Thermodynamic investigation of systems related
to TWIP steels

Bonnie Lindahl

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To my loving family who has always been there for me.
Education is not the learning of facts, but the training of the mind to think.

- Albert Einstein
Abstract

The world is facing serious challenges regarding environmental issues. Carbon dioxide levels increase every day. In an attempt to decrease carbon emissions the automotive industry searches for lighter, stronger materials. TWinning Induced Plasticity (TWIP) steels show an impressive combination of strength and ductility. The possibility of adding high amounts of aluminum that decreases the density while maintaining the mechanical properties makes this type of steel very interesting for use in automotive applications. The only thing keeping the TWIP steels from being used in the automotive industry is that the Yield Strength (YS) is too low. The TWIP steels usually have a YS around 400 MPa. For them to be useful in automotive applications YS around 600-700 MPa is necessary. One of the most promising ways of improving the YS is by precipitation hardening. This work has been performed within a European Research Fund for Coal and Steel (RFCS) project called Precipitation in High Manganese steels (PrecHiMn). As the name of the project suggests, the goal of this project has been to study the precipitation in TWIP steels. The precipitation hardening is achieved through the addition of carbide and carbonitride formers such as Nb, Ti and V. In order to build advanced models to simulate precipitation it is important to have a good understanding of the thermodynamics of systems related to TWIP steels.

The goal of this work has been to study the thermodynamic properties of systems related to TWIP steels, more specifically the system forming the matrix phases of TWIP steels. Therefore the Al-C-Fe-Mn system has been studied as well as the Al-Ti-V system. Complete thermodynamic descriptions that reproduce the experimental data well have been produced including descriptions of order-disorder transformations.
Sammandrag


Målet med detta arbete har varit att studera de termodynamiska egenskaperna hos system med anknytning till TWIP stål. Mer specifikt har systemet som bildar matrixfaserna i TWIP stål. Dfr har Al-C-Fe-Mn-systemet studerats liksom Al-Ti-V-systemet. Fullständiga termodynamiska beskrivningar som återger experimentella data väl har producerats inklusive beskrivningar av ordningsomvandlingar.
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Preface

If there is one thing I’ve learned in my PhD studies it’s that the more you know about something the more you realize that you don’t understand it. Thermodynamics is a very tricky subject and during these past 5 years I’ve found myself going back to the very basics more than once. Two steps forward, one step back. Modeling the thermodynamic properties of materials is an iterative process. Your results can always be improved and it is very hard to say that something is finished.

The biggest challenge for me during this period has been to let go. Letting other people read my texts and see my work before I think it’s perfect. Which is a good thing, because I don’t ever think anything I do is perfect. I would have gladly spent several more years perfecting this work, but now that task will fall on someone else.

CALPHAD modeling is something in between physics and mathematics. We use models that are based on thermodynamic properties and physical phenomena and add parameters that do not always have much physical meaning in order to be able to reproduce the properties of the system we are looking at. This usually means that physicists think that it’s not really a science at all. On the other hand people in industry sometimes think that it is too complicated and they would rather stick to what they are used to. But I have learned that with the right models, the CALPHAD method can be an incredibly powerful tool. I hope that this work will be useful, both for my industry partners to develop new materials but also for new Calphadians just starting their journey.

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List of appended papers


Contribution Statement: Bonnie Lindahl performed the thermodynamic modeling and prepared the draft manuscript.

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Other contributions


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Nomenclature

FCC – Face Centered Cubic
BCC – Body Centered Cubic
HCP – Hexagonal Close-Packed
CEF – Compound Energy Formalism
SFE – Stacking Fault Energy
2SL – two sublattice
4SL – four sublattice
DSA – Dynamic Strain Ageing
R-K – Redlich-Kister
BWG – Bragg-William-Gorsky
LOM – Light Optical Microscopy
SEM – Scanning Electron Microscopy
XRD – X-Ray Diffraction
DFT – Density Functional Theory
Chapter 1

Background/Introduction

This work has been performed within a European Research Fund for Coal and Steel (RFCS) project called Precipitation in High Manganese steels. The goal of this project has, as the title of the project suggests, been to study the precipitation in high manganese steels by means of experimental investigation and modeling work. In order to model the kinetics of precipitation it is important to have reliable thermodynamic descriptions. It was therefore part of this work to develop a thermodynamic database containing the most relevant elements for alloying these steels [1]. The database developed features the elements: Al, C, Fe, Mn, N, Nb, Si, Ti and V. Nb, Ti and V are carbide and nitride formers and Al-C-Fe-Mn forms the basis of the steel. In this work the Al-C-Fe-Mn system has been studied extensively with the addition of the ternary Al-Ti-V system. The thesis is divided into three parts. In chapter 1 some main features of TWIP steels as well as thermodynamic modeling using the Calphad approach are discussed. In chapter 2 thermodynamics of all the systems is discussed including all the subsystems. In chapter 3 some features of the database for the Al-C-Fe-Mn system are shown and compared to the previous description. Finally chapter 4 concludes the work and gives some suggestions on future work in this area.

1.1 TWIP steels

Steels with Twinning Induced Plasticity (TWIP) have in the past years become very interesting engineering materials due to the combination of high strength and high ductility. A special interest has been shown by the automotive industry. The formation of twins when the alloy is deformed is a perfect fit for parts on a car intended to absorb energy on impact. In the automotive industry there are always efforts to make lighter cars in order to decrease fuel consumption. Therefore the possibility to alloy the steel with high amounts of aluminum making L-IP steels, Lightweight steels with Induced Plasticity, has been explored. Some TWIP alloys are already in use in industry but for some applications the yield strength of these alloys is still far too low. Several ways to improve the
yield strength in these alloys have been explored. One of the improvements that seems the most promising is precipitation hardening by the addition of carbide and nitride formers such as Ti, Nb and V.

In recent years TWIP steels have attracted a lot of attention and the number of publications in the last decade is very large compared to previous years \[2\]. The main interest for these steels comes from the automotive industry where the aim is increased passenger safety. Reduction of CO\(_2\) emissions due to weight reduction is also a very attractive point for these materials. The TWIP steels are similar to the TRIP-steels (TRansformation Induced Plasticity) in that they undergo microstructural changes during deformation. In the case of the TRIP steels, they go through a phase transition under plastic deformation to form martensite whereas the TWIP-steels form twins. The definition of what constitutes a TWIP steel is not always clear, one reason being that it is quite common that a single grade can exhibit both twinning and formation of \(\epsilon\)-martensite on deformation. Most authors agree that the definition should be linked to the Stacking Fault Energy (SFE). According to Sato et al. \[3\] the \(\gamma \rightarrow \epsilon\) transformation will be the dominating mechanism for alloys having SFEs lower than 20 \(mJ/m^2\). The microstructure of TWIP steels is usually austenitic since it is in the FCC-phase the twins can form. There are efforts being made to produce duplex grades as well where the twins would only form in parts of the material making it even more flexible. There are several types of TWIP steels, they are generally divided into two main categories; High and low carbon steels. The high carbon steels are usually referred to as Hadfield steels and the low carbon variants can be e.g. shape memory alloys.

### 1.1.1 History of TWIP steels

The TWIP steels were originally called High Manganese steels since this is the type of steel that this kind of twinning-effect was first found in. The forefather of the High manganese steels is the so-called Hadfield steel, discovered by Sir Robert Hadfield in 1888 \[4\]. This steel, high in both manganese and carbon, exhibited an interesting combination of properties. It had very high strength but was also very tough. At this time there was no knowledge on the mechanisms behind these properties or even the microstructure, which was first described by Hall \[5\] and Krivobok \[6\] in 1929. They found that the material was austenitic, and so the limits for fully austenitic steels were studied by Tofaute and Linden in 1936 \[7\]. By this time it was still unclear why the material had the properties it did and it was not until 1935 that Chévenard made the assumption that a hard phase was formed during straining \[8\]. Troiano and McGuire suggested that there were two types of martensite, \(\alpha\) and \(\epsilon\), one formed from rapid cooling and the other formed under deformation \[9\]. The hexagonal \(\epsilon\) martensite was discovered by Schmidt \[10\] and was determined to be the source of the unusual properties of the manganese steels. During the 1950s, materials were discovered that displayed the high work hardening observed in Hadfield steels without containing any \(\epsilon\) martensite, and the idea of twins was formulated, see e.g. \[11\]. A while after this, the twins were formally confirmed by TEM studies, see e.g.
1.1.2 Twinning vs. $\epsilon$-martensite formation

One of the main phenomena being studied in the literature is the determining factor deciding whether the deformation of the material will be by martensite formation or twinning. There seem to be several different factors determining which will be the dominant deformation mechanism, which will be discussed further in the next section. One of the main factors regarding the twinning effect vs. $\epsilon$-martensite is the Stacking Fault Energy (SFE). According to Sato [3], additions of Al to Fe-Mn alloys strongly suppress the nucleation of $\epsilon$-martensite hence making it easier to form twins. However it also makes it easier to form $\alpha$-martensite, wherefore the best approach to achieve TWIP steels is to have high contents of manganese and small amounts of aluminum. Since manganese also suppresses the $\epsilon$ martensite transformation Bouaziz and co-workers [2] claim that the alloys which do not form $\epsilon$-martensite also do not form $\alpha$-martensite. Some authors have claimed that there exists a critical stress that must be overcome in order to form either mechanical twins or $\epsilon$-martensite, e.g. Bracke [13]. Some authors attribute the kind of deformation mechanism to the type of Stacking Fault (SF), extrinsic or intrinsic. Idrissi et al. [14] found in their work that the formation of intrinsic SFs in the sample deformed at 160 °C seems to agree with the mechanisms based on deviation, which predict the creation of intrinsic SFs prior to mechanical twinning. Furthermore, these models require the activation of multiple glide planes as observed in the present case. The authors conclude that their results indicate that there is a relationship between the type of stacking fault in the material and the deformation mechanism, extrinsic SFs for the formation of $\epsilon$-martensite and intrinsic SFs for the formation of mechanical twins.

