Computational Thermodynamics

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Thanks to: Paul Mason (Thermo-Calc), Shengyen Li and Min Soo Park for providing many slides!
Outline

• Motivation
• Fundamental Thermodynamics Concepts
  – Basic Thermodynamics
  – Thermodynamics and Phase Stability
• Computational Thermodynamics
  – CALPHAD Approach
  – Thermodynamic Models
  – Assessment of Models
  – Limitations and opportunities
• Applications
  – Phase Stability Co-Ni-Ga
  – Alloy Design (TRIP Steels)
  – Coupling to Phase-Field Models of Microstructure Evolution
Motivation
Thermodynamics: Big Picture

Equilibrium Properties

Equilibrium Properties

Property Relations

Phase Stability

Materials Evolution

Driving Force for Phase Transitions


[2011 Park Acta Mater]

[2001 Bhadehshia]

[2001 Hillert J. Alloys Compnd.]
Thermodynamics: Bigger Picture

The mapping between microscopic degrees of freedom and macroscopic features of materials is only possible through a thermodynamic formalism.
Fundamentals of Thermodynamics
Thermodynamics - Definitions

• A science concerning the state of a system when left alone, and when interacting with the surroundings.
• Such state is known as equilibrium state.
• By “system” we mean any portion of the world that can be defined for considerations of the changes that may occur under varying conditions.
• The system may be separated from the surroundings by a real or imaginary wall, that usually is considered to be part of the surroundings, and defines interactions between the system and the surroundings.
• A couple of Thermodynamics quotes:
  • “Thermodynamics is the study of the restrictions on the possible properties of matter that follow from the symmetry properties of the fundamental laws of physics” - Callen, H. B. (ca. 1960s)
  • “Kinetics is the poor man’s Thermodynamics” - Ceder, G. (ca. 2003)
  • “Lisa: In this house we obey the laws of Thermodynamics” – Simpson, H. (ca. 1995)

Thanks to: Paul Mason

Thermo-Calc Software
Thermodynamic Equilibrium

• Maximum Entropy:
  – The equilibrium value of any non-constrained internal variable is such that maximizes the entropy of a system.
  – dS=0 @ equilibrium

• Minimum Energy:
  – The equilibrium value of any non-constrained internal variable is such that minimizes the internal energy of a system
  – dU=0 @ equilibrium

Generalized Extremum Principle:
\[ \delta z = dU - TdS - \sum_i Y_idX_i < 0 \]

In practice, we do not control U or S. Imposing alternative boundary conditions, such as T, P etc requires usage of other thermodynamic potentials (enthalpy, Gibbs/Helmholtz free energies, Grand Potential, etc)

Thermodynamics is useful as long as we identify proper thermodynamic potential
Equilibrium in Systems at constant $T$, $P$

Using extremum principle and combined 1st and 2nd Law:

$$dU - TdS + PdV + TdS + SdT - PdV - VdP \leq 0$$

$$dT = 0 \quad dP = 0$$

$$d\left(U - TS + PV\right) \leq 0$$

$$dG = \sum_i \mu_i dN_i \leq 0$$

At constant $P$ and $T$, any change that minimizes $G$ (Gibbs Free Energy) will be spontaneous
In a heterogeneous system at constant (T,P), phases will exchange matter—subject to boundary constraints---in order to minimize the Gibbs free energy:

\[ dG_{\text{System}} = \sum_{i=1}^{p} \sum_{j=1}^{c} \mu_j^i dN_j^i < 0 \]

Both phases will exchange B and W (if interphase boundary is permeable to both components) until Gibbs energy is minimized

\[ dG = 0 \]
Gibbs Energy and Equilibrium

Equilibrium

Equilibrium condition for isobaric systems (P = const):

\[ G = \Sigma N_j G_j = \text{minimum} \]

where \( N_j \) is the number of moles, and \( G_j \) is the Gibbs energy of phase \( j \)

Thanks to: Paul Mason

Thermo-Calc Software
Thermodynamics and Phase Stability

- **Phase**: A chemically and structurally homogeneous portion of material, generally described by a distinct value of some parameters.

