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THERMO-CALC & DICTRA, Computational Tools For Materials Science

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Abstract. Software for calculation of phase diagrams and thermodynamic properties have been developed since the 1970's. Software and computers have now developed to a level where such calculations can be used as tools for material and process development. In the present paper some of the latest software developments at Thermo-Calc Software are presented together with application examples. It is shown how advanced thermodynamic calculations have become more accessible since:

- A more user-friendly windows version of Thermo-Calc, TCW, has been developed.
- There is an increasing amount of thermodynamic databases for different materials available.
- Thermo-Calc can be accessed from user-written software through several different programming interfaces are available which enables access to the thermodynamic software from a user-written software. Accurate data for thermodynamic properties and phase equilibria can then easily be incorporated into software written in e.g. C++, Matlab and FORTRAN.

Thermo-Calc Software also produces DICTRA, a software for simulation of diffusion controlled phase transformations. Using DICTRA it is possible to simulate processes such as homogenization, carburising, microsegregation and coarsening in multicomponent alloys. The different models in the DICTRA software are briefly presented in the present paper together with some application examples. © 2002 Elsevier Science Ltd. All rights reserved.

1.1. Introduction

Thermodynamic calculation and kinetic simulation have become important approaches in understanding material properties and processes. This paper describe some of the software developed to solve different problems in primary processes such as melting, alloying, refining, casting, solidification, sintering, reheating and in other more product oriented areas such as heat treatment, annealing, surface treatments, sintering, corrosion as well as in the case of environmental issues and give a few examples of such solutions.

The first section of the paper describes the development and facilities available in Thermo-Calc in its original form. The following part describes the new Thermo-Calc Windows (TCW) version. The simplicity to use TCW is illustrated by a detailed step-by-step example, where each part of user action regarding database handling, setting conditions and result presentation is covered. There is also comparison between the capabilities of the current versions of the two incarnations of Thermo-Calc. At the end of this section the Scheil-Gulliver simulation in TCW is presented by an example from the Al-Mg-Si system.

The following section of the paper moves into non-equilibrium calculations by the use of the DICTRA program for diffusion controlled phase transformations. An outline of the inner workings of the DICTRA is presented covering diffusion coefficients, diffusional flux in single phase regions as well as the five available transformation modes: Moving Phase Boundary, Dispersed System, Coarsening, Cell and Cooperative Growth model. A number of applications of DICTRA to real world problems is referenced and partly explained in more detail.

Finally, the possibilities of using Thermo-Calc programming interface will be presented; first an example using the TQ-interface giving commented pseudo code for a T_0 -temperature calculation. Secondly, results from an application using the MATLAB toolbox for thermodynamic calculations implemented by the TC-API C-language interface is presented.

1.1.1 General

Thermo-Calc is a powerful and flexible software and database package for all kinds of phase equilibrium, phase diagram and phase transformation calculations and thermodynamic assessments; with its application-oriented interface, many types of process simulations can also be performed. It has been developed for complex heterogeneous interaction systems with strongly non-ideal solution phases [1,2] and can be applied to any thermodynamic system in the fields of chemistry, metallurgy, material science, alloy development, geochemistry, semiconductors etc. depending on the kind of database it is connected to. It is based on the work of Mats Hillert [3] and makes use of a very general algorithm to find the equilibrium state of a system. The implementation of these ideas was made by Bo Jansson and is described in his thesis [4]. This technique allows much more flexibility for the user setting the external conditions for his equilibrium state than any other thermodynamic software. Thermo-Calc is for example the only software that allows explicit conditions on individual phase compositions or configuration whereas most software can handle conditions on the overall composition only. For example, activities and chemical potentials of the components, volumes, enthalpies, entropies etc can also be set as conditions. Many quantities that must be calculated by so called "target calculations", i.e. a double minimization procedure, with other software can be calculated directly and much faster with Thermo-Calc. The flexible way to set conditions is particularly useful when Thermo-Calc is used as a subroutine package in application programs, for example in microstructure evolution or process simulations. For diagram calculations the facility that each condition is set separately and that any condition can be used as axis variable means that Thermo-Calc can calculate innumerable types of diagrams. Thermo-Calc was designed originally for multi-component systems and all its facilities are available for systems with up to 40 components.

The first version of Thermo-Calc was released in 1981. There has been an update almost every year and the most recent, version P, will be publicly available in 2002. The first description of Thermo-Calc was published 1985 [1] and later [5]. The most recent description and documentation are available in the manuals available at www.thermocalc.se.

1.1.2 Software Versions

Today, Thermo-Calc is available in two versions, Thermo-Calc Classic that is the most powerful version and provides the expert user almost any possible combination of condition and stepping/mapping options. The "simple-to-use" Windows 95/98/Me/NT/2000 version TCW provides almost the same facilities to material science and process engineers and occasional users with less interest to learn the details of the software. An exhaustive description of TCW will be given on the following pages.

1.2. Modularity of Thermo-Calc Classic

Thermo-Calc consists of several modules for specific purposes and the various tasks the user may be interested to perform. The TDB module is used for retrieving databases or data files. The GES module is used for listing system information and thermodynamic/kinetic data, or interactively manipulating and entering such data. The POLY module can calculate various complex heterogeneous equilibria, and its post processor, the POST module, make it possible to plot many kinds of phase diagrams and property diagrams. The PARROT module provides a useful and flexible tool for data evaluation and assessment of experimental data. The TAB module tabulates various properties for pure substances or mixtures or chemical reactions.

Some special easy-to-use modules are also available within Thermo-Calc, which just require rather simple responses to some questions for performing certain types of calculation or simulation. The BIN and TERN modules are designed to plot phase diagrams and property diagrams for various binary and ternary systems respectively. Figure 1 and 2 demonstrates examples for a binary system (Fe-C) and a ternary system (Al-Fe-Mn), respectively.

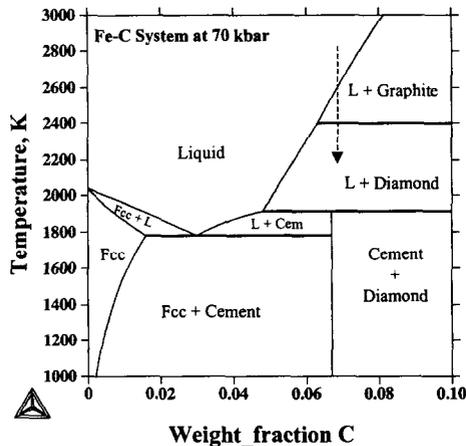


Figure 1

Figure 1 shows that at a pressure of 70 kbar Fe could be used as a catalyst for the production of diamond from graphite in the temperature range from 1900 to 2400 K [6].

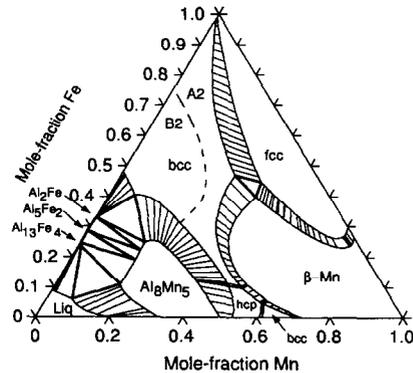


Figure 2

Figure 2 shows stability fields of various phases at 1273 K, which are calculated using carefully assessed thermodynamic data in the Al-Fe-Mn alloy systems [7]. For instance, the Al_2Fe phase has a very small solubility of Mn; the ordering of the bcc phase changes the position of the phase boundary (between disordered A2 and ordered B2) to Al_2Fe and Al_8Mn_5 with 1-2 atomic percent.

The POT module is used to illustrate gas speciation and partial pressures in gas-bearing interaction systems. The POURBAIX module is used to plot pH-Eh and other aqueous property diagrams for heterogeneous interactions involving complex aqueous solutions. The SCHEIL module is designed to simulate solidification processes where no kinetic description is needed, using the Scheil-Gulliver model. The REACTOR module is used to simulate mass transfer and energy transport in multi-staged steady-state processes.

Thermo-Calc employs many comprehensive thermodynamic models for various materials and interfaces with a wide spectrum of assessed and validated databases for specific material systems. The user may build on this collected knowledge to develop and add his own modules by utilising this programming interface called TQ Interface, which has been developed [8] and found very useful for application-oriented property calculations and process simulations.

Thermo-Calc forms the basis for some other thermodynamic/kinetic software systems. The DICTRA program [9,10], described later on, is specially designed for simulating various diffusion-controlled phase transformation processes occurred in some materials under high temperatures.

1.2.1 Thermo-Calc Classic User Interface

All the modules are interactive and except the very simplest modules the user has a menu of commands to select from. A command is usually a whole sentence and that makes it understandable. When a module requires input from the user it will write a prompt. In order to minimize the typing required by the user all commands can be abbreviated. In most cases a command needs some additional information in order to be executed and the user is then asked questions. In most cases the program will suggest a default value, which is taken as answer if the user just presses the RETURN key. An experienced user who knows what questions the command will ask can type the answers after the command on the same line. It is also possible to create macro files with frequently used command sequences.

All modules have a user's guide in the documentation set and these manuals can also be obtain as on-line help by use of the "help" and "information" commands or by giving a question mark as answer to a question the user does not understand.

```

ThermoCalc
Thermo-Calc version N on WinNT
Copyright (1993,2000) Foundation for Computational Thermodynamics,
Stockholm, Sweden
Double precision version linked at Fri Aug 24 11:31:57
For use at: TCAB
By only: TCAB Staff

SYS:go poly

POLY version 3.30, Feb 1996
POLY_3:?
ADD_INITIAL_EQUILIBRIUM  HELP
AMEND_STORED_EQUILIBRIA  INFORMATION
BACK                     LIST_AXIS_VARIABLE
CHANGE_STATUS            LIST_CONDITIONS
COMPUTE_EQUILIBRIUM      LIST_EQUILIBRIUM
COMPUTE_TRANSITION        LIST_INITIAL_EQUILIBRIA
CREATE_NEW_EQUILIBRIUM    LIST_STATUS
DEFINE_COMPONENTS         LIST_SYMBOLS
DEFINE_DIAGRAM            LOAD_INITIAL_EQUILIBRIUM
DEFINE_MATERIAL           MACRO_FILE_OPEN
DELETE_INITIAL_EQUILIB    MAP
DELETE_SYMBOL            POST
ENTER_SYMBOL              READ_WORKSPACES
EVALUATE_FUNCTIONS        RECOVER_START_VALUES
EXIT                      REINITIATE_MODULE
GOTO_MODULE               SAVE_WORKSPACES
POLY_3:                   SELECT_EQUILIBRIUM
                           SET_ALL_START_VALUES
                           SET_AXIS_VARIABLE
                           SET_CONDITION
                           SET_INPUT_AMOUNTS
                           SET_INTERACTIVE
                           SET_NUMERICAL_LIMITS
                           SET_REFERENCE_STATE
                           SET_START_CONSTITUTION
                           SET_START_VALUE
                           SHOW_VALUE
                           SPECIAL_OPTIONS
                           STEP_WITH_OPTIONS
                           TABULATE

```

1.2.2 Equilibrium calculations

The current version of the equilibrium module is POLY developed by Bo Jansson [2]. It has a very powerful and general set of commands to specify almost any kind of equilibrium or phase diagram calculation. Each condition necessary for the calculation is set separately and examples of conditions are:

- Value of the temperature, pressure, enthalpy, volume or entropy etc.
- Activities or chemical potentials of components
- Overall composition in total number of moles or mass or in mole or mass fractions
- Specifying some or all stable phases
- Some compositions or constitution of a phase
- General functions of state variables, e.g. the congruent melting point of Pyrrhotite in the binary Fe-S system can be calculated directly by giving $X(\text{Liquid,S})-X(\text{Pyrrhotite,S})=0$ as one of the conditions.

By combining various types of conditions the user can directly calculate many types of equilibria that he would find by trial and error only by using other software for equilibrium calculations. This means that the user may calculate directly how the "input" to a process should be by setting desired "output" as conditions. It is a unique feature in POLY, not available in most other software for thermodynamic calculations, that conditions on individual phases like the composition of a phase or its enthalpy can be set.

In POLY the user also can define functions of state variables and use these as conditions or for plotting the final results. The user is thus not limited to a set of predefined diagrams but can combine conditions as he wishes for generating a diagram. Below is a non-exhausting list of possible types of calculations available to users of Thermo-Calc:

- Phase diagrams (binary, ternary, isothermal, isoplethal etc, up to 5 independent axis variables)
- Thermodynamic properties of substances, compounds and solution phases
- Thermodynamic properties of chemical reactions
- Property diagrams (Fraction of phases, Gibbs Energy, Enthalpy, Cp, etc.)
- Pourbaix diagrams and other diagrams for aqueous-involving interaction systems
- Partial pressures of gases, chemical potentials of volatile species (up to 1000 species)
- Scheil-Gulliver solidification simulations
- Liquidus surfaces for multicomponent alloys
- Thermodynamic factors, driving forces for nucleation
- Metastable equilibria, para-equilibria
- Transport properties of aqueous solutions
- Special quantities: *e.g.*, T_0 , A_3 -temperature, adiabatic flame temperatures, chill factors, slopes of liquidus/solidus and phase boundaries etc.
- Oxide-layer formation of steel surface, steel/alloy refining
- Evolution of hydrothermal, metamorphic, volcanic, sedimentary, weathering processes
- Speciation in corrosion, recycling, remelting, sintering, incineration, combustion
- CVD diagrams, thin-film formation
- Chemical ordering-disordering, CVM calculations
- Magnetic properties of alloys
- Thermodynamics of steady-state reactors
- Establishment and modification of datasets or databases
- Simulation of Carnot cycles, Boyles law and other teaching facilities
- "Anything you can think of which represents an equilibrium ..."