1.1.3 Stacking Fault Energy (SFE)

When a perfect dislocation dissociates into two Shockley partials it is separated by a stacking fault. The SFE in a material is linked to the separation distance between the two Shockley partials, the lower the SFE the larger the distance [15]. There are different ways to estimate or predict the SFE, one experimental method and two calculation methods [16]. The SFE can be measured using TEM investigations observing the inscribed dislocation node radius [17]. The SFE can also be predicted using a model based on thermodynamics [18]. Lastly the SFE can be calculated using \textit{ab-initio} methods [15, 19]. Adler et al. [20] proposed an equation for calculating the SFE in FCC-metals based on thermodynamic considerations:

$$SFE_{\text{intrinsic}} = 2\rho\Delta G^{\gamma \rightarrow \epsilon} + 2\sigma^{\gamma / \epsilon}$$

(1.1)

This equation was revised by Saeed-Akbari et al. [16] to take the effect of grain size into account.

$$SFE_{\text{intrinsic}} = 2\rho\Delta G^{\gamma \rightarrow \epsilon} + 2\sigma^{\gamma / \epsilon} + 2\rho\Delta G_{ex}$$

(1.2)
where \(2\rho \Delta G_{ex}\) is the contribution to the SFE due to grain size. Aluminum increases the SFE of FCC-alloys. Decreasing the grain size will also increase the SFE. Hedström [21] stated that the grain boundaries will act as barriers for the growth of martensite laths, therefore the reduction of grain size will result in less strain induced martensite. Saeed-Akbari et al. [16] have studied the effect of temperature, alloying elements and grain size on the SFE. They showed that the effects of temperature and aluminum content are greater than that of the grain size. The sensitivity to temperature changes decreases with the amount of Mn. It seems like a low SFE is essential for the formation of mechanical twins, however, according to some authors, this is not the only trigger. Bouaziz et al. [22] have previously reported that alloys with similar SFE exhibit different deformation mechanisms depending on the carbon content in the material. The dissociation of perfect dislocations because of the low SFE makes it harder for other perfect dislocations to cross slip and therefore makes the glide of perfect dislocations mainly planar.

### 1.1.4 Plasticity mechanisms

Materials usually deform by deformation glide but mechanical twinning and \(\epsilon\) martensite formation are competitive mechanisms for deformation [2]. There are several different explanations for the interesting combination of flow stress and ductility that the high manganese steels exhibit. The property most attributed to the interesting qualities that the TWIP steels exhibit is a very high work hardening effect. The main explanations are an atypical Dynamic Strain Aging (DSA) and deformation mechanisms besides dislocation glide, e.g. twinning. The DSA is noticeable due to serrated stress-strain curves and negative strain rate sensitivity. Due to the fact that this phenomenon only occurs in alloys containing carbon, it is thought to be the result of the dynamic interaction between the mobile carbon atoms and dislocations. It has been described in terms of Portevin-LeChatelier (PLC) effect. The DSA leads to the formation of PLC (Portevin-LeChatelier) bands. The PLC bands are caused by localized strain and are similar to neck formation in that the PLC bands form in an angle to the straining direction. The cause of the high work hardening in the high manganese steels is cause for controversy in the literature, where some authors claim that it is caused mostly by the mechanical twins [23] and others say that the main cause is the DSA mechanism. Bouaziz et al. [2] claim that it is only the appearance of mechanical twins (or strain induced \(\epsilon\)-martensite) that can account for all the features during the work hardening. Kim et al. stated in their work [24] that the DSA probably is a result of the dynamic interaction between mobile obstacles, such as interstitial atoms, and dislocations during deformation. The authors claim that this theory is further strengthened by the fact that the serrations in the stress-strain curve do not seem to appear in carbon-free alloys see e.g [25]. During deformation parts of the dislocation can be temporarily arrested at obstacles, such as forest junctions. The longer the arrest time the more it will contribute to the stress. The movement of the mobile dislocations is interrupted by forest dislocations or solute atoms during
the waiting time. The interstitial solutes, such as carbon, diffuse toward the arrested mobile dislocation during the aging time and immobilize them. The activation energy of carbon diffusion is too high at room temperature to be able to account for the room-temperature DSA in FCC alloys. The activation energy for the diffusion of a complex vacancy such as Snoek locking is theoretically low enough to be possible. Although the DSA leads to higher strain hardening it may also cause an unwanted lowering of the ductility. The other theory is that the work hardening mainly can be attributed to the formation of mechanical twins during deformation. Bouaziz et al. \[2\] state that TWIP steels have excellent strain-hardening properties because of a reduction in the mean free path for dislocation glide due to deformation twinning. Adler and co-workers \[20\] also claim that twinning is the main explanation for the strengthening in TWIP steels. They are of the opinion that the hardening in Hadfield steels can almost entirely be attributed to the formation of twins during deformation. However some special properties compared to other materials exhibiting twins can be attributed to pseudo twins or some unknown interaction between the Mn and C atoms. Carbon atoms in the octahedral sites will become trapped in the tetrahedral sites inside the twinned regions, if the energy barrier for diffusion is too high, contributing to the hardening of these materials.

1.1.5 Twin formation

There are also some different theories on how the formation of twins in these materials takes place. In a recent review Idrissi \[26\] explains that there are mainly three theories on how the twins form. The theories are based on the different mechanisms dominating the actual formation and the type of SF and they are: (1) pole mechanism which produces perfect twins without SF, (2) deviation process which produce intrinsic SF together with the nucleation of Frank or stair-rod sessile dislocations and (3) extrinsic stacking faults (models based on the interaction between extrinsic SF).

(1) Venables \[27\] proposed that prismatic glide sources would dissociate under stress into a Frank partial dislocation (pole dislocation) and a Shockley twinning partial. The created Shockley partial would then move away from the sessile Frank partial leaving behind a large intrinsic stacking fault. When the Shockley partial has created a semicircle it will wind down to the underlying close packed plane. If this process is repeated on every plane, a twin structure is created. Hirth \[28\] proposed a similar kind of pole dislocation but with different types of dislocations.

(2) The most common theories based on deviation processes are that of Cohen and Weertman \[29\] and that of Mori and Fujita \[30\]. Cohen and Weertman \[29\] proposed that a perfect dislocation would dissociate into a sessile Frank partial screw dislocation and a glissile Shockley partial when converging with a Lomer-Cottrel barrier. The deformation twinning would occur on the conjugate plane. For each Shockley partial emitted a sessile
Frank partial is created. Mori and Fujita [30] suggested the dissociation of a Shockley partial dislocation gliding in the primary plane into a stair-rod sessile dislocation at the intersection of the primary and conjugate plane. This phenomenon is also known as the stair-rod cross-slip. Both of these models require both multiple glide planes and high stress concentrations to happen in order to get dislocation dissociation in the twinning plane.

The last type of model, the one based on the presence of an extrinsic stacking fault is dominated by the theory by Mahajan and Chin [31]. It describes two perfect dislocations on the same plane turning into three Shockley partial on three consecutive adjacent close-packed planes. This would result in an extrinsic stacking fault configuration that acts as a three-layer nucleus for twinning. A macro twin would form if several of these twin nuclei grew into each other.

There have also been models which specifically describe the formation of twins in the Hadfield-type TWIP-steels. One of the most commonly referred to of these is the MTN-model proposed by Miura, Takamura and Narita [32]. Idrissi’s study showed that it is only possible that the Pole mechanism with deviation and the MTN-model could describe the formation of twins in these steels.

