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Theoretical understanding of stability of alloys for hard-coating applications and design.

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Abstract

The performance of modern hard coating materials puts high demands on properties such as hardness, thermal stability and oxidation resistance. These properties not only depend on the chemical composition, but also on the structure of the material on a nanoscale. This kind of nanostructuring will change during use and can be both beneficial and detrimental as materials grown under non-equilibrium conditions transforms under heat treatment or pressure into other structures with significantly different properties. This thesis aims to reveal the physics behind the processes of phase stability and transformations and how this can be utilized to improve on the properties of this class of alloys. This has been achieved through the application of various methods of first-principles calculations and analysis of the results on the basis of thermodynamics and electronic structure theory.

Within multicomponent transition metal aluminum nitride alloys (TMAIN) a number of studies have been carried out and presented here on ways of improving high temperature stability and hardness. Most (TMAI)N and TMN prefer a cubic B1 structure while AlN is stable in a hexagonal B4 phase, but for the purposes of hard coatings the metastable cubic B1 AlN phase, isostructural with the TMN phase is desired. It will be shown how the introduction of additional alloying components, such as Cr, into (TiAl)N changes the thermodynamic stability of phases so that new intermediary and metastable phases are formed during decomposition. In the case of such a (CrAl)N phase it is shown to have greater thermodynamic stability in the cubic phase than the pure AlN, resulting in improved high temperature hardness. Also, the importance of treating not just the binodal decomposition through the formation energy relative to end products but also the impact of spinodal decomposition from its second derivative due to the topology of formation energy surfaces is emphasized in the thesis. The impact of pressure on the AlN phase has also been studied through the calculation of a P-T diagram of AlN as part of a (TiAl)N alloy.

During the study of chemical alloying of TM components into AlN the alloying of low concentrations of these TM were treated in great detail. What is generally referred to as the AlN phase in decomposition is not entirely pure and can be expected to contain traces of any alloying components, such as Ti and Cr or whatever other metals may be present. Low concentration alloying of Cr, on the order of 5-10% is also shown to be stable with regard to isostructural decomposition. Detailed analysis of the effect of Ti and Cr impurities in AlN has been carried out along with a systematic search of AlN alloyed with small amounts of other TM components. The impact of these impurities on the electronic structure and thermodynamic properties is analyzed and the general trends will be explained through the occupation of impurity states by d-like electrons.

Theoretical treatment of such impurities is not straightforward however. AlN is an s-p semiconductor with a wide band gap while TM impurities generate states of a d-like nature situated inside the band gap. Such localized impurity states are expected to give rise to magnetic effects due to spin dependent exchange, in addition strong correlation effects might have to be taken into account. For that reason the use of hybrid functionals with orbital corrections according to the mHSE+Vw scheme, developed specifically for this class of materials, has been used and shown to influence the results during calculation of impurities of Ti and Cr.

In nanocomposite multilayered structures, composed of very thin layers of one material sandwiched between slabs of another, such as layers of SiN between TiN or ZrN, the material properties are greatly affected by the interfaces. In addition to the thermodynamic effects and lattice strains of the interfaces one also has to consider the atomic vibrational motion in the interface structure. Hence, dynamical stability of these thin multilayers is of great importance. As part of this thesis, results on the thermodynamic and dynamical stability of both TiN-SiN layers and ZrN-SiN will be presented. It will be shown that due to considerable dynamical instability in the interface structure of monolayered B1 SiN sandwiched between isostructural layers of B1 ZrN along (111) interfaces this structure cannot be expected to grow, instead preferring the stable (001) direction of growth.

Populärvetenskaplig sammanfattning

Prestandan hos moderna material för hårda ytbeläggningar ställer höga krav på flera material egenskaper, inklusive hårdhet, temperatur stabilitet, oxidations beständighet mm. Många av dessa egenskaper beror på den struktur som materialet antar på nanometer skalan. Dessa strukturer kan också förändras under användning, som följd av hög temperatur och tryck. Förståelse för de processer som är inblandade i den strukturella stabiliteten hos dessa material blir av stor vikt och denna avhandling syftar att öka förståelsen av dessa via teoretiska datorberäkningar.

I legeringar av övergångsmetaller och aluminium nitrid (TMAIN) beror mycket av materialegenskaperna på bildandet av regioner av AlN och nitrider av övergångsmetallerna (TMN). TMN föredrar i allmänhet en kubisk struktur medan AlN är stabil i en hexagonal struktur, men för dessa hårda legeringar är kubisk AlN att föredra då bildandet av hexagonal AlN kan ha negativa konsekvenser för materialets hårdhet. Ett antal metoder för att stabilisera kubisk AlN har studerats, inklusive effekten av tryck och temperatur så väl som kemisk legering med ytterligare komponenter och hur det påverkar den sönderfallsprocessen så att det bildas metastabila mellanfaser vilka tillåter mera fördelaktiga egenskaper. Det noteras också hur fas stabilitet påverkas inte enbart av de termodynamiska förhållandena mellan slutprodukter utan även av topologin hos energiytorna vilket resulterar i metastabila tillfälliga faser med potentiellt fördelaktiga egenskaper. Effekten av tryck och temperatur på stabiliteten har också observerats genom beräkning av ett fasdiagram för AlN satt i perspektiv av att fasen befinner sig i en TiAlN legering.

Genom studien av kemisk legering av metaller i AlN så hanterades även situationer med låga koncentrationer av legeringskomponenter. Dels en systematisk genomsökning av AlN med olika TM komponenter där trender i elektronstruktur och termodynamiska storheter diskuteras och förklaras genom elektronernas besättning av olika atomlika elektrontillstånd. Men AlN är en halvledare där banden består av s-p orbitaler och övergångsmetallerna introducerar störellektroner av d-orbital natur i strukturen. Kombinationen av olika typer av orbitaler kan vara svår att hantera med de mer traditionella metoder som används för beräkning av materialegenskaper. Dessutom kan dessa störellektroner resultera i magnetiska egenskaper som skiljer sig drastiskt från de ingående komponenternas. För att bättre kunna hantera den elektroniska strukturen hos dessa störellektroner har vi använt en metod kallad mHSE+Vw, utvecklad speciellt för hantering av material av denna karaktär, på strukturer av AlN med tillsatser av Ti och Cr.

I nanokomposit multilager ligger tunna skikt av ett material mellan regioner av ett annat, exempel inkluderar lager av SiN mellan TiN eller ZrN. I dessa material

påverkas stabiliteten till stor del av gränsytorna och utöver andra egenskaper måste även hänsyn tas till den dynamiska stabiliteten på atomnivå. I alla material vibrerar atomerna runt jämnviktspositioner, men om atomerna inte kan finna sådana jämnviktspositioner för en viss struktur kan det inte heller hålla en stabil kristallstruktur. I denna studie presenteras hur den dynamiska instabiliteten hos lager av SiN mellan ZrN påverkar tillväxtordning och kan förhindra att vissa strukturer kan bildas.

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Chapter 1 - Introduction

1.1 Hard coating materials

Industrial machining tools present high demands on material properties, including high hardness, high temperature stability and oxidation resistance, as a few examples. One way to improve such properties is to coat a tool with a thin layer of a harder material such as transition metal nitrides (TMN). Using hard coatings on top of another material will serve to protect the underlying material and combines high strength substrates with a high hardness coating that protects from scratches or wear. That way lifetime is extended, allowing for higher performance materials resulting in more efficient and less cost-intensive application. As such development of new and advanced materials with increasingly beneficial properties becomes of great importance.

The material properties of hard coating alloys depend not only on chemical composition but also on structuring of various phases on a microscopic scale. A phase is a homogenous region of a material with a distinct and homogenous crystal structure and chemical composition. A bulk material may contain multiple domains, each of which is a specific phase separated from each other by phase boundaries. This phase structuring can change during use through phase transformations driven by alloy thermodynamics when conditions such as temperature and pressure changes, resulting in changes in material properties, a process that can be both detrimental or beneficial. One commonly used material in hard coating applications is (TiAl)N, which developed out of alloying TiN with AlN in the 1980s. As-deposited (TiAl)N in a single, homogeneously mixed phase is of little use in applications but heating the material will cause phase transformations separating the alloy into coherent domains of cubic TiN and AlN, increasing the hardness as the temperature increases up to 7-800°C. Further heating up to and beyond 900°C results in a sharp decrease in hardness due to further phase transformations as the metastable c-AlN transforms into a stable, hexagonal w-AlN phase[1].

A thorough understanding of the thermodynamics of phase stability and how one can use them to influence the transformation process in order to maintain beneficial microstructuring at ever more extreme conditions is of significant importance. While experimental observations are always useful and will provide accurate and reliable results on the properties of specific alloys, theoretical and computational work is also of great value and a field of growing importance, especially in terms of understanding the processes underlying the observable phenomena. Shortcomings of doing experiments alone include that they don't necessarily explain the why of a specific transformation; in addition experiments are very expensive and time consuming and it

is not possible to try out every conceivable material without having some idea of what to look for. Theoretical understanding in combination with modern computer simulations can give greater predictive power in trying to find potentially superior materials in advance of experiments. Thanks to the advances in computer technology of the past decades such calculations are also becoming more accurate and reliable, future advances will serve to make this field of research even more important.

Fundamental to the properties of any material is the principles of quantum mechanics, atoms bond into molecules and solids due to the interactions between electrons and nuclei[2]. These interactions are described through quantum mechanical equations such as the Schrödinger equation. However, direct application of such methods on a system of many interacting particles is in the general application completely unreasonable due to the large amount of particles and degrees of freedom. One of the most important steps leading up to the modern treatment of atomic theory was the development of Density Functional Theory (DFT), the basic principle of which is to change the problem of multiple interacting particles into another, consisting of individual, non-interacting particles inside an effective potential generated by the external potential as well as the total electron density. DFT was given its first practical methodology through the work of Hohenberg, Kohn and Sham in the 1960s. The theorems of Hohenberg and Kohn as well as the Kohn-Sham equation gave us the fundamental tools by which the electronic structure of materials can be determined. But it would take until the 1980s before computer technology reached the level where calculations started to become practical. The continued development of ever more powerful computers allow for more sophisticated calculations to be carried out on a wider range of materials.

1.2 Outline

The purpose of this thesis is to bring greater understanding to some of the processes involved in the phase stability and transformations of alloys used in hard coating applications. In particular how they respond to pressure, temperature and chemical alloying of additional component elements, but also how certain multilayer structures are dependent on the dynamical stability due to atomic vibrations.

The thesis will begin with a section on the theory used in this work. First the fundamental principles of quantum mechanics, many-body theory and density functional theory (DFT) as well as the different computational methods used in this work. I will follow this with a discussion on phonons and lattice vibrations and how they are calculated. There is also a chapter on the theory of alloys, including a number of ways how the atomic structure of the alloy can be modeled for the sake of calculations. There will also be a discussion on the principles of thermodynamic stability and phase decompositions.

Once the theory used has been established I continue with describing my own work, first a discussion on the behavior of multicomponent alloys of (TiAl)N, (TiCrAl)N and (TiZrAl)N, such as how the specific topology of the formation energy surface can result in the formation of intermediary metastable phases that improve material properties. The specific topology of the formation energy surface can also be seen to stabilize certain alloy phases despite them being thermodynamically unstable. Results on the pressure-temperature dependence of the AlN phase in (TiAl)N will also be presented. Of importance throughout this is how the phase decomposition and resulting material properties depend on the conditions of the AlN phase and how this

can be exploited. From this I will lead on to further discussion of the AlN phase and how it is affected by alloying with small concentrations of TM impurities, what happens to their electronic structure, how they can form magnetic phases even though the individual components are non-magnetic and how that impacts thermodynamic properties and overall phase stability of alloys. These sections will include both detailed calculations on Ti and Cr impurities as well as a systematic search across all TM to learn about general trends. Finally there will be a section on nanocomposite materials consisting of layers of transition metal nitrides (TMN) surrounding thin layers of SiN and how they are affected not only by the thermodynamics of the interfaces but also by the dynamical stability of atomic vibrations in the interface layers.

Finally, the thesis will conclude with a summary and a list of all publications that are part of this work.

Chapter 2 - Fundamental Theory

This chapter will detail the theoretical background and methods used throughout this thesis. First the density functional theory will be introduced, along with the methods through which it has been applied and various methods for describing the exchange-correlation effect, which is the biggest bottleneck of this method responsible for turning it into an approximate rather than exact theory. There will also be a section on the theoretical understanding of phonons and how they influence the behavior of materials along with a method for calculating these, the density functional perturbation theory. Finally a section will describe certain aspects of electron-phonon coupling along with an example relating to scattering processes.

2.1 Density functional theory

While the theory of quantum mechanics contains all the fundamentals for understanding materials on an atomic scale, the direct application of it in interacting many-body systems becomes unmanageable due to the large number of particles and parameters involved. The method of Density Functional Theory (DFT) overcomes this by treating the system as non-interacting electrons located in an effective potential generated by the total electron density as well as the external potential from sources such as the atomic nuclei[2-3]. While the total wave function has three degrees of freedom per electron, excluding spin, the electron density is a scalar function dependent on three degrees of freedom total, excluding spin, regardless of the number of electrons involved. An early version of a theory based on the density as opposed to the wave functions, the Thomas-Fermi theory, was developed during the 1920s[4-5] but failed due to being too crude and involving too many simplifications. A fundamentally exact method was developed in the 1960s by Hohenberg, Kohn and Sham[6-7] and with the help of improvements in computers during the 1980s and onwards it has become possible to carry out reliable calculations of materials on an atomic scale.

2.1.1 Quantum mechanics and many-body systems.

Quantum mechanics dictates how atoms and electrons interact with each other on a fundamental level. One way to describe quantum particles is through the Schrödinger picture, where the particles are treated in the form of waves. In this picture the fundamental relation that allows for the state of any quantum system to be described in the form of a wave function Ψ is the well-known Schrödinger equation[8].

$$i \frac{\partial \Psi}{\partial t} = H \Psi \quad (2.1)$$

In this equation H is the Hamiltonian operator, given a system of electrons and nuclei it takes the form

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{e^2}{4\pi\epsilon_0} \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.2)$$

where the terms represent the kinetic energy for electrons and nuclei as well as the electrostatic interactions between electrons, electrons and nuclei, and between nuclei. Ψ is the wavefunction describing the full state of all the particles of the system. This wave function has parameters based on coordinates for each of the electrons, $\mathbf{r}_i$, coordinates for each of the nuclei, $\mathbf{R}_I$, as well as their respective spin, σ_i and σ_I and the time t . As the number of particles increases the number of parameters increases as well. In an atomic system only single electrons can be solved analytically with the Schrödinger equation and the full numeric solution of many particle systems quickly becomes far too complex to be carried out. Approximations are essential for the effective solution of many body problems like this. If we assume that the Hamiltonian is not explicitly dependent on time then the time and spatial coordinates of the wave function can be separated and the time-independent Schrödinger equation can be used to obtain the stationary states.

$$E\Phi = H\Phi \quad (2.3)$$

Now the wave-function Φ is the time-independent, or stationary state, component of Ψ and E is the constant total energy of the system. The time-dependence is treated separately and is independent of the actual system configuration and external potentials. Another important approximation is the Born-Oppenheimer approximation[9], which is based on the fact that since the nuclei are several orders of magnitude heavier than the electrons their dynamics will also be correspondingly slower. This means that it is possible to decouple the dynamics of the electrons from the nuclei and treat the wave-function of the electrons as if the nuclei present a constant external potential while their kinetic energy is zero. This way the electrons can find their stationary states according to eq (2.3) without being significantly affected by the time-dependent dynamics of the nuclei. Also, the interaction between the nuclei becomes constant and can be neglected. If the atomic structure is periodic, then the Bloch theorem[10] demonstrates that the solutions to the Schrödinger equation has the property according to eq (2.4) where $u_{i,k}(\mathbf{r})$ is a periodic function with the periodicity of the external potential. In other words, the wave function can be described as a plane wave multiplied by a periodic function and therefore calculations can be carried out on just the periodically repeated unit cell.

$$\psi_{i,k}(\mathbf{r}) = e^{ik \cdot \mathbf{r}} u_{i,k}(\mathbf{r}) \quad (2.4)$$

Despite all these approximations, the many body problem is still unsolvable through direct application of the Schrödinger equation. In a system of n electrons there is still a total of $3n$ degrees of freedom, which is far too many for any practical consideration. One method that can be used is the Hartree-Fock approximation[11],

and while it does not reduce the amount of parameters it eliminates some parts of the electron correlation by treating the wave function as a Slater determinant. However, the dominant method within electron structure theory and atomic calculations is the DFT, due to the relative simplicity of being able to treat the system of multiple particles as a background electron density.

The above text mentions the spin as being part of the wave function, but the spin cannot be directly obtained from the Schrödinger equation and has been considered here in a simplified ad-hoc manner. A full understanding of fermions requires the use of relativistic functions such as the Dirac equation. But the Dirac equation is cumbersome and for the sake of clarity and without losing any significant points, throughout this and the following chapters the description is made through the non-relativistic theory according to Schrödinger.

2.1.2 Hartree-Fock

The purpose of DFT is to circumvent the difficulties of many-body calculations, in particular the large number of parameters, by replacing the problem with another, simpler, effective system. But there are times when it is practical, or necessary to do some form of many-body calculations instead. One well-known method for this is through the Hartree-Fock (HF) approximation, first developed by Fock[11] as an enhancement to the equations by Hartree[12]. Assuming no spin-orbit interactions one begins with the writing of an anti-symmetrized many-body wave function in the form of a Slater determinant.

$$\Phi = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_1(\mathbf{r}_2, \sigma_2) & \cdots \\ \phi_2(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_2, \sigma_2) & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} \quad (2.5)$$

Here the $\phi_i(\mathbf{r}_j, \sigma_j)$ are the single particle wave-functions, defined as a product of the position based wave-function $\psi_i^\sigma(\mathbf{r}_j)$ and the spin variable $\alpha_i(\sigma_j)$. If the spin variables are orthonormal and the Hamiltonian is spin independent then it is possible to show that the expectation value is as follows:

$$\begin{aligned} \langle \Phi | \hat{H} | \Phi \rangle &= \sum_{i,\sigma} \int d\mathbf{r} \psi_i^{\sigma*}(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) \\ &+ \frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma_i*}(\mathbf{r}) \psi_j^{\sigma_j*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^{\sigma_i}(\mathbf{r}) \psi_j^{\sigma_j}(\mathbf{r}') \\ &- \frac{1}{2} \sum_{i,j,\sigma} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma*}(\mathbf{r}) \psi_j^{\sigma*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^\sigma(\mathbf{r}) \psi_i^\sigma(\mathbf{r}') \end{aligned} \quad (2.6)$$

The first term is the sum of single particle expectation values, summed over each orbital. The second term is the direct interaction energy between electrons and the third is the exchange energy. The exchange term depends only on interaction between same spin electrons due to the orthonormality between spin orbitals. The summations include the self-interaction terms $i = j$ since they cancel each other out between the direct and exchange terms. The objective of the Hartree-Fock approach is to minimize the total energy due to all degrees of freedom, a daunting task in most situations due to the large number of parameters.