[Ken Jackson, University of Arizona]

- The **stable** phases at each temperature and composition are summarized in a **phase diagram** made up of boundaries between single and multiple phase regions.
- Multi-phase regions imply separation to the boundaries in proportions consistent with conserving overall composition.
Thermodynamics of Phase Diagrams

\[ G = \sum_{\phi} N^\phi G_m^\phi(T, P, x^\phi_i) \]

\[ \frac{\partial G}{\partial x^\phi_i} = 0 \]

Or

\[ \mu_i^\alpha = G_m^\alpha + \sum_{j=1}^{n-1} (\delta_{ij} - x_j^\alpha) \frac{\partial G_m^\alpha}{\partial x_j^\alpha} \]

\[ \mu_i^1 = \mu_i^2 = \ldots = \mu_i^\phi \quad (i = 1, n) \]

Thanks to: Paul Mason
Macro-Micro Thermodynamics
Microscopic DOF and Thermodynamics

- Macroscopic conditions \((V, T, N, P)\) translate to the microscopic world as boundary conditions.
- Microscopic system defined by extensive variables that are constant in the macroscopic world \((E,V,N), (V,N)\).
- The probability distribution from the microscopic system and its Hamiltonian are related to macroscopic thermodynamics.
Thermodynamic Modeling

• Thermodynamics always holds
  – Independent of models used

• For practical applications, it is necessary to mathematically describe thermodynamic properties

• Models need to be capable of describing Gibbs (other) energies of phases

• Usual approaches in materials science:
  – Empirical Models
  – Semi-empirical descriptions
    • Molecular Dynamics
    • Monte Carlo
  – First-principles:
    • Quantum-mechanical methods

• Current approach: Combine modeling approaches at all levels

Obtaining Thermodynamics from Microscopic Behavior

- Thermodynamics of phase stability result from *macroscopic behavior*
- Need to go from microscopic description to macroscopic behavior

**MD:**
Time average of system over a dynamic trajectory

**MC:**
Weighted average of properties of microscopic states
Phase Stability from Purely Atomistic Methods


Predictions of phase stability from combination of statistical mechanics and microscopic modeling (MC using ab initio-calculated interactions)
- Rigorous
- Topologically Correct
- Not very accurate (if to be used for alloy design, for example)
  - As we will see later: errors of a few meV correspond to 100’s of °C
- These methods are very difficult to apply in cases of multi-component, multi-phase systems
Computational Thermodynamics/CALPHAD Method
What is Computational thermodynamics / CALPHAD?

“CALPHAD (Computer Coupling of Phase Diagrams and Thermo chemistry) aims to promote computational thermodynamics through development of models to represent thermodynamic properties for various phases which permit prediction of properties of multicomponent systems from those of binary and ternary subsystems, critical assessment of data and their incorporation into self-consistent databases, development of software to optimize and derive thermodynamic parameters and the development and use of databanks for calculations to improve understanding of various industrial and technological processes.”

http://www.calphad.org

Larry Kaufman
What is Computational thermodynamics / CALPHAD? (2)

- Modeling of Gibbs energies of individual phases
- Coupling of phase equilibria and thermo-chemistry
- Internally consistent thermodynamics of multi-phase, multi-component systems
- Prediction of thermodynamic properties and phase equilibria

Thanks to: Paul Mason

Thermo-Calc Software
What is Computational thermodynamics / CALPHAD (3)

Method

Thermodynamic Database

Description of Gibbs free energy for the individual phases

Minimization of the total Gibbs free energy under given conditions.

\[ G_m^\phi(T, P, x_i^\phi) \]

\[ G = \sum_\phi N^\phi G_m^\phi(T, P, x_i^\phi) \]

\[ \frac{\partial G}{\partial x_i^\phi} = 0 \]

Result

Alloy 1

R- and μ-phase

600 800 1000 1200 1400

Temperature (°C)

Fraction of Phase

Thanks to: Paul Mason

Thermo-Calc Software
$64,000 Question

How do we get

\[ G^\phi_m(T, P, x^\phi_i) \]
CALPHAD Method for Thermodynamic Modeling
Thermodynamic Modeling

• The CALPHAD method[1]:
  – Use of empirical models to describe Gibbs energies of phases
  – Model parameters are fitted through using experimental data:
    • Phase boundaries
    • Thermochemical measurements
    • Invariant Reactions
  – In recent years ab initio calculations have been used to aid the model development[2]

• Applications:
  – Phase diagram calculations
  – Phase fractions
  – Extrapolations to higher-order systems
  – Solidification sequences

CALPHAD Methodology

Thanks to: Paul Mason

Thermo-Calc Software
Thermodynamic Modeling

Thermochemical measurements:
- enthalpy, entropy, heat capacity, activity

Phase equilibria:
- liquidus, solidus, phase boundary,

Gibbs Energy of individual Phases

Applications

Fewer experimental measurements

Experimental measurements

G = U − TS + PV ≡ H − TS

dG = −SdT + VdP + \sum_{i} \mu_i dN_i

‘easy’ to extrapolate:

Pure elements → Binary → Ternary → Multi-component

http://www.calphad.org
The CALPHAD Approach

\[ G_m^\phi = f(x^\phi_i, P, T) \]