### 1.1.6 Improvement of the Yield Stress (YS)

The main characteristic of the TWIP steels is the unusual and very interesting combination of Ultimate Tensile Strength (UTS) and ductility. The main problem with these alloys however is that they generally have to low values on the Yield Strength (YS) which is a very important factor in most applications and for automotive applications specifically. Several different routes to improve the YS of these steels have been investigated in the literature. The most promising ways seem to be: grain refinement, pre-straining by rolling and precipitation strengthening. In the automotive industry, a reasonable YS would be 600-700 MPa but most TWIP-alloys have a YS around about 400 MPa. With grain refinement it is possible to reach a YS of 600-700 MPa if the grain size is reduced to approximately 1 µm. Unfortunately the smallest grain size achievable in the industrial processes is about 2.5 µm. With pre-straining by rolling, it is possible to achieve great improvements in the YS and still keep much of the ductility in the material. However this method gives the material an instantaneous reduction of the strain hardening coefficient. The pre-straining will also introduce a substantial anisotropy into the material. To prevent the anisotropy and to regain some of the strain hardening it is possible to perform recovery and partial recrystallization of the material. It has been found that this might be an interesting route to take and the best results are achieved after the largest cold rolling reduction and the lower temperature limit [33]. Last but not least there is the method of precipitation strengthening which is currently being thoroughly investigated. It is important to be careful when it comes to precipitation strengthening since most of the precipitates are unwanted. They are unwanted
for two reasons; firstly most of the precipitates are carbides which are very brittle and secondly it will tie up most of the carbon which will minimize the strain-hardening. It seems like some alloying elements will have positive effects on the mechanical properties of the material. The most promising elements are Nb and V but also Ti and W seem to have some interesting influences. So far, improvements of up to 400 MPa on the YS have been achieved. The influence of interstitial alloying elements on the strength of the material is not as great as in ferritic alloys for these materials. However it can be seen that the influence on the dislocation glide is quite large at lower temperatures. If the temperature is increased it will however reach a critical value at which a plateau will be reached. Glide in these alloys is thermally activated at low temperatures.

1.2 Thermodynamic modeling (CALPHAD)

The Calphad technique is a method for describing the thermodynamic properties of alloy systems. In this method the Gibbs energy for each phase is described by a mathematical expression containing adjustable model parameters that can be optimized to reproduce experimental or ab initio data on thermodynamic properties or phase diagram data. CALPHAD is an acronym meaning Calculation of PHase Diagrams but the approach has expanded and can do much more than just calculate phase diagrams. These days CALPHAD is often said to mean Computational coupling of thermochemistry and phase diagrams.

1.2.1 Phase models

Pure elements

The descriptions of all unary systems in this work are taken from [34]. Efforts are presently being made to describe the unary systems using more physics based models but since the present work has been focused on building a multi-component database, it is based on the old unaries. The Gibbs energy of each phase is described by a polynomial in temperature

\[ \circ \gamma_i - H_{SER} = a + bT + cT \ln T + dT^2 + eT^3 + f T^{-1} \]  

(1.3)

where \( H_{SER} \) is the reference state, usually in thermodynamic databases the reference used is the enthalpy of the stable configuration of the pure element at room temperature, i.e. 298 K or 25 °C. The \( a \)-term represents enthalpy, \( b \) can be evaluated using information regarding entropy and the rest of the terms represent the heat capacity (\( C_p \)). The Gibbs energy can also be described as a function of pressure but this has not been considered in the present work.

7
Compound Energy Formalism

All phase models can be said to be based on the Compound Energy Formalism (CEF) developed by Hillert [35, 36, 37, 38, 39].

\[ G^\theta_m - H^{SER} = srf G^\theta_m + \text{cnf} S^\theta_m \cdot T + E G^\theta_m + \text{phys} G^\theta_m \]  
(1.4)

where \( srf G^\theta_m \) is the surface of reference, \( \text{cnf} S^\theta_m \) is the configurational entropy and \( E G^\theta_m \) is the excess Gibbs energy.

\[ srf G^\theta_m = \sum_{I_0} P_{I_0}(Y)^s G^\theta_{I_0} \]  
(1.5)

\[ \text{cnf} S^\theta_m = -R \sum_{s=1}^{n} a_s \sum_{i} y_i^{(s)} \ln y_i^{(s)} \]  
(1.6)

\[ E G^\theta_m = \sum_{I_1} P_{I_1}(Y)L_{I_1}^{\theta} + \sum_{I_2} P_{I_2}(Y)L_{I_2}^{\theta} + \cdots \]  
(1.7)

where \( I \) defines a constituent array containing the combination of all the species being considered. If the constituent array is of the zeroth order all the end-member compounds are described by \( P_{I_0}(Y) \). \( ^s G^\theta_{I_0} \) represents a nonmagnetic compound energy. \( R \) is the gas constant and \( a_s \) is the number of sites for sublattice \( s \). \( I_1 \) forms an array with all possible combinations with mixing on one sublattice and \( I_2 \) contains mixing on two. \( L_{I_1}^{\theta} \) is an interaction parameter describing the deviation from ideal mixing when there is interaction on one sublattice and similarly \( L_{I_2}^{\theta} \) describes the deviation from ideal mixing when there is simultaneous mixing on two sublattices. \( \text{phys} G^\theta_m \) in eq. [1.4] is the contribution to the Gibbs energy due to physical phenomena such as magnetism. The magnetic contribution was described by Hillert and Jarl [40].

\[ \text{mag} G^\theta_m = nRTf(\tau)\ln(\beta + 1) \]  
(1.8)

where \( \tau = \frac{T}{T_C} \), \( T \) is the thermodynamic temperature and \( T_C \) is the Curie temperature. \( \beta \) is the average magnetic moment.

Substitutional solutions

The simplest form of the CEF is the substitutional solution model. The substitutional solution model assumes that atoms mix randomly on a single lattice. This is often true for melts and terminal phases such as FCC, BCC and HCP when it comes to metallic elements. The mathematical expression for the sub-
stitutional solution model is:

\[ G_m^\theta - H^{SER} = \sum_i x_i \theta G_i^\theta + RT \sum_i x_i \ln x_i + \sum_{i,j} x_i x_j I_{i,j}^\theta + \sum_{i,j,k} x_i x_j x_k I_{i,j,k}^\theta + \text{phys} G_m^\theta \] (1.9)

where \( x_i \) is the mole fraction of element \( i \), \( \theta G_i^\theta \) is the non-magnetic lattice stability of \( \theta \) for pure \( i \). \( I_{i,j}^\theta \) is the binary interaction parameter describing the deviation from non-ideality in the mixing between \( i \) and \( j \). The composition dependence of the interaction parameter can be described using a Redlich-Kister (R-K) polynomial [41]

\[ I_{i,j}^\theta = \sum_{v=0}^{n} v L_{i,j}(x_i - x_j)^v \] (1.10)

where \( v L_{i,j} \) is the interaction parameter of \( v \):th order and can be expanded according to

\[ v L_{i,j} = A + B \cdot T \] (1.11)

where \( A \) and \( B \) are model parameters to be optimized to reproduce experimental data. If necessary, it is possible to add more parameters. The contributions to the Gibbs energy from the different parameters are shown in Fig. [41]

Stoichiometric compounds and phases with limited solubility

Some phases only exist at a single composition. They are then described as stoichiometric compounds which can be described similarly to the pure elements according to equation [1.3]. If there is no available information on \( C_p \) the energy of the phase can be described using the Neumann-Kopp approximation which means that the \( C_p \) is taken as the weighted average of the pure elements. The Gibbs energy of the compound \( I_n J_m \) is thus described by

\[ \Delta G_{I_n J_m} = G_{I_n J_m} - n \theta G_1^\theta - m \theta G_J^\theta = \Delta H_f - T \Delta S_f \] (1.12)

where \( \theta G_1^\theta \) resp. \( \theta G_J^\theta \) is the Gibbs energy of the stable configuration of pure \( I \) and \( J \) respectively, at ambient temperature and pressure. \( \Delta H_f \) is the enthalpy of formation and \( \Delta S_f \) is the entropy of formation.

There are many cases when compound phases show some deviation from ideal stoichiometry, this can be accounted for by introducing defects. Anti-site
defects can be introduced by allowing an element to occupy the sublattice of another element, e.g. \((A)_n(B)_m\). The Gibbs energy will then be described by:

\[
G_A^{A_nB_m} - H^{SER} = y_A'y_A''G_{A_nA_{m}} + y_B'y_B''G_{B_nB_m} + mRT(y_A''lny_A'' + y_B''lny_B'') + y_A'y_B' I_{A,B} \tag{1.13}
\]

where \(y_i^s\) is the site fraction of \(i\) on sublattice \(s\), \(G_A^{A_nB_m}\) is the lattice stability of \(A_nB_m\) for pure \(A\) and \(G_{A,B}^{A_nB_m}\) is the formation energy of the compound \(A_nB_m\) from the pure elements.

It is also possible to add vacancy defects in a similar way.

