Thermodynamic modelling of the $\gamma/\gamma'$ phases in the Calphad approach

Nathalie Dupin

Calcul Thermodynamique

Bochum, 2014 september 17th
Why Calphad?

- multicomponent calculations
- agreement with experiments
Why Calphad?

THERMO-CALC (2013.10.28:16.48) :IN738LC
DATABASE:USER
B(CR)=16.1, B(CO)=8.58, B(FE)=8E-2, B(MO)=1.74, B(W)=2.6, B(TA)=1.69,
B(AL)=3.44, B(TI)=3.44, B(NB)=0.82, B(C)=0.12, B=100, P=1E5;

ATD on Selective Laser Melted alloy

- melting 258 kJ/kg
- $\gamma'$ dissolution 60 kJ/kg
$\Rightarrow$ about 40% $\gamma'$ in supersaturation

Why Calphad?

René-N4/René-N5 at 1293 °C for 100 h

C. Campbell, NIST
Early Al-Ni


Fig. 3—Calculated Ni-Al phase diagram.
Early Al-Ni
Evolution of the models

Early Al-Ni


\[ \gamma : \text{fcc solution phase} \]
\[
G^{fcc} = x_{Al} G_{Al}^{fcc} + x_{Ni} G_{Ni}^{fcc} \\
+ RT \left( x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni} \right) \\
+ x_{Al} x_{Ni} \left[ L0 + (x_{Al} - x_{Ni})L1 \right]
\]

\[ \gamma' : \text{stoichiometric Ni}_3\text{Al} \]
\[
G^{Ni_3Al} = a + bT + cT^2 + dT^3
\]
Evolution of the models

Early Al-Ni


\[ \gamma : \text{fcc solution phase} \]

\[ G^{fcc} = x_{Al} G^{fcc}_{Al} + x_{Ni} G^{fcc}_{Ni} + R T (x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni}) + x_{Al} x_{Ni} [L0 + (x_{Al} - x_{Ni})L1] \]

\[ \gamma' : \text{stoichiometric Ni}_3\text{Al} \]

\[ G^{Ni_3Al} = a + b T + c T^2 + d T^3 \]
Compound Energy Formalism

N. Saunders in “Superalloys 1996” eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101

Fig. 1. Calculated Ni-Al phase diagram with experimental phase boundaries superimposed
Evolution of the models

Compound Energy Formalism

N. Saunders in “Superalloys 1996” eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101

\[ \gamma : \text{fcc solution phase} \]

\[ G^{fcc} = \sum_{i} x_i G^{fcc}_i + RT \sum_{i} x_i \ln x_i + x_s G^{fcc} \]

\[ \gamma' : (\text{Al,Ni})_3(\text{Al,Ni}) \text{ CEF} \]

\[ G^{\gamma'} = \sum_{i} \sum_{j} y_i' y_j'' G_{i3j}^{\gamma'} \]

\[ + RT \left( \frac{3}{4} \sum_{i} y_i' \ln y_i' + \frac{1}{4} \sum_{i} y_i'' \ln y_i'' \right) + x_s G^{\gamma'} \]

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Evolution of the models

Compound Energy Formalism

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\[ \gamma : \text{fcc solution phase} \]

\[ G_{\text{fcc}}^\gamma = \sum_i x_i G_{i, \text{fcc}}^\gamma + RT \sum_i x_i \ln x_i + x_s G_{\text{fcc}}^\gamma \]

\[ \gamma' : (\text{Al,Ni})_3(\text{Al,Ni}) \text{ CEF} \]

\[ G_{\gamma'} = \sum_i \sum_j y_i y_j' y_j'' G_{i,j}^{\gamma'} \]

\[ x_s G_{\gamma'} = \sum_i \sum_{j>i} \sum_k y_i' y_j' y_k' \left( L_0^{\gamma'}_{ij;k} + (y_i' - y_j') L_1^{\gamma'}_{ij;k} \right) + \sum_i \sum_{j>i} \sum_k y_i'' y_j'' y_k' \left( L_0^{\gamma'}_{k;ij} + (y_i'' - y_j'') L_1^{\gamma'}_{k;ij} \right) \]

