Experimental and theoretical study of carbides in the Co-Cr-C system

Structure, alloying and stability

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Abstract

The research presented in this thesis explores the structure, alloying and stability of the carbides in the Co-Cr-C system by using the CALPHAD approach supported by experimental measurements and ab initio calculations.

WC-Co based cemented carbide materials consist of hard WC grains and a ductile Co-based binder. Cr is usually added to cemented carbides for the purpose of reducing grain growth during sintering or to increase corrosion resistance. The Co-Cr-C system is highly relevant for Cr-containing cemented carbides. For example, it determines the allowable C-content interval in the quaternary W-Co-Cr-C system with respect to the formation of unwanted Cr-based carbides.

The CALPHAD method is based on critical assessment of model parameters constituting phenomenological expressions of the Gibbs energy and its derivatives, e.g. enthalpy, entropy and heat capacity. A thermodynamic assessment based on the CALPHAD method relies heavily on the available experimental or ab initio calculated information.

The crystal structures of Cr$_{23}$C$_6$ and Cr$_3$C$_2$ have previously been accurately determined. However, various authors reported different crystal structures for the Cr$_7$C$_3$ carbide. A combined experimental and ab initio investigation of the crystal structure of Cr$_7$C$_3$ and M$_7$C$_3$ (M=Co,Cr) was thus performed. Furthermore, the stabilities of all end-member compounds of the mixed carbide at 0 K were determined by ab initio calculations.

Available experimental information on phase equilibria with carbides in the Co-Cr-C system was found to be insufficient to describe all the features in the phase diagram. Therefore, the liquid + M$_{23}$C$_6$ + M$_7$C$_3$ and M$_7$C$_3$ + M$_3$C$_2$ + graphite equilibria (M=Co,Cr) were investigated experimentally with focus on the solubility of Co in the M$_{23}$C$_6$, M$_7$C$_3$ and M$_3$C$_2$ carbides.

Finally, a reassessment of the thermodynamic description of the Co-Cr-C system was performed, which resulted in a set of thermodynamic models and parameters that accurately describe all of the considered information.

Applied experimental methods and theoretical models are explained throughout the thesis. Important examples from the appended papers are also given.
Preface

The research presented in this thesis is based on the following appended papers:

I. Bartek Kaplan, Andreas Markström, Andreas Blomqvist, Susanne Norgren and Malin Selleby
   *Thermodynamic analysis of the Co-Cr-C system.*
   Submitted to Calphad (Jan. 2014).
   My contribution: Data collection and analysis, thermodynamic assessment, writing the manuscript.

II. Bartek Kaplan, Andreas Markström, Susanne Norgren and Malin Selleby
    *Experimental determination of the solubility of Co in the Cr-based carbides Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$.*
    My contribution: Planning and performing the experiments, data collection and analysis, thermodynamic calculations, writing the manuscript.

III. Bartek Kaplan, Andreas Blomqvist, Cecilia Århammar, Malin Selleby and Susanne Norgren
    *Structural determination of (Cr,Co)$_7$C$_3$.*
    Proceedings of the 18th Plansee Seminar, Reutte, Austria, June 2013.
    My contribution: Planning and performing the experiments, data collection and analysis, thermodynamic calculations, writing the manuscript.

All *ab initio* calculations in Papers I and III were performed by Dr. Andreas Blomqvist from Sandvik Coromant R&D.
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Chapter 1

Introduction

WC-Co cemented carbides were originally invented in the 1920’s as a replacement for the expensive diamond drawing dies used in the production of tungsten wire [1]. Nowadays, they are used in various forms and in numerous other applications e.g. metal cutting (turning or milling), rock drilling, steel rolling, tire studs, ski pole tips and various wear parts.

The microstructure of a typical WC-Co cemented carbide consists of a large fraction of hard and brittle WC grains (>80 vol.%) embedded in a ductile Co-based binder. This two-phase structure combines the properties of both the WC grains and the binder creating a very hard material with sufficient toughness for e.g. metal cutting applications. Additionally, the large fraction of WC in the material and its high melting temperature makes production of cemented carbides via conventional metallurgy impractical. Therefore, powder metallurgical methods are applied instead, where WC and Co raw material powders are mixed, milled and compacted to a desired shape followed by liquid phase sintering through melting of the binder phase. Strict control of the carbon content, within a very narrow range, is very important to avoid the formation of other phases than WC and binder, i.e. graphite or M₆C/M₁₂C (M=Co,W), see Figure 1.1.

Many features in the final cemented carbide material are affected by the choice of raw materials, milling conditions and sintering temperature. One of the most important features in a cemented carbide material is the average grain size (and grain size distribution) of the WC phase, since it is closely related to the mechanical properties. A smaller average grain size leads to increased hardness and thus improved wear resistance. On the other hand, a larger average WC grain size increases the toughness of the material. The toughness can also be adjusted with the volume fraction of the binder phase, where a larger fraction gives a more ductile material.

Control of the average WC grain size is usually achieved by choice of raw material powders, milling time and alloying with grain growth inhibitors, where Cr is
Figure 1.1: Isoplethal section in the WC-Co system at 10wt.%Co calculated using the Thermo-Calc software package [2] and the description of Markström et al. [3].

a well-known grain growth inhibitor in cemented carbide production [4]. Adding Cr to the WC-Co system means that the degrees of freedom are increased and thus it is possible for more phases to form, other than binder and WC, depending on the carbon content.

In the study of Zackrisson et al. [5] it was shown that $M_7C_3$ ($M=Cr,Co,W$) was the first carbide to form when adding Cr in excess of the solubility in the binder phase in WC-Co base cemented carbides. Additionally, a large solubility of Co in $M_7C_3$ was determined, which motivated Markström et al. [6] to experimentally determine the maximum solubility of Co in $M_7C_3$ ($M=Cr,Co$), i.e. in the Co-Cr-C system. The main issues addressed in this thesis are the maximum solubility of Co in the remaining two stable carbides, $M_{23}C_6$ and $M_3C_2$, Paper II, and the crystal structure of $M_7C_3$ ($M=Cr,Co$), Paper III. Such information is very desirable in the field of computational thermodynamics, where by using the CALPHAD (CALculation of PHAse Diagrams) method [7] self-consistent thermodynamic databases are developed, e.g. for the Co-Cr-C system, as shown in Paper I.

The CALPHAD method is based on phenomenological models of the Gibbs energy. It is very important that all thermodynamic descriptions are consistent
with respect to their lower order systems and the models chosen for all phases. For example, a binary system A-B constitutes one of three binary systems in several ternaries A-B-C, A-B-D and A-B-E. If one of the ternary systems (A-B-C) was evaluated based on a different evaluation of one of the constituent binaries (e.g. A-B) it will be incompatible with the other ternaries and thus extrapolation into a quaternary system will be impossible. This is especially important for the unary evaluations since they form the foundation of any database, which is often illustrated with an inverted pyramid, see figure 1.2. Therefore, the critically evaluated and self-consistent set of thermodynamic parameters for the elements by Dinsdale [8] is most often the first choice for any thermodynamic assessment.

