Phase field modeling of Spinodal decomposition in TiAlN

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TiAlN thin films are used commercially in the cutting tool industry as wear protection of the inserts. During cutting, the inserts are subjected to high temperatures (~ 900 °C and sometimes higher). The objective of this work is to simulate the material behavior at such high temperatures. TiAlN has been studied experimentally at least for two decades, but no microstructure simulations have so far been performed. In this thesis two models are presented, one based on regular solution and one that takes into account clustering effects on the thermodynamic data. Both models include anisotropic elasticity and lattice parameters deviation from Vegard’s law. The input parameters used in the simulations are ab initio calculations and experimental data.

Methods for extracting diffusivities and activation energies as well as Young’s modulus from phase field results are presented. Specifically, strains, von Mises stresses, energies, and microstructure evolution have been studied during the spinodal decomposition of TiAlN. It has been found that strains and stresses are generated during the decomposition i.e. von Mises stresses ranging between 5 and 7.5 GPa are typically seen. The stresses give rise to a strongly composition dependent elastic energy that together with the composition dependent gradient energy determine the decomposed microstructure. Hence, the evolving microstructure depends strongly on the global composition. Morphologies ranging from isotropic, round domains to entangled outstretched domains can be achieved by changing the Al content. Moreover, the compositional wavelength of the evolved domains during decomposition is also composition dependent and it decreases with increasing Al content. Comparing the compositional wavelength evolution extracted from simulations and small angle X-ray scattering experiments show that the decomposition of TiAlN occurs in two stages; first an initial stage of constant wavelength and then a second stage with an increasing wavelength are observed. This finding is characteristic for spinodal decomposition and offers conclusive evidence that an ordering transformation occurs. The Young’s modulus evolution for Ti_{0.33}Al_{0.67}N shows an increase of 5% to ~398 GPa during the simulated decomposition.
This work was performed between October 2009 and September 2012 in the Nanostructured Material group at the Department of Physics, Chemistry and Biology at Linköping University. The aim of the project in this thesis is to set up models, using the phase field method, for simulating spinodal decomposition in TiAlN, which has resulted in the three papers included here. The work has been performed within the Vinnova Excellence center, FunMat in Theme 2, with the industrial partners Seco Tools AB, Sandvik and Ionbond.
Included Papers

Paper I

Strain evolution during spinodal decomposition of TiAlN thin films
L. Rogström, J. Ullbrand, J. Almer, L. Hultman, B. Jansson, and M. Odén

Paper II

Early stage spinodal decomposition and microstructure evolution in TiAlN – A combined in-situ SAXS and phase field study
Manuscript in final preparation

Paper III

Microstructure evolution of TiAlN – a phase field study
J. Ullbrand, K. Grönhagen, F. Tasnádi, B. Jansson, and M. Odén
In Manuscript
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Paper I

Paper II

Paper III
1 Introduction

Thin films are used in a variety of applications, e.g. optical coatings on windows, decoration on cellphones, or as in this study for coating cutting tool inserts to increase their wear resistance. During cutting the insert is exposed to high temperatures [1] and high pressures [2]. To increase productivity in the industry there is a constant demand for higher cutting speeds, and inserts that can sustain these extreme conditions. TiAlN is one of the coating materials on the market that shows an increased hardness at elevated temperatures (age hardening) [3], and remains wear resistant. The underlying mechanism of this age hardening is assigned to spinodal decomposition, causing compositional variations and strain fields. Small nuclei of hexagonal-AlN (h-AlN) are also likely to be of importance, as discussed in Paper I. To address the age hardening mechanism, the spinodal decomposition has been studied using the phase field method based on thermodynamic considerations. With the phase field method, meso-scale phenomena such as solidification, solid state transformations, nucleation and growth, and dislocation movements can be studied [4].

1.1 Aim of the thesis

This work is based on the phase field method; applied to study the spinodal decomposition in thin films of TiAlN. The interest lies in predicting and explaining properties of the phase transformation and together with experimental studies get a more complete picture of the mechanisms involved. The focus has been to use the available experimental and calculated data of the system, in order
to predict microstructure evolution and domain sizes, as well as the corresponding Young's modulus. An attempt has also been made to estimate the diffusivity constant and activation energy of TiAlN from simulations coupled with experimental data.

1.2 Outline

The thesis is organized as follows: Chapter 2 is an introduction to cutting tool materials and coating synthesis processes, followed by the description of TiAlN. The last section of the chapter gives a brief introduction to suitable experimental techniques which give data sets comparable with the simulation output. Chapter 3 describes, in general terms, the two phase transformations that are considered in the thin film application of TiAlN, nucleation and growth, and spinodal decomposition. The following chapter, Chapter 4, is an introduction to phase field modeling with focus on the Cahn Hilliard model. The functional, as well as the differential equation, and the gradient energy term are derived. In the last section, the sharp-interface Allen–Cahn model is briefly described. Chapter 5 describes the model, and it is divided into four sections. Section one derives the specific partial differential equations used, section two the boundary conditions, section three describes the input parameters including an introduction to elasticity theory, and finally section four describes the output parameters. Chapter 6 describes the analysis methods used, their restrictions and validity. In Chapter 7 I summarize the included papers and conclude the thesis. In the end of the thesis the three papers are appended.
2 Cutting tools and TiAlN

Cutting tool inserts are used in a wide range of industrial applications, such as aerospace and automotive fields. Important properties for a cutting insert are inertness, wear resistance, toughness, oxidation resistance, thermally sustainability etc., all of which are customized for the application. To tune these properties, a common method of choice is to use a substrate of a hard material and coat it with a thin film of desired properties. The most coated substrate, used in 80–90% of the cases for cutting inserts, is cemented carbide [5] and one of the most used hard coatings is TiAlN. In this chapter a background and an introduction to hard coatings and TiAlN are given. In the end a few selective experimental characterization techniques are described.

2.1 Cemented carbide

Cemented carbide consists of hard WC grains (~80%) in a Co binder matrix. Its desirable properties as a substrate stem from the fact that it is sintered from a powder, and can therefore come in a variety of shapes. It is both hard, due to the WC grains and tough due to the Co binder. The properties of cemented carbide are tuned by the composition of the composite and grain size of the WC [6]. Usually, different cubic carbo-nitrides are added to increase its hardness at higher temperatures. Another tuning technique is to introduce compositional gradients in the substrate to control the stress state, and get a harder material at the substrate to thin film interface, and a tougher material further away from the film surface [7,8]. Even though these properties seem ideal, the wear resistance of the insert is
improved by a thin coating deposited by Chemical Vapor deposition (CVD) or Physical Vapor Deposition (PVD) techniques.

2.2 CVD and PVD

CVD and PVD are the two coating deposition methods for cutting tools.

In CVD an exothermal chemical reaction between introduced gases and the substrate generates the film [9]. There exist several types of CVD, the two major classes are high pressure and low pressure CVD. In CVD, a certain amount of energy is introduced to drive the chemical reactions, how this energy is added depends on the type, e.g. thermal heating, and plasma assisted heating. This produces thermodynamically stable thick films where the final films are limited to available chemical reactions and known catalysts. CVD is the most widespread technique which delivers uniform films with excellent adhesion to cemented carbide, covering substrate cavities [10]. A drawback of the technique is that hazardous gases may be formed as a byproduct during the process [9].

In PVD a vaporized metal is transported to the substrate where it condensates. There exist several types of PVD techniques depending on how the cathode material is vaporized. The one considered here is cathodic arc evaporation, where solid cathodes are evaporated by a localized high current, low voltage arc moving on the cathode surface, causing high local temperatures [11] and crater spots of the cathode [12,13]. A crater spot is only active for a short time before the arc dies and is re-ignited at another spot close by. If light elements such as N₂ are to be incorporated in the film, it can be introduced as a gas, which reacts with the high velocity vapor of electrons and positively charged ions. The plasma is transported e.g. by applying a negative bias to the substrate where the ions condensates. The high velocity vapor impinges the film during growth and rearranges atoms. Its energy is lost by e.g. collisions and the energetic cost for new bond formation [13].

PVD is preferable for creating thermodynamically unstable films where a combination of low temperature, to limit surface diffusion, and high energy ions are used. Another advantage is that it is a fast reproducible method that can be applied to sharp cutting edges. Point defects and compressive stresses, as well as small grains, are characteristics properties for PVD films known to increase the hardness [14,15]. The point defects and grain boundaries are acting as obstacles for
dislocation movement, by the strain field surrounding the defects, and the compressive stresses are known to increase the time until fracture when applying a load [16]. The amount of incorporated defects depends on the kinetic energy of the vapor and increases with increasing negative substrate bias [17]. The small grain size is a result of impingement of new species (droplets, neutrals and metals) to the growing film that enhances re-nucleation[14]. All these beneficial effects have led to an increase in PVD usage. A drawback of the method is that the high residual stresses also sets a limit for the thickness of PVD films [18]. Additionally, macro particles, in the case of arc-evaporation, are incorporated into the growing film, affecting its properties e.g. causing voids and roughness and changes in the composition [13,19,20].

The focus of this work is thermodynamically unstable TiAlN films that is produced by arc evaporation, but let us start from the beginning, with TiC.

2.3 From TiC to TiAlN

In 1968, the first commercial coating, TiC, was deposited on cemented carbide with CVD [21]. Just a few years later, the gold-colored TiN coatings, also deposited by CVD, with a higher toughness than TiC were released. The CVD technique was at the time preferable since the PVD coatings struggled with e.g. adhesion and rate problems. In 1979, the PVD coating of TiN emerged on the market [22]. From that point, the number of PVD coatings used commercially has increased steadily. Today are e.g. TiCN and TiAlN, with increased wear and oxidation resistance, as well as oxides deposited with PVD [22]. Aluminum was added to TiN to increase the oxidation resistance, which it successfully did by forming a stable oxide layer [23] on top of the thin film. But not only did the oxidation resistance increase, there was also an observed retained hardness at high temperatures, so called age hardening [3].

Recent development of hard coatings revolves around designing and controlling texture [18], nanostructures such as multilayers [22,24], and experimenting with crystal grains in amorphous matrices. TiAlCrN coatings have been developed, exhibiting improved wear resistance at elevated temperatures compared to TiAlN, for performance at faster cutting speeds [25]. Still, the interesting phenomena of age hardening with increasing temperature in e.g.
TiAlN and TiAlCrN are not fully understood. In this work the focus is to study TiAlN, which is the material system with more published experimental and theoretical data.

2.4 The material system TiAlN

When performing microstructural phase field simulations, a wide range of material input parameters are needed, and hence the availability of data is of importance. TiAlN is a well-known material system that has been studied with various experimental and computational methods, for a review see e.g. [26]. In this section a short review of the literature on TiAlN is given.

2.4.1 Thermodynamics

According to ab-initio calculations, TiAlN, exhibits a large miscibility gap [27], which does not close until the alloy melts at \( \sim 3000 \) K [28]. This is assigned to the difference in electronic configuration in Ti and Al, where the d states of Ti cannot bond to Al [29], due to the lacking d-state of Al. Consistently, early experimental results show that only a few at. % of AlN is dissolvable in TiN at equilibrium conditions [28]. It is possible to deposit thermodynamically unstable thin films of NaCl structured cubic-TiAlN (c-TiAlN) by PVD up to a maximum Al content of \( \sim 70 \) at. %. Above this, h-AlN grows [30–32]. There is a spinodal region inside the miscibility gap, for approximately Al>20 at.%, where the phase transformation to the c-TiN and metastable c-AlN domains occur [27]. If enough free energy is available the equilibrium phase of h-AlN can nucleate in the metastable c-AlN domains. Outside the spinodal but inside the miscibility gap, the transformation to the stable c-TiN and h-AlN takes place by nucleation and growth. The system has been studied by Differential Scanning Calorimetry (DSC), where three exothermal peaks appear during thermal treatment, see Paper I or ref. [33]. The first peak is identified as annihilation of defects, the second to latent heat release during the spinodal decomposition, and the third peak to the transformation of c-AlN to h-AlN.
2.4.2 Properties

Hörling et al. studied how the lifetime of the tool was affected by composition, and showed an increased lifetime with Al content [31]. An age hardening effect, appreciated during cutting when high temperatures and pressures evolve [26,34], has also been observed and attributed to spinodal decomposition [3]. During the spinodal decomposition coherency strains develop see e.g. Paper I. Further studies confirmed that the decomposed structure has a coherent cubic lattice with compositional fluctuations, see e.g. Paper II or ref. [35]. Recently, atom probe measurements confirms that diffuse interfaces, characteristic for spinodal decomposition, exist after annealing [36,37]. The knowledge of TiAlN has also been expanded by theoretical calculations of the elastic constants [38], and the lattice parameter dependence on composition, see Paper I or refs. [29,39]. These results are presented in section 5.3, and are used as input parameters in the simulations performed within this work.