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Compound Energy Formalism

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\[ \gamma : \text{fcc solution phase} \]

\[ G^{fcc} = \sum_i x_i G^{fcc}_i + id G^{fcc} + xs G^{fcc} \]

\[ \gamma' : (Al,Ni)_3(Al,Ni) \text{ CEF} \]

\[ G^{\gamma'} = \sum_i \sum_j y'_i y''_j G^{\gamma'}_{i,j} + id G^{\gamma'} + xs G^{\gamma'} \]

\[ G^{\gamma'\gamma'}_{i:i} = G^{fcc}_i \]
Order-Disorder CEF

Order-Disorder CEF


\[ \gamma \text{ and } \gamma': \text{ a single description} \]
\[ (\text{Al},\text{Ni})_3(\text{Al},\text{Ni}) \text{ CEF} \]

- constraints between \( u_i \)
  ensure \( (dG = 0)y_i' = y_i'' \)
- order independent contribution from L0 and L1
Order-Disorder CEF


\[ y_i' = y_i'' \]

\[ y_i' \neq y_i'' \]
Splitting Order-Disorder CEF


\[ G_m = G_m^{\text{dis}}(x_i) + G_m^{\text{ord}}(y_i', y_i'') - G_m^{\text{ord}}(x_i) \]

\[ G_{A:B} = G_{A:A:B:B} \]
\[ G_{B:A} = G_{B:B:B:A} \]
\[ 0L_{A:B} = 0L \]
\[ 1L_{A:B} = 1L \]
\[ 0L_{B:A} = 0L \]
\[ 1L_{B:A} = 1L \]
Splitting Order-Disorder CEF


\[ \gamma \text{ and } \gamma' : \text{a single CEF} \]

- splitting disorder description
  \[ G = G^{\text{dis}}(x) + G^{\text{ord}}(y) - G^{\text{ord}}(x) \]

- disorder stability: \( 2\text{SL}=4\text{SL} \)

- \( G_{\text{Al}_3\text{Ni}} = \frac{1}{3} G_{\text{Ni}_3\text{Al}} \)
  \( \frac{1}{4} G_{\text{Al}_2\text{Ni}_2} = \frac{1}{3} G_{\text{Ni}_3\text{Al}} \)

as \( \text{Al}_3\text{Ni} \) and \( \text{Al}_2\text{Ni}_2 \) not known experimentally
Splitting Order-Disorder

\[ G = G^{\text{dis}}(x) + G^{\text{ord}}(y) - G^{\text{ord}}(x) \]

- introduced to be able to assess separately the disordered phase
- the meaning of the \( G^{\text{ord}}(y) \) parameters is lost, only \( G^{\text{ord}}(y) - G^{\text{ord}}(x) \) is meaningful
- easy extrapolation in multicomponent even if many systems do not contribute to ordering
2SL = 4SL

\[ G^{2SL} = \sum_{i} \sum_{j} y_i y_j G^{2SL}_{ij} + RT \left( \frac{3}{4} \sum_i y_i \ln y_i + \frac{1}{4} \sum_i y_i'' \ln y_i'' \right) + x_s G^{2SL} \]
\[ 2\text{SL} = 4\text{SL} \]

\[
G^{2\text{SL}} = \sum_i \sum_j y_i' y_j'' G_{ij}^{2\text{SL}} + RT \left( \frac{3}{4} \sum_i y_i' \ln y_i' + \frac{1}{4} \sum_i y_i'' \ln y_i'' \right) + x_s G^{2\text{SL}}
\]

\[
G^{4\text{SL}} = \sum_i \sum_j y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl}^{4\text{SL}} + RT \sum_s \frac{1}{4} \sum_i y_i^s \ln y_i^s + x_s G^{4\text{SL}}
\]
2SL = 4SL

\[ G^{2SL} = \sum_i \sum_j y'_i y''_j G^{2SL}_{ij} + RT \left( \frac{3}{4} \sum_i y'_i \ln y'_i + \frac{1}{4} \sum_i y''_i \ln y''_i \right) + xsG^{2SL} \]

\[ G^{4SL} = \sum_i \sum_j y_\alpha^i y_\beta^j y_\gamma^k y_\delta^l G^{4SL}_{ijkl} + RT \sum_s \frac{1}{4} \sum_i y^s_i \ln y^s_i + xsG^{4SL} \]

The fcc lattice is built built on regular tetrahedra.

Equivalence of the 4SL ⇒ stability of the disorder (A1)
2SL = 4SL

From crystallographic symmetry, the following configurations are equivalent.
2SL = 4SL

From crystallographic symmetry, the following configurations are equivalent.

