods are most widespread and especially for hard coatings magnetron sputtering and arc evaporation are commonly used [11]. In magnetron sputtering an ionized sputtering gas is used to bombard the solid target material in a way controlled by the magnetrons. [12]. It results in a controlled removal of target-atoms (ions and electrons). When these sputtered species reach the substrate a film may form. In the case of nitrides the film growth most often takes place in the presence of N_2 .

3.1 Reactive Cathodic Arc Evaporation

Cathodic arc evaporation is based on an arc or discharge between a cathode and an anode. The cathode consists of a material that contains the elements or some of elements of the thin film that is to be synthesized. For the deposition systems used for this thesis, a mechanical trigger acting as an anode has contact with the cathode a short time and when these are separated a discharge is formed [13]. The effect of the arc is that electrons, atoms and ions are evaporated from a locally heated spot. Due to the electric field in the arc the emitted electrons are accelerated and when these collide with the evaporated atoms ionization occurs. The net result is plasma with a high degree of ionization [14].

Generally, the substrates are negatively biased for the purpose to attract positive ions to the surfaces of the substrates and when ions reach the surface condensation occurs and this leads to nucleation and growth of a film [15]. It is also possible to let in a gas into the deposition chamber causing a reaction with the ions [16] and in the context of this thesis this gas was N_2 , which was the source of nitrogen to the studied nitride films.

Figure 1 shows schematically a deposition chamber.

For this work two different commercial deposition systems were used, but the principles behind the processes are the same. For Paper I, a system that is illustrated in Figure 1 was used. Here a TiAl cathode was used and the specially designed *c*-BN substrates were mounted in rows with clamps on a rotating drum at the same height as the center of the used cathode with the consequence of giving the same composition of all the thin films. During deposition the drum was rotating with 3 rpm. For Paper II a system with two cathodes mounted on the same height was used, where one cathode consisted of pure Zr and the other was a TiAl cathode. In this case, WC-Co substrates were used, that furthermore were mounted in columns on a fixture with each column having different distances from both cathodes. The idea was to get a composition gradient with different compositions in

every row. In this case the drum was stationary (no rotation) to ensure homogenous coating.

3.2 Thin Film Growth

Thin film growth includes many different processes, mechanisms and phenomena of which some of the most important for polycrystalline film growth are nucleation, crystal growth and coalescence. Film growth is a complex process and the mentioned phenomena do not only occur sequentially, but are part of many of the film growth stages. The outcome is finally a continuous film [17].

Primary nucleation means that adatoms i.e. atoms that have stuck to the substrate surface, form clusters (nuclei). For a nucleus to form a thermodynamical criterion have to be fulfilled and this is described with the critical nucleus size and if this size is not reached, the cluster is not stable and do not survive [18]. Nucleation occurs not only in the first stage of film growth and therefore there also exists concepts as repeated and secondary nucleation [19].

Crystal growth or island growth is when individual dispersed crystals grow from many nuclei, but when this occurs the final orientation is not always decided. This can later be changed, when it grows as part of a polycrystalline structure and there is for the collective behavior of the polycrystalline film a dependence of for instance grain size and surface conditions [17].

Coalescence is when larger islands grow at the expense of smaller ones, which happens when two islands come in contact with each other. The interfusing of the islands lead to a reorganization and the new island will become one single crystal. There are different mechanisms for coalescence, but the driving force is always to reduce overall surface energy or interface energy [19].

4. Materials Science

4.1 Phases and Phase Transformations

This work is basically about crystalline solids i.e. the studied materials have an ordered repeated structure even though these can consist of millions of atoms. The repeated structure is described as a lattice. Because the lattices are ordered, a unit cell that builds up the lattice can be distinguished [20]. For this thesis the most important unit cells are the body centered (bcc), faced centered cubic (fcc) and hexagonal clos packed (hcp) and a phase of a solid refers here to its crystal structure.

However, the phase of a material is not unchangeable, but transformations can occur due to changes in for instance temperature and pressure. Additionally, the phase of a material often depends on its composition. When doing experiments one or more factors are often set constant and another is varied i.e. the controlling factor [21]. For this work, temperature is always the controlling factor and for Paper 1 also time is considered. A phase transformation is governed by thermodynamics and kinetics and depending on situation and circumstances it can occur through different processes, which are described in the following two sections.