2.5 Characterization techniques

A variety of techniques for coating characterization exists. Here, a selection of the ones used in the included papers will be presented. The aim is not to give a full description, but rather give a brief overview of the techniques.

2.5.1 WAXS and SAXS

Wide Angle X-ray Scattering (WAXS) and Small Angle X-ray Scattering (SAXS) are both non-destructive methods that use X-rays to gain information on elemental composition, phases, texture, strain, and grain size (WAXS), as well as particle shape and size (SAXS). The same basic theory applies to both techniques, but the scattering angles studied are different. Electron waves fulfilling Bragg’s law

$$2d \sin(\theta) = m \cdot \lambda$$

scatter by the atomic planes and interfere constructively. The intensity of the scattered electrons is detected as a function of angle. Here, d is the distance between atomic planes, \(\theta\) the scattering angle, and m an integer coupled to the order of diffraction, and \(\lambda\) the beam wavelength. In order to observe diffraction,
the beam needs to be in the same order of magnitude as the plane distance, i.e. in the 1–100 Å range.

For WAXS, scattering angles larger than 5° are detected and Å-size features of the electronic density are studied. The detected peaks give a fingerprint of the material. Elemental information, crystal structure, its crystalline quality and texture are given by the peak position, and the grain size and micro strain by the peak broadening.

With SAXS, scattering angles around 0–5° from the transmitted center spot is detected, and modulations of 1–10 nm in the electronic density are studied. With SAXS, the 2D intensity depends on larger modulations of the electronic structure that arises from composition fluctuations, structure differences, pores or voids. By assuming a particle shape and using the maximum entropy method, a particle distribution and its scattered intensity, \( I \), can be calculated, after Potton [40].

\[
I = \int G_j(q, D) f(D) dD, \quad j = 1 \ldots M
\]  

(2.2)

Here \( G_j(q, D) \) is the scattering intensity function for a single particle with scattering vector \( q \) and diameter \( D \). \( f(D) \) is the volume distribution function of the particles integrated over the small change in the diameter, \( D \). \( G_j(q, D) \) can be calculated by assuming a shape of the particles and \( f(D) \) can be extracted from experiments. If the volume distribution is assumed to be the same for all particles, the integral is reduced to a sum. Applying the maximization method of the configurationally entropy on the volume distribution function gives:

\[
S = - \sum_{i=1}^{N} \left( \frac{f(D_i) \Delta D_i}{b_i} \log \left( \frac{f(D_i) \Delta D_i}{b_i} \right) \right), \quad j = 1 \ldots M,
\]  

(2.3)

where the sum is over a range of size dimensions, \( D_i \). The size distribution function can then be determined in comparison with the measured data. A summary of the method is written by Jemian [41]. From the measured intensity plot, direction-dependent, average sizes of the composition fluctuations can be extracted, and the sizes can be determined by comparing the measured intensities with the calculated intensities as described above.
2.5.2 DSC

With DSC it is possible to study the enthalpy exchange during phase transformations. The same property can be extracted from the phase field simulations, and therefore the method act as a bridge between theory and experiments. Basically, the setup consists of two sample holders on two thermocouples situated on a balance in a controlled atmosphere. The temperature is strictly measured for both sample holders, which are surrounded by heating elements. The balance measures any mass losses during transformations and the DSC may be connected to a mass spectrometer to identify any released gases. The difference in energy between the reference and the sample holder is measured. In that way the enthalpy variations during a phase transformation can be measured. Apart from measuring the enthalpies involved in a transformation, the method may be used to calculate activation energies for diffusion [33], an important input parameter in the phase field modeling.
3 Phase Transformations

A phase is a part of a system with a certain state. In thermodynamics, minimization of the free energy, which is a function of the state variables, e.g. $F(T,V)$, $G(T,P)$ gives the equilibrium state of the system. Pressure, volume, temperature, entropy, the number of particles, the chemical potential, as well as the composition are examples of state variables. In solid thin films, a phase as defined above is characterized by its volume or lattice. A phase transformation is thus a change of state. Gibbs [42] classified phase transformations into heterogeneous and homogenous transformations. Heterogeneous transformations are characterized by a local change of the phase leading to sharp interfaces. Homogenous phase transformations are described by widespread phase changes that occur gradually leading to diffuse interfaces. Examples of heterogeneous phase transformations are solidification and condensation. A common example of homogenous transformations are ordering reactions in a solid. Phase transformations can further be classified by the order. A first order transformation shows a discontinuity in the first derivative of the state function, a second order transformation has a discontinuity in the second derivative etc.

3.1 Phase stability and driving force

The stability of a phase and the driving force for a specific phase transformation is commonly discussed and sometimes a subject of confusion. All state variables oscillate due to thermal fluctuations in the system. If the state is stable, these fluctuations will not grow. A stable state is described by a global minimum in the
state function, and any fluctuation will cause an increase in the free energy. A metastable state has a local minimum in the state function, and is stable for sufficiently small variations, but above a critical level of the fluctuations, the system will become unstable and transform to another phase. An unstable state is unstable with respect to all fluctuations, since any variation will decrease the free energy of the system. The driving force is a measure of how far away from equilibrium a state is. The further away, the larger the driving force. If a driving force for the transformation exists, the transformation is defined as irreversible.

3.2 Nucleation and growth

Heterogeneous phase transformations of metastable states always occur by nucleation and growth [43], and is the most common phase transformation in metals [16]. A critical nucleus of the new phase with a sharp or thin interface is formed within the parent phase, and then the nucleus grows by interface movement. The critical size of the nucleus is determined by the minimization of the global free energy; the sum of the free energy decrease accompanied by the volume of the new phase, and the free energy increase due to the interface formation. The increase in free energy due to the interface formation results in an activation barrier that needs to be overcome for the phase transformation to occur. To reduce the activation barrier, the nuclei are formed at surfaces of impurities, grain boundaries or other surfaces. The barrier reduction is an effect of the reduced surface energy at impurities, and in the case of destruction of the defect, a further reduction of the free energy occurs [16]. The nuclei continue to grow in order to reduce the interface/volume ratio until they hit each other. Smaller nuclei will decay in size and larger nuclei will grow due to the differences in chemical potential surrounding nuclei with different sizes. The interface between the precipitate and the parent phase, is important for the kinetics and shape of the growing precipitate. The interface may be coherent, semi-coherent or incoherent depending on the degree of lattice mismatch between the precipitate and the matrix. If the interface is coherent, the two structures have similar lattices, if it is semi-coherent, some set of planes in the precipitate have the same lattice parameter as the matrix, and if it is incoherent, the precipitate and matrix have different lattices.
TiAlN possesses a miscibility gap for close to all compositions [27]. Within the miscibility gap, but outside the spinodal regime, h-AlN nucleate with incoherent to semi coherent interfaces to the parent c-TiAlN phase [35].

In Figure 3.1 a free energy surface outside the spinodal region, but inside the miscibility gap is shown after Hillert [44,45]. The free energy change, $\Delta F$, is determined by a compositional wavelength and amplitude. For very short wavelengths a growth in amplitude increase the free energy. For “wavelengths” larger than a critical one, an energy barrier, in form of a critical nucleus (marked by dots) needs to be overcome in order to reach the free energy valley (dashed line). To reach the equilibrium state in the energy valley the amplitude of the nucleus needs to increase i.e. the nucleus purifies. This is in contrast to regular nucleation and growth outside the miscibility gap where the nucleus possess the equilibrium composition when it is nucleated. The interface thickness and the activation energy of the nucleus vary from the miscibility line towards the spinodal. At the miscibility and the spinodal line the critical nucleus size is infinite. In between the critical size goes through a minimum. From the center towards the spinodal the compositional interface becomes more diffuse as the amplitude difference between matrix and nucleus decrease. This results in decreased activation energy for nucleation when one moves towards the spinodal regime. This was first addressed by Hillert [44,45] and later by Cahn et al. [46]. More recent publications on the matter are Grönhagen et al. [47] and Philippe et al. [48].

Figure 3.1. The nucleation and growth process in terms of amplitude and wavelength. The dots represent the critical nucleus depending on the compositional wavelength. The dashed lines show the metastable states. The lowest nucleation barrier is found at infinite wavelength. To reach the free energy valley the amplitude of the nucleus needs to grow. After Hillert [44,45].
An example of nucleation and growth phenomena that have been studied by phase field modeling is solidification, for example Ni [49], AlCu [50], and Ni based alloys [51]). Solidification starts with the formation of a nucleus, and often continues with an anisotropic growth depending on surface energies and preferred growth direction of the crystallographic planes, giving rise to dendrites. In particular, precipitation in Ni-based alloys [52,53], have been the subject of intense phase field modeling. Other examples of phase field modeled transformations occurring by nucleation and growth are the austenite to ferrite transformation in steel [54–56], and the recently studied precipitation hardening in Mg–Y–Nd [57], the latter performed using the software Micress [58].

3.3 Spinodal decomposition

Spinodal decomposition is an example of a homogenous isostructural transformation that is diffusion driven and occurs for unstable states. The global composition during the transformation is constant, but increasing composition fluctuations lead to formation of domains separated by diffuse interfaces. For diffusion-driven processes, also called thermally-driven processes, a certain temperature is needed for the transformation. A sufficient temperature will make the formation of a vacancy and a jump (in the case of vacancy diffusion) of an atom possible. Spinodal decomposition occurs for states with a negative second derivative of the free energy with respect to composition, i.e. states within the chemical spinodal region in a miscibility gap in a phase diagram. Within the miscibility gap, a coherent miscibility gap and a coherent spinodal is defined if the equilibrium domains possess different elastically properties or lattice parameters. The coherent spinodal is narrower both in temperature and compositional extension compared to the chemical spinodal. The coherent spinodal takes into account the decrease in free energy due to formation of coherent strain.

Hillert [44,45] showed that there exists a critical wavelength of the compositional fluctuations which amplitude, according to Cahn [59], initially will grow exponentially until higher order terms becomes important. In Figure 3.2 a, the effect of different compositional wavelengths and amplitudes on the change in free energy is shown for a binary mixture of equal amounts of A and B atoms inside a symmetric spinodal regime. A symmetric spinodal regime has its peak
value of the free energy at $A_{0.5}B_{0.5}$. As shown, any wavelengths larger than the critical wavelength (indicated by an arrow in the figure) that grows in amplitude will decrease the free energy. No nucleus is needed, as shown by the dotted states at zero amplitude. For shorter wavelength than the critical wavelength, the free energy increases as the amplitude of the wave increases. The free energy valley becomes deeper for longer wavelengths. In the initial state of spinodal decomposition high frequencies are reduced, and any wavelength larger than the critical will grow, i.e. the compositional fluctuation purifies. But, as seen from the figure every wavelength is associated with a specific free energy value; in order to decrease the total free energy a longer wavelength need to develop and grow on the expense of shorter ones, that will decay in amplitude and vanish. Hence the free energy decrease of the longer wavelength will cover the cost for the shorter wavelength to decay. An infinite wavelength would give the largest free energy decrease, but would involve long range diffusion. The fastest growing wavelength is determined by the free energy decrease and the energy needed for the diffusion length considered.