$L1_2$ configurations

\[ G_{AAAB}^{4SL} = G_{AABA}^{4SL} = G_{ABAA}^{4SL} = G_{BAAA}^{4SL} \]

Standing also for excess parameters

\[ L_{AB:**:*:*}^{4SL} = L_{*:*:*AB:**}^{4SL} = L_{*:*:*AB:*}^{4SL} = L_{*:*:*:*AB}^{4SL} \]
Evolution of the models

Splitting Order-Disorder CEF

2SL = 4SL

From crystallographic symmetry, the following configurations are equivalent.

\[ L_{10} \text{ configurations} \]

\[ G_{AABB}^{4SL} = G_{ABAB}^{4SL} = G_{BAAB}^{4SL} = G_{ABBA}^{4SL} = G_{BABA}^{4SL} = G_{BBAA}^{4SL} \]
2SL = 4SL

\[ G^{2SL}_{A3B} = G^{4SL}_{AAAB} \]
\[ G^{2SL}_{AB3} = G^{4SL}_{ABBB} \]
\[ L0^{2SL}_{AB:A} = -1.5G^{4SL}_{AABB} + 1.5G^{4SL}_{AAAB} + 1.5G^{4SL}_{AAAB} + 3\ L0^{4SL}_{AB:*:*:*} \]
\[ L0^{2SL}_{AB:B} = +1.5G^{4SL}_{ABBB} + 1.5G^{4SL}_{AAAB} - 1.5G^{4SL}_{AAAB} + 3\ L0^{4SL}_{AB:*:*:*} \]
\[ L0^{2SL}_{A:AB} = L0^{4SL}_{AB:*:*:*} \]
\[ L0^{2SL}_{B:AB} = L0^{4SL}_{AB:*:*:*} \]
\[ L1^{2SL}_{AB:A} = 0.5G^{4SL}_{ABBB} - 1.5G^{4SL}_{AABB} + 1.5G^{4SL}_{AAAB} + 3\ L1^{4SL}_{AB:*:*:*} \]
\[ L1^{2SL}_{AB:B} = -1.5G^{4SL}_{ABBB} + 1.5G^{4SL}_{AABB} - 0.5G^{4SL}_{AAAB} + 3\ L1^{4SL}_{AB:*:*:*} \]
\[ L1^{2SL}_{A:AB} = L1^{4SL}_{AB:*:*:*} \]
\[ L1^{2SL}_{B:AB} = L1^{4SL}_{AB:*:*:*} \]
$2\text{SL} = 4\text{SL}$

\[ y_i^\alpha = y_i^\beta = y_i^\gamma = y_i^\delta \]

\[ y_i^\alpha = y_i^\beta = y_i^\gamma \neq y_i^\delta \]

\[ y_i^\alpha = y_i^\beta \neq y_i^\gamma = y_i^\delta \]
$$2\text{SL} = 4\text{SL}$$

Similar to Shockley fcc prototype considering a single and constant nearest neighbours energy with BWG entropy.

W. Shockley, J. Chem. Phys., 6 (1938), 130
\[ 2\text{SL} = 4\text{SL} \]

\[ G = \sum_{i} \sum_{j} \sum_{k} \sum_{l} y_{i}^{\alpha} y_{j}^{\beta} y_{k}^{\gamma} y_{l}^{\delta} G_{ijkl} \]

\[ + RT \sum_{s} \sum_{i} \frac{1}{4} y_{i}^{s} \ln y_{i}^{s} \]

with \[ G_{A3B} = 3 \epsilon_{AB}, \quad G_{A2B2} = 4 \epsilon_{AB} \]

\[ \triangleright \text{Tetrahedron CVM prototype using the same pairwise energy} \]

Bad topology, bad critical temperature
Splitting Order-Disorder CEF
Splitting Order-Disorder CEF

Evolution of the models
Splitting Order-Disorder CEF

Evolution of the models

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Splitting Order-Disorder CEF

Despite its physical weakness, this model allowed to describe reasonably experimental data in Al-Ni as well as many ternary systems and allowed to set up a multicomponent database, today known as the commercial database TCNI6.

N. Dupin, B. Sundman, Scandinavian J. Metall., 30 (2001) 184
4SL Order-Disorder CEF

A way to get proper fcc phase diagram topology with the CEF

Figure 1: The assessed Au-Cu phase diagram using CEF

B. Sundman, S. G. Fries, W. A. Oates, Calphad, 22 (1998), 335
4SL Order-Disorder CEF

A way to get proper fcc phase diagram topology with the CEF

\[ G = \sum_i \sum_j \sum_k \sum_l y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl} \]

\[ + RT \sum_s \sum_i \frac{1}{4} y_i^s \ln y_i^s \]

\[ + \sum_s \sum_{r>s} y_A^s y_B^s y_A^r y_B^r L_{AB:AB:*:*} \]