Phase Equilibria

Thermochemistry

Structure*
Example: Fe-Cr-C (Important in Steels)
Thermodynamic Models: Formalism
Thermodynamic Modeling

• Pure elements

\[ G_m - H_m^{SER} = a + bT + cT \ln(T) + \sum d_i T^i \]

• Stoichiometric compounds
  - Gibbs energy of formation

\[ G^{A_xB_y} = o G^{A_xB_y} + \Delta_f G^{A_xB_y} \]

\[ o G^{A_xB_y} = xG_A^{SER} + yG_B^{SER} \]

\[ \Delta_f G = a + bT \]

• Solution phases

\[ G_m = G_m^0 + \Delta G_m^{ideal} + \Delta G_m^{xs} + \Delta G_m^{ph} \]

reference surface
excess term
configurational contribution
physical contribution
Thermodynamic Modeling: Binary Solutions

\[ G_m = G_m^0 + \Delta G_m^{\text{ideal}} + \Delta G_m^{xs} \]

\[ G_m^0 = x_A G_A^o + x_B G_B^o \]

\[ \Delta G_m^{\text{ideal}} = RT \left( x_A \ln x_A + x_B \ln x_B \right) \]

\[ \Delta G_m^{xs} = x_A x_B^0 L_{A,B} \]

\[ ^0 L_{A,B} = a + bT \]

\[ \Delta S_m^{xs} = -x_A x_B b \]

\[ \Delta H_m^{xs} = x_A x_B a \]

\[ \Delta C_P^{xs} = 0 \]

Deviation from ideality is described by model (interaction) parameters

Thanks to: Paul Mason  
Thermo-Calc Software
Endothermic/Exothermic Non-ideal Solutions

Thanks to: Paul Mason  
Thermo-Calc Software
Real Solid Solutions

\[ \Delta G_m^{xs} = x_A x_B \sum_{k=0}^{\infty} L_{A,B} (x_A - x_B)^k \]

\[ = x_A x_B \left( 0 L_{A,B} + 1 L_{A,B} (x_A - x_B) + 2 L_{A,B} (x_A - x_B)^2 \ldots \right) \]

Deviations from ideality are modeled using so-called “interaction parameters”

Origin of formalism: simple generalization of regular solution model

Thanks to: Paul Mason Thermo-Calc Software
Extrapolations to Higher-order Systems

\[ G_m = G_m^0 + \Delta G_m^{ideal} + \Delta G_m^{xs} \]

\[ G_m^0 = x_A G_A^o + x_B G_B^o + x_C G_C^o \]

\[ \Delta G_m^{ideal} = RT \left( x_A \ln x_A + x_B \ln x_B + x_C \ln x_C \right) \]

\[ \Delta G_m^{xs} = \sum_i \sum_{j>i} x_i x_j I_{ij} + \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k I_{ijk} + \ldots \]

From Binary

From Ternary

As long as thermodynamic descriptions are mutually-consistent, it is possible to extrapolate to arbitrary order (provided model parameters are assessed against experiments)

Thanks to: Paul Mason Thermo-Calc Software
What about more complicated phases?

- Sublattice Model
  - (Also known as the Compound Energy Formalism, CEF)
  - Sublattice:
    - Crystallographic position with specific point group symmetry
- SM models interactions between and within sublattices
- Entropies are given through mean-field approximations
- Applications:
  - Interstitial and substitutional solution phases
  - Intermetallics
  - Oxides
Compound Energy Formalism (CEF)

Fcc

\[
G_m^\phi = \sum_M \sum_I y_M y_I \cdot G_{M:I}^\phi + RT \left( a \sum_M y_M \ln y_M + c \sum_I y_I \ln y_I \right) + E G_m^\phi + G_m^{\phi mg}
\]

- \(G_{M:I}^\phi\) is the Gibbs energy of formation of the compound \(M_aI_c\)
- \(a\) and \(c\) are the site ratios
- The excess and physical contributions are as for a regular solution on each sublattice

Thanks to: Paul Mason

Thermo-Calc Software 37
Compound Energy Formalism (CEF)

More complex structures need more sublattices

\[
M_6C \text{ Carbide} \\
(Co,Fe)_2(Co,Cr,Fe,Mo, Si,V,W)_2(Mo,W)_2(C)_1
\]

\[
G_m = \sum y^1_i y^2_j y^3_k G_{i,j;j;C} + RT \sum \sum n^S y^S_J \ln(y^S_J) + E G_m
\]

Thanks to: Paul Mason

Thermo-Calc Software
Sublattice (CEF) Model Formalisms

- **Formula:**
  \[
  (A,B)_k (C,E)_l
  \]