Stability of a phase is an important concept and in phase diagrams the phase for each condition refers to the stable phase. Material systems in

nature tend to be stable and if an unstable phase would appear, nature would aim to transform it to the stable phase. Thermodynamically, this is described with help of the free energy of the material system and the striving for stability is then expressed as minimization of the free energy.

For this thesis Gibbs' free energy, G , is used for a material system and with the enthalpy, H , the temperature, T , and the entropy, S , of the system it is expressed [22]:

$$G = H - TS \quad (1)$$

The minimization of energy gives then the condition for equilibrium as:

$$dG = 0 \quad (2)$$

The equilibrium condition is also fulfilled for non-global minima and in this case the phase is referred as a metastable phase.

4.2 Nucleation and Growth

A new phase can be formed by the forming and growth of nuclei, because the increase of size of a nucleus decreases the free energy. However, the forming itself of the nucleus increases the free energy and first when the nucleus has reached the critical radius, further growth leads to decrease of free energy. Thus, there is an activation energy barrier that has to be exceeded first. When the nucleation starts at a grain boundary or an impurity, it is considered as heterogeneous nucleation [23]. The growth

needs addition of atoms from the surrounding and thus diffusion takes place and this occurs downhill the concentration gradient [24].

4.3 Spinodal Decomposition

It is sometimes possible to obtain alloys i.e. solid solutions consisting of two or more constituents that are immiscible. In a phase diagram a region where these are immiscible is referred to a miscibility gap. The material system is characterized by not being resistant to infinitesimal changes that for instance could be a fluctuation of composition [25]. This means that there is no barrier to nucleation except barriers for diffusion and in contrast with nucleation and growth uphill diffusion takes place, i.e. diffusion of an element A occurs towards regions with higher A-concentration [26]. Subsequently, if there is a region enriched of one element this region will become even more enriched of the same element due to the spinodal decomposition [27].

The conditions for spinodal decomposition can be described thermodynamically with Gibb's free energy of mixing. For illustration, here an alloy between two constituents is used. In order to compare the solid solution between these and the two separate phases, the Gibb's free energy of mixing, ΔG_{mix} , is taken into consideration. ΔG_{mix} is the difference between Gibb's free energy of the multicomponent alloy and the free energy of the state, where the constituents coexist. These phases are not necessarily stable, but could also be metastable. Often this is expressed as a function of a composition variable i.e. the mole or atomic fraction of one of the constituents [27]. In this case this is denoted x_A . The ΔG_{mix} is in general a measure of the stability of a system or the tendency for

decomposition and in this context it is a measure of the driving force for spinodal decomposition.

Figure 2 shows the Gibbs' free energy of mixing as a function of composition. At point B, there is a maximum and a fluctuation of composition will always lead to a decrease in the total free energy and thus this point is unstable. However, the system is not only unstable at B, but also at all points between A and C, and this is the spinodal region. The reason is that the second derivative with respect to composition is smaller than zero, $\frac{\partial^2 \Delta G_{mix}}{\partial x_A^2} < 0$, that has the implication that any small fluctuation will lead to a decrease of the overall energy. The opposite condition, $\frac{\partial^2 \Delta G_{mix}}{\partial x_A^2} > 0$, will lead to separation by the nucleation and growth mechanism [24].

At an early stage, the precipitates are coherent in the sense that there is no lattice mismatch, even though there is a lattice mismatch when comparing them in their pure states. The maintenance of the coherency implies a strain in the lattices that in fact affects the hardness, because it affects the movement of dislocations [28]. If relaxation occurs after the spinodal decomposition, it implies increased lattice mismatch that also affects the hardness and thus there is an evolution of the hardness from initial solid solution and the precipitates.

Figure 2 shows the Gibbs' free energy of mixing for a binary system with a spinodal region.

4.4 Hardness and age hardening

The most important mechanical property of thin films for machining is hardness and therefore it is of relevance of this work. During machining with cutting inserts coated with TiAlN the temperature can reach 1000 °C [29,30] and thus not only hardness in the as-deposited state is of interest, but also the changes of hardness with temperature and time. Hardness in this context means the ability to resist against plastic deformation. One factor leading to a drop of hardness is movement of dislocations and one of the effects of the movement is slipping which in turn means a deformation. Consequently, design of hard composite materials aims to hinder this motion and one way of achieving that is to introduce coherency strains that

increases the energy needed for a dislocation to move between the domains [31].

