Open Calphad macro examples

This is a short description of the macro files used to test Open Calphad (OC) and to demonstrate its facilities.

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Contents

1 Introduction

Open Calphad is an initiative of a group of scientists interested to develop a free software for thermodynamic calculations in multicomponent systems. It can be downloaded from

http://www.opencalphad.org or as a prerelease from the opencalphad repository at

http://www.github.com/sundmanbo/opencalphad

There is extensive documentation and several publications[15Sun1, 15Sun2] describing this initiative and the software. For a general description of the Calphad technique and application please read [98Sau] and for a description of thermodynamic modeling and assessments see [07Luk]. For a comprehensive introduction to thermodynamics see [08Hil].

The OC software is modular and includes

- basic libraries for numeric and command handling,
- the General Thermodynamic Package (GTP) for thermodynamic models,
- the Hillert Minimizing System (HMS) for equilibrium calculations,
- the Step, Map and Plot (SMP) package for step, map and plotting connected to the GNUPLOT graphical software,
- the Database Development System (DDS) for assessment of experimental and theoretical data in terms of thermodynamic model parameters,
- the Application Software Interface (OCASI) to provide thermodynamic data to other software including multi-threading and an isoC binding for C++ and other programming languages.

The software code is free with a GNU GPL license. Most of the software is written in the new Fortran 08 standard. Any skilled programmer interested use it in applications, develop or add to the software is welcome. The software has been tested for use in parallel with the OpenMP standard. For the use of OC in commercial software another license is needed.

The graphics are generated by GNUPLOT, which is another free software the user must install separately. The OC software creates a command and data file, ocgnu.plt, that can be run by GNUPLOT from the OC software. I have not bothered to implement all facilities provided by GNUPLOT but the ocgnu.plt file can be edited for users who are interested to explore the extensive faciliteis of GNUPLOT.

OC has a classical command interface, there is no "click and run" facility. If you prefer that please use a commercial software or you are welcome to develop one for OC.

The macro files contain commands to execute the OC software. Study the macros to learn how to calculate various things. They contain comment lines, which start with "@$" and "stops","@&". After each plot the user must click in the graphical window to continue.

The macros are regularly used to test for errors in the software during the development. There are two "super macro" all.OCM and all2.OCM, which executes all the macros. The reason for two macros is that there are some "memory leaks" in the Windows OS as all memory used is not returned after finishing a calculation. As shown by the examples there are still many more errors inside OC to fix also.

2 Macros

Changes in the command structure (new commands, new questions etc) require changes in the macro files and old macro files many not work on a new release and vice versa. The commands here are for OC version 3.

After installing OC please verify our installation by executing all the macros. The data files needed are provided with the macro files.

2.1 Single equilibrium calculations

The macros contain single equilibrium calculations. There are no diagrams.

2.1.1 Equilibria in pure Fe

Macro file unary.OCM

Calculation of single equilibrium for a pure element, Fe. Initially OC could not change the set of stable phases when it had to replace the only stable phase with another if the Gibbs phase rule did not allow it to have two stable phases.

The example just shows how to set various conditions of a simple system, including enthalpy, H. It shows that if you first makes a calculation for conditions on T, P and the size of the system N, you can then set the calculated enthalpy value as condition and release the condition of T to recalculate that temperature. And if you change the value of H then T will change and maybe also the stable phase.

Currently there is a bug that one cannot combine a condition on the mass of the system (B) and the enthalpy. Another bug is that OC cannot step across a phase boundary in a unary (or binary) system. It can step across a change in the set of stable phases for multicomponent systems as shown in example 2.2.1

2.1.2 Equilibria and melting T of a 6 component high speed steel (HSS)

Macro file melting.OCM

Calculations of equilibria in a multicomponent steel. As the previous example it shows the flexible way of setting conditions. First a straightforward calculation with T, P and mole fractions. Then the command **calculate transition** is used to calculate the melting temperature directly.

Then the carbon content of the fcc phase, x(fcc,c), is set as condition rather than the overall carbon content, x(c). Then we set the status of the liquid phase as fix with zero amount, and the condition on T is released to calculate the new melting T. Then the current value of the enthalpy, H, is set as condition and the size of the system, N is released. The equilibrium of the system does not change, just the way we control the system.

When the enthalpy of the system is changed the size of the system changes as that is the only way it can change its enthalpy.

2.2 Property diagram calculations

These are calculations with a single independent axis variable.

2.2.1 Diagrams for phase fractions, compositions, heat content and heat capacity for a HSS

Macro file step1.OCM

A similar steel like in the example 2.1.2 is used. In these steels there is normally a cubic carbide stable and this is described by the same model for FCC phase as the austenite. To make it easier to identify these two phases we can enter a second composition set with additional pre- and suffixes and predefined default composition limits. The software will try to find the composition set with closest default composition if it has two composition sets stable for a phase. We must then also set a default composition for the austenite (the first composition set).

