Thermodynamic calculation of Al-Mn-Zn system

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Content

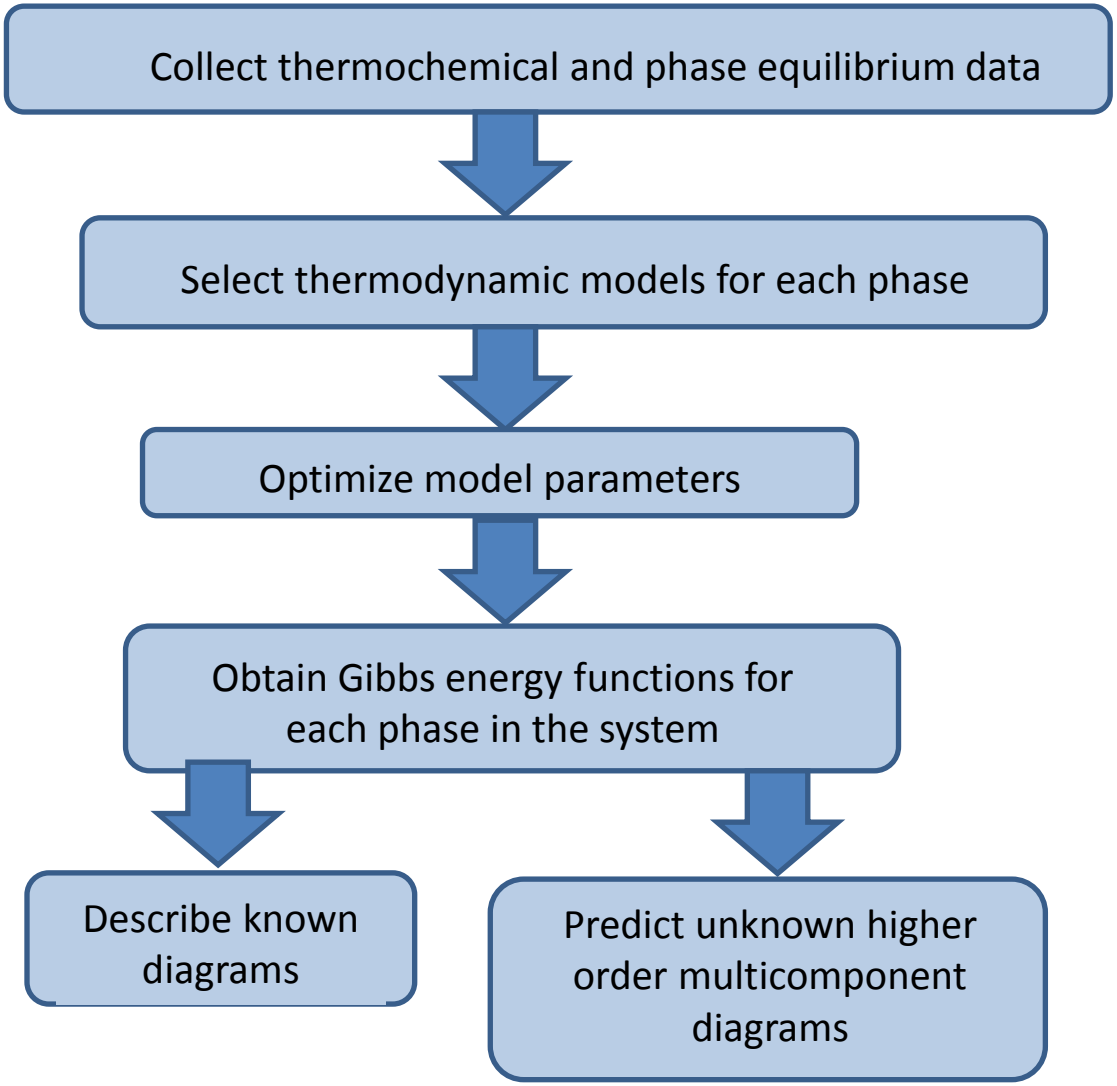
- Introduction
- Thermodynamic calculation approach
- Thermodynamic modeling of Al-Mn, Al-Zn, Mn-Zn system.
- Thermodynamic calculation of Al-Mn-Zn ternary system.
- Conclusion

