Calculation of solidification of steels under back diffusion conditions using ChemSheet

Risto Pajarre
Technical Research Centre of Finland

Business from technology

Back diffusion

- In solidifying steels, in addition to thermodynamics also diffusion and convection control the phase formation.
- To avoid computationally intensive diffusion calculations, the problems are often solved using approximate solutions based on some simplifying assumption such as:
  - Full equilibrium (diffusion is assumed to be fast enough that equilibrium between solid and liquid is always maintained
  - Scheil cooling, where once formed solid is assumed to be effectively inert. Liquid is assumed to be completely mixed and local chemical equilibrium is assumed on the advancing solidification front.
- The ability in ChemSheet (or ChemApp) calculations to set constraints on arbitrary constituents, reactions or phase transformations allows also equally easy use of more sophisticated assumptions for back diffusion, such as:
  - paraequilibrium, where the small interstitial solutes in solid iron are assumed to be able to move between solid and liquid, while the larger metal atoms in solid are assumed immobile.

Paraequilibrium calculation schema

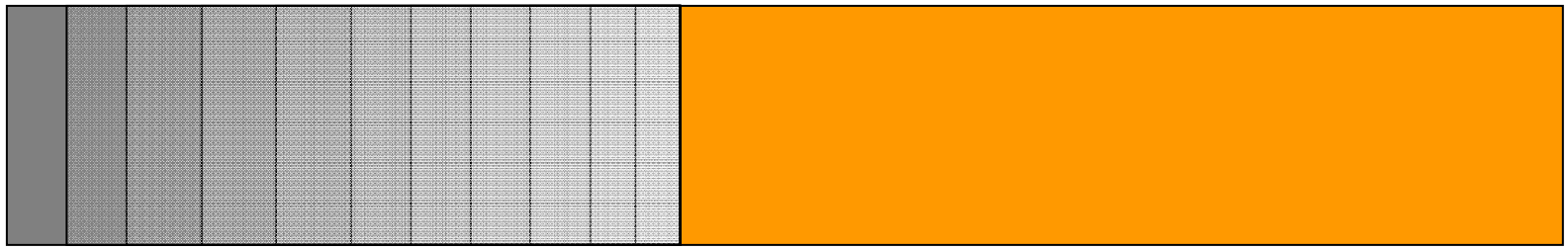
Previously formed solid, partially "inert"

- no diffusion of at least some constituents to or from melt
- Those constituents that can diffuse between solid and melt are assumed to reach chemical equilibrium between the phases
- Having all constituents inert in a solid phase leads to Scheil-Gulliver behaviour, if none is inert, full equilibrium is reached

Remaining melt assumed to reach equilibrium (with the effect of diffusive mass transfer from solid included) in the new temperature. The corresponding amount of new solid is formed

Calculation schema (II)

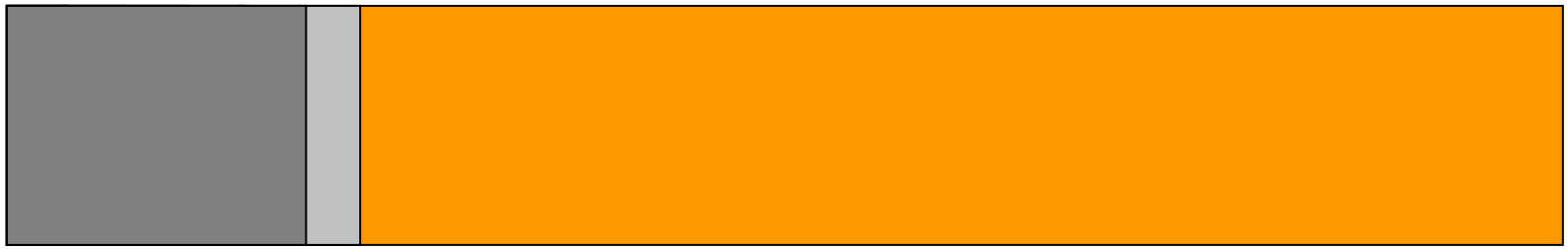
Applying the outlined calculation procedure directly leads to system with one new solid layer (which has depending on the composition, temperature and thermochemistry one or more solid phases) for each cooling step.



This is initially cumbersome to implement, and becomes impossible after a while using ChemApp because of the number of components required.