In Figure 3.2 (b), the free energy change due to different wavelengths and amplitudes are shown for a binary system, with an off peak composition inside a symmetric spinodal region. In this case, there exist wavelengths smaller than the critical one where a free energy decrease can occur by nucleation. The nuclei increase their amplitude, to reach the free energy valley. As in the case of symmetric composition, for wavelengths larger than the critical, the system decreases its energy without any energy barrier as the amplitude increases. As one moves from the center of the spinodal region towards the spinodal line the critical wavelength increases and hence probability for nucleation increases. As mentioned already, at the spinodal line the wavelength is infinite, and outside the spinodal line phase transformation occurs by nucleation and growth.

The critical wavelength does not only vary with composition, but also with temperature. The critical wavelength decreases with temperature, resulting in a maximum driving force for decomposition at the bottom of the miscibility gap, for the composition at the peak of the free energy. On the other hand, the diffusion is faster at higher temperatures, and therefore the transformation rate goes through a maximum for a certain temperature, usually far up in the spinodal regime.
In summary, the critical wavelength varies within the spinodal regime. Systems with compositions at the peak of the free energy are unstable against any fluctuation larger than the critical wavelength, and off peak compositions possess a degree of metastability since for short wavelengths fluctuations an energy barrier is needed to overcome to reach the decreased free energy state, i.e. a nucleus needs to form. The metastability increases with temperature.

![Diagram](image.png)

**Figure 3.2** (a) Symmetric composition in a symmetric spinodal. (b) Asymmetric composition in a symmetric spinodal. Free energy of a system with spinodal decomposition in terms of amplitude and wavelength. The dots represent the critical nucleus depending on the wavelength. The dashed lines show the metastable states. The metastable states can be reached for wavelengths longer than the critical without any barrier in the free energy. After Hillert [44,45].

(a) Any wavelength above the critical will grow. A longer wavelength grows and ends deeper in the free energy valley, but a certain wavelength is always connected with a specific end value of the free energy. To decrease the free energy longer wavelengths need to grow on the expanse of shorter.

(b) For an asymmetric composition in a symmetric miscibility gap there exists wavelengths where a critical nucleus can be formed by overcoming an energy barrier. For wavelengths larger than a critical no energy barrier exists.
Many ternary nitrides are predicted to decompose spinodally, e.g. ZrAlN [60], ScAlN, CrAlN and HfAlN [61]. TiAlN is one of the nitrides that undergo spinodal decomposition, and as a result age hardening occurs, as described in section 2.4. In stainless steel, embrittlement is a result of spinodal decomposition at low temperatures. Therefore, much research has been made in the area and phase field modeling have been applied [62,63]. Spinodal decomposition is commonly occurring on a nano-scale and can be a fast process that is hard to detect and track experimentally. The system Al-Ag decomposes spinodally, but has concurrent nucleation and growth mechanisms. The material system was studied both by experiments and by phase field modeling [64].
4 Phase field Modeling

For a metallurgist, the micro- and nanostructure of a material can reveal a lot about macroscopic properties. The composition, size, orientation and shape of grains as well as the nanostructure inside the grains, are all features that determine the macroscopic properties, and may even give an insight to the formation of the material. Macroscopic properties determined by the microstructure/nanostructure are hardness, ductility, toughness, and wear resistance, which all are important for industry and manufacturers.

By simulating the microstructure/nanostructure of materials, a deeper understanding of the formation and evolution of the material and its properties can be achieved. An up-coming method for performing these simulations is the phase field method based on thermodynamic descriptions given by CALPHAD type databases, experimental data or data calculated from first principles. For a general review of the phase field method see e.g. Loginova et al. [65], Chen et al. [66], and Moelens et al. [4]. The strength of the phase field method is the way it handles sharp interfaces, as very thin, smoothly varying transition regions, which eliminates the need of tracking the position of interfaces, typically needed in solving free boundary problems.

4.1 Diffusive interfaces by Van der Waals, Hillert, and Cahn–Hilliard

The roots of the diffusive interface method goes back to 1893, when van der Waals claimed the existence of a diffuse interface in transformation between liquid
and vapor [67]. Much later, in 1956, Hillert reviewed the existing nucleation theories by Borelius, Becker, and Hobstetter, and presented a new theory for thermodynamically unstable materials, “homogenous nucleation of exchange transformations”, later named spinodal decomposition [44]. His major contribution was to abandon the nucleation size concept for a wavelength description of the composition variations in spinodal decomposition. He succeeded in calculating (by “machine”) the solution to a compositional fluctuation between discrete lattice planes in 1D, taking nearest neighbors into account. The waves were characterized by amplitude and wavelength, and could determine a critical wavelength for spinodal decomposition as seen in section 3.3.

In 1958, Cahn and Hilliard developed Hillert’s discrete model, into a continuous 3D model applicable to spinodal decomposition and other ordering transformations with diffusive interfaces [68]. This model is today widely used and referred to as the Cahn–Hilliard model or equation.

### 4.1.1 The free energy functional

Cahn and Hilliard’s approach was to Taylor–expand the free energy around the mean composition, at a given point

\[
f (c, \nabla c, \nabla^2 c, ...) =
\]

\[
f_0(c) + \sum_i L_i \frac{\partial c}{\partial x_i} + \sum_{ij} \kappa^{(1)}_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j} + \left( \frac{1}{2} \right) \sum_{ij} \kappa^{(2)}_{ij} \left( \frac{\partial c}{\partial x_i} \right) \left( \frac{\partial c}{\partial x_j} \right).
\]

(4.1)

where

\[
L_i = \left[ \frac{\partial f}{\partial \left( \frac{\partial c}{\partial x_i} \right)} \right]_0
\]

(4.2)

\[
\kappa^{(1)}_{ij} = \left[ \frac{\partial f}{\partial \left( \frac{\partial^2 c}{\partial x_i \partial x_j} \right)} \right]_0
\]
Simplifying by assuming a cubic symmetry,

\[ L_i = 0 \]
\[ \kappa_{ij}^{(1)} = \kappa_1 = \left. \frac{\partial f}{\partial \nabla c} \right|_0 \text{ for } i = j, \]
\[ \kappa_{ij}^{(1)} = 0 \text{ for } i \neq j, \] \hspace{2cm} (4.3)
\[ \kappa_{ij}^{(2)} = \kappa_2 = \left. \frac{\partial^2 f}{\partial |\nabla c|^2} \right|_0 \text{ for } i = j, \]
\[ \kappa_{ij}^{(2)} = 0 \text{ for } i \neq j. \]

The total free energy functional is given by the integration of the Taylor-expansion over the volume,

\[ F = N \int_V [f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 (\nabla c)^2 + \cdots] dV, \] \hspace{2cm} (4.4)

where \( N \) is the number of atoms. By using the divergence theorem,

\[ \int_V (\kappa_1 \nabla^2 c) dV = -\int_V (\partial f/\partial c)(\nabla c)^2 dV + \int_S (\kappa_2 \nabla c \cdot n) dS, \] \hspace{2cm} (4.5)

Cahn and Hilliard derived the free energy functional after approximating the surface integral to zero,

\[ F = N \int_V [f_0(c) + \kappa (\nabla c)^2 + \cdots] dV \] \hspace{2cm} (4.6)

where

\[ \kappa = -\frac{\partial \kappa_1}{\partial c} + \kappa_2. \] \hspace{2cm} (4.7)
The first term in the functional describes the homogenous free energy and the second term is the free energy associated with a gradient in the composition. In this work, the gradient energy is treated in the same manner as Cahn–Hilliard did since the system studied here also is cubic.

4.1.2 The Gradient energy using pairwise nearest neighbors

The difference in internal energy for a regular binary homogenous solution and an inhomogeneous (with composition gradients) system can be developed by considering atomic pairwise interactions of the nearest neighbors. The atoms are randomly distributed in the homogenous case. Assuming a Face Centered Cubic (FCC) crystal with 12 nearest neighbors, \( Z \), with a bonding energy \( \varepsilon_{ij} \), the homogenous energy is

\[
E_{\text{hom}} = \frac{ZN_A}{2} \sum_{ij} x_{ij} \varepsilon_{ij} = 6N_A \cdot (x_{AA} \varepsilon_{AA} + x_{BB} \varepsilon_{BB} + x_{AB} \varepsilon_{AB} + x_{BA} \varepsilon_{BA}),
\]

where \( x_{ij} \) is the molar fraction of atoms. The \( \frac{1}{2} \) comes from that one bond is shared by two atoms. By using that the molar fractions of the two species sum to one and that the bonding energy of a AB bond is equal to a BA bond,

\[
x_A + x_B = 1 \quad \text{and} \quad \varepsilon_{AB} = \varepsilon_{BA}
\]

the homogenous internal energy is derived,

\[
E_{\text{hom}} = 6N_A \cdot (x_A x_B (2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}) + x_A \varepsilon_A + x_B \varepsilon_B).
\]

Two cases exists:

\[
2\varepsilon_{AB} < (\varepsilon_{AA} + \varepsilon_{BB}) \Rightarrow E_{\text{hom}} < 0 \quad (i)
\]

\[
2\varepsilon_{AB} > (\varepsilon_{AA} + \varepsilon_{BB}) \Rightarrow E_{\text{hom}} > 0 \quad (ii)
\]

where (i) implies that mixing and (ii) ordering is preferable for the system.
The approach to derive the internal energy of a pairwise inhomogeneous system is similar. Consider a compositional gradient in one direction. The atom considered at the origin can either be an A or B atom, bonded to an A or B atom in the neighboring plane located in the \( +x \) or in the \( -x \) direction at a distance \( b \).

Here the lattice parameter \( b \) is assumed to be independent of composition, and the bonding energy is only dependent on the interaction distance, and the distribution of the atoms is locally random. We are again interested in the internal energy per atom and count the number of bonds per atom. In this case the atom in the origin is connected to two atoms in the gradient direction; one in the \( +x \)-direction and one in the \( -x \)-direction, giving rise to \( \frac{1}{2} \) bond per atom in each direction.

\[
E_{\text{inhom}} = \frac{ZN_A}{2} \sum_{i,j} (x_i^+ \epsilon_{i,j} + x_i^- \epsilon_{i,j}) = \\
\frac{1}{2} \cdot (x_A x_A^+ \epsilon_{AA} + x_A x_B^+ \epsilon_{AB} + x_A x_A^- \epsilon_{AA} + x_A x_B^- \epsilon_{AB}) + \\
\frac{1}{2} \cdot (x_B x_A^+ \epsilon_{BA} + x_B x_B^+ \epsilon_{BB} + x_B x_A^- \epsilon_{BA} + x_B x_B^- \epsilon_{BB})
\]

To get a continuous description, let us Taylor expand \( x_A^+, x_B^+, x_A^-, \) and \( x_B^- \) around the original composition (origo),

\[
x_A^+ = x_A + \frac{\partial x_A}{\partial \xi} b + \frac{\partial^2 x_A}{\partial \xi^2} \frac{b^2}{2}, \quad x_B^+ = x_B + \frac{\partial x_B}{\partial \xi} b + \frac{\partial^2 x_B}{\partial \xi^2} \frac{b^2}{2},
\]

\[
x_A^- = x_A - \frac{\partial x_A}{\partial \xi} b + \frac{\partial^2 x_A}{\partial \xi^2} \frac{b^2}{2}, \quad x_B^- = x_B - \frac{\partial x_B}{\partial \xi} b + \frac{\partial^2 x_B}{\partial \xi^2} \frac{b^2}{2}
\]

where \( \xi \) is an infinitesimal distance in the \( x \)-direction. By using eq. (4.9) and eq. (4.13), and only considering derivatives up to the second order, the expression for the inhomogeneous internal energy becomes

\[
E_{\text{inhom}} = E_{\text{hom}} + \frac{N_A}{2} \left[ x_A (\epsilon_{AA} - 2\epsilon_{AB} + \epsilon_{BB}) + \epsilon_{AB} - \epsilon_{BB} \right] \frac{\partial^2 x_A}{\partial \xi^2} \frac{b^2}{2}
\]