Introduction

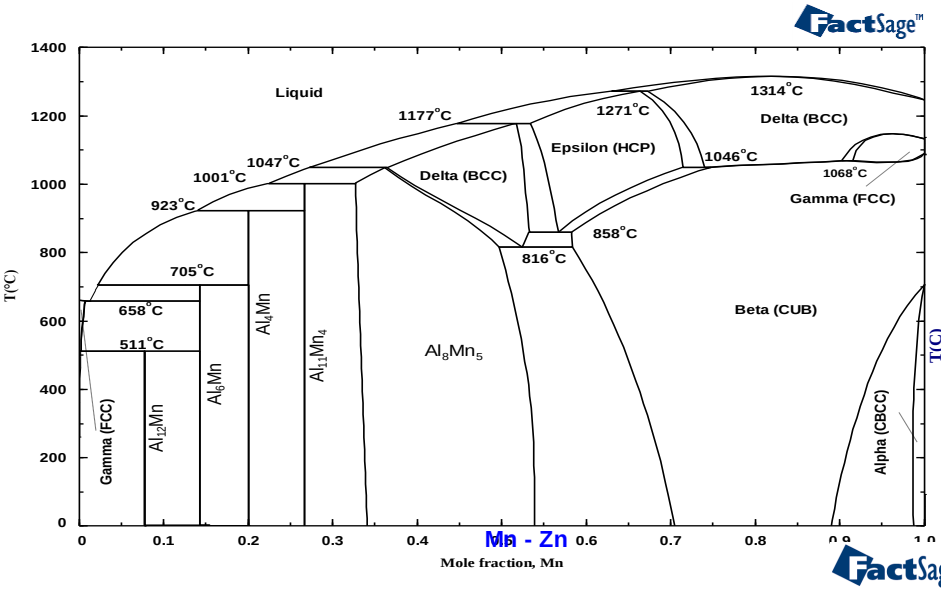
Phase diagrams are the foundation in performing basic materials research in such fields as solidification, crystal growth, joining, phase transformation, etc. Also, a phase diagram also serves as a road map for materials design and process optimization.

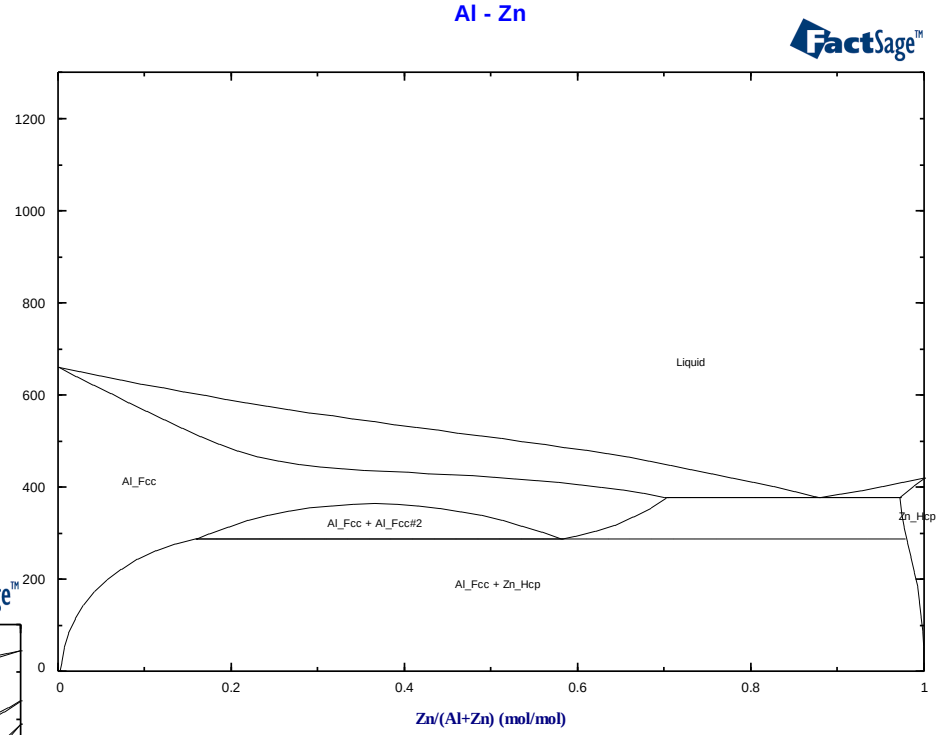
In an alloy with several alloying elements, the phase relationships are very complex. In order to investigate and understand these complex phase relationships effectively, it is very useful to develop thermodynamic databases containing model parameters giving the thermodynamic properties of all phases as functions of temperature and composition. Using Gibbs free energy minimization software such as FactSage .