While this approximation provides both a cancelation of the self-interaction terms and the introduction of an exact exchange energy term, the main drawback is the initial

description of the total wave function as being made up of independent single particle wave functions. Consequently it does not include correlation effects, making it an approximation rather than exact theory. Despite this the Hartree-Fock approximation can still give good results and has seen use in quantum chemistry applications. As will be discussed later in this thesis there are ways of combining the exact exchange of HF with a DFT method to improve on the exchange-correlation functionals.

2.1.3 Hohenberg-Kohn theorems

The early methods of density based theory according to Thomas and Fermi[4-5] was based on the density of a homogenous gas with density equal to that of the local density at a given point. They also neglected both exchange and correlations and even though Dirac later extended their scheme with an approximation for exchange[13] the method remains too inaccurate for modern use. The foundation for the modern description of DFT was developed by Hohenberg and Kohn in their influential 1964 paper[6]. Their intention was to develop DFT as an exact theory of many-body systems and in this paper they presented two theorems that serve as the basis for the theory that follows.

1. For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, this potential is determined uniquely up to a constant, by the ground state particle density $n_0(\mathbf{r})$.
2. A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

According to the first theorem, if we can determine the electron density of the system, then we can also determine the external potential on individual electrons and with that all properties of the system. In addition, the second theorem tells us that if we can find a density that minimizes the energy then we also know that we have both the correct ground state density and energy. All that is needed is the energy functional $E[n]$, which is not given by these two theorems.

2.1.4 Kohn-Sham equation

The two theorems of Hohenberg and Kohn tells us that the ground state electron density $n_0(\mathbf{r})$ can give us any properties of the system and that this exact density can be obtained from the external potential $V_{ext}(\mathbf{r})$. What they did not provide was a scheme for actually obtaining these things. This was accomplished a year after the publication of the Hohenberg-Kohn theorems when another paper was published that presented a method for actually solving the density functional problem. This paper by Kohn and Sham [7] introduced the Kohn-Sham equation, which has become the foundation for the modern methods of density functional theory. Kohn and Sham proposed replacing the system of many bodies of interacting particles with non-interacting particles that have the same total density as the real system. The external potential is then replaced with an effective potential $V_{KS}(\mathbf{r})$ generated both by external influence as well as the total electron density $n(\mathbf{r})$ defined as the sum of the square of all electron eigenfunctions $\psi_i(\mathbf{r})$.

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (2.7)$$

Since the individual electrons are non-interacting according to KS, applying the one-electron Schrödinger equation can solve the problem. In addition, if we assume a steady-state system it is possible to use the time-independent version.

$$\left(-\frac{\hbar}{2m} \nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2.8)$$

The effective potential is then defined as follows:

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (2.9)$$

The first term is the external potential, generated by for instance the ionic cores, electric fields etc. The second term is the Hartree energy, imposed by the electron density rather than individual electrons, and the last term is the exchange-correlation potential, with $E_{xc}[n(\mathbf{r})]$ as the exchange-correlation energy functional. Since the potential depends on the electron density, which in turn depends on the potential the solution will require a self-consistent scheme. This equation, according to (2.8) and (2.9) is called the Kohn-Sham equation and is in principle exact. The only exception is the exchange-correlation term for which no exact form exists, meaning it has to be approximated. The Kohn-Sham equation itself is independent of the actual form of the exchange-correlation functional and methods for approximating it can be developed independently. There are multiple ways in which these functionals can be designed and the development of new methods is an ongoing process. The choice of which methods to use is also a non-trivial matter and some methods, commonly used and new ones, will be discussed later in this thesis. But in general the Kohn-Sham equations are exact and any physical system will be well defined, exactly reproducible and unique, according to the Hohenberg-Kohn theorems. In addition, assuming an exact exchange correlation functional the solution would be exact as well. But no such exact functional exists so the exact solution is in practice not a possibility.

Through the Kohn-Sham equation, it is possible to obtain the single electron wave functions where the N lowest spin-dependent levels are occupied, where N is the total number of electrons in the system, or $N/2$ levels in a spin-degenerate system. The total wave function is then the combination of all the one-electron wave functions. The obvious advantage is that the problem can now be solved as a simple 3-D equation as opposed to a 3N-D Schrödinger equation.

2.1.5 Exchange-correlation functionals

As mentioned in the previous section, the Kohn-Sham equation is exact with the exception of the exchange-correlation functional, here given as $E_{xc}[n(\mathbf{r})]$ in a general form. But since the exact form of the exchange-correlation is not known, various approximations are needed and several methods for determining the exchange-correlation exist, the preferred choice may depend greatly on the system that is being calculated, and depending on the system and property calculated, one method may be preferable over another. Development of new methods is an ongoing process and a

few of these methods, old and established as well as new methods recently developed, will be described here.

Local density approximation (LDA)

The simplest, and earliest, method for determining the exchange correlation is the so-called local density approximation (LDA). It was proposed by Kohn and Sham in their original paper[7] and is based on the assumption that the exchange-correlation in any point is equal to the exchange-correlation of a homogenous electron gas of the same density.

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{hom}(n(\mathbf{r})) \quad (2.10)$$

In this equation $\varepsilon_{xc}^{hom}(n(\mathbf{r}))$ is the exchange-correlation energy of a single electron in a homogenous electron gas of density $n(\mathbf{r})$ and it can be determined with good accuracy as the exchange energy is an analytical expression and the correlation energy, whatever energy isn't included in the exchange, has been determined with great accuracy through Monte Carlo calculations[14]. This approximation works well in solids with an electronic structure close to that of a homogenous electron gas, such as nearly-free-electron metals but starts to fail as the charge density changes rapidly. The worst approximation would be for atoms or solids with highly localized charge distribution.

Another problem with the LDA method is the spurious self-interaction energy it generates[15]. In the Hartree-Fock method the self-term in the Hartree interaction is exactly canceled by the exchange term. However, due to inexact exchange energy in the local approximation this self-term is only approximately canceled. What remains is negligible in the homogenous gas but can be quite large in a system of localized charge, such as an atom. Despite these issues LDA has proven itself useful in many situation, even some very inhomogenous cases. It has also served as the groundwork for other, improved, methods that have been developed from it.

Generalized Gradient Approximation (GGA)

While the LDA is a very useful, and in some cases accurate, method it also has flaws. One other method that has been developed to try to address some of the problems that LDA has is the Generalized Gradient Approximation (GGA). There is no single method for determining a GGA functional but multiple functionals have been developed[16-18]. One of the most popular, and the one mainly used for the work in this thesis, is the one by Perdew, Burke and Ernzerhof[19]

The main point of the GGA is to incorporate not only the local value of the electron density $n(\mathbf{r})$ into the functional, but also its gradient $\nabla n(\mathbf{r})$. GGA functionals are described in a generalized form similar to the one for the LDA.

$$\begin{aligned} E_{xc}[n(\mathbf{r})] &= \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) \\ &= \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{hom}(n(\mathbf{r})) F_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) \end{aligned} \quad (2.11)$$

In this form $\varepsilon_{xc}^{hom}(n(\mathbf{r}))$ is the same as in the case of LDA and $F_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$ is a dimensionless functional that scales the exchange-correlation. Several different forms of this function have been developed, each one designed to meet specific criteria. Use

of GGA functionals will improve on results compared to LDA in many cases; most notably it improves on the determination of lattice parameter in several materials. GGA is not always an improvement on LDA though and each GGA functional has its own advantages and disadvantages.

There are also a number of situations where both LDA and GGA fail. They are both still based in a (semi)local theory of non-interacting particles and treat many-body effects in an approximation, as such they suffer problems in self-interaction as well as incorrect exchange and correlations. This can result in underestimation of band gaps and they also tend to fail in treating highly correlated systems such as localized electron impurity states. As will be seen, this extends to some of the materials discussed within this thesis.

LDA+U

One way for treating systems of strongly correlated electrons is the LDA+U[20-22] developed by Anisimov. This method is useful in materials consisting of both localized d-orbitals and delocalized s and p orbitals for instance, due to its introduction of an orbital dependent correction to the potential that treats the d-d orbital interactions without altering the s and p interactions. This is accomplished through the interaction energy according to a Hubbard Hamiltonian[23]. The new energy functional is defined as

$$E_{DFT+U} = E_{DFT} - U \frac{N(N-1)}{2} + \frac{1}{2} U \sum_{i \neq j} n_i n_j \quad (2.12)$$

Here the second term is the coulomb energy of d-d interactions according to DFT and is subtracted while the third term is the Hubbard interaction energy between the same. $N = \sum_i n_i$ is the total number of correlated electrons treated by this method summed over all relevant orbitals where n_i is the occupation number for orbital i . The U is called the Hubbard U and is related to the coulomb interaction between electrons and has to be determined separately, often taken as the value that best reproduces experimental results. From this equation one can derive a correction to individual electron orbitals according to

$$\varepsilon_i = \frac{\partial E_{DFT+U}}{\partial n_i} = \varepsilon_{DFT+U} + U \left(\frac{1}{2} - n_i \right) \quad (2.13)$$

In this form it is seen that the DFT orbital energies are shifted down $-U/2$ for occupied orbitals ($n_i = 1$) and up by the same amount for unoccupied orbitals ($n_i = 0$).

It is possible to rewrite the above energy functional in the following form that will be seen to be useful in the upcoming sections.

$$E_{DFT+U} = E_{DFT} + \frac{1}{2} U_{eff} \sum_i (n_i - \langle n_i \rangle)^2 \quad (2.14)$$

Here, the $U_{eff} = U + J$, where J is the Stoner J . Additionally the following potential correction for a specific orbital n_i can be obtained.

$$\Delta V_i^{DFT+U} = U_{eff} \left(\frac{1}{2} - n_i \right) \quad (2.15)$$

As such, the DFT+U method can be applied to a subset of strongly correlated orbitals, while the remaining are treated under normal (semi)local DFT.

2.1.6 Hybrid functionals

Another class of functionals are the hybrid-DFT functionals[24]. They are based on the idea of mixing in the exact exchange energy from Hartree-Fock with the approximation given by the semilocal DFT. Apart from a more exact exchange energy this can give improvements in terms of the self-interaction error seen in LDA and GGA. But due to its consideration of wave function as based on independent single particle orbitals it will not include correlations, which have to be drawn exclusively from the DFT functional. This correlation may still be improved as the exchange affects the wave functions and indirectly the correlation component. One common method for hybrid treatment is the PBE0 functional[25], defined from the following expression where α is the parameter of mixing as a portion of the exchange from the DFT is replaced by the exchange from HF as defined in the last term of eq (2.6).

$$E_{xc}^{PBE0}(n, \{\psi_i\}) = E_{xc}^{PBE}(n) + \alpha E_x^{HF}(\{\psi_i\}) - \alpha E_x^{PBE}(n) \quad (2.16)$$

Another version of hybrid functionals is the HSE06 method[26-27]. This method is similar to the PBE0 hybrid, except it limits itself to mixing the short-range (sr) exchange, the exchange energy within an adjustable cutoff radius.

$$E_{xc}^{HSE06}(n, \{\psi_i\}) = E_{xc}^{PBE}(n) + \alpha E_x^{HF, sr}(\{\psi_i\}) - \alpha E_x^{PBE, sr}(n) \quad (2.17)$$

There are still limitations in this method however, since this correction only applies to exchange energy and the mixing parameter is applied to all orbital interactions equally.

2.1.7 HSE06+Vw

The method of hybrid-DFT+Vw was developed by Ivády et al[28-29] and came out of a discovery of similarities between DFT+U and hybrid functionals in terms of corrections to energy and potential. In these papers Ivády *et al* showed that the correction to exchange energy of the subsystem of correlated orbitals i through the application of a hybrid functional can be described as

$$\Delta E_x^{hybrid} = \frac{\alpha(F^0 - J^0)}{2} \sum_i (n_i - (n_i)^2) \quad (2.18)$$

In this n_i are the occupation numbers of the considered orbitals, F^0 and J^0 are the spherically averaged unscreened direct and exchange parameters of the Coulomb interaction. The correction to the potential in turn is given by

$$\Delta V_i^{hybrid, x} = \alpha(F^0 - J^0) \left(\frac{1}{2} - n_i \right) \quad (2.19)$$

The similarity to the equivalent equations for LDA+U, eq (2.14) and (2.15), is obvious. As discussed above in the section on hybrid functionals, α is the mixing parameter between HF and DFT exchange and it is the same for all orbitals, giving a homogenous screening of all electron-electron interactions. This can make treatment of a system consisting of different types of orbitals, such as sp^3 and d , problematic. But with the discovery that these correction terms are mathematically similar to those of DFT+U it becomes possible to apply the formalism of DFT+U to introduce additional orbital dependent screening

$$V_i(w) = w \left(\frac{1}{2} - n_i \right) \quad (2.20)$$

to localized orbitals in a hybrid functional. Here w is an energy correction parameter to be determined separately. In addition to being able to treat all orbitals in an efficient and accurate way this method is based on other methods that are well used and already implemented in existing codes. As such, it may be implemented with the tools already in place for hybrid functionals and the DFT+U scheme.

Determining the parameter w

In order to make use of this method, one has to have a value for w . The U in DFT+U scheme is typically determined so that the results best match experiments. In principle that could be done here as well but one method for determining w self-consistently, provided by Ivády[29], is to make use of and fulfilling the generalized Koopman's theorem (gKT)[30-32]. The Koopman theorem states that the KS eigenvalue of the highest occupied (lowest empty) orbital is equal to the change in total energy if an electron is removed (added) to the system assuming all other orbitals remain unchanged. From this, the non-Koopman's energy E_i^{NK} [32] is defined as the difference in energy between the highest occupied (lowest empty) KS eigenvalue ε_i and the change in total energy ΔE_N due to removing (adding) an electron. Consequently, the non-Koopman's energy may be applied as a measure of the quality of a functional by observing how the total energy changes as orbital occupations change. One has to consider though, that in a charged periodic system there will be an incorrect interaction between the localized charge density and its periodically repeated image that needs to be corrected for as well.

$$E_i^{NK} = (\varepsilon_i + \delta\varepsilon_{N-N_0}^{cc}) - \Delta E_N \quad (2.21)$$

In this equation $\delta\varepsilon_{N-N_0}^{cc}$ is the mentioned charge correction to the KS orbital energy and should be zero if there are no electron impurities (N electrons) and

$$\Delta E_N = (E_N + \delta E_{N-N_0}^{cc}) - (E_{N-1} + \delta E_{N-1-N_0}^{cc}) \quad (2.22)$$

represents the change in total energy as an electron is removed from the system. Here E_N and E_{N-1} are the total energies of a system of N and $N - 1$ electrons respectively. $\delta E_{N-N_0}^{cc}$ and $\delta E_{N-1-N_0}^{cc}$ are the charge corrections for the two systems respectively when N_0 is the number of electrons in the charge neutral state. Charge correction, both to orbitals and total energy, should be zero in the system of N_0 electrons, when there are no electron defects. Only if the total charge is non-zero is it really relevant. Fulfilling the gKT then becomes the problem of finding the w that gives a non-Koopman's energy of zero. In practice this means that one has to calculate total energy and orbital eigenvalues for both a system of N and $N - 1$ electrons for at least two different values of w , since the correction is linear in this parameter a linear interpolation can be done to find the correct value.

Figure 2.1: A comparison of the result of calculating Cr impurities in a cubic B1 structure of AlN using mHSE+Vw with a value of $w = 0$ (a) and $w = -3.4$ (b). Light red is the total DOS and blue is the d-orbital projection only.

Finding the correct value for w can be important as illustrated in Figure 2.1, where the electron density of states (DOS) of Cr impurities in cubic B1 AlN has been calculated. Figure 2.1b shows the result when using a value for w of -3.4 , determined to give the non-Koopman's energy as zero. Figure 2.1a shows the result if one used a value of 0 instead, in this case the occupied d-states are situated inside the valence band and no longer take the form of localized orbitals inside the band gap. These results were obtained by using a modified version of HSE06 referred to as mHSE, that has the range separator parameter adjusted specifically to improve on the representation of the band gap of AlN. Use of some other general mixing parameter and range separators might give different results but the correction terms would still be required in order to obtain accurate results for all orbitals. This example helps illustrate the value of this method and how important it is to find the correct value for w .

2.1.8 Green's function

The methods, based on Hamiltonian wave functions and the Kohn-Sham equations as described above are well known, well implemented in codes and considered to be both effective and reliable. Sometimes it may be necessary or preferable to apply some alternate method, one alternative method is to base the calculations on the use of the Green's function technique[2,33]. Often the wave-function methods are more

efficient and can give better energy and geometric relaxations in many systems. However, under some circumstances the Green's function can still be very useful. For instance the coherent potential approximation that will be presented in section 3.2.1 makes use of the Green's function formalism described here and has shown itself to be an efficient method for calculations of disordered systems.

Unlike the Schrödinger equation, which is a wave equation for the particle, the Green's function considers the scattering properties of the electrons instead. The single-particle Green's function describes the propagation of a particle of energy E from point $\mathbf{r}$ to point $\mathbf{r}'$ under the influence of an external potential $V(\mathbf{r})$.

$$\left[-\frac{\hbar}{2m} \nabla^2 + V(\mathbf{r}) - E \right] G(\mathbf{r}, \mathbf{r}', E) = -\delta(\mathbf{r} - \mathbf{r}') \quad (2.23)$$

The solution of the Green's function can be related to the wave function solutions ϕ_α , with energy eigenvalues ε_α , from the Kohn-Sham equation through the spectral representation.

$$G(\mathbf{r}, \mathbf{r}', E + i\xi) = \sum_{\alpha} \frac{\psi_{\alpha}(E, \mathbf{r}) \psi_{\alpha}^*(E, \mathbf{r}')}{E + i\xi - \varepsilon_{\alpha}} \quad (2.24)$$

With the Green's function known it is possible to obtain properties such as electron density

$$n(\mathbf{r}) = -\frac{2}{\pi} \int_{-\infty}^{E_F} dE \operatorname{Im} G(\mathbf{r}, \mathbf{r}', E) \quad (2.25)$$

or the electron density of states.

$$n(E) = -\frac{2}{\pi} \int_V d\mathbf{r} \operatorname{Im} G(\mathbf{r}, \mathbf{r}', E) \quad (2.26)$$

In material science, the Green's function is often presented in the form of multiple scattering theory according to Korringa-Kohn-Rostoker (KKR) [34-35]. The fundamental point of this is that atoms are considered as scattering centers and then solving the problem based on the condition that the incoming wave at each center is equal to the outgoing waves from all other centers. Within a muffin-tin (MT) representation of the crystal potential, then the Green's function can be presented in the following mixed coordinate-atomic position representation.

$$\begin{aligned} G(\mathbf{r} + \mathbf{R}_i, \mathbf{r}' + \mathbf{R}_j, E) &= \sum_{LL'} R_{il}(\mathbf{r}, E) g_{LL'}^{ij}(\mathbf{r}', E) R_{jl'}(\mathbf{r}', E) \\ &- \delta_{ij} \sum_L R_{il}(\mathbf{r}, E) H_{jl}(E) \end{aligned} \quad (2.27)$$

Coordinates $\mathbf{r}$ and $\mathbf{r}'$ are inside the MT spheres centered at positions $\mathbf{R}_i$ and $\mathbf{R}_j$ respectively. E is the electron energy relative to the interstitial region, called the MT-zero. L is the angular-moment quantum numbers l and m . R_{il} and H_{jl} are the regular and irregular solutions, respectively, of the Schrödinger equation inside the atomic sphere i for a given orbital angular momentum l and energy E .