Calculation schema (III)

As a simplification, in the calculations it has been assumed that to calculate the chemical potential for the diffusive species in the solid, the layered structure can be replaced by one layer where the solid phases have a weighted average composition of those they have in the individual layers



It is still possible to keep track on the composition of the individual layers as they are formed

System structure (viewed by using CSFAP)

- In the example case we have one **liquid** ('Fe-liquid') and two **solid** ('FCC_A1' and 'M7C3') phases
- In the data file, there are two copies of the solid phases, the second one with the '**_restricted**' suffix

Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C3
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1

System structure (viewed by using CSFAP)

- The amounts of substances in the '_restricted' phases are prevented from equilibrating with the liquid by new system components, specific for the constrained phases

Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C3
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1

System structure (viewed by using CSFAP)

- Auxiliary pseudo phases can be used to lift any individual restrictions by allowing the formation of the corresponding pseudo phase

Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C3
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1

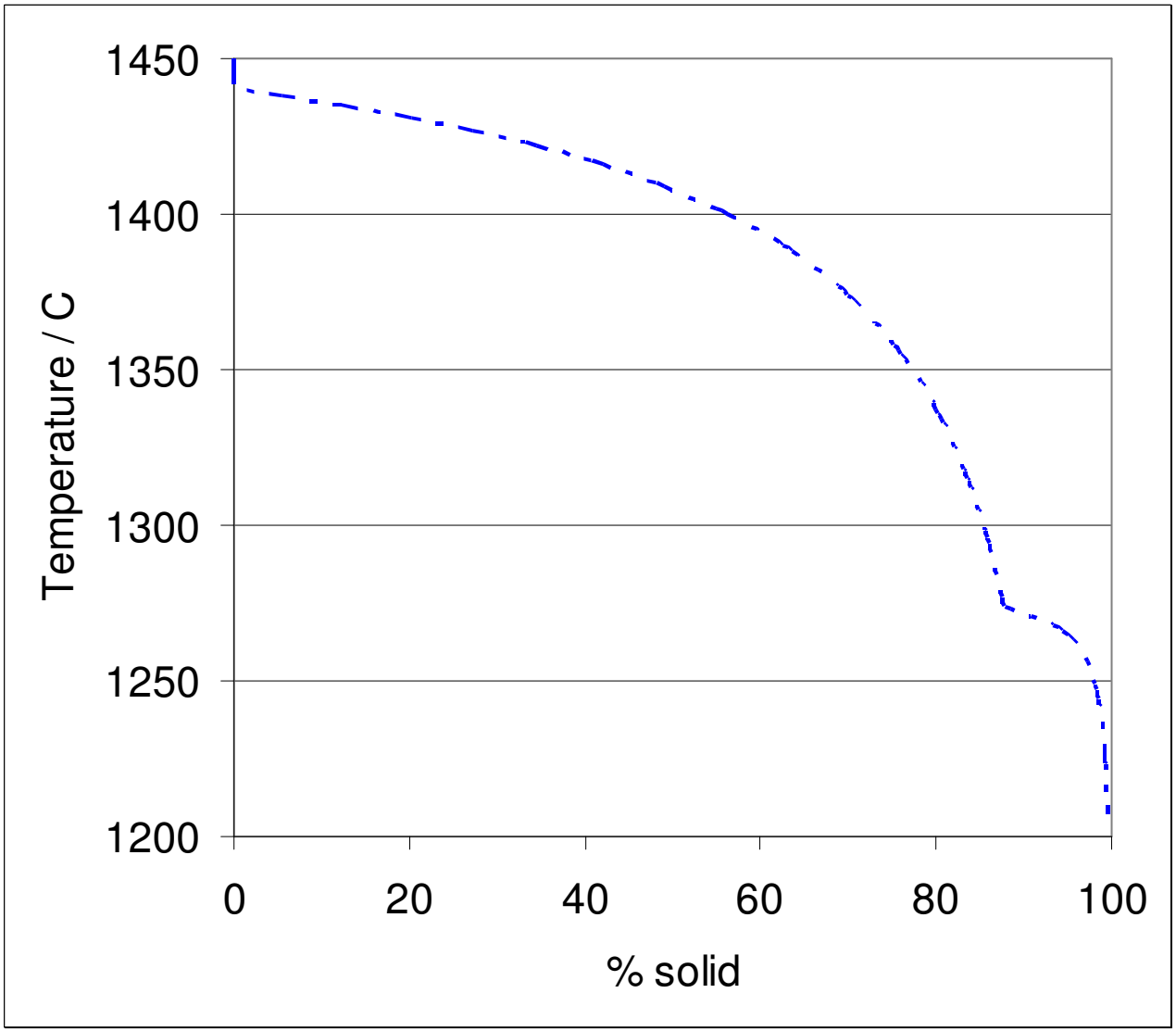
$$\mu_i^0 \equiv 0$$

System structure (viewed by using CSFAP)

- Auxiliary pseudo phases can be used to lift any individual restrictions by allowing the formation of corresponding pseudo phase
  - When all of them are 'Dormant' we have the Scheil cooling behaviour

Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C3
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1