Figure 3 shows age hardening for $Ti_{0.44}Zr_{0.17}Al_{0.40}N$.

Age hardening is a phenomenon that implies a higher hardness as precipitates in a solid solution form causing obstacles for dislocation motion [32]. If the formation is associated with an increase of temperature, this is beneficial for machining. In this study age hardening was observed for cubic $Ti_{0.44}Zr_{0.17}Al_{0.40}N$ correlated to the decomposition in Equation 3. Figure 3 shows the evolution of hardness with temperature for this specific

composition and it also shows age hardening. The increase of hardness after annealing at 1000°C is related to the spinodal decomposition in step 1 in the equation and it was also shown that the precipitates are coherent. Furthermore, the drop at 1100°C is related to the second step in the equation, when cubic AlN transforms to hexagonal AlN.

4.5 Theoretical Calculations

The calculations in this work aim to determine the phase stability of $Ti_xZr_yAl_zN$ by calculating Gibb's free energy of mixing with the Gibb's free energy defined in Equation 1 and where x, y and z are the fractions of each element and T is a given temperature. The free energy of mixing is then expressed in this case [6]:

$$\Delta G(x, y, z) = G(Ti_xZr_yAl_zN) - xG(TiN) - yG(ZrN) - zG(AlN) \quad (4)$$

The enthalpy, H , is calculated quantum mechanically by ab initio calculations in the density functional theory (DFT) framework and the entropy, S , is calculated with the mean-field approximation. For the enthalpy, H , different kinds of terms can be taken into account for instance a term for the relaxation energy [33] and another for vibrational energy. Here, it is described how the energy of a system with its atoms placed ideally in a lattice is calculated. In Paper II, where also relaxation energy is considered, the total energy for the ideal lattice is denoted E_{chem} and here also in the same way.

The main idea for determining E_{chem} is to solve the Schrödinger equation of the entire lattice, but this is not analytically possible for all cases and

therefore approximations are needed. The first approximation is to consider the nucleus as stationary, because it has a relatively much higher mass than electrons and this is referred to the Born-Oppenheimer approximation [34]. Instead of constructing complicated wave functions within DFT functionals of electron densities are used. This reduces the complexity of the problem, because the electron densities are only functions of three spatial coordinates. A lattice can have millions of atoms, but because of the periodicity in a crystal the Bloch-theorem states that the problem can be reduced by solving a unit cell and then expand the solution to the entire lattice [35]. If the crystal is not perfect, supercells are constructed out of the cells in order to get periodical boundary conditions.

For calculations of the entropy, S , only configuration entropy is considered and vibrational contributions are not considered and this is valid, when the difference in lattice parameter is small. The configuration entropy depends on the number of the configurations of the atoms in the lattice. For the calculations the mean field approximation was used and with this the configurations depend on the average compositions of each element together with the Boltzmann constant, k_B , and is expressed [33]:

$$S = k_B(x \ln x + y \ln y + z \ln z) \quad (5)$$

5. Material Systems

5.1 TiAlN

During the 1980's TiN was the most used hard coating for wear resistance until TiAlN was introduced later in the same decade [36]. Then cutting inserts coated with TiN already had shown to increase the cutting performance [37], but by adding Al the performance was even more pronounced, because it led to better wear resistance and oxidation resistance [38]. One of the reasons to improved wear resistance was the age hardening effect, that later was observed and explained [3]. The improved oxidation resistance was later explained due to an Al_2O_3 layer that is formed at elevated temperatures and this layer acts as a protection against oxygen diffusion into the film [39].