1.2.3 Diagrams and graphics

Any conditions in POLY can be used as axis variable and one may step in the axis variable and calculate how any other quantity depends on the axis variable. After the STEP command the user may select any state variable to be plotted as dependent quantity. An example of this in a multi-component system is how the amounts or compositions of the stable phases vary with temperature. Another example is how the activity of a component varies with the composition.

One may also set two or more (max 5) conditions as axis variables and the program will then calculate phase diagrams. Due to the generality of Thermo-Calc all types of phase diagrams can be calculated in almost the same way. With Thermo-Calc one may calculate many types of diagrams that no one has thought of before.

In POLY there is a postprocessor, which allows the user to select the axis variables to be used in the plot. They may be different from those used in the calculation and the user may define functions to be plotted on the axis and scaling and size can be set interactively.

1.2.4 Models, Databases and Assessment

Successful applications of a thermochemistry software result from powerful calculation methods, but also comprehensive thermodynamic/kinetic models, internally consistent databases and effective assessment performance.

In the Gibbs Energy System (GES module) the thermodynamic data needed for the calculations are stored. Normally these data have been retrieved from a database but the user can interactively list or amend the data. A large number of models for the composition dependence of the Gibbs energy have been implemented in GES and the most important ones are:

- The regular solution model with binary Redlich-Kister parameters and composition dependent ternary parameters according to Hillert [11]
- The compound energy formalism with up to 10 sublattices and Redlich-Kister and composition dependent ternary interaction parameters on all sublattices [12,13]
- Molecules, associates and ions can be constituents in any sublattice
- The two-sublattice ionic liquid model [14]
- The associate model [15]
- The Kapoor-Frohberg-Gaye cell model for liquid oxides [16]
- The modified dilute solution model [17]
- The CVM tetrahedron model for binaries [18,19]
- SIT (Specific Interaction Theory) model for aqueous solutions
- The Inden model for magnetic ordering [20]
- The Pitzer model for aqueous solutions including the Debye-Huckel term.
- Revised Helgeson-Kirkham-Flowers model.
- Chemical ordering using an extended Bragg-Williams model formalism

Many of the models listed above are actually special cases of the generalized compound energy formalism [21]. A review of most of the models implemented in Thermo-Calc can be found in [2]. All parameters in the models can be temperature and pressure dependent.

There is a wide spectrum of thermodynamic databases connected with the TDB module, for example

General Databases with data for compounds and solutions

- SSUB SGTE Substances database. Data for 4000 condensed compounds or gaseous species.
- SSOL SGTE Solutions database. A general database with data for many different systems.
- BIN SGTE Binary Alloy Solutions database.

Databases for alloys

- TC-FE2000 TC Steels/Alloys database, updated in 1999. Covers the iron rich corner within the Al-B-C-Co-Cr-Cu-Fe-Mg-Mn-Mo-N-Nb-Ni-O-P-S-Si-Ti-V-W system.
- TC-NI TCAB Ni-based superalloys database. Contains 7 elements: Al Co Cr Ni Ti W Re
- TT-Al Al-based alloys database. 15 elements: Al B C Cr Cu Fe Mg Mn Ni Si Sr Ti V Zn Zr
- TT-Ti Ti-based alloys database. 17 elements: Ti Al Cr Cu Fe Mo Nb Ni Si Sn Ta V Zr C O N B
- TT-Mg Mg-based alloys database. Contains 9 elements: Mg Al Cu Ce La Mn Si Zn Zr
- TT-Ni Ni-based superalloys. 16 elements: Ni Al Co Cr Fe Hf Mo Nb Re Ta Ti W Zr B C N

Databases for slags, molten salts and ionic systems

- SLAG IRSID Fe-containing slags database. Liquid slag and condensed oxides for the $\text{Al}_2\text{O}_3\text{-CaO-FeO-Fe}_2\text{O}_3\text{-MgO-SiO}_2$ system including data for Na, Cr, Ni, P and S
- ION TC Ionic database for some oxides, sulfides and nitrides.
- SALT SGTE Molten salts database.

Databases for environmental aspects (toxic species metallurgical and chemical processes)

- TC-ER TCAB Recycling/Remelting database. 30 elements Gas, Liquid, Solid and Slag phase
- TC-ES TCAB Sintering/Incineration/Combustion database. As TC-ER

Databases for aqueous solutions

- TC-AQ TC Aqueous solution database (using SIT & PITZ models). To combine with SSUB, SSOL, TC-FE2000, SLAG, ION, TC-NI, TC-ER1/ER2, TT-Al/Ti/Ni, and GEOCHEM
- AQS UU Aqueous solution database (using HKF model). As TC-AQ

Databases for nuclear materials

- NUCLMAT AEA Pure radionuclides database (596 species, version 2).
- NUCLOX AEA Nuclear oxide solutions database (version 4).
- AGCDIN AEA Ag-Cd-In solutions database.
- SIUZRO AEA Si-U-Zr-O metal-metaloxide solutions database.

Databases for geochemistry

- GEOCHEM UU Geochemical/environmental database. 500 minerals and 46 elements.

Databases for semiconductors

- G35 ISC Group III-V Binary semiconductors database. 15 binary systems.

Many more databases are available for special purposes, please contact info@thermocalc.se for details

The further development of thermodynamic/kinetic models and databases is required for many application fields of materials science and engineering. Thermo-Calc provides a powerful tool for such purposes, i.e., the PARROT module can be used to perform assessment of experimental data on thermochemistry, phase diagram, and kinetic processes, and evaluation of parameters for thermodynamic/kinetic models and databases.

1.2.5 Future of Thermo-Calc Classic

The new version of Thermo-Calc Classic P will contain some improvements in the area of equilibrium calculations but also extends into non-equilibrium calculations.

In some cases it is of interest to find the composition where two phases have the same Gibbs energy rather than the same chemical potential of the components. Such point is often referred to as a T_0 point. If one axis is selected as stepping axis the T_0 -line and can now be mapped directly by the new version of Thermo-Calc.

Another non-equilibrium state that the new version can calculate is the so-called para equilibrium transformation. If one component in an alloy can diffuse much faster than the others it is possible to have a partly partitionless transformation where a new phase can form with different content of the mobile component but without with the same composition of the slow diffusing components. Such para-equilibrium points and lines can now be directly calculated in Thermo-Calc.

Equilibrium calculations in complex multi-component system can in some cases have difficulties to find a stable minimum in the Gibbs energy for the system under the given conditions. These problems can often be

caused by the existence of miscibility gaps in the Gibbs energy description of one or several phases under consideration. The new version of POLY has a check for internal phase stability implemented to improve the situation in such cases. This check will detect and give a warning if the equilibrium calculation is inside a spinodal region of a miscibility gap. In the next release of Thermo-Calc the POLY program will automatically correct the composition of the phases to avoid such regions of instability.

Other minor improvements are:

- Enhanced mapping algorithm to speed up calculations and ensure that all equilibrium lines are mapped.
- Improved combination of datasets from different thermodynamic and kinetic databases
- Database names are now stored in GES to be presented on listings and plots.
- A number of smaller improvements regarding listings and user interaction
- Bug corrections

1.3. Application Examples In Materials Chemistry

Resulting from the features as described above, Thermo-Calc can be used to calculate all kinds of thermodynamic functions of materials over wide temperature-pressure-composition ranges, to calculate phase equilibria and speciation in complex homogeneous and heterogeneous interaction systems. It can simulate mass transfer and energy transport in some dynamic processes (e.g., multi-staged steady-state reactors, one-/two-dimensional diffusions). It has been applied worldwide in materials science and engineering [5,6]. Some of such application examples are briefly described below.

1.3.1 Higher Order Phase Diagrams and Property Diagrams:

Thermo-Calc is able to calculate any kind of section (in chemical potentials or compositions) in complex multicomponent systems with up to forty components; among these composition parameters and temperature and pressure conditions, five can be defined as independent variables for plotting phase diagram sections and isopleths.

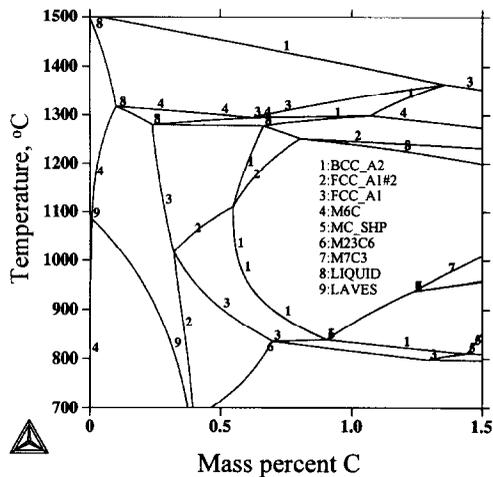


Figure 3

Figure 3 shows an example of calculated phase diagram for a M42 high speed steel with constant amounts (in weight percent) of Cr(4)-Mo(5)-W(8)-V(2)-Mn(0.3)-Si(0.3) and 0 to 1.5wt% of carbon. A line illustrates where a new phase appears or disappears, and a number representing a phase is located on the side where the phase is stable.

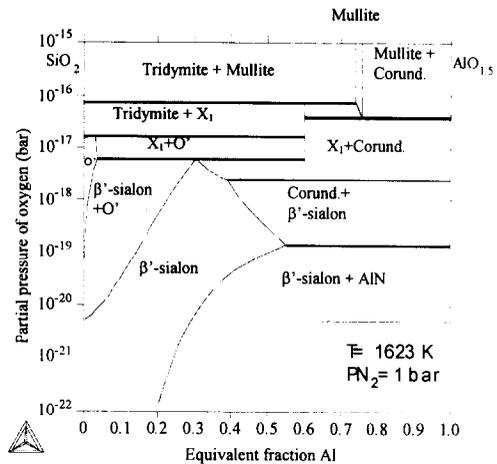


Figure 4

Figure 4 shows how suitable conditions for synthesis of β' -sialon from mixed SiO_2 and Al_2O_3 powder by reduction-nitridation [22] can be simulated. By making thermodynamic calculations in the Si-Al-O-N system, one can determine the optimal values of controlling temperature, partial pressures of oxygen and nitrogen, and Si:Al ratio in the precursor mixtures for synthesis processes. This figure shows that β' -sialon is stable with a certain region of oxygen and nitrogen partial pressures

1.3.2 Phase Equilibrium Involving Aqueous Solutions:

If interacting with an aqueous solution, a solid material may be dissolved into the aqueous phase, or be oxidized or reduced to some other phases. Thermo-Calc can make complex equilibrium calculations for such heterogeneous interactions in both supercritical and subcritical regions. With the POURBAIX module, aqueous database, and the normal POLY module, many types of property diagrams can be made by defining the x/y axis in the POST module as acidity (pH), electronic potential (Eh), electronic affinity and activity (Ah and pe), ionic strength, total ionic concentration, water activity, osmotic coefficient, molalities and activities of various aqueous species, as well temperature, pressure, salinity, and so on [23]. An example of this is shown in figure 5 below.

1.3.3 Approximate Simulation of Solidification Processes:

It is often satisfactory to approach some diffusion processes, such as compositional variation in segregation occurring when an alloy solidifies, by utilizing local equilibrium approximation in Thermo-Calc. The SCHEIL module within Thermo-Calc applies the Scheil-Gulliver model to deal with solidification problems of alloys [24]. This assumes that the diffusion coefficients in the liquid phase are equal to infinity whereas in the solid phases they are equal to zero, and that local equilibrium is always held at the phase interface between the liquid and solid phases. An example of this is shown in figure 6 below. More details on Scheil-Gulliver simulation will be provided in the section on TCW. Another case is corrosion resistance in sensitization occurring in heat-affected zone of steel during welding and during long-time service at a fairly high temperature [6].