![Figure 1.2: Illustration of the dependency of thermodynamic descriptions based on the number of components.](image)

Thermodynamic parameters are usually evaluated by a least-squares fit to a chosen set of experimental and/or ab initio calculated data. Allotropes of the stable structure in unary systems from room temperature (occasionally from absolute zero) up to 6000 K are mainly evaluated based on heat capacities, enthalpies of formation and phase transformation temperatures. For the evaluation of binary, ternary or higher-order systems, data like activities, equilibrium tie-lines and invariant equilibria are important since they provide information on the composition of the equilibrium phases. Higher order systems, i.e. quaternary and higher, are rarely evaluated due to lack of reliable experimental information.

Once a consistent set of thermodynamic parameters of all unary, binary and ternary subsystems for a system of interest is available it is possible to calculate multicomponent equilibria by extrapolation. Accurate predictions obviously require that the lower order systems are well determined.
Chapter 2

Experimental techniques

2.1 Design of model alloys

All model alloys presented in this thesis were designed with the aid of thermodynamic calculations. The aim was to produce well defined samples, which would reveal important features of the phase relations in the Co-Cr-C system. Features of importance were determined to be the maximum solubility of Co in M\textsubscript{3}C\textsubscript{2} and M\textsubscript{23}C\textsubscript{6} and the crystal structure of M\textsubscript{7}C\textsubscript{3} (M=Cr,Co).

2.1.1 Maximum solubility of Co in Cr-carbides

As mentioned in the introduction the maximum solubility of Co in M\textsubscript{7}C\textsubscript{3} has already been studied at a number of temperatures by Markström et al. [6], by synthesizing samples in the liquid/fcc + M\textsubscript{7}C\textsubscript{3} + graphite three-phase equilibrium. Similarly, in Paper II, samples in the liquid + M\textsubscript{23}C\textsubscript{6} + M\textsubscript{7}C\textsubscript{3} and M\textsubscript{7}C\textsubscript{3} + M\textsubscript{3}C\textsubscript{2} + graphite three-phase equilibria respectively were prepared. These equilibria are illustrated in Figure 2.1. Once the bulk composition of a sample falls within a three-phase region, such as those mentioned above, the composition of the present equilibrium phases is fixed at that temperature as dictated by the Gibbs phase rule.

The liquid + M\textsubscript{7}C\textsubscript{3} + graphite three-phase equilibrium shown in Figure 2.1 is based on the experimentally determined solubility of Co in M\textsubscript{7}C\textsubscript{3}. Therefore, it can be concluded that the maximum solubility of Co in M\textsubscript{3}C\textsubscript{2} is much smaller since the extent of the M\textsubscript{7}C\textsubscript{3} + M\textsubscript{3}C\textsubscript{2} + graphite phase field is limited by the maximum solubility of Co in M\textsubscript{7}C\textsubscript{3}. This makes the choice of bulk composition of the alloy easy and the samples for studying the M\textsubscript{7}C\textsubscript{3} + M\textsubscript{3}C\textsubscript{2} + graphite equilibrium were thus designed to contain 40 at. % C, 10 at. % Co and 50 at. % Cr. Compacted samples were then heat treated at 1523 K and 1723 K for 300 h and 100 h respectively.
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In the case of the liquid + $\text{M}_{23}\text{C}_6 + \text{M}_7\text{C}_3$ equilibrium the possible solubility of Co in $\text{M}_{23}\text{C}_6$ is not as limited as for $\text{M}_3\text{C}_2$ in the $\text{M}_7\text{C}_3 + \text{M}_3\text{C}_2 + \text{graphite}$ equilibrium. However, the thermodynamic description of Markström et al. [6] could be used as a guide for designing the bulk alloy composition.

Figure 2.1: Isothermal section of the Co-Cr-C system at 1623 K, calculated using the Thermo-Calc software package [2] and the description of Markström et al. [6].

The calculated isothermal section shown in Figure 2.1 suggests that the solubility of Co in $\text{M}_{23}\text{C}_6$ is much lower than in $\text{M}_7\text{C}_3$. Therefore, a series of samples in the vicinity of the calculated three-phase region, at constant carbon content, were designed. After sintering at 1723 K for 10 h the microstructure was investigated on polished cross-sections of the samples and the number of present phases could then be determined. According to Figure 2.1 the possible outcomes would be the desired liquid + $\text{M}_{23}\text{C}_6 + \text{M}_7\text{C}_3$ equilibrium or either of the two $\text{M}_{23}\text{C}_6 + \text{M}_7\text{C}_3$ or liquid + $\text{M}_7\text{C}_3$ two-phase equilibria. Once the desired three-phase equilibrium was observed, two more samples with the same bulk composition were sintered at 1623 K and 1773 K respectively in order to determine the temperature dependence of the solubility.

2.1.2 The crystal structure of $\text{M}_7\text{C}_3$

The crystal structure of $\text{M}_7\text{C}_3$ ($\text{M}=\text{Cr,Co}$), and to a certain extent the site occupancies of Co and Cr, were investigated in Paper III by combining experimental and theoretical techniques. The idea for the experimental study was to synthesize
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a sample with a large fraction of carbide particles and with an appreciable amount of dissolved Co in $M_7C_3$.

Design of the bulk composition was relatively easy, since the extent of the liquid + $M_{23}C_6 + M_7C_3$ and the liquid + $M_7C_3 +$ graphite equilibrium phase fields were already known based on the results from Paper II and the work of Markström et al. [6] respectively. Thus, a sample, with its bulk composition in the liquid + $M_7C_3$ phase field and sintered at 1723 K for 10 h was selected.

2.2 Powder metallurgy

The primary experimental technique employed in the present work is very similar to the so-called "equilibrated alloy"-technique, where an alloy is created by arc melting of raw materials and subsequently heat treated for a long time to ensure equilibrium.

In the present work, powder metallurgical techniques were applied instead of arc melting. A typical powder metallurgical process consists of several steps, the most important being:

- Choice of raw material powders.
- Choice of additives, e.g. pressing aid or milling media.
- Mixing or milling of the powders to ensure homogeneity.
- Compaction of samples or components to a desired shape.
- Heat treatment (solid- or liquid-phase sintering).

Arc melting of the raw materials will cause them to react and form stable or metastable phases and structures upon cooling, which may be very difficult or even impossible to get rid of by equilibration at some lower temperature. Therefore, one of the main advantages in using powder metallurgy instead of arc melting is the possibility to react the raw materials at the desired temperature and thus avoid any frozen-in structures. Furthermore, volatile elements often cause a significant mass loss in the sample during arc melting making the bulk composition difficult to control. This problem is easily avoided by applying powder metallurgical methods.

2.2.1 Raw material powders

The choice of raw material powders is very important and several aspects must be considered before a choice can be made. Purity is the first and most important aspect for alloys where the equilibrium state is of interest. Usually, all raw
material powders contain a non-negligible content of oxygen due to the large surface/volume ratio, which facilitates oxidation. Fortunately, any oxygen is usually present as an outer oxide layer on the surfaces of the powder particles. These can be readily reduced during the heat treatment in a sample with a carefully weighed-in surplus of carbon. Other impurities may be present due to the synthesis route of the raw material powder and are thus inherent from the process itself. These can be very difficult to remove completely but it is usually not a problem to keep the impurity contents at acceptable levels in high-quality raw material powders.