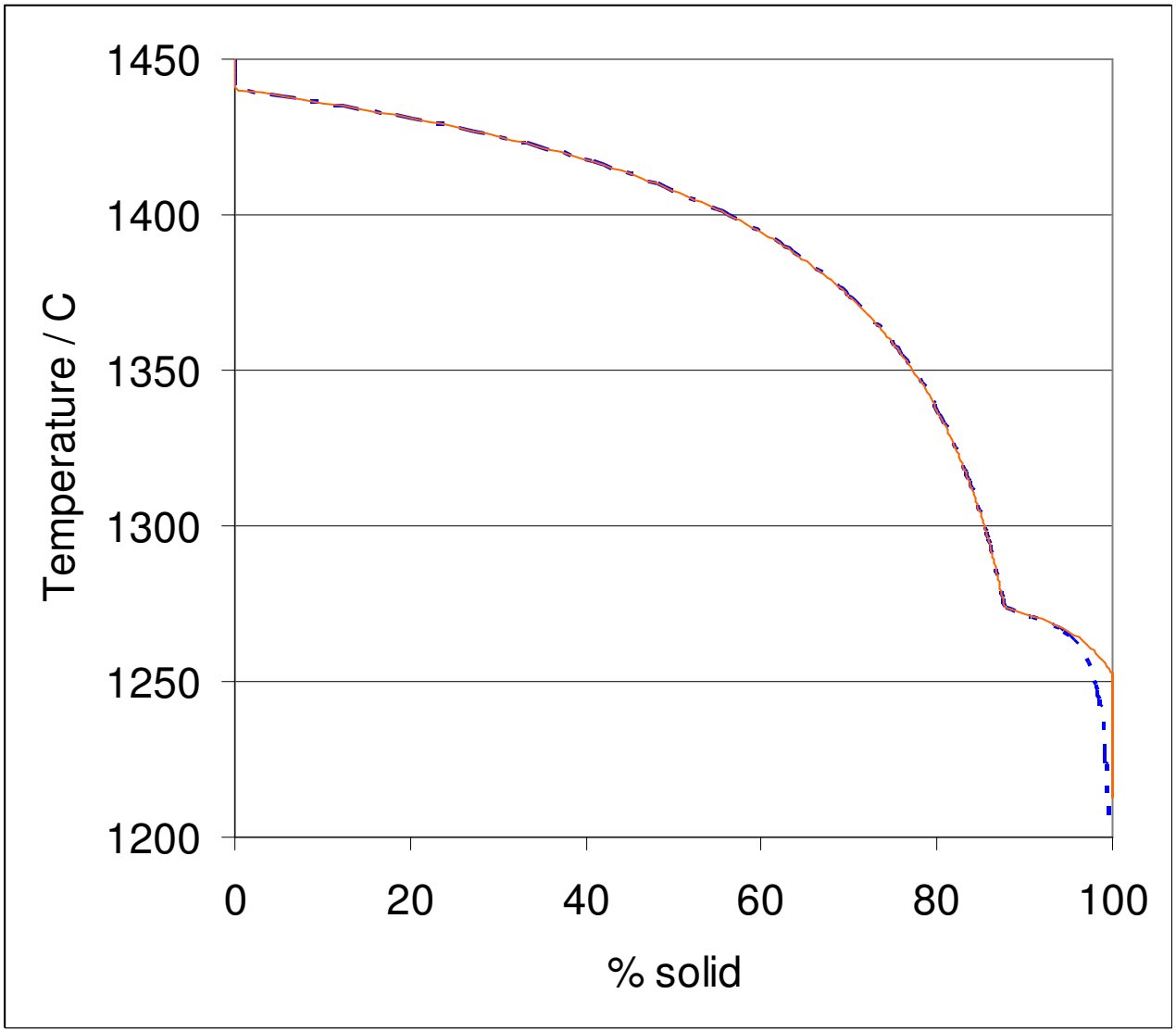
Composition:
10.84% Cr,
0.95% C in Fe



System structure (viewed by using CSFAP)

- When the formation of 'R_Cr_M7C3+' and 'R_Fe_M7C3+' are allowed, free transfer of matter from the phase 'M7C3_restricted' is allowed. In respect to FCC phase, we still have the Scheil behaviour