- **Site Fraction:**
  \[
  y_i^S = \frac{n_i^S}{n_{va} + \sum_i n_i^S}
  \]

- **Mean-Field Entropy:**
  \[
  -TS_{\text{mix}}^{\text{ideal}} = RT \sum_S N^S \sum_i y_i^S \ln(y_i^S)
  \]

- **Excess Gibbs Energy:**
  \[
  G_{m}^{xs} = y_A^I y_B^I L_A^0 + y_D^I y_E^I L_D^0 + \cdots
  \]

- **Total Gibbs Energy:**
  \[
  G_{m}^{\text{Tot}} = G_{m}^{\text{ref}} - TS_{\text{mix}}^{\text{ideal}} + G_{m}^{xs}
  \]

- **Reference Gibbs Energy**
  \[
  G_{m}^{\text{ref}} = y_A^I y_D^I G_{AD}^0 + y_B^I y_D^I G_{BD}^0 + y_A^I y_E^I G_{AE}^0 + y_B^I y_E^I G_{BE}^0
  \]
CEF: Anti-site Point Defects

- CuTi (P4/nmm)
- Experimentally, this phase exhibits anti-site point defects:

Model:

\[(Cu, Ti)_1(Cu, Ti)_1\]
Sublattice model can be used to describe order/disorder transitions:

Example: \((A,B)_{0.5}(A,B)_{0.5}\)

- When fully disordered:
  \[ y_A^I = y_A^II \]

- When order:
  \[ y_A^I \neq y_A^II \]

\[
T_{Tr} = \frac{- (G_{A:B} + G_{B:A}) \cdot x_A \cdot x_B}{R}
\]

\[ G_{A:B} = G_{B:A} < 0 \quad G_{A:A} = G_{B:B} = 0 \]
CEF: Order/Disorder: Fe-Al

Bcc in Fe-Al undergoes an order/disorder phase transition
CEF: CALPHAD Model for B2 Phases

- **Sublattice model:**
  \[(A,B,Va)_{0.5}(A,B,Va)_{0.5}(Va)_3\]

- **Gibbs energy model:**

  \[
  G_m^{ex} = xs G_m^{dis} + \Delta \text{ord} G_m
  \]

  \[
  xs G_m = G_m(x_i) + \Delta \text{ord} G
  \]

  \[
  \Delta \text{ord} G = \Delta G^{ord*}(y_i,y'_i) - \Delta G^{ord*}(x_i,x_i)
  \]

- **Within CALPHAD method, need to define correct references**

- **Example:**

  - \((Ni,Al,Ru)_{0.5}(Ni,Al,Ru)_{0.5}(Va)_3\)
  - It is necessary to define Gibbs energies of several stable, metastable (and even unstable) end-members:
    - \((Ni)_{0.5}(Al)_{0.5}(Va)_3\)
    - \((Ru)_{0.5}(Al)_{0.5}(Va)_3\)
    - \((Ni)_{0.5}(Ru)_{0.5}(Va)_3\)
    - \((Al)_{0.5}(Al)_{0.5}(Va)_3\)
    - \((Ni)_{0.5}(Ni)_{0.5}(Va)_3\)
    - \((Ru)_{0.5}(Ru)_{0.5}(Va)_3\)
CEF: Point Defects in B2 Phases

- Defect structure in sublattice model:

\[ (A, B, Va)_1 (A, B, Va)_1 \]

- Parameters:
  - References:
    \[ ^0G_{A:A}, ^0G_{B:B}, ^0G_{C:C} \]
  - Symmetry:
    \[ \Delta^0G_{A:B} = \Delta^0G_{B:A} \quad \text{Formation Energies} \]
    \[ \Delta^0G_{Va:B} = \Delta^0G_{B:Va} \quad \text{Formation Energies, Vacancies} \]
    \[ \Delta^0G_{A:Va} = \Delta^0G_{Va:A} \]
  - \( d_{1\text{NN}} \sim d_{2\text{NN}} \)
    - Sublattice interactions necessary:

\[ L_{A,VA:B}, L_{A:B, Va} \]

CEF: Modeling of Oxides- Charge Conservation

• SM/CEF can also be used to describe free energies of oxides:

\[
(A^{+2}, E^{+3})_1 (E^{+3}, A^{+2})_2 (O^{-2})_4
\]

– Gibbs energies must be minimized under charge and mass conservation constraints
  • Conservación de componentes
  • Conservación de carga

• This model has been effectively used to describe thermodynamics of many oxide systems
CEF Application to Oxides, Example: TiO