with \( G_{A3B} = 3 \epsilon_{AB} \), \( G_{A2B2} = 4 \epsilon_{AB} \),

and \( L_{AB:AB:*:*} = \epsilon_{AB} \) (reciprocal)

\[ \Delta \text{Tetrahedron CVM prototype using} \]

the same pairwise energy
4SL Order-Disorder CEF

A way to get proper fcc phase diagram topology with the CEF

Evolution of the models  4SL SOD CEF

4SL Order-Disorder CEF
B. Sundman, N. Dupin, JEEP 2003, Lyon

\[ G = G^{\text{dis}}(x) + G^{\text{ord}}(y) - G^{\text{ord}}(x) \]

- splitting disorder description
- \( G^{\text{dis}}(x) = G^{\text{ord}}(x) \)
- \( G_{\text{Al}_3\text{Ni}} \) and \( G_{\text{Al}_2\text{Ni}_2} \) assessed from FP
- Reciprocal interaction parameter allows proper fcc metastable topology

\( \gamma \) and \( \gamma' \) : a single CEF
4SL Order-Disorder CEF
B. Sundman, N. Dupin, JEEP 2003, Lyon
4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon

\[ G^{ord}(y) = \]
\[ \sum_{i} \sum_{j} \sum_{k} \sum_{l} y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl}^{ord} \]
\[ + \frac{1}{4} RT \sum_{s} \sum_{i} y_i^s \ln y_i^s \]
\[ + \sum_{s} \sum_{i} \sum_{j > i} y_i^s y_j^s L_{ij:ij:ij:ij}^{ord} \]
\[ + \sum_{s} \sum_{r > s} \sum_{i} \sum_{j > i} y_i^s y_j^s y_i^r y_j^r L_{ij:ij:ij:ij}^{ord} \]
4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon

\[ G^{ord}(y) = \sum_{i} \sum_{j} \sum_{k} \sum_{l} y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl}^{ord} \]
\[ + \frac{1}{4} RT \sum_{s} \sum_{i} y_i^s \ln y_i^s \]
\[ + \sum_{s} \sum_{i} \sum_{j>i} y_i^s y_j^s L_{ij}^{ord}^{*:*:*:*} \]

\[ G^{dis}(x) = \sum_{i} G_i^{dis} + RT \sum_{i} x_i \ln x_i + \sum_{i} \sum_{j>i} x_i x_j \sum_{n} (x_i - x_j) L_{ij}^{dis} \]

**with** \( L_{0ij}^{dis} = G_{i3j}^{ord} + 1.5 G_{i2j2}^{ord} + G_{ij3}^{ord} + 1.5 L_{ij}^{ord}^{*:*:*:*} + 4 L_{ij}^{ord}^{*:*:*:*} \)

4SL Order-Disorder CEF
B. Sundman, N. Dupin, JEEP 2003, Lyon

4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon
Application to ternaries

N. Dupin et al., Grenoble 2006
Application to ternaries

\[ G_{Al_2FeNi} = 2u_{AlFe}(Al_3Fe) + 2u_{AlNi}(Al_3Ni) + u_{FeNi}(Fe_2Ni_2) \]

N. Dupin et al., Grenoble 2006
Application to ternaries

X.G. Lu et al., Calphad 33 (2009) 450.
Conclusions

- In order to derive a Calphad thermodynamic description of quality, experimental phase diagram, crystallographic structure, enthalpy of mixing, of formation, of transition, Cp, activities, chemical potentials, ... should be taken into account as well as FP enthalpies of formation, cell volume, defects, CE-CVM/MC phase diagram...
Conclusions

- In order to derive a Calphad thermodynamic description of quality, experimental phase diagram, crystallographic structure, enthalpy of mixing, of formation, of transition, Cp, activities, chemical potentials, ... should be taken into account as well as FP enthalpies of formation, cell volume, defects, CE-CVM/MC phase diagram...

- The current multicomponent thermodynamic database could be improved by the use of a real 4SL model.
Conclusions

- In order to derive a Calphad thermodynamic description of quality, *experimental* phase diagram, crystallographic structure, enthalpy of mixing, of formation, of transition, Cp, activities, chemical potentials, ... should be taken into account as well as FP enthalpies of formation, cell volume, defects, CE-CVM/MC phase diagram...

- The current multicomponent thermodynamic database could be improved by the use of a real 4SL model.

- Will another better model appear soon? When will a more *accurate* approximation describe a 10 elements system with appealing computational time, appealing agreement with experiments?