**Ordered phases**

Ordered compounds can also be described using the CEF. All elements are then allowed to occupy all sublattices i.e. \((A,B)_m(A,B)_n\). There are several ordered compounds that can be regarded as superstructures to the terminal phases FCC, BCC and HCP. Depending on the number of sublattices used, a different number of ordered compounds can be described. In this work, the FCC, BCC and \(\kappa\) phases have been described using models with four sublattices (4SL) for the substitutional elements. The phases were described using the partitioning model (also known as the split CEF) in which the chemical ordering is described as an
addition to the Gibbs energy in a similar way as is done for magnetism

\[ G_{\text{phase}} = G_{\text{dis}} + \Delta G_{\text{ord}} \]  

(1.14)

\[ \Delta G_{\text{ord}} = G_{\text{ord}}(y_i^{(s)}) - G_{\text{ord}}(y_i^{(s)} = x_i) \]  

(1.15)

where \( G_{\text{ord}} \) is calculated twice so that the contribution becomes zero if the phase is disordered i.e. \( y_i' = y_i'' = y_i''' = x_i \).

Using a 4 SL model for the substitutional elements creates many end-member compounds whose energies need to be determined. In order to limit the internal degrees of freedom and improve extrapolations into higher order systems the Bragg-William-Gorsky (BWG) approximation [42, 43] has been implemented in this work.

Ordering in BCC alloys using a 4SL model is discussed further in paper II.

1.2.2 Extrapolation into higher order systems

The mathematical functions for each phase are stored in a database. Using this database many different thermodynamic equilibria and thermodynamic properties can be calculated.

Once the binary systems are evaluated they can be combined and used to extrapolate into higher order systems. There are several methods for conducting these extrapolations. Illustration of some of the available methods are shown in Fig. 1.2. The composition from which the binary values will be taken are evaluated in different ways. The first two methods, the Kohler method and the Muggianu method are symmetrical methods, where the compositions are evaluated in a similar manner for all the binaries and the last, the Toop method, is an asymmetrical method. In this work, the Muggianu extrapolations have been used for all systems.

![Illustrations for evaluating the binary composition from which the energy value will be taken.](image)

Figure 1.2: Illustrations for evaluating the binary composition from which the energy value will be taken.

The interaction parameters become less relevant the more elements that are involved. Therefore the highest order systems that are usually evaluated are the
Because of the relatively simple mathematics involved it is possible to describe the thermodynamic properties of multicomponent alloys. When building thermodynamic databases it is necessary to use the same descriptions for the lower order systems for the higher order descriptions to be compatible. Therefore it happens that ternary or higher order systems have to be reassessed even though good evaluations of those particular systems are available, if the lower order systems are improved.

1.2.3 Data evaluation

One of the most important stages of the thermodynamic assessment process and probably the most time consuming one is critically assessing the available experimental data. Choosing the “correct” set of data to fit to is crucial in order to get good extrapolations into higher order systems.

In the cases when thermochemical data is missing, a good approximation can often be to use data calculated using ab initio methods such as Density Functional Theory (DFT). It is important to be careful when using ab initio calculated data. The lattice stabilities in Calphad and DFT do not always match. With some elements such as FCC vanadium, the mismatch is very large, making it almost impossible to use some types of data at all directly. Fig. 1.3 shows the enthalpy of formation calculated with Calphad and DFT respectively across the entire composition range in the Al-V system.

As can be seen, the enthalpy for the different phases matches well on the Al-side, but on the V-side the mismatch is quite large. This means that this data cannot be used directly, specifically near the V-side. It is possible however
to look at the trends. In the case shown in Fig. 1.3 the enthalpy of formation for FCC and HCP phases has been optimized to reproduce the trend so that the curves for FCC, BCC and HCP cross at the point that they do according to the DFT data.

The assessment process is an iterative process. Even if binary experimental data are reproduced with a thermodynamic description it can sometimes prove to extrapolate badly into higher order systems. This is usually due to lack of thermochemical data. In general, as few and as small parameters as possible are desired. If it is necessary to use many large parameters in higher order systems, it is usually a sign that one or several of the lower order systems need to be reassessed.
Chapter 2

Assessed systems

Within the PrecHiMn project a database containing the elements Al, C, Fe, Mn, Ti, V, N, Nb, Si has been developed. My work has been to assess some of the subsystems, the Al-C-Fe-Mn system and its subsystems as well as the Al-Ti-V system and its subsystems. Table 2.1 shows a summary of all the binary and ternary systems used within this work. Table 2.2 shows all of the phases in the Al-C-Fe-Mn system and table 2.3 all the phases in the Al-Ti-V system. In the following, the available thermodynamic assessments of all the systems dealt with in this work are discussed. In the cases when there were no satisfactory descriptions, new thermodynamic assessments have been performed.

Table 2.1: Descriptions of binary systems used in this work.

<table>
<thead>
<tr>
<th>Binary systems</th>
<th>Ternary systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-C</td>
<td>Connetable et al. [44]</td>
</tr>
<tr>
<td>Al-Fe</td>
<td>Sundman et al. [45]</td>
</tr>
<tr>
<td>Al-Mn</td>
<td>Du et al. [46]</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>Witusiewicz et al. [47]</td>
</tr>
<tr>
<td>Al-V</td>
<td>Lindahl et al. [paper III]</td>
</tr>
<tr>
<td>C-Mn</td>
<td>Djurovic et al. [49]</td>
</tr>
<tr>
<td>Ti-V</td>
<td>Saunders [51]</td>
</tr>
</tbody>
</table>

2.1 Binary systems

In order to have accurate thermodynamic descriptions of multicomponent alloys, it is very important to have sound descriptions of the lower order systems. In the following, the available binary systems are discussed. It was found that there are sufficient available thermodynamic assessments for all binary systems.
Table 2.2: Phases in the Al-C-Fe-Mn system.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Strukturbericht</th>
<th>Space group</th>
<th>Pearson symbol</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terminal phases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td>(Al,C,Fe,Mn)$_1$</td>
</tr>
<tr>
<td>FCC</td>
<td>A1</td>
<td>Fm$\overline{3}$m</td>
<td>cF4</td>
<td>(Al,Fe,Mn)$_1$(C,Va)$_1$</td>
</tr>
<tr>
<td>BCC</td>
<td>A2</td>
<td>Im$\overline{3}$m</td>
<td>cI2</td>
<td>(Al,Fe,Mn)$_1$(C,Va)$_3$</td>
</tr>
<tr>
<td>HCP</td>
<td>A3</td>
<td>P6$_3$/mmc</td>
<td>hP2</td>
<td>(Al,Fe,Mn)$<em>1$(C,Va)$</em>{1.5}$</td>
</tr>
<tr>
<td>$\alpha$-Mn</td>
<td>A12</td>
<td>I4$\overline{3}$m</td>
<td>cI58</td>
<td>(Al,Fe,Mn)$_1$(C,Va)$_1$</td>
</tr>
<tr>
<td>$\beta$-Mn</td>
<td>A13</td>
<td>P4$_1$32</td>
<td>cP20</td>
<td>(Al,Fe,Mn)$_1$(C,Va)$_1$</td>
</tr>
<tr>
<td><strong>Carbides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_4$C$_3$</td>
<td>-</td>
<td>R3m</td>
<td>hR21</td>
<td>(Al)$_2$(C)$_3$</td>
</tr>
<tr>
<td>M$_2$3C$_6$</td>
<td>-</td>
<td>Fm$\overline{3}$m</td>
<td>cF116</td>
<td>(Fe,Mn)$_{20}$(Fe,Mn)$_3$(C)$_6$</td>
</tr>
<tr>
<td>cementite</td>
<td>-</td>
<td>Pmmm</td>
<td>oP16</td>
<td>(Fe,Mn)$_3$(C)$_1$</td>
</tr>
<tr>
<td>M$_3$C$_2$</td>
<td>-</td>
<td>C2/c</td>
<td>mS28</td>
<td>(Fe,Mn)$_5$(C)$_2$</td>
</tr>
<tr>
<td>M$_7$C$_3$</td>
<td>-</td>
<td>Pmma</td>
<td>oP40</td>
<td>(Fe,Mn)$_7$(C)$_3$</td>
</tr>
<tr>
<td>Graphite</td>
<td>-</td>
<td>P6$_3$/mmc</td>
<td>hP4</td>
<td>(C)$_1$</td>
</tr>
<tr>
<td><strong>Aluminides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_8$Fe$_5$</td>
<td>D$_{8h}$</td>
<td>I4$\overline{3}$m</td>
<td>hR26</td>
<td>(Al,Fe)$_5$(Al,Fe)$_5$</td>
</tr>
<tr>
<td>Al$_2$Fe</td>
<td>-</td>
<td>P1</td>
<td>aP18</td>
<td>(Al)$_2$(Fe,Mn)$_1$</td>
</tr>
<tr>
<td>Al$_3$Fe$_2$</td>
<td>-</td>
<td>Cmcm</td>
<td>(Al)$_5$(Fe,Mn)$_2$</td>
<td></td>
</tr>
<tr>
<td>Al$_{13}$Fe$_4$</td>
<td>-</td>
<td>C2/m</td>
<td>mC102</td>
<td>(Al)$<em>{6275}$(Fe,Mn)$</em>{0.235}$(Al, Va)$_{0.1375}$</td>
</tr>
<tr>
<td>Al$_{12}$Mn</td>
<td>-</td>
<td>I$\overline{3}$m</td>
<td>cI26</td>
<td>(Al)$_{12}$(Fe,Mn)$_1$</td>
</tr>
<tr>
<td>Al$_6$Mn</td>
<td>D$_{2h}$</td>
<td>Cmcm</td>
<td>oC28</td>
<td>(Al)$_6$(Fe,Mn)$_1$</td>
</tr>
<tr>
<td>R-Al$_4$Mn</td>
<td>-</td>
<td>P6$_3$/m</td>
<td>hP586</td>
<td>(Al)$<em>{461}$(Mn)$</em>{107}$</td>
</tr>
<tr>
<td>U-Al$_4$Mn</td>
<td>-</td>
<td>P6$_3$/mmc</td>
<td>hP574</td>
<td>(Al)$_4$(Fe,Mn)$_1$</td>
</tr>
<tr>
<td>LT Al$_{11}$Mn$_4$</td>
<td>-</td>
<td>P1</td>
<td>aP15</td>
<td>(Al)$_{11}$(Mn)$_4$</td>
</tr>
<tr>
<td>HT Al$_{11}$Mn$_4$</td>
<td>-</td>
<td>Pn$2_1$a</td>
<td>oP156</td>
<td>(Al,Mn)$<em>{29}$(Mn)$</em>{10}$</td>
</tr>
<tr>
<td>Al$_5$Mn$_5$</td>
<td>D$_{8h10}$</td>
<td>R3m</td>
<td>cI52</td>
<td>(Al)$_{12}$(Mn)$_5$(Al,Fe,Mn)$_9$</td>
</tr>
<tr>
<td><strong>Metastable Carbides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M$_2$C</td>
<td>-</td>
<td>Pnmm</td>
<td>oP6</td>
<td></td>
</tr>
</tbody>
</table>