- TiO (HT) has a NaCl crystal structure
- Complex defect structure:
  - Multiple valences
  - Interstitials

\[
(Ti^{+2}, Ti^{+3}, Va) (Ti, Va) (O^{-2})
\]

Interstitials
As oxygen concentration increases:
- Fraction of interstitial Ti decreases
- Oxidation state changes from Ti$^{+2}$ to Ti$^{+3}$

Oxidation state controls optical and electronic properties of this oxide phase
Thermodynamic models handle EOS & all kinds of thermodynamic properties for various systems. Some of the most important models are:

- **Component-Energy Model** (*interaction on up to ten sublattices)*:
  - Redlich-Kister polynomials (Muggianu or Kohler extrapolation)
  - Stoichiometric constraints
  - Interstitial solution
  - Chemical ordering
  - Ionic constituents

- **Two-Sublattice Ionic Liquid Model**

- **Associated Model**

- **Quasi-chemical Model**

- **Kapoor-Frohberg Cell Model**

- **Inden Model for magnetic ordering**

- **CVM (Cluster Variation Methods) for chemical ordering**

- **Birch-Murnaghan Model** (pressure-dependency) for minerals/alloys

- **SUPERFLUID Model** for C-H-O-S-N-Ar fluid & gaseous mixtures

- **DHLL, SIT, HKF and PITZ Models** for aqueous solutions

- **Flory-Huggins Model** for polymers
CALPHAD Method: Assessment of Model Parameters
Thermodynamic Databases

• A (thermodynamic) database in our understanding means a collection of polynomials describing the Gibbs energy of individual phases of a system as a function of temperature, (pressure) and composition.

Assessed thermodynamic database consist of model parameters which describe as accurately as possible experimental data on binary, ternary systems and higher order systems. The models are based on physical principles which make it possible to extrapolate to commercially interesting multicomponent systems. Extrapolation from several assessed lower order systems require that these systems are internally consistent and this take time and effort to achieve.
Thermodynamic Databases

- Unary systems. \( G = G(T) \) for all stable \textbf{and} metastable phases included in database.
- Binary systems (or parts of). \( G = G(T,x) \) for stable and metastable phases, including binary phases.
- Ternary systems (or parts of). See above.
- Higher order systems (parts of).

Thanks to: Paul Mason \[ \text{Techo-Calc Software} \]
The CALPHAD method.

**Theory**
- Quantum Mechanics
- Statistical Thermodynamics

**Estimates**

**Experiments**
- DTA, Calorimetry
- EMF, Vapor pressure
- Metallography, X-Ray diffraction

**Models**
- with adjustable Parameters
  - Thermodynamic Functions
    - \( G, H, S, C_P = f(T, P, x, \ldots) \)

**Equilibrium Calculations**
- Storage Databases, Publications

**Thermodynamic Optimization**
- Ab-initio calculation

**Applications**

**Graphical Representation**

**Phase Diagrams**

**Equilibria**
Sources of thermodynamic data

Two types of data

- Basic thermodynamic and phase equilibrium data – the building blocks of thermodynamic databases
  - Experimental
    - Phase equilibrium (phase diagrams) for binary and ternary system (liquidus/solidus/phase boundary)
    - Thermodynamic data for compounds/stoichiometric phases
    - Activity measurements etc
  - Theoretical
    - Estimation and Ab initio calculations

- Higher order (multi-component data) – validation for alloys etc
  - Experimental
    - Cp, liquidus/solidus/phase boundary data etc for “real” alloys
    - Volume fraction of carbides etc

Thanks to: Paul Mason

Thermo-Calc Software
Higher order systems: Real alloys for validation

Figure 10.37 Comparison between calculated and experimental (Jernkonteret 1977) solidus and liquidus values of a range of steels.
From: Saunders & Miedownik: "Calphad - a comprehensive review"

Thanks to: Paul Mason Thermo-Calc Software
CALPHAD from DFT
Limitations of the CALPHAD approach

• CALPHAD models are only as good as the experimental data used to fit them

• On many occasions, this information is lacking:
  – Limited solubility
  – Thermochemistry at low temperature difficult to measure due to kinetic effects
  – Phases of interest are not even thermodynamically stable
    • Metastable, even unstable
  – Experimental difficulties make determination of thermochemical properties cumbersome

• What to do?
  – Ab-initio methods
Beyond 0K

- DFT yields ground state electronic structure+energy
- As T increases, internal degrees of freedom in the structure need to be taken into account
- Thermally-excited DOFs can be considered using relatively simple approaches (in this case implemented in the ATAT code by A. van de Walle)
Thermodynamic Calculations