By comparing eq. (4.14) and eq. (4.4) it is clear that \( k_2 \) is zero, and
According to eq. (4.7), $\kappa$ is the derivative with respect to composition,

$$\kappa = -\frac{\partial k_1}{\partial x_A} = -\frac{N_A}{2} (\epsilon_{AA} - 2\epsilon_{AB} + \epsilon_{BB}) \frac{b^2}{2}.$$  \hspace{1cm} (4.16)

When looking at the expression for $\kappa$, there is a certain similarity with the enthalpy of mixing, or the excess enthalpy of mixing, for a regular solution model

$$\Delta H_{\text{mix}} = \Delta H_{\text{exc}} = N_AZ \frac{1}{2} (-\epsilon_{AA} + 2\epsilon_{AB} - \epsilon_{BB}) x_A x_B$$  \hspace{1cm} (4.17)

Hence,

$$\kappa = \frac{\Delta H_{\text{exc}}}{x_A x_B} \frac{b^2}{2} = \Delta H_{\text{bond}} \frac{b^2}{2}.$$  \hspace{1cm} (4.18)

where $\Delta H_{\text{bond}}$ is

$$\Delta H_{\text{bond}} = N_AZ \frac{1}{2} (-\epsilon_{AA} + 2\epsilon_{AB} - \epsilon_{BB}).$$  \hspace{1cm} (4.19)

For derivation of three and four body interaction energies for nearest neighbors see Lass et al. [69].

### 4.2 The Cahn Hilliard equation for simulation of diffuse interfaces

The starting point for a derivation of the Cahn Hilliard equation governed by a diffuse interface is the functional of eq. (4.6). The divergence theorem and the fact that the average composition during spinodal decomposition is conserved give the equation of continuity:

$$\frac{1}{V_m} \frac{\partial x_k}{\partial t} = -\nabla \cdot J_k$$  \hspace{1cm} (4.20)
where $V_m$ is the molar volume approximated as constant and $x_k$ is the molar fraction of element $k$. Onsager’s linear law [70] of irreversible thermodynamics couples the flow of matter to the chemical potential by:

$$J_k = -L_k \nabla \left( \frac{\partial G}{\partial x_k} \right).$$  \hspace{1cm} (4.21)

The variation principle, applied to eq. (4.6)

$$\frac{\delta G}{\delta x_k} = \frac{\partial G_m}{\partial x_k} - \nabla \left( \frac{\partial G}{\partial \nabla x_k} \right)$$  \hspace{1cm} (4.22)

gives

$$\frac{\delta G}{\delta x_k} = \frac{\partial G_m}{\partial x_k} - \nabla (2\kappa \nabla x_k).$$  \hspace{1cm} (4.23)

By putting eq. (4.23) and (4.21) into eq. (4.20), the Cahn Hilliard equation results:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot L_k \nabla \left( \frac{\partial G_m}{\partial x_k} - \nabla (2\kappa \nabla x_k) \right).$$  \hspace{1cm} (4.24)

The variable $\kappa$ is to a first approximation independent of composition, see eq. (4.16), and usually the gradient energy is written as $-2\kappa \nabla^2 x_k$.

The parameter $L_k$, that entered by Onsager’s law, is connected to the mobility, and for a binary system given by:

$$L_k = (1 - x_k)x_k \cdot (x_k M_{1-k} + x_{1-k} M_k)$$  \hspace{1cm} (4.25)

The simulation model in this thesis is based on the Cahn Hilliard equation, eq. (4.24) extended by introducing an elasticity term, see Chapter 5.

### 4.3 The Allen–Cahn model for simulation of sharp interfaces

The second type of phase field model is the Allen–Cahn model for sharp interfaces, typically used for simulating nucleation and growth. Instead of the gradient energy in the functional of the free energy of Cahn–Hilliard, a non-
conserved order parameter is introduced. The order parameter keeps track of which phase the region belongs to, i.e. nuclei or matrix. The Gibbs’ free energy functional then is:

$$G = \int_{\Omega} \left( \frac{G_m(x, \phi)}{V_m} + \epsilon_\phi^2 |\nabla \phi|^2 \right) d\Omega$$

(4.26)

and $G_m$ is postulated as

$$G_m = (1 - P(\phi))G^\alpha_m + P(\phi)G^\beta_m + g(\phi)W$$

(4.27)

where $G^\alpha_m$ and $G^\beta_m$ is the free energy for phase $\alpha$ and $\beta$ respectively, $P(\phi)$ is an interpolating function that takes the values $P(0) = 0$ and $P(1) = 1$. The last term in the equation, $g(\phi)$, is a double well potential where $W$ determines the height of the potential. By applying a similar route as in the previous section, the Allen Cahn equation can be derived. Starting with the order parameter, a non-conserved parameter, one uses the time dependent Ginzburg-Landau equation,

$$\frac{\partial \phi}{\partial t} = -M \frac{\delta G}{\delta \phi}$$

(4.28)

and by using the variation principle,

$$\frac{\delta G}{\delta \phi} = \frac{1}{V_m} \frac{\partial G_m}{\partial \phi} - 2\epsilon^2 \nabla^2 \phi,$$

(4.29)

one arrives at

$$\frac{\partial \phi}{\partial t} = -M \left( \frac{1}{V_m} \frac{\partial G_m}{\partial \phi} - 2\epsilon^2 \nabla^2 \phi \right).$$

(4.30)

To the conserved concentration the equation of continuity, eq.(4.20), and Onsager linear law, (4.21), gives

$$\frac{\partial x}{\partial t} = \nabla \cdot \left( L_k \left( \frac{\partial^2 G_m}{\partial x_k^2} \nabla x + \frac{\partial^2 G_m}{\partial x_k \partial \phi} \nabla \phi \right) \right).$$

(4.31)

The two eqs. (4.30) and (4.31) are the two basic equations solved in a system with sharp interfaces.
5 The Model

A modified version of the Cahn–Hilliard equation has been used to simulate the spinodal decomposition in TiAlN, where an elasticity term is introduced. Two different models have been used in the three papers; one based on regular solution and one taking into account the effect of clustering of atoms on the free energy. In Paper I, the Gibbs’ free energy data was taken from \textit{ab initio} calculations of TiAlN from ref. [27], and an ideal entropy was assumed. In Papers II and III the enthalpy and entropy were taken from equilibrium calculations at 2000 K from ref. [27], where clustering effects are considered. In all cases, elasticity was included [71] since it has been shown from micrographs of TiAlN that the decomposed structure is highly anisotropic [34]. Experimentally measured initial strains of the thin films were taken into account in the models of Paper I and II, by setting the appropriate boundary conditions. Such strains were excluded in Paper III due to the lack of experimental data for some of the specific compositions simulated. The modeling is performed in 2D, and solved by the commercial software Flex PDE [72] using the Finite Element Method (FEM).

5.1 Cahn Hilliard equation with Elasticity

For the simulation of TiAlN a continuous phase field approach in two dimensions is used, where (TiAl)N is approximated as a pseudo-binary system consisting of TiN and AlN. The nitrogen content is homogenous throughout the simulation box, and the model only accounts for substitutional diffusion of Ti and
Al on the metal sublattice. An initial fluctuation of the composition is imposed to start the decomposition, i.e., to mimic the effect of randomly occurring compositional variations due to thermal fluctuations in a real sample. An alternative is to set up a fluctuation of the free energy and keep it during the simulations. As the compositional fluctuations in the box are small in amplitude with a short wavelength and randomized they will not influence the resulting microstructure evolving during decomposition.

For each node in the mesh of the simulation box, the composition is solved for each time step. The driving force of the decomposition is the minimization of the system’s Gibbs’ free energy, $\Delta G$, where the difference compared to the pure TiN and AlN is given by the functional

$$\Delta G = \frac{1}{V_m} \left( \int_{\Omega} \left( \Delta G_m(x_k) + \kappa |\nabla x_k|^2 + \Delta E_{el,m}(x_k) \right) \, d\Omega \right). \quad (5.1)$$

Here, $\Delta G_m$ is the Gibbs’ free energy of mixing per mole for a homogeneous system, $\kappa$ is the gradient energy coefficient, and an additional factor is introduced, $E_{el,m}$, the elastic energy per mole. The integration is performed over the whole volume, $\Omega$. The molar volume, $V_m$, is approximated as constant. By following the scheme introduced in section 4.1.2 and 4.2, the modified Cahn–Hilliard equation is,

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ L_k \nabla \left( \frac{\partial \Delta G_m}{\partial x_k} - 2 \nabla \kappa \nabla x_k + \frac{\partial \Delta E_{el,m}}{\partial x_k} \right) \right] \quad (5.2)$$

where $L_k$ is connected to the mobility. If one uses the approximation for a dilute solution to convert mobility into diffusion, the $L_k$ for a binary system is described by:

$$L_k = (1 - x_k)x_k \cdot (x_k M_{1-k} + x_{1-k} M_k)$$

$$\approx (1 - x_k)x_k \cdot \frac{x_k D_{1-k} + x_{1-k} D_k}{RT}$$

$$= (1 - x_k)x_k \cdot \frac{D_{1-k}}{(RT)}. \quad (5.3)$$
where $R$ is the gas constant, and $T$ is the temperature. The mobility depends on the self-diffusivity constants, $D_k$, which in all three papers are assumed to be equal and constant for Ti and Al;

$$D_k = D_{1-k} = D_0 \cdot e^{-\frac{Q}{RT}} \quad \text{(5.4)}$$

where $D_0$ is the diffusivity constant and $Q$ is the activation energy, given in J/mole.

There are three contributions to the driving force in the Cahn–Hilliard equation, eq. (5.2). The first term is the free energy of mixing per mole,

$$\Delta G_m(x_k) = \Delta G_{\text{mix}} = \Delta G_{\text{ideal}} + \Delta G_{\text{exc}} \quad \text{(5.5)}$$

where the ideal Gibbs’ free energy, $\Delta G_{\text{ideal}}$ is

$$\Delta G_{\text{ideal}} = \Delta H_{\text{ideal}} - T \Delta S_{\text{ideal}} = -T \Delta S_{\text{ideal}}$$

$$= RT [x_k \ln x_k + (1 - x_k) \ln (1 - x_k)], \quad \text{(5.6)}$$

since the ideal enthalpy of mixing is zero and the ideal entropy only considers configurationally entropy. In the same manner as $\Delta G_{\text{ideal}}$, $\Delta G_{\text{exc}}$ may be written as

$$\Delta G_{\text{exc}} = \Delta H_{\text{exc}} - T \Delta S_{\text{exc}} \quad \text{(5.7)}$$

In the model, $\Delta H_{\text{exc}}$ is independent of temperature and the excess entropy is,

$$\Delta S_{\text{exc}} = - \left( \frac{\partial \Delta G_{\text{exc}}}{\partial T} \right)_{pN} \quad \text{(5.8)}$$