The miscibility of AlN in TiN and is not high, but with PVD it is possible to form metastable TiAlN solid solutions with fcc structure in the miscibility gap [40]. The $\text{Ti}_{x-1}\text{Al}_x\text{N}$ with two different compositions in this thesis has shown to be fcc and metastable. Because the solution is thermodynamically metastable elevation of temperature leads to spinodal decomposition i.e. to a state with a lower free energy and the products are *c*-TiN and *c*-AlN, see step one in Equation 4. However, the free energy can be even more lowered and that is by the phase transformation of *c*-AlN into its stable *h*-AlN phase [2,41], see step 2 in Equation 4. This second

transformation occurs by nucleation and growth [42]. Step 1 in the decomposition has been shown to start at around 800°C during isothermal annealing for 2 hours [2]. Age hardening is an effect of the spinodal decomposition and a drop of hardness is associated with the second phase transformation [3].

Concerning the pressure behavior of TiAlN, it has been shown theoretically that a pressure of 4 GPa at 0 K increases the solubility of Al in $Ti_{x-1}Al_xN$ and thus improving the stability of the system [43]. Before, it was also theoretically shown that the mixing enthalpy, i.e. the free energy of mixing at 0 K, increases as a consequence of applied pressure that in turn promotes spinodal decomposition. This mixing enthalpy was calculated for 0, 10 15 and 20 GPa [5]. Calculations have furthermore shown that the *h*-AlN phase is stabilized by pressure itself or temperature itself or an increase of these together [44,45].

Experimentally, it was later observed in line with calculations that a pressure of 2 GPa and a temperature of 900°C promotes the spinodal decomposition and this was done by comparing an annealed deposited cutting insert at ambient pressure with one used in a cutting test [46]. The stabilization of *h*-AlN has also been confirmed. This experiment was performed with a powder sample of TiAlN and with some different combinations of temperature and pressure. The temperatures were in the range 900 to 1700°C and pressure in the range 8 to 14 GPa [45]. In Paper I the contribution from this work to the studies about HPHT behavior of TiAlN is presented.

5.2 TiZrAlN

The studied TiZrAlN in this work is cubic. The evolution of Zr-based nitrides started with the binary ZrN, because it has high hardness [47] and good oxidation resistance [48]. When Ti was added, it was shown that the driving force for phase separation in *c*-TiZrN is low and even after annealing at 1200°C for 2 hours, the system remains in its multicomponent cubic phase. The subsequence is that the hardness is high also after annealing above 1000°C [49].

Another studied system is the addition of Al instead of Ti and for ZrAlN it has been shown that the miscibility gap is large [38], but because of the lattice mismatch between Al and Zr spinodal decomposition do not occur and instead *h*-AlN is formed by nucleation and growth while the cubic lattice approaches *c*-ZrN [50]. For the *c*-ZrAlN also age hardening has been observed [51].

The *c*-TiZrAlN system behaves differently from *c*-TiZrN and *c*-ZrAlN with respect to decomposition. A recent theoretical study showed that the system is not thermodynamic stable at 0 K and that it is tended to decompose through spinodal decomposition [7]. In Paper II the contribution to the studies of TiZrAlN from this work is presented. Hans Lind in Paper II made a similar calculation of the mixing enthalpy or the Gibb's free energy at 0 K, which is shown in Figure 4. It is seen that a mixture with a low Ti content and a Zr:Ti ratio of 1:1 is not stable. By increasing the Ti content, the composition gets less unstable. The TiZrN mixture has a very low tendency for decomposition. It seems that *c*-AlN is the most stable phase, but the calculations do not takes the hexagonal phase into account and the

transformation into *h*-AlN is still expected. The calculations show that Al is not tended to be mixed with Ti and especially not Zr.

Figure 4 shows the calculated mixing enthalpy i.e. Gibb's free energy at 0 K of *c*-TiZrAlN.

5.3 Tungsten Carbide

Tungsten carbide is one kind of cemented carbide and it is produced by sintering of powder of the composites together with a binder material [52].

In Paper II WC-Co is used as the substrate of the deposited films, where Co acts as the binder metal. Tungsten carbide is widely used for machining of for instance carbon steel and stainless steel [53] and the used substrates were commercial cutting inserts with hexagonal WC phase and cubic Co phase. The advantages of tungsten carbide are its high hardness and good wear resistance [52]. In comparison with diamond and PCBN it is cheaper to produce.