Specific Heat of hcp_Mg

Enthalpy of hcp_Mg

Entropy of hcp_Mg

Phonon DOS

Calculation
Experiments
Applications
Design of Co-Ni-Ga Alloys
Background And Motivation

- Co-Ni-Ga and Co-Ni-Al have emerged as a promising high temperature SMAs
- In Co-Ni-Ga and Co-Ni-Al systems, the austenite phase has B2-type ordering (no full L21 ordering)
- Increased ductility and optimization of SM properties can be achieved by careful alloy design
  - Precipitation of ductile fcc phases along grain boundaries enhances ductility
  - Control of B2 composition as well as presence of ordered L12 precipitates determines Ms temperature (among other things) and stability of SM properties
  - Need to prevent precipitation of undesirable phases (Ni5Ga3, for example)

(Okawa, 2001; 2006)

Phase Stability in CoNiGa and corresponding microstructure:

Left: no fcc precipitates
Right: fcc precipitates

Karaman (2008)

(Liu, 2006)
Phase Diagram and Microstructures:

(Liu, 2006)
Phase Stability and Alloy Design

- **Phase** constitution changes dramatically with composition and temperature
- **Alloy** design in multi-phase SMAs solely through empirical approaches is quite challenging
- **Thermodynamics**, thermodynamic modeling and phase-stability prediction can be used to understand complex equilibria
- **Challenges:**
  - Not enough experimental data available
    - Most experimental investigation concentrates around target SM compositions
- **Opportunities:**
  - Ab initio data can supplement experimental data to develop accurate thermodynamic models to predict phase stability
Application of DFT in Thermodynamic Modeling of Co-Ni-Ga Alloys

• True ground state in Ni-Ga?
  – $\text{Ni}_5\text{Ga}_3$ and other Ni-Ga intermetallics ($\text{Ni}_{13}\text{Ga}_9$) may affect performance in some alloy compositions

• Can DFT be used to validate new CALPHAD model for Co-Ga binary system?

• Is there ternary ordering to L21 in Co-Ni-Ga alloys?

• Is it possible to reduce DOF in models for ternary Co-Ni-Ga phases
  – Interactions and parameters grow geometrically with numbers of components
Ground State in Ni-Ga

- Experiments have difficulty in sampling ground state
- Some phases stable at high temperature may become unstable at low temperatures
- Important to determine ground state for development of robust thermodynamic models
Ni-Ga Ground State

- Ni5Ga3 and Ni13Ga9 are true ground states in Ni-Ga
- They project into ternary (dissolve significant amounts of Co)
- B2 (NiGa) may not be true ground state (decomposition, transformation?)
- Ni
- Somewhat unrelated to SMAs:
  - NiGa4 is not a phase in the system
  - New phase predicted with PdGa5 prototype
Thermodynamic modeling in Co-Ga

• Accurate thermodynamic model for Co-Ga system is essential to extrapolate to Co-Ni-Ga ternary
• The beta phase (B2) description is very important, as it dominates the central region of the ternary Co-Ni-Ga system where the shape memory effect is observed
• In earlier Co-Ga models, B2 phase becomes stable at high temperatures

Message:
Fitting parameters to known temperature ranges may lead to erroneous extrapolations
Thermodynamic Model and Phase Stability Prediction in **Co-Ga**
DFT used to validate Thermodynamic Models

- Comparison of calculated enthalpies of formation at 298 K with DFT calculations
- DFT results **WERE NOT** used to fit model parameters

<table>
<thead>
<tr>
<th>Phase</th>
<th>GGA</th>
<th>LDA</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$ (Ga:Co)</td>
<td>$-26,900$</td>
<td>$-39,400$</td>
<td>$-37,833$</td>
</tr>
<tr>
<td>$\beta$ (Ga:Va)</td>
<td>$7,700$</td>
<td>$8,600$</td>
<td>$7,250$</td>
</tr>
<tr>
<td>CoGa$_3$</td>
<td>$-25,900$</td>
<td>$-32,400$</td>
<td>$-28,666$</td>
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</table>

- Comparison of calculated lattice parameters from DFT calculations with experiments

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice parameters (Å)</th>
<th>LDA</th>
<th>GGA</th>
<th>Experiments</th>
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</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>$a$</td>
<td>$2.813$</td>
<td>$2.886$</td>
<td>$2.880$ [34]</td>
</tr>
</tbody>
</table>
Comparison with thermochemical measurements

a) Enthalpies of formation of liquid alloys at 1537 K

b) Enthalpies of formation of intermediate phases at 298 K
The Ternary Co-Ni-Ga phase diagram