The factor $g_{LL'}^{ij}(E)$ is called the scattering path operator; it describes the propagation of states with energy E between two different lattice sites. In a periodic system with a single atomic species, the scattering path operator is given by the following integral.

$$g_{LL'}^{ij}(E) = \frac{1}{\Omega_{BZ}} \int_{BZ} d\mathbf{k} (m(E) - B(\mathbf{k}, E))_{LL'}^{-1} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \quad (2.28)$$

Here, Ω_{BZ} is the brillouin zone volume, $m(E)$ is the inverse of the scattering matrix and $B(\mathbf{k}, E)$ is the Fourier transform of the structure constant matrix.

2.1.9 Plane wave method

In order to solve the Kohn-Sham equations numerically, some suitable representation has to be provided. Most methods for calculating solids are based on the atomic structure being periodic. According to the Bloch theorem[10], if the underlying structure and potential are periodic, then the wave function solutions have the following property:

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r}) \quad (2.29)$$

In this, $u_{i,\mathbf{k}}(\mathbf{r})$ is a periodic function with the same periodicity as the background potential and $e^{i\mathbf{k}\cdot\mathbf{r}}$ is a periodic function with the same periodicity as the potential. This periodic function can be Fourier expanded into

$$u_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.30)$$

where $\mathbf{G}$ are reciprocal lattice vectors. Given this periodicity and series expansion of the wave function it becomes natural to define $\psi_i(\mathbf{r})$ in the form of an expansion of plane wave components[2].

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.31)$$

Here the summation is over reciprocal lattice vectors $\mathbf{G}$, $c_{i,\mathbf{k}}$ are the expansion coefficients in the basis of the orthonormal plane waves. If one inserts the Fourier expanded wave function (eq 2.31) along with an equivalently expanded potential into the Schrödinger equation it is possible to arrive at a set of matrix equations from which the expansion coefficients can easily be determined through diagonalization.

One problem with this method is that strong Coulomb interactions near the atomic core causes the wave function to change rapidly, resulting in the necessity for a very large number of plane wave components and very large matrices that take significant amounts of memory and time to solve. A number of methods exist to get around this problem, one of them is to use so-called pseudopotentials.

2.1.10 Pseudopotentials.

A pseudopotential is a means of replacing the consideration of both the strong Coulomb potential of the nucleus as well as the interactions of the core electrons with an effective ionic potential acting on the valence electrons[2]. The basis for this technique is the assumption that due to the strong localization of core electrons they will not be expected to interact to any significant degree with the valence electrons.

As long as there is no need to explicitly consider the effects of core states then this provides an effective approximation, capable of greatly reducing computational effort as only the valence electrons need to be calculated. Additionally, the pseudopotential can be designed in such a way to provide smoother wave functions in the core region for the valence electrons, thus requiring fewer components in plane wave expansion techniques. A pseudopotential also has to be constructed in such a way that outside some cutoff radius R_C , both the potential and the wave function has to coincide with the exact ones. Both wave function and pseudopotential also has to be continuous at this cutoff point but beyond that the pseudopotential can be constructed in many different ways, reproducing different results inside the cutoff. That way it is possible to construct different potentials to suit the needs of the specific material considered. Two common types of pseudopotentials are the norm-conserving and the ultrasoft, each with their own advantages and disadvantages.

The *ab-initio* norm-conserving pseudopotential is based on the idea that the norm, or the charge, of the real and the pseudo wave function inside the cutoff radius should be the same, even though the general form is not. This guarantees that the wave function outside the cutoff sphere retains the correct shape. However, in order to maintain good accuracy and transferability, so that the pseudopotential works for the same atoms in all materials, the cutoff radius R_C has to be chosen as small. But a small cutoff results in ‘hard’ pseudopotentials that require a large number of plane wave components for calculation. Inversely, a soft pseudopotential requires a large cutoff and reduces transferability.

Another type of pseudopotential is the ultrasoft pseudopotentials, developed by Blöchl[36] and Vanderbilt[37] as extensions of the norm-conserving. In this form the norm-conservation condition is relaxed, allowing for calculation of much smoother pseudo wave functions requiring less expansion components. To still allow for accuracy an auxiliary function is provided that corrects for the error in removing norm-conservation. The disadvantage is that the ultrasoft pseudopotentials require more complex equations that are more time consuming to calculate. There is generally a net gain in efficiency though, as the wave function is easier to represent in a plane wave expansion. However, ultrasoft pseudopotentials suffer a loss of information about electron states inside the core, but that should not affect the results on the valence states.

2.1.11 Projector augmented wave

Another way to handle the electronic structure problem is through the projector augmented wave (PAW) method, originally by Blöchl[38] and later expanded on by Kresse[39], in this the actual wave function projects on smooth auxiliary functions that are more mathematically convenient. Through its use of auxiliary functions and algorithms the PAW method shares some similarities to the ultrasoft pseudopotentials. The main difference is that the auxiliary functions still contain all the information on the full all-electron wave function through the transformations, allowing for more accurate results on energy in and around the nuclei region and providing greater transferability of potentials.

2.2 Phonons

Early in this chapter it was stated that according to the Born-Oppenheimer approximation it was possible to decouple the dynamics of the electrons from the

ionic dynamics, due to the much slower velocity of the nuclei relative to the electrons. This allowed for the calculation of electronic structure without having to consider the dynamics of the atoms at the same time. That does not mean that the vibrational effects can be ignored however, atomic vibrations will have a profound effects on a number of material properties, including structural stability, superconductivity, thermal conductivity and heat expansion. Additionally, if one wants to calculate the material properties at finite temperature the vibrations should ideally be considered as well since they are the main contributor to heat and temperature effects. Even at $T = 0K$, vibrations influence material properties through the zero-point motions. The theory of crystal lattice vibrations, or phonons as the quantized vibrations that appear in periodic solids are called, started in the early 20th century by Born and von Kármán[40] and is summarized in the 1954 book by Born and Huang[41].

2.2.1 Lattice dynamics from electronic structure

The early work on lattice vibrations by Born, von Karman and Huang laid out the general principles of the dynamics of a crystal, such as the dynamical matrix and how it relates to the vibrational frequencies. But their work did not explain the relationship with the electronic structure, nor did it suggest a practical method for determining these things in real materials. A more detailed study of the relationship between electronic structure and crystal vibrations were not carried out until the late 60s and early 70s[42-43]. Together with the development of density functional theory in the 60s[6-7] and density-functional perturbation theory (DFPT)[44-45] a working method for calculating vibrational properties of crystals from first-principles had been achieved[2,46]. Other methods, like molecular dynamics[47] and the small displacement method[48-49] exist as well, but the DFPT is the method used in this work and as such described here.

Within the Born-Oppenheimer approximation, the lattice-dynamics of an ionic system is defined by the Hamiltonian

$$H_{BO}(\mathbf{R}) = - \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}) \quad (2.32)$$

where $\mathbf{R}_I$ is the coordinate of the I th nucleus, M_I is its mass, $\mathbf{R} \equiv \{\mathbf{R}_I\}$ is the set of all the nuclear coordinates and $E(\mathbf{R})$ is the ground-state energy of the system of electrons within the field of the fixed nuclei with coordinates $\mathbf{R}$, called the *Born-Oppenheimer energy surface*. The equilibrium geometry, $\mathbf{R}_0$, of the system is given when the forces, defined as the first derivative of the energy surface according to the Hellman-Feynman theorem[50], acting on individual nuclei vanish.

$$\mathbf{F}_I(\mathbf{R}_0) = - \frac{\partial E(\mathbf{R}_0)}{\partial (\mathbf{R}_I)} = 0 \quad (2.33)$$

It is convenient to apply the harmonic approximation by doing a series expansion of the Born-Oppenheimer energy surface and neglecting all terms beyond the second order expansion, resulting in the following set of equations.

$$E(\mathbf{R}) = E_0 + \sum_I \Phi_I \mathbf{R}_I + \frac{1}{2} \sum_{I,J} \Phi_{I,J} \mathbf{R}_I \mathbf{R}_J \quad (2.34)$$

$$\Phi_I = \left. \frac{\partial E(\mathbf{R})}{\partial(\mathbf{R}_I)} \right|_{\mathbf{R}=\mathbf{R}_0} \equiv 0 \quad (2.35)$$

$$\Phi_{I,J} = \left. \frac{\partial^2 E(\mathbf{R})}{\partial(\mathbf{R}_I)\partial(\mathbf{R}_J)} \right|_{\mathbf{R}=\mathbf{R}_0} \quad (2.36)$$

The constant term E_0 is typically taken as the electronic ground-state energy and can for the sake of the lattice dynamics be considered as zero. The first order expansion terms are the forces and they are by definition zero as the derivative in eq (2.35) is taken at the equilibrium. The second order terms, eq (2.36) are known as the (2nd order) *interatomic force constants*. The force constants make up a $3N \times 3N$ matrix where N is the total number of interacting atoms within the system and the 3 is for the dimensions. Within the harmonic approximation they will provide a full description of the dynamics of the atomic system. For instance the vibrational frequencies ω are given by the eigenvalues of the force constant matrix scaled by nuclear masses.

$$\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\mathbf{R})}{\partial(\mathbf{R}_I)\partial(\mathbf{R}_J)} - \omega^2 \right| = 0 \quad (2.37)$$

Determination of the vibrational frequencies then become the problem of determining the force constant matrix, or rather the second derivatives of the Born-Oppenheimer energy surface which can be given in the following form.

$$\begin{aligned} \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} = & \int \frac{\partial n_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_J} \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} + \int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial^2 V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} d\mathbf{r} \\ & + \frac{\partial^2 E_N(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} \end{aligned} \quad (2.38)$$

Here, $V_{\mathbf{R}}(\mathbf{r})$ is the potential of electron-nuclei interaction energy and $E_N(\mathbf{R})$ is the electrostatic energy of the nuclei interaction. There is also a dependence of the electron charge density $n_{\mathbf{R}}(\mathbf{r})$ and its linear response to a distortion in nuclear geometry, $\partial n_{\mathbf{R}}(\mathbf{r})/\partial \mathbf{R}_J$ in the given nuclear configuration $\mathbf{R}$. The first is acquired through density functional theory and the second through the theory of density functional perturbation theory.

2.2.2 Density functional perturbation theory

The previous chapter described how the interatomic force constants and lattice vibrational frequencies can be determined through the electron density and its linear response term. This chapter will focus on how to calculate the linear response term from density functional theory through the method known as density functional perturbation theory (DFPT)[2,44-46].

The linear response term $\partial n_{\mathbf{R}}(\mathbf{r})/\partial \mathbf{R}_J$ is obtained through the linearization of the equations for the Kohn-Sham equation (2.8) and (2.9) and the electron density (2.7). Linearization of the electron density leads to

$$\Delta n(\mathbf{r}) = 2Re \sum_{i=1}^N \psi_n^*(\mathbf{r}) \Delta \psi_n(\mathbf{r}) \quad (2.39)$$

The finite-difference operator Δ^λ , where the superscript λ represents some set of parameters, is formally defined as

$$\Delta^\lambda F = \sum_i \frac{\partial F_\lambda}{\partial \lambda_i} \Delta \lambda_i \quad (2.40)$$

In all equations λ will be omitted. Since the potential is real, the product of the wave function and its complex conjugate will be real and the specification of only using the real component in eq (2.39) above can be dropped. The variation of KS orbitals $\Delta\psi_n$ is obtained through standard perturbation theory:

$$(H_{KS} - \varepsilon_n)|\Delta\psi_n\rangle = -(\Delta V_{KS} - \Delta\varepsilon_n)|\psi_n\rangle \quad (2.41)$$

where

$$H_{KS} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{KS}(\mathbf{r}) \quad (2.42)$$

is the regular, unperturbed KS Hamiltonian.

$$\Delta V_{KS}(\mathbf{r}) = \Delta V_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int d\mathbf{r}' \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{dv_{xc}}{dn} \Delta n(\mathbf{r}) \quad (2.43)$$

is the first-order correction to the KS potential V_{KS} according to eq (2.9) and

$$\Delta\varepsilon_n = \langle \psi_n | \Delta V_{KS} | \psi_n \rangle \quad (2.44)$$

is the variation of the KS eigenvalues. These equations, (2.39) to (2.43), form a set of equations that have to be solved self-consistently, analogous to those for the solution of the Kohn-Sham equation. This solution applies to insulators and semiconductors with a band gap, in metals the perturbation may result in a change in orbital occupations. To account for this a number of modifications have to be done to the above equations[46,51].

2.2.3 Quasi-harmonic approximation

In the discussion above the assumption that the atoms vibrate according to harmonic oscillators was made, but in the harmonic approximation (HA) the vibrational contribution to the structural energy is independent of interatomic distance, or volume. Consequently the HA will not be able to determine thermal expansion, it also predicts infinite thermal conductivity and an independence of temperature on the vibrational spectra to name a few deficiencies. While formal treatment of anharmonicity can be accomplished by a number of different methods, including the temperature dependent effective potential (TDEP) by Hellman[52-53], they can be time consuming and difficult to manage. Another method that is capable of correcting for several of the problems with the harmonic approximation, without requiring any explicit calculation of anharmonicity, is the so-called quasi-harmonic approximation (QHA)[54].

According to QHA, the crystal free energy is determined in the same manner as in the harmonic approximation with one noteworthy difference.

$$F = U_0(V) + \sum_{jq} \frac{\hbar\omega_{jq}(V)}{2} + k_B T \ln \left(1 - e^{\left(-\frac{\hbar\omega_{jq}(V)}{k_B T} \right)} \right) \quad (2.45)$$

In this, $U_0(V)$ is the volume dependent zero-temperature energy, determined from the electronic structure only and $\omega_{jq}(V)$ are the phonon frequencies as a function of Brillouin zone vectors $\mathbf{q}$ and modes j . The difference from the standard harmonic

approximation is that the vibrational frequencies $\omega_{jq}(V)$ are now also volume dependent and determined separately for each volume. This is also the only explicit appearance of volume through the expression. Even though the determination of these phonon frequencies is done through methods based on harmonic approximations, recalculating them for multiple volumes instead of using the volume independent frequencies from the equilibrium still allows for the introduction of a degree of anharmonicity and allows for calculation of a number of temperature dependent thermodynamic properties.

2.3 Raman scattering and electron-phonon interactions

Raman scattering is the process whereby particles such as neutrons or photons are scattered off of the phonons in order to experimentally observe the phonon dispersion relations. A higher order, but weaker, process is the two-phonon Raman scattering, where the inbound particles scatter off of two phonons before leaving the crystal.[55] An important difference between the two processes is that in the single phonon scattering the conservation laws allow for absorption only of specific energies and momentum corresponding to specific phonon modes.

$$\begin{aligned} E' &= E + \hbar\omega_s(\mathbf{k}) \\ \mathbf{p}' &= \mathbf{p} + \hbar\mathbf{k} + \hbar\mathbf{K} \end{aligned} \tag{2.46}$$

where $\mathbf{k}$ and s are wave vector and mode of the absorbed phonon and $\mathbf{K}$ is a reciprocal lattice vector. In the two-phonon process the scattered particles are capable of absorbing a much broader spectrum of energies since the two absorbed phonons could have almost any combination of energy and momenta.

$$\begin{aligned} E' &= E + \hbar\omega_s(\mathbf{k}) + \hbar\omega_{s'}(\mathbf{k}') \\ \mathbf{p}' &= \mathbf{p} + \hbar\mathbf{k} + \hbar\mathbf{k}' + \hbar\mathbf{K} \end{aligned} \tag{2.47}$$

This would mean that the while the single Raman spectrum shows discrete energy peaks and scattering in specific directions depending on the scattering phonons, the two-phonon process shows a wide band that is observable in all directions. This generally makes the two processes easily distinguishable from each other.

Additionally, the multi phonon process has been known since the 1980s to provide insight into not only the dispersions themselves, but also electron-phonon interactions and superconductivity as two-phonon Raman responses have been shown to be strong in materials of relatively high T_c , $\sim 10\text{K}$ such as NbC or TaC while absent in low $T_c < 1\text{K}$ like HfC[56]. Strong two-phonon Raman has also been tied to the same processes of electron-phonon scattering that gives rise to softening anomalies (dips) in the phonon dispersions[57-58]. These electron-phonon scattering processes are usually linked to nesting features of the Fermi surface[59-60].

Figure 2.2: Comparison of calculated phonon dispersions of NbC under uniform compression of 88% of bulk volume to a two-phonon Raman spectrum of NbC inclusions in bulk Nb. Each of the peaks in the two-phonon spectra matches reasonably well with the anomalies in the calculated dispersion. The frequencies of the experimental data has been halved in this diagram, to account for the scattering off two phonon.

While the two-phonon process is usually quite weak and appears in the form of a broad distribution, an unusually strong two-phonon response was detected in NbC inclusions inside bulk Nb samples, these results were presented in paper IX. Not only was this scattering much stronger than anything previously observed, it also presented itself in the form of distinct peaks. This allowed for direct comparison between the experimentally observed scattering peaks and the anomalies in a calculated phonon dispersion diagram, see fig 2.2. Calculations done on NbC under bulk equilibrium conditions showed a moderate correspondence between the scattering peaks and the phonon anomalies, but there is some debate as to the actual structure and interface connection between Nb and NbC. If one assumes that the (111) plane of NbC connects to the (110) plane of Nb the NbC inclusions will end up under volume compression of 0.87. Calculation of phonon spectra under a uniform compression of 0.88, as demonstrated in the figure, gives a reasonably good agreement between experimental scattering and calculated anomalies. This would suggest that each of these peaks represent a greatly enhanced two-phonon scattering off of the phonons at the anomalies and that each peak represents scattering off the same phonon anomaly twice. While no clear explanation for why the two-phonon response was enhanced in this way is available, it appears that the electron-phonon interaction has been enhanced, possibly due to compressive strain or interaction with the coherent Nb bulk sample.