By using eqs. (5.5), and (5.6) the first term of the modified Cahn–Hilliard equation, eq. (5.2), may be rewritten:
\[ \nabla \cdot \left[ L_k \nabla \left( \frac{\partial (\Delta G_{\text{ideal}} + \Delta G_{\text{exc}})}{\partial x_k} \right) \right] = \]
\[ \nabla \cdot \left[ L_k \left( \frac{\partial^2 \Delta G_{\text{ideal}}}{\partial x_k^2} \nabla x_k + \frac{\partial^2 \Delta G_{\text{exc}}}{\partial x_k^2} \nabla x_k \right) \right] = \]
\[ \nabla \cdot \left[ L_k \left( \frac{RT}{(1 - x_k)x_k} \nabla x_k + \frac{\partial^2 \Delta G_{\text{exc}}}{\partial x_k^2} \nabla x_k \right) \right] = \]
\[ \nabla \cdot \left[ D_{k(1-k)} \left( 1 + \frac{(1 - x_k)x_k \partial^2 \Delta G_{\text{exc}}}{RT \partial x_k^2} \right) \nabla x_k \right] , \]
and finalized,
\[ \frac{\partial x_k}{\partial t} = \nabla \cdot \left[ D_{k(1-k)} \left( 1 + \frac{(1 - x_k)x_k \partial^2 \Delta G_{\text{exc}}}{RT \partial x_k^2} \right) \nabla x_k \right] + L_k \nabla \left( -2\nu_k \nabla x_k + \frac{\partial \Delta E_{\text{el},m}}{\partial x_k} \right) , \]
\[ \frac{(1 - x_k)x_k \partial^2 \Delta G_{\text{exc}}}{\partial x_k^2} \]
is usually called the thermodynamic factor \[73,74\]. The second term in eq. (5.2), or third in (5.10), is the gradient energy and is already described in Chapter 4, by eq. (4.18). The third term of eq. (5.2), or fourth in (5.10), is the contribution from elastic energy in 3D where plain strain is considered. For a review of elasticity, see e.g. Nye \[75\] or section 5.3.3. The elastic energy, described using the Voigt notation, is
\[ \Delta E_{\text{el},m}(x_k) = \frac{V_m}{2} \left( \sigma_{x x} \varepsilon_x + \sigma_{y y} \varepsilon_y + \sigma_{z z} \varepsilon_z + \right. \]
\[ \left. \sigma_{x y} \varepsilon_{x y} + \sigma_{y z} \varepsilon_{y z} + \sigma_{x z} \varepsilon_{x z} \right) \]
where the stress, \(\sigma\), for a cubic crystal is
The strain relative to the initial conditions is
\[
\sigma_x = C_{11}\epsilon_x + C_{12}\epsilon_y + C_{13}\epsilon_z \tag{5.13}
\]
\[
\sigma_y = C_{12}\epsilon_x + C_{11}\epsilon_y + C_{13}\epsilon_z \tag{5.14}
\]
\[
\sigma_z = C_{13}\epsilon_x + C_{12}\epsilon_y + C_{11}\epsilon_z \tag{5.15}
\]
\[
\sigma_{yz} = C_{44}\epsilon_{yz}, \quad \sigma_{xz} = C_{44}\epsilon_{xz}, \quad \sigma_{xy} = C_{44}\epsilon_{xy}. \tag{5.16}
\]

The relation between \( \epsilon^* \) and the real strain \( \epsilon \) is
\[
\epsilon = \frac{\epsilon^* - \epsilon_m}{1 + \epsilon_m} = \frac{a - a_r}{a_r}, \tag{5.19}
\]
where \( \epsilon_m \) is the so called eigenstrain, and \( \epsilon^* \) is the strain relative to the initial lattice parameter given by the global composition. To the right side, the definition of strain is given in terms of lattice parameters where \( a \) is the lattice parameter given by the distortions and \( a_r \) is the relaxed lattice parameter.

The eigen-strain compensates for the fact that when the composition changes the relaxed lattice parameter changes as well. The eigen-strain can be seen as a correction from the initial relaxed lattice parameter, \( a_{r\text{init}} \), to the actual relaxed lattice parameter, \( a_r \), of the specific composition:
\[
\epsilon_m = \frac{a_r - a_{r\text{init}}}{a_{r\text{init}}}. \tag{5.20}
\]

The strain, \( \epsilon^* \), is not the real strain since the distortions are relative to the initial lattice and lattice parameter, which is considered fixed during the simulation, hence \( \epsilon^* \) can be expressed in lattice parameters by
It follows from eq. (5.20) and (5.21) that eq. (5.19) is true. Observe that the eigen-strain is not contributing to shear strains and hence is not assigned with a in eq. (5.18).

The elastic strain in eq. (5.12) is the difference between the actual strain and the unconstrained coherency misfit. The partial derivative of the elastic energy with respect to the composition is calculated by changing the composition slightly and calculating the slope

\[
\frac{\partial E_{el,m}}{\partial x_k} = \frac{\Delta E_{el,m}(x_k + dx_k) - \Delta E_{el,m}(x_k)}{dx_k}
\]  

The elastic energy term is solved without any further approximations.

The condition that the total forces acting on the box is zero, gives the solution of the displacement vectorsu, v and w:

\[
\frac{\partial \sigma_x}{\partial x} + \frac{\partial \sigma_y}{\partial y} + \frac{\partial \sigma_z}{\partial z} = 0,
\]

\[
\frac{\partial \sigma_y}{\partial y} + \frac{\partial \sigma_z}{\partial x} + \frac{\partial \sigma_z}{\partial z} = 0,
\]

\[
\frac{\partial \sigma_z}{\partial z} + \frac{\partial \sigma_x}{\partial x} + \frac{\partial \sigma_y}{\partial y} = 0.
\]

respectively.

5.2 Boundary conditions and modeling details

The boundary conditions of a partial differential equation give the unique solution to the problem. The boundary conditions for the displacement vectors are of Dirchlet type (a value for the variable is set on the boundary), and for the composition of Neumann type (the flow is zero). In Paper I and II experimentally measured initial strains, were set as Dirchlet values as boundary conditions of the displacement vectors. In Paper III the boundary conditions for the displacement
vectors were again used to strain the simulation box to determine the time evolution of the Young's modulus.

The partial differential equations, eqs. (5.23), (5.24), (5.25) and (5.10) are solved in the written order; first the forces are set to zero solving for the displacement variables $u$, $v$ and $w$, respectively, and then the modified Cahn–Hilliard equation is solved for the composition in two steps, due to the limitation of the second order Partial Differential Equation (PDE) solver, Flex PDE. The gradient term is an fourth order PDE and therefore eq. (5.10) is divided into two second order PDEs. The equations for the displacement vectors are solved simultaneously as well as the two equations governing the composition evolution. The solution of the Cahn Hilliard equation gives the composition at a given time. The equation is solved at every node in FEM box and the result is the compositional variation in time and space.

5.3 Input parameters

The aim of this work is not to model spinodal decomposition in general, but specifically the spinodal decomposition of c-TiAlN. To achieve that, input parameters for the material must be taken either from experimental work or calculations.

5.3.1 Thermodynamic description

The thermodynamic data is the foundation of the model, and needs to be realistic to be able to predict correct properties of TiAlN. In the included papers the thermodynamic data, $\Delta G_m(x_k)$ and $\Delta H_{exc}$ is taken from Alling et al. [27]. In Paper I the $\Delta H_{exc}$ was used together with the ideal entropy to describe the Gibbs’ free energy by a regular solution model. In Paper II and III the excess enthalpy and entropy was included. The non-equilibrium state of the thin films around 1173 K was assumed to have the same clustering degree as the equilibrium state of TiAlN at 2000 K. According to eq. (5.10) the thermodynamic factor involving $\Delta G_{exc}$ and the gradient energy, $\kappa$, is needed as input data and should be derived from $g_m(x_k)$ and $\Delta H_{exc}$, the available data of the material system.
Figure 5.1 Thermodynamic data of 2000 K, 4000 K, 6000 K, 8000 K, and 10 000 K. Data from Alling [27].
(a) Gibbs’ free energy of mixing. The Gibbs’ free energy curve for 2000 K shows that the spinodal covers all compositions above Al content ~0.15. Maximum is positioned for an Al content of ~0.7. From these curves the spinodal seems to close already at 4000 K.

(b) Enthalpy of mixing. The asymmetry of the enthalpy of mixing curve is decreasing with temperature, from a peak position of ~0.65 in Al content for 10000 K to almost symmetrical at 2000 K.

(c) Entropy of mixing. The asymmetry of the entropy curves are decreasing with temperature. It is almost symmetrical at 10000 K. At 2000 K the peak position is at ~0.3 in Al content.

The total Gibbs’ free energy and excess enthalpy, as well as the total entropy times temperature, are plotted above for various temperatures from Alling [27]. As seen in Figure 5.1 (b), and (c), the enthalpy of mixing is symmetric at 2000 K, with a peak value of ~0.5 in Al content, and the entropy curve has its peak position for an Al content ~0.3. As a result, the Gibbs’ free energy curve plotted in Figure 5.1 (a), has its peak position for the Al content of ~0.7. In the simulation model, we take the thermodynamic data calculated for the equilibrium clustering at 2000 K and use that as the clustering degree for the unstable thin film of TiAlN. By using eq. (5.5) and (5.6), the excess Gibbs’ free energy is easily derived from $\Delta G_m(x_k)$ and $\Delta H_{exc}$. The $\Delta G_{exc}$ term is usually assumed to take the form of a Redlich-Kister (RK) polynomial [73,74,76]:

$$\Delta G_{exc} = x_k(1-x_k) \sum_{n=0}^{3} (x_k - (1-x_k))^n \cdot L_n^G$$  \hspace{1cm} (5.26)

To match the given data at 2000 K, the polynomial was applied to an order of n=3. The same procedure was applied to $\Delta S_{exc}$ data at 2000 K after deriving it from $\Delta G_{exc}$ and $\Delta H_{exc}$ by rearranging eq.(5.7).

$$\Delta S_{exc} = x_k(1-x_k) \sum_{n=0}^{3} (x_k - (1-x_k))^n \cdot L_n^S$$  \hspace{1cm} (5.27)

The temperature dependence of the $L$ parameters is to a first approximation usually assumed to be linearly dependent on temperature [74].
To get the temperature dependency of the free energy around 1173 K where the simulations are performed $\Delta G_{\text{exc}}$ is to a first approximation described in the same manner as the temperature-dependent $L$ parameters,

$$
\Delta G_{\text{exc}}(x, T) = \Delta G_{\text{exc}}(x, 2000) + \frac{\partial}{\partial T}(\Delta G_{\text{exc}}(x, 2000K))(T - 2000) \\
= \Delta G_{\text{exc}}(x, 2000) + [-S_{\text{exc}}(x, 2000)](T - 2000)
$$  \hspace{1cm} (5.29)

with a perfect match at 2000 K. The model gives an accurate equilibrium description around 2000 K but rapidly fails to give the equilibrium properties for large temperature deviations. In this model the interest is not to get the thermodynamic description for a system in thermodynamic equilibrium at 1173 K, but for a metastable or even thermodynamically unstable thin film at 1173 K. The clustering degree is assumed to be the same as the equilibrium state at 2000 K. The temperature dependence on the free energy is then described by

$$
\Delta G_{\text{exc}}(x, T) = x_k(1 - x_k)L(x, k),
$$  \hspace{1cm} (5.30)

where

$$
L(x, k) = \sum_{n=0}^{3}(x_k - (1 - x_k))^i \cdot L_n(T),
$$  \hspace{1cm} (5.31)

and

$$
L_n(T) = L_n^0 + L_n^\Delta \cdot (T - 2000). \hspace{1cm} (5.32)
$$

From this function, tabulated data of the thermodynamic factor is used as input data and later interpolated on the fly by Flex PDE. To get the gradient energy, one needs to make use of eq. (4.18) and hence $\Delta H_{\text{bond}}$ is needed. Using eq. (5.7) the enthalpy of mixing is described by
\[ \Delta H_{\text{exc}} = \Delta G_{\text{exc}} + T \Delta S_{\text{exc}}, \]  

(5.33)

and using eq. (5.8) again as well as eq. (5.30), \( \Delta H_{\text{bond}} \) can be expressed as:

\[ \Delta H_{\text{bond}} = \frac{\Delta H_{\text{exc}}}{x_k(1-x_k)} = \frac{\Delta G_{\text{exc}} + T \Delta S_{\text{exc}}}{x_k(1-x_k)} = L(x, k) - T \frac{\partial}{\partial T} L(x, k). \]  

(5.34)

Tabulated data of \( \Delta H_{\text{bond}} \) is used as input data. The \( b \) parameter in the expression of the gradient energy is covered in section 5.3.5.