except for the Al-V system. A summary of the binary systems used in this work is shown in table 2.1.

**Al-C**

The Al-C system was first assessed by Gröbner [52]. In his description he only included the stable phases in this system i.e. liquid, FCC (Al), graphite (C) and the intermetallic compound Al$_4$C$_3$. In 2008 Connetable et al. [44] reassessed the system adding a very slight solubility of carbon in FCC (Al) and descriptions of the metastable phases BCC and $\kappa$ where also added. The phase diagrams according to the different sets of parameters are shown in Fig. 2.1. The description by Connetable et al. [44] is used in this work.
Table 2.3: Phases in the Al-Ti-V system.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Strukturbericht</th>
<th>Space group</th>
<th>Pearson symbol</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal phases</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCC</td>
<td>A1</td>
<td>Fm$\bar{3}$m</td>
<td>cF4</td>
<td>(Al,Ti)$_1$ (Va)$_1$</td>
</tr>
<tr>
<td>BCC</td>
<td>A2</td>
<td>Im$\bar{3}$m</td>
<td>cI2</td>
<td>(Al,Ti)$_1$ (Va)$_3$</td>
</tr>
<tr>
<td>HCP</td>
<td>A3</td>
<td>P6$_3$/mmc</td>
<td>hP2</td>
<td>(Al,Ti)$<em>1$ (Va)$</em>{0.5}$</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCC</td>
<td>B2</td>
<td>Pm$\bar{3}$m</td>
<td>cI2</td>
<td>(Al,Ti)$<em>{0.5}$ (Al,Ti)$</em>{0.5}$ (Va)$_3$</td>
</tr>
<tr>
<td>AlTi$_3$</td>
<td>D0$_{19}$</td>
<td>P6$_3$/mmc</td>
<td>hP8</td>
<td>(Al,Ti)$_3$(Al,Ti)$_1$</td>
</tr>
<tr>
<td>AlTi</td>
<td>L1$_0$</td>
<td>P4/mmm</td>
<td>tP4</td>
<td>(Al,Ti)$_1$(Al,Ti)$_1$</td>
</tr>
<tr>
<td>Al$_2$Ti</td>
<td></td>
<td>I4$_1$/amd</td>
<td>tI24</td>
<td>(Al,Ti)$_2$(Al,Ti)$_1$</td>
</tr>
<tr>
<td>Al$_5$Ti$_2$</td>
<td></td>
<td>P4/mmm</td>
<td>tP28</td>
<td>(Al,Ti)$_5$(Al,Ti)$_2$</td>
</tr>
<tr>
<td>Al$_3$M</td>
<td>D0$_{22}$</td>
<td>I4/mmm</td>
<td>tI8</td>
<td>(Al,Ti,V)$_3$(Al,Ti,V)$_1$</td>
</tr>
<tr>
<td>L Al$_3$Ti</td>
<td></td>
<td>I4/mmm</td>
<td>tI32</td>
<td>(Al,Ti)$_3$(Al,Ti)$_1$</td>
</tr>
<tr>
<td>Al$_8$V$_5$</td>
<td>D8$_2$</td>
<td>143m</td>
<td>cI52</td>
<td>(Al)$_6$(Al,V)$_2$(Al,V)$_3$(V)$_2$</td>
</tr>
<tr>
<td>Stoichiometric phases</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_5$Ti$_3$</td>
<td></td>
<td>P4/mbm</td>
<td>tP32</td>
<td>(Al)$_5$(Ti)$_3$</td>
</tr>
<tr>
<td>Al$_{23}$V$_4$</td>
<td></td>
<td>P6$_3$/mmc</td>
<td>hP54</td>
<td>(Al)$_{23}$(V)$_4$</td>
</tr>
<tr>
<td>Al$_{45}$V$_7$</td>
<td></td>
<td>C2/m</td>
<td>mC104</td>
<td>(Al)$_{45}$(V)$_7$</td>
</tr>
<tr>
<td>Al$_{21}$V$_2$</td>
<td></td>
<td>Fd$\bar{3}$m</td>
<td>cF184</td>
<td>(Al)$_{21}$(V)$_2$</td>
</tr>
</tbody>
</table>

Figure 2.1: Binary phase diagram for the Al-C system.

**Al-Fe**

The first complete thermodynamic assessment of the Al-Fe system was performed by Saunders [53]. In 1993 Kattner and Burton [54] reviewed the experimental data and the published diagram. They published the generally accepted
diagram along with experimental data. Not all of the parameters were published though since the models at that time weren’t sophisticated enough to deal with the D0₃ phase. Seiersten [55] made the first complete thermodynamic assessment of the system with a complete set of parameters. The BCC phase was modeled with a 2SL model. This was later published as a part of the COST 507 project [56]. In 2008 Du et al. [57] modified Seiersten’s assessment to fit new experimental data on the congruent melting of Al₁₃Fe₄. The same year Connetable et al. [44] reassessed the Al-C-Fe system including reassessments of the binary Al-Fe and Al-C systems. Jacobs and Schmid-Fetzer [58] made a thermodynamic assessment of the system based on the assessment of Seiersten but introduced vacancy defects into the models for BCC and FeAl₃. Sundman et al. [45] assessed the entire system, this assessment was also based on the one by Seiersten with the changes made by Du et al. [57], but a 4SL model was used for the BCC phase in order to describe the ordered D0₃ phase. The new experimental information since the assessment of Seiersten was reviewed in this work. Phase diagrams calculated with descriptions with available thermodynamic model parameters are shown in Fig. 2.2. The description by Sundman et al. [45] has been used in this work.

**Al-Mn**

The Al-Mn system has been assessed a number of times in the literature. Due to vague experimental results, especially concerning the Al₈Mn₅ phase and it’s disordering into the BCC phase, the assessments have given quite different results. Kaufman & Nesor [59] performed an initial assessment of the Al-Mn system. Their calculated diagram was quite different from the experimental phase diagram. In 1992 Jansson [60] reassessed the system. The BCC phase in the middle of the system was ignored in this description.

Later, in 1999, Liu et al. [61] again reassessed the Al-Mn system, this time including the phase region of BCC in the middle of the phase diagram. They also used a 2SL model for the BCC phase in order to describe the second order phase transition from A₂ to B₂ in that same phase region according to experimental data from [62].

Ohno et al. [63] slightly adjusted the description by Liu et al. [61] making the Al₁₁Mn₄ phase stable down to room temperature and also slightly adjusted the two phase region between Al₈Mn₅ and β-Mn.