Chapter 3 - Alloy Models

The previous chapter detailed the fundamental theory that is involved in the determination of material properties. But before any calculations can be performed it is first necessary to provide a model for the atomic structure itself. If the material has a periodic atomic structure, then according to the Bloch theorem the electron density is periodic with the same periodicity as the primitive unit cell and it is possible to perform calculations on this finite periodic structure. But this is an idealized situation, real materials are not perfectly periodic, there are impurities and defects, materials can be disordered and they can be built up of nanostructured phases with interfaces between different domain regions. Atoms are also not stationary in real materials and their dynamics do not in general obey the periodicity of the underlying lattice if such exists. In a method such as Molecular Dynamics, one has to increase the model size beyond the primitive unit cell in order to get sufficient statistical averages and to be able to capture long wavelength phonons.

But molecular dynamics was not used throughout the work presented in this thesis and will not be discussed here. Instead disordered materials, interfacial structures and dilute alloys have been treated. In a disordered alloy the atoms are distributed in a more or less random way across the periodic lattice sites (not to be confused with amorphous structures). In such a disordered situation there is no ‘primitive unit cell’ that incorporates the full nature of the structure, the complete ‘primitive cell’ would be the size of the whole physical structure. This applies to disorder on any concentration, including low concentration impurity alloys. There are also nanostructured alloys of different phase domain regions and even if one can treat each individual domain as periodic and chemically pure, the interfacial regions still affect material properties. Actual materials consist of $\sim 10^{23}$ atoms per gram of the material, this is an entirely impractical situation for simulation under any method of atomic scale modeling where first-principles calculations are at most capable of handling hundreds, or in the extreme, a few thousand atoms. Consequently, some model has to be used for representing the macroscopic material as smaller components. Throughout this thesis two different methods have been used, supercells and effective medium, both of which are presented in this chapter.

3.1 Supercells

While actual devices and material components have sizes of mm or even larger, electron interactions are not that long ranged, they tend to decay quickly and become insignificant at distances of only a few primitive unit cells of the basic lattice. The actual coherence length is dependent on structure, material components and electronic

structure, metallic systems tend to have longer range interactions than other materials. However, there is always some distance R beyond which atomic interactions can be said to disappear or at least are small enough that they can be neglected. One can define a translationally invariant system, larger than this cutoff radius R , on which calculations can be carried out using the same methods and theorems as in the case of a primitive unit cell. This is the basis for the use of supercells, which are created by repeating the primitive unit cell of the underlying lattice symmetry a number of times in each direction until a sufficiently large structure on which the atoms can be appropriately distributed is obtained[33]. Periodic boundary conditions can be applied to this structure and Bloch's theorem and any methods based on translational invariance can be used. Supercells can be used for disordered alloys as well as impurities and defects as long as they are large enough that atoms do not interact with themselves across the translational symmetry boundaries. Interfacial boundary effects can also be treated with this method. It is also important to consider how the atoms are distributed, both in terms of alloy components, concentration and size of the supercell, in order to adequately represent the physical system that is to be represented.

Figure 3.1: An example of a supercell structure. A $2 \times 4 \times 2$ repeating wurtzite structure with 3 different atomic species on two different sublattices.

3.1.1 Special quasirandom structure

When one reduces an infinitely large substitutionally disordered alloy to a periodically repeating supercell structure of finite size it is not enough to simply assign atoms randomly across the lattice since it might result in a clustering of local environment that misrepresents the average of the actual system being modeled. One method designed to get around this problem was presented by Zunger et al [61-62] and is known as the special quasirandom structure (SQS). The basic idea of the SQS is to selectively distribute atoms throughout the supercell in such a way that the average coordination order throughout the whole structure is similar to that of the

infinitely large bulk structure of a completely random order. Ideally this would require that atomic correlation functions are the same as in the infinite random alloy across all coordination shells. Accomplishing this in a finite supercell is impossible, both because atoms can't be organized on a finite size structure in a way to accomplish this with perfection and because of the periodicity of the supercell. However, it is not necessary either, since interactions within clusters decrease quickly with distance it is only necessary to approximate the random order on the short-range coordination shells. The objective then becomes to find a structure where the correlation functions are zero for the coordination shells where effective interactions are significant and vice versa, when the correlation functions are non-zero, the effective interactions have to be zero.

One has to be careful in the application of this method though, the smaller the supercell is, the harder it becomes to find a structure with the right correlation functions at larger distances. Interaction strength and range is also dependent on the material, while one SQS might be suitable for one material it may not do for another. Small supercells can also have problems in accounting for relaxation effects as atoms are distorted away from ideal lattice sites due to atomic interactions.

3.2 Effective medium

An alternative to the method of supercells is to replace the actual medium of different atoms arranged along the lattice with an alternate, effective medium, designed to average the properties of the actual medium in some way and to create something simpler that can be calculated more easily. The simplest effective medium method is the virtual crystal approximation (VCA) in which the electron potential of different atomic sites is averaged. If the alloy has the makeup A_xB_{1-x} then it is replaced with a system of a single component C , where the electron potential of sites C , $V_{eff}(C)$, is the average of those for sites A and B . This is however an oversimplification and typically works poorly since the potential is not a self-averaging property of the system. The general principle is interesting though, being able to replace a medium of randomly distributed atoms with another with translational invariance would simplify calculations greatly.

3.2.1 Coherent potential approximation

The VCA failed because the potential was not self-averaging, but another property that is self-averaging is the Green's function and the electron scattering behavior within the crystal. As such the goal instead becomes to find an effective single-component medium with a Green's function that averages the scattering properties of the original structure. The coherent potential approximation (CPA)[33], originally proposed by Soven [63] for electronic system calculations, strives to achieve just this. This original formulation was somewhat impractical and was later reformulated by Györfy[64] in the terminology of the multiple scattering theory of Korringa-Kohn-Rostoker (KKR)[34-35]. In this form the CPA method has proven itself efficient at calculating disordered alloys.

Figure 3.2: A schematic representation of the principle of the CPA method. The leftmost image shows a two-dimensional crystal consisting of two different atomic species. The two figures to the right show how each separate atomic species is located inside the medium of effective atomic scatterers.

The objective of the CPA is to replace individual atoms of the crystal structure with effective scatterers with an effective coherent potential $\tilde{m}$ with effective scattering path operator $\tilde{g}$, placed on the sites of the underlying crystal lattice. Into this effective medium, the unique atomic components are placed in the form of impurities. The operator $\tilde{g}$ is determined from multiple-scattering theory.

$$\tilde{g}(E) = \frac{1}{\Omega_{BZ}} \int_{BZ} d\mathbf{k} \frac{1}{\tilde{m}(E) - B(\mathbf{k}, E)} \quad (3.1)$$

The given CPA condition is that effective scattering path operator $\tilde{g}(E)$ of the scatterers should average the on-site operators, $g^i(E)$, of the individual alloy components i embedded inside this effective medium.

$$\tilde{g}(E) = \sum_i c_i g^i(E) \quad (3.2)$$

These component path operators $g^i(E)$ are obtained from a single-site Dyson equation.

$$g^i(E) = \frac{1}{1 + \tilde{g}(E)[m^i(E) - \tilde{m}(E)]} \tilde{g}(E) \quad (3.3)$$

In this, $m^i(E)$, are potential function matrix elements of alloy component i . This set of equations, (3.1) to (3.3), are solved self-consistently to obtain the effective medium. Once this effective medium has been established, the methods of chapter 2.1.8 can be applied.

The benefit of this technique is that one does not have to consider the problems of supercells, such as how to order atoms within the structure to get the effect of an infinitely large random arrangement of atoms. Treatment of impurities also become rather natural as spurious self-interaction in too small supercells is no longer an issue either. Most importantly also, disordered alloys and impurities can be treated without the need for time-consuming calculations of very large supercells. The effective medium calculations are instead done on small and simple structures allowing for very fast calculations compared to a 100 atom supercell model. While there are several benefits, there are also deficiencies as certain material properties cannot be treated within this idealized medium, local environment effects, local relaxation, charge transfer, force calculation to name a few. For some of these it may be possible

to apply additional models to calculate them on top of the CPA calculations. Madelung screening can be calculated by use of a model requiring the input of a set of appropriate parameters. Through the use of the independent sublattice model (ISM)[65] a significant portion of the lattice relaxation effect can be treated as well, this method also requires the use of separately determined parameters defining the relaxation energies.

There exists also techniques that aim to combine the benefits of effective medium and supercells, the Locally Self-consistent Green's Function method (LSGF)[66-67] combines fast calculations of effective medium with some local environment effects of supercells. While this technique has shown itself useful in some systems it is not used within this thesis.

3.3 Alloy thermodynamics

The equilibrium structure and phase transformations of the alloy are determined by principles of thermodynamics that will be described throughout this chapter. A phase is a homogenous region of a material with a distinct crystal structure and chemical composition. A bulk material may contain multiple domains, each of which is a specific phase and are separated from each other by phase boundaries[1,33]. The phase structure of a material will have significant impact on material properties and as chemical composition, temperature and pressure changes the relative stability of different phases will change as well and the material will undergo phase transformations seeking to obtain the structure with the lowest total free energy[33]. The fundamental property in the thermodynamic relations discussed here is the Gibbs' free energy, G :

$$G = E + pV - TS = H - TS \quad (3.4)$$

Here E is the energy determined through electronic calculations, H is the enthalpy, p is the pressure, V is the volume, TS is the temperature T dependent free energy term. The entropy S can be made up of a number of different sources, including configurational and vibrational. Configurational entropy appears in a disordered alloy consisting of two or more components distributed across each sublattice. On a lattice consisting of n different components the configurational entropy becomes:

$$S_{conf} = -k_B \sum_{i=1}^n x_i \ln x_i \quad (3.5)$$

In this equation k_B is Boltzmann's constant and x_i is the concentration of alloy component i . Vibrational free energy in the harmonic approximation is given as

$$F_{vibr} = -k_B T \ln Z_{vibr} = \sum_{jq} \frac{\hbar \omega_{jq}}{2} + k_B T \ln \left(1 - e^{-\left(\frac{\hbar \omega_{jq}}{k_B T}\right)} \right) \quad (3.6)$$

This expression is the same as the last two terms in equation (2.45) in the chapter on the QHA method, except for the lack of volume dependence. Note that F_{vibr} represents that whole TS_{vibr} term. The equilibrium phase structure and configuration is the one with the lowest Gibbs' free energy. For solid solutions the formation free energy ΔG_{mix} can be determined as well and serves to describe whether a certain solution is thermodynamically unstable or not.

Fig 3.3: (a) Isostructural cubic mixing enthalpy of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ at pressures $P = 0$ GPa and $P = 10$ GPa (b) Mixing enthalpy of cubic rock salt (thick lines) and hexagonal wurtzite (thin lines) $\text{Ti}_{1-x}\text{Al}_x\text{N}$ compared to the stable c-TiN and w-AlN.

$$\Delta G_{mix} = G_{solution} - \sum_i x_i G_i \quad (3.7)$$

Here $G_{solution}$ is the free energy of the solution, x_i and G_i are the concentration and free energy of the end product i of phase separation. If ΔG_{mix} is positive then the solution is unstable and should decompose into separated phases, if it is negative then the solution is stable. At 0K the same expression can be applied to the enthalpy H for solution and components to determine the mixing enthalpy ΔH_{mix} .

From the free energy and formation energy one can determine a phase diagram that tells you whether a certain solution is stable, or which phases are expected for temperatures/pressure/concentration etc. But alloys can be grown under non-equilibrium conditions and while the thermodynamics suggest it should separate, thermal barriers will prevent the dynamics needed for rearrangements so that metastable non-equilibrium states can exist at low temperatures. Additionally, the decomposition of a solution from one state with positive formation energy into the stable end products is referred to as a process of binodal decomposition, another form of decomposition that needs to be considered is spinodal decomposition, caused by small, continuous changes in compositions as atoms order themselves. For spinodal decomposition to occur the total energy has to decrease with any small change in composition, which can mathematically be described by the second derivative of the formation energy due to a change in composition being negative.

$$\frac{\partial^2 G}{\partial x^2} < 0 \quad (3.8)$$

In the case of a multicomponent alloy of more than two components the second directional derivative has to be negative in some compositional direction for such a change to occur, it can reasonably be assumed that the change would occur in whichever direction has the lowest negative second derivative and consequently the largest gain in free energy from the change in composition.

Binodal decomposition is only of relevance if there is some initial nucleation of a phase region from which the separation can grow, otherwise the regions have to begin growing through spinodal decomposition. Spinodal decomposition is expected to be the initial decomposition process in carefully grown alloys of homogenous atomic distribution. Spinodal decomposition has been considered in a number of studies[1,65,68-69] and papers II and III demonstrate the value of considering spinodal decomposition in addition to the binodal within multicomponent alloys.

Chapter 4 - Results

4.1 Multicomponent alloys

Metal nitrides such as (TiAl)N are commonly used materials in hard coating applications. They are favored due to properties such as high temperature hardness[1,70-72], high melting point and oxidation resistance[73-78]. (TiAl)N alloys are in general not thermodynamically stable but they can be grown in non-equilibrium configuration by various deposition techniques[1]. Subsequent processes of heat treatment of the as-deposited alloy along with applied pressure causes phase transformation into other, more stable phases, greatly affecting the composition and nanostructure of the material[1, 65, 68-69, 79-87]. Indeed, many of the desired properties, in particular the high temperature hardness, are obtained specifically as a result of these transformation processes. Consequently, understanding how these processes occur, how they affect material properties and how we can exploit them in order to develop more advanced materials has significant importance.

In the case of (TiAl)N alloys the stable end phases are c-TiN and w-AlN, but despite the rather large positive formation energy of the disordered (TiAl)N phase, which would allow for spinodal decomposition, the alloy remains metastable in the as-deposited configuration due to the presence of thermal barriers preventing rearrangement on an atomic scale. However, when the deposited alloy is heated, a phase separation occurs, first separation of c-(TiAl)N into coherent c-TiN and c-AlN which happens at around 800°C, depending on the relative concentrations. This is the desired state of the alloy as lattice strains between the two coherent phases serve to enhance hardness, in addition this change in structure will also persist as the material is cooled. But c-AlN is not stable either, additional heating beyond 900°C will cause further restructuring into the stable w-AlN structure. This is an irreversible process that results in significant softening of the material, effectively rendering it useless for any practical applications, see Fig 4.1. This phase separation process is driven by the electronic structure of the material, AlN is a wide band gap semiconductor and TiN is metallic with decent conductivity and moderate DOS at the Fermi level. (TiAl)N on the other hand will go through a metal to semiconductor transition as composition changes, with a large and unfavorable DOS at the Fermi level, resulting in instability and decomposition.

Fig 4.1: Hardness of TiN (black), $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ (blue) as well as multilayered $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}/\text{TiN}$ (red) coatings. The values are from [72]. TiN quickly drops off in hardness as temperature decreases. (TiAl)N alloys on the other hand experience an increase in hardness around 7-800°C followed by a sharp dropoff beyond 900°C.

Another material that has seen use is (CrAl)N. It does not go through the same age hardening process as (TiAl)N, but is seen to have better oxidation resistance[81,85,88-92]. (CrAl)N is also thermodynamically less unstable than (TiAl)N, allowing for solubility of larger amounts of Al before the onset of the hexagonal phase as well as the appearance of isostructural stability at low concentrations of Cr. (ZrAl)N is another alloy that has received interest in literature[93-99]. In more recent work, focus has been made on alloying further components into the material where it has been seen that the thermal stability of (TiAl)N can be enhanced by addition of alloy components such as Cr[101-108] or Zr[109-112]. Other metal additions have been considered as well[113-115].

4.1.1 Improving thermal stability through metastable intermediary phases

In paper II it was shown how one can predict and tailor the formation of metastable phases during spinodal decomposition in order to improve overall material properties. Theoretical methods were used to predict the formation of coherent (CrAl)N and (TiCr)N phases during the spinodal decomposition. The presence of Cr inside the AlN phase is expected to delay the onset of the detrimental transformation into wurtzite AlN, resulting in an improved thermal stability compared to that of (TiAl)N.

Fig 4.2: Formation free energy surface and decomposition diagram for TiCrAlN single structured alloys. a) and c) Formation free energy surface at $T=0\text{K}$ and $T=1300\text{K}$ respectively. b) and d) Spinodal decomposition diagram at $T=0\text{K}$ and $T=1300\text{K}$ respectively. The background is the formation energy and the arrows indicate the most favorable direction of decomposition.

Figures 4.2a) and 4.2c) show the formation energy surface at 0K and 1300K respectively. The formation energy is defined in accordance with eq (3.7) in chapter 3.3 with the end phases of isostructural decomposition defined as cubic TiN, CrN and AlN. At low temperatures the alloy is thermodynamically unstable at almost all compositions, only for some compositions of (TiCr)N with around 10% Ti is the alloy seen to be stable. As temperature increases up to 1300K (TiCr)N becomes stable at all compositions, there are also some compositions of (CrAl)N at around 5-10% Cr that are stable with regards to isostructural decomposition even though they are still unstable with regard to the formation of hexagonal AlN. The strongest instabilities are observed in compositions of mainly (TiAl)N with little to no Cr present. Processes of binodal decomposition would be expected to drive a phase separation into a structure consisting of regions of c-(TiCr)N and h-AlN. But the binodal decomposition, given from the thermodynamic instability of the composition relative to the stable end products is not the only decomposition process to consider. Without the presence of regions of initial nucleation the decomposition would have to occur through a process

of spinodal decomposition. Spinodal decomposition is not determined by the value of the formation energy; instead the governing property is the second derivative of the formation energy surface, see eq (3.8). In a binary alloy spinodal decomposition will occur if this second derivative is negative, the strength of the process is determined by the magnitude of the second derivative. $\text{Ti}_x\text{Cr}_y\text{Al}_z\text{N}$ where $z = 1 - x - y$, is a ternary compound with formation energies on a two-dimensional surface, as such one needs to consider the two-dimensional second directional derivative for determining spinodal decomposition behavior. In addition it can reasonably be assumed that decomposition will occur in the direction within configurational composition space with the largest negative value of the second derivative. Figures 4.2b and 4.2d presents the spinodal decomposition trends in the form of arrows, the arrows mark the direction in which this second derivative has the largest magnitude, suggesting it is the direction in which spinodal decomposition is likely to occur. If the second derivative is positive in all directions, as it is near (TiCr)N, then no arrows are shown. In addition, the size of the arrows marks the relative strength of the decomposition. What is seen is that at most compositions the dominant decomposition trend is between TiN and AlN with little to no favor for the separation of CrN through spinodal decomposition. This trend holds both at 0K and 1300K even though thermal barriers prevent any phase separation at low temperatures. The diagrams show that if one has an alloy of (TiCrAl)N it can be expected that spinodal decomposition drives a separation into domain regions of stable c-(TiCr)N and a phase of c-(CrAl)N with low content of Cr that is isostructurally stable at high temperature. While the diagrams indicate that CrAlN is stable with regards to isostructural decomposition it will not be stable compared to transformation into CrN and hexagonal AlN. But since spinodal decomposition is a primarily isostructural process it can still be expected that c-CrAlN phases form as an intermediary phase.