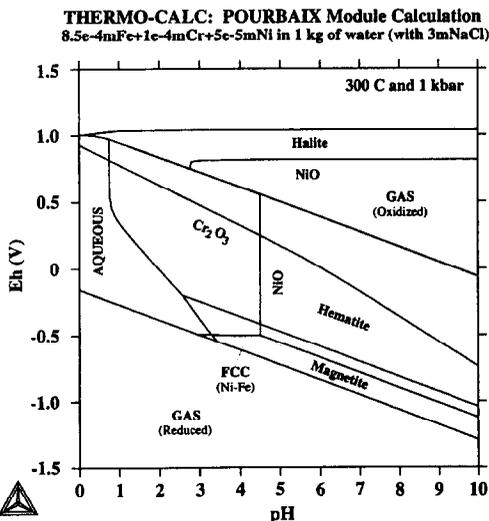


Figure 5

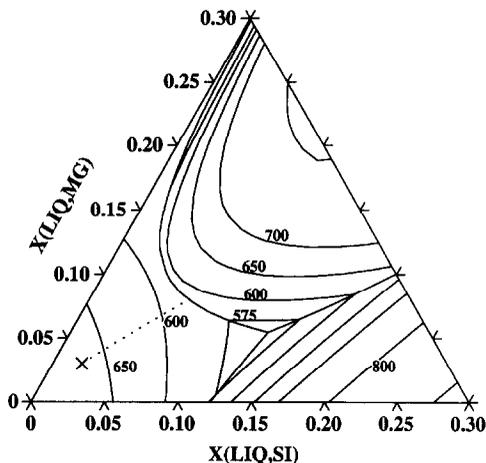


Figure 6

Figure 5 presents the so-called Pourbaix diagram (Eh-pH), and IS-pH diagram calculated by the POURBAIX module, for an alloy system Fe-Cr-Ni ($8.5 \cdot 10^{-4}m$ Fe, $10^{-4}m$ Cr and $5 \cdot 10^{-5}m$ Ni) which interacts with 1 kg of water containing 3m NaCl solution. The calculations show that under equilibrium state the alloys may be alternated to various oxides, or sulphides, or completely be dissolved into water, depending on how the pH-Eh condition of the system is controlled.

Figure 6 outlines the liquid surface of the Al-Mg-Si and the solidification path of an Al-Mg-Si alloy with 3%Mg and 2%Si [7].

2. Thermo-Calc for windows, TCW

2.1 Introduction

Thermo-Calc for Windows (TCW) is the new Windows version of the Thermo-Calc software. TCW has a graphical user interface, which makes calculation of multicomponent phase diagrams and property diagrams easy and intuitive for a new user. Simply by clicking in the graphical user interface, GUI, a new user can perform complex thermodynamic calculations. The first version of TCW, TCW1.0, was released in June 2000. Following user feedback and demands, a new version with increased functionality has been developed and this version, TCW 2.0, will be released in the end of 2001. In the current paper it is TCW 2.0, which is presented and it is hereafter only called TCW.

2.2 The software

2.2.1 Functionality

TCW uses the same thermodynamic databases and the same calculation engine as the classic version of the Thermo-Calc software. It thus provides most of the functionality found in the classical version of Thermo-Calc, TCC. However, some functions in TCC have not yet been implemented. In Table 1 below a comparison is made of the functionality of TCW vs. TCC.

Table 1 A comparison of the functionality available in TCC and TCW

Calculation of:	Multicomponent phase diagrams e.g. isothermal and isoplethal sections	X	X
	Equilibrium phase fractions and compositions as a function of temperature for multicomponent materials	X	X
	Thermodynamic properties, activities, enthalpies, chemical potentials, C_p ...	X	X
	User defined functions of thermodynamic state variables and plotting of these functions e.g. PRE-numbers for stainless steel.	X	X
	Microsegregation during solidification with the Scheil module	X	X
	Pourbaix diagrams for aqueous solutions	X	
Possibility to	Export diagram coordinates to a text-file	X	X
	Compare with other diagram or experimental data	X	X
	Optimize thermodynamic parameters, creating own databases (PARROT)	X	
Amending composition sets for miscibility gaps		X	X
Setting start values for phase compositions		X	X
Changing reference state for a component		X	X
Redefining components (e.g. using MgO, SiO ₂ and O instead of Mg, Si, O)		X	X
Using user defined start points in phase diagram calculations (ADD_INITIAL_EQUILBRIUM)		X	
Point and click labeling of phase fields in plotted diagrams			X
Complex user defined macros		X	

2.2.2. Output Facilities

The diagrams produced in TCW can be printed directly or saved as a graphical file in several different formats such as, Portable Networks Graphics (.png), Windows bitmap (.bmp), Acrobat (.pdf), JPEG (.jpg), TIFF (.tif) and Post Script (.ps). It is also possible to save the coordinates of a calculated diagram on a text file for further processing outside TCW.

2.2.3 Availability and system requirements

TCW is at present available for the PC/Windows environment. TCW can be used with Windows NT3/NT4/XP/2000/95/98/Me. The system requirements are a screen resolution of 800x600 or better and a CPU equivalent or better than a Pentium 200Mhz.

2.3 Applications

Since TCW can perform most of the calculations that are possible in TCC the applications of the software are numerous. The details of two application examples are shown here as illustrations of how calculations are performed.

2.3.1 Application example 1

Calculation of a phase fractions and phase compositions in a duplex stainless steel.

The STEP-calculation where temperature is varied for a fix composition is probably the most commonly used Thermo-Calc calculation. This example demonstrates such a calculation for a duplex stainless steel with the composition Fe-25Cr-7Ni-4Mo-0.27N-0.3Si-0.3Mn (wt%).

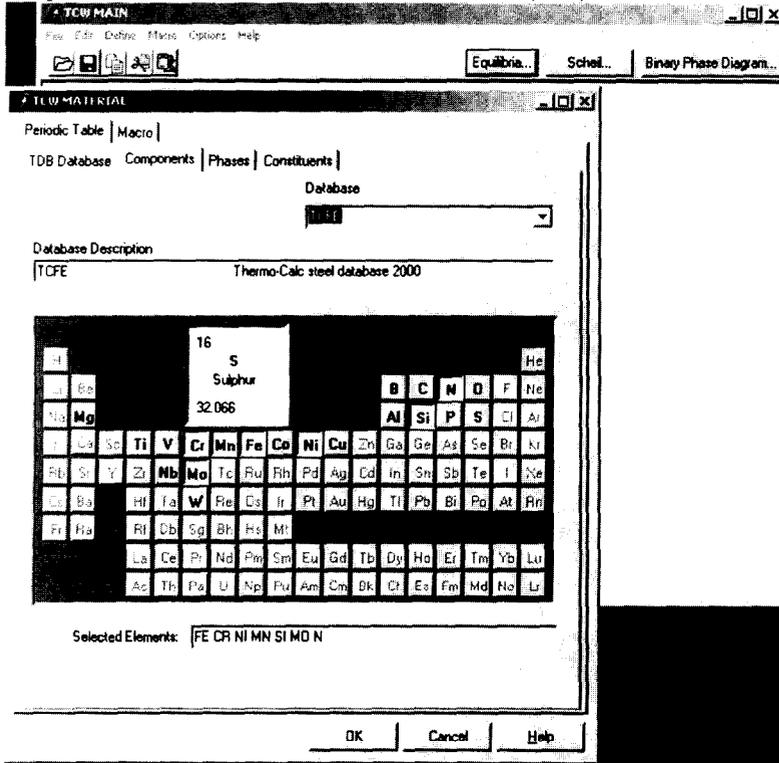


Figure 7. The graphical user interface of TCW. When pressing the Equilibria button in the TCW MAIN window the TCW MATERIAL window appears. This window is used to define the elements and the thermodynamic database that is to be used in the calculation. For a duplex stainless steel the TCFE2000 steel database is the most suitable thermodynamic database. Different colours show selected elements (red), available elements (black) and non-available elements (grey). Here Fe, Cr, Ni, Mn, Si, Mo and N have been selected by simply clicking on them. After this OK is pressed and the thermodynamic data is retrieved.

TCW MAIN

File Edit Define Macro Options Help

Equilibria... Sched... Binary Phase Diagram...

DEGREES OF FREEDOM 0

Temperature 1373. Pressure 1.000000E+05
 Number of moles of components 1.00000E+00. Mass 5.53220E+01
 Total Gibbs energy -7.79441E+04. Enthalpy 4.09326E+04. Volume 6.78638E-06

Component	Moles	W-Fraction	Activity	Potential	Ref State
CR	2.6599E-01	2.5000E-01	2.1399E-03	-7.0173E+04	SER
FE	6.2537E-01	6.3130E-01	1.3979E-03	-7.5034E+04	SER
MN	3.0210E-03	3.0000E-03	2.3689E-06	-1.4787E+05	SER
MO	2.3065E-02	4.0000E-02	4.3707E-04	-8.8306E+04	SER
N	1.0664E-02	2.7000E-03	6.1953E-07	-1.6318E+05	SER
NI	6.5983E-02	7.0000E-02	1.1290E-04	-1.0376E+05	SER
SI	5.9092E-03	3.0000E-03	5.3247E-09	-2.1748E+05	SER

BCC_A2#1 STATUS ENTERED Driving force 0.0000E+00
 Number of moles 4.8208E-01. Mass 2.6882E+01
 Mass fractions:
 FE 6.25896E-01 MO 4.91337E-02 N 4.49639E-04
 CR 2.66312E-01 SI 3.49767E-03
 NI 5.22392E-02 MN 2.47191E-03

FCC_A1#1 STATUS ENTERED Driving force 0.0000E+00
 Number of moles 5.1792E-01. Mass 2.8440E+01
 Mass fractions:
 FE 6.36408E-01 MO 3.13665E-02 SI 2.52958E-03
 CR 2.34582E-01 N 4.82711E-03
 NI 8.67881E-02 MN 3.49917E-03

TCW CONDITIONS

Number of Missing Conditions 0

Temperature 1373 K
 Pressure 100000 Pa

System Size Moles 1

Default Unit Mass-percent

Component	Value	Unit
CR	25	Default
FE		Default
MN	0.3	Default
MO	4	Default
N	0.27	Default
NI	7	Default
SI	0.3	Default

All Defined Conditions

```
T=1373
P=100000
N=1
W(CR)=2.5E-1
W(MN)=3E-3
W(MO)=4E-2
W(N)=2.7E-3
W(NI)=7E-2
W(SI)=3E-3
```

Fixed Phases

Map/Step Definition...

OK Cancel Help

Figure 8. The conditions for calculating an initial phase equilibrium is specified. Here the composition (Fe-25Cr-7Ni-4Mo-0.27N-0.3Si-0.3Mn in wt%) has been entered together with the temperature (1373K), system size (1 mole) and pressure (100000Pa). When Apply is pressed the equilibrium state is calculated for these conditions. We find that the equilibrium state, listed in the TCW MAIN window, is a mixture of ferrite (BCC_A2#1) and austenite (FCC_A1#1). The composition of the phases is also listed.

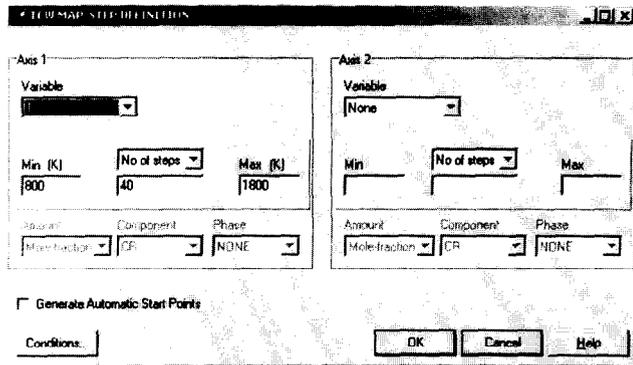


Figure 9. In order to perform equilibrium calculations for the same composition at various temperatures we specify T as the variable for Axis 1. The temperature interval and number of temperature increments is also specified here. When OK is pressed the STEP calculation is performed.

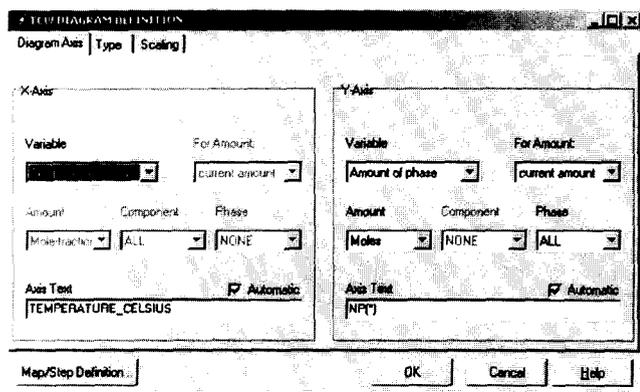


Figure 10. When the calculation is finished the TCW DIAGRAM DEFINITION window appears. This window is used to define the diagram that is to be plotted. It is often interesting to see how the fraction of different phases in an alloy varies with temperature. Such a diagram is defined here by selecting temperature and amount of phase as the axis variables.