5.4 PCBN

PCBN inserts mainly consisting of *c*-BN are used for machining of hardened steel because it has advantages compared with cemented carbide and diamond. It is harder than cemented carbide and though it is softer than diamond it has the advantage of not being reactive with iron based alloys. The *c*-BN is the hardest material known next to diamond and has hardness around 50 GPa while diamond has around 90 GPa. Other benefits are high thermal conductivity and low chemical reactivity [54].

At room temperature the hexagonal phase of BN is stable and *c*-BN is synthesized by a HPHT process [55]. During HPHT conditions it is stable and therefore the tendency for revert phase transformation during machining is very low. In order to produce the PCBN another HPHT process is used i.e. sintering of *c*-BN powder and the other components of the composite. The used PCBN substrate in Paper I consists of *c*-BN ~90% and the rest is the binding material consisting of stable *h*-AlN, AlB₂ and traces of AlB₁₂. The composite is commercial, but for this work specially designed substrates instead of inserts were used.

6. HPHT experiments

The HPHT experiments were performed with a BELT system at Element Six in Robertsfors, Sweden. The BELT was invented to produce synthesized diamond and was also the first system making that possible commercially. Pressure is created mechanically and temperature by the means of resistive heating. The system has the capability to create and maintain pressures up to 10 GPa and temperatures up to 2000 °C during the time space of hours [56]. Figure 5 shows in a simplified way how one part of the system is constructed and with the arms this part is moved into another part of the press, where loads are created hydraulically. The pressure in the tube is created mechanically by applying forces on the dies. From the anvils the forces are transmitted to the tube that contains the samples and the material of the tube acts as the resistance for the resistive heating.

However, Element Six does not work with all possible pressures and temperatures and thus the HPHT conditions of the experiments had to be adapted to their production conditions and to their experience of creating high pressures and temperatures. In the experiments, the pressure was set constant to 5.35 ± 0.15 GPa, while the holding temperature was either 1050 °C or 1300 °C and with a holding time of either 6 minutes or 66 minutes. The tube was mounted in the BELT press at room temperature and ambient pressure. The heating power was during a first step of 2 minutes ramped to

half of the full power and during a second step of 10 minutes ramped to full power followed by a holding step of either 6 or 66 minutes. The cooling was during a first step of 6 minutes to half of the full power followed by a second step of 11 minutes to zero power.

Figure 5 is a simple illustration of one main part of the BELT press.

Each material piece was contained in a specially designed capsule illustrated in Figure 6. Four capsules were put in the pressure medium that finally was contained in a tube that was specially designed for this purpose. The capsule is first designed to create and maintain pressure and second to give a support in order not to destroy the sample. The separation discs were put in the capsule to make the recovery of the samples after the experiments easier. The inside of the capsule that during the experiments was in contact with the film side of the PCBN piece was deposited by spraying with Al_2O_3 and TiO_2 and this was to avoid chemical reactions between the thin film and the Nb-cup that otherwise would in contact with the sample. Temperature determination was based on previous measurements on a similar tube with the same design and the same

pressure medium and the pressures were determined with the used load and by the dimensions of the parts of the capsule. In order to recover the samples after each experiment the capsule and pressure medium were crushed with a hammer, the ceramic mechanical support by turning and the Nb-cup first by a blasting step followed by the use of pliers and scalpel. For some samples the Al_2O_3 and TiO_2 coating had sintered on the film surface and this cladding was not possible to remove.

Figure 6 shows schematically the construction of the capsule. The white space between parts is only there to make distinction between the parts.

7. Characterization Techniques

7.1 X-ray diffraction

X-ray diffraction (XRD) is an analytical technique based on the concept of constructive interference between X-rays. The phenomenon of constructive interference was first observed and explained for visible light. However, other kinds of waves can be used and even electrons, because they possess wave properties. In the case of a crystal or a lattice, atoms are formed repeatedly and regularly. Atoms are then aligned equidistantly in different planes and furthermore such planes in different directions can be distinguished [57]. In order to get diffraction, the wavelength of the incident beam has to be in the same order as the distance between parallel planes, which are in the order of a few Å. A wavelength in that order belongs precisely to the x-ray spectrum of electromagnetic radiation. If two different beams scatter from two parallel planes and the both scattered beams are still coherent, superposition of the beams will lead to constructive interference or diffraction. This condition can be expressed with Bragg's law [58]:

$$2d\sin(\theta) = m\lambda \quad (7)$$

Here d is the distance or spacing between two neighboring parallel planes, θ the incident angle of the beam and λ is the wavelength of the used wave. In Figure 7 XRD is schematically illustrated. One advantage of XRD is that it is a nondestructive technique [59].

