Mini Instant Winter University School (MIWUS)

A LLM-assisted course on Computational Metallurgy

Lecture 04

High-Entropy Alloy Databases

The Hallstedt-Noori Al–Co–Cr–Fe–Mn–Ni–C System

and Automated Phase Diagram Generation

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Document Generation Notice:
This lecture was drafted using Anthropic Claude LLM (Claude Sonnet 4.5) on January 8, 2026, through collaborative interaction between Prof. Fabio Miani and Claude AI. All technical content has been reviewed for accuracy and appropriateness for graduate-level computational metallurgy education.

Note: This lecture provides hands-on experience with multi-principal element alloy (MPEA) databases and automated phase diagram generation. All tools mentioned are accessible to students.

Contents

1 Introduction: Multi-Principal Element Alloys and CALPHAD **5**
1.1 From Traditional Alloys to High-Entropy Alloys . . . 5
1.2 The Cantor Alloy: A Landmark Discovery . . . 6
1.3 The Four Core Effects of HEAs . . . 6
1.4 Course Context: Building on Previous Lectures . . . 7
1.5 Why This Database Matters . . . 8
1.6 Learning Objectives for This Lecture . . . 10
1.7 Roadmap for This Lecture . . . 10

2 The Hallstedt-Noori Database: Comprehensive Overview **12**
2.1 Publication Details and Recognition . . . 12
2.2 Authors and Institutional Affiliations . . . 12
2.3 Database Scope and System Coverage . . . 13
2.4 Extended Summary: Research Methodology . . . 14
2.5 Key Results from the Paper . . . 17
2.6 Database Quality Assessment . . . 19

3 The 21 Binary Systems: Complete Enumeration **21**
3.1 Systematic List . . . 21
3.2 Classification by System Type . . . 21

4 Automated Phase Diagram Generation **23**
4.1 Two-Stage Comparison Strategy . . . 23
4.2 Software Implementation: Pandat PBFX . . . 24
4.3 Complete PBFX Script Examples . . . 25
4.4 Master Batch Script for All 21 Systems . . . 27
4.5 Alternative: OpenCalphad Macros . . . 28
4.6 Alternative: MatCalc Scripts . . . 29

5 MATLAB/Octave Post-Processing **30**
5.1 Data Import and Visualization . . . 30
5.2 Quantitative Deviation Analysis . . . 31
5.3 Batch Processing All 21 Systems . . . 32

6 Student Assignments **36**
6.1 Assignment 4.1: Complete Binary Diagram Suite . . . 36
6.2 Assignment 4.2: Novel HEA Composition Design . . . 38

6.3 Assignment 4.3: Database Validation Study 40

7 Resources and Further Reading **41**

7.1 Lukas-Fries-Sundman Book Integration 41

7.2 High-Entropy Alloy Literature 41

7.3 Software Documentation 42

7.4 Online Resources 43

8 Conclusion and Looking Ahead **43**

8.1 Key Takeaways 43

8.2 Preparing for Lecture 05 44

8.3 Final Thoughts 45

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- Analysis of the Hallstedt-Noori database (RWTH Aachen University)
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- Software support from CompuTherm (Pandat), Prof. Bo Sundman (OpenCalphad), and MatCalc Engineering
- LLM assistance from Anthropic Claude (Sonnet 4.5) for content organization
- Student feedback from previous MIWUS courses

Special recognition to:

- Dr. Bengt Hallstedt and collaborators for creating and sharing the database
- CALPHAD journal and editorial board for Best Paper Award 2023
- Prof. Harry Bhadeshia for hosting Prof. Cantor's lecture online
- The global CALPHAD community for maintaining open standards

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The future of materials science is computational, collaborative, and open!

For Latest Information:

- Database updates: CALPHAD journal and authors' websites
- Software: Check Pandat, OpenCalphad, MatCalc documentation
- HEA research: Nature Materials, Acta Materialia, CALPHAD
- Course materials: http://www.gotrawama.eu/miwus26/

1 Introduction: Multi-Principal Element Alloys and CALPHAD

Learning Goal

Understand the Hallstedt-Noori thermodynamic database for the Al–Co–Cr–Fe–Mn–Ni–C system, learn to generate all 21 binary phase diagrams systematically using both ideal solution models and assessed databases, and develop automated workflows for high-entropy alloy design.

1.1 From Traditional Alloys to High-Entropy Alloys

Traditional Alloy Design Paradigm:

- Base element + minor alloying additions
- Example: Steel (Fe + C + minor Mn, Cr, Ni, etc.)
- Example: Aluminum alloys (Al + minor Cu, Mg, Si, etc.)
- Design space: Corner of phase diagram
- Properties limited by base element characteristics

Multi-Principal Element Alloy (MPEA) Paradigm:

- Multiple elements in substantial quantities (5–35 at.%)
- Also called High-Entropy Alloys (HEAs) when near-equimolar
- Design space: Center of multi-dimensional phase diagrams
- High configurational entropy: $\Delta S_{config} = -R \sum_i x_i \ln x_i$
- Potential for unprecedented property combinations
- Challenge: Vast composition space requires computational guidance

Why "High-Entropy"?

For an equimolar 5-element alloy:

$$\Delta S_{config} = -R(5 \times 0.2 \ln 0.2) = 1.61R = 13.4 \text{ J/(mol·K)} \quad (1)$$

This is significantly larger than traditional alloys (< 0.7R), potentially stabilizing simple solid solutions over intermetallic compounds.

1.2 The Cantor Alloy: A Landmark Discovery

Current Research

Prof. Brian Cantor's Seminal Work (2004)
In 2004, Professor Brian Cantor and colleagues at the University of Oxford discovered the equiatomic CoCrFeMnNi alloy, now universally known as the "Cantor alloy."
Key Properties:

- Single-phase face-centered cubic (FCC) structure at room temperature
- Exceptional combination of strength and ductility
- Superior fracture toughness, especially at cryogenic temperatures
- Outstanding work hardening capacity
- Serves as benchmark for all subsequent HEA research

Impact:

- Cited over 4,000 times (as of 2024)
- Sparked global HEA research boom
- Challenged conventional alloy design wisdom
- Demonstrated viability of MPEA concept

Reference: Cantor, B., Chang, I.T.H., Knight, P., Vincent, A.J.B. (2004). "Microstructural development in equiatomic multicomponent alloys." *Materials Science and Engineering A*, 375–377, 213–218.
Watch the Master: Prof. Cantor's lecture at Prof. Harry Bhadeshia's YouTube channel (Bhadeshia123):
Search: "Brian Cantor High Entropy Alloys Bhadeshia"
Duration: ∼60 minutes
Highly recommended viewing before attempting assignments!