Colleagues associated with this project carried out experiments that were able to confirm these predictions on the decomposition process. In these experiments, alloys of $\text{Ti}_{0.31}\text{Cr}_{0.07}\text{Al}_{0.62}\text{N}$ were grown and heat treated up to a temperature of 1400°C where it was shown that as temperature increases the structure goes from c-(TiCrAl)N to c-(TiCr)N and c-(CrAl)N with an associated increase in hardness at around 800°C. As temperature was increased further, the alloy goes through continued phase transformations into c-(TiCr)N and h-AlN at just above 1000°C, approximately 100°C higher than the equivalent for (TiAl)N decomposition into h-AlN phase.

4.1.2 Spinodal decomposition in (TiZrAl)N

Another multicomponent alloy that has received attention in hard coating applications is (TiZrAl)N, this material has also been shown to promote cubic phases and retard the formation of detrimental wurtzite AlN while maintaining high hardness, as much as ~40 GPa at temperatures as high as 1100°C[109]. (TiCrAl)N accomplished the high temperature hardness through the formation of metastable c-(CrAl)N phases with greater stability than c-AlN, but (ZrAl)N is known to be even less stable than (TiAl)N[95,99] so a metastable (ZrAl)N phase could not be the cause. In the investigation of the phase stability and decomposition processes presented here and in paper III, an explanation for this stability was not made but other vital observations were made instead and will serve as an example of how phase decomposition of a thermodynamically unstable structure can be prevented because of its resistance to spinodal decomposition.

Figure 4.3: Formation free energy a) and spinodal decomposition diagram b) for (TiZrAl)N at a temperature of 1300K. The two circles mark compositions used in related experimental work. Like in Fig 4.2 above the arrows in the decomposition graph marks the most favorable direction of spinodal decomposition

The formation energy of monostructured c-TiZrAlN at 1300K is presented in figure 4.2. The formation energy is defined in accordance with eq (3.7) where the decomposition end phases are c-TiN, c-ZrN and c-AlN. This shows that (TiZrAl)N is a highly unstable alloy with very large positive formation energy at almost all compositions, especially along the (ZrAl)N compositional edge where it is more than twice as large as that of (TiAl)N presented both here and in the previous chapter. Only for a few compositions of (TiZr)N does the formation energy become negative at this temperature. In addition, the spinodal decomposition trend based on the second derivative of the formation energy also illustrates the strong separation tendency between ZrN and AlN that dominate at most configurations. Even at very low concentrations of ZrN, as little as 5%, the separation of ZrN is still dominant over the

separation between TiN and AlN, even though a (TiAl)N phase can still be expected to separate into TiN and AlN once the ZrN has separated out.

However, the formation energy surface of (TiZrAl)N is highly asymmetric with higher formation energies near the AlN end. This behavior has in past studies of (TiAl)N been attributed to the specific electronic structure of (TiAl)N and the unfavorable Ti-Al bonds[65]. Zr and Ti have the same valency so this behavior can be expected to be present for Zr as well and as can be seen, it is not only present in (ZrAl)N but even stronger as the formation energy peak is situated even closer to the AlN end than for (TiAl)N. Due to this strong asymmetry of the formation energy between AlN and (TiZr)N, the formation energy surface is distinctly flattened at low concentrations of AlN, resulting in a much weaker trend for spinodal decomposition. At high temperatures and high concentrations of ZrN (> 75-80%) the energy surface even turns concave with positive second derivative in all directions. Under these circumstances it is expected that the spinodal decomposition is suppressed, but since the formation energy is still positive the alloy is thermodynamically unstable with regard to binodal decomposition. Consequently, if there is initial nucleation a phase separation can still occur, but it will be greatly suppressed due to the lack of spinodal decomposition. A solid solution of (TiZrAl)N can still be expected to exist, even at elevated temperatures. And given the surface topology of (TiZrAl)N high temperatures only serves to increase the resilience against spinodal decomposition, even though the increased thermal motion should facilitate atomic rearrangements.

Experiments done in conjunction with these calculations proved this observation as alloys of moderate Zr-content was shown to quickly phase separate into c-AlN and c-(TiZr)N while other compositions of high Zr-content decomposed very slowly, even at very high temperatures. And when they did decompose it was observation that this behavior was more consistent with binodal as opposed to spinodal phase separation.

4.1.3 Pressure and temperature effects on (TiAl)N

Another important factor for the stabilization of the cubic AlN phase can be attributed to pressure and temperature as both can affect the phase stability. The hexagonal w-AlN phase is more stable than the cubic c-AlN at ambient conditions, but since the volume of the cubic phase is less than that of the hexagonal, high-pressure conditions will stabilize it, see fig 4.4. Different experiments and calculations have in the past shown that the cubic to hexagonal transition of AlN lies between 12-17 GPa [116-118]. This is an observation that would extend to the AlN phase of (TiAl)N alloys. Even so, few past studies have considered the impact of both pressure and temperature on the phase stability of (TiAl)N. Paper IV details such a study, consisting of both experimental and theoretical work.

Figure 4.4: Left: Energy binding curves of rock-salt (blue) and wurtzite (black) AlN. The wurtzite phase is the more stable due to its lower equilibrium energy, but the rock-salt phase has a lower equilibrium volume, resulting in a stabilization of the B1 phase at high pressure. Right: A phase diagram of the AlN phase inside a TiAlN alloy. The solid curve represents the calculated transition point as a function of pressure and temperature. The dashed line at 2700°C marks the high temperature limit for the calculations and the approximate melting point of AlN. The squares and hexagons are experimental observations on the AlN phase inside a TiAlN alloy.

In this paper, calculations were made to determine a phase diagram of AlN over variations of both pressure and temperature by means of calculation of phonon properties at high temperature. In these calculations, at 0K the transition pressure from hexagonal to cubic is 13.9 GPa. But as temperature increased the hexagonal AlN phase was seen to experience greater thermal expansion than the cubic. Phase stability is dictated by the Gibbs free energy, eq (3.4), and the transition occurs when the free energy for both structures is the same, $G_{B1} = G_{B4}$. With this and eq (3.4) it can be shown that if the difference in volume increases then the transition pressure decreases. Consequently, the transition pressure decreases as the temperature increases. While the pressure, 10-14 GPa, and the temperature range for a significant decrease in the transition pressure, 1500-2000K, is far beyond industrial applications it is clear that both factors still act to stabilize the cubic phase. And while the pressure is not enough to completely stabilize the c-AlN phase under normal operational conditions, it could be enough to slow down the phase transition. In addition, the high pressure is also expected to slow down the diffusion processes that cause the decomposition itself, leading to additional stability.

In addition, the experiments on (TiAl)N gave the transition pressure as slightly lower than the theoretically predicted, with a difference of ~ 2 GPa. This can likely be attributed to either strain in the phase boundaries helping to stabilize the cubic phase or that there could be some impurities of Ti within the AlN doing the same. Adding impurities of $\sim 3\%$ Ti (1 Ti to 31 Al) reduces the transition pressure at 0K by ~ 3 GPa. An even greater amount of Ti, 1 Ti to 7 Al at 12.5% Ti, decreases it by an additional 1.5 GPa. The introduction of small amounts of Ti, as well as Cr as seen in the discussion of (TiCrAl)N, stabilizes the cubic phase of AlN, a line of investigation that will be further discussed in the following sections.

4.2 Dilute (TMAI)N alloys

In the previous section on multicomponent alloys two important points have been demonstrated. First that a very important aspect of the detrimental phase decomposition is the transition of cubic AlN into a hexagonal AlN phase. Second, that a small amount of Cr and Ti can serve to stabilize the cubic phase relative to the hexagonal and even though it does not stabilize it completely, there is enough of an effect to delay the phase transformation. While Ti added into AlN is generally unstable due to positive formation energy and spinodal decomposition, there may still be some amount of Ti present in what is generally referred to as the ‘AlN-phase’. (CrAl)N is also known to be stable with regard to isostructural decomposition with Cr concentration of about 5-10%, even if it is still not thermodynamically stable with regard to transformation into a hexagonal AlN phase.

AlN is a strongly ionized wide band gap III-V semiconductor with an s-p bonding structure[119-120]. Each Al atom contributes 3 valence electrons and 5 valence electrons come from each N-site, most of this charge will be situated on the N-sites or the Al-N bonds. Adding substitutional TM defects, TM_{Al} , on the Al sites will make 3 of the valence electrons from these impurity atoms bond with the overall host band structure while any remaining electrons form localized impurity states of a d-orbital character within the band gap, centered on the TM sites. In addition, these localized states will become magnetic due to spin dependent exchange[121-124]. Tetrahedrally bonded CrAlN of 5-10% Cr has demonstrated ferromagnetism with a Curie temperature of 900K[125-128] despite AlN being non-magnetic and CrN being anti-ferromagnetic/paramagnetic[92,131]. Other works have suggested ferromagnetism in AlN with Ti impurities[132] as well. This class of materials is generally known as Dilute Magnetic Semiconductors (DMS) and has seen some interest through the development of materials for spintronic applications but these considerations have not been brought to the study of hard coating materials. Also, past studies have been focused on impurities in the tetrahedrally bonded AlN, as opposed to the cubic B1 AlN, which does appear in alloying with TMN.

These studies have primarily made use of standard DFT methods, and while they have been able to provide generally good results, they do suffer some limitations in the treatment of systems consisting of delocalized s-p-orbitals and strongly correlated localized d-orbitals. DFT is also known to underestimate semiconductor band gaps. Incorrect determination of band gap can, apart from giving wrong estimations of use in electronic materials, also result in the spurious placement of impurity states within the conduction band[124]. A recently developed method, the HSE06+Vw[28-29], intended specifically for this kind of electronic structure and detailed earlier in this thesis has been shown to give improved results through the use of hybrid functionals along with an orbital dependent correction scheme similar to that of LDA+U.

4.2.1 Ti and Cr impurities in AlN

In an attempt to learn more about the effect of low concentration of Ti and Cr impurities in AlN, in paper VI calculations were carried out on 64 atom supercells in both B1 and B4 structures, with both single and double impurities in different configurations generating simulated impurity concentrations of 3.125% or 6.25% on the metal sublattice. Even so, the purpose of this study was not to test specific concentrations but to study the effect of local impurities, local environment and magnetism on the structural stability of AlN phases in nanostructured metal nitride

thin films. Since this study originated from the (TMAI)N alloy systems, where the concentration is relatively high and the TM substituted AlN phase regions will be interfaced with metallic TMN regions we have not considered charged impurities and only neutral impurities have been treated. An additional purpose of this work has been to test out the effect of the HSE06+Vw method, to see how much the results are affected by this methods treatment of correlations and many body effects. For this purpose calculations were done with both standard semi-local DFT, using exchange-correlation density functionals according to Perdew-Burke-Ernzerhof (PBE)[19] and a variant mHSE+Vw[28-29] with a modified parameter for range separation compared to regular HSE06. By the methods described in previous chapters the w correction term was determined by the criteria of obtaining a non-Koopman energy of 0. This resulted in values of $w \approx 0$ for Ti impurities in both structures and $w \approx -1.7$ for Cr impurities in a B4 structure and $w \approx -3.4$ for Cr impurities in a B1 structure. As such, use of mHSE+Vw for Ti-impurities becomes the same as mHSE only and will be called mHSE from now on. Cr impurities may prove more problematic since different value for w should be used for the two structures and the choice of w will affect the total energy beyond merely the correction to the specific orbitals. Consequently, it then becomes necessary to make comparisons of the total energy with the same w even if it means one of the structures has received incorrect treatment..

Electronic Structure

Figure 4.5: The electronic DOS of a single Ti impurity in AlN, calculated with both PBE (top) and mHSE (bottom) in both B1 structure (left) and B4 structure (right). Light red is total DOS and blue are the d-orbitals.

The use of the hybrid functional has little effect on the host AlN band structure except for the width of the band gap, experimentally it has been determined to around 6 -6.1 eV[133] in the hexagonal B4 phase. Calculating the band gap with DFT gave a value of 4.1 eV in the w-AlN structure. The hybrid functional calculations managed to improve this result to 5.7 eV, a not insignificant improvement as incorrect band gap can result in faulty placement of impurity states inside the conduction band[124]. Any substitutional TM_{Al} impurities added to the AlN host will not greatly affect the host band structure while the additional impurity valence electrons generate localized atomic like orbital states within the band gap. A single impurity of Ti has 4 valence electrons, 3 of those are bonded to the host structure while the remaining one occupies the impurity states within the band gap. The result from calculation of a single, isolated, impurity within the AlN host is seen in figure 4.5, where the electron DOS has been calculated in both cubic B1 and hexagonal B4 structures, as well as with both PBE and mHSE functionals. In the B1 structure, for both functionals, the impurity states within the band gap maintain a purely t_{2g} nature, pointing along the [110] fcc directions, towards the Al sites and away from the large charge concentration on the N-sites in the [100] directions. The e_g orbitals on the other hand are well separated from the t_{2g} orbitals and situated inside the conduction band, regardless of functional used. There is also additional splitting that has broken the orbital symmetry so that all occupation is on the d_{yz} orbital only and while present in both methods, there is an increased splitting in the mHSE caused by increased correlations making it more obvious there. In the hexagonal structure the impurities do not have this well-defined separation into the cubic symmetry triplet and doublet. While not so obvious with Ti-impurities that hold a single impurity electron, impurities with more electrons, like Cr (fig 4.6) or Fe (next chapter, fig 4.13), show more clearly how all 5 states in the spin-up channel fills before the spin-down channel start to occupy.

Apart from the increased splitting of occupied and unoccupied orbitals generated by the use of hybrids, there is also a lowering of the energy of the occupied orbitals compared to that of the PBE calculations by about 0.5 eV when using the valence band edge as a reference point. In the B1 structure PBE calculations placed the impurity states at 2.5 eV above the valence band while mHSE placed them at 2 eV above the valence band. In the B4 structure the impurity bands were located 3.5 eV and 2.9 eV above the valence band respectively. According to this the mHSE suggests less instability of Ti impurities compared to that of DFT, something that is seen in the formation energy ΔG_{mix} (eq 3.7) as well, which is 28 meV/atom according to PBE and 21 meV/atom according to mHSE. The impurity level in the B1 structure is also significantly lower than the same in B4, indicating that the impurities would serve to stabilize the B1 structure relative to the B4 as well.

Figure 4.6: The electronic DOS of a single Cr impurity in AlN, calculated with both PBE (top) and mHSE+Vw (bottom) in both B1 structure (left) and B4 structure (right). Light red is total DOS and blue are the d-orbitals.

Cr impurities present a different situation for the electronic structure, as there are enough valence electrons now to fill the t_{2g} triplet in the up-spin channel of the B1 structure. The DOS is presented in figure 4.6 and according to this the occupied states are situated just above the valence band, both in the (semi)local and the hybrid calculations with little difference. One has to remember, however, that the actual level of the orbitals depends on the w parameter. In this calculation a value of $w = -3.4$ was used, this was the value determined to provide a non-Koopman energy of zero, but values closer to zero would lower the orbital energy levels until it merges with the band. If $w = 0$ the d-orbital states were entirely inside the valence band, rather than being inside the band gap as was seen in figure 2.1, emphasizing the necessity for the use of correction terms like this. Same as in the case of Ti-impurities, using the hybrid method increased the separation between the occupied states and the unoccupied, but since the Cr impurity fills the triplet state there is no degeneracy and none of the symmetry breaking noted in the case of Ti-impurities. There is also significantly less impact of the correlations and less difference between the DFT and hybrid calculations.

Local environment and magnetic phases

As has been said, TM impurities like Ti and Cr in AlN should be magnetic, but in what phases and how strong are they relative to each other. Additionally, the local environment should have an impact on both magnetic phases and structural stability. A comparison of energies of different magnetic phases, non-magnetic (NM),

ferromagnetic (FM) and anti-ferromagnetic (AFM) was made for a number of different configurations of two impurity atoms using both the PBE and mHSE+Vw methods. For this purpose a number of different configurations of impurity atoms were set up, three are presented here for B1 and B4 structures respectively. The B1 supercell is a $4 \times 2 \times 4$ fcc lattice and the B4 supercell is a $2 \times 4 \times 2$ hexagonal lattice, both structures have a total of 64 atoms. In the B1 structures the structures are two atoms whose relative positions were determined through the techniques of SQS and fairly well separated (1), two impurities as nearest neighbors along the $[110]$ direction of the metal fcc sublattice (2) and two atoms as second nearest neighbors along the $[100]$ direction (3). Consequently structure (1) is intended to represent, as far as possible, an infinitely large random arranged alloy, structure (2) has two close lying impurities with overlapping t_{2g} orbitals and structure (3) have the impurities close by, but screened by a N-atom between them and the t_{2g} orbitals are all pointing towards Al-sites. The three B4 structures are two impurity atoms arranged according to SQS technique (1), two impurities as close neighbors in the same plane (2) and two impurities as near neighbors in the same hexagonal lattice primitive cell(3). All these atomic configurations are presented in figure 4.7.

Figure 4.7: Diagram showing relative positions of the impurity atoms in the different configurations of the B1 structure (top) and the B4 structure (bottom) of AlN. With the first atom in position 0, the second atom in each of the three different configurations are labeled as 1 to 3 respectively. Because of periodic boundary conditions atoms 0 and 2 are repeated on the edges of the B1 structure. For the sake of clarity, not all atoms are displayed in the figure. The lines show the actual supercell boundary. See the text for a detailed description of the specific impurity configurations.