The latest description of the Al-Mn system was by Du et al. [46]. They included two more phases in the high-Al region (RAl₄Mn and Al₁₁Mn₄ (HT)) and disregarded the ordering in BCC. The solubility of Al in α-Mn was also drastically decreased compared to previous versions. The phase diagrams from the different descriptions are shown in Fig. 2.3. In this work the description by Du et al. has been used together with information on the ordering in the BCC phase from Djurovic [64].
Figure 2.2: Binary phase diagram for the Al-Fe system.

**Al-Ti**

The Al-Ti system is an important system and has therefore been studied several times in the literature. The system is a complex one, with many intermetallic phases. Some regions in the phase diagram have been proven to be very difficult to determine experimentally wherefore different results have been achieved by different assessors. The first attempt of a thermodynamic assessment of this system was carried out by Kaufman and Nesor [65] in their binary phase diagram compilation from 1978. They treated all the intermetallic phases as stoichiometric compounds. In 1988 Murray [66] improved the assessment by adding a solubility range to the TiAl(L1₀)-phase and also treated the order-disorder transformations for BCC, FCC and HCP using the Bragg-William approximation. The same year Gros et al. [67] published a thermodynamic description for the Ti-rich side of the phase diagram including only phase equilibria for
the BCC, HCP, Liquid and Ti₃Al(D0₁₉) phases. In 1992 Kattner et al. [68] re-assessed the Al-Ti system and added descriptions of two more stoichiometric phases (Al₂Ti and Al₅Ti₂). This assessment also treats the order-disorder transformations and accepts a different reaction for the formation of α-Ti, namely:

\[ \text{Liquid} + \beta - Ti \rightarrow \alpha - Ti \]

Instead of the reaction accepted by Murray:

\[ \beta - Ti + TiAl(L1₀) \rightarrow \alpha - Ti \]

Because of experimental information from McCulloogh et al. [69], Kattner et al. also added a solubility range to the TiAl₃(D0₁₉)-phase. The assessment by Kattner et al. was in 1997 modified by Zhang et al. [70] to better fit data on intrinsic defect concentration in AlTi(L1₀). However, not many changes were
made to the stable phase diagram. Because previous assessments had described
the ordered and disordered phases with the same primitive structure using in-
dependent expressions of the Gibbs energy Ohnuma et al. [71] re-evaluated the
Gibbs energies of the FCC, BCC, HCP phases and their ordered counterparts
in 2000. They included a stable A2/B2 transformation and based their evalua-
tion on their own experiments carried out while carefully controlling the oxygen
contamination. In 2008 Witusiewicz et al. [47] reassessed the system putting
more focus on the Al-rich side of the phase diagram. They improved the fit
to the experimental data compared to previous assessments. The work deter-
mined that the melting behavior of the BCC-phase is congruent and included
the order-disorder phenomenon in the BCC-phase. The nature of the formation
of the AlTi$_3$ (D0$_{19}$) is dependent on whether the A2-B2 ordering is considered
or not. The Al$_5$Ti$_3$ phase is considered to be stable since it doesn’t interfere
with the rest of the system. The field in the middle of the phase diagram is
modeled as AlTi (L1$_0$) and ζ (Ti$_{2+x}$Al$_{5-x}$). The most recent assessment was
performed by Wang et al. [72] in 2012. The most important contribution of
this work is the addition of anti-site defects which will not be considered in the
present work. The phase diagrams calculated from the parameters published by
Ohnuma et al. [71] and Witusiewicz et al. [47] are shown in Fig. 2.4

![Phase Diagrams](image)

(a) Ohnuma et al. [71]  
(b) Witusiewicz et al. [47]

Figure 2.4: Binary phase diagrams for the Al-Ti system.

The assessment of Witusiewicz et al. [47] has been used in the present work.

Al-V

Okamoto [73, 74] has reviewed the phase diagram information available for the
Al-V system. The first assessment of the available experimental data of this
system was performed by Murray [75]. Her assessment was mainly based on
experimental information from Bailey et al. [76] on invariant reactions and infor-
mation from Willey [77] and Eremenko et al. [78] on dilute liquids. The
The system contains three solution phases, Liquid, FCC (Al) with a very narrow solubility range of vanadium (0-0.3% V) and BCC (V) with an extensive solubility range (0-50% Al). The system also contains 5 compound phases: Al_{21}V_2, Al_{15}V_7, Al_{21}V_4, Al_4V (D0_{22}) and Al_8V_5 modeled as stoichiometric phases due to lack of experimental information in the assessment by Murray. During the COST 507 project Saunders [79] assessed the Al-V system. Complete expressions for the Gibbs energy were published to describe all the phases. All the intermetallic compounds were described as stoichiometric. The phase Al_{45}V_7 was described as Al_{7}V and the Al_{21}V_2 as Al_{10}V. The temperatures of the invariant reactions are similar to those published by Murray [66]. In the year 2000 Richter and Ipser [80] re-investigated the Al-V phase diagram experimentally on the Al-rich side i.e. up to 50% V. They found the same intermetallic compounds as had been reported earlier but the invariant points for the formation of Al_8V_5 and Al_3V varied considerably from earlier reported values. They were 1681 K and 1543 K respectively compared to the values used by Murray (and Saunders) 1943 (1932.7) K and 1633 (1640.1) K. The most recent assessment for this system and the one used in the present work is due to Gong et al. [81]. Their assessment puts a higher weight on the more recent experimental results from Richter and Ipser [80] and puts more focus on the development of a crystallographically correct model for the Al_8V_5 phase. The parameters for this phase were developed in steps starting with a stoichiometric model and then using those parameters as starting values for the increasingly complex model until arriving at the model (Al)_{6/13}(Al,V)_{2/13}(Al,V)_{3/13}(V)_{2/13}. The solution phases i.e. liquid, FCC and BCC were modeled with Redlich-Kister polynomials based on the unaries published by SGTE [34] and the remaining compound phases mentioned earlier were modeled as stoichiometric. The phase diagrams produced from the parameters from Saunders [79] and Gong et al. [81] are shown in Fig. 2.5.

Figure 2.5: Binary phase diagram for the Al-V system.
None of the available descriptions describe the thermodynamic properties and the phase diagram data well enough. The assessment by Saunders [79] was published before the experimental data by Richter and Ipser [80] was available and the description by Gong et al. [81] extrapolates poorly. The Al-V system have been reassessed in this work.

Details on the thermodynamic assessment of the Al-V system can be found in paper III. The thermochemical properties of the Al-V system has been studied by Kubaschewski and Heymer [82], Meschel and Kleppa [83], Neckel and Nowotny [84] and Samokhval et al. [85]. The results of the different studies are shown in Fig. 2.6.

The values differ quite drastically. The data from Kubaschewski and Heymer [82] suggest that there should be a minimum at \(x_V = 0.2\) while the other data suggest that the minimum should be around \(x_V = 0.4\). In paper III both the data from Meschel and Kleppa [83] Kubaschewski and Heymer [82] were used in two different optimization procedures. The produced sets of parameters were used to extrapolate into the ternary Al-Ti-V system and it was found that the data from Kubaschewski and Heymer [82] were more reasonable. The produced Al-V phase diagram is shown in Fig. 2.7.

**C-Fe**

The thermodynamic properties of the C-Fe system have been investigated several times in the past [88, 36, 89, 90]. The most widely used assessment was made by Gustafson [48]. He based his description on the one by Ågren [90] but used a substitutional solution model with a single sublattice for the liquid phase so that the phase diagram could be calculated across the entire composition range. Later, Franke [91] reevaluated the parameters by Gustafson and
removed an inverse miscibility gap in the liquid at high temperatures. Hallstedt et al. [92] reevaluated the thermodynamic properties of the cementite phase and found that the Kopp-Neuman rule wasn’t adequate. Djurovic et al. [50] used *ab initio* calculations to establish the enthalpies of formation of the metastable iron carbides. Recently Naraghi et al [93] reassessed the entire C-Fe system using new descriptions of the unaries. In this work, the description by Gustafson [48] with the additions by Hallstedt et al. [92] and Djurovic et al. [50] is used.

C-Mn

The C-Mn system has been described 3 times in the literature. The first assessment was done by Lee [94] before the standardization of the descriptions of the pure elements [34]. The second assessment was performed by Huang [95] at approximately the same time. Later Djurovic et al. [49] improved the description by Huang including new experimental data and used *ab initio* calculated enthalpies for the carbides. The phase diagrams for the two most recent descriptions are shown in Fig. 2.9. The description by Djurovic [49] has been used in this work.