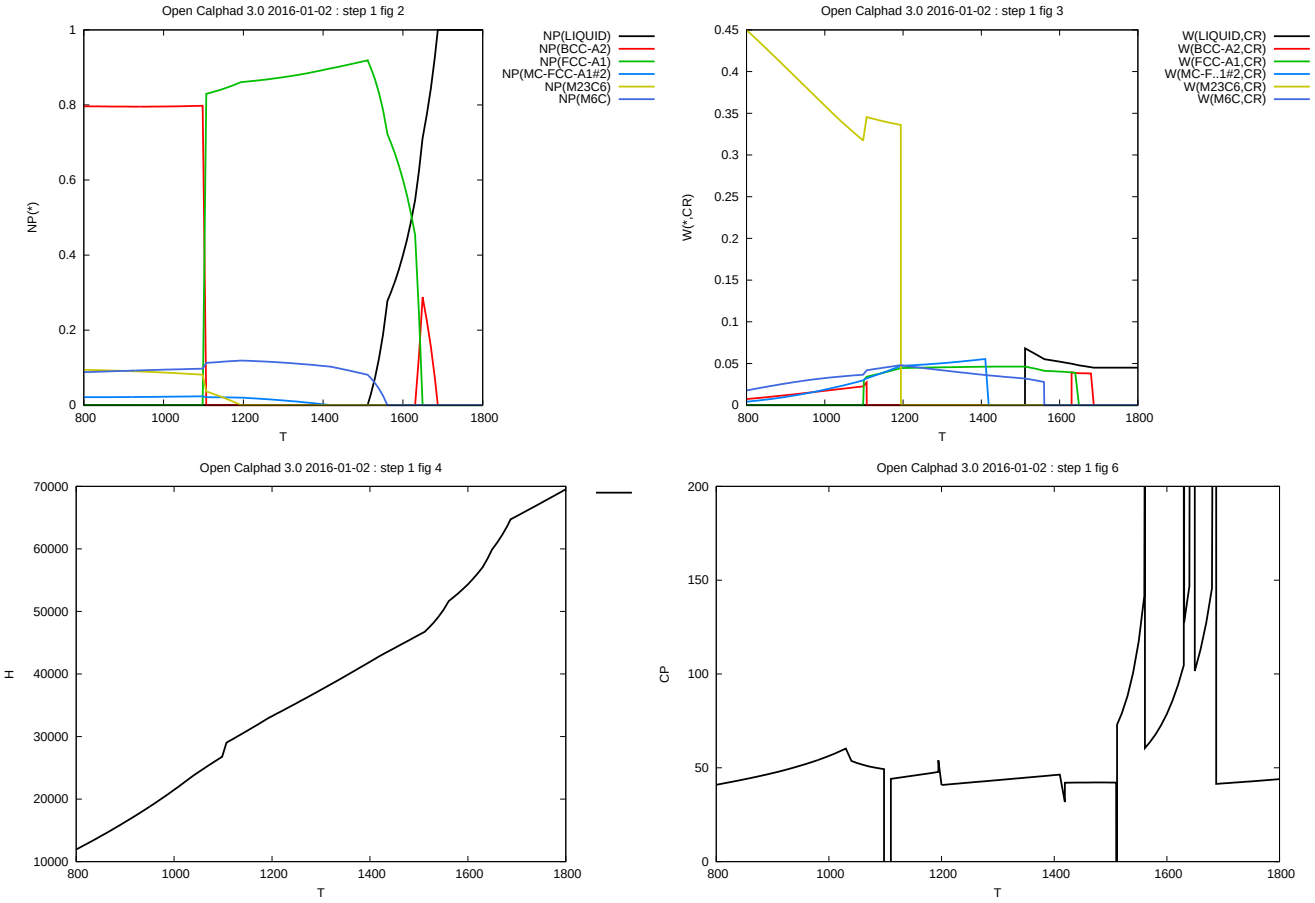
When we list the result after the equilibrium calculation we find two FCC phases, one with the MC prefix which is high in carbon. That is the cubic carbide, the other FCC phase is the austenite.

Then we set T as an axis variable with the limits 800 and 1800 K and an increment of 10 and calculate equilibria along this axis. During the calculation the exact T value for phase changes is calculated and all calculated equilibria are stored. They can be listed and also the list of all stored node points with phase changes. Any property value or derived symbol for these equilibria can be listed or plotted.

For plotting the GNUPLOT software is used. The OC interface to GNUPLOT uses only a minimum of the extensive facilities of GNUPLOT. The first plot is how the amount (in moles) of the phases varies. The second plot the Cr content in the stable phases, then a plot of the enthalpy variation and finally we enter and plot a symbol $C_P = H.T$ which is

the partial derivative of the enthalpy with respect to T, i.e. the heat capacity, but across a phase transition it also includes what is normally called the latent heat.

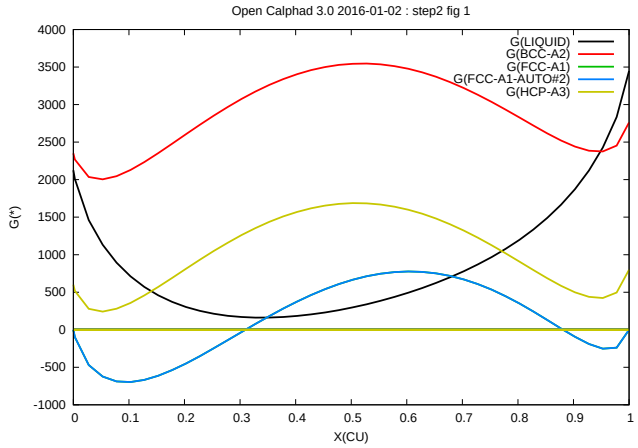
There is a software bug that the plot of C_P shows negative values at the phase changes because the storing of calculated equilibria is not fully compatible with such a calculation.