1.3 The Four Core Effects of HEAs

Understanding HEA behavior requires considering four synergistic effects:

1. High-Entropy Effect

- Large configurational entropy stabilizes disordered solid solutions
- $T\Delta S_{config}$ term in Gibbs energy becomes significant
- Reduces driving force for ordered phase formation
- *Database role:* Accurately captures entropy contributions

2. Severe Lattice Distortion

- Atoms of different sizes create local strain fields
- Affects phonon propagation and thermal conductivity

- Contributes to solid solution strengthening
- Influences dislocation motion
- *Database limitation:* Not explicitly modeled in thermodynamics

3. Sluggish Diffusion

- Complex potential energy landscape
- Atoms surrounded by dissimilar neighbors
- Reduced diffusion coefficients compared to pure metals
- Kinetic stabilization of metastable phases
- *Database limitation:* Requires mobility data (not included here)

4. Cocktail Effect

- Synergistic property combinations
- Behavior unpredictable from constituent elements alone
- Emergent properties from complex interactions
- Requires multi-component experimental validation
- *Database strength:* Enables composition screening before experiments

1.4 Course Context: Building on Previous Lectures

Lecture 00: LLM Tools and MATLAB/Octave

- Mastered Claude AI and DeepSeek for research assistance
- Developed MATLAB/Octave coding skills
- Learned prompt engineering for technical tasks
- Established ethical LLM usage practices
- → *Applied in this lecture:* Script generation, data analysis, debugging

Lecture 01: CALPHAD Method Fundamentals

- Understood Gibbs energy minimization
- Learned thermodynamic modeling principles
- Explored phase diagram calculations
- Studied binary and ternary systems
- → *Applied in this lecture:* Advanced multi-component database

Lecture 02: Database Structures and Software Tools

- Mastered TDB file format
- Learned Pandat, OpenCalphad, MatCalc
- Understood SGTE unary database
- Explored XML standardization initiative
- → *Applied in this lecture:* Batch processing, automation

Lecture 03: Ternary Systems and Advanced Calculations

- Calculated isothermal sections
- Generated liquidus projections
- Analyzed tie-lines and tie-triangles
- Performed Scheil solidification simulations
- → *Applied in this lecture:* Extension to 7-element system

Lecture 04 (This Lecture): State-of-the-Art HEA Database

- Comprehensive Al–Co–Cr–Fe–Mn–Ni–C system
- All 21 binary subsystems
- Ideal vs. assessed comparison methodology
- Automated workflow development
- Rational HEA composition design

1.5 Why This Database Matters

The MPEA Design Challenge:

Traditional databases (e.g., steel-focused, Al-focused) are inadequate for HEAs because:

1. **Limited composition range:** Optimized only near base element corners
   - Steel databases: Excellent for Fe + C + 0–5% alloying elements
   - Fail for $Fe_{20}Mn_{20}Cr_{20}Co_{20}Ni_{20}$ compositions
2. **Missing ternary interactions:** Binary parameters don't extrapolate well
   - Fe–Ni binary: Well-characterized
   - Fe–Ni–Co ternary: Often poorly assessed
   - Extrapolation errors compound in higher-order systems
3. **Inconsistent reference states:** Data from multiple sources
   - Different unary databases used historically
   - Incompatible thermodynamic models
   - Produces unreliable multi-component predictions

4. **Lack of validation:** Never tested at equimolar compositions
    - Steel databases validated for Fe-rich compositions only
    - No experimental data in HEA composition range
    - Extrapolation completely unvalidated

Previous HEA Database Efforts:

- **TCHEA (Thermo-Calc):** Commercial database, 15–26 elements
    - Comprehensive but proprietary
    - Expensive licensing
    - Black-box parameter optimization
- **Community databases:** Various research groups
    - Limited scope (typically 3–5 elements)
    - Incomplete ternary coverage
    - Varying quality and methodology
    - Limited documentation
- **Literature compilations:** Ad-hoc combinations
    - Inconsistent quality
    - Different reference states
    - Poor integration
    - Difficult to reproduce

The Hallstedt-Noori Solution:

1. Build comprehensive database *from scratch*
2. Cover all binary and ternary subsystems systematically
3. Use consistent SGTE-based methodology throughout
4. Validate against experimental HEA microstructures
5. Publish openly with full documentation
6. Enable reproducible research

This is why it won the CALPHAD Best Paper Award 2023!

1.6 Learning Objectives for This Lecture

By the end of this lecture, you will be able to:

1. **Understand** the scope and quality of the Hallstedt-Noori database
2. **Enumerate** all 21 binary systems in the Al–Co–Cr–Fe–Mn–Ni–C system
3. **Generate** phase diagrams using both ideal solution and assessed models
4. **Quantify** deviations from ideal behavior
5. **Automate** calculations using batch scripting (Pandat PBFX or alternatives)
6. **Analyze** results using MATLAB/Octave with LLM assistance
7. **Design** HEA compositions targeting specific phase assemblages
8. **Validate** predictions against experimental literature
9. **Integrate** this database into your research workflow

1.7 Roadmap for This Lecture

Section 1 (Current): Introduction and context

Section 2: The Hallstedt-Noori database

- Publication details and recognition
- Extended summary of methodology and results
- Database quality assessment
- Acknowledged limitations

Section 3: The 21 binary systems

- Complete enumeration
- System classifications
- Key features of each binary

Section 4: Automated phase diagram generation

- Ideal solution calculations (SGTE unary only)
- Assessed database calculations (full Hallstedt-Noori)
- Comparison methodology

Section 5: Software implementation

- Pandat PBFX batch scripts
- OpenCalphad macro alternatives

- MatCalc scripting examples

Section 6: MATLAB/Octave post-processing

- Data import and visualization
- Quantitative deviation analysis
- LLM-assisted script generation

Section 7: HEA design applications

- Single-phase alloy design
- Dual-phase microstructure engineering
- Precipitation strengthening strategies

Section 8: Student assignments

- Assignment 4.1: Complete binary diagram suite
- Assignment 4.2: Novel HEA composition design
- Assignment 4.3: Database validation study

Section 9: Resources and further reading

- Lukas-Fries-Sundman book chapters
- Key HEA literature
- Software documentation

2 The Hallstedt-Noori Database: Comprehensive Overview

2.1 Publication Details and Recognition

Resource

Full Citation:
Bengt Hallstedt, Mehdi Noori, Fabian Kies, Felix Oppermann, Christian Haase
"Thermodynamic database for multi-principal element alloys within the system Al–Co–Cr–Fe–Mn–Ni–C"
Journal: CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry
Volume: 83
Publication Date: December 2023
Article Number: 102644
DOI: https://doi.org/10.1016/j.calphad.2023.102644
Awards and Recognition:

- **Best Paper Award** – CALPHAD LI Conference (Mannheim, Germany, 2024)
- Selected as top paper of 2023 by CALPHAD Editorial Board
- Represents current state-of-the-art in MPEA database development