Figure 7 illustrates the Bragg-Brentano geometry for X-ray diffraction.

In ex-situ measurements for this thesis a wavelength of $\lambda=1.540598 \text{ \AA}$ was used and furthermore the commonly Bragg-Brentano technique or θ - 2θ scan was used for XRD measurements. The idea is to vary the incident angle θ and for each angle measure the intensity. As can be seen in Figure 7 the incident angle and the diffracted angle are the same, however in the diffraction diagram the intensity is plotted as a function of the 2θ angle. With this setup only grains that have an orientation so that some of their

(hkl) planes are parallel to the surface of the sample can be identified in the corresponding diffractogram [60]

7.2 Transmission Electron Microscopy

Before the formulation of the electron Rayleigh's criterion of the resolution of a light-optical microscope (LOM) was formulated according to [61]:

$$r = 0.61 \frac{\lambda}{n \sin(\Theta)} \quad (8)$$

Here, r is the resolution limit, λ the wavelength of light, n the refractive index of the medium between the object and the lens. Visible light has roughly a wavelength between 400 and 700 nm and thus there is a lower limit of what can be resolved with light. Electrons have de Broglie wavelengths and it is possible to obtain wavelengths smaller than the ones for optical light. It is thus with the use of beams of electrons instead of photons possible to build microscopes with higher resolution than a LOM and it has been shown that Rayleigh's criterion is valid in this context too. In the studies of this thesis an acceleration voltage of 200 keV was used and it gives the relativistic de Broglie wavelength of 0.0025 nm [62].

The samples used in this work have a thickness less than 100 nm [63] and the electrons interact with the sample in different ways. These can be transmitted, absorbed, scattered or backscattered, but for TEM the advantage is mainly taken of transmission and scattering. Contrast is caused by differences in diffraction, phase, thickness and mass. By blocking diffracted beams with an aperture in the back focal plan a

brightfield (BF) image is obtained and this increases the diffraction contrast, because diffracted areas then appear darker [64]. A BF micrograph is shown in Figure 8.

Figure 8 shows a BF micrograph of PCBN deposited with TiAlN. The brightest areas in the bottom left corner are from c-BN grains that do not cause much diffraction due to the lower masses of B and N.

Bragg's law in Equation 7 is always satisfied for diffracted beams in a TEM and in the back focal plane the diffraction pattern was formed. For this thesis electron diffraction (ED) and in particular selected area electron diffraction (SAED) is used to determine crystal structure.

Figure 9 shows an SAED pattern of c-TiAlN. In this figure the diffracted planes represented with the rings are indexed.

For SAED only beams from a specific area for instance from a single grain is selected by blocking beams from all other areas with an aperture and therefore only beams from this selected area are collected in the back focal

plane. The diffraction pattern consists either of dots or rings. In Figure 9 there is an SAED pattern from an area of *c*-TiAlN coating.

Furthermore, for this thesis also scanning TEM (STEM) was used for which a nanoprobe is used for scanning all over the specimen [65] and when a high angle annular dark field (HAADF) detector is used, mass contrast is significant. When a HAADF detector combined with a high energy dispersive x-ray spectroscopy (EDX) detector is used, an elemental map can be obtained from the detected data. This is because the x-rays emitted when electrons interact with matter are characteristic for each element.

Another used analytical technique related to TEM is Electron Energy-Loss Spectroscopy (EELS). For EELS inelastic scattering between an incident electron and atoms are used that leads to excitation of the atom with the effect that the incident electron loses energy. The energy loss is dependent on from which subshell of the element the excitation occurs and the energy-loss is shown in an EELS spectrum [66].

7.3 TEM Sample Preparation

A sample for TEM needs to be electron transparent and that is thinner than 100 μm . For this study two different methods to prepare samples were used and the choice of method depended on the substrate used. For Paper I conventional sample preparation was used due to the tungsten carbide substrate (WC-Co) while with the harder PCBN substrate in Paper II that was not possible and instead focused ion beam (FIB) was used. The

drawback of a FIB sample is that it is in general thicker than a conventionally prepared one.