Figure 4.8: The energy of two Ti-impurities in AlN for the different configurations. The reference zero-point is taken as the energy of the most stable configuration and magnetic phase. a) B1 PBE, b) B1 mHSE c) B4 PBE d) B4 mHSE. The different atomic configurations are arranged along the x-axis

Figure 4.8 shows the relative energies of two Ti-atoms within a 64 atom AlN supercell for different magnetic phases and atomic configurations. In the B1 structure, the lowest energy is when the two Ti-atoms are nearest neighbors, forming a Ti-Ti bond. This is expected since it has already been shown in the past that Ti-Ti bonds are energetically far more favorable than Ti-Al bonds[65]. It is also seen that magnetic phases are favored over the non-magnetic, especially so according to the hybrid calculation, but while the DFT calculations indicate that Ti-impurities should be ferromagnetic the hybrid calculation show that they should be anti-ferromagnetic in structures 2 and 3 and lacking significant magnetic interaction when the Ti-atoms are more well separated in structure 1. A paper by Zunger[124] gives a possible explanation for this difference in magnetic phases. According to Zunger, FM impurities can only appear in a situation of partially occupied states. The interactions between neighboring sites splits the impurity states into a set of bonding-antibonding states for each spin channel. In the FM configuration the filling begins with the bonding states, but if the orbital is filled then the single spin channel has to be occupied with non-bonding states as well, making it energetically unfavorable. In the anti-ferromagnetic case a filled orbital can occupy both spin channels in order to keep all electrons in a bonding state. Hybrid-DFT calculations showed a very strong symmetry breaking (fig 4.5b) that separated the triplet into a singlet and a doublet,

Figure 4.9: Relative energies of two Cr-impurities in different configurations in AlN. B1 used $w=-3.4$ and B4 used $w=-1.7$. a) B1 PBE b) B1 mHSE+Vw c) B4 PBE d) mHSE+Vw.

where the singlet is fully filled, and as such cannot be ferromagnetic. In the DFT calculation the t_{2g} orbitals experience little to no symmetry breaking, (see fig 4.5a) resulting in a partially filled triplet orbital and allowing for ferromagnetism. There is also an oddly weak magnetization of structure 2 in B4 that is only seen when using hybrid functionals, no clear explanation for that is available at this time, but it appears that for this particular configuration the magnetic strength is weakened, something that is not seen in standard DFT.

Cr impurities have a total of 3 valence electrons per atom, with the cubic symmetry of the B1 structure it is enough to fill the up-spin triplet in magnetic phases resulting in the relatively stable phases as seen in past works[81,91-92] including paper II, where it was seen that the isostructural formation energy of dilute (CrAl)N is almost zero, or even negative at higher temperatures. However, in non-magnetic configurations the three electrons can only fill the triplet half-way and as such the non-magnetic Cr impurities become much more unfavorable than for Ti. And since the triplet state is filled only the AFM phase is possible, but this is only significant in structure 2, where the energy difference between FM and AFM is 0.12 eV/Cr-atom for both PBE and hybrid-DFT. Another difference from the Ti-impurities is that there is little difference between the different atomic configurations in the magnetic structures, this is also due to the filled t_{2g} orbitals resulting in less orbital interaction between the Cr sites.

Phase stabilities

This research project was approached from the point of determining how impurities affected the relative phase stability and formation energy of cubic and hexagonal AlN. So far it has been shown the impact that different impurity configurations and magnetic phases has on the dilute alloys. The differences between the (semi)local and the hybrid-DFT functionals has also been demonstrated. This chapter will focus on the structural stability, in terms of formation energy and the relative stability between the hexagonal and cubic phases.

Fig 4.10: Formation energy of a) Ti in B1 structure and b) Cr in B1 structure. Shown are single impurities and two impurities. Green markers are for PBE results and red are for mHSE+Vw, circles are NM, triangles are FM and squares are AFM. In this plot, no distinction is made between the different atomic configurations, but the actual values of formation energy are given in table 1. The blue line is the formation energy as determined by methods of coherent potential approximation(33). In the Ti-plot, for the sake of clarity, the PBE and mHSE+Vw points have been shifted sideways from the actual concentration line, which is marked by the dashed line. No results on formation energy of Cr-impurities with mHSE+Vw method are presented, since common values of w for bulk CrN and AlN with Cr-impurities could not be obtained.

Figure 4.10 demonstrates these variances through the formation energy of both single and double impurities as calculated with the different functionals, magnetic phases and atomic configurations of Ti and Cr impurities in the B1 structure. Table 1 holds all the relevant data values. The formation energy ΔG_{mix} is defined as in chapter 3 and eq (3.7), for B1 the decomposition end phases are c-TiN and c-AlN and for B4 they are c-TiN and w-AlN. There is a notable decrease in formation energy of the magnetic phases when using the mHSE+Vw method on Ti-impurities, which is consistent across B1 and B4 structures. The formation energy of a single non-magnetic Ti-impurity calculated with standard DFT was 0.0301 eV/atom, but factoring in magnetism and using hybrid functionals this drops to 0.0214 eV/atom. The local environment also has an effect, in the calculations with two impurities an SQS generated structure, in this case represented by structure 1, calculated without magnetism had a formation energy of 0.0571 eV/atom according to DFT, but the anti-ferromagnetic structure 2 had an energy of only 0.0339 eV/atom when calculated with the hybrid functional. Clustering is seen to be a factor under these circumstances, but this study made no attempt to evaluate the degree of clustering in a random alloy, and

standard SQS methods for generating supercells takes no consideration to the thermodynamics of different bondings.

PBE B1 Ti	Single TM	Structure 1	Structure 2	Structure 3
NM	0.030	0.0571	0.0417	0.0547
FM	0.028	0.0536	0.0406	0.0499
AFM	---	0.0547	0.0409	0.0540
mHSE B1 Ti				
NM	0.0323	0.0637	0.0363	0.0583
FM	0.0214	0.0393	0.0354	0.0473
AFM	---	0.0395	0.0339	0.0410
PBE B4 Ti				
NM	0.0387	0.0755	0.0648	0.0627
FM	0.0354	0.0696	0.0619	0.0608
AFM	---	0.0700	0.0636	0.0627
mHSE B4 Ti				
NM	0.0433	0.0828	0.0594	0.0586
FM	0.0272	0.0541	0.0567	0.0522
AFM	----	0.0542	0.0587	0.0541
PBE B1 Cr				
NM	0.0255	0.0553	0.0255	0.0415
FM	0.0035	0.0069	0.0077	0.0080
AFM		0.0068	0.0038	0.0066
PBE B4 Cr				
NM	0.0410	0.0822	0.0724	0.0662
FM	0.0252	0.0501	0.0391	0.0431
AFM		0.0503	0.0461	0.0476

Table 1: Formation energy values from the DFT calculation on impurities. The values for Ti and Cr impurities in the B1 structure are plotted in figure 4.2. The formation energy for impurities in B1 AlN is taken relative to cubic TiN and cubic AlN, the formation energy for impurities in B4 AlN is taken relative to cubic TiN and wurtzite AlN. Ti-impurities were calculated with $w = 0$ while Cr impurities in B1 and B4 were calculated with $w = -3.4$ and $w = -1.7$ respectively.

The first column is the single impurity. The other columns are double impurities in different configurations.

The rows are the non-magnetic (NM), ferro-magnetic (FM) and anti-ferromagnetic (AFM) phases. When there is only a single impurity only FM was possible to calculate and as such no AFM phase data is available.

Energies are given in eV/atom, for the single impurity the level for the zero energy is set to the energy of the FM phase and for double impurities the zero is set to the atomic configuration with the lowest energy.

* These AFM calculations relaxed into states with weak to no magnetic moment on individual sites. The AFM states did not appear to be computationally stable.

In addition to the formation energy, there is also the relative stability between the B1 and the B4 structures to consider. This relative stability can be defined as the difference in equilibrium enthalpy between the cubic (B1) and wurtzite (B4) phases, formulated in here.

$$\Delta H_{B1-B4} = H_{B1}^{(TM-Al)N} - H_{B4}^{(TM-Al)N} \quad (4.1)$$

According to PBE functionals, the equilibrium energy difference between B1 and B4 structures is 0.17 eV/atom, hybrid functionals will lower this to 0.15 eV/atom, suggesting that DFT methods exaggerate the instability of the B1 phase. Comparing the B1 and B4 structures of AlN with Ti and Cr impurities shows that the energy difference drops by about the same amount, 0.02 eV/atom, when using hybrid-DFT, so it is plausible that this stabilization is inherent to the AlN phase only and not due to the impurities. Magnetism has little effect on the relative stability between B1 and B4 AlN with Ti. Cr impurities on the other hand show a greater stability for the B1 phase as long as magnetism is treated, but (CrAl)N has always been treated as magnetic anyway.

	Ti PBE	Ti mHSE	Cr PBE	Cr mHSE+Vw $w = -1.7$	Cr mHSE+Vw $w = -3.4$
NM	0.158	0.135	0.151	0.137	0.136
FM	0.159	0.140	0.145	0.120	0.120

Table 2: Energy difference in equilibrium energy between B1 and B4 structures with a single impurity. Since energy comparison is only possible if the same value for w is used in the mHSE+Vw method, comparison is made for both $w = -1.7$ and $w = -3.4$ in the case of Cr. As a reference, the value for pure AlN is 0.172 eV/atom according to PBE calculations and 0.150 eV/atom according to mHSE.

4.2.2 Systematic search

Small amounts of Ti and Cr can serve to stabilize the cubic AlN phase within the nanostructured alloy, delaying the onset of detrimental hexagonal AlN. In another study, presented in paper V, it was also investigated how other impurity components could affect the relative stability of cubic and hexagonal AlN. A search was made for TM impurities, which when dissolved in AlN minimized the structural enthalpy difference between the cubic and wurtzite phases at equilibrium, see eq 4.1. At the time of this work we did not consider the solubility of these impurities in AlN and merely assumed the presence of such, a not entirely unreasonable assumption considering the possibility to grow alloys under non-equilibrium conditions, the decomposition processes and the low concentrations to be considered. Also, while in the impurity studies mentioned above, techniques based on hybrid functionals and orbital corrections were used and were seen to affect the results, such calculations would be too time consuming in a general search for potential candidate materials requiring a large amount of calculations. In addition, those advanced calculations showed that standard DFT was reasonably accurate on a qualitative level, even if being somewhat inadequate on a quantitative level. When considering the difference between the two structures as will be done here, any difference between the two functional treatments could be attributed to effects inherent to AlN and not due to the

Figure 4.11: The relative stability of B1 and B4 phases of AlN with impurities given as the enthalpy difference in eV/atom according to eq (4.1). The dotted line marks the enthalpy difference for pure AlN as a reference and comparison. The blue columns marks the results with magnetism on the impurity site and the red are without magnetism.

impurities. As such, since the purpose of this study was to obtain a general overview of TM impurities in AlN, a standard DFT method was applied with single impurities within a 16 atom supercell. This was deemed sufficient to see the general impact on relative stabilities and electronic structure.

Figure 4.11 shows the results on the enthalpy difference with different impurities. The dotted line in the figure marks the enthalpy difference in pure AlN with no alloying components and is 0.1722 eV/atom, it is marked here for reference. Results are presented both with magnetism calculated on the impurity site (blue columns) and non-magnetic (red columns). While in most impurities there was little to no effect on the enthalpy difference whether the system was magnetic or not, there is a significant difference with impurities of Mn, Fe and Co. Apart from these anomalies in the magnetic calculations, to be discussed further down, there is a clear trend with relative stabilization of the B1 phase compared to the B4 with impurities from within the middle of the periodic table, especially in groups 6 to 9 with platinum metals Ru, Rh, Os and Ir as potential candidates. Co might also be an interesting material, as well as the non-magnetic phase of Fe could indicate it as a material to investigate if the magnetic phase can be suppressed somehow, no method for doing such is given here. The platinum metals are both rare and expensive however, and might be unsuitable candidates for that reason, but both Fe and Co are common and readily available materials for potential applications. It can be seen from these results that Cr inclusions

Figure 4.12: Change in volume of AlN according to eq (4.2) as impurities were added. Blue columns are for the B1 structure and red is the B4.

provide one of the best alloy components for stabilizing c-AlN and even if the other candidate materials can be synthesized they may not be more effective, or they will provide other limitations to their use such as cost or magnetism.

Another factor affected by the introduction of an impurity is the equilibrium volume and a large change in volume may indicate instability. Also, lower volume of the B1 phase suggests that it can be stabilized at high pressure as was discussed in chapter 4.1.2 regarding the pressure-temperature phase diagram of (TiAl)N. As such the phase stability can be affected by equilibrium volume as well as the enthalpy. This change in volume, ΔV_{alloy} , given in percent of the AlN volume is presented in figure 4.12.

$$\Delta V_{alloy} = (V_{(TM-Al)N} - V_{AlN}) / V_{AlN} \quad (4.2)$$

A similar trend to that of enthalpy is seen in the volume as well with elemental impurities from the middle of the periodic table having a smaller impact on the volume than those on the sides. It is also noteworthy that for the elements in the middle of the periodic table the volume of the B1 phase increases by less than for the B4 phase, for Mn, Fe and Co inclusions the volume even decreases in the B1 phase relative to the volume of AlN. Although it is not a proof of solubility potential we know that (TiAl)N and (CrAl)N where the impurities have a small impact on volume can be synthesized in metastable form[1,81, 91], (ZrAl)N with a larger increase in volume is far more unstable and is harder to grow in a wide range of compositions[96,111]. Also, when the volume of the B1 phase decreases relative to

that of the B4 phase, the transition pressure may be lowered beyond the effect caused by changes in the equilibrium enthalpy as well. The transition pressure is defined as the pressure when the Gibbs' free energy G is equal for both structures.

$$G(P, T) = E(P) - TS + P \quad (4.3)$$

If the Gibbs' free energy is to be equal for the two structures and given an assumption that $T = 0$ and that $E(P)$ is unchanged for the two structures respectively, then if the volume between the two structures increases it becomes easy to see that the transition pressure has to increase in compensation. The assumption does not hold fully, while $E(P)$ is unchanged a change in pressure P changes the energy E as well, in addition there is a dependence between P and V and not just between P and ΔV but this is not enough to cause a problem regarding the direction of change, only the magnitude.

Figure 4.13: Electronic DOS for Fe impurities in AlN calculated with PBE functionals. a) B1 structure b) B4 structure. Fe has 8 valence electrons, 3 of those are bonded in the host band structure and the remaining 5 fill the impurity states. In the B1 structure the impurities make up a triplet-doublet structure, unlike the B4 structure.

As mentioned, Mn, Fe and Co gave different results in the non-magnetic and the magnetic calculations, with the magnetic calculations breaking the trends seen through the other impurities with significantly higher difference in enthalpy compared

to other impurities close to them in the periodic table. The cause for these results can be attributed to the different electronic structure of the impurities within cubic and hexagonal phases, something that results in different magnetic phases and occupation of impurity states. As mentioned in chapter 4.2.1, the cubic crystal symmetry of the B1 structure results in the separation of impurity states into a triplet-doublet structure where the triplet will fill in both spin channels before starting to occupy the doublet. This splitting is not present in the hexagonal crystal structure where all five spin up states become occupied before the electrons can start occupying the spin down channel. The effect on Fe impurities is presented in figure 4.13 as an example, Fe has 8 valence electrons, 3 of those become bonded with the host AlN band structure while the remaining 5 occupy impurity states within the band gap. In the B1 structure the triplet will occupy first with 3 electrons in the up-channel and the remaining 2 in the down channel, resulting in partially occupied states and an unfavorable occupation at the Fermi level. In the B4 structure on the other hand the 5 electrons will fully occupy the up spin channel with no occupation in the down spin channel. With filled orbitals and a DOS of zero at the Fermi level this structure will gain in favor. Co impurities provide 6 electrons, in the B1 structure the triplet fills in both spin channels, resulting in a non-magnetic phase that gains in favor compared to the B4 that now has electrons in a partially filled down spin channel. If Fe and Co impurities were considered as non-magnetic the electrons they provide would be insufficient to fill the now spin-degenerate states, resulting in a more unfavorable situation, which can be seen in the energy difference as it becomes lower compared to the magnetic case. The same is not seen in the elements of higher periods, there the magnetic interactions are too weak for the magnetic phases to become relevant. Ru barely shows any magnetism and Os, Rh and Ir it is even less to nothing.

Figure 4.14 shows the magnetic moment of each impurity element. While it is presented as the total magnetic moment of the supercell the majority of it is situated on the impurity site in most cases. Restricting discussions to period 4 elements, as period 5 and 6 elements were not consistently magnetic in these calculations, the magnetic moment in the B1 structure maxes out at 3 for Cr impurities when the up spin channel of the t_{2g} triplet is filled, at this point the magnetic moment is the same for both structures. As the number of valence electrons increases after this they will occupy the down spin channel until the triplet is filled in both spin channels at the Co impurities which becomes non-magnetic. In the B4 structure on the other hand the magnetic moment maxes out at 5 with Fe impurities.

Figure 4.14: Calculated magnetic moment for each TM impurity in the two structures. The magnetism effect is only significant in period 4 impurities. Magnetic moments are given in units of Bohr magnetons μ_B .

The conclusion is that without magnetism the B1 structure will increase in stability as the triplet fills with group 9 TM impurities, at this point the B4 structure has only partially filled orbitals with occupation at the Fermi level reducing its stability. When the number of impurity electrons increase beyond group 9 the doublet will start to fill in the B1 structure resulting in a far less favorable state. This explains the optimal states at group 9 impurities Co, Rh and Ir in the non-magnetic calculations. If the impurity states are magnetic the stability of the B1 structure will max out in group 6 with Cr impurities instead as the triplet is filled in the up channel with the B4 structure gaining favor as the electrons fill the up-spin channel for Fe and B1 again gaining favor as the triplet is filled in both channels for the B1 structure. It is also seen that magnetism is strong enough that it has to be taken into consideration for period 4 elements with 3d valence electrons. If the valence electrons are 4d or 5d the magnetic interactions decrease enough that magnetism is no longer a significant issue in group 6 to 9 impurities and the stability of the B1 maxes out Rh and Ir.

4.3 Nanocomposite multilayers

Transition metal nitride nanocomposites, such as nc-TiN-SiN have demonstrated exceptional hardness along with high oxidation resistance and thermal stability[134-138]. They have received considerable attention for the purposes of hard coating materials under extreme conditions, such as industrial grade metal cutting tools. However, SiN is highly immiscible in TiN so no bulk phase of (TiSi)N

can be expected, instead there is a phase separation during material deposition that will separate the component materials into nanometer sized grains of TiN separated by thin layers, a few atoms thick at most, of SiN in a so called tissue phase. The high hardness can be attributed to a combination of the small grains of TiN which prevent dislocations and the strong intergranular bonds of the SiN tissue phase which prevent boundary sliding[139]. For a full understanding of the improvement in hardness it is important to understand the structuring of the TiN and SiN in the interface, a subject that has received interest in past studies where a number of different suggestions have been made for the structure of the SiN interface layer[140-141]. In the past, the SiN tissue phase was considered to be amorphous[134], later reformulated to x-ray amorphous[142]. More recent studies have proposed the formation of stable crystalline phases of only a few monolayers (ML) of SiN between TiN interfaces[143-147]. Theoretical studies have considered different geometries for these SiN phases, including a hypothetical B1 structure[148-150]. It has later been shown that this B1 structure, as well as a tetrahedrally bonded zincblende B3, for the interface region are dynamically unstable, both in bulk and interfaces[151] even though they have been seen to have some stability if the SiN tissue phase is thin enough. Dynamical instability appears when the atoms are not in a stable equilibrium state without restoring forces from a small distortion due to vibrations for instance. It is most conveniently read out of the phonon dispersions where imaginary phonon frequencies indicate the instability. The cause of this dynamical instability can be attributed to the unfavorable 1:1 stoichiometry[151] and instead pseudo-B3 Si_3N_4 phases based on on L1_2 - and D0_{22} -distributions of Si-vacancies were suggested and presented in paper VII.