5.3.2 Visualization of the thermodynamic description

Visualization is important in order to better understand the properties of the thermodynamic model. In the previous chapter, the input data based on the total free energy, enthalpy and entropy was plotted. In this section, the total free energy and entropy, as well as the gradient energy term and the driving force for decomposition of the set up models are plotted in Figure 5.2 and 5.3.

The Gibbs’ free energy of the regular solution is highly asymmetric with a sharp peak at Al content of \(~0.7\) as seen in Figure 5.2 (a). Taking clustering effects into account, the peak decreases and the shape of the free energy curve flattens out, even though the maximum value is in the same region for both models. The peak position of the curve with clustering is slightly shifted towards lower Al content, \(~0.6\).

The entropy curves in Figure 5.2 (b) shows that the ideal entropy is highest for all compositions, as expected, since it corresponds to a total random configuration of the atoms. By considering the clustering of atoms, at the degree given by equilibrium conditions at 2000 K, the total entropy is decreased by the amount represented by \( \Delta S_{\text{exc}} \). The decrease is largest for compositions close to an Al content of \(~0.67\), and hence the clustering is more severe and energetically preferable at the compositions surrounded by the dip in the \( \Delta S_{\text{exc}} \) curve. The total entropy is given by the sum of the ideal and the excess entropy, recall eqs. (5.5)-(5.7). The peak of the total entropy is at an Al content of \(~0.3\) resembling the more disordered configurations. Higher entropy of a system stabilizes the system’s state.
Figure 5.2 Thermodynamic data of the two different models at 1173 K; the regular solution model, used in Paper I, and the clustered model, used in Paper II and Paper III.

(a) Gibbs’ free energy of mixing for the regular solution model (dashed line), and the clustered model (solid line).

(b) Ideal entropy of mixing term, (blue dashed line), total entropy of mixing term, (solid line), and excess entropy of mixing term (black dashed line) of the clustered model.
From these curves one might conclude that the driving force for decomposition is largest for the regular solution model due to the higher Gibbs’ free energy of mixing. But, the gradient energy and the elastic energy that evolves during decomposition will increase the free energy, reducing the rate of the

Figure 5.3
(a) Gradient energy at 1173K for the ideal and clustered model.
(b) Spinodal (line) and coherent spinodal (dashed line) for the clustered (gray line) and ideal model (black line).

From these curves one might conclude that the driving force for decomposition is largest for the regular solution model due to the higher Gibbs’ free energy of mixing. But, the gradient energy and the elastic energy that evolves during decomposition will increase the free energy, reducing the rate of the
decomposition as well as the driving force. Therefore, no clear conclusion can be drawn without knowing the values for the gradient energy and elastic energy. In this model, the gradient energy is closely related to the enthalpy of mixing; a higher enthalpy of mixing is causing a higher gradient energy. The enthalpy of mixing curves, show peak values of 10 kJ/mole and 20 kJ/mole, for the clustered and regular solution model respectively. Without considering the elastic energy, the rate decrease of the decomposition caused by the gradient energy should be slightly larger in the case of the regular solution model compared to the model with clustered entropy.

This is confirmed by studying the graphs of the gradient energy term, Figure 5.3 (a). Furthermore, the effect should decrease for compositions in lower Al content.

With the thermodynamic data available it is possible to describe the driving force taking into account gradient energies and approximately even the elastic energy, as given in Figure 5.3 (b). It is evident that the two models have a driving force for spinodal decomposition since:

$$\frac{d^2G}{dx_k^2} < 0,$$

is true for most compositions. The spinodal line is defined as

$$\frac{d^2G}{dx_k^2} = 0.$$

The spinodal region at 1173 K can be defined from Figure 5.3 (b). At an Al content above 0.75 (0 K) the hexagonal phase is lower in energy than the cubic phase and is therefore expected to grow [77]. This is also readily observed experimentally see refs. [30–32].

In the regular solution model, it is clear that the driving force should be larger and more composition dependent than in the clustered model. Hence, taking into account clustering stabilizes the c-TiAlN phase. In the clustered model, an extended driving force for decomposition of low Al content alloys is observed with respect to the regular solution model; where the spinodal region is shifted from x=0.22 to x=0.13 in Ti_{1-x}Al_x content. Taking into account the elasticity effects, the spinodal region is decreased to x=0.33 and x=0.17 for the regular
solution model and the clustered model, respectively. Here the driving force for decomposition including elasticity is calculated following ref. [78] using a composition dependent Young’s modulus, $E$, [38] but a Poisson’s’ constant, \( \nu = 0.22 \) valid for TiN [79].

\[
\frac{d^2 G}{dx_k^2} = -2\eta^2 E' V_m, \tag{5.37}
\]

where

\[
\eta = \frac{1}{a(x_k)} \left( \frac{da(x_k)}{dx_k} \right) \quad \text{and} \quad E' = \frac{E(x_k)}{1 - \nu(TiN)}, \tag{5.38}
\]

and $a$ is the lattice parameter, from refs. [29,39] and Paper I.

### 5.3.3 Elastic constants

The application of stress to a solid body changes the shape of the solid. As long as the stress on the material is below the elastic limit, the strain and shape is recovered when the stress is removed. Above the elastic limit, plastic deformation occurs followed by fracture. Ternary nitrides are usually described having a mix of metallic, covalent and ionic bonding properties [26]. As a result, the elastic behavior varies with the amount of AlN incorporated in the thin film. The work done by the stresses is stored as elastic energy in the bonds of the material and given by the area under the stress strain graph, recall eq. (5.12) and see Figure 5.4.

![Schematic stress-strain graph showing the recoverable elasticity region and the plastic deformation region. A brittle material does not necessarily enter the plasticity region before fracture.](image.png)
Elastic theory is a well-covered area by several authors see e.g. Nye [75], but is reviewed here to give the reader an idea how it is connected to the phase field model. For small stresses, Hooke’s law is valid:

\[ \epsilon_{ij} = S_{ijkl} \sigma_{kl} \]  (5.39)

and the strain is proportional to the applied stress. The strain in one dimension is defined as the increased length of a body under stress divided by its original length, and is therefore a dimensionless quantity. Stress is force per area applied to the surface of a body. The proportionality constant, \( S \) in eq. (5.55) is called the elastic compliance tensor. Another way of describing the proportionality is by the elastic stiffness tensor, \( C \).

\[ \sigma_{ij} = C_{ijkl} \epsilon_{kl}, \quad C_{ijkl} = \frac{1}{S_{ijkl}} \]  (5.40)

The indices \( i,j,k,l \) run from 1 to 3 for the three dimensions. In this work, the elastic stiffness is used as described in section 5.1. Before entering to the detailed description of the fourth rank elastic stiffness tensor, the second order stress and strain tensor is introduced.

The stress is a second rank tensor and has nine components, as shown in Figure 5.5. The \( i \) index gives the direction of the stress, \( j \) gives the direction normal to the surface the stress is acting on. The stresses with indices \( i = j \) are called normal stresses and when \( i \neq j \) they are called shear stresses. The symmetry of the tensor, if no body torques are present, gives

\[ \sigma_{ij} = \sigma_{ji} \]  (5.41)

This reduces to a vector using the Voigt notation,

\[ \sigma_{ij} \leftrightarrow \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \leftrightarrow \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yx} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} \]  (5.42)
Figure 5.5. The practical meaning of the stress indices. The “i” indices give the direction of the stress, “j” give the direction normal to the surface the stress is acting on.

If there are body forces present, e.g., gravity, the equation of motion can be described by

$$\frac{\partial \sigma_{ii}}{\partial x_j} + \rho g_i = \rho a_i, \quad (5.43)$$

where \( \rho \) is the density and \( g \) is the body force per unit mass in the \( i \) direction and \( a \) is the acceleration in the \( i \) direction. If the body is in static equilibrium no acceleration is present, and if no body forces are present, the equation of motion reduces to

$$\frac{\partial \sigma_{ii}}{\partial x_j} = 0, \quad (5.44)$$

which is the condition used in the modeling to get the displacement vectors, see eqs. (5.23)–(5.25).

Consider a general distortion of a body, the \( i \) index give the direction of the distortion and \( j \) the coordinate of the original point in \( x, y, \) or \( z \) direction, as seen by
The symmetric part, the strain tensor, is described by

$$e_{ij} = \frac{\partial u_i}{\partial x_j}$$  \hspace{1cm} (5.45)

The symmetric part, the strain tensor, is described by

$$e_{ij} = \frac{1}{2}(e_{ij} + e_{ji}) = \epsilon_{ij},$$  \hspace{1cm} (5.46)

and the antisymmetric part (pure rotation) by

$$\omega_{ij} = \frac{1}{2}(e_{ij} - e_{ji}) - \omega_{ji}.$$  \hspace{1cm} (5.47)

The strains with indices \(i = j\) and \(i \neq j\) is the tensile or compressive strains and shear strains, respectively. The tensile or compressive strain have the displacement of the body in the same direction as the strain and orthogonal to a surface. The shear strain has the displacement parallel to a surface and can be accompanied with rotation. Consider two elements drawn parallel to the \(x\) and \(y\) axes respectively, separated with an angle \(\pi/2\). Then \(\epsilon_{12}\) is the rotation counterclockwise of the \(x\) element and \(\epsilon_{21}\) is the clockwise rotation of the \(y\) element. A rotation with the same angle in the same direction i.e. \(\epsilon_{12}\) and \(\epsilon_{21}\) have opposite signs, and the same value; would not give rise to any strain as seen from eq. (5.46). Instead, rigid body rotation would occur, belonging to the antisymmetrical part of the tensor. But, a rotation against or away from each other i.e. \(\epsilon_{12}\) and \(\epsilon_{21}\) have equal signs would give rise to strain. Consider the example above and the condition that the two elements are moving towards each other \((\epsilon_{12} > 0\) and \(\epsilon_{21} > 0\)) then the movement is accompanied by strain and the angle is decreased to approximately \(\frac{\pi}{2} - 2 \cdot \epsilon_{21}\). By the symmetry condition of the strain tensor it may be reduced to a vector using the Voigt notation again

$$\epsilon_{ij} \leftrightarrow \left[ \begin{array}{ccc} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{array} \right] \leftrightarrow \left[ \begin{array}{c} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yx} \\ \epsilon_{zy} \\ \epsilon_{xz} \end{array} \right]$$  \hspace{1cm} (5.48)
Returning to the elastic compliance/stiffness tensors and eq. (5.40) again one finds that for every strain component there are nine stress components, and since there are nine strain components in the full matrix there are 81 elements in the full compliance/stiffness tensor. Fortunately due to previously described, and some further, symmetry conditions the number of non-zero elements will be reduced. By the observation that when shearing of a plane occur, the two strain components $\varepsilon_{ki}\varepsilon_{ik}$ for $k \neq i$ always come in pairs, as well as $C_{ijkl}C_{ijkl}$. Further reduction of the stiffness tensor is possible. Observe e.g.

$$\sigma_{ij} = C_{ij12}\varepsilon_{12} + C_{ij21}\varepsilon_{21} = (C_{ij12} + C_{ij21})\varepsilon_{12}, \quad (5.49)$$

and since the strain components by symmetry are equal, by convention

$$C_{ijkl} = C_{ijlk}. \quad (5.50)$$

More, the stress tensor is also symmetric,

$$\sigma_{ij} = C_{ij33}\varepsilon_{33} = \sigma_{ji} = C_{ji33}\varepsilon_{33}. \quad (5.51)$$

From eq. (5.51) it follows that

$$C_{ijkl} = C_{jikl}. \quad (5.52)$$

The tensor has now been reduced to 36 non-zero elements. Using Voigt notation again where $iji$ and $kji$ transforms as

11 $\rightarrow$ 1; 22 $\rightarrow$ 2; 33 $\rightarrow$ 3; 32,23 $\rightarrow$ 4; 31,13 $\rightarrow$ 5, 12,21 $\rightarrow$ 6. \quad (5.53)

the fourth ordered tensor may be reduced to a second order matrix. Furthermore, the second order matrix is symmetric and the number of elements is reduced to 21. Finally, TiAlN possess cubic–symmetry and the matrix may be simplified accordingly. Most of the 21 components are zero and only the diagonal and 6 elements more are non-zero;
The three elastic stiffness constants, $C_{11}$, $C_{12}$, and $C_{44}$ for TiAlN have been calculated by Tasnádi et al. [38] for zero temperature, see Figure 5.5. The elastic constants will change with temperature but at the time the model was set up, no other data of the system was found. How temperature will affect the elastic constants is hard to estimate exactly, but the stiffness is expected to decrease with temperature. In our case, the anisotropy is the important factor for the microstructure and hence, if the stiffness decrease is composition dependent the anisotropy of the system may increase as well as decrease. The calculations were performed by calculating the sound velocities, since a higher velocity is caused by a stiffer bonding. For a cubic system three elastic constants exist, $C_{11}$, $C_{12}$ and $C_{44}$. $C_{11}$ is associated with deforming in $x$-direction, $C_{12}$ and $C_{44}$ is associated with shearing of the crystal. For visualization, the stiffness constants are plotted in Figure 5.5 below together with the Zener anisotropy defined in as [80,81]

\[
A = \frac{-2C44}{C11 - C12}
\]  

The Zener anisotropy indicates the elastically soft directions. If the value is equal to one, the crystal is isotropic, below and above one the elasticity is anisotropic.