2.2.2 Diagrams for Gibbs energy curves for Ag-Cu

Macro file step2.OCM

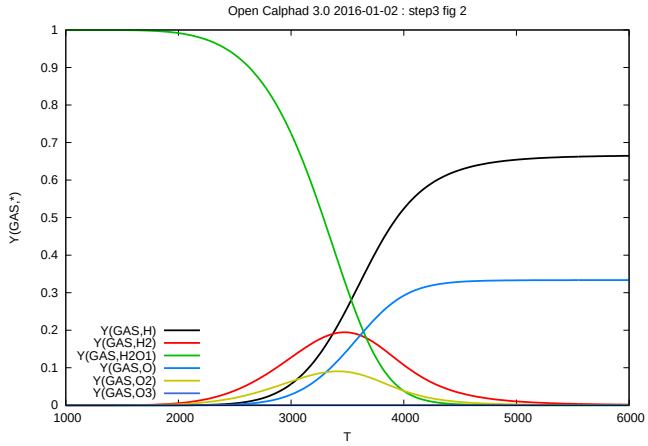
This was my first calculation of Gibbs energy curves with OC so I have kept it. In this and several other plots there are spurious horizontal and vertical lines due to the current simple interface to GNUPLOT.

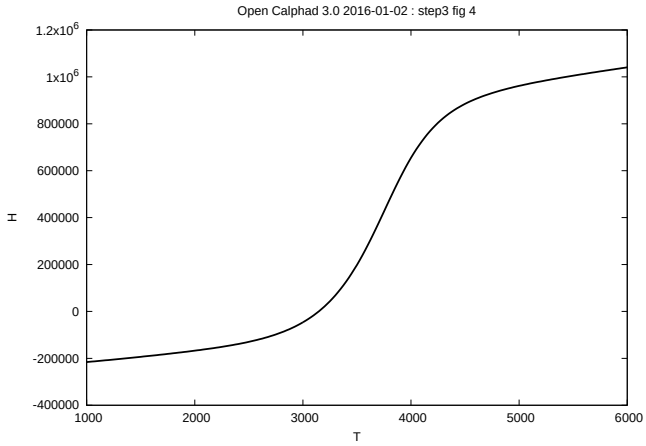


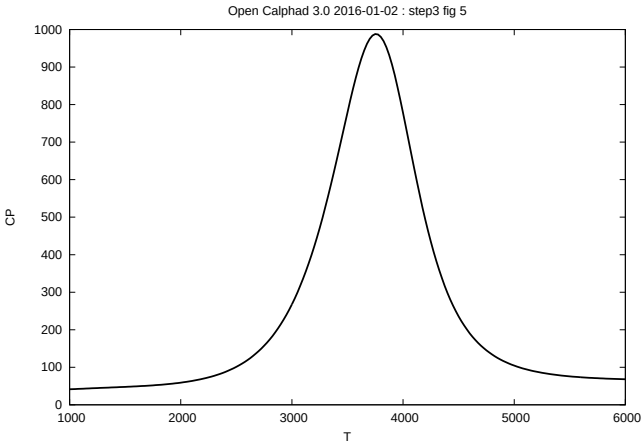
2.2.3 Diagrams for gas phase speciation, heat content and heat capacity

Macro file step3.OCM

This calculates the speciation of H_2O in a gas phase between 1000 and 6000 K. At low T the system consists of just the H_2O molecule but around 2000 K it splits up in several molecules and above 5000 K only atomic H and O are present. This changes the configurational entropy and enthalpy and thus also the heat capacity as shown.