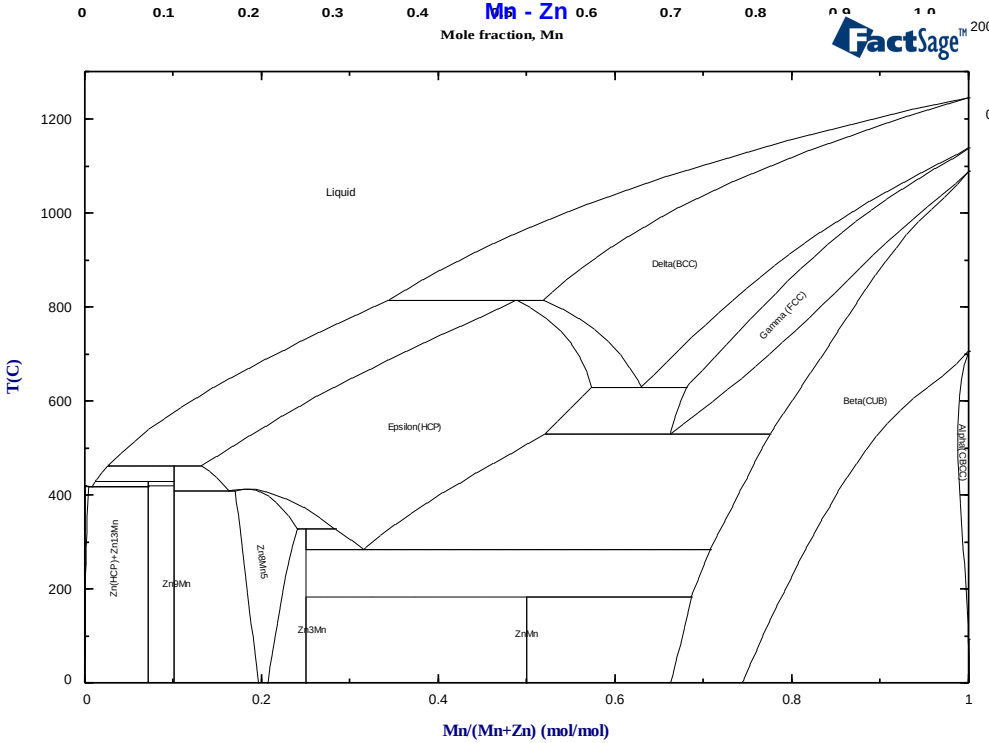
Thermodynamic Calculation Approach



Thermodynamic modeling of Al-Mn, Al-Zn, Mn-Zn system







Three binary phase diagrams were calculated by current ternary model

Modified Quasichemical Model(MQM) for the liquid phase.

Substitutional Solution Model (SSM) for the solid solution

Stoichiometric Model(ST) for the compound

The advantages of Modified Quasichemical Model(MQM)

- It permits the composition of maximum short range ordering in a binary system to be freely chosen
- It expresses the energy of pair formation as a function of composition which can be expanded as a polynomial in the pair fraction
- The coordination numbers are permitted to vary with the composition
- The model can be extended to multicomponent systems

Equation of each model

MQM $$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i\geq 1} g^{i0}_{AB} X^{i}_{AA} + \sum_{j\geq 1} g^{0j}_{AB} X^{j}_{BB}$$

Δg_{AB} is the change in the Gibbs energy for the formation of 2 moles of A-B pair

Δg^{o}_{AB} g^{i0}_{AB} g^{0j}_{AB} are the parameters of model which related to the temperature

SSM The Gibbs energy, per mole of the phase for the A-B binary system is given by:

$$\Delta G^{\phi} = x_A {}^{o}G_A + x_B {}^{o}G_B + RT\left(x_A \ln x_A + x_B \ln x_B\right) + {}^{ex}G^{\phi}$$

where $${}^{ex}G^{\phi} = x_A x_B \left[{}^{0}L^{\phi}_{A,B} + \left(x_A - x_B\right)^{1} L^{\phi}_{A,B} + \left(x_A - x_B\right)^{2} {}^{2}L^{\phi}_{A,B} \right]$$

$${}^{n}L^{\phi}_{A,B} = C + DT$$

C and D are the parameters to be determined during the optimization

ST $$\Delta G_{A_pB_q} = {}^{o}G^{A_pB_q} - p\,{}^{o}G^{(A)}_{A} - q\,{}^{o}G^{(B)}_{B} = C + DT$$

where *p* and *q* are the site fractions in the two sublattices of the compound A*p*B*q* and the *C* and *D* values are to be optimized using experimental data.