- Thermodynamic model developed with DFT and experimental data
- ‘Negative’ evidence was also used
  - Absence of phases at specific compositions/temperatures were used as exp. data
- Developed through extrapolations from binaries with third-order corrections
- Additional Experiments were used to validate models

Isothermal section at 1000° C
Co$_{30}$Ni$_{45}$Ga$_{25}$ 1077 °C (1350K) 24 hrs WQ

THERMO-CALC (2010.02.02:15.21) :
DATABASE: USER
X(CO)=0.3, X(NI)=0.45, N=1, P=1E5;

Co$_{30}$Ni$_{45}$Ga$_{25}$

Intensities (arb. unit)

γ(111), M(111)
M(200)
γ(200)
M(220)
γ(220)
M(030)

50% (±2) γ
Applications
Computational+Experimental Design of TRIP Steel

Shengyen Li
THE Martensitic transformation results in large elastic and plastic strains.” - Bhadeshia, 2004

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<thead>
<tr>
<th>Phase Mixture in Fe-0.2C-1.5Mn wt% at 300K</th>
<th>Stored Energy J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite, Graphite, and Cementite</td>
<td>0</td>
</tr>
<tr>
<td>Ferrite and Cementite</td>
<td>70</td>
</tr>
<tr>
<td>Paraequilibrium Ferrite and Cementite</td>
<td>385</td>
</tr>
<tr>
<td>Bainite and Paraequilibrium Cementite</td>
<td>785</td>
</tr>
<tr>
<td>Martensite</td>
<td>1214</td>
</tr>
</tbody>
</table>

Targets: **Maximize the retained Austenite**

- Bainite transformation rate
- Carbon enrichment after heat treatment
- The Martensitic transformation (if possible)
- Volume Fraction of each Phase at each stage
Two-Step Heat Treatment

Two-Step Heat Treatment

\[ T_{IA} \quad \text{IA} \]

\[ T_{BIT} \quad \text{BIT} \]

\[ Vf_{2}(Mar) \]

\[ Vf_{1}(Bai) \]

\[ Vf_{1}(Mar) \]

\[ Vf(Fer) \]

\[ Vf_{4}(Aus) \]
Phase diagram under equilibrium and para-equilibrium conditions of Fe-0.32C-1.42Mn-1.56Si
Bainitic transformation is diffusional in nucleation process and diffusionless in growth process.

\[ \Delta G_{\text{MAX}} < \Delta G_{\text{N}} \]

\[ \Delta G^{\gamma \rightarrow \alpha} < -400 \]
• During BIT, carbon is repelled from Bainite and enriches Austenite.
• With the higher carbon content, the driving force to transform Austenite is lower.
• While the driving force is less than the stored energy (400J/mol), Austenite is no longer to transform into Bainite.
• Carbon stabilized the retained Austenite.
• If the carbon content is high enough, the retained Austenite does not transform into Martensite at operating temperature (room temperature is set in this work.)
• The red triangle stands for the optimum heat treated condition; there is no Martensite in the product.
Diffusion controlled TTT Diagram

Incubation time
This formula is proposed by Bhadeshia 1982

\[ \tau = \frac{T^{20}}{(\Delta G)^p} \exp \left( \frac{Q}{RT} + c \right) \]

Diffusion controlled model
This is implemented by Luzginova (2008)

\[ f = 1 - \exp \left( -K_1 \cdot v_0 \cdot \exp \left( -\frac{K_2 Q_C^y}{RT} \right) \cdot \Delta t^2 \right) \]
TTT Diagram – Jacques Model

This model is proposed by Jacques in 2006

\[ dV^e_B = \left( I_p + I_a \right) \cdot u_b \cdot \exp \left[ -\frac{G^{\gamma\rightarrow\alpha}_{np}}{RT} \right] \, dt \]

\[ dI_p = N_0 \cdot s_\gamma \cdot \nu \cdot E_p \, dt \]

\[ dI_a = I_p \cdot \frac{2D_\gamma}{\pi \cdot l_b} \cdot \beta_a \cdot E_p \, dt \]
This model is proposed by Jacques in 2006

\[ dV_B^e = (I_p + I_a) \cdot u_b \cdot \exp \left[ \frac{G_{np}^{\gamma \rightarrow \alpha}}{RT} \right] dt \]

\[ dI_p = N_0 \cdot s_\gamma \cdot v \cdot E_p \, dt \]

\[ dI_a = I_p \cdot \frac{2D_\gamma}{\pi \cdot l_b} \cdot \beta_a \cdot E_p \, dt \]
TTT Diagram – Jacques Model