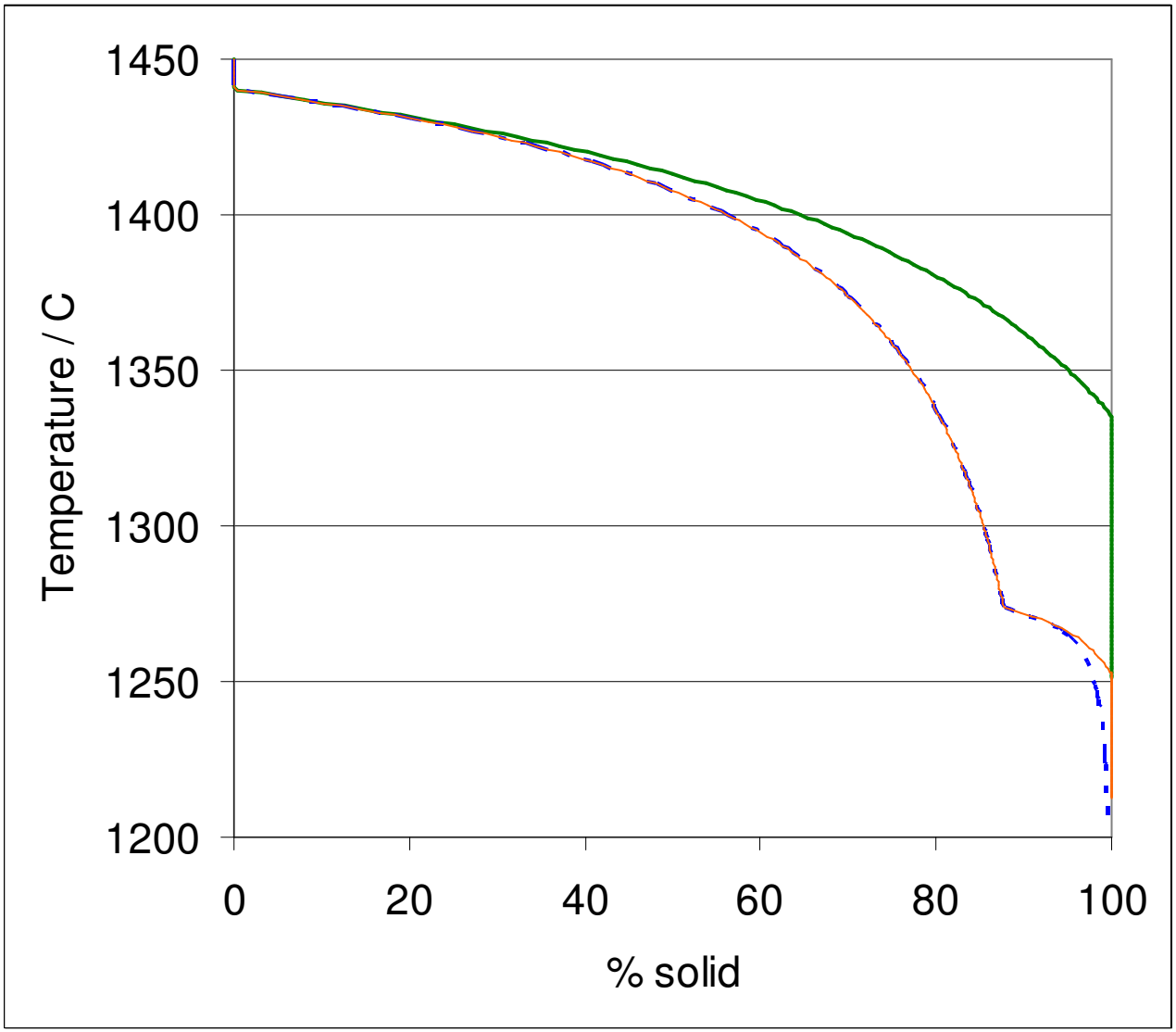
Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1


1450
1400
1350
1300
1250
1200
Temperature / C
0
20
40
60
80
100
% solid

System structure (viewed by using CSFAP)

- When additionally also the formation of 'R_Cr_FCC+', 'R_Fe_FCC+' and 'R_C_FCC-' are allowed we always reach full equilibrium between the solids and liquid

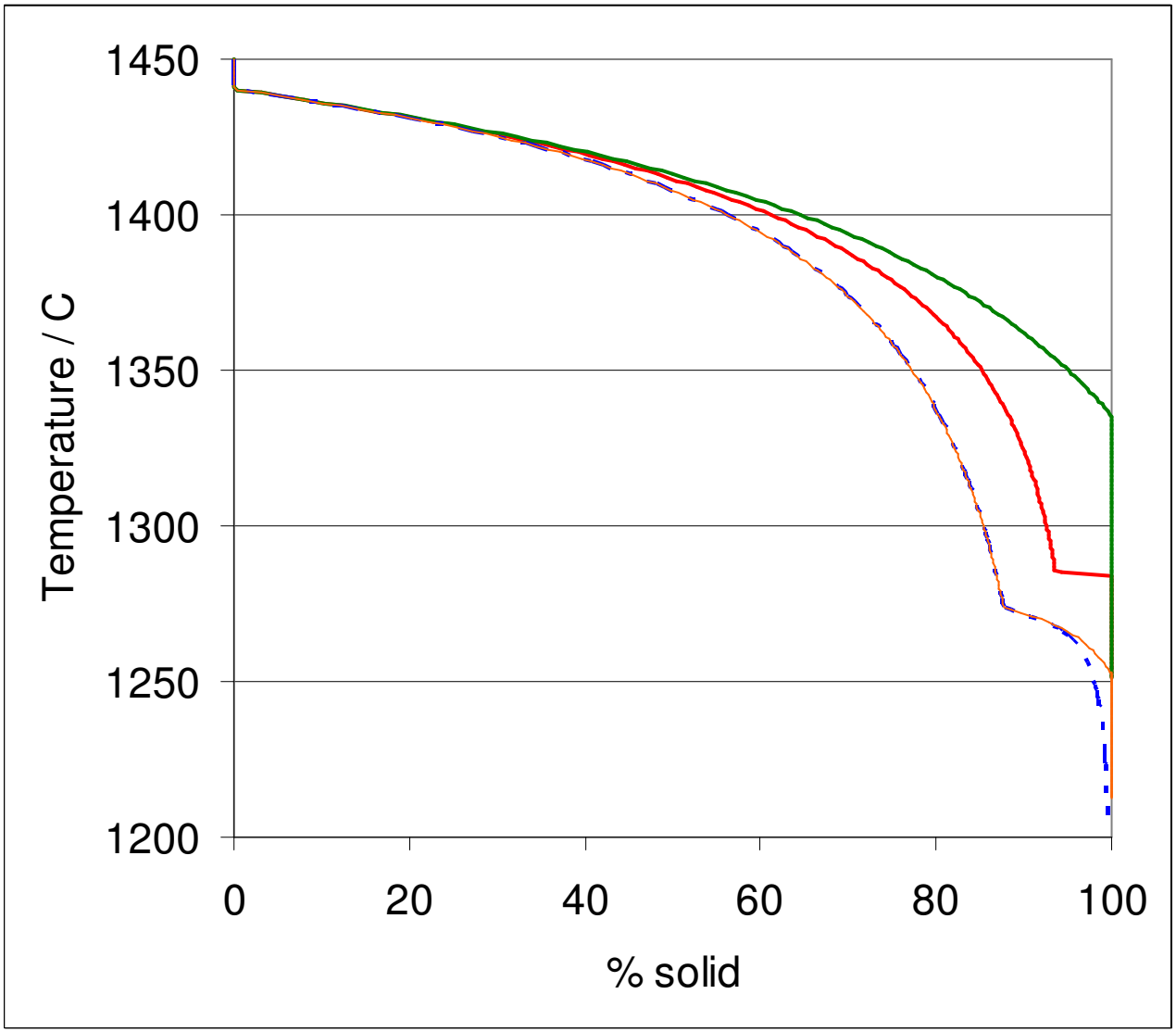
Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1