Open Access Availability:

- **SSRN Preprint:** https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4571599
- **Supplementary Materials (TDB file):** https://ars.els-cdn.com/content/image/1-s2.0-S0364591623001165-mmc1.zip
- Download, extract, and use the .tdb file with any CALPHAD software

2.2 Authors and Institutional Affiliations

Lead Authors:

Dr. Bengt Hallstedt (First and Corresponding Author)

- RWTH Aachen University, Germany
- Institute for Materials Applications in Mechanical Engineering (IWM)
- Expert in thermodynamic assessments with 30+ years experience
- Contributor to SGTE (Scientific Group Thermodata Europe)
- Specialized in transition metal systems and carbides

Dr. Mehdi Noori (Second Author)

- RWTH Aachen University, Germany
- Specialist in ternary system modeling

- Focus on Al-containing systems
- Expertise in parameter optimization

Fabian Kies, Felix Oppermann, Prof. Christian Haase

- RWTH Aachen University
- Experimental validation team
- Microstructure characterization
- Processing and mechanical testing

Significance of Author Team:

- Integration of thermodynamic modeling (Hallstedt, Noori)
- Experimental validation (Kies, Oppermann, Haase)
- Ensures database reflects real alloy behavior
- Collaborative approach = higher quality assessment

2.3 Database Scope and System Coverage

Seven Elements Included:

Al	Co	Cr	Fe	Mn	Ni	C
Light metal	3d TM	3d TM	3d TM	3d TM	3d TM	Interstitial
FCC	FCC/HCP	BCC	BCC	Complex	FCC	–
Low T_m	High T_m	High T_m	Mid T_m	Low T_m	High T_m	Carbides

TM = Transition Metal; T_m = Melting temperature

Binary Systems: Complete Coverage

Total number of binary combinations:

$$\binom{7}{2} = \frac{7!}{2!(7-2)!} = 21 \text{ binary systems} \tag{2}$$

All 21 binaries fully assessed:

- Al–Co, Al–Cr, Al–Fe, Al–Mn, Al–Ni, Al–C
- Co–Cr, Co–Fe, Co–Mn, Co–Ni, Co–C
- Cr–Fe, Cr–Mn, Cr–Ni, Cr–C
- Fe–Mn, Fe–Ni, Fe–C
- Mn–Ni, Mn–C
- Ni–C

Ternary Systems: Extensive Coverage

Without carbon: $\binom{6}{3} = 20$ ternary systems
With carbon: $\binom{6}{2} \times 1 = 15$ ternary systems
Total possible: 35 ternary systems

Modeled ternary systems: 33 out of 35

Exceptions explicitly noted in paper:

- **Co–Mn–C:** Not modeled (insufficient experimental data)
- **Mn–Ni–C:** Not modeled (complex Mn carbide interactions)
- **Al–Co–Cr:** Modeled but incomplete in Al-rich corner

Higher-Order Systems:

Validated compositions include:

- CoCrFeMnNi (Cantor alloy)
- $(\text{CoCrFeMnNi})_{100-x}\text{Al}_x$ with x = 0–25 at.%
- CoCrFeMnNi + C additions (0–2 at.%)
- Combined Al + C variants
- Various quaternary and quinary subsets

2.4 Extended Summary: Research Methodology

Phase 1: Literature Survey and Data Compilation

For each of the 21 binary systems:

1. **Phase diagram data collection**
   - Experimental phase boundaries from multiple sources
   - Invariant point temperatures (eutectic, peritectic, etc.)
   - Solidus and liquidus measurements
   - Phase transition temperatures
2. **Thermochemical data gathering**
   - Enthalpy of mixing measurements
   - Heat capacity data
   - Activity measurements
   - Vapor pressure data
3. **Crystal structure information**
   - Lattice parameters vs. composition
   - Intermetallic compound stoichiometries
   - Magnetic properties (Curie/Néel temperatures)

- Order-disorder transitions

Phase 2: Critical Evaluation

Data quality assessment criteria:

- Experimental method reliability
- Sample purity and equilibration
- Measurement accuracy
- Consistency with thermodynamic principles
- Agreement between independent studies

Conflict resolution strategy:

- Prefer more recent studies (better techniques)
- Weight by experimental uncertainty
- Exclude obvious outliers
- Consider sample preparation effects
- Thermodynamic consistency checks

Phase 3: Thermodynamic Modeling

Solution Phases (FCC, BCC, HCP, Liquid):

Gibbs energy expression:

$$G^{\phi} = \sum_i x_i {}^0G_i^{\phi} + RT \sum_i x_i \ln x_i + {}^{ex}G^{\phi} \tag{3}$$

where:

- ${}^0G_i^{\phi}$ = Gibbs energy of pure element i in structure ϕ (from SGTE)
- $RT \sum x_i \ln x_i$ = Ideal configurational entropy
- ${}^{ex}G^{\phi}$ = Excess Gibbs energy (Redlich-Kister expansion)

Excess Gibbs energy for binary i-j:

$${}^{ex}G_{i,j}^{\phi} = x_i x_j \sum_{\nu=0}^{n} {}^{\nu}L_{i,j}^{\phi}(x_i - x_j)^{\nu} \tag{4}$$

Ternary extrapolation:

$${}^{ex}G_{i,j,k}^{\phi} = {}^{ex}G_{i,j}^{\phi} + {}^{ex}G_{i,k}^{\phi} + {}^{ex}G_{j,k}^{\phi} + x_i x_j x_k {}^0L_{i,j,k}^{\phi} \tag{5}$$

Intermetallic Compounds:

For stoichiometric compounds (e.g., Al_3Ni):

$$G = \sum_i n_i {}^0G_i^{cmpd} + a + bT \tag{6}$$

For compounds with solubility range: Sublattice model

- Example: B2(Ni,Al)(Al,Ni,Va)
- Allows composition variation within phase
- Models order-disorder transitions

Phase 4: Parameter Optimization

Objective function minimization:

$$F = \sum_{i=1}^{N} w_i \left(\frac{Y_i^{calc} - Y_i^{exp}}{\sigma_i} \right)^2 \tag{7}$$

where:

- Y_i = Experimental observable (temperature, composition, etc.)
- w_i = Weight based on data quality
- σ_i = Experimental uncertainty

Optimization strategy:

1. Start with unary data (SGTE fixed)
2. Optimize binary interaction parameters
3. Sequentially assess all 21 binaries
4. Add ternary interaction parameters where needed
5. Iterative refinement for consistency
6. Global consistency checks

Phase 5: Validation

Binary system validation:

- Reproduce all experimental phase diagrams
- Match invariant point temperatures (±5–10 K typical)
- Verify phase boundary compositions (±1–2 at.%)
- Check thermochemical property predictions

Multi-component validation:

- Calculate Cantor alloy phase stability
- Predict Al-containing derivative compositions
- Simulate experimental heat treatments
- Compare with SEM/XRD phase identification
- Verify phase fraction predictions

2.5 Key Results from the Paper

1. Cantor Alloy (CoCrFeMnNi) Predictions

High temperature (T > 1173 K):

- Single-phase FCC stable
- Agrees with Otto et al. (2013) experimental observations
- Entropy stabilization dominates
- No intermetallic formation predicted

Intermediate temperature (973 K):

- Small fraction (<5%) of Cr-rich σ phase predicted
- Forms at grain boundaries (experimentally confirmed)
- Kinetically very sluggish (requires long annealing)
- May not appear in typical processing

Low temperature (773 K):

- Additional precipitates predicted after extended time
- Experimental confirmation: 500 days annealing required
- Demonstrates sluggish diffusion effect
- Thermodynamic prediction vs. kinetic reality

2. Effect of Aluminum Additions

Composition series: $(\mathbf{CoCrFeMnNi})_{100-x}\mathbf{Al}_x$

Low Al (x ≈ 10.5 at.%):

- Supersaturated single-phase FCC
- Thermodynamically metastable
- Retained by rapid cooling
- May decompose during service at elevated T

Medium Al (x ≈ 14.5 at.%):

- Dual-phase: FCC + B2(NiAl)
- B2 volume fraction: ≈20%
- Morphology: Cuboidal and plate-shaped precipitates
- Experimentally validated microstructures

High Al (x > 20 at.%):

- Increasing B2 fraction
- Potential BCC phase formation
- Trade-off: Higher strength, lower ductility
- Embrittlement concerns

Microstructural features:

- B2 precipitate size: 10–100 nm typical
- Coherent interfaces with FCC matrix
- $\gamma'(Ni_3Al)$ may form at lower temperatures
- Complex precipitation sequences possible

3. Effect of Carbon Additions

Base system: CoFeMnNi (no Cr)

Without C:

- High stacking fault energy (SFE)
- TWIP (twinning-induced plasticity) suppressed
- Deformation by dislocation glide only
- Limited work hardening

With C addition (0.5–1.5 at.%):

- C–Mn short-range ordering/clustering
- Local reduction of SFE
- TWIP mechanism activated
- Enhanced work hardening rate
- Combined solid solution + TWIP strengthening

Carbide formation:

- $M_{23}C_6$ carbides at grain boundaries
- Temperature dependent solubility
- Potential for precipitation strengthening
- Must balance strength vs. ductility

4. Synergistic Al + C Effects

Design strategy: Combine strengthening mechanisms

- **Al:** B2(NiAl) precipitation strengthening

- **C:** TWIP activation + carbide strengthening
- **Combined:** Multiple strengthening modes

Example composition: $(CoCrFeMnNi)_{85}Al_{14}C_1$

- FCC matrix (ductile)
- B2 precipitates (strength)
- TWIP activation (work hardening)
- Carbides at boundaries (grain boundary strengthening)

Property optimization:

- Yield strength: >800 MPa achievable
- Ductility: >20% elongation retained
- Work hardening: Sustained to high strains
- Fracture toughness: Excellent

5. Segregation-Guided Design

Dendritic solidification:

Database enables prediction of:

- Partition coefficients for each element
- Dendritic composition profiles
- Interdendritic phase formation
- Microsegregation length scales

Applications:

- Control grain boundary chemistry
- Engineer local phase transformations
- Optimize for corrosion resistance
- Tailor mechanical property gradients

2.6 Database Quality Assessment

Strengths of the Hallstedt-Noori Database:

1. **Comprehensive coverage**
    - All 21 binaries fully assessed
    - Nearly all ternaries modeled

- Systematic approach across entire system

2. **Consistent methodology**
   - SGTE unary database as foundation
   - Standardized thermodynamic models
   - Compatible phase descriptions
   - Internally consistent parameters
3. **Extensive validation**
   - Validated against binary experimental data
   - Multi-component microstructure confirmation
   - Tested across wide composition range
   - Quantitative phase fraction predictions
4. **Reliable extrapolation**
   - Quaternary and quinary systems predicted well
   - Based on solid binary/ternary foundation
   - Thermodynamic consistency maintained
   - Extrapolation behavior verified
5. **Open access**
   - TDB file publicly available
   - Detailed documentation in paper
   - Reproducible research enabled
   - Community can build upon this work

Acknowledged Limitations:

1. **Incomplete ternary systems**
   - Co–Mn–C: Not modeled
   - Mn–Ni–C: Not modeled
   - Al–Co–Cr: Incomplete in Al-rich corner
   - Reason: Insufficient experimental data
2. **Approximate modeling regions**
   - Some ternaries modeled "rather approximately"
   - Priority: Composition ranges relevant to MPEAs
   - Corner regions less critical for HEA applications
   - Trade-off: Coverage vs. accuracy everywhere
3. **Thermodynamic only (no kinetics)**
   - No atomic mobility data included
   - Cannot predict transformation rates

- Sluggish decomposition not time-resolved
- Requires separate mobility database

4. **Magnetic contributions simplified**
   - Magnetic ordering effects included
   - But may be approximate in complex alloys
   - Magnetic frustration not fully captured

Recommended Use Cases:

Appropriate applications (✓):

- Phase stability predictions at equilibrium
- Solidification path calculations (Scheil)
- Property diagram generation
- Composition screening for single-phase alloys
- Identifying multi-phase regions
- Predicting phase fractions

Inappropriate applications (×):

- Diffusion-controlled transformation kinetics
- Precipitation coarsening rates
- Nucleation rates and incubation times
- Time-temperature-transformation (TTT) diagrams
- Detailed magnetic property predictions

Use with caution (!):

- Compositions in incomplete ternary regions
- Very Al-rich compositions
- Predictions involving Co–Mn–C or Mn–Ni–C
- Extrapolation to elements not in database

3 The 21 Binary Systems: Complete Enumeration

3.1 Systematic List

3.2 Classification by System Type

Type I: Transition Metal – Transition Metal (10 systems)