Thermodynamic calculation of Al-Mn-Zn ternary System

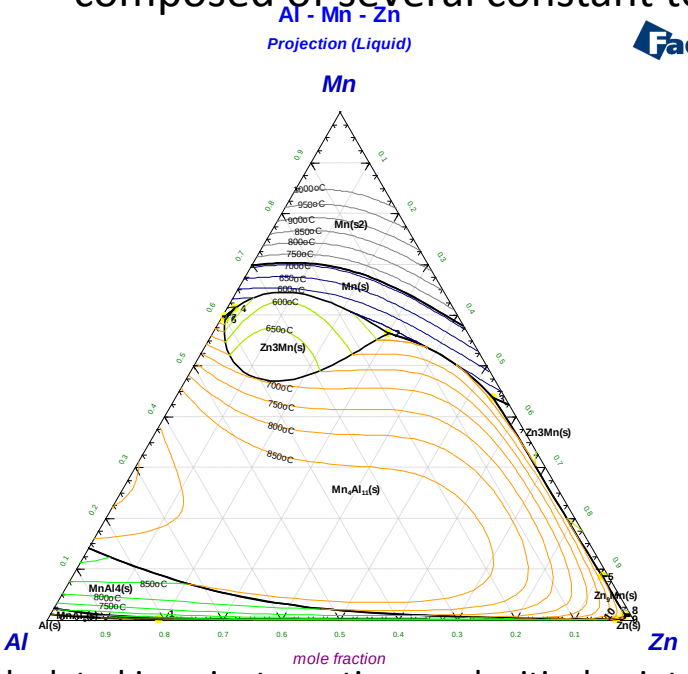
A simple extrapolation of the Al-Mn, Al-Zn and Mn-Zn system to construct the ternary Al-Mn-Zn has been carried out using Kohler extrapolation technique without the use of any ternary interaction parameter.

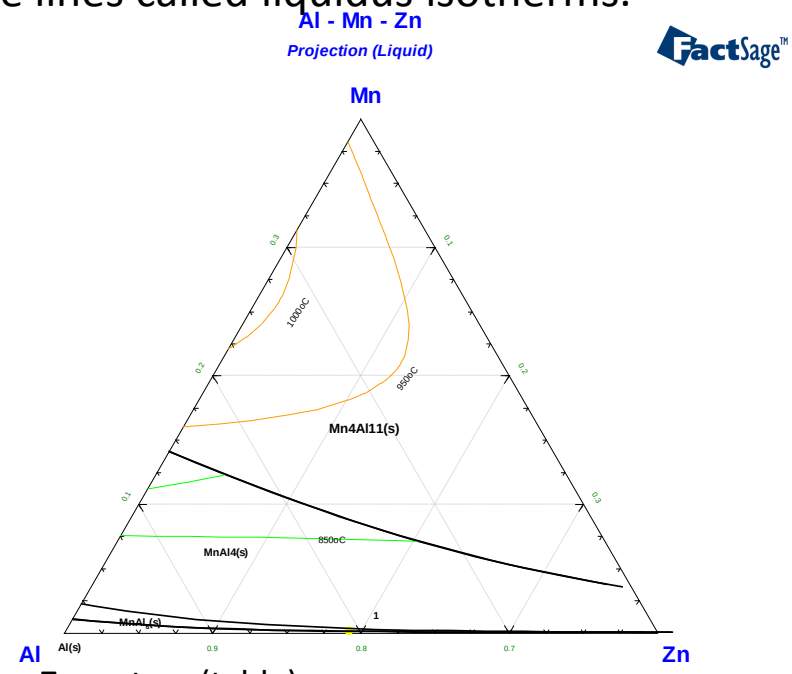
For modeling purposes, Alpha_CBCC, Beta_CUB, Delta_BCC and Gamma_FCC phases in both Al-Mn and Mn-Zn system were formally treated as the same phase. The thermodynamic properties of these phase were estimated from the binary model parameters.

The previous optimizations of the Al-Mn, Al-Zn and Mn-Zn systems were combined in order to calculate the polythermal projection of the liquidus of the Al-Mn-Zn system. The thermodynamic properties of the ternary liquid phase were calculated by the MQM from the binary model parameters

Calculated liquidus projection of Al-Mn-Zn system

The polythermal or liquidus projection is a two dimensional representation of the ternary liquidus surface on the Gibbs triangle which is mainly composed of several constant temperature lines called liquidus isotherms.