1450
1400
1350
1300
1250
1200
Temperature / C
0
20
40
60
80
100
% solid

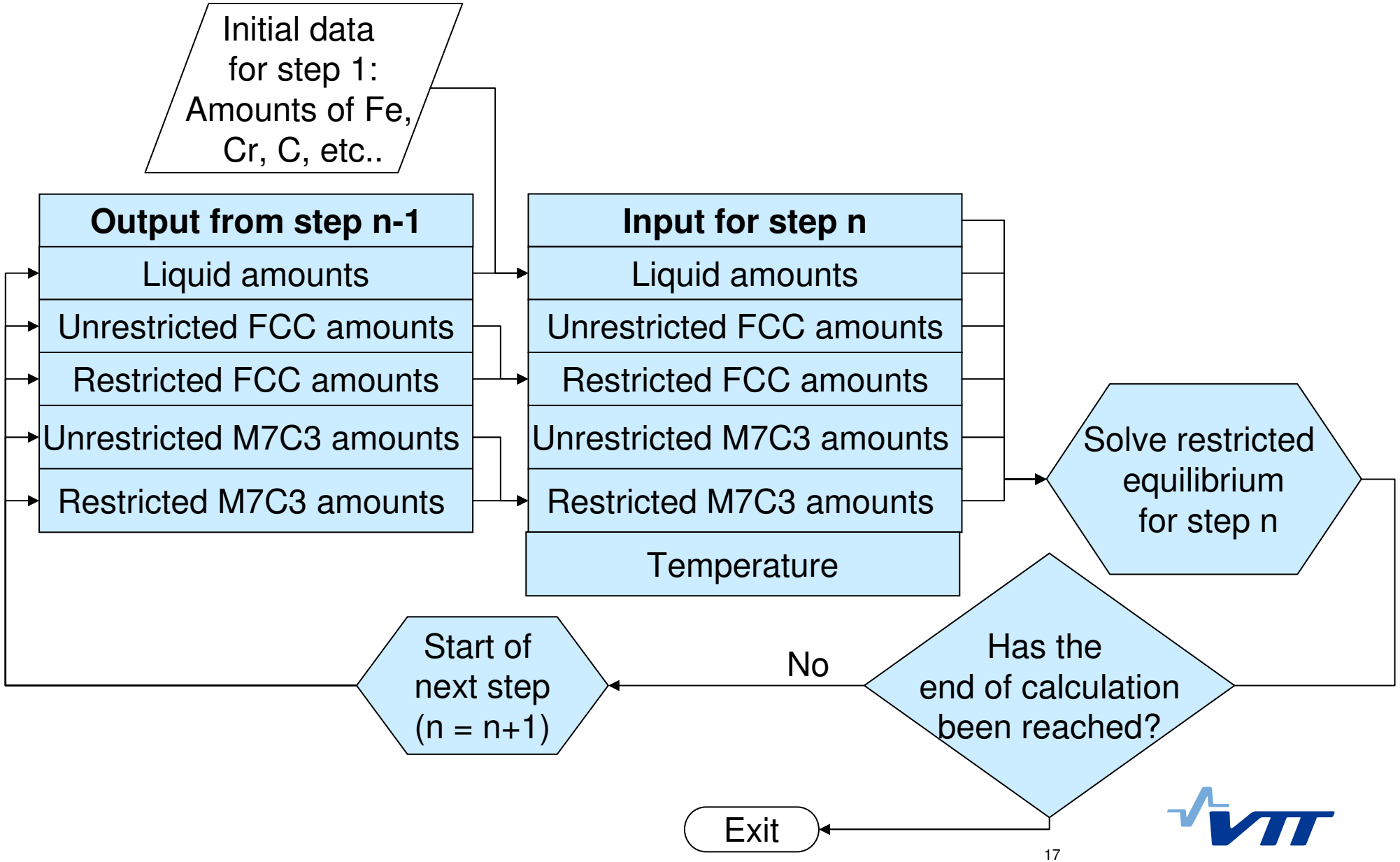
System structure (viewed by using CSFAP)