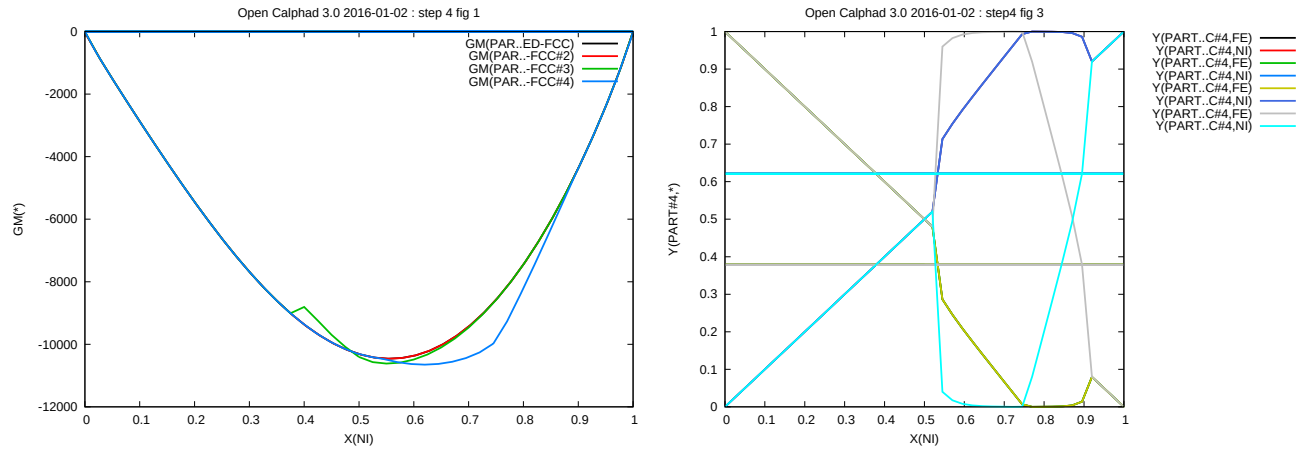




2.2.4 Diagrams for constitution and Gibbs energy curves for ordered FCC in Fe-Ni using DFT data

Macro file step4.OCM

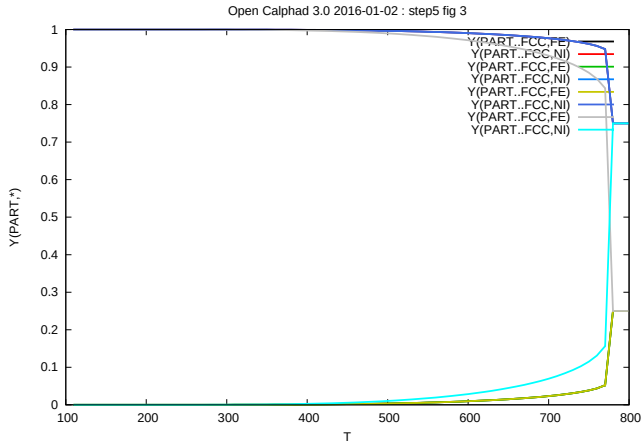
DFT calculated values for the different ordered forms of FCC in the Fe-Ni system is used to calculate the Gibbs energy curves and sublattice occupancy.

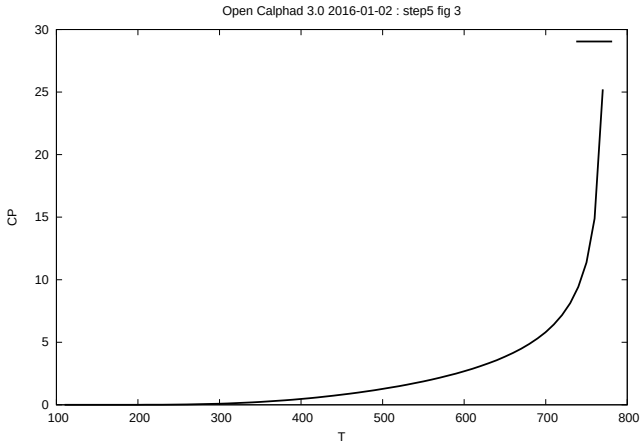


2.2.5 Diagrams for constitution and heat capacity for DFT calculated ordered FCC in Fe-Ni at Ni_3Fe

Macro file step5.OCM

The same DFT data used for a fixed composition $FeNi_3$ to calculate the constituent fractions and their contribution to the heat capacity.

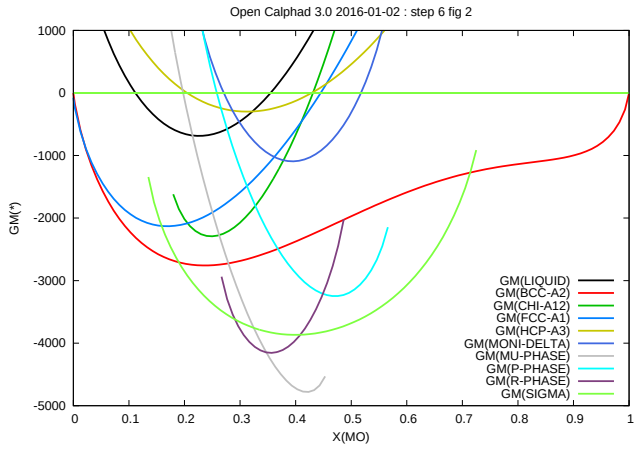




2.2.6 Diagram for Gibbs energy curves for Fe-Mo at 1500 K

Macro file step6.OCM

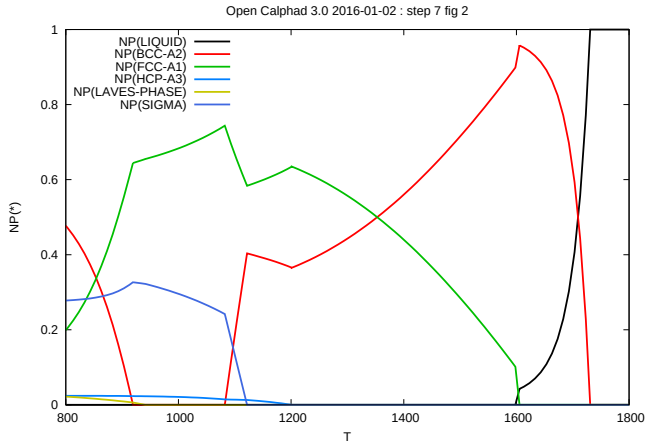
The Gibbs energy curves for the phases in the Fe-Mo system at 1400 K.