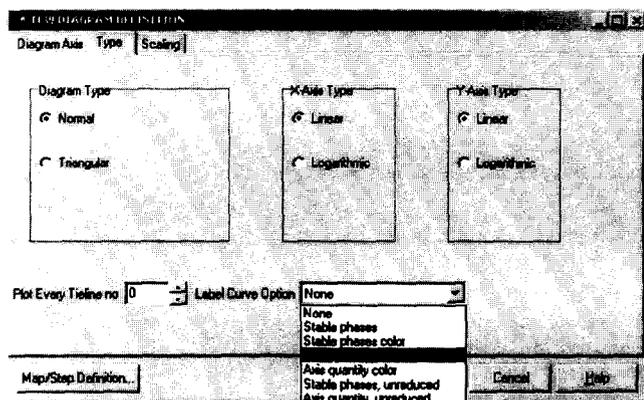


Figure 11. A suitable curve labelling is chosen to assist in identifying the curves for the different phases.

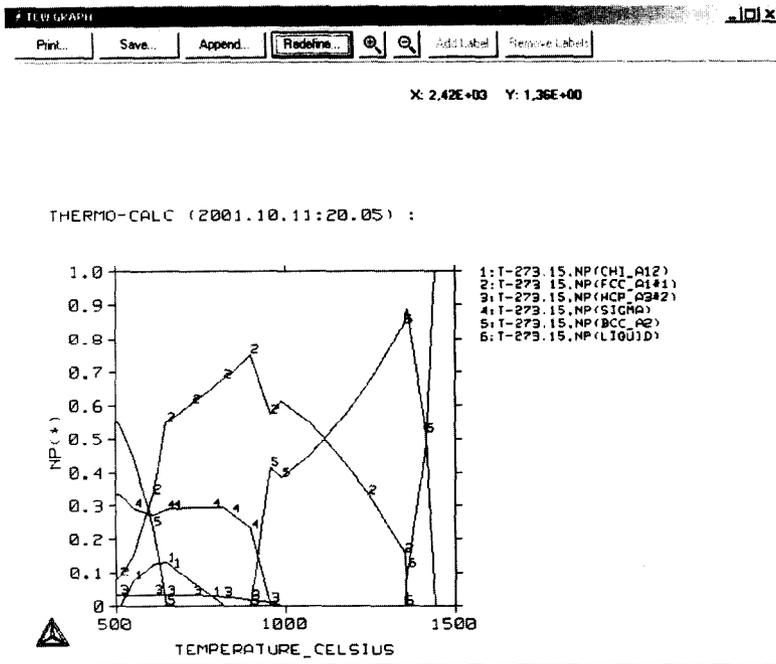


Figure 12. The TCW GRAPH window containing the diagram calculated for mole fraction of stable phases as a function of temperature for the duplex stainless steel. It is also possible to plot the different curves in different colours in order to easily identify the phases.

The diagram shows where there is risk for forming secondary phases such as Cr_2N (HCP_A3#2) and sigma phase, which have a detrimental effect on the material properties.

The Print button prints a paper copy of the diagram. Using the Save button saves the diagram in graphical formats or gives the possibility of exporting the coordinates of the curves to a text file. The Append button is used for comparing with experimental data or a previously calculated diagram. Redefine is used to change axis variables, axis scaling, labelling of the curves and more. The magnifying glasses are used to zoom in or out in the diagram. Add Label and Remove Labels are used to label phase fields in phase diagrams. X: and Y: show the pointer position in diagram coordinates enabling a fast and precise reading of some special point in a diagram.

From the same calculation many more diagrams can be plotted. Using the redefine button one can plot for example the composition of the ferrite phase.

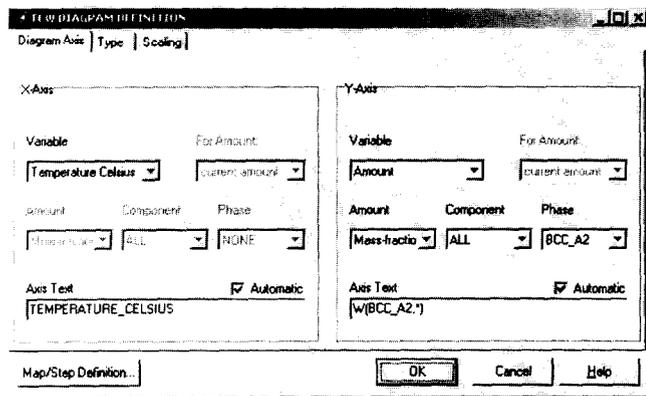


Figure 13. The chemical composition of the phases is often important from a practical point of view since the composition is often related to physical properties such as corrosion resistance and mechanical properties. The chemical composition of the ferrite is easily plotted. The data is already available from the calculation and we can select mass-fraction of all elements in the ferrite (BCC_A2) as the new Y-axis variable. This is done in the TCW DIAGRAM DEFINITION window, which appears when pressing Redefine in the TCW GRAPH window.

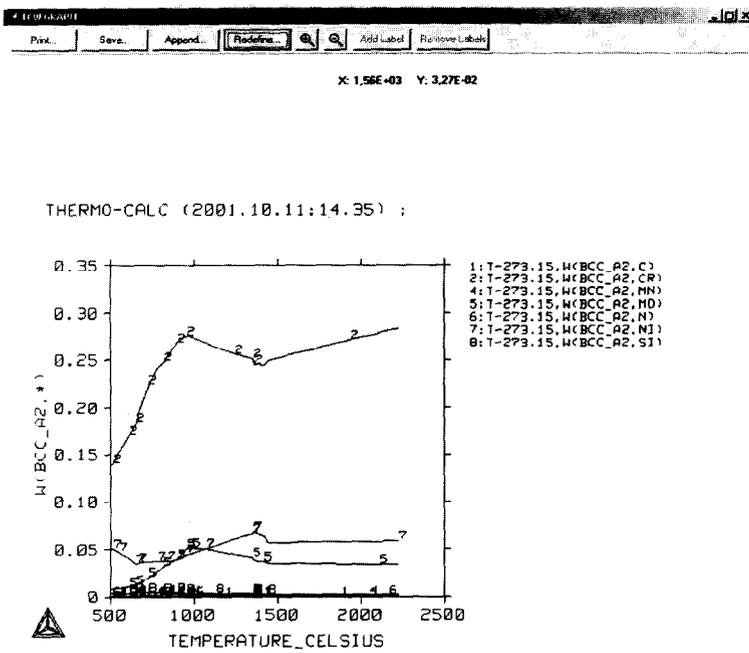


Figure 14. The equilibrium chemical composition of the ferrite as a function of annealing temperature. At temperatures below 1000°C the content of chromium and molybdenum decreases since secondary phases such as sigma phase and Cr_2N are stable in this temperature region.

2.3.2 Application example 2:

Calculation of solidification in an Al-3Mg-2Si alloy using the Scheil module.

TCW contains a Scheil module for calculating the effect of microsegregation on solidification. Using this module it is easy to perform a Scheil calculation for a multicomponent alloy. The model uses the Scheil-Gulliver model for which the basic assumptions are:

- Fast diffusion in the liquid phase (homogenous composition in this phase)
- No diffusion in the solid phase

This application example shows a Scheil calculation for a ternary Al-3Mg-2Si alloy.

After pressing the Scheil button in the TCW MAIN window, the TER98 thermodynamic database and the elements Al, Mg and Si are selected in a similar way as in the previous example.

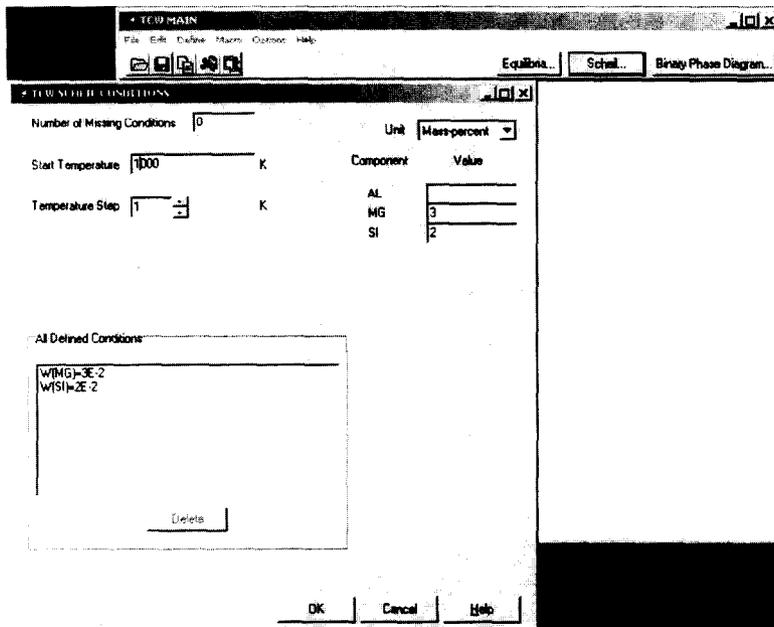


Figure 15. In the TCW SCHEIL CONDITIONS window the composition of the system, start temperature for the calculation and the temperature step are specified. When the OK button is pressed the calculation is performed.

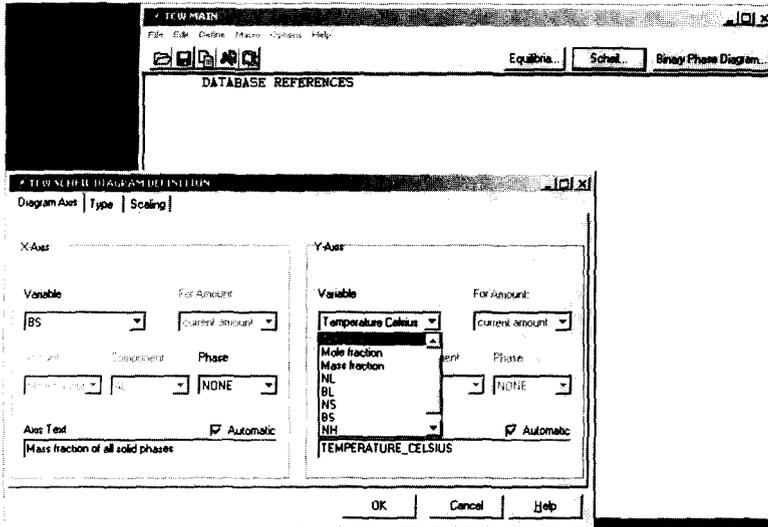


Figure 16. The TCW SCHEIL DIAGRAM DEFINITION window is used to define the diagrams to be plotted from the calculation. First a plot of temperature vs. mass fraction of all solid phases is defined.

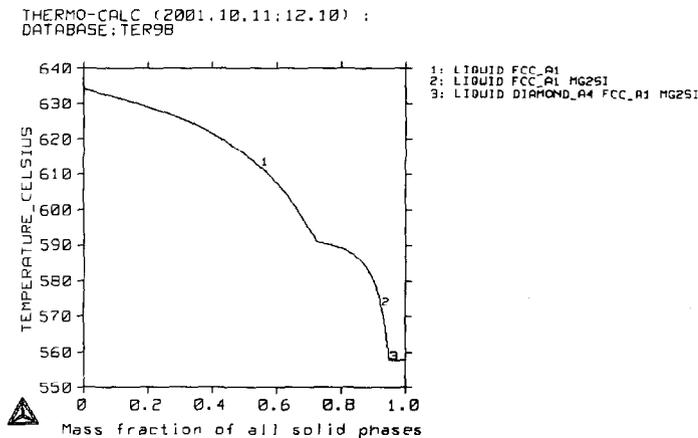


Figure 17. The plotted diagram shows how the mass fraction of solid material varies with temperature. The calculated liquidus temperature is thus 634°C and the material is completely solidified at 558°C. The numbers label the different solidification reactions. In the first segment of the curve, labelled 1, liquid is transformed to the Al-rich FCC-phase. In the second segment of the curve, labelled 2, the solidification reaction is $\text{Liq.} \Rightarrow \text{FCC} + \text{Mg}_2\text{Si}$. The third and final stage, labelled 3, is the $\text{Liq.} \Rightarrow \text{FCC} + \text{Mg}_2\text{Si} + \text{Si}(\text{DIAMOND})$ reaction.

It is also interesting to plot the latent heat evolution during the solidification. This is easily done by changing axis variables in the diagram in the TCW DIAGRAM DEFINITION window

THERMO-CALC (2001.10.11:12.23) ;
 DATABASE: TER98

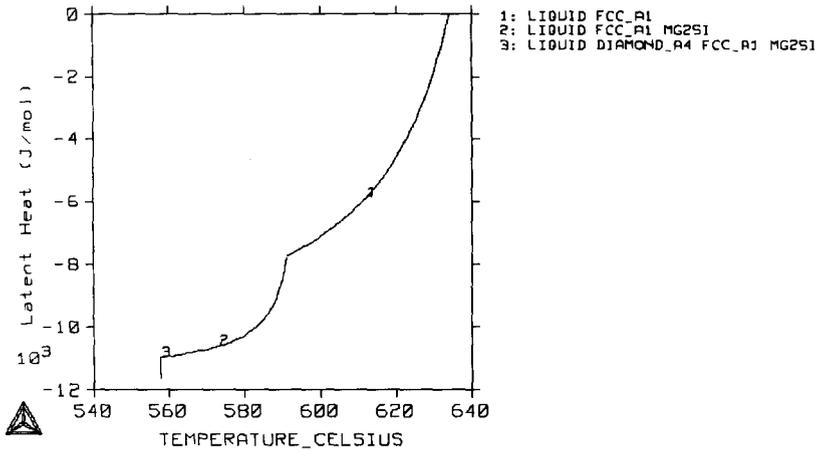


Figure 18. The plotted diagram showing the latent heat evolution during the solidification.