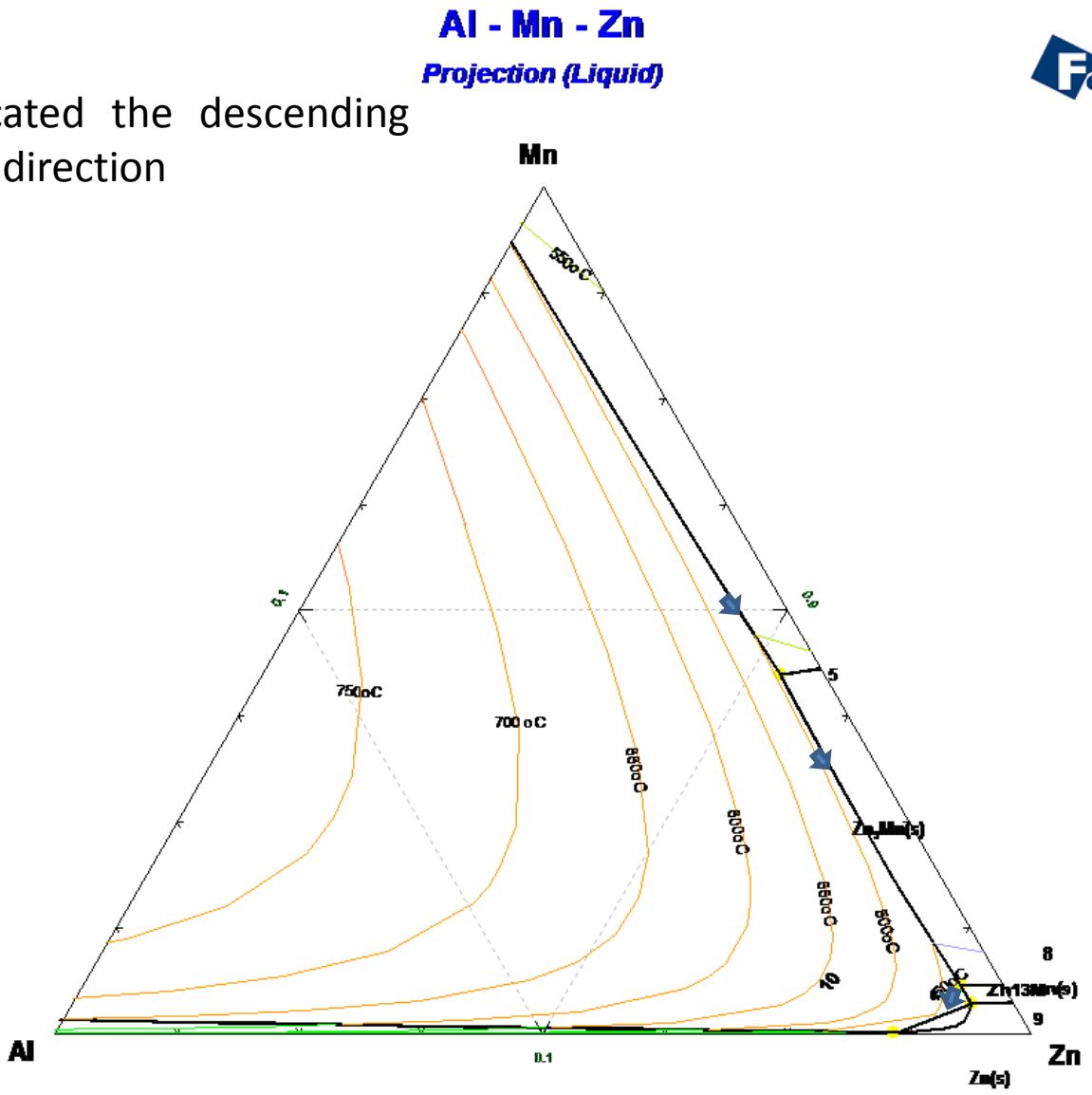


Calculated invariant reactions and critical points in the Al- Mn –Zn system (table)