Figure 5.5 shows that the elastic constants are nearly linearly dependent of the composition and in the model the data is approximated to linear functions. The figure confirms that TiN is stiffer and AlN is more compliant, additionally it shows that when the Al content is approximately 0.3 the system is elastically isotropic. According to Cahn [81] cubic systems with $A<1$ and $A>1$ have elastically soft directions in the $\{111\}$ and the $\{100\}$ directions, respectively, which has been observed in TiAlN [34]. The evolution of the microstructure on compositions and the evolution of Young’s modulus are studied in Paper III.
5.3.4 Lattice parameters and Vegard’s law

Only one lattice parameter is needed to describe the cubic unit cell of TiAlN for a specific composition. But, the composition varies in space and time during the decomposition and hence the lattice parameter as a function of composition is needed. The lattice parameters are used for calculating the eigen-strain, the initial molar volume (see section 5.1), and the interaction parameter in the gradient energy (section 4.1.2). The composition dependent lattice parameters have been calculated \textit{ab initio} [29,39], and measured experimentally (the latter for a limited range of compositions) and presented in Paper I. For both sets of data, a clear deviation from Vegard’s linear law is seen. This deviation is important for the strain, since it will give a decrease in volume during the decomposition, and hence increase the strain in non-decomposed TiAlN regions.

The amount of elastic energy stored in the material is determined by the values of the elastic constants and the strains. Coherent strains are generated during decomposition due to the lattice mismatch between decomposed TiN-rich and AlN-rich regions. Furthermore, the mechanical strains, due to e.g. the shape of
the domains, also contribute to the elastic energy. Since the decomposition is a fast process, and in practice the material during a cutting operation is decomposed, as seen from Paper I and Paper II, the end values of the strains and the elastic constants are very important for the hardness and toughness. Both the strain and elastic constants depend on the lattice parameters and therefore it is important to have correct input data for pure c-TiN and c-AlN. The latter is not possible to synthesize in an unstrained state, hence the calculated lattice parameter is not experimentally confirmed.

It is important to have the correct lattice parameters, not only for the eigenstrain but also for the molar volume and interaction parameter, \( b \), in the gradient term. An increase in the initial molar volume constant will slow down the decomposition since the elastic energy is increased. An increase in the interaction parameter increases the cost for having a gradient and therefore also decreases the decomposition rate.

5.3.5 Diffusion and activation energies

The composition independent diffusivity used in the simulations mainly affects the timescale in the simulations. In practice the diffusivity is highly dependent on composition and should affect the decomposition rate and possibly even the purity levels of the domains. Unfortunately the diffusivity constant, \( D_0 \), in TiAlN is unknown, and in a trial simulation the total diffusivity, \( D \), was set to match experimental knowledge, i.e. the microstructure should be decomposed after annealing at 1173 K for 2 hours. The activation energy has been determined experimentally by Hörling et al. [33] using DSC, and from that value combined with the total diffusivity in the trial simulation, the unknown diffusivity constant, \( D_0 \), could be calculated. From Paper II a more detailed attempt to determine the diffusivity constants and activation energies for TiAlN was performed, for method descriptions and details see section 6.3.

5.4 Output parameters

The output variables are calculated at every node in the simulation box, in every time step. The variables within this model are the displacement vectors in x-
and y-direction and the composition. Properties depending on these variables may be evaluated and plotted in every time step.

The validity of the simulation can be seen by the behavior of the mean energies and mean composition, as well as the variables themselves. The mean composition should be constant throughout the simulation and the free energies should decrease.

The time evolution of mean, max and min parameters as well as the correlation to other variables can be plotted. Typically studied parameters within this work are; strains (Paper I), wavelength evolution (Paper II), stresses, mobility, energies (Paper III), and composition. Another possibility is to compare simulation data with experiments and get new properties e.g. diffusivity values (Paper II). Macroscopic properties like the von Mises stresses or Young’s modulus evolution (Paper III) are also possible to extract. Furthermore, the simulations offer an opportunity to separate complicated effects observed in experiments. In Paper I the strain effect of the formation of h-AlN and the strain effect of spinodal decomposition are separated.

An example of what can be presented by the output parameters is the microstructure plot shown below, where white represents AlN and black TiN.

![Microstructure plot](image)

*Figure 5.6 Micrograph of Ti$_{0.33}$Al$_{0.67}$N after 40 s simulated at 1173 K. White regions represent Al rich domains and black regions represent Ti rich domains.*
6 Analysis

This chapter describes the analysis methods used, and gives results not included in the papers. In addition four complex matters are considered: (i) how to get a proper domain size evolution from the anisotropic decomposed microstructure, (ii) how to get the proper critical wavelength when elasticity is included, (iii) how to determine the unknown diffusion constants and activation energies of TiAlN, (iv) how to determine mechanical properties from the simulated microstructure.

6.1 Autocorrelation function

A simple way of extracting size information from micrographs, is by counting the number of domains in a specific region or direction, and divide it by the total area or length. This method is not very reproducible, and several regions need to be studied to get trustworthy statistics. Characteristics of a spinodally decomposed microstructure are the existence of one minimum wavelength and a distribution of much longer wavelengths, correlating to the stretched-out domains. The size description does not seem to give any physical meaning for such a situation. In spinodal decomposed microstructures the proper “size” to study is the wavelength. For this situation, the number of wavelengths in a certain direction can be counted and the mean length determined, but the same restrictions stated above remains. A
complication is that the thickness of the interface needs to be extracted from the wavelength, in order to get the domain size, and that the microstructure in the case of TiAlN is asymmetric and aligned in the \{100\} directions. For the simulated microstructure there are several ways to calculate the domain size. A method suggested by Jansson [82] is to integrate the area of the gradients, estimate the thickness of the interface, (which is approximately constant during coarsening of the microstructure), and estimate the length of the interface. The total area is then divided by twice the length of the interface to get an estimate of the domain size. This gives an average size of the two evolving domain types, restricted to the time after the decomposition. The drawback is that no information of the wavelength at the initial time of the decomposition can be given. In the second paper the autocorrelation function of the composition is used instead to extract the size evolution for all simulation times. The method suits the microstructure since it studies the repetition of domains represented by waves. All the data in a micrograph is considered, and the statistics represents the information available. The autocorrelation can be used to extract crystallographic directional dependent wavelengths, and hence reflect the asymmetric microstructure, or used as a whole to get an averaged size of the domains. The drawback with this method is that the interface thickness will contribute to the domain size resulting in an overestimated size. The error is largest in the beginning of the decomposition, where the relative interface thickness is large with respect to the domain size, and decreases during decomposition (interface thickness is decreasing), and is further reduced during coarsening (constant interface thickness and increasing domain size).

6.2 Critical wavelength

Theoretically, the critical wavelength, $\lambda_{\text{crit}}$, and the fastest growing wavelength, $\lambda_{\text{max}}$, in the paper of Cahn [83] is:

$$\lambda_{\text{crit}} = 2\pi \sqrt{-\frac{\kappa}{G}}, \quad \lambda_{\text{max}} = \sqrt{2} \cdot \lambda_{\text{crit}}. \quad (6.1)$$

In practice the critical wavelength is never observed, in contrast to the fastest growing wavelength. To get an estimate of the difference between the fastest
growing wavelength and the observed plateau wavelength given by the autocorrelation function, the critical and fastest growing wavelength were calculated by eq. (6.1). The results are presented in Figure 6.1 for both 1123 K and 1173 K for the ideal and clustered model.

![Graph showing composition dependent wavelengths](image)

*Figure 6.1. Composition dependent $\lambda_{\text{crit}}$ and $\lambda_{\text{max}}$ for the ideal model and the clustered model at 1123 K and 1173 K respectively, calculated without taking into account elasticity.*

The shape of the critical wavelengths are in accordance with expectations; shortest for the peak positions of the Gibbs’ free energy, in accordance with Hillert’s theory presented in section 3.3, and infinite at the spinodal line. Hillert stated that in a symmetric miscibility gap the critical wavelength is shortest for the peak composition $A_{0.5}B_{0.5}$. In our case, with an asymmetric miscibility gap the shortest wavelength is observed for $\text{T}_{0.33}\text{Al}_{0.67}\text{N}$, the peak composition of the miscibility gap. The same result is also readily derived by studying the driving force see eq. (6.1) that is for high Al content alloys at low temperatures as seen in Figure 5.3 (b). The effect of increasing the temperature gives a small shift of the wavelengths towards larger values. The calculated fastest growing wavelength,
presented in Figure 6.1, is as expected smaller than the values given by the autocorrelation function, see Paper II. A method was implemented to see if there was consistency between the fastest growing wavelength calculated from the thermodynamic data, and calculated in the same manner on the fly in the simulations. In the first time steps of the simulation the fastest growing wavelength is determined by eq.(6.1) in every point in the simulation box, and the value encountered from the initial composition is extracted. The resulting initial wavelength is still larger than the calculated one from the thermodynamic data, but smaller than the one given by the autocorrelation function.

For the two compositions, Ti$_{0.5}$Al$_{0.5}$N and Ti$_{0.33}$Al$_{0.67}$N, the effect of the elasticity on the critical wavelength were studied with the autocorrelation function. In both cases the fastest growing wavelength increased when including the elasticity. This could of course be due to the anisotropy of the microstructure, that increase with elastic anisotropy which in turn increase with Al content for the compositions studied. There is no complete analytical expression for the critical wavelength where the elasticity is included. Note that the autocorrelation function itself is not the best choice for determining the fastest growing wavelength, since the microstructure in any given direction consists of several wavelengths, and hence the method always overestimates the size. A suggestion would be to study the Fourier transform of the autocorrelation function, rather than the function itself, to determine the frequencies and wavelengths. To get good results from the suggested method, good statistics i.e. a large area of the micrograph is needed.