It is also interesting to see how the alloying elements segregate during the solidification. This can be visualised by plotting the composition of the liquid as a function of temperature.

THERMO-CALC (2001.10.11:12.29) ;
 DATABASE: TER98

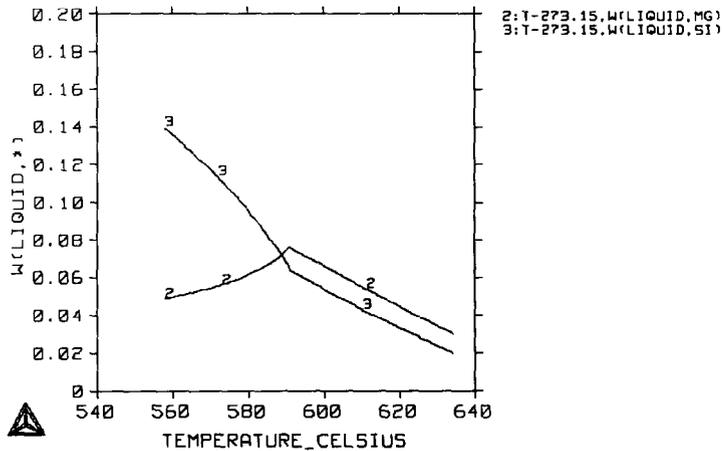


Figure 19. The plotted diagram shows the composition of the liquid as a function of temperature. Initially the content of both Mg and Si increases. When the precipitation of Mg_2Si starts around 595°C the Mg content in the liquid decreases, while the Si content continues to increase.

The different models in the DICTRA software have been used to simulate many different processes of practical and scientific interest. Some areas of application are

- Homogenisation of alloys [25]
- Carburization and decarburization of steels [26]
- Carburization of High-Temperature alloys [27, 28]
- Nitriding of steels [29-31]
- Diffusion during sintering of cemented carbides [32]
- Nitrocarburizing of steels [31]
- Austenite/ferrite diffusional transformations in steels [7,32-34]
- Growth or dissolution of individual particles [9,35 and 36]
- Solidification of alloys [25]
- Transient liquid phase bonding of alloys [37]
- Calculation of TTT-diagrams [38]
- Growth or dissolution of intermediate phases in alloy compounds [30]
- Interdiffusion in compound materials [10,27, 39]
- Interdiffusion in coating/substrate compounds [40 and 41]
- Coarsening of a particle distribution [42]
- Gradient sintering of cemented carbides [43]
- Growth of pearlite in alloyed steels [44]
- Sigma phase precipitation in stainless steel [45]
- Post weld heat treatment of welds between dissimilar materials [27,39 and 46]

DICTRA has thus been applied to many different types of materials and problems using the different models available. The DICTRA section of the present paper is intended as a general description of the software and its applications. For more detailed information regarding DICTRA, the reader is referred to the paper by Borgenstam et al. [47]

3.2 Models in DICTRA

3.2.1 The one-phase model

The one-phase model is the most basic model. The multicomponent diffusion equation for an n-component system

$$J_k = - \sum_{j=1}^{n-1} D_{kj}^n \frac{\partial c_j}{\partial z} \quad (1)$$

is solved in one phase applying a numerical procedure for a system of coupled parabolic partial differential equations [48]. J_k is the diffusive flux of element k, D_{ij}^n is (n-1)x(n-1) matrix of diffusivities and $\frac{\partial c_j}{\partial z}$ is the concentration gradient of element j. The numerical procedure for solving the equations can handle non-linearities caused by a varying diffusion-coefficient matrix or non-linear boundary conditions. Boundary conditions of many different kinds such as composition, activity, chemical potential or fluxes of the elements can be entered. These quantities can also be entered as functions of time, temperature and pressure. Some examples of applications for this model are.

- *Homogenisation of one-phase alloys*
- *Carburizing and decarburizing of steels*

3.2.2. Moving boundary model

The moving boundary model treats problems where diffusion causes a phase transformation, e.g. growth or dissolution of individual particles in a matrix phase. In the model two one-phase regions are separated by a phase interface and the migration of the interface is determined by the rate of diffusion to and from the interface.

Consider the phase transformation between a phase α and its adjacent phase β as shown in Figure 21. α phase growing into β in a binary system under isothermal conditions. The corresponding concentration profile is shown in lower left part of the figure and the phase diagram in the lower right part of the figure. In order to conserve the number of moles of a component k , a flux balance equation can be formulated as,

$$v^\alpha c_k^\alpha - v^\beta c_k^\beta = J_k^\alpha - J_k^\beta \quad k=1,2,\dots,n \quad (2)$$

where v^α and v^β denotes the interface migration rate in the α and β phases respectively, c_k^α and c_k^β are the concentrations of component k in α and β close to the phase interface and J_k^α and J_k^β are the corresponding diffusional fluxes.

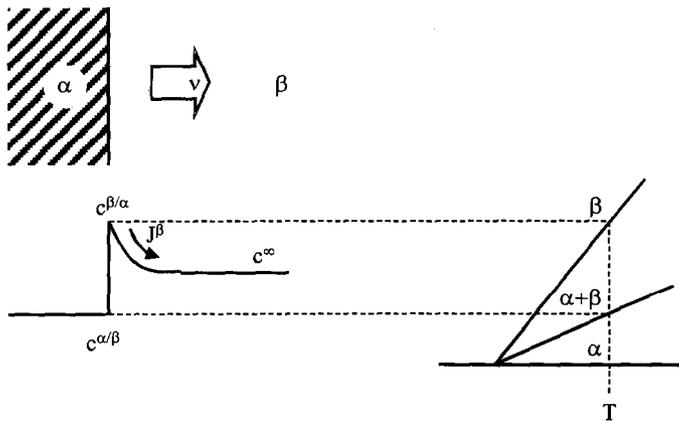


Figure 21. α phase growing into β in a binary system under isothermal conditions. The corresponding concentration profile is shown in lower left part of the figure and the phase diagram in the lower right part of the figure. Figure taken from reference 46.

The integration in time is carried out by initially calculating the boundary conditions at the phase interface. Thermodynamic equilibrium is assumed to hold locally at the interface. This assumption, usually referred to as the local equilibrium hypothesis, is commonly applied and allows the boundary conditions to be determined. After this the diffusion problem in each one-phase region can be solved. Finally, the migration rate of the phase interface is determined by solving the flux-balance equation, Eq. 2. In the multicomponent case this will generate a system of non-linear equations, which has to be solved by an iterative procedure.

Examples of problems, which have been treated with this model, are:

- $\gamma \rightarrow \alpha$ transformations in steels
- Carbide dissolution during austenitizing of steel
- Certain aspects of solidification

3.2.3 Model for diffusion in dispersed systems

The model for diffusion in dispersed systems was developed in order to treat problems involving diffusion **through** microstructures containing dispersed precipitates of secondary phases. For example, carburization of high-temperature alloys, where long range diffusion of carbon occurs in an austenitic matrix with dispersed carbides.

In this model it is assumed that there exists a continuous phase, the matrix phase, in which there are one or more dispersed phases. Diffusion is assumed to take place only in the matrix phase. The dispersed phases act as point sinks or sources of solute atoms in the simulation and their fraction and composition is calculated from the average composition in each node, assuming that equilibrium holds locally in each volume element.

The calculation scheme is described in Figure 22 and consists of two steps. The first step is the so-called diffusion step, which is simply a one-phase problem since it is assumed that all diffusion occurs in a matrix phase. However, due to the composition change in the matrix during the diffusion step, there is a change in the average composition at every node. The new equilibrium is calculated from the new average composition using Thermo-Calc, and the diffusion step is then repeated with the new composition profile in the matrix phase, and so on.

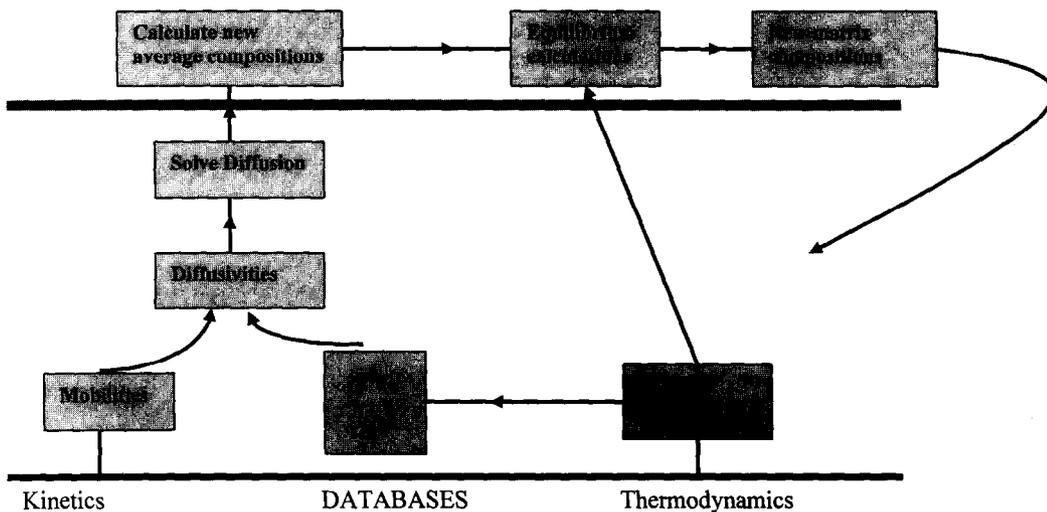


Figure 22. The calculation scheme used in the model for diffusion in dispersed systems. [49]

This model is suitable to any application where long-range diffusion occurs in a single continuous phase containing dispersed particles. Here long-range means distances which are long compared to the inter-particle spacing. Examples of applications for this model are:

- Carburization of high-temperature alloys
- Interdiffusion in composite materials
- Gradient sintering of cemented carbide work-tool pieces

3.2.4 The "cell" model

All models discussed so far consider one cell. It is however possible to connect two or more cells. The boundary between the cells will then be an immobile interface where it is assumed that diffusional equilibrium holds i.e. the diffusion potential, Φ for an element is the same at all cell boundaries. The diffusion potential for element i is defined as

$$\Phi_i = \mu_i - \mu_n \quad \text{if } i \text{ is a substitutional element} \quad (3)$$

$$\Phi_i = \mu_i \quad \text{if } i \text{ is an interstitial element}$$

where μ_n is the chemical potential of an arbitrarily chosen reference element n , usually the major element. Furthermore, it is required that the total amount of each component is constant in the system of cells. In order to maintain the overall massbalance the net flow of atoms between the cells is assumed to be zero. The flow is equal to the flux J times A the outer area of the cell. The diffusion potentials will then be iteratively determined until such an activity is found that will yield a zero net sum of flows. The cell model is quite versatile and some possible calculations are shown in Figure 23 below.

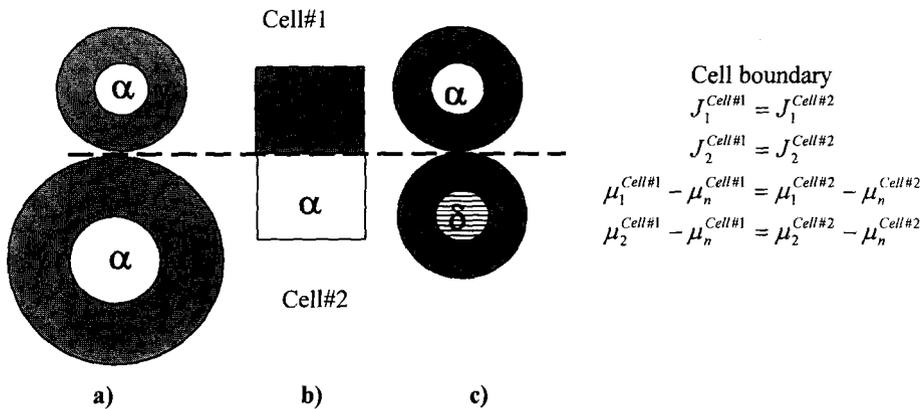


Figure 23. Some possible calculation using the cell model. a) Dissolution reaction considering a size distribution of precipitates. b) Diffusion at a phase interface, which is immobile e.g. due to coherency. c) Dissolution of several spherical precipitates of different phases.