- Finally, when the formation of 'R_Cr_FCC+', 'R_Fe_FCC+' are *not* allowed but the formation of 'R_C_FCC-' is, the amounts of metallic components in formed FCC phase are 'frozen' but the transfer of additional carbon to the solid is allowed resulting in the paraequilibrium state.

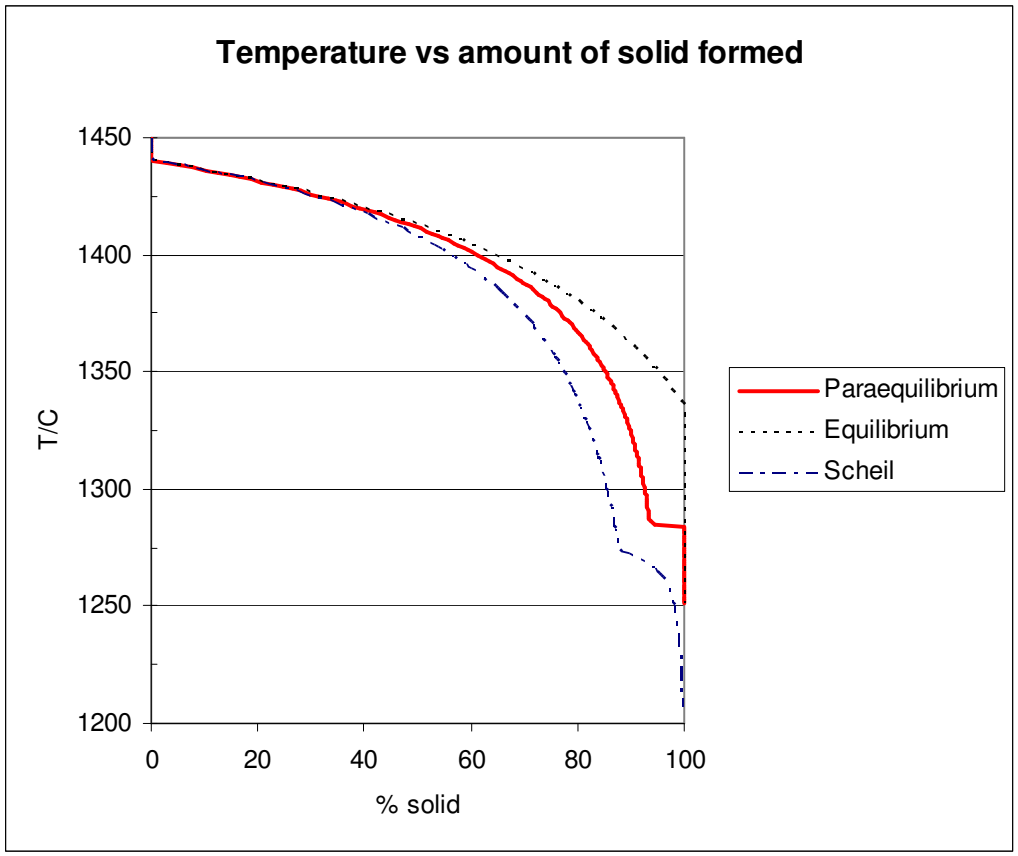
Phase	Component	Fe	Cr	C	*Cr_FCC	*Fe_FCC	*C_FCC	*Cr_M7C3	*Fe_M7C3
Fe-LIQUID	C	0	0	1	0	0	0	0	0
Fe-LIQUID	Cr	0	1	0	0	0	0	0	0
Fe-LIQUID	Fe	1	0	0	0	0	0	0	0
FCC_A1	Cr1C1	0	1	1	0	0	0	0	0
FCC_A1	Cr	0	1	0	0	0	0	0	0
FCC_A1	Fe1C1	1	0	1	0	0	0	0	0
FCC_A1	Fe	1	0	0	0	0	0	0	0
FCC_A1_restricted	Cr1C1	0	1	1	1	0	1	0	0
FCC_A1_restricted	Cr	0	1	0	1	0	0	0	0
FCC_A1_restricted	Fe1C1	1	0	1	0	1	1	0	0
FCC_A1_restricted	Fe	1	0	0	0	1	0	0	0
M7C3	Cr:C	0	7	3	0	0	0	0	0
M7C3	Fe:C	7	0	3	0	0	0	0	0
M7C3_restricted	Cr:C	0	7	3	0	0	0	7	0
M7C3_restricted	Fe:C	7	0	3	0	0	0	0	7
R_Cr_FCC+	R_Cr_FCC+	0	0	0	1	0	0	0	0
R_Cr_FCC-	R_Cr_FCC-	0	0	0	-1	0	0	0	0
R_Fe_FCC+	R_Fe_FCC+	0	0	0	0	1	0	0	0
R_Fe_FCC-	R_Fe_FCC-	0	0	0	0	-1	0	0	0
R_C_FCC+	R_C_FCC+	0	0	0	0	0	1	0	0
R_C_FCC-	R_C_FCC-	0	0	0	0	0	-1	0	0
R_Cr_M7C3+	R_Cr_M7C3+	0	0	0	0	0	0	1	0
R_Cr_M7C3-	R_Cr_M7C3-	0	0	0	0	0	0	-1	0
R_Fe_M7C3+	R_Fe_M7C3+	0	0	0	0	0	0	0	1
R_Fe_M7C3-	R_Fe_M7C3-	0	0	0	0	0	0	0	-1