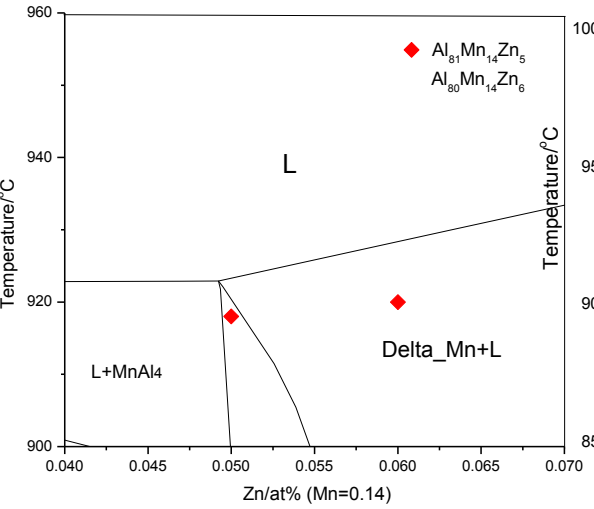
Number	Reaction	T (^{o}C)	Type *	Composition (at %)		
				Mn	Al	Zn
1	L ⇔ Al_fcc + Al12Mn + Al6Mn	552.34	E1	1	80	19
2	L ⇔ Al11Mn4+ Mn_cbcc +MnZn3	524.1	E2	56.3	13.5	30.2
3	L ⇔ Al11Mn4 + Mn_cbcc + MnZn3	508.71	E3	43.7	2	54.3
4	L + Mn_cbcc ⇔ MnZn3 + MnZn	494.29	P1	61.4	37.1	1.5
5	L + MnZn3 ⇔ Mn4Al11 +MnZn9	491.26	P2	8.5	1	90.5
6	L + MnZn3 ⇔ Al11Mn4 +MnZn	461.39	P3	59	40	1
7	L ⇔ Al11Mn4+Mn_cbcc + MnZn	439.42	E4	60	39	1
8	L +MnZn9 ⇔ Al11Mn4 +MnZn13	424.15	P4	1.1	0.9	98
9	L + MnZn13 ⇔ Al11Mn4 + `Zn(HCP)	411.05	P5	0.7	0.8	98.5
10	L ⇔ $Al_{11}Mn_4$ + Al4Mn+Zn(HCP)	404.73	E5	0.02	2.8	97.18

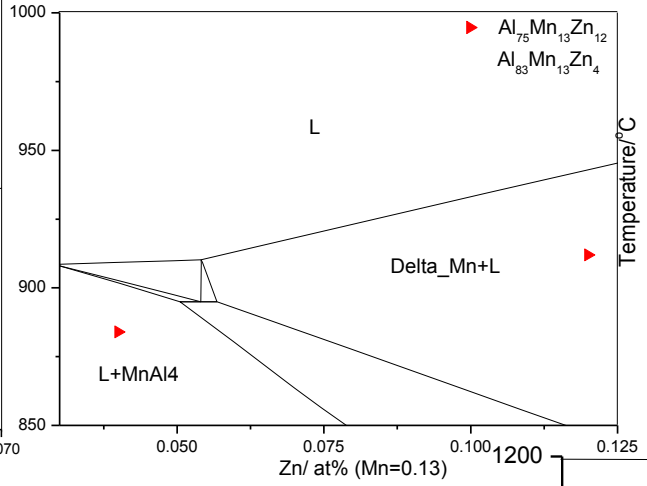
Zoomed Zn-rich corner

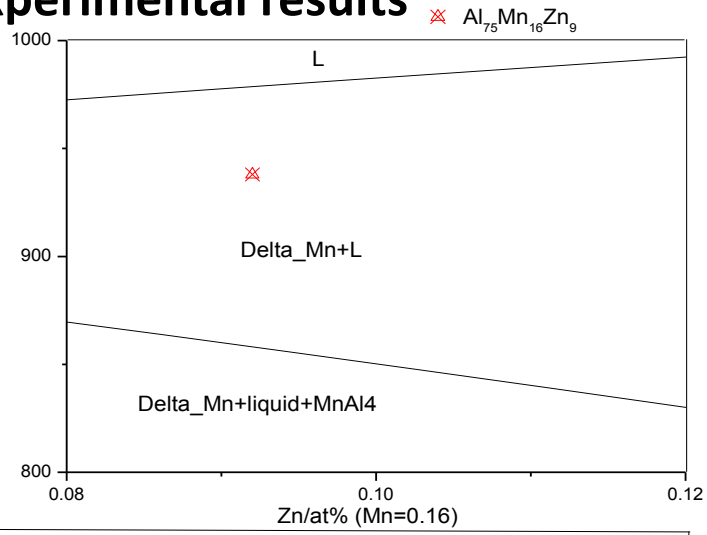
Arrows indicated the descending temperature direction