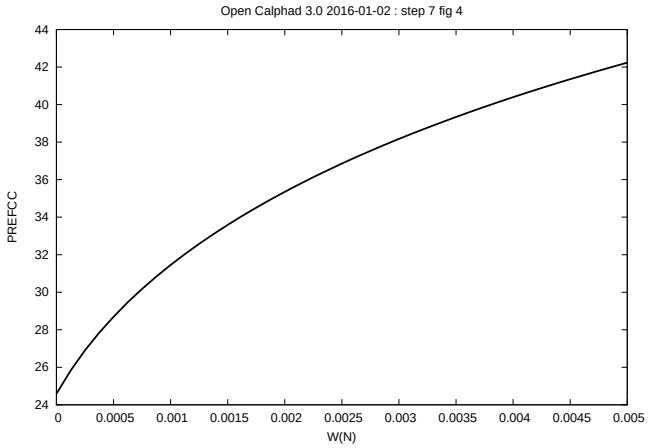


2.2.7 Diagram for phase fractions and PRE for a duplex stainless steel

Macro file step7.OCM

This example calculate the phase fraction fractions of a duplex stainless steel and show how to calculate the PRE (Pitting corrosion Resistance Equivalence) as a function of the nitrogen content at temperature of the duplex structure.

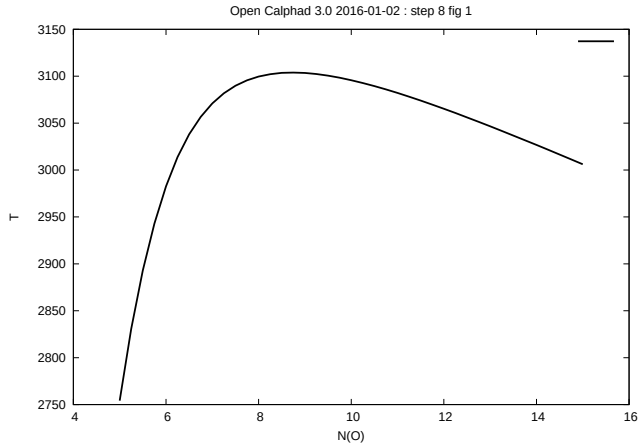


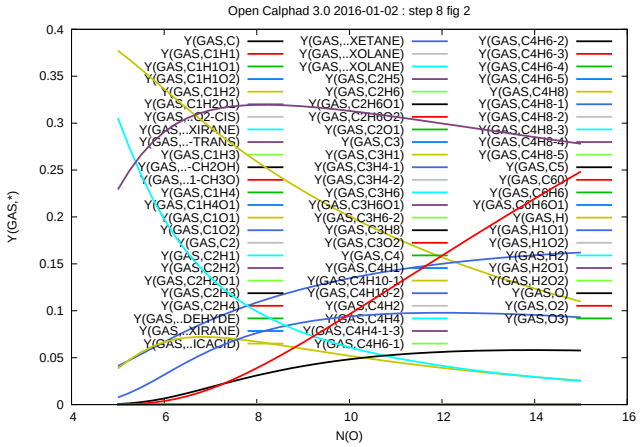


2.2.8 Adiabatic flame temperature of propane (C_3H_8) as function of the amount of O

Macro file step8.OCM

In this example we first calculate the adiabatic flame temperature of propan (C_3H_8) in pure oxygen. First using a stoichiometric fraction of N(O)=7, then at variable oxygen content. We also show how a variation of the chemical potential of carbon affects the amount of carbon.





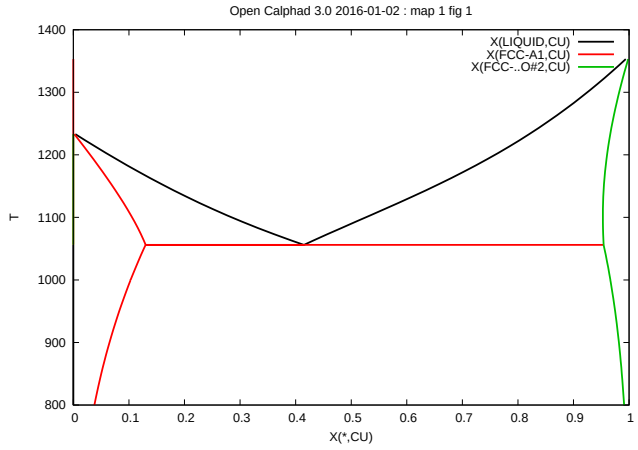
2.3 Phase diagram calculations

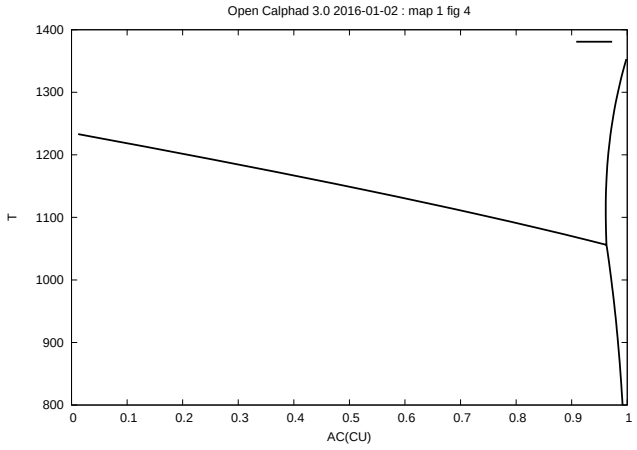
Only binary diagrams works properly. Ternary isopleths cannot be plotted at present and other higher order diagrams usually have some missing lines.

2.3.1 Phase diagram for Au-Cu plotted with various axis variables

Macro file map1.OCM

The simple eutectic binary phase diagram for Au-Cu. There is a miscibility gap in the FCC phase which is detected by the grid minimizer.