Some possible applications for this model is thus

- *Dissolution of a particle distribution.*
- *Simultaneous dissolution of particles of several different phases*

3.2.5 The coarsening model

This model was developed in order to treat coarsening, i.e. Ostwald ripening [42]. It uses the assumption that coarsening of a system can be described by performing calculations on a single particle of maximum size at the centre of a spherical cell. It is assumed that the particle size distribution obeys the Lifshitz-Slyozov-Wagner distribution, i.e. that the maximum particle size is 1.5 times the average size. In this model a contribution from the interfacial energy is added to the Gibbs energy function for the particle, see Figure 24.

$$\Delta G_m = \frac{2\sigma V_m}{r} \quad (4)$$

where σ is the interfacial energy, r the radius of the particle and V_m is the molar volume. It is assumed that equilibrium between particles of average size and the matrix holds locally at the cell boundary taking into account the contribution of the interfacial energy in Gibbs energy. The particle of the maximum size will have a smaller Gibbs energy addition than the particles of average size giving a difference in composition close to the interface between the maximum particle and matrix and the outer cell boundary. This difference will make the maximum particle grow. In order to maintain the total composition in the cell its size will increase accordingly. Figure 24 below show a schematic picture of this model.

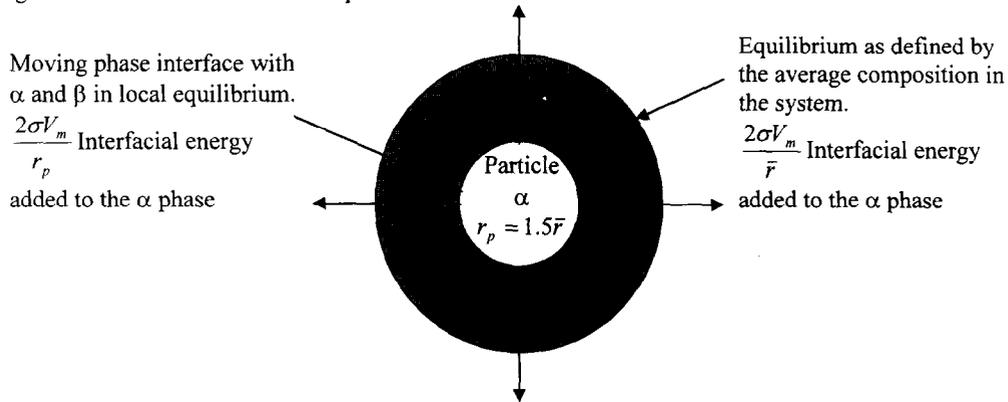


Figure 24. Schematic picture of the coarsening model.

Examples where this model can be used are

- Coarsening of γ' particles
- Coarsening of carbides in austenite
- Coarsening of carbo-nitrides in ferrite

3.2.6 The cooperative growth model

The cooperative growth model was developed to simulate the reaction $\gamma \rightarrow \alpha + \beta$ where α and β grow cooperatively as a lamellar aggregate into a γ matrix in both binary and multicomponent alloys [44].

In this model the theory for boundary and volume diffusion controlled lamellar growth of eutectics and eutectoids as presented by Hillert [50], have been modified to handle mixed boundary and volume diffusion control for treating growth of lamellar phases, e.g. growth of pearlite in steels. This has been achieved by introducing so-called effective diffusion coefficients. Substitutional alloying elements are here assumed to redistribute by boundary diffusion.

Several assumptions have been made. A steady-state growth rate controlled by diffusion in front of the aggregate was assumed. All diffusivities were assumed independent of alloying effects and diffusion inside the lamella was assumed negligible. Furthermore it was assumed that the transformation front is approximately planar and that local equilibrium holds across the γ/α and γ/β interfaces.

This model has been applied on

- Growth of pearlite in binary and multicomponent systems

3.3 Diffusion in DICTRA

3.3.1. Introduction

DICTRA solves the multicomponent diffusion equation, Eq. 1, according to the Onsager extension of Fick's law [50]. In equation 1., the flux of element k depends on the concentration gradients of the other elements in the system as well as the concentration profiles in multicomponent systems can often have a different appearance than in binary systems. In ternary and higher order systems an element can even diffuse "up" it's own concentration gradient, so called up-hill diffusion. In Figure 25 below an example of this is given.

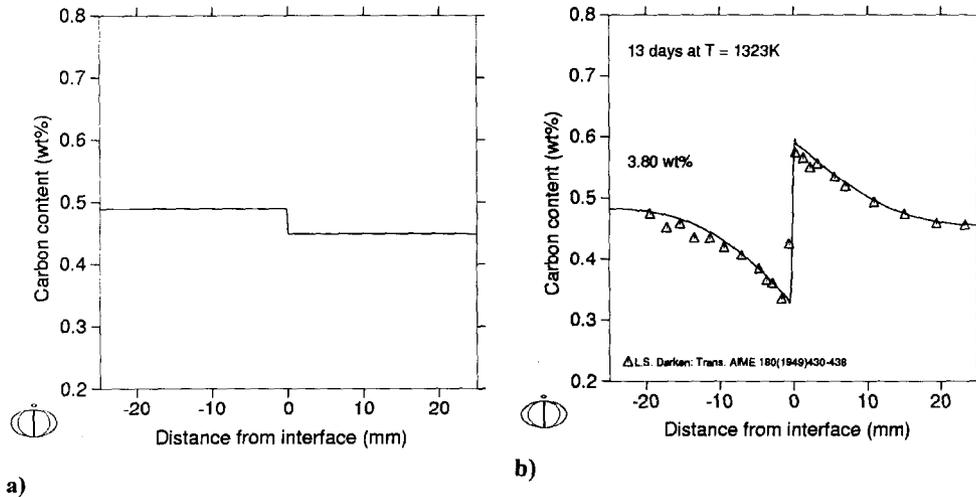


Figure 25. DICTRA simulation of diffusion in a weld between a Fe-3.8Si-0.49C alloy and a Fe-0.05Si-0.45C alloy for a heat treatment of 13 days at 1323K. In a) the initial concentration profile for carbon is shown. In b) the concentration profile after 13 days at 1323K is shown together with experimental measurements from [52].

In Figure 25 it can be seen how carbon at the interface diffuses "up" its own concentration gradient, from a region of low carbon content to a region of higher carbon content. This is caused by a gradient in silicon content at the joint. In equation 1 it is the off-diagonal elements D_{kj}^n with $k \neq j$ that accounts for effects of gradients in other alloying elements which can cause up-hill diffusion.

3.3.2 The Diffusion Matrix, D_{kj}^n

The DICTRA simulations are based on databases with thermodynamic and diffusion data. For thermodynamic data the same databases as in Thermo-Calc can be used. Diffusion data is stored as mobilities in databases and by combining mobilities with thermodynamic data it is possible to calculate the diffusion matrix D_{kj}^n .

The databases with mobilities are created through an assessment procedure similar to the one for thermodynamic databases. Experimental data are collected and selected from the literature. Parameters in the mobility models are optimised to give the best possible description of the experimental data. The optimised parameters are then

stored in mobility databases. From these databases it is then possible to calculate the temperature and concentration dependent diffusion matrix D_{kj}^n as shown in Figure 26 below.

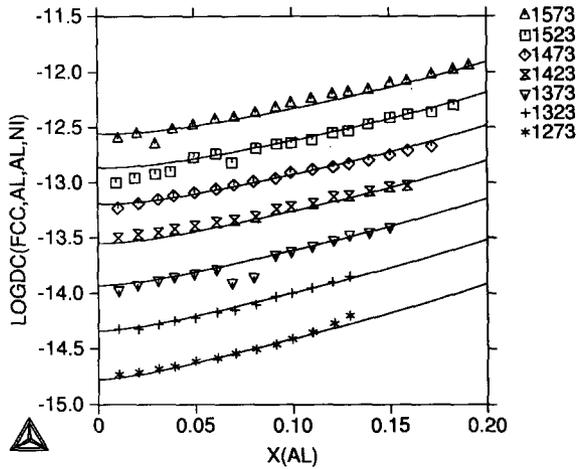


Figure 26. Logarithm of the interdiffusion coefficient in the FCC-phase of the Ni-Al system plotted against mole-fraction of aluminium for different temperatures (1273,1323,1373,1423,1473,1523and 1573K). The figure is taken from [53]. Solid lines are calculated using DICTRA and the symbols are experimental measurements [54].

As mentioned above the diffusion matrix in DICTRA is temperature and concentration dependent. An effort has also been made to incorporate other effects on the diffusion coefficients. The ferromagnetic transformation occurring in e.g. BCC-Fe has a marked effect on the diffusion in this phase. This is practically important in e.g. steels. A model for the effect of the ferromagnetic transformation on the diffusion coefficients was implemented. This is shown in Figure 27 below.

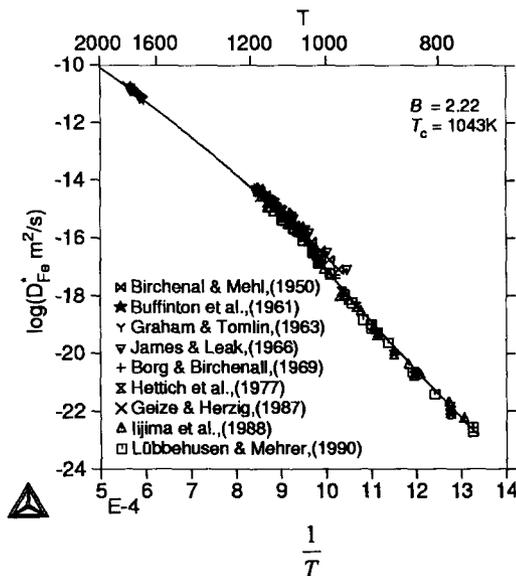


Figure 27. Logarithm of the self diffusion coefficient of iron plotted against the inverse of temperature. Note the deviation from linearity around the Curie temperature 1043K. The solid line is calculated using DICTRA and the symbols denote experimental measurements. The figure is taken from[55].

3.4 Application Examples

In the following section some successful applications of DICTRA will be reviewed.

3.4.1 Microsegregation behavior during solidification and homogenisation of a high-alloy multicomponent steel.

Lippard *et al.* [25]. used DICTRA to simulate the microsegregation behavior of a Fe-13.4Co-11.1Ni-3.1Cr-1.2Mo-0.23C alloy. The solidification was simulated using a computational cell defined as the half-width of the secondary dendrite arm spacing.

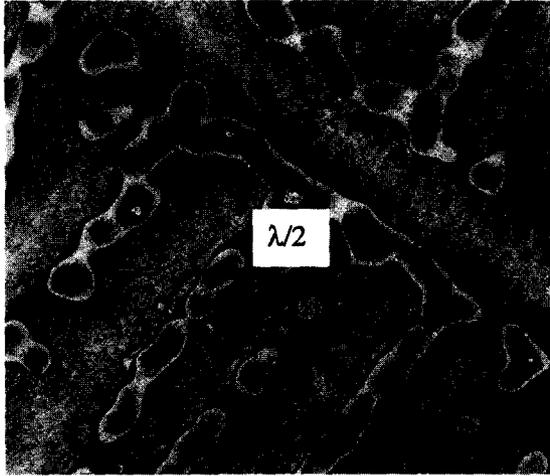


Figure 28. Example of cast microstructure showing the half-width of the secondary dendrite arm spacing ($\lambda/2$) used as computational cell in the DICTRA simulations.

The simulation were carried out using the moving boundary model and considering growth of the austenite into the liquid. The full six-component system was treated. The input data to the simulation was over-all composition, cooling rate and the secondary dendrite arm spacing.

From this it is possible to simulate the growth of the solid FCC-phase into the liquid. The operating tie-line for the Austenite/Liquid phase interface is calculated in Thermo-Calc. This tieline will shift during the simulation. The multicomponent diffusion equation is solved in both the liquid and the austenite and thus back diffusion in the solid phase is considered. After the simulation is performed output data such as fraction of solid phase as a function of temperature or composition profiles can be plotted.

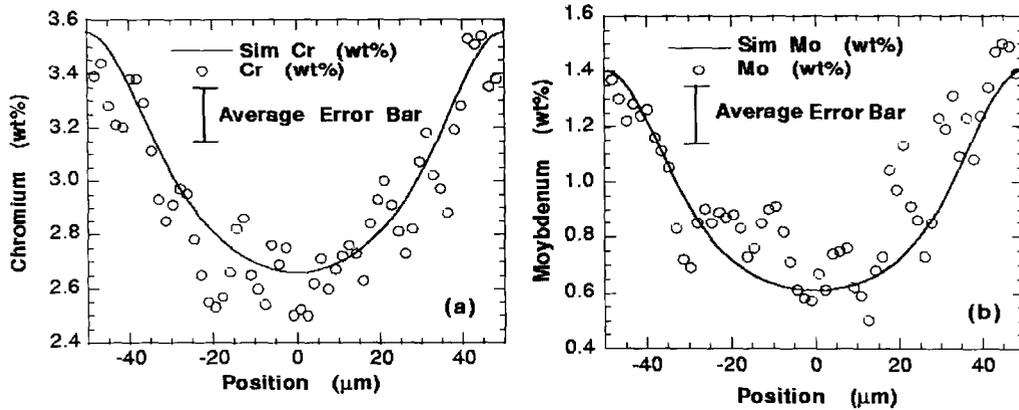


Figure 29. Composition profile for chromium and molybdenum across a secondary dendrite arm spacing. The solid curve is a result from a DICTRA simulation and the points are experimental measurements using SEM/EDS. Figure from [25]

Lippard et al. thus managed to obtain a very nice agreement between the simulations and the experimental measurements for this multicomponent steel.