Another important aspect is the initial state of the raw material. One must consider if the best choice is to add a pure element or if a compound is better suited. In Paper II it is explained that a large fraction of metallic particles considerably affects the possibility of obtaining a dense compact during compaction due to elastic recoil. A high density is desirable since it facilitates equilibration throughout the sample, particularly if the heat treatment is conducted in solid state. Therefore, in Paper II, Cr was added in the form of a carbide powder, $\text{Cr}_3\text{C}_2$ or $\text{Cr}_7\text{C}_3$, depending on the desired final equilibrium state.

### 2.2.2 Homogenization and compaction of the powder mixture

Eventually, when the choice of raw materials and desired bulk composition has been made, the powder is usually wet-milled in a conventional powder metallurgical process in order to homogenize the powder and reduce the particle size.

Wet-milling in its simplest form is conducted by adding the powder mixture together with milling bodies (hard cylindrical or spherical bodies), milling liquid and other additives, e.g. wax or PolyEthylene Glycol (PEG) as a pressing aid, into a cylindrical rotating drum. The milling liquid is usually based on some sort of alcohol, e.g. ethanol, and besides from protecting the powder from excessive oxidation during milling it also dissolves the pressing aid. After milling the powder is granulated by spray drying.

The use of milling bodies and pressing aid could introduce unwanted impurities. Unless the milling bodies themselves are very similar in composition to the investigated alloy, contamination is very likely. Furthermore, the addition of a pressed aid requires a more complex heat treatment with prolonged stages at different temperatures in order for it to be fully removed. Therefore, in the research presented in this thesis, milling was replaced by dry mixing of the raw material powders in a multi-axial shaker.

Compaction by single action pressing of small quantities of a homogenized powder mixture is usually straightforward and is simplified by adding PEG or wax. The pressing aid acts as a lubricant between the powder particles and between the powder and the die. The absence of such a pressing aid makes it more difficult to obtain a compact with an acceptable green density from an industrial
perspective, since more porosity will remain after sintering of a loosely packed compact. However, compaction to an acceptable density of a powder without pressing aid is in no way impossible if the equilibrium state of the alloy is more important than the resulting mechanical properties of the sintered body.

2.2.3 Heat treatment

The time for the reaction of the raw materials and the time needed to reach equilibrium in a powder metallurgical compact subjected to a heat treatment is shorter than for an as-cast alloy produced by arc melting, primarily due to shorter diffusion distances. Homogeneity can, to a large extent, be ensured already during the production of the powder and is facilitated by e.g. finer powder particle size and sufficient mixing or milling time.

Before any heat treatment is performed a suitable container for the sample must be selected. Reactions between the sample and the container can often prove to be disastrous and are therefore unwanted but can be impossible to avoid entirely. If a sample with an excess of carbon (for example in the form of graphite) is to be heat treated, a suitable container would be one made of graphite. Such was the case in Paper II, where the $M_7C_3 + M_3C_2 +$ graphite equilibrium was studied.

In the study of the liquid $+ M_{23}C_6 + M_7C_3$ equilibrium, also performed in Paper II, there was no graphite present at the desired equilibrium temperature and bulk alloy composition. In such cases, one should chose a container which is as inert as possible, usually made of a very stable oxide e.g. $\text{Al}_2\text{O}_3$. Although Cr forms a $\text{Cr}_2\text{O}_3$ oxide, which is isomorphous with alumina, the reaction is slow and the loss of Cr through this reaction in the samples described in Paper II negligible.

Atmospheric conditions in the furnace must also be considered. An inert atmosphere is desirable and can consist of either an inert gas, e.g. argon, or vacuum. Vacuum facilitates the reduction of impurity oxides but is not always feasible due to furnace limitations. All model alloys presented in this thesis were synthesized by powder metallurgical methods and heat treated either in vacuum or in a protective atmosphere of high-purity argon gas. The specific details concerning the synthesis of the different samples are given in Papers II and III respectively.

Finally, once the desired time at the desired equilibrium temperature has been reached the sample must be cooled down to ambient temperature. It is very important that the cooling is fast enough to not allow for any significant changes to occur in the sample e.g. phase transformations or change of composition in any of the constituent phases. This can sometimes be very difficult or impossible to achieve, for example in an equilibrium with liquid, as in Paper II, where the liquid inevitably will solidify. Liquids often dissolve much more of the alloying elements than the solid solution phases and thus precipitation upon cooling must be expected and accounted for during analysis of the sample.
2.3 Analysis of equilibrated samples

Equilibria are characterized by the number of phases, components (e.g. elements) and the external conditions as stated by the Gibbs phase rule. As mentioned in the introduction, information on the composition of the phases in equilibrium at a given temperature is of fundamental importance for modeling the thermodynamic properties. In order to make sure that the desired equilibrium has been reached the constituent phases in an equilibrated sample must be identified. This is usually done by inspecting the microstructure of the sample.

The microstructure of an alloy can be investigated in detail with several techniques. Direct imaging by light optical or electron microscopy can reveal the number of phases. Extensions of these techniques include compositional analysis of the phases constituting the microstructure, making it a very valuable tool for determining phase equilibria. If a phase cannot be identified via imaging of the microstructure or compositional analysis it is possible to use X-Ray Diffraction (XRD) in an attempt to identify the constituent phases in a sample by comparing the collected diffraction pattern to a database with well determined patterns.

2.3.1 Sample preparation and light optical microscopy

Before any analysis can be performed, a section (or cross-section) of a region of interest in a sample must be prepared by appropriate methods. Conventional grinding and polishing techniques most often yield acceptable results for imaging of the microstructure.

Light Optical Microscopy (LOM) is nowadays an often largely underestimated tool, which is readily available for almost every materials scientist. First and foremost, it is a very cheap piece of equipment, requiring very little technical skills and training (in comparison to other, more advanced instruments), which can in combination with appropriate etching reveal e.g. the constituent phases, see Figure 2.2 and the present state of a sample (porosity, incomplete reaction of raw materials etc.). It is therefore the obvious first step for investigating almost any metallic or ceramic sample.

2.3.2 Electron microscopy

As the name foretells, in Scanning Electron Microscopy (SEM) electrons are used instead of visible light to image the microstructure of a sample. This is done by scanning an electron beam over a designated surface of a sample and counting the number of electrons that reach the detector at every position of the beam. The number of electrons at each point are then translated to contrast values by a computer and a grayscale image is produced.
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Figure 2.2: Light optical micrograph of sample A3 from Paper II etched with the Murakami etching reagent. The constituent phases can be distinguished based on their color and were identified with WDS (section 2.3.3) and XRD (section 2.3.4).

When the electron beam interacts with a sample, the incoming electrons, apart from generating X-rays, are scattered in various ways allowing for different types of imaging to be performed by using different types of detectors. The two most commonly detected electrons are classified as Secondary Electrons (SE) and Back-Scattered Electrons (BSE). The SE signal is detected by applying a positive bias on a detector to collect electrons that were not directly back-scattered but exhibit a random path. This signal gives information about the topography of a sample and is useful for studying e.g. fracture surfaces or other microscopic features. On the other hand, the number of elastically back-scattered electrons depend on the average atomic number of the analyzed phase and thus an image containing information on the composition of the sample can be generated. Heavy elements produce more back-scattered electrons and thus regions enriched in heavier elements appear brighter. This is very helpful for distinguishing the constituent phases, see Figure 2.3.