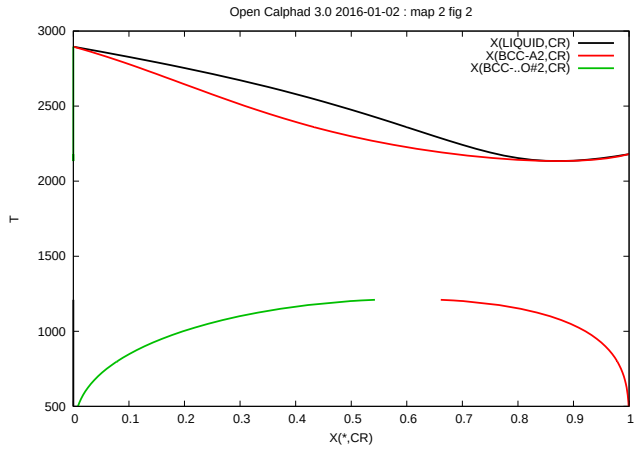


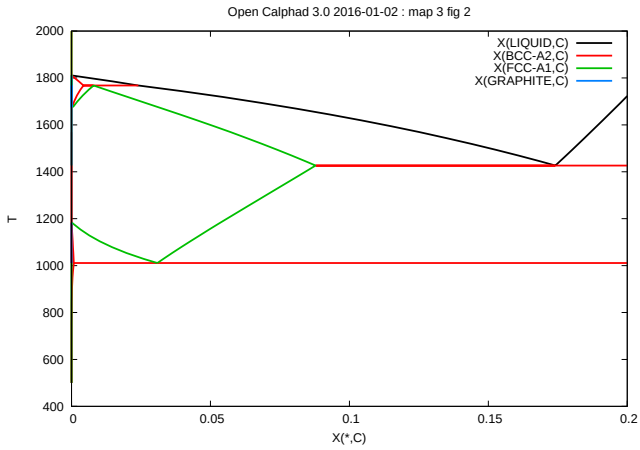


2.3.2 Phase diagram for Cr-Mo with miscibility gap

Macro file map2.OCM

There is also a miscibility gap in the BCC phase in the Cr-Mo system. As can be seen the mapping fails to calculate the top of this miscibility gap.





2.3.3 Phase diagram for C-Fe

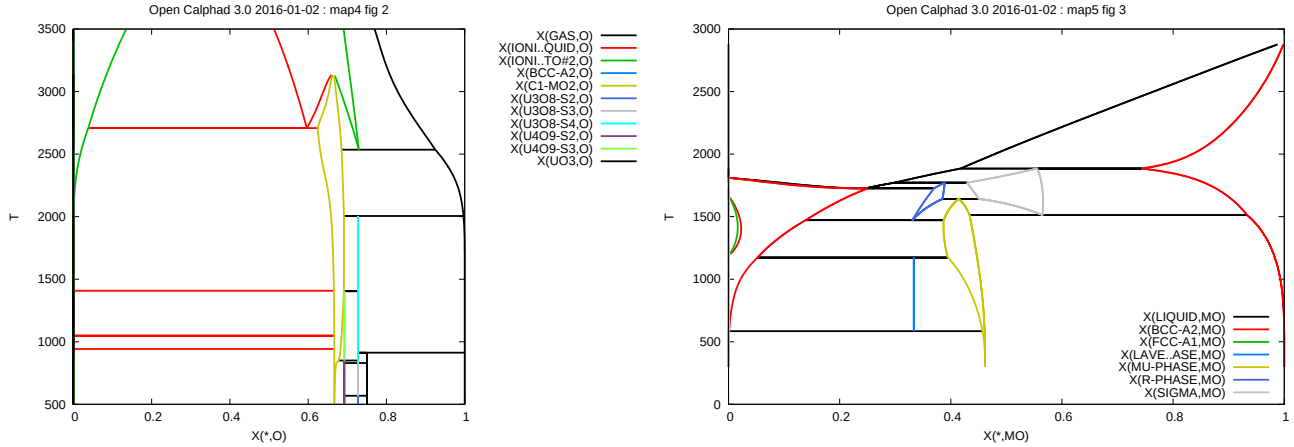
Macro file map3.OCM

The phase diagram for C-Fe system is a must.

2.3.4 Phase diagram for O-U

Macro file map4.OCM

The phase diagram for O-U requires to start points as the mapping does not manage to pass the congruent melting point.