3.4.2 Transient Liquid-Phase Bonding in the Ni-Al-B System

Transient liquid phase bonding is a joining method which uses the formation of a transient liquid phase between the materials which should be joined. This is obtained by inserting a low-melting filler material which will wet the contacting base materials and subsequently solidify isothermally due to diffusion of a fast diffusing element. This was studied experimentally and using DICTRA by Cambell and Boettinger[37]. in the Ni-Al-B system. They used a Ni-1.9B filler to join two pieces of Ni-5Al material. After the heating to 1315°C the Ni-1.9B filler melts and after this the liquid shrinks when B diffuses away from the liquid region.

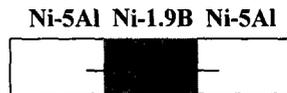


Figure 30 Schematic picture of the transient liquid phase bonding process studied.

Using the moving boundary model Campbell and Boettinger managed to successfully simulate the width of the liquid region and composition profiles as shown in Figure 31 and 32 below.

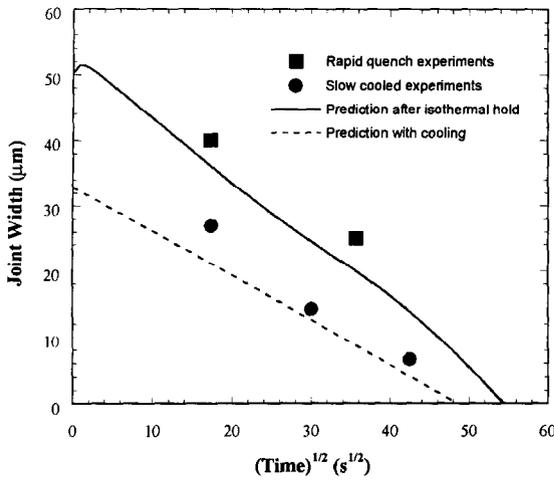


Figure 31. Experimental and predicted liquid widths as a function of the square root of time. Figure from [37].

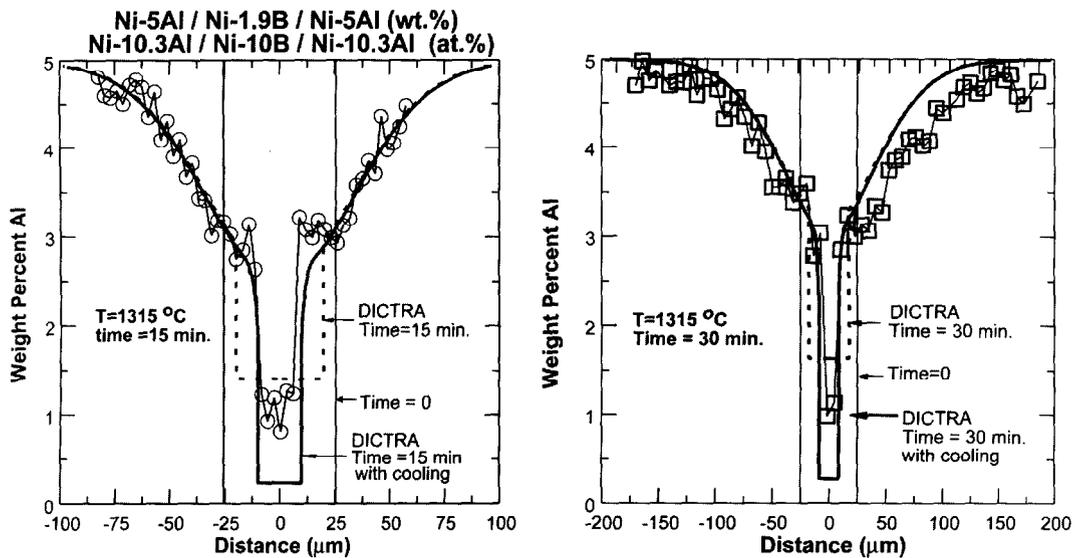


Figure 32. Comparison of the experimental and predicted Al composition profiles at (a) 900 s and (b) 1800 s. Figure from [37].

3.4.3. Complex Carbide Growth, Dissolution and coarsening in a Modified 12pct Chromium Steel

Bjärbo and Hättstrand[56] used DICTRA to model the growth dissolution and coarsening of carbides in a Fe-10.5Cr-1Mo-1W-0.14C steel. Experimental studies showed formation of two carbides, M_7C_3 and $M_{23}C_6$. The M_7C_3 carbide formed initially but was later dissolved and replaced by the $M_{23}C_6$ carbide. This was in agreement with Thermo-Calc calculations showing $M_{23}C_6$ to be the only stable carbide. The process was modelled by Bjärbo and Hättstrand using a cell calculation according to Figure 33 below.

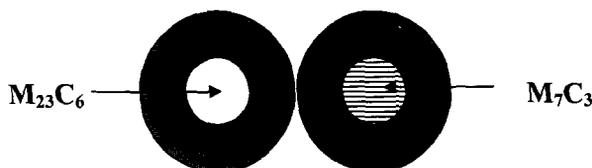


Figure 33. Schematic figure of cell calculation used by Bjärbo and Hättstrand.

With the cell calculation Bjärbo and Hättstrand succeeded in modelling the precipitation reaction consisting of an initial growth of both M_7C_3 and $M_{23}C_6$ and subsequently M_7C_3 starts to dissolve when the diffusion fields from the two particles overlap. Figure 34 below shows the result from simulations and experiments.

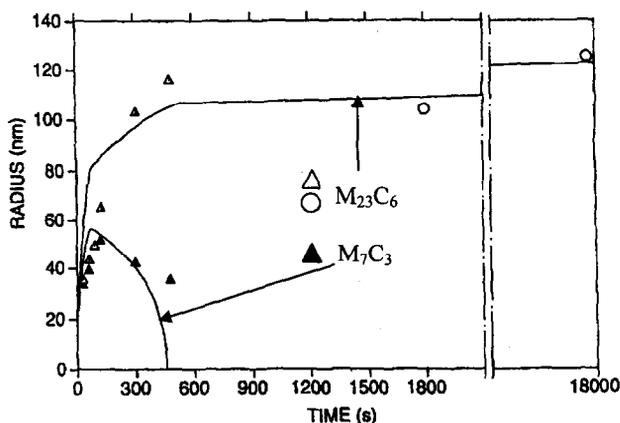


Figure 34. Carbide radius as a function of heat treatment time. Solid lines are results from the DICTRA simulation and the symbols are experimental measurements. Figure from [56]

Bjärbo and Hättstrand also performed coarsening calculations to model the final coarsening of the $M_{23}C_6$ carbide after the growth and dissolution step was finished. The results from this calculation is shown in Figure 35 below.

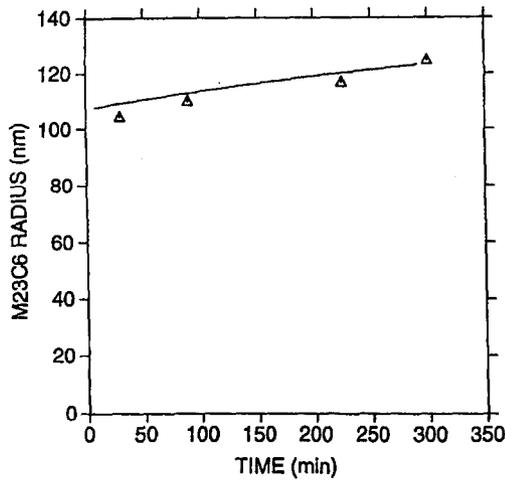


Figure 35. Coarsening of the $M_{23}C_6$ carbide. Solid curve shows the result from a DICTRA simulation while the symbols are experimental measurements. Figure from [56]

3.5 User Interface

The DICTRA software is divided into several different modules for performing different tasks e.g. retrieving data, setting up a simulation or plotting the results. The user interface is very similar to the user interface in Thermo-Calc Classic with a command line interface where commands are typed. All commands can be abbreviated for convenience.

After gaining some experience with the software, it is possible to construct macro-files, which set up and execute a simulation. Virtually all experienced users use macro-files and it is possible to set up a simulation in a very short time (minutes) using this feature.

There are complete help facilities for the users. A list of available commands can be retrieved by simply typing a ? at the command prompt and there are also descriptions of all commands available.

4 Thermo-Calc Programming Interfaces, TC-PI

4.1 Introduction

The Thermo-Calc programming interfaces make it possible to access Thermo-Calc from a user-written application. Using a programming interface it is easy to use Thermo-Calc as a subroutine in the application to obtain thermodynamic properties and phase equilibria. Some examples of quantities that can be calculated using the programming interfaces are:

- Amount of phases
- Composition of phases
- Enthalpies
- C_p
- Liquidus or solidus temperatures
- Partition coefficients
- Invariant temperatures

At present there are three different programming interfaces available, TQ-Interface, TC-API and TC-Toolbox. These are presented below

4.2 TQ-Interface

TQ is an application program interface of Thermo-Calc, it is intended for application programmers to write application programs using the Thermo-Calc kernel without bothering of how actual thermodynamic data or equilibrium calculations are performed. The thermodynamic properties and phase equilibrium data, which can be obtained by using TQ include most of the quantities that are available from Thermo-Calc.

With the TQ interface, it is easy to program. The subroutines and functions available in the TQ interface can be classified into categories according to their purposes:

- Initialization
- System data manipulation
- Defining conditions for an equilibrium calculation.
- Performing calculation.
- Obtaining results

The TQ interface is written in Fortran and available on most platforms e.g. PC-Windows NT/2000/95/98/Me, PC-Linux and many UNIX platforms (Sparc, Solaris, HP, IBM, Compaq). It is supplied in the form of object or library files that can be readily linked to an application program.

A programming example using this interface for calculating the T_0 -temperature is given below. The T_0 -temperature is the temperature where the Gibbs energy for two phases, having the same composition, is equal. It is thus the theoretical limit for a diffusionless transformation.

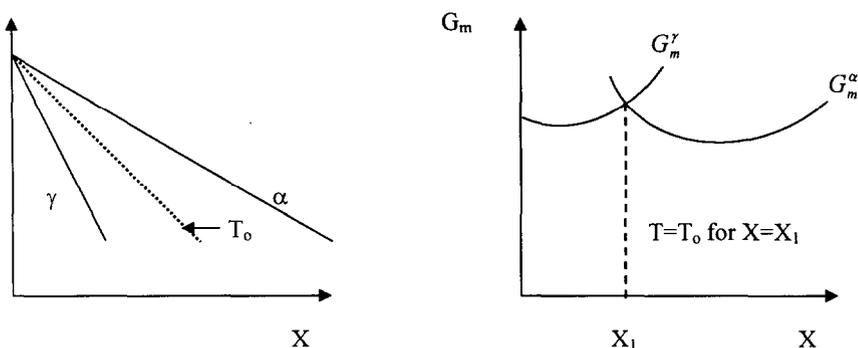


Figure 37. Schematic picture showing the principle for calculating the T_0 -temperature

Below is the pseudocode for calculating the T_0 -temperature using the TQ-interface.

A number of lines initialising the program

Do the calculation from minimum carbon content (X_{min}) to maximum carbon content (X_{max}) with the increment dX

```
do 2000, XC=Xmin, Xmax, dX
  Tmax=Tmax0
  Tmin=Tmin0
  T=(Tmax0+Tmin0)*0.5
  P=101325
  N=1.0
  its=0
```

Suspend both phases

```
call tqcsp(iph1, 'SUSPENDED', 0, iwsg)
call tqcsp(iph2, 'SUSPENDED', 0, iwsg)
```

Set conditions for temperature (T), pressure (P), System size (N) and Composition (X)

```
call tqsetc('P', -1, -1, P, numcon, iwsg)
call tqsetc('T', -1, -1, T, numcon, iwsg)
call tqsetc('N', -1, -1, N, numcon, iwsg)
call tqsetc('X', -1, icmp, XC, numcon, iwsg)
```

```
100 continue
  its=its+1
  call tqsetc('T', -1, -1, T, numcon, iwsg)
```

Calculate the Gibbs free energy for the two phases and store them in gm1 and gm2.

```
call tqcsp(iph1, 'ENTERED', 1, iwsg)
call tqcsp(iph2, 'SUSPENDED', 0, iwsg)
call tqce(' ', 0, 0, 0.0, iwsg)
gm1 = tqggm(iph1, iwsg)
```

C

```

call tqcsp(iph1,'SUSPENDED',0,iwsg)
call tqcsp(iph2,'ENTERED',1,iwsg)
call tqce(' ',0,0,0.0,iwsg)
gm2 = tqggm(iph2,iwsg)

```

C

Calculate the relative difference between gm1 and gm2. If it is small enough the temperature is approximately the T0-temperature

```

gmd=(gm1-gm2)/gm1
if (abs(gmd).le.eps) goto 200

```

We did not find the solution, adjust the temperature and do one more iteration.

```

if (gmd.lt.0) then
  Tmin=T
  T=(T+Tmax)*0.5
endif
if (gmd.gt.0) then
  Tmax=T
  T=(T+Tmin)*0.5
endif
goto 100

```

C

```

200 continue

```

We have found the solution for this composition. Write out composition, T0-temperature and number of iterations.

```

write(*,*)' X(C),T,its ',XC,T,its

```

```

2000 continue
end

```

4.4 TC-API

The TC-API (Thermo-Calc Application Programming Interface) is a general programming interface for integrating thermodynamics into user applications in MS-Windows and Linux environments. TCW and TC-Toolbox is based on this programming interface.