A problem arises when two phases exhibit a very large difference in average atomic number, e.g. graphite and a metallic FCC solid solution of Cr and Co. Graphite is pure carbon with atomic number 6 while the FCC phase has an average atomic number close to 25. Graphite will thus appear black, which in turn makes it difficult to distinguish from pores. This is where LOM becomes a very valuable tool, where upon imaging the pores will be black and graphite will appear clearly as a dark gray phase, see Figure 2.4. Of course, the constituent phases can also be identified based on direct analysis of their composition.

Another advantage of SEM compared to LOM is the possibility to reach a
much higher magnification thanks to the much smaller wavelength of electrons compared to visible light. This particular advantage is not critical for determining phase equilibria because in order to obtain reliable information of the equilibrium phase composition the single phase regions (or grains/crystallites) must be large enough to rule out any surface energy effects.

Figure 2.3: BSE micrograph of the sample studied in Paper III. The constituent phases can be distinguished based on atomic number contrast and were identified with WDS (section 2.3.3) and XRD (section 2.3.4).

Figure 2.4: Light optical micrograph of sample B2 from Paper II, as polished. The graphite phase can be clearly distinguished from the pore.

The surface energy of a grain increases if the surface area to volume ratio increases, i.e. when a grain is small, which can affect the equilibrium composition of
the constituent phases [9]. Furthermore, the interaction between the electron beam and the sample takes place in a volume rather than directly at the surface [10], see Figure 2.5.

![Interaction Volume Diagram](image)

**Figure 2.5**: Schematic drawing of a typical interaction volume between the incident electron beam and the sample. The regions from which the different signals are emitted are indicated.

### 2.3.3 In-situ analysis of phase composition

Analysis of the composition of each phase in a sample is nowadays standard procedure for determining phase equilibria. This can be done by using appropriate modules connected to a SEM. Two distinct techniques for compositional analysis in SEM analysis are widely used: Energy- and Wavelength Dispersive X-Ray Spectroscopy (EDS and WDS respectively). Both techniques are based on the fact that the incoming electron beam excites electrons in the studied sample, which in turn produces X-rays, characteristic for each element, as the electrons fall back to their initial orbitals [10]. The main difference between the two techniques lies in the measured quantity of the characteristic X-ray photons. As the name implies,
in EDS analysis the energy and intensity of the incoming photons are measured while in WDS the wavelength and the intensity are the measured quantities. The energy, or wavelength, is characteristic for each element and thus reveals which elements are present while the intensity is a measure of the concentration. As already mentioned the produced X-rays originate from an interaction volume between the incident electron beam and the sample (Figure 2.5). Even though the size of the interaction volume varies, its diameter can rarely be smaller than 1 \( \mu m \). Since both EDS and WDS rely on the produced X-rays for analysis of the composition this effectively limits the minimum size a single phase region can have in order for the analysis to be reliable.

In general, EDS provides a much faster analysis than WDS while WDS is more accurate. The reason why EDS analysis is faster is due to the possibility for simultaneous detection of all elements. This is usually not feasible for WDS because the incoming X-rays must first be diffracted by a crystal, with a well determined crystal structure, so that only photons of the correct wavelength are detected. On the other hand, the peak resolution when using WDS is much better compared to EDS, see Figure 2.6, which explains the much better accuracy.

Figure 2.6: Part of the X-ray spectrum of Co collected using WDS (top) and EDS (bottom). Resolution is clearly improved when using WDS.
This makes EDS the first choice for e.g. qualitative determination of the composition or elemental mapping and WDS is thus most often used for quantitative analyses where accuracy is of importance. However, both methods can be used for quantitative analysis if proper standardization is performed. Standardization is important since it enables quantification of the measured intensity into a composition. This is done by relating the measured intensity of the sample to the standard and its already known composition, which is usually expressed as [10]:

\[
C_{\text{spl}}^i = \frac{I_{\text{spl}}^i}{I_{\text{std}}^i} \cdot C_{\text{std}}^i
\]

where \( C \) and \( I \) denote concentration and intensity, the superscript \( \text{spl} \) and \( \text{std} \) refer to the sample and standard respectively and the subscript \( i \) refers to the measured element. Furthermore, standardization must be performed for each phase using well defined samples. Ideally the composition of the phases in the standard samples should be similar to the phases in the analyzed samples. For example, in Paper II, WDS analysis of the solubility of Co in Cr carbides was performed. The standards used to measure the Cr and C contents were also Cr carbides but in their pure stoichiometric form, i.e. well defined C content and without any dissolved Co. Using a sample of pure Co for analyzing the Co content in the carbides was not ideal but necessary since there are no stable pure Co-carbides [11]. Also, Co was the minority element and thus the error of measurement for this element would only give a small contribution to the total error, compared to the Cr and C measurements.

Measured intensities must be corrected due to the so-called ZAF (Z = atomic number, A = absorption, F = fluorescence) effects. The factor \( Z \) depends on the average atomic number of the phase and the factor \( A \) on the mass absorption coefficient of the element. Fluorescence is a process where characteristic X-rays generated by one of the constituent elements in a phase have enough energy to excite electrons in another element and thus generate secondary X-rays. This secondary radiation can in some cases yield a non-negligible intensity which must be corrected for. The better the standard the closer the correction factor is to unity, i.e. a smaller correction is needed. In Paper III, the use of pure Co as a standard resulted in a total correction factor around 0.82-0.85 for the Co content while the use of a Cr carbide standard resulted in a total correction factor of almost exactly 1.0 for the Cr content, effectively demonstrating the importance of choosing a suitable standard.

In the research presented in this thesis, WDS was used for determining the composition of the equilibrium phases in all samples in Paper II. Elemental mapping with EDS was used to verify homogeneity of the single phase regions.
2.3.4 Phase identification and structure determination by X-ray diffraction

For quite some time the available techniques for analysis of equilibrated samples for the purpose of determining phase diagrams were limited to mainly XRD, LOM and a few other techniques [12]. Phase diagrams were determined by e.g. synthesizing a series of samples, with increasing content of one of the alloying elements. The number of phases could then be determined by LOM, combined with appropriate etching, and the phases could in turn be identified by XRD. Furthermore, phase boundaries could be determined quite accurately with the aid of XRD, i.e. by determining the lattice parameters of the phases. For example, in a binary system the lattice parameters of a phase in a single-phase region change continuously until a two-phase region is reached. In such a two-phase region, at constant temperature, the phase compositions are fixed and thus only the phase fractions change with composition along an equilibrium tie-line. This means that the lattice parameters of both phases are fixed in the two-phase region. Therefore, the lattice parameters of a phase, as a function of composition, can be extrapolated from the single-phase region to the lattice parameters of the same phase in the two-phase region (a horizontal line). The phase boundary can then be identified as the composition at which the two lines cross.