2.3.5 Phase diagram for Fe-Mo

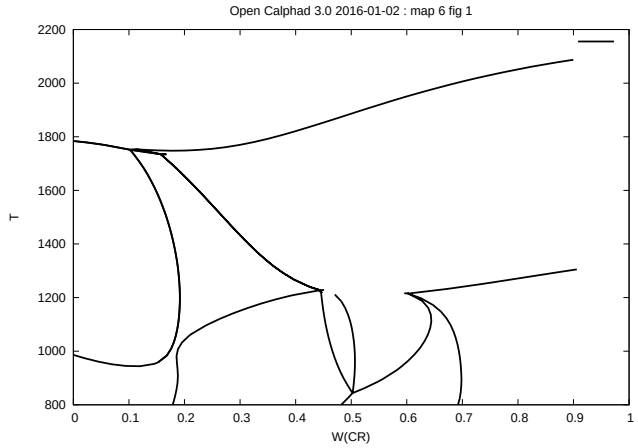
Macro file map5.OCM

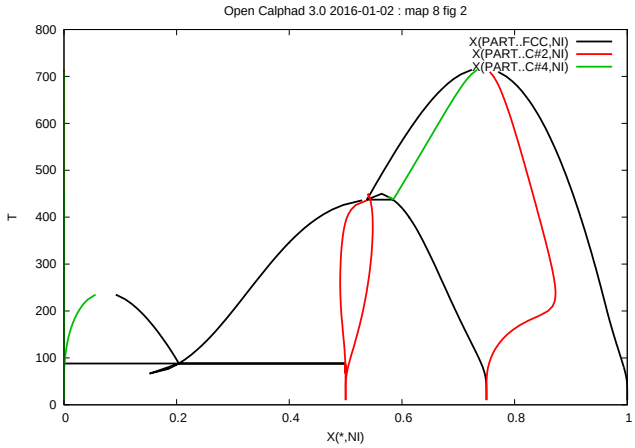
The Fe-Mo system requires also a separate start point for the γ-loop. The main problem to map it was the peritectic equilibrium between BCC+LIQUID+R-phase, the difference between the peritectic temperature and the minimum in the bcc/liquid solubility lines is less than 0.2 K.

2.3.6 Isopleth phase diagram for an 18-8 stainless steel: Cr-Fe-Ni

Macro file map6.OCM

This is an isopleth for 8 mass% Ni and varying amount of Cr. The calculated lines are correct but several lines are missing. This will be considered in the next version of OC.





2.3.7 Metastable phase diagram for ordered FCC in Fe-Ni using DFT data

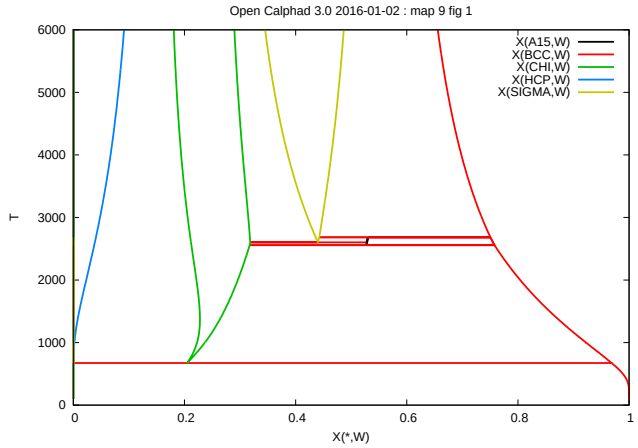
Macro file map8.OCM

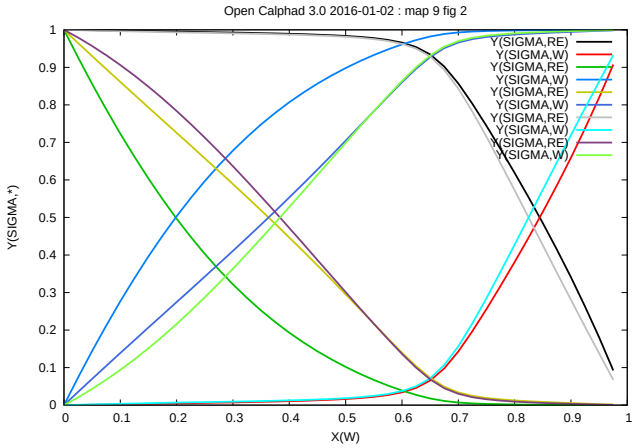
The phase diagram for metastable fcc-Ni using the same DFT data as in the earlier STEP calculations. This requires 3 startpoints. The $L1_2$ and the $L1_0$ ordered forms are well described. The miscibility gap on the Al-rich side is sometimes calculated, sometimes it fails. It is metastable because Fe should be bcc at these temperatures.

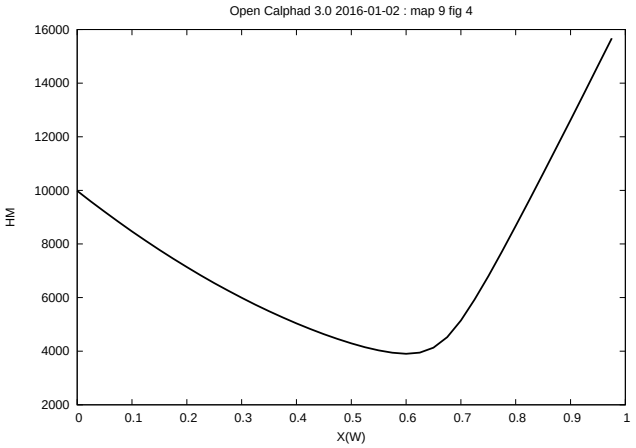
2.3.8 Metastable Re-W phase diagram based on DFT calculated data