4.3.1 TiN-SiN

In terms of single layers of B1 SiN embedded in TiN, studies have shown that structural relaxations in the interface layer were essential for the stabilization. Along an (001) interface orientation the Si and N atoms were seen to distort by as much as 14% of the Si-Si spacing[150]. Those relaxations allowed the system to transition from one with extremely high dynamic instability due to lattice vibrations, to one with only a very small instability and only a few imaginary phonon modes in a limited part of reciprocal space. It has been indicated that small dynamical instabilities such as this can be stabilized through thermal effects[152-153]. That way, this kind of interface may still form under practical circumstances. However, this same work by Marten also showed that there was stronger dynamical stability of interfaces arranged along the (111) direction, after relaxation the phonon spectra experienced no dynamical instabilities at all when all the phonon modes were positive and real valued. Even so, the 1:1 stoichiometry turned out to be thermodynamically unstable compared to the 3:4 through the vacancy formation energy. As such, Si-vacancies can still be expected in such interfaces.

Throughout paper VII these kind of structures were considered further with more structures and thicker layers of SiN embedded between TiN. Calculations were done on both single monolayers (1ML) and three monolayers (3ML) of SiN in a cubic but tetrahedrally bonded B3 symmetry as well as a multilayered pseudo-B3 structure with Si-vacancies in a D0_{22} -style ordering. These calculations showed that in a N-terminated 1ML B3 structure, the interfaces were stable, both in regards to vacancy formation on either Si- or N-sites as well as the dynamics of vibrations, which show real valued phonon frequencies across the whole spectrum. This can likely be

attributed to the polar nature of the interface layer and the tetrahedral bonding around the Si-sites that connect to 4 N-atoms each while the total Si:N stoichiometry is only 1:2 within the interface. This makes it a possible candidate for single ML of a SiN tissue phase embedded between TiN.

But as more layers were added to the SiN interface the stoichiometry approached 1:1, especially near the center of the interface and the electronic structure and stability became closer to that of bulk SiN resulting in thermodynamic instability. The pseudo-B3 D0₂₂-ordered interface structure has a 3:4 stoichiometry where each Si-atom has 4 N-nearest neighbors and the N-atoms closest to the center of the SiN-interface each have the ideal 3 Si-atoms as nearest neighbors. This interface is closer to a known stable bulk structure for SiN and indeed, it was seen that it was stable with regards to formation of vacancies on both Si and N sites. It was not possible to calculate dynamical stability on these larger structures however, due to the large supercells and extensive computational costs. But bulk B3-D0₂₂ Si₃N₄ is dynamically stable and 1ML calculations showed that the interface was stabilized in contact with the TiN(001) layer.

4.3.2 ZrN-SiN

Another material that has received attention is ZrN-SiN, a material similar to the nanocomposites based on Ti discussed above. They show similar types of structures to nc-TiN/a-Si₃N₄ yet demonstrate different behaviors in phase segregation[154-155]. While Zr atoms have a similar electronic structure to Ti, they are significantly larger and the lattice parameter of bulk c-ZrN is much larger than that of c-TiN. Because of this larger mismatch of atomic size between the Si atoms and the Zr compared to Ti one would expect an even stronger immiscibility, which has been demonstrated in the past [156]. This can be expected to lead to different structure of the separated SiN_x tissue phase compared to what has been demonstrated in TiN-SiN nanocomposites. It has been shown that while the SiN interfaces in TiN-SiN prefer an orientation along the (111) direction, in ZrN they always align according to the (200) direction[157]. The stability of ZrN-SiN interfaces was studied in paper VIII where it was shown that this is due to a significant change in the dynamical stability of the superstructures compared to that of TiN-SiN, in particular the appearance of an extreme dynamic instability of 1ML of SiN between TiN(111) layers.

Fig 4.15: Figures of the atomic structure model. Left: Ideal 001 interface structure. Right: Ideal 111 interface. Red spheres are Zr atoms, blue are N and green are Si.

In this study, monolayers of B1 SiN was layered between slabs of B1 ZrN with interfaces arranged along both the (100) and the (111) direction, these structures are illustrated in figure 4.15. Calculations carried out on single monolayers of SiN in a 1:1 stoichiometry along (100) interfaces (see fig 4.16) showed that while the structure was dynamically unstable within the ideal lattice configuration, an observation which is consistent with previous work on TiN-SiN [150], it stabilized after suitable relaxations within the interface layers. There is a difference however; as according to Marten [150], in the case of TiN slabs, a relaxation could not fully stabilize the material and some imaginary phonon frequencies remained around the X-direction. But in ZrN-SiN (001) the interfaces were able to fully stabilize from a dynamic perspective after relaxations. Figure 4.16a show first the energy surface as the Si atom is moved across the in-plane surface by different percentages of lattice parameter, the lower left corner is representative of the ideal lattice configuration while the ridge follows the N-Si-N (110) direction. The stable configuration is achieved with a dislocation of the Si-atom by as much as 15% of the Si-Si spacing along the Si-Si (100) direction. Figure 4.16b also shows that the N-atoms are distorted by an equal amount in the opposite direction, the result is that some of the Si-N bonds are brought closer and strengthened while others are weakened. Before the relaxation (fig 4.16c) there are imaginary phonon frequencies in all directions showing complete dynamic instability but after relaxations the superstructure shows full dynamic stability as the phonon frequencies are positive and real valued in all directions (fig 4.16d).

Figure 4.16: Phonon spectra and related relaxations for 001 interface in a 1x1 inplane superstructure. a) Energy surface as the Si atom is moved to a fixed position relative to ideal lattice point (bottom left corner) and surrounding atoms are allowed to relax their positions relative to that. b) Atomic structure of the SiN interface layer after relaxations into the equilibrium state, green is Si, blue is N, empty circles are ideal positions and filled are final positions after relaxation. c) Phonon spectra in ideal crystal structure, there are imaginary phonon frequencies along the entire spectra indicating extreme dynamical instability. d) Phonon spectra after relaxation. The imaginary frequencies are gone and the system has stabilized.

In the (111) interface structure the situation changes, any attempt to relax the material, whether in a 1x1 in-plane superstructure with a single Si-atom or in larger 2x2 superstructures with a total of 4 Si-sites, allowing for the treatment of Si-vacancies in a 3:4 stoichiometry, the relaxations failed to reach a stable crystalline structure, instead relaxing into something that appears amorphous. While the 1x1 in-plane superstructure at first glance looks like a properly relaxed and stable structure, this only happened due to the limited degrees of freedom from the single N-atom and Si-atom in the interface. The phonon calculations revealed the instability through the presence of imaginary phonon frequencies across the entire spectrum, see fig 4.17b, even after the relaxation. The added degrees of freedom provided by the larger 2x2 supercells better showed the instability in relaxation, both with and without vacancies, into what clearly looks amorphous, fig 4.17a. This relaxed state was also heavily dependent on the initial state of the calculations and a small change of lattice parameters could be enough to give an entirely different relaxation pathway. While the phonon calculations could not be done on the 2x2 structures due to the computational costs, it would be a redundant operation as a stable relaxed equilibrium configuration is necessary for successful calculations of phonons, which is essentially the criterion for dynamical instability. These results were confirmed by experiments done in conjunction with these calculations where any attempt to deliberately grow

Figure 4.17: a) Atomic arrangement in the SiN monolayer given a 2x2 inplane supercell on a (111) interface orientation. It is effectively amorphous in arrangement. Note that the Si-atoms and the N-atoms are located across three different atomic layers with the Si-atoms in the middle layer and N-atoms above and below. Also, the coordinates of the atoms are given relative to the hexagonal basis vectors so the atoms are not actually on a cubic basis as it might appear in the figure. b) Phonon dispersions for a (111) interface orientation given a 1x1 inplane supercell after atomic relaxations. There are imaginary phonon frequencies across all directions.

ZrN-SiN nanocomposite tissue phases in the (111) direction failed and instead they quickly rearranged themselves into a (002) growth direction. In addition no clear SiN layers could be discerned, unlike what could be seen when deliberately growing on a (002) substrate. We attribute this instability to a complex topology of the many-dimensional energy surface provided by the atomic configuration in the interface, a topology that lacks any clear minima or equilibrium points.

Chapter 5 - Conclusions

Within this thesis the processes behind alloy thermodynamics and phase stability has been discussed, starting with the basic principles of physics, such as quantum mechanics. More practical methods of calculations have been presented, such as density functional theory (DFT). The governing principles of thermodynamics were also presented before a number of examples were brought up that illustrate some important ways through which phase stability is influenced.

Through studies of multicomponent alloying of (TiCrAl)N it has been demonstrated how it is possible to tailor different metastable intermediary phases during decomposition in order to improve on the desired material properties such as hardness. In alloys of (TiZrAl)N it was seen how phase separation through spinodal decomposition could be suppressed due to the specific topology of the formation free energy surface despite an unfavorable thermodynamic instability. It has also been demonstrated how pressure and temperature can affect the phase transformation process.

Due to the observations that additional alloying components can suppress the transformation of the AlN phase, studies were made on dilute (TMAI)N alloys where small amounts of TM impurities were added to AlN and calculated. It was shown how such impurities generate magnetic phases in otherwise non-magnetic component materials along with how those magnetic phases and local environment effects influence phase stability. New methods of density functionals were applied to remedy some of the deficiencies of standard (semi)local DFT on this class of materials, which was seen to have an effect on the results, affecting electronic structure, magnetic phases and energetics.

Nanocomposite multilayer structures such as TiN-SiN and ZrN-SiN were presented as well, discussions were made on structural properties, thermodynamic stability of the SiN tissue phases as well as, most importantly, the dynamical stability. It was shown that isostructural B1 ZrN-SiN experiences extreme dynamical instabilities if attempted to be grown in a (111) interface layer, while stabilizing well in a (001) interface. This is unlike TiN-SiN which could be stabilized in a (111) interface, although other studies indicate a pseudo-B3 Si₃N₄ tissue phase may be preferred in thicker layers.

Chapter 6 - Bibliography

- [1] P.H. Mayrhofer, C. Mitterer, L. Hultman and H. Clemens, Progress in Materials Science **51**, 1032 (2006)
- [2] R.M. Martin, Electronic structure, basic theory and practical methods. Cambridge University Press (2004)
- [3] K. Burke, The ABC of DFT, dft.uci.edu/doc/g1.pdf (2007)
- [4] L.H. Thomas, Math. Proc. Cambridge Philos. Soc. **23**, 542 (1927)
- [5] E. Fermi, Rend. Accad. Naz. Lincei, **6**, 602 (1927)
- [6] P. Hohenberg and W. Kohn, Physical Review **136**, B864 (1964)
- [7] W. Kohn and L. Sham, Physical Review **140**, A1133 (1965)
- [8] E. Schrödinger, Physical Review **28**, 1049 (1926)
- [9] M. Born and R. Oppenheimer, Annalen der Physik **84**, 457 (1927)
- [10] F. Bloch. Z. Physik A. **52**, 555 (1928)
- [11] V. Fock. Z. Physik **61**, 126 (1930)
- [12] D.R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89,111,426 (1928)
- [13] P.A.M. Dirac, Proc. Cambridge Phil. Roy. Soc. **26**, 376 (1930)
- [14] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980)
- [15] J.P. Perdew and A. Zunger, **23**, 5048 (1981)
- [16] A.D. Becke, Phys. Rev. A **38**, 3098 (1988)
- [17] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)
- [18] J.P. Perdew and K. Burke, Int. J. Quant. Chem. **57**, 309 (1996)
- [19] J.P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)
- [20] V.I. Anisimov, J. Zaanen and O.K. Andersen, Phys. Rev. B **44**, 943 (1991)
- [21] V.I. Anisimov, I.V. Solov'yev, M.A. Korotin, M.T. Czyzyk, G.A. Sawatzky, Phys. Rev. B **48**, 16929 (1993)
- [22] V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997)
- [23] J. Hubbard, P. Roy. Soc. A, **281**, 401 (1964)

- [24] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993)
- [25] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999)
- [26] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003)
- [27] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006)
- [28] V. Ivády, I.A. Abrikosov, E. Janzén, and A. Gali, Phys. Rev. B **87**, 205201 (2013)
- [29] V. Ivády, R. Armiento, K. Szász, E. Janzén, A. Gali and I.A. Abrikosov, Phys. Rev. B **90**, 035146 (2014)
- [30] S. Lany and A. Zunger, Phys. Rev. B **80**, 085202 (2009)
- [31] S. Lany and A. Zunger, Phys. Rev. B **81**, 205209 (2010).
- [32] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, Phys. Rev. B **82**, 115121 (2010)
- [33] A.V. Ruban and I.A. Abrikosov, Reports on Progress in Physics **71**, 046501 (2008)
- [34] J. Korrington, Physica (Utrecht) **13**, 392 (1947)
- [35] W. Kohn and N. Rostocker Phys. Rev. **94**, 1111 (1954)
- [36] P.E. Blöchl, Phys. Rev. B **41**, 5414 (1990)
- [37] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)
- [38] P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994)
- [39] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999)
- [40] M. Born and T. von Kármán, Physi. Z **13**, 297 (1912)
- [41] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford (1954)
- [42] P.D. De Cicco, F.A. Johnson, Proc. R. Soc. London A **310**, 111 (1969)
- [43] R. Pick, M.H. Cohen and R.M. Martin, Phys. Rev. B **1**, 910 (1970)
- [44] E.N. Zein, 1984, Fiz. Tverd. Tela (Leningrad) **26** 3024 [Sov. Phys. Solid State **26**, 1825 (1984)]
- [45] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)
- [46] S. Baroni, S. de Gironcoli and A.D. Corso, Rev. Mod. Phys. **73**, 515 (2001)
- [47] D. Marx and J. Hutter, *Ab initio molecular dynamics: basic theory and advanced methods*, Cambridge University Press (2009)
- [48] G. Kresse, J. Furthmüller and J. Hafner, Europhys. Lett. **32**, 729 (1995)
- [49] D. Alf. G.D. Price and M.J. Gillan, Phys. Rev. B **64**, 045123 (2001)
- [50] R.P. Feynman, Phys. Rev. **56**, 340 (1939)
- [51] S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995)
- [52] O. Hellman, I.A. Abrikosov and S.I. Simak, Physical Review B **84**, 180301 (2011)

- [53] O. Hellman, P. Steneteg, I.A. Abrikosov and S.I. Simak, Phys. Rev. B **87**, 104111 (2013)
- [54] S. Baroni, P. Giannozzi, and E. Isaev, Rev. Mineral. Geochem. **71**, 39 (2010) [arXiv:1112.4977v1 (2011)]
- [55] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Brooks-Cole (1976)
- [56] H. Wipf, M.V. Klein, and W.S. Williams, Phys. Stat. Sol. (b) **108**, 489 (1981)
- [57] M.V. Klein, Phys. Rev. B **24**, 4208 (1981).
- [58] C. M. Varma and W. Weber, Phys. Rev. B **19**, 6142 (1979).
- [59] B.M. Klein, L.L. Boyer and D.A. Papaconstantopoulos, Solid State Commun. **20**, 937 (1976)
- [60] E.I. Isaev, S.I. Simak, I.A. Abrikosov, R. Ahuja, Y.K. Vekilov, M.I. Katsnelson, A.I. Lichtenstein, and B. Johansson, J. Appl. Phys. **101**, 123519 (2007).
- [61] A. Zunger, S.H. Wei, L.G. Ferreira and J.E. Bernard Phys.Rev. Lett. **65** 353 (1990)
- [62] S.H. Wei, L.G. Ferreira, J.E. Bernard and A. Zunger, Phys.Rev. B **42**, 9622 (1990)
- [63] P. Soven, Phys. Rev. **156**, 809 (1967)
- [64] B.L. Györfy, Phys. Rev. B **5**, 2382 (1972)
- [65] B. Alling, A.V. Ruban, A. Karimi, O. Peil, S.I. Simak, L. Hultman, and I.A. Abrikosov, Phys. Rev. B **75**, 045123 (2007)
- [66] I.A. Abrikosov, A.M.N. Niklasson, S.I. Simak, B. Johansson, A.V. Ruban and H.L. Skriver, Phys. Rev. Lett. **76**, 4203 (1996)
- [67] I.A. Abrikosov, S.I. Simak, B. Johansson, A.V. Ruban and H.L. Skriver, Phys. Rev. B **59**, 11693 (1999)
- [68] R. Rachbauer, S. Massl, E. Stergar, D. Holec, D. Kiener, J. Keckes, J. Patscheider, M. Stiefel, H. Leitner and P.H. Mayrhofer, J. Appl. Phys. **110**, 023515 (2011)
- [69] P.H. Mayrhofer, A. Hörling, L. Karlsson, J. Sjöln, T. Larsson, C. Mitterer and L. Hultman, Appl. Phys. Lett. **83**, 2049 (2003)
- [70] A. Hörling, L. Hultman, M. Odén, J. Sjöln and L.J. Karlsson, Vac. Sci. Technol. A **20**, 1815 (2002)
- [71] A. Hörling, L. Hultman, M. Odén, J. Sjöln and L. Karlsson, Surf. Coat. Technol. **191**, 384 (2005)
- [72] A. Knutsson, M.P. Johansson, L. Karlsson, M. Odén, J. Appl. Phys. **108**, 044312 (2010)
- [73] G. Beensh-Marchwicka, L. Król-Stepniewska, P. Posadowski, Thin Solid Films **82**, 313 (1981)
- [74] O. Knotek, W.D. Münz, T. Leyendecker, J. Vac. Sci. Technol. A **5**, 2173-2179 (1987)