Fe-Mn

The Fe-Mn system was first assessed by Kaufman [59], Huang [96]. Reassessed the entire system using the sub-regular solution model for all phases. The magnetic model by Hillert and Jarl [10] was also implemented for the BCC/FCC equilibria. Later, Huang [97] reassessed the system again based on a new model for pure Mn, including a magnetic model. Some new experimental information was also taken under consideration. A description for the metastable HCP phase
was also added. Lee and Lee [94] presented a new version of the Fe-Mn system. It was reassessed because of a conflict in selection of model for pure Mn with [96]. The metastable HCP phase was not included in this assessment. Witusiewicz et al. [98] made a new assessment of the Fe-Mn system based on new experimental results on the enthalpy of mixing for liquid Fe-Mn alloys and enthalpy of formation of solid FCC and BCC alloys. A new description of the magnetic contribution to the heat capacity was proposed but not implemented since the current Thermo-Calc version did not support it. Nakano and Jacques [99] evaluated the influence of Mn on the SFE using the thermodynamic description of the Fe-Mn system evaluated by Huang [97] with reevaluated Gibbs energy functions for the HCP phase. Djurovic et al. [50] also reassessed the parameters for the HCP phase to better fit experimental information on the $\epsilon$-martensite from Cotes et al. [100]. The remaining Gibbs energy functions were taken from the assessment by Huang [97] since the authors are of the opinion that the revision
of the HCP phase by Nakano and Jacques [99] resulted in unacceptable values for the Gibbs energy at high Mn compositions and a miscibility gap that has not been seen in experiments. Furthermore the extension of the Gibbs energies for the FCC and BCC phases to high Mn values seems more reasonable in the assessment by Huang [97] than in the more recent assessment by Witusiewicz et al. [98]. The phase diagrams produced with the different descriptions are shown in Fig. 2.10. The description by Huang [97] together with the parameters for the HCP phase by Djurovic et al. [50] has been used in this work.

Figure 2.9: Binary phase diagram for the C-Mn system.

Figure 2.10: Binary phase diagrams for the Fe-Mn system.
Ti-V

The experimental information on the Ti-V system available before 1993 has been reviewed by Okamoto [101]. His review was mainly based on information from Murray [102]. The system contains only terminal phases, HCP (Ti), BCC and liquid. A thermodynamic description of this system was published by Saunders in the COST 507 project [51] and has been used in this work.

2.2 Ternary systems

Al-C-Fe

The most extensive experimental studies of the Al-C-Fe system were performed by Palm and Inden [103] and Oden [104]. Using this experimental information Ohtani et al. [105] assessed the Al-C-Fe system with the aid of ab initio calculations. Connetable et al. [44] reassessed the system using a more complex model for the $\kappa$-phase. Recently Phan et al. [106] reassessed the system and performed new experiments. The experiments agreed well with the previous studies. This assessment used the simpler model for the $\kappa$-phase and was therefore disregarded in the present work. Instead the description by Connetable et al. [44] has been used in this work.

According to the experimental investigation by Palm et al. [103] the solubility of Carbon in BCC seemed to decrease with temperature. This seems unlikely and therefore we decided to investigate this more closely. Measuring carbon contents is very difficult. Since it is a light element composition measurements using e.g. Energy Dispersive X-ray Spectroscopy (EDS) can only be made in a qualitative manner. The more accurate Wavelength Dispersive Spectroscopy (WDS) can be used for quantitative measurements of light elements. However very good reference samples are needed to get accurate values. In this work another route was taken. Two samples were prepared with different carbon contents, one that would be in the BCC one phase region according to the experimental investigation by [103] and the other that would be in the BCC + $\kappa$ two phase region. The two samples were prepared by Arcelor Mittal with compositions 18 mass-% Al 0.05 mass-% C and 18 mass-% Al 0.1 mass-% C. The samples were heat treated at 1100 °C for 200 h in evacuated silica tubes and quenched in brine. After quenching the samples were ground and polished and etched in 4% nital for 1 min and investigated with Light Optical Microscopy (LOM). The microstructures are shown in Fig. 2.11.

As can be seen in Fig. 2.11 a second phase has precipitated. Examining this sample with X-Ray Diffraction (XRD) confirms that the second phase is the $\kappa$-phase. The shape of the $\kappa$-phase precipitates suggests that the phase might have formed during cooling and not during the heat treatment or that the sample had not reached equilibrium. Longer heat treatment is needed to clarify this.
Al-C-Mn

The phase equilibria in the Al-C-Mn system are not well determined. Most of the studies conducted for this system were focused on the magnetic metastable $\tau$-phase [107, 108, 109]. The Al-C-Mn system has only been assessed once in the literature by Chin et al. [110]. This assessment was based on the binary systems Gröbner [52] (Al-C), Jansson [60] (Al-Mn) and Huang [95] (C-Mn) and used a simplified model for the $\kappa$-phase. In the present work a new assessment has been performed of the Al-C-Mn system describing the $\kappa$-phase with the 5SL model. Details on this assessment can be found in paper IV.

Al-Fe-Mn

The Al-Fe-Mn system has been studied quite extensively in the literature and the phase equilibria are well determined, at least in the iron rich part of the system. The first thermodynamic assessment of this system was by Jansson [111], using the binary systems by Seiersten [55] (Al-Fe), Jansson [60] (Al-Mn) and Huang [97] (Fe-Mn). Liu et al. [112] re-assessed the Fe-rich part of the Al-Fe-Mn system including the FCC, BCC, $\beta$-Mn and liquid phases. The parameters for the binary systems were taken from Huang [97] (Fe-Mn), Jansson [60] (Al-Mn) and the parameters for Al-Fe were newly optimized. The magnetism was described using the model proposed by Nishisawa [113]. In 2006, Umino reassessed the Al-Fe-Mn system using a 2SL model for the BCC phase in order to be able to describe the second order phase transition into the ordered B2 compound. The assessment was based on the binary systems by Ohnuma et al. [114] (Al-Fe), Liu et al. [61] (Al-Mn) and Huang [97] (Fe-Mn). In the present work the Al-Fe-Mn system was reassessed. The binary systems used are the ones shown in table 2.1. The details of this assessment can be found in paper I.

In paper I the order-disorder transformation in the BCC phase is modeled using a 2SL model. This makes it possible to describe the transition into the
ordered B2 configuration. As reported by another ordered configuration of the BCC phase, D0₃ also appears in the Al-Fe-Mn system. In order to be able to describe the D0₃ ordering it is necessary to use a 4SL model. In paper II the evaluation of the parameters for a 4SL model for the ternary Al-Fe-Mn system is reported.

**Al-Ti-V**

As mentioned in the introduction precipitation hardening is one of the most promising ways to increase the yield strength of TWIP alloys. The precipitation is achieved by the addition of carbide and nitride formers to the alloys. The most common carbide and nitride formers are Nb, Ti and V. In order to fully understand this system properly, evaluations of the thermodynamics of all the lower order systems are necessary. It was found that no thermodynamic assessment of the Al-Ti-V system was available in the literature. The Al-Ti-V system is also important since it contains the most widely used titanium alloy Ti-6Al-4V.

Combining the previously available binary descriptions, Al-Ti (Witusiewicz et al. [47]), Al-V (Gong et al. [81]) and Ti-V (Saunders [79]), produces isothermal sections that deviate drastically from experimental data. Some of the sections together with experimental data from Ahmed and Flower [116] and Maeda [117] are shown in Fig. 2.12.

![Figure 2.12: Extrapolated isothermal sections using descriptions by (Al-Ti), (Al-V) and (Ti-V). Experimental phase boundary information is from Maeda [117] and Ahmed and Flower [116].](image-url)
The isothermal sections deviate quite drastically from experimental data at low temperatures. The main reason for the deviation is a miscibility gap in the BCC phase that originates from the Al-V system. Since no other sufficient description of the Al-V system existed it was reassessed in this work.

Combining the new description of the Al-V system with the binary descriptions by Witusiewicz et al. [98] (Al-Ti) and Saunders [51] (Ti-V) the extrapolations are greatly improved and agree well with the experimental data from Ahmed and Flower [116] and Maeda [117] without the addition of ternary parameters as can be seen in Fig. 2.13.

Figure 2.13: Extrapolations into ternary Al-Ti-V using assessment of Al-V derived in this work. The experimental points are from Ahmed and Flower [116] (○) and Maeda [117] (○).

C-Fe-Mn

The C-Fe-Mn system has been evaluated twice in the literature. The first assessment was made by Huang [118], who based her assessment on the binary descriptions by Gustafson [48] (C-Fe), Huang [95] (C-Mn) and Huang [97] (Fe-Mn). Within the PrecHiMn project Djurovic et al. [50] reassessed the C-Fe-Mn system based on the binary systems listed in table 2.1. This assessment used experimental data published after the assessment by Huang and using \textit{ab initio} calculations to determine the enthalpies of formation for the carbides at 0 K. The description by Djurovic et al. [50] has been used in this work.
Chapter 3

Applications of the database

The basis of all TWIP and L-IP steels is the quaternary Al-C-Fe-Mn system. In this work, the thermodynamic properties of this system have been studied. All the phases in this system are shown in Table 2.2.