Nowadays, WDS and EDS techniques have replaced XRD as the primary analysis technique for determination of phase boundaries, often with improved accuracy. XRD is therefore mainly used for phase identification and occasionally determination of the crystal structure of newly discovered phases.

Identification of the phases in equilibrated alloys usually involves analysis of polycrystalline samples. XRD measurements are then often referred to as powder X-ray diffraction. In general, the method is based on irradiating a sample with X-rays and detecting the diffracted photons as a function of the angle between the incoming beam and the sample surface. Constructive and destructive interference will then produce a spectrum of peaks which can be compared to reference spectra of well determined phases. Constructive interference can only occur when Bragg’s law is satisfied [13], i.e. when the path difference between two parallel beams is an integral multiple of the wavelength according to:

\[ n\lambda = 2d \sin \theta \] (2.2)

where \( n \) is an integer, \( \lambda \) is the wavelength of the photons, \( d \) is the interplanar spacing and \( \theta \) is the Bragg angle. The position of the peaks then corresponds to the lattice parameters and the intensity of the diffracted X-rays is dependent on the element. The usefulness of this technique has led to the development of crystallographic databases containing a multitude of published structures and their
corresponding spectra [14, 15]. These can be used as reference patterns for phase identification. However, since these patterns are composition dependent, upon comparison between e.g. a pure Cr carbide, Cr$_7$C$_3$, and one with dissolved Co, M$_7$C$_3$, a shift between the peak positions for the two spectra will be observed, corresponding to the change in lattice parameter. This well-known fact was demonstrated in Paper III.

As mentioned previously, a collected XRD spectrum can also be used for the determination of the crystal structure of a phase. Rietveld refinement [13] of powder X-ray diffraction spectra was performed in Paper III to determine the structure of (Cr,Co)$_7$C$_3$. The method is based on least-squares minimization of the difference between measured and calculated intensities at each 2$\theta$ step given by:

\[ R = \sum_i w_i (Y_{io} - Y_{ic})^2 \]  

(2.3)

where $Y_{io}$ and $Y_{ic}$ are the observed and calculated intensities at each 2$\theta$ step respectively and $w_i$ is a weighting factor. Calculation of the intensity forms the foundation of Rietveld refinement and is based on unit cell size, atom positions, site occupancy factors, scale factors, background intensity and several profile parameters describing peak shapes and widths. Needless to say, structure refinement using the Rietveld method thus requires a fairly accurate initial guess of the crystal structure of the investigated material.
Chapter 3

Thermodynamic modeling

Most activities within the field of thermodynamic modeling (a.k.a. computational thermodynamics) today can be sorted into one of two groups; CALPHAD (CALculation of PHAse Diagrams) and \textit{ab initio} (or first principles). In this chapter, a brief introduction to both subjects is given, with focus on the CALPHAD method.

3.1 The CALPHAD method

As briefly mentioned in the introduction, the foundation of the CALPHAD method \cite{7} lies in phenomenological models of the Gibbs energy, where model parameters for all stable, metastable and unstable phases present in a system are evaluated with the aid of various pieces of experimental and theoretical information. The reason for modeling the Gibbs energy is because it is minimized for conditions reflecting constant temperature, pressure and composition \cite{9}, which are easily controlled during an experiment. Normally, the Gibbs energy for each phase and for each contribution is modeled separately, since the Gibbs energy is additive. The total molar Gibbs energy of a phase, $\theta$, is then expressed as:

$$G_m^{\theta} = srf G_m^{\theta} - T \cdot cnf S_m^{\theta} + mag G_m^{\theta} + E G_m^{\theta}$$

where $T$ is temperature and the terms represent:

- surface of reference, $srf G_m^{\theta}$
- configurational entropy, $cnf S_m^{\theta}$
- magnetic effects, $mag G_m^{\theta}$
- excess Gibbs energy, $E G_m^{\theta}$
The surface of reference contains contributions from all end-members, e.g. pure elements or compounds, and is usually described as a "mechanical mixture" of the components. If the surface of reference term were to be subtracted from eq. 3.1 the remaining quantity would represent the Gibbs energy of mixing, which thus consists of the configurational entropy and the excess Gibbs energy (assuming negligible magnetic effects). The configurational entropy represents ideal mixing of the components and is usually not sufficient to describe any but the simplest of cases. Therefore, an excess term, capable of describing the deviation from ideal behaviour, is most often necessary. The above is visualized in Figure 3.1. In the simplest case, the excess term describes the type of interaction, positive or negative, between two components. The components have a strong tendency for mixing if the interaction is negative. If it is positive, it is likely that a miscibility gap will be the result.

![Figure 3.1: Schematic drawing of the different contributions to the Gibbs energy as a function of composition for a hypothetical A-B system.](image)

Since only differences or changes of the Gibbs energy from one state to another are of interest, a reference state must always be selected (not to be confused with the surface of reference). Typically, the Standard Element Reference (SER) is the default reference state for any CALPHAD-type calculation, i.e. the enthalpy of the constituent elements in their stable states at 298.15 K and 1 bar. Entropy is defined as equal to zero at 0 K.
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3.1.1 Modeling of pure components

The Gibbs energy of pure components, i.e. elements or other end-member constituents or stoichiometric compounds, is usually modeled with a power series in temperature. Taking SER as the reference state the expression for the molar Gibbs energy becomes:

\[ \alpha G_{\text{end}}^\theta - \sum_i k_i H_i = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 \ldots \] (3.2)

where the subscript \( \text{end} \) denotes the stoichiometry (e.g. \( A_2B \)), \( \theta \) denotes the phase name, \( i \) denotes the element (e.g. A or B) and the coefficients \( a \) to \( f \) are the available parameters for fitting of experimental information. The coefficient \( k_i \) represents the fraction of atoms of species \( i \) per formula unit.

Equation 3.2 is differentiable and since the enthalpy \( (H) \), entropy \( (S) \) and heat capacity \( (c_p) \) are all derivatives of the Gibbs energy they can, at constant pressure and composition, be derived as (the superscript “\( \text{end} \)” is omitted for clarity):

\[ H_{\text{end}}^\theta = G_{\text{end}}^\theta - T \left( \frac{\partial G_{\text{end}}^\theta}{\partial T} \right) = a - cT - dT^2 + 2eT^{-1} - 2fT^3 \ldots \] (3.3)

\[ S_{\text{end}}^\theta = -\left( \frac{\partial G_{\text{end}}^\theta}{\partial T} \right) = -b - c(1 + \ln T) - 2dT + eT^{-2} - 3fT^2 \ldots \] (3.4)

\[ c_p^\theta = -T \left( \frac{\partial^2 G_{\text{end}}^\theta}{\partial T^2} \right) = -c - 2dT - 2eT^{-2} - 6fT^2 \ldots \] (3.5)

The number of parameters used to model the Gibbs energy according to eq. 3.2 is usually limited by the available experimental information. However, as seen from eqs. 3.3-3.5, at least \( a \), \( b \) and \( c \) need to be determined in order for these quantities to be defined.

A limitation of this kind of polynomial is its inability to describe the Gibbs energy below 298.15 K, due to the \( cT \ln T \) and \( T^{-n} \) terms of eq. 3.2 and its derivatives. As 0 K is approached, these terms approach \(-\infty\) and \( \infty \) respectively, which is completely artificial. This limitation is usually not critical for most alloy systems.