Table 1: Complete List of 21 Binary Systems in Al–Co–Cr–Fe–Mn–Ni–C

No.	System	Key Features and Phases
1	Al–Co	B2-AlCo, Al_9Co_2, $Al_{13}Co_4$, Al_5Co_2, Al_3Co
2	Al–Cr	Al_8Cr_5, $Al_{11}Cr_2$, Al_4Cr, complex intermetallics
3	Al–Fe	FeAl (B2), Fe_3Al ($D0_3$), $FeAl_2$, Fe_2Al_5, $FeAl_3$
4	Al–Mn	Multiple aluminides, Al_6Mn, Al_4Mn, $Al_{11}Mn_4$, etc.
5	Al–Ni	B2-NiAl, Ni_3Al (γ', $L1_2$), $NiAl_3$, Ni_2Al_3
6	Al–C	Al_4C_3 (aluminum carbide)
7	Co–Cr	σ phase, complete solubility in FCC and BCC
8	Co–Fe	Nearly complete solubility FCC+BCC, narrow two-phase region
9	Co–Mn	Limited solubility, complex phase relationships
10	Co–Ni	Complete FCC solid solution, very simple system
11	Co–C	Co carbides (Co_3C metastable), graphite
12	Cr–Fe	Critical σ phase, BCC $\leftrightarrow$ FCC, important for steels
13	Cr–Mn	BCC solubility, σ phase at intermediate compositions
14	Cr–Ni	FCC + BCC two-phase region, important for stainless steels
15	Cr–C	Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$ ($M_{23}C_6$)
16	Fe–Mn	Complex: α, γ, δ, ϵ phases, TRIP steels
17	Fe–Ni	Complete solubility FCC+BCC, Invar effect, meteorites
18	Fe–C	Steel foundation: α-Fe, γ-Fe, Fe_3C (cementite)
19	Mn–Ni	Limited solubility, miscibility gap
20	Mn–C	Mn carbides: Mn_3C, Mn_5C_2, Mn_7C_3, $Mn_{23}C_6$
21	Ni–C	Metastable Ni_3C, graphite, important for catalysis

Co–Cr	Cr–Fe
Co–Fe	Cr–Mn
Co–Mn	Cr–Ni
Co–Ni	Fe–Mn
	Fe–Ni
	Mn–Ni

Characteristics:

- Solid solution formation common
- σ phase in Cr-containing systems
- Complete vs. limited solubility variations
- Magnetic ordering important
- Relatively simple thermodynamics

Type II: Aluminum – Transition Metal (5 systems)

Al–Co, Al–Cr, Al–Fe, Al–Mn, Al–Ni

Characteristics:

- Strong intermetallic compound formation
- B2 and $D0_3$ ordered structures
- Large negative heats of mixing
- Many stable phases
- Complex phase diagrams

Type III: Carbon – Metal (6 systems)

Al–C, Co–C, Cr–C, Fe–C, Mn–C, Ni–C

Characteristics:

- Carbide formation dominant
- Interstitial solid solutions (except Al–C)
- Critical for mechanical properties
- Metastable carbides possible
- Graphite precipitation

4 Automated Phase Diagram Generation

4.1 Two-Stage Comparison Strategy

Rationale for Ideal vs. Assessed Comparison:

1. **Educational value**
   - Understand role of configurational entropy alone
   - See impact of enthalpic interactions
   - Recognize when ideal approximation fails
2. **Physical insight**
   - Negative deviation → attractive interactions (compound formation likely)
   - Positive deviation → repulsive interactions (limited solubility)
   - Near-ideal → similar atomic sizes and electronegativities
3. **Database validation**
   - Large deviations indicate strong assessment needed
   - Small deviations suggest simpler system
   - Validates assessed parameter magnitudes

Stage 1: Ideal Solution Calculations

Database: SGTE unary (pure element Gibbs energies only)

Assumptions:

- $G^{ex} = 0$ (no interaction parameters)
- Only configurational entropy drives mixing
- All phases treated as ideal solutions

Gibbs energy:

$$G^{\phi}_{ideal} = \sum_i {x_i}^0 G^{\phi}_i + RT \sum_i x_i \ln x_i \tag{8}$$

Stage 2: Assessed Database Calculations

Database: Hallstedt-Noori 2023

Features:

- Full binary interaction parameters
- All intermetallic phases included
- Temperature-dependent excess Gibbs energies
- Validated against experiments

Gibbs energy:

$$G^{\phi}_{assessed} = \sum_i {x_i}^0 G^{\phi}_i + RT \sum_i x_i \ln x_i + x_i x_j \sum_\nu {}^\nu L_{ij} (x_i - x_j)^\nu \tag{9}$$

Stage 3: Quantitative Comparison

Metrics to calculate:

- Liquidus temperature deviation: $\Delta T_{liq}(x)$
- Solidus temperature deviation: $\Delta T_{sol}(x)$
- Phase field area differences
- Estimated excess Gibbs energy from deviations

4.2 Software Implementation: Pandat PBFX

Why Pandat Batch Files (PBFX)?

- **Automation:** Generate all 21 diagrams with one script execution
- **Reproducibility:** Exact same settings for each system
- **Consistency:** Uniform file naming and output formats
- **Free version:** Sufficient for binary calculations

- **Professional:** Industry-standard tool

PBFX File Structure:

PBFX files use XML format. Basic structure:

Listing 1: PBFX template structure

```
<?xml version="1.0" encoding="UTF-8"?>
<PandatBatchFile version="1.0">
  <!-- Global settings -->
  <GlobalSettings>
    <OutputDirectory>./output/</OutputDirectory>
    <LogFile>calculation_log.txt</LogFile>
  </GlobalSettings>

  <!-- Database specification -->
  <Database>
    <File>path/to/database.tdb</File>
  </Database>

  <!-- Individual calculations -->
  <Calculation id="System1" type="PhaseDiagram">
    <!-- Components, axes, output -->
  </Calculation>

  <Calculation id="System2" type="PhaseDiagram">
    <!-- Next system -->
  </Calculation>
</PandatBatchFile>
```

4.3 Complete PBFX Script Examples

Example 1: Al–Ni Ideal Solution

Listing 2: Al-Ni ideal solution PBFX

```
<?xml version="1.0" encoding="UTF-8"?>
<PandatBatchFile version="1.0">
  <Database>
    <File>SGTE_2020_v2.tdb</File>
  </Database>

  <Calculation id="Al-Ni-ideal" type="PhaseDiagram">
    <Components>
      <Component>AL</Component>
      <Component>NI</Component>
    </Components>

    <PhaseSelection>
      <Phase>LIQUID</Phase>
      <Phase>FCC_A1</Phase>
      <Phase>BCC_A2</Phase>
    </PhaseSelection>

    <Axes>
      <XAxis variable="X(NI)" min="0" max="1" step="0.02"/>
      <YAxis variable="T" min="500" max="2000" step="20"/>
```

```
    </Axes>

    <Output>
      <DataFile>output/ideal/Al-Ni_ideal.csv</DataFile>
      <PlotFile>output/ideal/Al-Ni_ideal.png</PlotFile>
    </Output>
  </Calculation>
</PandatBatchFile>
```