The addition of Al to these steels can sometimes be problematic. With the wrong composition a hard and very brittle phase called $\kappa$ can form. It is very important to have accurate thermodynamic descriptions of this system in order to properly predict what compositions are safe to use without forming this $\kappa$-phase.

The $\kappa$-phase is a carbide that appears in ternary or higher order systems containing Al. It is a perovskite phase with Strukturbericht designation E2$_1$ and the formula M$_3$AlC, where M in this case would be Fe or Mn. The atomic structure of the $\kappa$ phase is seen in Fig. 3.1 and can be regarded as an ordered form of FCC with ordering on both the substitutional and the interstitial sublattices where the carbon atoms order on the octahedral sites.

Currently there are no models that can describe simultaneous ordering on both the substitutional and the interstitial lattices so the model proposed by Connetable et al. [44] has been adopted in this work.

\[(M_1, M_2)_{0.25}(M_1, M_2...)_{0.25}(M_1, M_2...)_{0.25}(C,Va)_{0.25}\] \hspace{1cm} (3.1)

In a previous description of the Al-C-Fe-Mn system by Chin et al. [110] the $\kappa$-phase was described using a much less advanced model

\[(Fe, Mn)_3(Al)_{1}(C, Va)_{1}\] \hspace{1cm} (3.2)

Although this is an important system, the phase equilibria have not been studied many times. The most extensive experimental study of this system was by Ishida et al. [120]. They investigated the Fe-rich part of this system at 20 and 30 mass-% Mn at 900, 1000, 1100 and 1200 °C. In Figs. 3.2 – 3.9 comparisons are made
Figure 3.1: cubic unit cell of the \( \kappa \)-phase figure produced using the VESTA program [119].

between the thermodynamic description of the Al-C-Fe-Mn system produced in this work and the experimental data from Ishida et al. [120] and the same comparison using the description from Chin et al. [110, 107].

The overall fit to the experimental data is good and exhibits a clear improvement compared to the previous description. The extension of the FCC phase region is somewhat underestimated, see e.g. Fig. 3.5. In e.g. Fig. 3.3 the \( \text{M}_2\text{C}_2 \)-carbide forms a three-phase region together with FCC and \( \kappa \). By suspending this phase the fit to the experimental data is improved further. It might be because the kinetics of the carbide are slow similarly to that of graphite or because the stability of the carbide is overestimated in the current description. Similar
Figure 3.3: Isothermal sections at 20 mass-% Mn, 1000 °C. Comparison between the description by Chin et al. [110] and current work. Experimental data is from Ishida et al. [120].

Figure 3.4: Isothermal sections at 20 mass-% Mn, 1100 °C. Comparison between the description by Chin et al. [110] and current work. Experimental data is from Ishida et al. [120].

Phase regions form in the description by Chin et al. [110] although they do not appear in the published isothermal sections, indicating that they hindered the carbide from appearing in their calculations.

The database for the Al-C-Fe-Mn system will be available for download together with paper IV.
3.1 Experimental investigation

As mentioned in the beginning of this chapter the phase equilibria in the quaternary Al-C-Fe-Mn system have previously been studied by Ishida et al. [120]. In the present work new samples were prepared by our project partners to confirm the results by Ishida et al. [120] and investigate the phase relations at higher Mn-contents. The sample compositions are shown in table 3.1. The samples
were heat treated at 900 and 1050 °C and then quenched in brine. Details on the experimental investigation can be found in paper IV.

After heat treatment the samples were all examined using Scanning Electron Microscopy (SEM) and in some samples, where it was necessary to clarify which phases were present, they were also examined using XRD. The phases present in the different samples at different temperatures are shown in table 3.2.

In Figs. 3.10 and 3.11 the experimental phase equilibria are compared to the
Figure 3.9: Isothermal sections at 30 mass-% Mn, 1200 °C. Comparison between
the description by Chin et al. [110] and current work. Experimental data is
from Ishida et al. [120].

Table 3.1: Composition of quaternary samples studied in this work, the amounts
are given in mass-%.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Al</th>
<th>C</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>TKSE1</td>
<td>1.5</td>
<td>0.3</td>
<td>78.2</td>
<td>20</td>
</tr>
<tr>
<td>T1</td>
<td>10</td>
<td>2</td>
<td>58</td>
<td>30</td>
</tr>
<tr>
<td>T6</td>
<td>10</td>
<td>1</td>
<td>49</td>
<td>40</td>
</tr>
<tr>
<td>T7</td>
<td>10</td>
<td>3</td>
<td>47</td>
<td>40</td>
</tr>
<tr>
<td>T8</td>
<td>5</td>
<td>3.5</td>
<td>51.5</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3.2: Comparison between calculations and experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature [°C]</th>
<th>Phases (experimental)</th>
<th>Phases (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TKSE1</td>
<td>900</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td>T1</td>
<td>900</td>
<td>FCC+κ</td>
<td>FCC+κ</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>FCC+κ</td>
<td>FCC+κ</td>
</tr>
<tr>
<td>T6</td>
<td>900</td>
<td>FCC</td>
<td>FCC+BCC</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>FCC</td>
<td>FCC+BCC</td>
</tr>
<tr>
<td>T7</td>
<td>1050</td>
<td>FCC+κ</td>
<td>FCC+κ</td>
</tr>
<tr>
<td>T8</td>
<td>1050</td>
<td>FCC+κ+carbide</td>
<td>FCC+κ+M5C2</td>
</tr>
</tbody>
</table>

thermodynamic description developed in this work as well as the description by
Chin et al. [110].

The current thermodynamic description provides an improvement also at
higher Mn-contents.
Figure 3.10: Isothermal sections at 10 mass-% Al including experimental data from this work. Comparison between description produced in current work and description by Chin et al \[110\].
Figure 3.11: Isoplethal sections at 40 mass-% Mn including experimental data from this work. Comparison between description produced in current work and description by Chin et al. [110]

(a) 900 °C this work
(b) 1050 °C this work
(c) 900 °C Chin et al. [110]
(d) 1050 °C Chin et al. [110]
Chapter 4

Conclusions and Future work

4.1 Conclusions

In this work, the thermodynamic properties of systems related to TWIP steels have been studied, specifically thermodynamic descriptions for the Al-C-Fe-Mn and Al-Ti-V systems have been developed. All the available subsystems have been critically evaluated and new thermodynamic descriptions have been developed when necessary. The FCC, BCC and $\kappa$ phases are described using models with 4 sublattices for the substitutional elements in order to be able to describe order-disorder transformations. The modeling of complicated ordered compounds such as the D0$_3$ compound is not merely of academic interest. Brittle compounds such as these can form from the BCC phase during production in industry which means that knowledge of the thermodynamics of ordered compounds is crucial for successful production of viable products. When modeling the ordering in BCC alloys it was found that assessing the formation energy of ordered compounds in binary systems, even the ones where the ordered compounds are metastable can greatly improve the extrapolations.

In the cases where no experimental information is available the use of DFT can greatly improve the thermodynamic descriptions. In this work, enthalpies of formation calculated using DFT have been used, not only when there is a lack of experimental data but also to confirm the available experimental data. When using data calculated using DFT or other ab initio methods it is important to realize that the reference states might be different.

Within this work some experimental investigations have been undertaken. Samples within the Al-C-Fe-Mn system have been heat treated to reach equilibrium, quenched and investigated mainly using microscopy. It has been found that it is problematic using elements with very different melting temperatures and the high vapor pressure of manganese may cause problems. It is crucial to let the samples properly reach equilibrium before characterizing their prop-
erties, otherwise the results can be misleading. Within the PrecHiMn project, a thermodynamic database including Al, C, Fe, Mn, Ti, V, Nb, N has been created.

4.2 Future work

In order to fully understand the thermodynamics of TWIP steels the twin formation needs to be studied further. Specifically, more attention needs to be given to the meta-stable HCP phases. Modeling the volume dependence would also be of great interest.

The Al-Ti-V system is quite well described without ternary parameters. The information on the BCC solvus can be fitted using ternary parameters. The solubility of vanadium in the AlTi (L1₀) and AlTi₃ (D0₁₉) is underestimated, especially in the AlTi phase. According to the experimental data, the AlTi phase should extend quite far toward the Al-V system. Using the current description, the AlTi phase is described as a separate phase instead of as an ordered form of FCC. Describing the AlTi phase separately causes a miscibility gap near the Ti side that prevents further solubility of vanadium. Fig. 4.1 shows the metastable AlTi phase diagram.

![Figure 4.1: Metastable AlTi (L1₀) phase diagram for the Al-Ti system.](image_url)

The Al-Ti system needs to be reassessed treating the AlTi phase as an ordered form of FCC in order to properly describe the ternary Al-Ti-V system.


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