3.1.2 Modeling of magnetic effects

Magnetism and its effect on the Gibbs energy of a system cannot be ignored for most metals. For a pure component, at the ferro- to paramagnetic transition temperature, the heat capacity approaches infinity. This tendency must be adequately
described in order for the model to accurately reflect the thermodynamic properties of the system. Furthermore, the importance of magnetic effects was clearly demonstrated when CALPHAD-type models predicted magnetically induced miscibility gaps between ferro- and paramagnetic regions, the so-called Nishizawa horn, for alloy systems before any conclusive experimental evidence could be found [12]. Such a miscibility gap occurs in the Co-Cr system, an important subsystem to Co-Cr-C, and is shown in Figure 3.2.

Figure 3.2: Magnetically induced miscibility gap (Nishizawa horn) on the Co-rich side of the Co-Cr phase diagram. The dotted line is the Curie temperature of the FCC phase. Calculated using Thermo-Calc [2] and the thermodynamic description of Kusoffsky and Jansson [16].

The magnetic contribution is usually modeled according to the description of the magnetic effect on the heat capacity by Inden [17], which was later incorporated in a Gibbs energy expression by Hillert and Jarl [18]:

$$ mag C_m^w = nRT \ln (\beta + 1) f(\tau) $$  

where $n$ is the number of atoms per formula unit, $R$ is the ideal gas constant, $T$ is temperature and $\beta$ is the average magnetic moment. $\tau$ is a dimensionless temperature defined as $\tau = T/T_C$, where $T_C$ is the Curie temperature. The function $f(\tau)$ is divided into two intervals, i.e. for $\tau < 1$ and $\tau > 1$, in order to be able to account for the earlier mentioned effect of the magnetic transition on the heat capacity. The two intervals are described as:
\[ \tau < 1 : f(\tau) = 1 - \left( \frac{79\tau^{-1}}{140p} + \frac{474}{497}(p^{-1} - 1) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right) A^{-1} \quad (3.7) \]

\[ \tau > 1 : f(\tau) = \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) A^{-1} \quad (3.8) \]

where \( p \) depends on the crystal structure and \( A \) is:

\[ A = \left( \frac{518}{1125} \right) + \left( \frac{11692}{15975} \right) (p^{-1} - 1) \quad (3.9) \]

The composition dependence of \( T_C \) for a phase in e.g. a binary system is usually a linear combination according to:

\[ T_C = T_C^i x_i + T_C^j x_j \quad (3.10) \]

where \( T_C^i \) and \( T_C^j \) are the Curie temperatures of the pure components \( i \) and \( j \) respectively. If allowed by the quality and amount of experimental data, a polynomial, such as eq. 3.12, may be used to introduce a more complex composition dependence.

### 3.1.3 The substitutional solution model

Substitutional solution models are characterized by their wide use and simplicity. For example, most liquids are modeled as substitutional solutions if there is no tendency for e.g. short-range ordering, but it can also be applied to solid solutions.

The full model, for an arbitrary number of components, is written as:

\[ G_m^\theta = \sum_i x_i^0 G_i^\theta + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j I_{ij}^\theta + \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k I_{ijk}^\theta \quad (3.11) \]

where \( x_i \) denotes the mole fraction of component \( i \), the first term is the surface of reference, the second is the configurational entropy and the last two are the binary and ternary excess Gibbs energies respectively. \( I_{ij}^\theta \) represents the binary interaction between constituents \( i \) and \( j \). The reason for multiplying it with \( x_i x_j \) is to make sure that no excess energy persists at the end-points, i.e. where \( x_i = 1 \) and \( \sum_j x_j = 0 \) and similarly for the ternary interaction.

If \( I_{ij}^\theta \) and \( I_{ijk}^\theta \) are taken as constant values (negative or positive), the solution is said to be regular. The regular solution model can be extended to sub-regular, sub-sub-regular etc. by expressing the binary excess term to be a function of composition using a Redlich-Kister polynomial [19]:
\[ I_{i,j}^\theta = \sum_{v=0}^{n} v L_{i,j}^\theta (x_i - x_j)^v \]  

(3.12)

where parameters of even and uneven order are symmetric and asymmetric respectively.

For ternary interactions, the excess term is written:

\[ I_{i,j,k}^\theta = v_i L_{i,j,k}^\theta + v_j L_{i,j,k}^\theta + v_k L_{i,j,k}^\theta \]  

(3.13)

where \( v_i, v_j \) and \( v_k \) are normalized mole fractions, which facilitate extrapolations into multicomponent systems according to [20]:

\[ v_i = x_i + \frac{(1 - x_i - x_j - x_k)}{3} \]  

(3.14)

\[ v_j = x_j + \frac{(1 - x_i - x_j - x_k)}{3} \]  

(3.15)

\[ v_k = x_k + \frac{(1 - x_i - x_j - x_k)}{3} \]  

(3.16)

Each \( L \) (binary or ternary) can also be expressed as a temperature dependent quantity according to:

\[ v L_{i,j}^\theta = a + bT \]  

(3.17)

### 3.1.4 The compound energy formalism

The Compound Energy Formalism (CEF) [21] is used for solid solution phases or compounds, where preferential sites for certain constituents are important, e.g. carbon in carbides, or if other types of ordering are present, e.g. intermetallic phases. These types of phases require the introduction of the concept of sublattices and site fractions (instead of mole fractions).

For a phase with an arbitrary number of components and sublattices, the CEF is written:

\[ G_m = \sum y_i^s \prod n_i y_i^s \ln y_i^s + \Sigma n_i G_{\text{end}} + RT \sum n_i y_i^s \ln y_i^s + E G_m + \text{mag} G_m \]  

(3.18)

where \( y_i^s \) denotes the site fraction of component \( i \) on sublattice \( s \) and \( n_i \) is the stoichiometric coefficient of sublattice \( s \). The excess term is written:

\[ E G_m = \prod y_i^s \sum y_B^t I_{A,B:D:G...} + \prod y_i^s \sum y_B^t y_D^t I_{A,B:D,E:G...} + ... \]  

(3.19)
where commas and colons between constituents in the \( I \)-parameters separate constituents within a sublattice and in different sublattices respectively.

For clarity, modeling of a hypothetical non-magnetic compound described by the chemical formula \((A,B)_{a}(C,D)_{b}\), i.e. a reciprocal solution, using the CEF is presented below:

\[
G_m = \sum_i \sum_j \alpha G_{i,j} y'_i y''_j + RT \left( a \sum_i y'_i \ln y'_i + b \sum_j y''_j \ln y''_j \right) + E G_m \tag{3.20}
\]

where \( y'_i \) and \( y''_j \) denotes the site fraction of components \( i \) (A or B) and \( j \) (C or D) on the first and second sublattice respectively. Note the similarities with the substitutional solution model, eq. 3.11.

The excess Gibbs energy contains sublattice- and composition-specific terms and is in this case written as:

\[
E G_m = y'_A y'_B \sum_j y''_j I_{A,B,j} + y''_C y''_D \sum_i y'_i I_{i,C,D} + y'_A y'_B y''_C y''_D I_{A,B,C,D} \tag{3.21}
\]

where the last term is the reciprocal parameter, i.e. a term which simultaneously describes the interaction of A and B on the first sublattice and of C and D on the second sublattice.