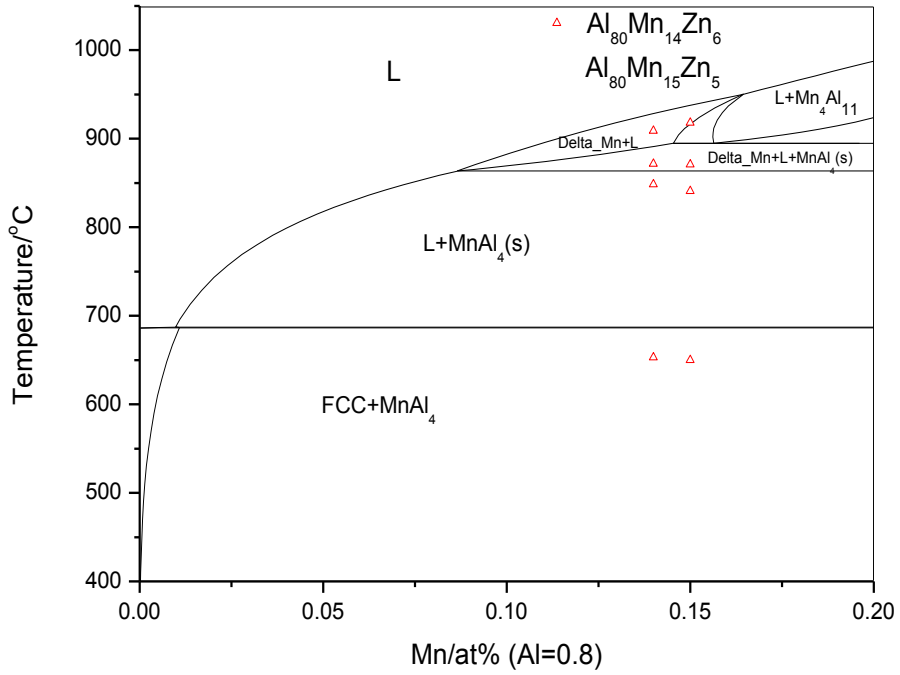


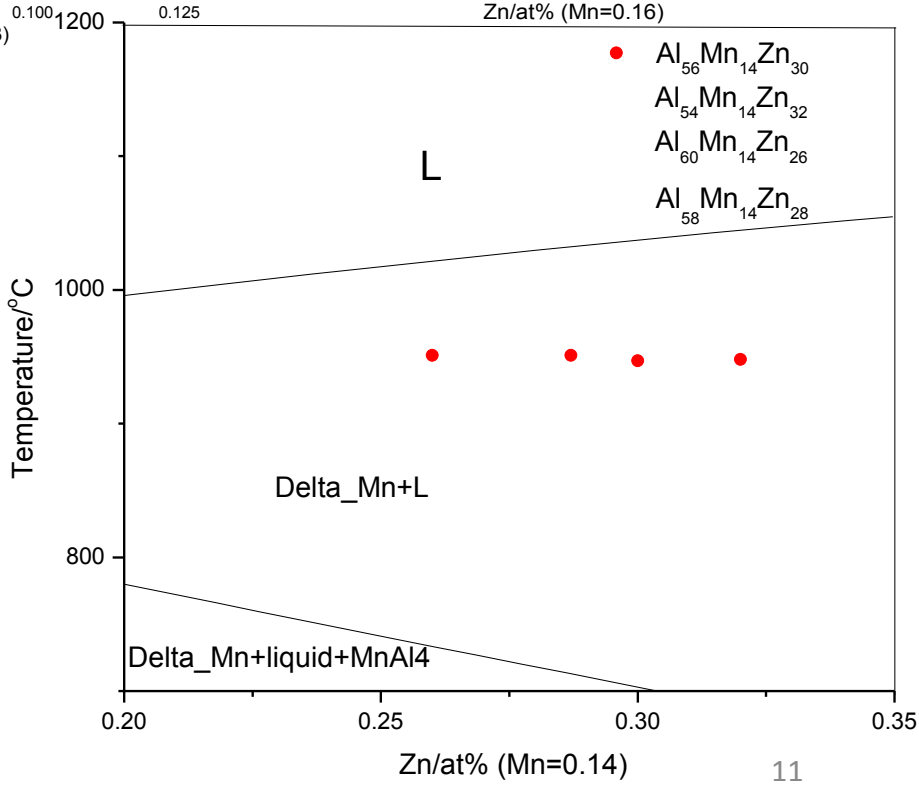
Calculated liqudus temperature compared with the experimental results