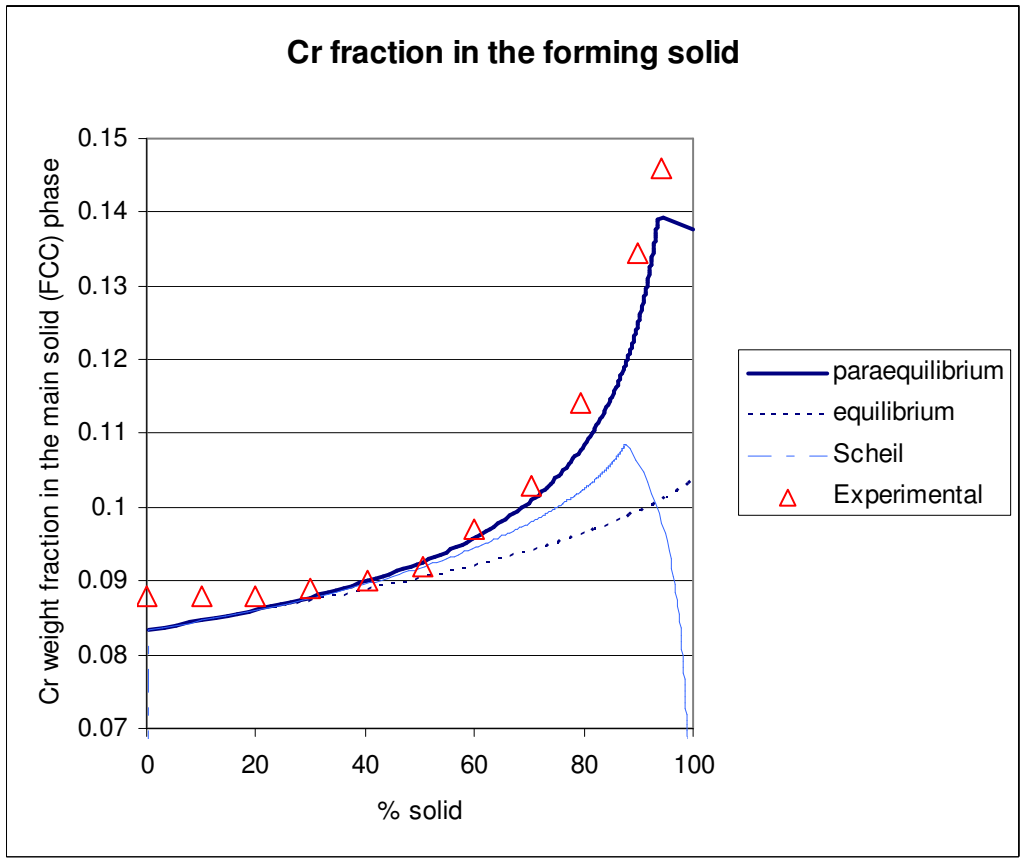

1450
1400
1350
1300
1250
1200
Temperature / C
0
20
40
60
80
100
% solid

Flow sheet schema

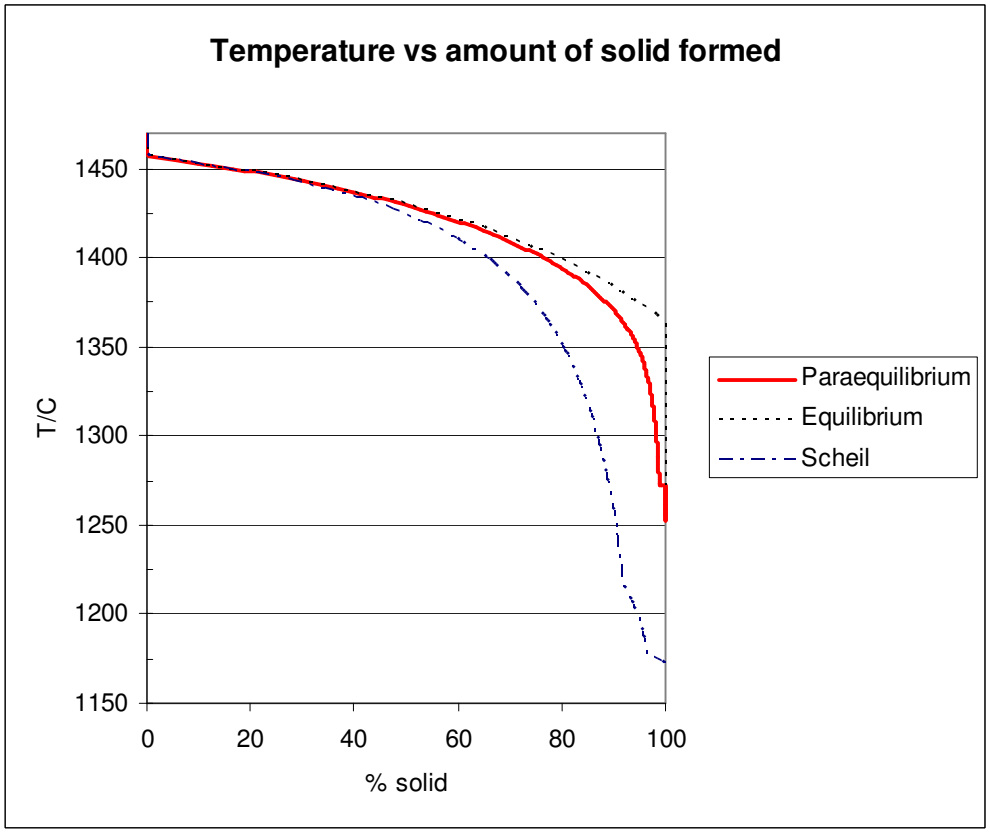