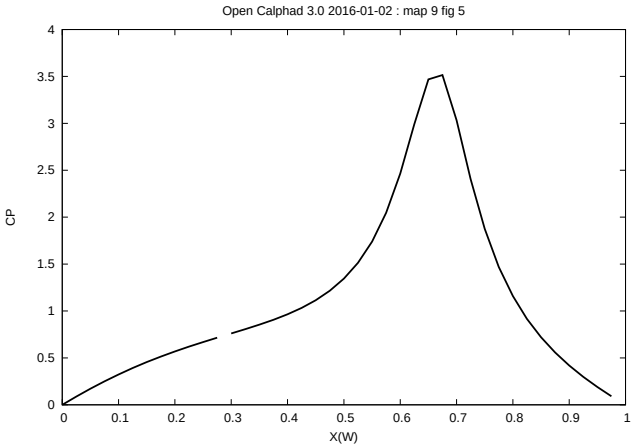
Macro file map9.OCM

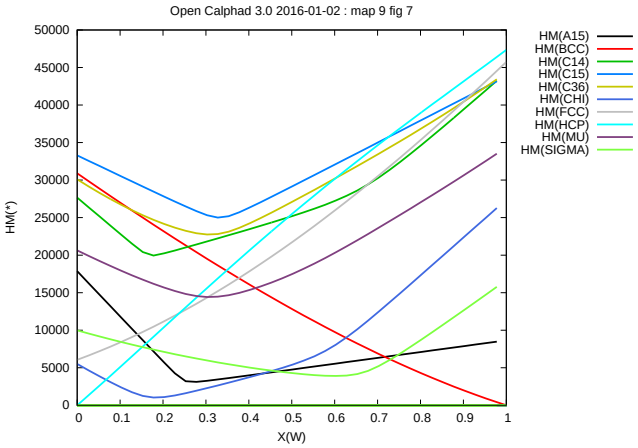
DFT calculated data for the TCP phases as well as bcc and hcp in the Re-W system is entered and the phase diagram calculated. Additionally STEP calculations giving site fractions for the σ phase and also the enthalpy and heat capacity. Finally the Gibbs energy and enthalpy curves for all phases are calculated and plotted.







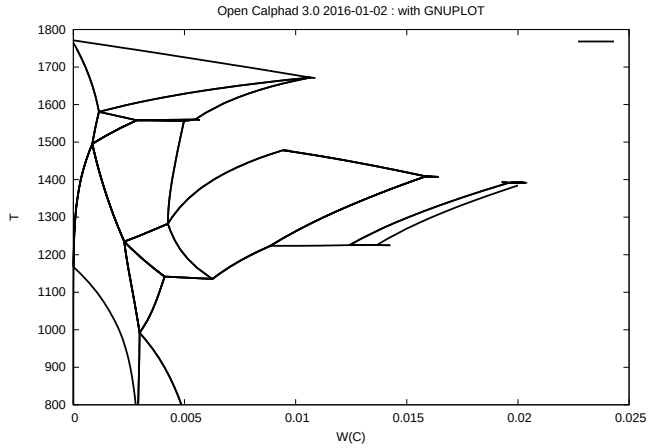




2.3.9 Incomplete isopleth calculation of a HSS

Macro file map7.OCM

The phase diagram for this 6 component High Speed Steel was much better when version 2 was released. So some things goes backward. For version 4 I will have a look at STEP and MAP again.



2.4 Miscellaneous calculations, assessments, parallel etc

This section may contain various examples.

2.4.1 Calculating 21 equilibria in parallel

Macro file parallel1.OCM

This macro was the first attempt to calculate in parallel using the enter many_equilibrium command. It is more or less superseded by the next more complex case.

2.4.2 Enter a table with 400 equilibria and calculate them in parallel

Macro file parallel2.OCM

In the macro some 400 equilibria are entered using the enter many_equilibria command. They are then calculated in parallel (by the parallel version of OC). On a PC with 4 CPU/2 treads the gain in speed is almost a factor of 4.

2.4.3 A calculation with 20 elements and 191 phases

Macro file allcost.OCM

This macro calculates a few equilibria with the largest free database I have access to, from the light alloy assessment project COST507. The quality of the database is questionable for multicomponent calculations but many binary and ternary systems are well assessed. In this case I was just interested to test OC with a very large system, 20 elements and 191 phases.

2.4.4 Setup of an assessment with fictitious binary experimental data

Macro file opttest1.OCM

A tentative start of an assessment of a phase in a binary system. Shows how to enter experimental data and optimizing coefficients and how the weighting can change the results.

2.4.5 Start of an assessment of the Cu-Mg binary system

Macro file opttest2.OCM

This enters a full set of experimental data for the Cu-Mg system and performs the first step in the assessment by fitting the data for the liquid phase. The enter many_equilibria command is used to enter several tables of experimental data.

The experimental data has been converted to an OC macro file from a Thermo-Calc POP file created by Malin Selleby and Christine Guéneau. In OC the experimental data is entered as a macro file.

The BIG problem with assessments in OC is that there is no PAR file. This is one of the difficult things to implement.

3 Summary

That is all

References

[98Sau] Nigel Saunders and Peter Miodownik, *Calphad*, Pergamon Materials series, Vol 1 (1998)

[07Luk] H Leo Lukas, Suzana G Fries and Bo Sundman, *Computational Thermodynamics*, Cambridge Univ Press (2007)

[08Hil] Mats Hillert, *Phase equilibria, phase diagrams and phase transformations*, 2nd ed., Cambridge University Press (2008)

[15Sun1] Bo Sundman, Ursula R Kattner, Mauro Palumbo and Suzana G Fries *OpenCalphad - a free thermodynamic software*, (Open Access) Integrating Materials and Manufacturing Innovation (2015) **4:**1

[15Sun2] Bo Sundman, Xiao-Gang Lu and Hiroshi Ohtani, Computational Materials Science, **101** (2015) 127-137.