Reciprocal solutions can be represented by a compositional square. The advantage of doing so is the possibility to visualize where in the system the interaction parameters are most effective. A zeroth order interaction parameter \( L \) will, due to its symmetric nature, have its largest contribution to the Gibbs energy when the site fractions of the mixing constituents are equal. From this, the compositional square in Figure 3.3 can be constructed.

![Figure 3.3: Compositional square for the reciprocal solution \((A,B)_{a}(C,D)_{b}\).](image)
Eq. 3.21 may of course be set as temperature dependent according to eq. 3.17 or extended by a Redlich-Kister polynomial, eq. 3.12, if a more complex composition dependence is required, or both.

CEF models, as described above with two or more sublattices, were used to describe the metallic solid solution phases and carbides exhibiting a solubility of the third element in Paper I for the Co-Cr-C system.

### 3.1.5 Recent developments in thermodynamic modeling

Continuous development of thermodynamic models has led to improved capabilities for describing certain phenomena. Chen and Sundman [22] presented a model capable of describing the Gibbs energy and its derivatives down to 0 K. Therefore, re-modeling of the unary descriptions, down to 0 K, is a currently ongoing activity within the CALPHAD community. Furthermore a more advanced and more physically sound model for treating magnetism and its effect on the Gibbs energy was recently presented by Xiong et al. [23].

### 3.2 Evaluation of metastable and unstable phases

Quite often, available information on a system or a particular phase of interest is quite sparse or contradictory, especially for the metastable or unstable end-members of compound phases. In such cases it may be possible to give values to certain parameters by approximation. A commonly used approximation is the well-known Kopp-Neumann rule, which states that the heat capacity of a compound can be approximated to be a sum of the fractional heat capacities of the constituent elements. From eq. 3.5 we see that knowledge on the heat capacity of an end-member compound allows the determination of all but two parameters in the Gibbs energy expression, \( a \) and \( b \) in eq. 3.2. The remaining two parameters can then be evaluated from experimental information on the solubility of the element in question in the stable end-member or by accounting for information from higher order systems. This method has been successfully applied by e.g. Gustafson [24] for determining the Gibbs energy of formation of the \( \text{M}_{20}\text{W}_{3}\text{C}_6 \) (M=Cr or Fe) end-member compounds.

#### 3.2.1 Ab initio calculations

Another way to determine the stability of a metastable or unstable phase is to apply quantum mechanical \textit{ab initio} calculations of the electronic structure of a selected compound with a fix crystal symmetry. The advantage of this method is that the only input required for a calculation is the crystal structure (symmetry and atomic
positions) and the atomic number of the constituent elements. Examples of this were given in Paper I, where the stabilities of stable and metastable end-member compositions of $M_{23}C_6$, $M_7C_3$ and $M_3C_2$ ($M=$Co or Cr) were calculated, and in Paper III, where the relative stabilities of two polymorphs of $M_7C_3$ ($M=$Co,Cr) were investigated.

The method used in the appended papers is based on Density Functional Theory (DFT) [25] coupled with statistical mechanics. With this method, the free energy (Gibbs or Helmholtz) of formation of a compound with fixed crystal symmetry and composition can be calculated as a function of temperature, within the Harmonic or Quasi Harmonic Approximation (HA and QHA respectively).

DFT calculations are based on solving the Schrödinger or Dirac equations numerically, where the interaction of electrons is treated by considering interaction between an electron and a fictitious electron density, thus transforming the many body problem to many one body problems. The calculations are most often performed within the Born-Oppenheimer approximation, which states that the motion of the nuclei can be neglected since the motion of the electrons is many orders of magnitude faster. Therefore, DFT is usually applied for 0 K ground state calculations and must be coupled with other techniques in order to be able to predict properties as a function of temperature. However, in many cases, phonon spectra can be calculated if the displacive forces on the atoms in the compounds are known. Thus, stabilities of compounds as a function of temperature can be calculated by statistical mechanics.

In Paper III the stable ground state structure of pure $Cr_7C_3$ was calculated to be the hexagonal polymorph, in accordance with earlier theoretical investigations. Despite this, most experimental investigations suggested that the carbide would be of orthorhombic symmetry. The resulting calculation of the relative hexagonal to orthorhombic stability as a function of temperature, using the above mentioned method, is shown in Figure 3.4. From this, it can be seen that the orthorhombic structure is stabilized with temperature with an approximate transition temperature of 500 K.

In general, the following computational steps are necessary for a successful calculation:

- Selection of a representative cell for the compound of interest.
- Calculation of the relaxed structure by DFT.
- Construction of a set supercells with appropriate displacements.
- Calculation of displacive forces on the atoms in each supercell.
- Calculation of phonon frequencies.
In this thesis, the calculation of relaxed structures and displacive forces at 0 K was performed with the Vienna Ab initio Simulation Package (VASP) [26]. Thermodynamic quantities as a function of temperature were then calculated with the Phonopy package [27]. Computational details are given in their respective papers.

![Figure 3.4: Calculated stability of the orthorhombic Cr$_7$C$_3$ relative to the hexagonal structure.](image)

3.3 Assessment procedure

Thermodynamic assessments are performed by determining appropriate values for all model parameters using numerical optimization routines taking into account all of the available experimental information. Reliability and compatibility issues of each piece of information must of course be resolved before an assessment can be performed. The next step is to choose suitable models for each phase based on their respective crystal (or amorphous) structures and preferential site occupancies, as described in sections 3.1.3-3.1.4 and Paper I.

Some commercially available software packages for thermodynamic calculations based on the CALPHAD [7] method, e.g. Thermo-Calc [2], also include a module for optimization of model parameters. The module used in this thesis, which is integrated in Thermo-Calc, is called PARROT [28] and is based on weighted least-squares minimization, similarly to eq. 2.3. Optimization of thermodynamic model parameters is an iterative procedure both from the numerical and the scientific point of view. For example, an assessor performs an optimization taking into account all the available information about the system in question.
CHAPTER 3. THERMODYNAMIC MODELING

Later, new experiments or theoretical calculations are performed, which disprove earlier findings or constitute entirely new datasets. Depending on the criticality of the newly uncovered information a system might have to be reassessed. Such was the case for the Co-Cr-C system, which to date has been assessed at least three times, first by Kusoffsky and Jansson [16], later by Markström et al. [6] and most recently in Paper I in this thesis.

Every assessment is to some extent unique and it is not possible to describe a fool-proof method for how it should be performed. However, there are some guidelines and "best-practice" remarks that should be followed. First of all, assuming that appropriate models are selected, the number of parameters must be considered. In PARROT, the difference between the number of experimental equilibria and the number of optimizable parameters simultaneously considered is always indicated and denoted as "Degrees of Freedom" (DoF). Optimization in PARROT is not possible if this value is negative since the risk of over-fitting would be imminent. However, over-fitting may still be an issue even if the DoF value is positive e.g. in the case of a symmetric miscibility gap. The presence of a miscibility gap indicates that the excess term should be positive. If the excess term is treated with a Redlich-Kister polynomial, eq. 3.12, only the symmetric interaction parameters, e.g. $^0L$ and sometimes $^2L$, are necessary. The Relative Standard Deviation (RSD) of any asymmetric interaction parameter, e.g. $^1L$, would thus be very high, indicating that the parameter lacks significance, and its resulting optimized value would be completely arbitrary.