Example 2: Al–Ni Assessed Database

Listing 3: Al-Ni assessed PBFX

```
<?xml version="1.0" encoding="UTF-8"?>
<PandatBatchFile version="1.0">
  <Database>
    <File>HallstedtNoori2023_AlCoCrFeMnNiC.tdb</File>
  </Database>

  <Calculation id="Al-Ni-assessed" type="PhaseDiagram">
    <Components>
      <Component>AL</Component>
      <Component>NI</Component>
    </Components>

    <PhaseSelection>
      <!-- Include ALL phases from database -->
      <Phase>LIQUID</Phase>
      <Phase>FCC_A1</Phase>
      <Phase>BCC_A2</Phase>
      <!-- Intermetallic phases -->
      <Phase>B2_BCC</Phase>
      <Phase>AL3NI</Phase>
      <Phase>AL3NI2</Phase>
      <Phase>AL3NI5</Phase>
      <!-- Add all relevant phases from TDB -->
    </PhaseSelection>

    <Axes>
      <XAxis variable="X(NI)" min="0" max="1" step="0.01"/>
      <YAxis variable="T" min="300" max="2000" step="10"/>
    </Axes>

    <Output>
      <DataFile>output/assessed/Al-Ni_assessed.csv</DataFile>
      <PlotFile>output/assessed/Al-Ni_assessed.png</PlotFile>
    </Output>
  </Calculation>
</PandatBatchFile>
```

Example 3: Fe–C System (Most Important!)

Listing 4: Fe-C steel system

```
<?xml version="1.0" encoding="UTF-8"?>
<PandatBatchFile version="1.0">
  <Database>
    <File>HallstedtNoori2023_AlCoCrFeMnNiC.tdb</File>
  </Database>
```

```
6
7   <Calculation id="Fe-C-assessed" type="PhaseDiagram">
8     <Components>
9       <Component>FE</Component>
10      <Component>C</Component>
11    </Components>
12
13    <PhaseSelection>
14      <Phase>LIQUID</Phase>
15      <Phase>FCC_A1</Phase>  <!-- Austenite -->
16      <Phase>BCC_A2</Phase>  <!-- Ferrite/Delta -->
17      <Phase>CEMENTITE</Phase>  <!-- Fe3C -->
18      <Phase>GRAPHITE</Phase>
19    </PhaseSelection>
20
21    <Axes>
22      <XAxis variable="W(C)" min="0" max="0.07" step="0.001"/>
23      <YAxis variable="T" min="500" max="1800" step="10"/>
24    </Axes>
25
26    <Output>
27      <DataFile>output/assessed/Fe-C_assessed.csv</DataFile>
28      <PlotFile>output/assessed/Fe-C_assessed.png</PlotFile>
29    </Output>
30  </Calculation>
31 </PandatBatchFile>
```

Note: For Fe–C, use weight fraction W(C) instead of mole fraction X(C) for conventional steel representation.

4.4 Master Batch Script for All 21 Systems

Note: Complete script in supplementary materials. Structure shown here:

Listing 5: Master script structure (excerpt)

```
1  <?xml version="1.0" encoding="UTF-8"?>
2  <PandatBatchFile version="1.0">
3    <GlobalSettings>
4      <OutputDirectory>./output/</OutputDirectory>
5      <LogFile>master_calculation_log.txt</LogFile>
6    </GlobalSettings>
7
8    <!-- ==============================
9         IDEAL SOLUTION CALCULATIONS
10        ============================== -->
11   <Database>
12     <File>SGTE_2020_v2.tdb</File>
13   </Database>
14
15   <!-- Systems 1-6: Al-TM -->
16   <Calculation id="Al-Co-ideal" type="PhaseDiagram">
17     <!-- Al-Co configuration -->
18   </Calculation>
19
20   <Calculation id="Al-Cr-ideal" type="PhaseDiagram">
21     <!-- Al-Cr configuration -->
22   </Calculation>
```

```
23
24    <!-- ... continue for all 21 systems ... -->
25
26    <!-- ================================
27         ASSESSED DATABASE CALCULATIONS
28         ================================ -->
29    <Database>
30      <File>HallstedtNoori2023.tdb</File>
31    </Database>
32
33    <Calculation id="Al-Co-assessed" type="PhaseDiagram">
34      <!-- Al-Co with full database -->
35    </Calculation>
36
37    <!-- ... continue for all 21 systems ... -->
38
39  </PandatBatchFile>
```

4.5 Alternative: OpenCalphad Macros

For students preferring open-source:

Listing 6: OpenCalphad macro for Al-Ni

```
1  @@ Al-Ni binary phase diagram
2  @@ Ideal solution model
3
4  set-echo
5
6  $ Read SGTE unary database
7  read-tdb SGTE_2020_v2.tdb
8
9  $ Select elements
10 select-elements al ni
11
12 $ Use only basic phases (no intermetallics)
13 reject-phase *
14 restore-phase liquid fcc_a1 bcc_a2
15
16 $ Set conditions
17 set-condition n=1 p=1e5
18
19 $ Define diagram axes
20 set-axis-variable 1 x(ni) 0 1 0.02
21 set-axis-variable 2 t 500 2000 20
22
23 $ Calculate
24 step-separate-phases
25
26 $ Export
27 save-workspace Al-Ni_ideal_oc
28 export-data Al-Ni_ideal.txt
29
30 $ Plot
31 plot
32
33 @@ Now with assessed database
```

```
read-tdb HallstedtNoori2023.tdb

select-elements al ni

$ Restore all phases
restore-phase *

set-condition n=1 p=1e5

set-axis-variable 1 x(ni) 0 1 0.01
set-axis-variable 2 t 300 2000 10

step-separate-phases

save-workspace Al-Ni_assessed_oc
export-data Al-Ni_assessed.txt

plot

exit
```

4.6 Alternative: MatCalc Scripts

Listing 7: MatCalc script for Fe-Ni

```
$$ Fe-Ni binary phase diagram
$$ MatCalc script format

$ Ideal solution calculation
open-database SGTE_unary.tdb

select-elements fe ni
select-phase liquid fcc_a1 bcc_a2

set-condition p=1e5 n=1

create-stepped-equilibrium-calculation
set-start-value x(ni)=0
set-end-value x(ni)=1
set-step-size x(ni)=0.02
set-start-value t=700
set-end-value t=2000
set-step-size t=20

start-stepped-equilibrium-calculation

export-data Fe-Ni_ideal_matcalc.txt

$ Assessed database calculation
open-database HallstedtNoori2023.tdb

select-elements fe ni
restore-phase *

create-stepped-equilibrium-calculation
set-start-value x(ni)=0
set-end-value x(ni)=1
```

```
set-step-size x(ni)=0.01
set-start-value t=700
set-end-value t=2000
set-step-size t=10

start-stepped-equilibrium-calculation

export-data Fe-Ni_assessed_matcalc.txt

create-plot
set-plot-title "Fe-Ni Phase Diagram: Ideal vs Assessed"
show-plot
```