Prime Nucleation

Autocatalytic Nucleation

Austenite

Fe-0.3C-1.42Mn-1.56Si
T=613K

$w(C_{Aus})$, %

$Vf(Bainite)$

Time, Second

Efficient Multifunctional Materials
Genetic Algorithm Alloy Design

Generate (a) TIA, (b) TBIT

1. Estimate the phase stability and chemical composition of Austenite after IA Treatment
2. Update the Alloy composition for BIT Treatment
3. Evaluate

Genetic Algorithm

1,000 Generations (10,000 Samples)

Good Genes

Bad Genes

Estimate the Thermodynamics state in Para-Equilibrium

Obtain the state of Austenite

Estimate the state of the alloy at 300k
**Genetic Algorithm**

**Randomly choose parents**

**Generating:** Randomly swap two positions or genes

**Compare the fitting value**

**Choose the better conditions as new parent and repeat the process**

**Mutating:**

- Parent: ABAABBBABABA

  - Mutating examples:
    - ABAAABBBABABA
    - ABABABBAAAAA
    - ABAAABBAAAAA

**Mating:**

- Parents: ABAABBBAAAAA
  - Parent: ABAABBBAAAAA
  - Parent: ABAABBBAAAAA

**Diagram:**

- Tree diagram showing the process of generating and mutating genetic algorithms.
Genetic Algorithm

<table>
<thead>
<tr>
<th></th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{IA}$</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>$T_{BIT}$</td>
<td>500</td>
<td>900</td>
</tr>
</tbody>
</table>
Applications
Coupling of CALPHAD+Phase Field Modeling:
Pb-free Soldering
Min Soo Park
Multiscale microstructure formation process

Dendrite polycrystals

Dendritic and Eutectic solidification

Influence of macroscopic solidification conditions

Map of morphologies of solidification

Intermetallic compounds in soldering reactions

Growth morphologies in Al-Si alloys for increasing solidification velocities
Solidification models

- **Classical model**
  - Pattern formation of solidification
  - Coupling equations between two neighboring phases
  - Free boundary and moving boundary (Stefan problem)
  - Difficulty of handling topology changes

- **Approach**: Phase-field modeling
  - WBM (Wheeler, Boettinger McFadden) model (Wheeler 1992)
  - Kim & Kim model (Kim 1999)
  - Steinbach model (Multi-phase field model) (Steinbach 1999)

### Classical model
- Sharp Interface
- Independent governing equations for each phases
- Phase boundaries
  - Discontinuous
  - Atomic scale

### Phase field model
- Diffusion Interface
- Integrated governing equations for all phases
- Phase boundaries
  - Continuous
  - Non-atomic scale
Phase field model

Wheeler, Boettinger, McFadden, Physical Review A V.45 No.10 pp.7424 1992

- New variable in governing equation \( \phi(x,t) \)
- Helmholtz free energy is a functional of the phase field

\[
F[\phi, \cdots, \nabla \phi, \cdots] = \int_{\Omega} \left[ f(\phi, \cdots) + \frac{1}{2} \varepsilon^2 (\nabla \phi)^2 + \cdots \right] d\Omega
\]

- Only contribution to the energy functional from local gradients is of the phase field

\[
\dot{\phi} \propto L\left( \frac{\delta F}{\delta \phi} \right) \quad \text{Ginzburg-Landau Equation}
\]

Simple, realistic physical phenomena
Continuous computation with simpler numerical algorithms
Less time-consuming implement
Intermetallic compound (IMC) growth during Lead-free soldering

Background
1. Interface reaction occurs when a molten metal contact with a compatible solid metal
2. The reaction involves interdiffusion between the liquid and solid metal and often result in the formation and growth of IMC at the interface. - Soldering process
3. The formation of an intermetallic layer is essential to ensure the metallurgical bonding at the solder joint.

Considerations
1. Metallurgical life cycle of solder joint
   - Solidification without defects
   - Withstanding external stresses, fatigue, thermal shock, vibration, impact and so on
2. Solidification on soldering processes
   - Nucleation, precipitation, interdiffusion, coarsening, Reaction with substrate, and so on
3. Selection of soldering alloys
   - Pb-based alloys v.s. Pb-free alloys

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Lead-free soldering on Cu/Sn system

Infinite thickness of Solder (Sn)

Phase diagrams (Cu-Sn system)

Free Energy Curves (250 C)

Morphological Evolution of η phase

Morphological Evolution of η+ε phase

Morphological Evolution of η+ε phase (Nucleation)
Lead-free soldering on Cu/Sn/Cu system

Finite thickness of Solder (Sn)

Morphological Evolution of $\eta$ phase

3D integration

Morphological Evolution of $\eta$ & $\varepsilon$ phase