The FIB instrument uses an ion beam of Ga ions with energies of 5-50 keV in order to mill in a material piece on microscopic level. This gives the user the possibility to cut in the material and thereby by controlling the beam a cross-section for TEM can be shaped. FIB uses a very fine focusing and the accuracy on nanoscale level is very high, but for this high vacuum is needed [68].

Furthermore, the instrument used here is a combination of a FIB and a SEM for imaging. FIB is used for bombardment of ions of the thin film and the substrate while SEM is used for imaging. When the ions hit the surface, the material will be sputtered. The user can choose where to bombard the surface with ions and thereby the user works with a controlled machining or milling process

For the sample preparation a variant of the liftout technique was used [69]. Briefly, this means that an area of interest is first deposited with platinum. The area around is milled or dug to an appropriate depth. After that, a needle is attached to the sample and the sample is lifted out and moved to a copper grid, where sample gets welded followed by a thinning with the ion beam until it gets electron transparent. The grid can afterwards easily be put on the sample holder of the TEM.

Conventional TEM preparation consists of the steps mechanical polishing and ion milling. First, the sample needs to be cut and fixed in the grid. This was achieved by cutting smaller pieces of the sample so that two pieces together with their film sides facing each other could fit into the grid followed by baking with graphite and araldite. Thereafter, diamond

abrasive cloths with different grain sizes were used with 1 μm grain size in the final step while the thickness of the sample was around 50 μm .

The ion milling is made with bombardment of Ar-ions with energies in steps from 5 keV to less than 1 keV. The samples are hit with an angle of 5° and in a vacuum chamber. The milling ought to be stopped when electron transparency is achieved and in total it took around 10 hours.

7.4 Nanoindentation

In order to measure hardness, nanoindentation was used and the main idea is to put a continuous load with a tip on the sample and at the same time register the changes of indentation depth. When the load, P for causing plastic deformation is known and the contact area is given, the hardness is given by [70]:

$$H = \frac{P}{A} \quad (9)$$

The indents are too small to have their sizes accurately estimated by an optical microscope. Instead the contact area is calculated with the knowledge of the shape of the tip together with the recorded contact depth [70]. For this thesis a diamond Berkovich tip with a pyramidal shape was always used. The contact area for the particular used tip as a function of indentation depth was obtained with indentations in fused silica with already known material properties.

The sample was baked into a cylinder of bakelite and the sample was tilted so that polishing would give a tapered cross-section and before

measurement the surface was cleaned with acetone and mounted in the instrument. The points where the indents were set were selected carefully with an optical microscope and macro-particles from to the deposition process were avoided. In order to minimize impact from the substrate, the indentation depth was less than 10% of the film thickness. For statistical purposes 40 points were selected for each sample.

8. Summary of the Included Papers

Paper I

High pressure and high temperature behavior of TiAlN coatings deposited on c-BN based substrates

Paper I deals with the HPHT behavior of TiAlN deposited on PCBN. The pressure was set constant to 5.35 GPa and the time were either 6 or 66 minutes while the temperature was 1050 °C or 1300 °C. For comparative reasons TiAlN films were also annealed at ambient pressure. The results showed that the decomposition is slower at higher pressure compared to ambient pressure and that no chemical interaction takes place between TiAlN and PCBN during the HPHT experiments. It is concluded that this film has the potential to protect a PCBN substrate during metal machining due to a high chemical integrity.

Paper II

High temperature phase decomposition in $Ti_xZr_yAl_zN$

Paper II is about the high temperature phase decomposition behavior of TiZrAlN and it takes advantage of both theoretical and experimental methods. Calculations of the mixing free energy and the second directional

derivatives showed that for Zr-poor compositions the tendency for phase separation between ZrN and AlN is strong while the driving force for spinodal decomposition for Zr-rich compositions is low. During spinodal decomposition TiZrN is formed and the calculations predict that this phase is stable at higher temperatures. The experiments used XRD and STEM to confirm that a low Zr-content thin film had decomposed according to calculations after annealing while in comparison a high Zr-content film had shown a significantly reduced decomposition rate.

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