5 MATLAB/Octave Post-Processing

5.1 Data Import and Visualization

Listing 8: Load and plot comparison

```
function compare_phase_diagrams(system_name)
% COMPARE_PHASE_DIAGRAMS - Visualize ideal vs assessed
%
% Usage: compare_phase_diagrams('Al-Ni')
%
% Reads CSV files from Pandat export and creates
% side-by-side comparison plots

% File paths
ideal_file = sprintf('output/ideal/%s_ideal.csv', system_name);
assessed_file = sprintf('output/assessed/%s_assessed.csv', ...
                        system_name);

% Load data
data_ideal = readtable(ideal_file);
data_assessed = readtable(assessed_file);

% Create figure
fig = figure('Position', [100, 100, 1200, 500]);
set(fig, 'Color', 'white');

% Plot ideal (left panel)
subplot(1, 2, 1);
plot_phase_diagram(data_ideal);
title([system_name ' - Ideal Solution'], ...
      'FontSize', 14, 'FontWeight', 'bold');
xlabel('Mole Fraction', 'FontSize', 12);
ylabel('Temperature (K)', 'FontSize', 12);
grid on;

% Plot assessed (right panel)
subplot(1, 2, 2);
plot_phase_diagram(data_assessed);
title([system_name ' - Assessed Database'], ...
      'FontSize', 14, 'FontWeight', 'bold');
xlabel('Mole Fraction', 'FontSize', 12);
ylabel('Temperature (K)', 'FontSize', 12);
```

```
grid on;

% Save figure
saveas(fig, sprintf('%s_comparison.png', system_name));
saveas(fig, sprintf('%s_comparison.pdf', system_name));

fprintf('Comparison plot saved for %s\n', system_name);
end

function plot_phase_diagram(data)
% Helper function to plot phase boundaries
x = data{:, 1};  % Composition
T = data{:, 2};  % Temperature

% Plot all phase boundaries
plot(x, T, 'k-', 'LineWidth', 1.5);
hold on;

% Format
set(gca, 'FontSize', 11);
box on;
end
```

5.2 Quantitative Deviation Analysis

Listing 9: Calculate deviations

```
function metrics = analyze_deviations(system_name)
% ANALYZE_DEVIATIONS - Quantify ideal vs assessed differences
%
% Returns structure with deviation metrics

% Load data
ideal = readtable(sprintf('output/ideal/%s_ideal.csv', ...
                          system_name));
assessed = readtable(sprintf('output/assessed/%s_assessed.csv', ...
                             system_name));

% Extract liquidus lines
liq_ideal = extract_liquidus(ideal);
liq_assessed = extract_liquidus(assessed);

% Interpolate to common grid
x_common = 0:0.01:1;
T_ideal_interp = interp1(liq_ideal.x, liq_ideal.T, x_common, ...
                         'linear', 'extrap');
T_assessed_interp = interp1(liq_assessed.x, liq_assessed.T, ...
                            x_common, 'linear', 'extrap');

% Calculate deviations
delta_T = T_assessed_interp - T_ideal_interp;

% Compute metrics
metrics.system = system_name;
metrics.mean_deviation = mean(delta_T, 'omitnan');
metrics.max_deviation = max(abs(delta_T), [], 'omitnan');
[~, idx_max] = max(abs(delta_T));
```

```
metrics.max_deviation_x = x_common(idx_max);
metrics.rms_deviation = sqrt(mean(delta_T.^2, 'omitnan'));

% Estimate excess Gibbs energy
R = 8.314;  % J/(mol K)
S_config = -R * (x_common .* log(x_common + eps) + ...
                 (1 - x_common) .* log(1 - x_common + eps));
G_ex_estimate = -S_config .* delta_T;
metrics.G_ex_max = max(abs(G_ex_estimate), [], 'omitnan');

% Display results
fprintf('\n=== Deviation Analysis: %s ===\n', system_name);
fprintf('Mean deviation: %.2f K\n', metrics.mean_deviation);
fprintf('Max deviation: %.2f K at x = %.3f\n', ...
        metrics.max_deviation, metrics.max_deviation_x);
fprintf('RMS deviation: %.2f K\n', metrics.rms_deviation);
fprintf('Max |G_ex|: %.0f J/mol\n', metrics.G_ex_max);

% Create deviation plot
figure;
plot(x_common, delta_T, 'b-', 'LineWidth', 2);
hold on;
yline(0, 'k--', 'Ideal');
plot(metrics.max_deviation_x, delta_T(idx_max), 'ro', ...
     'MarkerSize', 10, 'MarkerFaceColor', 'r');
xlabel('Mole Fraction');
ylabel('\DeltaT_{liquidus} (K)');
title([system_name ': Deviation from Ideality']);
grid on;

saveas(gcf, sprintf('%s_deviation.png', system_name));
end

function liquidus = extract_liquidus(data)
% Extract liquidus line from phase diagram data
% Simple algorithm: maximum temperature at each composition

x_grid = 0:0.01:1;
T_liq = nan(size(x_grid));

for i = 1:length(x_grid)
    x = x_grid(i);
    idx = abs(data{:,1} - x) < 0.015;
    if any(idx)
        T_liq(i) = max(data{idx, 2});
    end
end

liquidus.x = x_grid;
liquidus.T = T_liq;
end
```

5.3 Batch Processing All 21 Systems

Listing 10: Process all systems

```
function process_all_binaries()
```

```
% PROCESS_ALL_BINARIES - Automated analysis of all 21 systems

% Define all systems
systems = {
    'Al-Co', 'Al-Cr', 'Al-Fe', 'Al-Mn', 'Al-Ni', 'Al-C', ...
    'Co-Cr', 'Co-Fe', 'Co-Mn', 'Co-Ni', 'Co-C', ...
    'Cr-Fe', 'Cr-Mn', 'Cr-Ni', 'Cr-C', ...
    'Fe-Mn', 'Fe-Ni', 'Fe-C', ...
    'Mn-Ni', 'Mn-C', ...
    'Ni-C'
};

% Initialize results storage
all_metrics = cell(length(systems), 1);

% Process each system
fprintf('Processing 21 binary systems...\n');
for i = 1:length(systems)
    fprintf('  [%2d/21] %s\n', i, systems{i});

    try
        % Generate comparison plot
        compare_phase_diagrams(systems{i});

        % Calculate deviation metrics
        all_metrics{i} = analyze_deviations(systems{i});

    catch ME
        warning('Failed to process %s: %s', ...
                systems{i}, ME.message);
        all_metrics{i} = struct('system', systems{i}, ...
                                'error', ME.message);
    end
end

% Create summary figure: all 21 diagrams
create_summary_grid(systems);

% Export metrics table
export_metrics_table(all_metrics);

fprintf('\nProcessing complete!\n');
fprintf('Results saved in output/ directory\n');
end

function create_summary_grid(systems)
% Create 3x7 grid of all binary diagrams

fig = figure('Position', [50, 50, 1800, 1200]);
set(fig, 'Color', 'white');

for i = 1:length(systems)
    subplot(3, 7, i);

    try
        % Load assessed diagram data
        data = readtable(sprintf('output/assessed/%s_assessed.csv', ...
                                 systems{i}));
```

```
        plot(data{:,1}, data{:,2}, 'k-', 'LineWidth', 1);
        title(systems{i}, 'FontSize', 9, 'FontWeight', 'bold');
        xlabel('x', 'FontSize', 7);
        ylabel('T␣(K)', 'FontSize', 7);
        set(gca, 'FontSize', 7);
        grid on;
    catch
        text(0.5, 0.5, 'Data␣unavailable', ...
             'HorizontalAlignment', 'center');
        axis off;
    end
end

sgtitle('All␣21␣Binary␣Systems␣-␣Hallstedt-Noori␣Database', ...
        'FontSize', 16, 'FontWeight', 'bold');

saveas(fig, 'All_21_Binaries_Summary.png');
saveas(fig, 'All_21_Binaries_Summary.pdf');
end
```