- [75] H. Jehn, S. Hoffmann, V.E. Rückborn and W.D. Münz, *J. Vac. Sci. Technol. A* **4**, 2701-2705 (1986)
- [76] W.D. Münz, *J. Vac. Sci. Technol. A* **1986**, 4, 2717-2725.
- [77] McIntyre, J.E. Greene, G. Håkansson, J.E. Sundgren and W.D. Münz, *J. Appl. Phys.* **67**, 1542-1553 (1990)
- [78] H. Jehn, S. Hoffman, and W.D. Münz, *Metal* **42**, 658-669 (1988)
- [79] A. Madan, I.W. Kim, S.C. Cheng, P. Yashar, V.P. Dravid and S.A. Barnett, *Phys. Rev. Lett.* **78**, 1743 (1997)
- [80] A. Knutsson, M. P. Johansson, P. O. A. Persson, L. Hultman, and M. Odén, *Appl. Phys. Lett.* **93**, 143110 (2008)
- [81] B. Alling, T. Marten, I. A. Abrikosov, and A. Karimi, *J. Appl. Phys.* **102**, 044314 (2007)
- [82] B. Alling, A. Karimi, and I.A. Abrikosov, *Surf. Coat. Technol.* **203**, 883-886 (2008)
- [83] P.H. Mayrhofer, D. Music, J.M. Schneider, *Appl. Phys. Lett.* **88**, 071922 (2006)
- [84] B. Alling, M. Odén, L. Hultman and I.A. Abrikosov, *Appl. Phys. Lett.* **95**, 181906 (2009)
- [85] D. Holec, F. Rovere, P.H. Mayrhofer and P.B. Barna, *Scripta Mater.* **62**, 349-352 (2010)
- [86] A. Knutsson, J. Ullbrand, L. Rogström, N. Norrby, L.J.S. Johnson, L. Hultman, J. Almer, M.P. Johansson-Jöesaar, B. Jansson and M. Odén, *J. Appl. Phys.* **113**, 213518 (2013)
- [87] N. Norrby, L. Rogström, M.P. Johansson-Jöesaar, N. Schell, M. Odén, *Acta Mater.* **73**, 205-214 (2014)
- [88] A. Sugishima, H. Kajioka and Y. Makino, *Surf. Coat. Technol.* **97**, 590 (1997)
- [89] A.E. Reiter, V.H. Derflinger, B. Hanselmann, T. Bachmann and B. Sartory, *Surf. Coat. Technol.* **200**, 2114 (2005)
- [90] H. Willmann, P.H. Mayrhofer, P.O.Å. Persson, A.E. Reiter, L. Hultman and C. Mitterer, *Scripta Mater.* **54**, 1847 (2006)
- [91] P.H. Mayrhofer, D. Music, Th. Reeswinkel, H.G. Fuß and J.M. Schneider, *Acta Mater.* **56**, 2469 (2008)
- [92] B. Alling, L. Hultberg, L. Hultman and I.A. Abrikosov, *Appl. Phys. Lett.* **102**, 031910 (2013)
- [93] L. Rogström, L.J.S. Johnson, M.P. Johansson, M. Ahlgren, L. Hultman, and M. Odén, *Scripta Mater.* **62**, 739-741 (2010)
- [94] L. Rogström, L.J.S. Johnson, M.P. Johansson, M. Ahlgren, L. Hultman, and M. Odén, *Thin Solid Films* **519**, 694-699 (2010)
- [95] D. Holec, R. Rachbauer, L. Chen, L. Wang, D. Luef, and P. H. Mayrhofer, *Surf. Coat. Technol.* **206**, 1698-1704 (2011)
- [96] L. Rogström, M. Ahlgren, J. Almer, L. Hultman, and M. Odén, *J. Mater. Res.* **27**, 1716-1724 (2012)

- [97] P.H. Mayrhofer, D. Sonnleitner, M. Bartosik, and D. Holec, *Surf. Coat. Technol.* **244**, 52-56 (2014)
- [98] L. Rogström, M.P. Johansson, N. Ghafoor, L. Hultman, and M. Odén, *J. Vac. Sci. Technol. A* **30**, 031504 (2012)
- [99] S.H. Sheng, R.F. Zhang, and S. Veprek, *Acta Materialia* **56**, 968-976 (2008)
- [100] Q. Luo, W. M. Rainforth, L. A. Donohue, I. Wadsworth, and W. Münz, *Vacuum* **53**, 123 (1999)
- [101] A.E. Santana, A. Karimi, V.H. Derflinger, and A. Schütze, *Surf. Coat. Technol.* **177-178**, 334 (2004).
- [102] H.W. Hugosson, H. Högberg, M. Algren, M. Rodmar, and T.I. Selinder, *J. Appl. Phys.* **93**, 4505 (2003)
- [103] S.G. Harris, E.D. Doyle, A.C. Vlasveld, J. Audy, J.M. Long, and D. Quick, *Wear* **254**, 185 (2003)
- [104] Z.F. Zhou, P.L. Tam, P.W. Shum, and K.Y. Li, *Thin Solid Films* **517**, 5243 (2009)
- [105] A. I. Kovalev, D. L. Wainstein, A. Y. Rashkovskiy, G. S. Fox-Rabinovich, K. Yamamoto, S. Veldhuis, M. Aguirre, and B. D. Beake, *Vacuum* **84**, 184 (2009)
- [106] R. Forsén, M. Johansson, M. Odén and N. Ghafoor, *J. Vac. Sci. Technol. A* **30**, 061506 (2012)
- [107] R. Forsén, N. Ghafoor and M. Odén, *J. Appl. Phys.* **114**, 244303 (2013)
- [108] R. Forsén, M.P. Johansson, M. Odén and N. Ghafoor, *Thin Solid Films* **534**, 394-402 (2013)
- [109] L. Chen, D. Holec, D. Yong, and P. H. Mayrhofer, *Thin Solid Films* **519**, 5503-5510 (2011)
- [110] L. Rogström, N. Ghafoor, M. Ahlgren, and M. Odén, *Thin Solid Films* **520**, 6451-6454 (2012)
- [111] D. Holec, L. Zhou, R. Rachbauer, and P. H. Mayrhofer, *J. Appl. Phys.* **113**, 113510 (2013)
- [112] G. Abadias, I. A. Saladukhin, V. V. Uglov, S. V. Zlotski, and D. Eyidi, *Surf. Coat. Technol.* **237**, 187-195 (2013)
- [113] D. Holec, L. Zhou, R. Rachbauer and P.H. Mayrhofer, *J. Appl. Phys.* **113**, 113510 (2013)
- [114] R. Rachbauer, D. Holec, M. Lattemann, L. Hultman and P.H. Mayrhofer, *International Journal of Materials Research* **102**, 735-742 (2011)
- [115] R. Rachbauer, D. Holec and P.H. Mayrhofer, *Surf. Coat. Technol.* **211**, 98-103 (2012)
- [116] H. Vollstadt, E. Ito, M. Akaishi, S. Akimoto and O. Fukunaga, *Proc. Jpn. Acad. B* **66**, 7 (1990)
- [117] N.E. Christensen and I. Gorczyca, *Physical Review B* **47**, 4307 (1993)
- [118] A. Siegel, K. Parlinski and U. Wdowik, *Physical Review B* **74**, 104116 (2006)
- [119] E. Ruiz, S. Alvarez and P. Alemany, *Physical Review B* **49**, 7115 (1994)

- [120] W.Y. Ching and B.N. Harmon, Phys. Rev. B **34**, 5305 (1986)
- [121] H. Ohno, Science **281**, 951 (1998)
- [122] P. Mahadevan and A.Zunger, Physical Review B **69**, 115211 (2004)
- [123] C.G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004)
- [124] A. Zunger, S. Lany and H. Raebiger, Physics **3**, 53 (2010)
- [125] S.Y. Wu, H.X. Liu, L. Gu, R.K. Singh, L. Budd, M. van Schilfgaarde, M.R. McCartney, D.J. Smith and N. Newman, Appl. Phys. Lett. **82**, 3047 (2003)
- [126] D. Kumar, J. Antifakos, M.G. Blamire and Z.H. Barber, Appl. Phys. Lett. **84**, 5004 (2004)
- [127] H.X. Liu, S.Y. Wu, R.K. Singh, L. Gu, D.J. Smith, N. Newman, N.R. Dilley, L. Montes and M.B. Simmonds, Appl. Phys. Lett. **85**, 4076 (2004)
- [128] L.J. Shi, L.F. Zhu, Y.H. Zhao and B.G. Liu, Physical Review B **78**, 195206 (2008)
- [129] L. Corliss, N. Elliott and J. Hastings, Physical Review, **117**, 929 (1960)
- [130] B. Alling, T. Marten and I.A. Abrikosov, Physical Review B **82**, 184430 (2010)
- [131] P. Steneteg, B. Alling and I.A. Abrikosov, Physical Review B **85**, 144404 (2012)
- [132] S.W. Fan, K.L. Yao, Z.G. Huang, J. Zhang, G.Y. Gao and G.H. Du, Chemical Physics Letters **482**, 62 (2009)
- [133] Q. Guo and A. Yoshida, Jpn. J. Appl. Phys. **33**, 2453 (1994)
- [134] S. Veprek and S. Reiprich, Thin Solid Films **268**, 64 (1995)
- [135] S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova, and J. Prochazka, Thin Solid Films **476**, 1 (2005)
- [136] S. Veprek, J. Nanosci. Nanotechnol. **11**, 14 (2011)
- [137] L. Hultman, J. Bareno, A. Flink, H. Söderberg, K. Larsson, V. Petrova, M. Odén, J.E. Greene, and I. Petrov, Phys. Rev. B **75**, 155437 (2007)
- [138] A. Niederhofer, T. Bolom, P. Nesladek, K. Moto, C. Eggs, D. S. Patil, and S. Veprek, Surf. Coat. Technol. **146–147**, 183 (2001)
- [139] J. Schiotz, F.D. Di Tolla, and K.W. Jacobsen, Nature (London) **391**, 561 (1998)
- [140] R.F. Zhang, A.S. Argon, and S. Veprek, Phys. Rev. Lett. **102**, 015503 (2009)
- [141] R.F. Zhang, A.S. Argon, and S. Veprek, Phys. Rev. B **79**, 245426 (2009)
- [142] S. Veprek, High Press. Res. **26**, 119 (2006)
- [143] L. Hultman, J. Bareño, A. Flink, H. Söderberg, K. Larsson, V. Petrova, M. Odén, J.E. Greene, and I. Petrov, Phys. Rev. B **75**, 155437 (2007)
- [144] H. Söderberg, M. Odén, J.M. Molina-Aldareguia, and L. Hultman, J. Appl. Phys. **97**, 114327 (2005)
- [145] H. Söderberg, M. Odén, A. Flink, J. Birch, P.O.A. Persson, M. Beckers, and L. Hultman, J. Mater. Res. **22**, 3255 (2007)

- [146] S. Hao, B. Delley, S. Veprek, and C. Stampfl, Phys. Rev. Lett. **97**, 086102 (2006)
- [147] S. Hao, B. Delley, and C. Stampfl, Phys. Rev. B **74**, 035402 (2006)
- [148] R.F. Zhang, S.H. Sheng, and S. Veprek, Appl. Phys. Lett. **90**, 191903 (2007)
- [149] S. Veprek, A.S. Argon, and R.F. Zhang, Philos. Mag. Lett. **87**, 955 (2007)
- [150] T. Marten, E.I. Isaev, B. Alling, L. Hultman, and I. A. Abrikosov, Phys. Rev. B **81**, 212102 (2010)
- [151] B. Alling, E.I. Isaev, A. Flink, L. Hultman, and I.A. Abrikosov, Phys. Rev. B **78**, 132103 (2008)
- [152] C. Asker, A.B. Belonoshko, A.S. Mikhaylushkin, and I.A. Abrikosov, Phys. Rev. B **77**, 220102 (2008)
- [153] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Phys. Rev. Lett. **100**, 095901 (2008)
- [154] T. Mae, M. Nose, M. Zhou, T. Nagae, and K. Shimamura, Surf. Coat. Technol. **142–144**, 954 (2001)
- [155] S.H. Sheng, R.F. Zhang, and S. Veprek, Acta Mater. **59**, 297 (2011)
- [156] P.J. Martin, A. Bendavid, J.M. Cairney, and M. Hoffman, Surf. Coat. Technol. **200**, 2228 (2005)
- [157] Y. Dong, W. Zhao, J. Yue, and G. Li, Appl. Phys. Lett. **89**, 121916 (2006)

List of included Publications

Paper I

Phase Stability and Elasticity of TiAlN

I.A. Abrikosov, A. Knutsson, B. Alling, F. Tasnádi, H. Lind, L. Hultman and M. Odén, *Materials* **4**, 1599-1618 (2010)

Summary

A review of theoretical and experimental studies of the properties of TiAlN alloys. The basic thermodynamic principles that govern phase transformations and thermal stability are brought up, along with examples from both theory and experiments. Discussions are made on how this affects the various mechanical properties such as hardness and elasticity.

Author's Contribution

I participated in the writing and editing of the paper while working on similar alloy systems for papers II and III.

Paper II

Improving thermal stability of hard coating films via a concept of multicomponent alloying

H. Lind, R. Forsén, B. Alling, N. Ghafoor, F. Tasnádi, M.P. Johansson, I.A. Abrikosov and M. Odén, *Applied Physics Letters* **99**, 091903 (2011)

Summary

A combination of theoretical predictions and experimental verifications on the decomposition pathways of (TiCrAl)N. The paper demonstrates methods by which it is possible to predict phase decomposition pathways and use that to find metastable decomposition products that improve thermal stability and high temperature hardness of a material.

Author's Contribution

I carried out all calculations of free energy surface and phase stability of the alloy with guidance by supervisors and other co-authors. I partook greatly in discussions and analysis of the theoretical predictions. I was primary author and wrote most of the paper, with the experimental parts as the exception.

Paper III

High temperature phase decomposition in $Ti_xZr_yAl_zN$

H. Lind, R. Pilemalm, L. Rogström, F. Tasnádi, N. Ghafoor, R. Forsén, L.J.S. Johnson, M.P. Johansson-Jöesaar, M. Odén and I.A. Abrikosov, AIP Advances **4**, 127147 (2014)

Summary

A combination of theoretical calculations and experiments analyzing phase stability of (TiZrAl)N alloys. While (TiZrAl)N is thermodynamically unstable and will experience rapid decomposition for most compositions it was shown that for high Zr-content alloys it could resist spinodal decomposition due to peculiarities in the topology of the free energy surface.

Author's Contribution

I carried out all calculations and theoretical work. Alongside all co-authors I discussed and analyzed both theoretical and experimental results. I was primary author and wrote most of the paper except the experimental parts.

Paper IV

High pressure and high temperature stabilization of cubic AlN in $Ti_{0.60}Al_{0.40}N$

N. Norrby, H. Lind, G. Parakhonskiy, M.P. Johansson, F. Tasnádi, L.S. Dubrovinsky, N. Dubrovinskaia, I.A. Abrikosov and M. Odén, Journal of Applied Physics **113**, 053515 (2013)

Summary

A combined theoretical and experimental study on the effect of both temperature and pressure on the phase stability of the cubic AlN phase inside TiAlN. Through experiments and calculations we found the phase diagram describing the transition between cubic and hexagonal phases.

Author's Contribution

I carried out all first-principle calculations needed for determining the phase diagram. I partook in discussion on analyzing the results and wrote the theoretical parts of the paper. I also assisted in the editing process of the rest of the paper.

Paper V

Systematic theoretical search for alloys with increased thermal stability for advanced hard coating applications

H. Lind, F. Tasnádi and I.A. Abrikosov, New Journal of Physics **15**, 095010 (2013)

Summary

A theoretical analysis on the impact of small amounts of transition metals (TM) added into AlN on the relative stability of the cubic and hexagonal phases. A systematic search across all transition metals was carried out, leading to an observation of trends across the periodic table.

Author's Contribution

I carried out all calculations by myself and conducted most of the analysis by myself with occasional discussions and consultations with my supervisors. I was primary author and wrote most of the paper.

Paper VI

Ti and Cr impurities in cubic and hexagonal AlN

H. Lind, F. Tasnádi and I.A. Abrikosov, In Manuscript

Summary

Paper V did a systematic search across all TM using simple methods in order to observe general trends. In this paper more detailed calculations were on impurities of Ti and Cr, observing electronic structure, phase stability and magnetic phases. In addition, a more advanced method for treating exchange-correlation functionals, the mHSE+Vw, was applied.

Author's Contribution

I planned most of the calculations myself and carried them out myself. I did most of the analysis of the results myself. I was primary author and did most of the writing.

Paper VII

First-principles study of SiN_x/TiN(001) interface

T. Marten, B. Alling, E.I. Isaev, H. Lind, F. Tasnádi, L. Hultman and I.A. Abrikosov, Physical Review B **85**, 104106 (2012)

Summary

Theoretical calculations on the dynamic and thermodynamic stability of SiN_x interface layers between TiN. Studies of both monolayers and multilayers of SiN in a number of different configurations have been carried out. It is shown that otherwise unstable phases of SiN can become stabilized in monolayers, but in thick enough layers the SiN phase prefers a pseudo-B3 structure with a 3:4 stoichiometry

Author's Contribution

I partook in discussions and assisted in some computational work and analysis while I was working on my own project in paper VIII. I had a part in the editing of the paper.

Paper VIII

Anomalous epitaxial stability of (001) interfaces in ZrN/SiN_x multilayers

N. Ghafoor, H. Lind, F. Tasnádi, I.A. Abrikosov and M. Odén, APL Materials **2**, 046106 (2014)

Summary

An observation in theoretical calculations of an extreme dynamic instability of (111) directed interfaces between ZrN and SiN tissue phases initiated a set of experiments intended to observe growth directions and interface stability. These experiments confirmed the experiments prediction on instability as (111) interfaces did not grow.

Author's Contribution

I carried out all calculations and much of the analysis throughout the project. I wrote the theoretical parts of the manuscript and assisted in the editing of the rest.

Paper IX

Giant two-phonon Raman scattering from nanoscale NbC precipitates in Nb

C. Cao, R. Tao, D.C. Ford, R. Klie, T. Proslir, L. Cooley, A. Dzyuba, P. Zapol, M. Warren, H. Lind and J.F. Zasadzinski, Accepted for publication in Physical Review B

Summary

A very large two-phonon Raman response was observed in NbC inclusions inside a bulk Nb sample. This allowed for an unprecedented comparison of these Raman features with the softening regions in the phonon dispersion relations.

Author's Contribution

On the request of the other authors I carried out calculations of phonon dispersion relations in bulk NbC at both equilibrium conditions and uniform compressive strain. I partook in some discussion on the analysis of the results. I wrote a segment on the computational method used by myself and helped edit the written text.

Other Publications

Electric-field control of magnetization in biased semiconductor quantum wires and point contacts

H. Lind, I. Yakimenko and K.-F. Berggren, Physical Review B **83**, 075308 (2011)

This paper was written as the culmination of my masters thesis. It predicts spontaneous spin-splitting of states inside quantum-wires, driven by Hartree-Fock exchange.

Theoretical description of pressure-induced phase transitions: a case study of Ti-V alloys

I.A. Abrikosov, A.V. Ponomareva, A.Yu. Nikonov, A.M. Zharmukhambetova, I.Yu. Mosyagin, A.V. Lugovskoy, O. Hellman, H. Lind, A.I. Dmitriev and S.A. Barannikova, High Pressure Research, 2014

A general overview of phase stability under pressure. I contributed some of the presented data and worked with similar problems of pressure thermodynamics.

Papers

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-115405>