6.3 Diffusion and Activation Energies

A method for determining the diffusivity constant, $D_0$, and activation energies, $Q$, of TiAlN, from SAXS experiments coupled to simulation data was suggested in Paper II. The diffusivity is usually described by an Arrhenius type of equation

$$D = D_0 e^{\frac{Q}{RT}},$$

(6.2)

where $R$ is the gas constant and $T$ is the temperature. If the diffusivity constant is approximated to be independent of temperature [78], then the increase in coarsening rate between two temperatures is only dependent of $Q$. 


where $D_{T_2}$ and $D_{T_1}$ is the diffusivity at $T_2$ and $T_1$ respectively and $m$ is the number of times the rate is increased at $T_2$ compared to $T_1$. In Paper III this method was used for the radius evolution data for Ti$_{0.33}$Al$_{0.67}$N for 1123 K and 1173 K. The relation between $Q$ and $m$ can be plotted given any two temperatures, see Figure 6.2. Three graphs are plotted, for an increase in temperature of 50 K, 100 K and 200 K from 1123 K see Figure 6.2.

Figure 6.2 The activation energy determined by the number of times, $m$, the coarseing rate increases when the temperature is raised by $\Delta T$ from 1123 K.
Hence, by determining the increase in rate from the two different temperatures of the experimental data the activation energy can be extracted. To determine the diffusivity constant the simulated coarsening rate need to be used. An assumption is that the driving force is small and approximately constant. This is true for later stages of the coarsening. The number of times the rate of the experiments are faster/slower compared to simulations may be determined as well as a total diffusivity $D$ for the experiment. Together with the previously determined activation energy, the diffusion constant $D_0$ can be calculated:

\[
D_{\text{Exp}} = n \cdot D_{\text{Sim}} \rightarrow \\
D_0^{\text{Exp}} \cdot e^{\left(\frac{q_{\text{Exp}}}{RT}\right)} = n \cdot D_{\text{Sim}} \rightarrow \\
D_0^{\text{Exp}} = n \tau_1 \cdot \frac{D_{\text{Sim}}}{e^{\left(\frac{q_{\text{Exp}}}{RT_1}\right)}} = n \tau_2 \cdot \frac{D_{\text{Sim}}}{e^{\left(\frac{q_{\text{Exp}}}{RT_2}\right)}} 
\]

(6.4)

Here $n$ is the increase in rate between the simulations and the experiment for the two temperatures. For a certain composition, the diffusivity constants for the two temperatures should be in the same range if the above stated approximations are valid. The task is then to find the two m:s that fit the data and give similar diffusivity constant values. It is recommended to run new simulations to test the diffusivity constants and activation energies, and iterate the procedure until convergence is reached.

It was recognized that this method was hard to apply to $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$, both due to the deviating shape of the experimental data for $1173 \, \text{K}$ that were difficult to fit and/or due to validity problems of the stated approximations. One reason could be that the sample did not have time to enter the later stage of coarsening and still was influenced by changes in the driving force.

6.4 Energies

A good way to determine if the output of the model is physical is to study the evolution of energies with time. It is also interesting to study how the changes in microstructure are coupled to the energies, see Paper III. The free energy, as well as the entropy and enthalpy are expected to decrease during the decomposition.
On the contrary the elastic energy and the gradient energy should increase during decomposition. In Figure 6.3, the gradient energy and elastic energy evolution on composition is shown. The gradient energy is seen to increase slightly before the elastic energy for all compositions. Another observation is that the evolving gradient energy is largest for Ti$_{0.33}$Al$_{0.67}$N, but the elastic energy is largest for Ti$_{0.5}$Al$_{0.5}$N.

![Elastic energy and gradient energy evolution on composition.](image)

**Figure 6.3 Elastic energy and gradient energy evolution on composition.**

### 6.5 Strain and Stress

The stress/strain behavior in TiAlN is complex and far from completely understood. During the isostructural decomposition coherency strains between the forming domains evolve due to the mismatch in lattice parameter and elasticity. The simulated and measured strains are in the order of $10^{-3}$, see Paper I and the mean simulated stresses are in the order of 5 GPa, see Paper III. During coarsening the irregularities of the domains cause local strain fields, which can be much higher than the mean values. In Figure 6.4 a graph of the maximum and minimum strain on composition is shown. As seen the strain is always largest in the \{110\} direction.
The elastic energy on the other hand is largest in the \{100\} directions as seen in Paper III. The anisotropic elastic constants is causing the shape of the evolving domains to be aligned in the \{100\} directions and the elastic energy to accumulate in these directions as seen in Paper III.

![Graph showing maximum and minimum strain evolution on composition.](image)

Figure 6.4 Maximum and minimum strain evolution on composition.

6.6 Young’s modulus

One of the goals of simulating the microstructure of TiAlN is to get values on the mechanical properties connected to it. To estimate the hardness of a certain microstructure one needs to simulate plastic properties including dislocation movements, which is difficult and time consuming. In Paper III, a simple way of extracting the elastic properties of the evolved microstructure through the Young’s modulus is used. The Young’s modulus is defined for an isotropic material as the $C_{1111}$ elastic stiffness constant. The time evolution of Young’s modulus were determined from the microstructure by calculating the change in free energy when increasing strain is applied in one of the \{100\} directions. The change in free
energy upon strain were fitted to a second order polynomial, and by the relation in eq. (6.5)

\[ dF = \sigma_1 d\epsilon_1 = C_{11} \epsilon_1 d\epsilon_1 \rightarrow \]

\[ C_{11} = \frac{d^2F}{d\epsilon_1^2} = Y, \]  \hspace{1cm} (6.5)

which holds for isothermal and reversible work.
7 Summary of included Papers

In this chapter, a summary of the included papers and my contribution to each paper is given.

7.1 Paper I

In Paper I \textit{in-situ} wide angle X-ray scattering and phase field modeling were used to study the strain evolution on composition during decomposition of TiAlN. The TiAlN thin films were deposited by an industrial scale arc evaporation system using TiAl cathodes in a N\textsubscript{2} atmosphere at a substrate temperature of 500°C. Phase field simulations based on the regular solution model, using calculated enthalpy of mixing and lattice parameters from \textit{ab initio} were performed. In the simulations, experimentally measured initial strains were set as boundary conditions to mimic the difference in strain state of the in plane and growth direction for the thin film after deposition. The elasticity and the deviation from Vegard’s law were considered in the model. The elasticity model is described in detail.

During the decomposition strain evolves due to the lattice mismatch between the domains and elastic incompatibility. The experimentally observed compressive strain in the TiAlN phase evolving during decomposition was addressed the formation of small amount of h-AlN nuclei.

7.1.1 Contribution to Paper I

I set up the phase field model and analyzed the simulated data. I took part in writing the paper.
7.2 Paper II

In Paper II in-situ small angle X-ray scattering and phase field simulations were performed to study the compositional wavelength evolution during spinodal decomposition of TiAlN. The thin films were deposited by an industrial scale arc evaporation system using TiAl cathodes in a N$_2$ atmosphere at $\sim$400°C. Phase field simulations using thermodynamic data calculated by ab initio taking into account clustering, were performed. The model also included elasticity and the deviation from Vegard’s law on the lattice parameters. The simulations were performed by ramping with 110 °C/min up to a holding temperature of 900 °C, similar to the experimental conditions were performed. The autocorrelation function was used to extract the domain sizes of the simulated data. From the small-angle X-ray scattering data a size of the domains could be determined by assuming the domain shapes to be spherical. The scattering intensities were then compared to modeled intensities from a specific size distribution of the spherical shapes.

It was found that the compositional wavelength evolution of TiAlN during annealing matches the stages characteristic of spinodal decomposition. First, a constant compositional wavelength is observed when the domains purify. Then, an increased compositional wavelength caused by domain coarsening is observed. Furthermore, the initial wavelength dependence on composition and temperature were studied. By comparing the experimental and simulated domain size data, a diffusivity constant and an activation energy was calculated and determined to $1.4 \times 10^{-7}$ m$^2$/s and 3.14 eV at$^{-1}$ respectively.

7.2.1 Contribution to Paper II

I set up the phase field model and analyzed the simulated data as well as extracted the diffusivity constant and activation energies. I also performed the autocorrelation function analysis on the z-contrast images. I took part in writing the paper.
7.3 Summary of Paper III

In Paper III, a phase field model was set up to study the evolution of von Mises stresses, Young’s modulus and the microstructure, on composition of Ti$_{1-x}$Al$_x$N where $x$ varied between 0.3 and 0.75. The phase field simulations were performed using thermodynamic data calculated by \textit{ab initio} that takes into account clustering effects. The phase field model was described in detail as well as how the clustered data deviates from the regular solution model. In the model elasticity and the deviation from Vegard’s law on the lattice parameters are considered. The simulations were performed at a holding temperature of 1173 K, and the diffusivity and activation energy determined in Paper II was used as input parameters. To extract the Young’s modulus dependence of the microstructure, the simulated microstructure was strained in one \{100\} direction and the difference in Free energy was determined.

It was found that the von Mises stresses ranges between 5 and 7.5 GPa depending on the composition. Furthermore, the Young’s modulus was observed to increase with 5% during the decomposition, in the case of Ti$_{0.33}$Al$_{0.67}$N to a value of \approx 398 GPa. Several stages of the microstructure evolution were identified and coupled to the energy evolution and the composition. In general, initially, when the amplitude of the evolving compositional fluctuation is small, outstretched domains in random directions of the majority phase evolves. Later, AlN rich cores appear and the microstructure evolves in accordance to minimize the elastic energy. Finally, high curvature regions are eliminated and coarsening begins. It was found that the AlN rich domains always purifies first and reaches equilibrium values of pure AlN, in contrast to TiN domains that after decomposition show an amount of incorporated TiN, independent of the global composition. This is due to the increased driving force for high Al content alloys, preferring clustering of AlN.

7.3.1 Contribution to Paper III

I set up the phase field modeling, analyzed the data and wrote the paper.
8 Conclusions

In this Chapter a summary of the conclusions of the appended papers is given.

The strain evolution of TiAlN during annealing was studied by *in-situ* X-ray scattering experiments and phase field simulations. The decomposition give rise to more compressive strains in the experiments compared to the simulations. The reason is suggested to be attributed to small amount of h-AlN formed in the experiments, not considered in the simulations.

The wavelength evolution of the Ti and Al rich domains during spinodal decomposition and coarsening was studied by *in-situ* small angle X-ray scattering and phase field simulations. Two stages were revealed; in the first stage the wavelength is constant and in the second stage the wavelength increases. During the first stage the amplitude of the wavelength increases and during the second stage coarsening of the domain occurs, characteristics of spinodal decomposition. When the temperature is increased from 850° C to 900° C the decomposition rate and the initial wavelength of the domains increase. The initial wavelength is shorter for Ti\(_{0.33}\)Al\(_{0.67}\)N compared to Ti\(_{0.5}\)Al\(_{0.5}\)N. Furthermore, the diffusion constant and activation energy was extracted by comparing the simulations and experiments, and determined to 1.4·10\(^{-7}\) m\(^2\)/s and 3.14 eV at\(^{-1}\), respectively.

Von Mises stress, Young’s modulus and microstructure evolution was studied using the phase field method coupled with *ab initio* calculated clustered data for TiAlN. The composition of Ti\(_{1-x}\)Al\(_{x}\)N was varied between x = 0.3 and x = 0.75. It was found that the decomposition and coarsening rate increase with Al content.
due to the increase in driving force. Further, the microstructure changes from round domains to stretched out domains in the elastically soft \{100\} directions, and the compositional wavelength decreases when the Al content is increased. Several stages of the microstructure evolution was identified and described from energy considerations. It was found that the AlN rich domains always purifies first and to a higher degree, independent of the global composition due to the increased driving force, preferring clustering of AlN. The elastic energy and von Mises stresses are largest for Ti\(_{0.5}\)Al\(_{0.5}\)N. Typical mean values of the von Mises stresses are between 5 and 7.5 GPa depending on the composition studied. The Young's modulus increased with 5% during decomposition of Ti\(_{0.33}\)Al\(_{0.67}\)N to a value of \(~398\) GPa.
9 Bibliography


[34] N. Norrby, High pressure and high temperature behavior of TiAlN, Linköping University, 2012.


9 Bibliography