An important point to emphasize when using theoretically calculated data, such as described in section 3.2.1, to determine the stability of end-member compounds is to always fit the calculated heat capacity to the appropriate parameters. If this is not done, e.g. by only considering the calculated Gibbs energy, the calculated heat capacity from the optimized expression will most probably yield a constant value, i.e. the low-temperature part of the heat capacity will not be reproduced. Many other pitfalls exist and the interested reader is referred to ref. [7].

Finally, after a successful optimization, the parameters should be rounded off according to their RSD. Otherwise, the final parameter values will give the impression of an accuracy well beyond what is actually true. A convenient method for rounding off parameters in PARROT is described in ref. [7].
Chapter 4

Summary of appended papers

4.1 Paper I

Thermodynamic analysis of the Co-Cr-C system
Authors: Bartek Kaplan, Andreas Markström, Andreas Blomqvist, Susanne Norgren and Malin Selleby

A reassessment of the thermodynamic description of the Co-Cr-C system was performed to take into account recent experimental information on the solubility of Co in Cr-based carbides. Density functional theory calculations coupled with phonon calculations were performed to calculate the heat capacity and Gibbs energies of formation of stable and metastable carbides in the Co-Cr-C system as a function of temperature, within the limits of the harmonic or the quasi harmonic approximation. Resulting Gibbs energies were compared with earlier experiments and assessments, where calculated values for Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_7$C$_2$ were seen to fall within the experimental scatter. The calculated heat capacity and Gibbs energy of formation as a function of temperature for the metastable Co$_3$C$_2$ compound was used in the evaluation of the thermodynamic parameters. As a result, the new and improved thermodynamic description accounts for the solubility of Co in M$_3$C$_2$ in contrast to previous descriptions, where this was neglected due to a complete lack of experimental information. Furthermore, a better representation of previously reported liquidus temperatures is achieved, without increasing the number of parameters in the liquid phase. Other relevant features of the phase diagram and thermochemical properties were also well represented.
4.2 Paper II

Experimental determination of the solubility of Co in the Cr-based carbides \( \text{Cr}_{23}C_6 \), \( \text{Cr}_7C_3 \) and \( \text{Cr}_5C_2 \)
Authors: Bartek Kaplan, Andreas Markström, Susanne Norgren and Malin Selleby

The ternary Co-Cr-C system is a very important subsystem to e.g. multicomponent cemented carbide grades, such as W-Co-Cr-M-C (M=Ti,Ta,Nb,V,Zr,Hf), as well as Cr-alloyed Co-base alloys. In the case of the Co-Cr-C system there is a lack of reliable data on the solubility of Co in Cr-carbides. Therefore, this paper concerns an experimental study of the solubility of Co in all three of the Cr-based carbides, i.e. \( \text{Cr}_{23}C_6 \), \( \text{Cr}_7C_3 \) and \( \text{Cr}_5C_2 \). This was done by synthesizing appropriate samples in the \( \text{M}_7C_3+\text{M}_{23}C_6+\text{liquid} \) and \( \text{M}_7C_3+\text{M}_3C_2+\text{graphite} \) three-phase fields. The results show that the most recent thermodynamic description of the Co-Cr-C system is unable to reproduce the experimentally determined solubilities. Therefore, the present study provides important input for future alloy development and improvement of the thermodynamic description of the Co-Cr-C system.

4.3 Paper III

Structural determination of \((\text{Cr},\text{Co})_7C_3\)
Authors: Bartek Kaplan, Andreas Blomqvist, Cecilia Århammar, Malin Selleby and Susanne Norgren

Chromium is one of the most well-known WC grain growth inhibitors in cemented carbides. It is thus important to understand and to be able to thermodynamically model the prevailing phase equilibria in the WC-Co-Cr system. To do this it is important that the lower order systems, such as the Co-Cr-C system, are correctly described. Previous investigations have shown that the \( \text{M}_7C_3 \) (M=Cr,Co,W) phase is the first carbide to form when Cr is added in excess to the WC + fcc-Co/liquid + graphite phase field. However, the exact structure of this phase has not been investigated and there are many proposed structures already for the binary \( \text{Cr}_7C_3 \) carbide, ranging from trigonal, via hexagonal to orthorhombic symmetry. Recent investigations show that the hexagonal structure belonging to the \( \text{P6}_3\text{mc} \) space group is the stable structure at 0 K. In the present study the binary \( \text{Cr}_7C_3 \) carbide and a mixed \( \text{M}_7C_3 \) carbide are investigated. The structures of both carbides and preferential positions for Co atoms in the mixed carbide are investigated by XRD measurements in combination with ab initio calculations and Rietveld refinement.
Chapter 5

Concluding remarks

The purpose of the research presented in this thesis has been to improve the thermodynamic description of the Co-Cr-C system by performing experimental and theoretical investigations of certain features of the system and a subsequent thermodynamic assessment. Although this objective has been reached there still remain important issues that need to be dealt with in order to further improve the thermodynamic description.

First and foremost the stabilities of the Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$ end-member compounds, which were investigated by DFT-QHA calculations in Paper I, need to be revised based on careful experimentation and possibly more exact calculations. This is mostly due to the large scatter in reported experimentally determined Gibbs energies of formation, which has made accurate assessment of their stabilities difficult.

Many phase equilibria in the Co-Cr-C system at temperatures above 1373 K have up to now been determined experimentally, Paper II being the latest addition. However, such information at temperatures lower than 1373 K is severely lacking. The only available information at these temperatures was presented by Köster and Sperner [29] and was obtained from samples with very high impurity contents and suspicion of frozen-in equilibria from higher temperatures. This imposes a limit on the reliability of thermodynamic calculations in this system and in multicomponent extrapolations, if they are performed below this temperature. In the case of cemented carbides, this limitation is not critical due to the high temperatures required during production and processing of these materials. However, the Co-Cr-C system is an important subsystem to many other material classes, e.g. Co-base superalloys and Co-Cr medical alloys, where changes in the microstructure upon aging at temperatures below 1373 K are potentially critical.

Accurate knowledge on site occupancies of Co in M$_{23}$C$_6$, M$_7$C$_3$ and M$_3$C$_2$ (M=Co,Cr) is also of interest, since it would enable the selection of more realistic thermodynamic models. The main difficulty lies in the poor X-ray diffraction
contrast between Cr and Co, a problem which was encountered in Paper III. One possible way of resolving this problem is to study the carbides with neutron diffraction, where the contrast is good enough to allow for refinement of site occupancies using the Rietveld method. However, such measurements inevitably have to be performed with very expensive and scarce equipment.

As a final remark, it should be mentioned that most thermodynamic databases only contain critically assessed model parameters for unary, binary and ternary subsystems. Extrapolations to higher order systems must therefore be verified by careful experimental work. Unfortunately, this type of work is seldom performed.
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