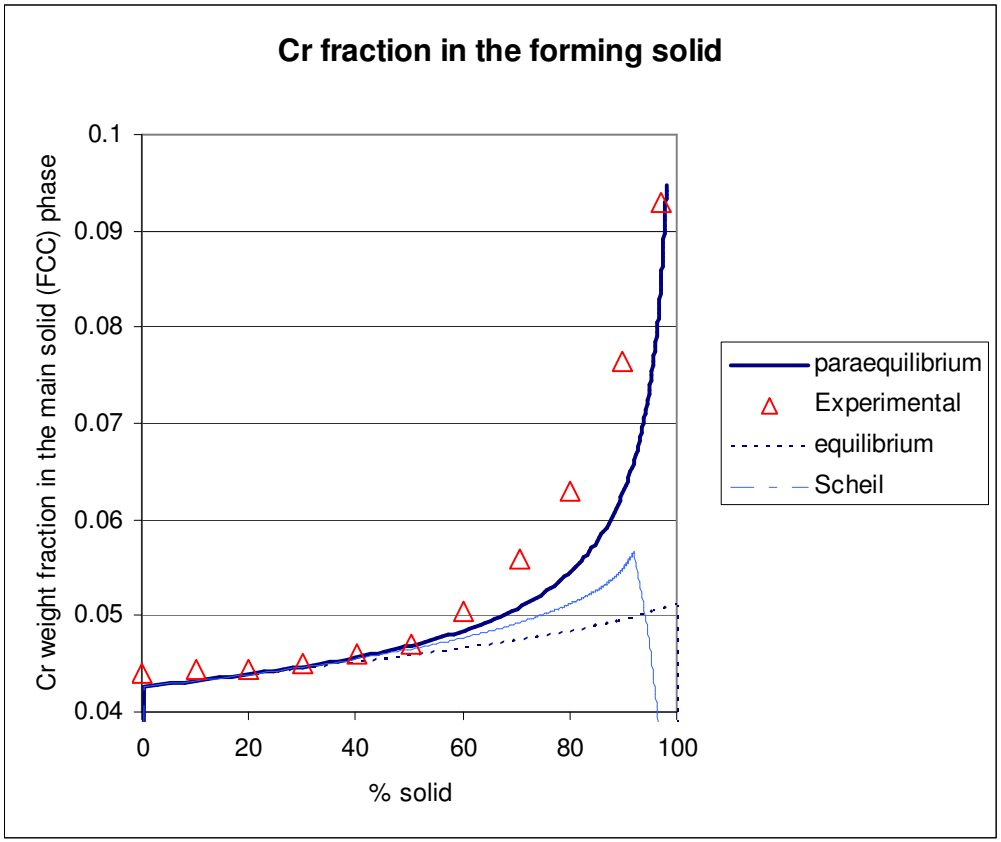
Result comparison





Composition: 10.84% Cr, 0.95% C. Cooling rate in experiment 0.167K/s





Composition: 5.34% Cr, 0.93% C. Cooling rate in experiment 0.167K/s