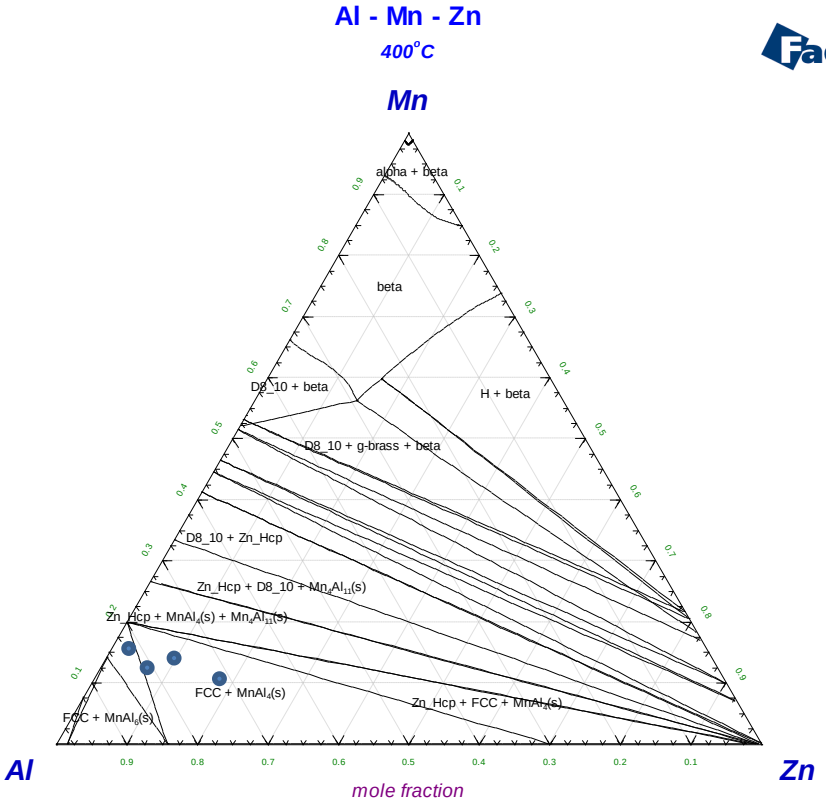


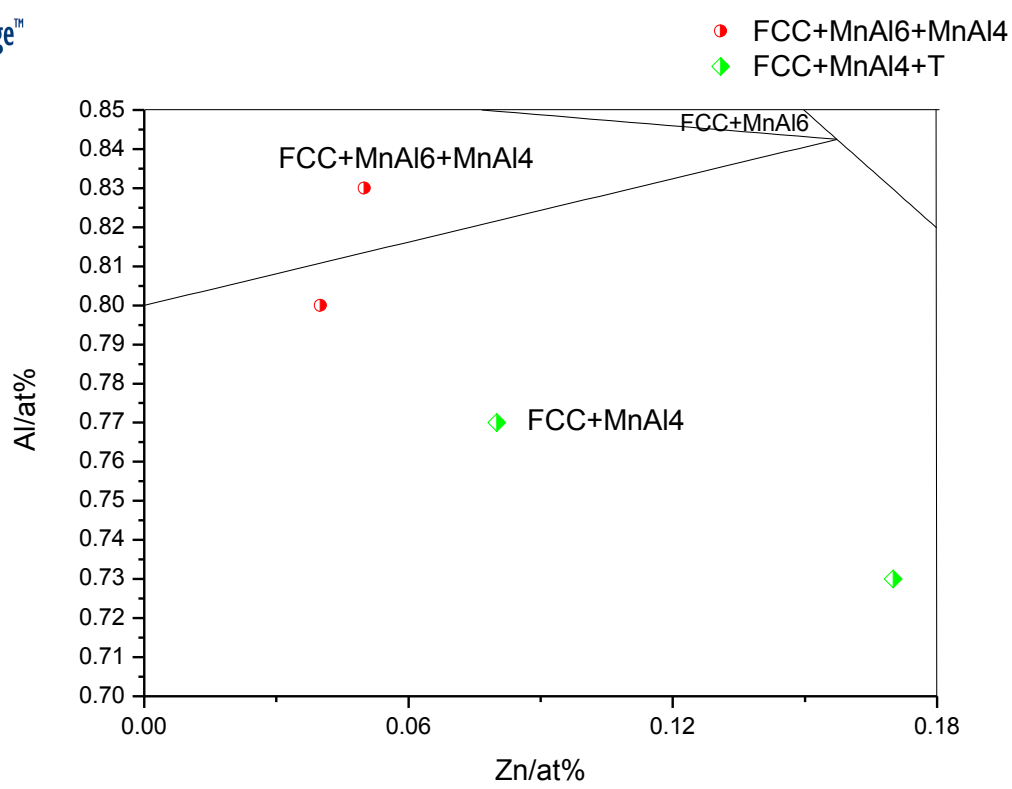






Calculated Isothermal section (vertical section at 400oC)





Calculated isothermal section compared with experimental results

Conclusion

- Thermodynamic modeling and calculation is a useful way to predict the complex system.
- Current calculation shows some discrepancies because the absence of ternary compounds data and ternary interaction parameters.
- Further experimental results will be used to construct and model the Al-Mn-Zn system.

Thank you