TC-API is similar in functionality as compared with the TQ-interface, it does however differ in some important aspects.

- The API is written in C and is therefore suited for interfacing with most other programming languages than FORTRAN.

- The API includes functionality of Thermo-Calc not available in the TQ-interface. It offers access to most of the used commands in the TDB, POLY-3 and POLY-3_Postprocessor modules and some important commands in the GES5 module.

4.5 TC-Toolbox

Thermo-Calc has also been implemented as a toolbox in the MATLAB® software, allowing access to Thermo-Calc from MATLAB programs. Using this it is possible to combine the MATLAB's functionality with Thermo-Calc. Below is an example of a calculation performed using the toolbox. It is a calculation of the liquidus surface for a ternary A-B-C surface performed and plotted using the TC-Toolbox in MATLAB.

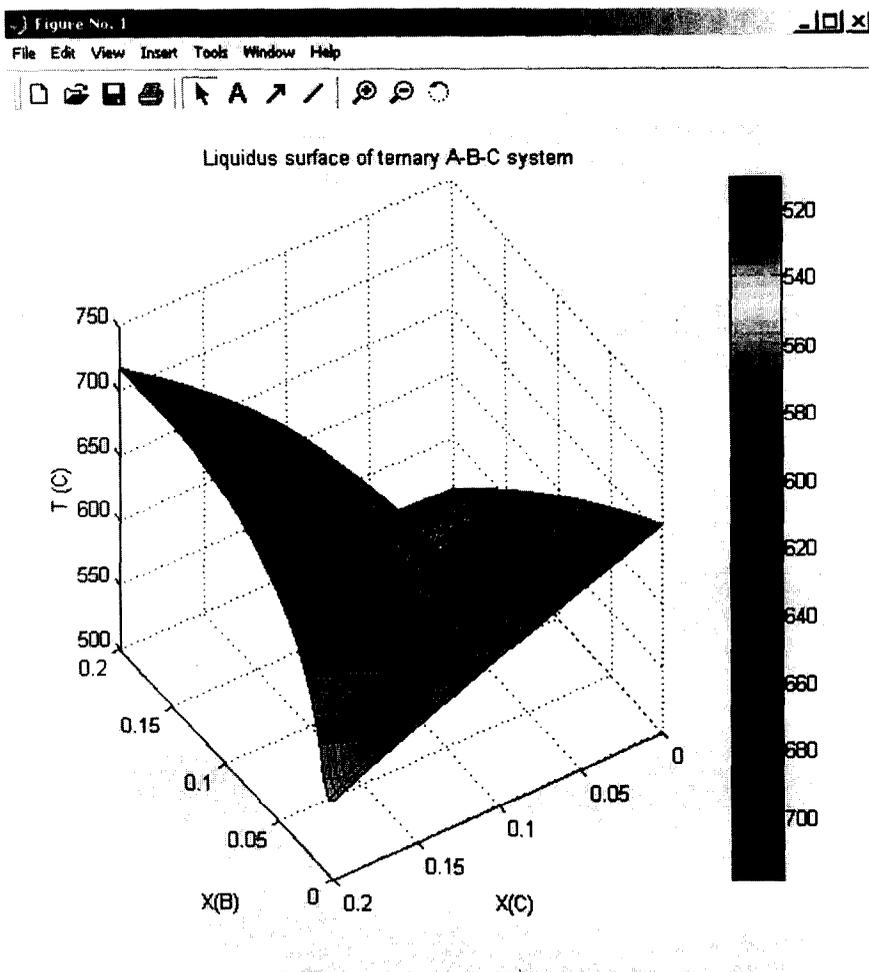


Figure 38. Liquidus surface of the A-B-C system calculated and plotted using TC-Toolbox in MATLAB.

Conclusion

Thermo-Calc is today an established tool for calculating thermodynamic properties and phase-equilibria in materials. Over the last years the software has been made more accessible.

- The development of a windows version, TCW, enables materials & process engineers to perform advanced calculations in an easy and intuitive way
- The amount of available high quality thermodynamic data is continuously increasing and thermodynamic databases for new applications e.g. environmental issues can now be used in Thermo-Calc.
- Programming interfaces allows Thermo-Calc to be used as part of another software providing thermodynamic and equilibrium data as a subroutine.

All this has made Thermo-Calc into a whole set of tools with multiple applicability in science and industry.

DICTRA has proven itself to be capable of simulating the rate of phase transformations and diffusion processes in multicomponent alloys. The unique feature of DICTRA is the implementation of several phase transformation mode models that adds microstructural information or constraints and local equilibrium constraints to the diffusional flux calculations. The application of DICTRA to many well known processes such as sintering, heat treatment or surface treatments has provided new insights both from a scientific and industrial point of view.

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References

1. B. Sundman, B. Jansson and J-O. Andersson, *CALPHAD*, **9** (1985) 153.
2. B. Sundman, *Anales de Fisica, Serie B*, **86** (1990) 69.
3. M. Hillert *Phase Equilibria Phase Diagrams and Phase Transformations*, (1999) Cambridge Univ. Press ISBN 0-521-56270-8.
4. B. Jansson, Thesis (1984) Royal Institute of Technology, Stockholm, Sweden.
5. B. Jansson, M. Schalin, M. Selleby and B. Sundman in *Computer Software in Chem. Extract. Metall.*, C.W. Bale and G.A. Irons, Editors, The Met Soc. of CIM, Quebec (1993) 57.
6. M. Hillert, private communication (1997).
7. Å. Jansson, Ph.D. Thesis, Royal Institute of Technology, Stockholm, Sweden (1997).
8. G. Eriksson, H. Sippola and B. Sundman, Thermodynamic Calculation Interface (TQ). Report to EC/Science Simulation Program "Computer Assisted Process Simulation" (1995).
9. J-O. Andersson, L. Höglund, B. Jönsson, J. Ågren in *Fundamentals and Applications of Ternary Diffusion*, G.R. Purdy, Editor, Pergamon Press, New York (1990) 153.
10. T. Helander and J. Ågren, *Metall. Mater. Trans. A*, **28A**, (1997) 303 .
11. M. Hillert, *Calphad*, (1980) 1.
12. M. Hillert, *Journal of Alloys and Compounds*, **320** (2001) 161-176.
13. K. Frisk and M. Selleby, *Journal of Alloys and Compounds*, **320** (2001) 177-188.
14. M. Hillert, B. Jansson, B. Sundman and J. Ågren, *Met Trans. A*, **16A**, (1985) 261.
15. A S Jordan in *Calculation of Phase Diagrams and Thermochemistry of Alloy Phases* eds. Y A Chang and J F Smith TMS-AIME, (1979) 100.
16. H. Gaye and J. Welfringer, *2nd Int Symp on "Metallurgical Slags and fluxes"*, Warrendale, P A, Met Soc of AIME, Eds H A Fine and D R Gaskell, (1984) 357.
17. M Hillert, *Met Trans A*, **17A** (1986) 1878.
18. R Kikuchi, *Phys Rev*, **81** (1951) 998.
19. B Sundman and T Mohri, *Z. Metallkd.*, **81** (1990) 251.
20. G Inden, *Z. Metallkd.*, **66** (1975) 725.
21. J-O Andersson, A Fernandez Guillermet, M Hillert, B Jansson and B Sundman, *Acta Met*, **34** (1986) 437.
22. L.F.S. Dumitrescu and B. Sundman, *J. Eur. Cera. Soc.*, **15** (1995) 89.
23. P-F. Shi and B. Sundman, Tech. Prog. Abs. CALPHAD XXVI (1997).
24. Q. Chen, L.F.S. Dumitrescu, L. Höglund, Å. Jansson, M-L. Malmström, S. Norgren, M. Schalin, M. Selleby, P-F. Shi, B. Sundman and A. Weidling, Tech. Prog. Abs. CALPHAD XXVI (1997).
25. H. E. Lippard, C. E. Campbell, T. Björklind, U. Borggren, P. Kellgren, V. P. Dravid and G. B. Olson, *Metall. Mater. Trans. B*, **29B** (1998) 205-210.
26. L. Sproge and J. Ågren, *J. Heat Treat.*, **6** (1988) 9-19.
27. A. Engström, L. Höglund and J. Ågren, *Metall. Mater. Trans.* **25A** (1994) 1127-1134.
28. A. Engström, L. Höglund and J. Ågren, *Mater. Sci. Forum*, **163-165** (1994) 725-730.
29. H. Du and J. Ågren, *Z. Metallkd.*, **86** (1995) 522-529.
30. H. Du, N. Lange and J. Ågren, *Surface Eng.*, **11** (1995) 301-308.
31. H. Du and J. Ågren, *Met. Trans. A*, **27A** (1996) 1073-1079.
32. S. Haglund and J. Ågren, *Acta Materialia*, **46**, (1998) 2801-2807.
33. J. Ågren, *Acta Metall.*, **30** (1982) 841-851.
34. S. Crusius, L. Höglund, G. Inden, U. Knoop and J. Ågren, *Z. Metallkd.*, **83** (1992) 729 – 738.
35. J. Ågren, *ISIJ Internat.*, **32** (1992) 291-296.
36. Z.-K. Liu, L. Höglund, B. Jönsson and J. Ågren, *Metall. Trans. A*, **22A** (1991) 1745-1752.
37. C. E. Campbell and W. J. Boettinger, *Metall. Mater. Trans. A*, **31A** (2000) 2835.
38. Z.-K. Liu, *Some aspects on theoretical calculation of TTT diagram; Solid-Solid Phase Transformations*, edited by W.C. Johnson, J.M. Howe, D.E. Laughlin and W.A. Soffa, The Minerals, Metals & Materials Society, 1994, pp. 39-44.
39. T. Helander, J.-O. Nilsson and J. Ågren, *ISIJ Internat.*, **37** (1997) 1139-1145.
40. A. Engström, J. E. Morral and John. Ågren, *Acta mater.*, **45** (1997) 1189-1199.
41. A. Engström and J. Ågren, *Defect and Diffusion Forum*, **143-147** (1997) 677-682.

42. Å. Gustafson, L. Höglund and J. Ågren, *Proceed. Advanced heat resistant steel for power generation* ed. by R. Viswanathan and J. Nutting, San Sebastian, Spain 1998, 270-276.
43. M. Ekroth, R. Frykholm, M. Lindholm, H.-O. André, and J. Ågren, *Acta Materialia*, **48** (2000) 2177-2185.
44. B.Jönsson, *internal report:TRITA-MAC-0478*, Department of Materials Science and Engineering, Royal Institute of Technology, S-100 44, Stockholm, Sweden 1992.
45. M. Schwind, J. Källqvist, J-O Nilsson, J. Ågren and H-O André, *Acta mater.*, **48** (2000) 2473-2481.
46. T. Helander, H.C.M. Andersson and M. Oskarsson, *Materials at High Temperatures* **17** (2000) 389-396.
47. A. Borgenstam, A Engström, L. Höglund and J. Ågren, *Journal of phase equilibria*, **21** (2000) 269-280.
48. J. Ågren, *J. Phys. Chem. Solids*, **43**(1982), 385-91.
49. A. Engström: Dissertation, Division of Physical Metallurgy, Royal Institute of Technology, S-10044, Stockholm, Sweden, (1996).
50. M. Hillert: *Acta met.*, **19**(1971) 769-78.
51. L. Onsager, *New York Academy of Sci. Annal*, **46** (1945/46) 241.
52. L.S. Darken, *Trans AIME*, **180** (1949) 430-438.
53. A. Engström and J. Ågren, *Z. Metallkd.*, **87** (1996) 92-97.
54. T. Yamamoto, T. Takashima, K. Nishida, *Trans Jpn. Inst. Met.*, **21** (1980) 601.
55. B. Jönsson, *Z. Metallkd.*, **83**(1992) 349-355.
56. A .Bjärbo and M. Hättestrand, *Metall. Mater. Trans A*, **32A** (2001) 19-27.