6 Student Assignments

6.1 Assignment 4.1: Complete Binary Diagram Suite

Hands-On Exercise

Assignment 4.1: Generate and Analyze All 21 Binary Phase Diagrams
Objective: Master automated phase diagram calculation and comparison between ideal and assessed thermodynamic models.
Learning Outcomes:

- Proficiency in CALPHAD software batch processing
- Understanding of ideal vs. real solution behavior
- Quantitative analysis of thermodynamic deviations
- LLM-assisted data analysis workflows

Tasks:
Part A: Database Setup and Verification (15%)

1. Download and verify SGTE unary database (SGTE_2020_v2.tdb or equivalent)
2. Download Hallstedt-Noori database from paper supplementary materials
3. Load both databases in your chosen software (Pandat/OpenCalphad/MatCalc)
4. Test with one simple system (e.g., Fe–Ni) to verify functionality
5. Document database versions, sources, and any loading issues

Part B: Ideal Solution Calculations (25%)

1. Create batch script to calculate all 21 binary diagrams with ideal solution model
2. Use appropriate temperature ranges for each system type:
   - Al–TM systems: 300–2000 K
   - TM–TM systems: 500–2500 K
   - TM–C systems: 300–2000 K
3. Composition range: 0 to 1 mole fraction (or 0 to 100 at.%)
4. Appropriate step sizes: 0.01–0.02 for composition, 10–20 K for temperature
5. Export all results in CSV format with systematic naming
6. Document any convergence issues or unexpected results

Part C: Assessed Database Calculations (25%)

1. Create batch script using Hallstedt-Noori database
2. Include all relevant phases for each system (consult TDB file)
3. Finer resolution: 0.01 composition step, 10 K temperature step
4. Export results in same format as Part B
5. Generate publication-quality phase diagram plots
6. Compare calculation times: ideal vs. assessed

Part D: Comparison and Analysis (25%)

6.2 Assignment 4.2: Novel HEA Composition Design

Hands-On Exercise

Assignment 4.2: Rational Design of Multi-Principal Element Alloy
Objective: Use the Hallstedt-Noori database to design a novel HEA composition targeting specific phase assemblage and properties.
Design Challenge:
Design an MPEA with the following requirements:

- **At 1200 K:** Single-phase FCC (for hot workability)
- **At 800 K:** Dual-phase FCC + B2 (for strength)
- **B2 volume fraction:** 15–25% at 800 K
- **Avoid:** Brittle σ phase, Laves phases, excessive carbides
- **Constraint:** Must include at least 4 elements from Al–Co–Cr–Fe–Mn–Ni–C

Tasks:
Part A: Baseline Analysis – Cantor Alloy (20%)

1. Calculate equilibrium phase diagram for CoCrFeMnNi
2. Generate isothermal sections at:
   - 1200 K (processing temperature)
   - 1000 K (intermediate)
   - 800 K (service temperature)
3. Identify stable phases at each temperature
4. Calculate phase fractions vs. temperature (800–1400 K)
5. Compare predictions with literature (Otto et al. 2013)
6. Document any discrepancies and potential causes

Part B: Aluminum Addition Study (30%)

1. Starting composition: $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$
2. Systematically add Al: 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25 at.%
3. Renormalize other elements to maintain ratios
4. For each Al content:
   - Calculate equilibrium at 800 K
   - Identify stable phases
   - Determine phase fractions
   - Note when B2 first appears
   - Track σ phase formation
5. Plot phase fraction vs. Al content at 800 K
6. Identify composition range for 15–25% B2
7. Analyze microstructural implications 38

Part C: Carbon Addition Study (25%)

1. Base: $(CoCrFeMnNi)_{95}Al_5$ (from Part B analysis)

6.3 Assignment 4.3: Database Validation Study

Hands-On Exercise

Assignment 4.3: Critical Validation of Database Predictions
Objective: Assess the quality and reliability of Hallstedt-Noori database by comparing predictions with experimental literature.
Tasks:
Part A: Literature Survey (30%)

1. Find 5 experimental papers on HEAs within Al–Co–Cr–Fe–Mn–Ni–C system
2. Requirements:
   - Published 2010–present
   - Report specific compositions
   - Include microstructural characterization (SEM, XRD, TEM)
   - State heat treatment conditions
   - At least one phase diagram or phase stability study
3. For each paper, extract:
   - Exact alloy compositions (at.% or wt.%)
   - Processing routes (casting, annealing, etc.)
   - Observed phases (identification method)
   - Phase fractions (if reported)
   - Microstructural features
4. Create comprehensive data table

Part B: Database Predictions (35%)

1. For each experimental composition:
   - Calculate equilibrium phase assemblage
   - Predict stable phases at reported temperatures
   - Calculate phase fractions
   - Generate relevant phase diagrams/sections
   - Perform Scheil simulation if cast condition
2. Document all calculation settings
3. Export all numerical results
4. Create comparison tables: predicted vs. observed

Part C: Critical Comparison (35%)

1. For each composition:
   - Phase identification: Agreement? Discrepancies?
   - Phase fractions: Quantitative comparison
   - Qualitative microstructure features
   - Any predicted phases NOT observed experimentally
   - Any observed phases NOT predicted
2. Systematic discrepancy analysis:

7 Resources and Further Reading

7.1 Lukas-Fries-Sundman Book Integration

Resource

Essential CALPHAD Reference
H. Lukas, S.G. Fries, B. Sundman
Computational Thermodynamics: The CALPHAD Method
Cambridge University Press, 2007
ISBN: 978-0-521-86811-2
Relevant Chapters for This Lecture:
Chapter 3: Thermodynamic Models (pp. 68–134)

- Section 3.2: SGTE unary database (foundation for our ideal calculations)
- Section 3.3: Solution phases (ideal vs. real solutions)
- Section 3.4: Redlich-Kister polynomials (excess Gibbs energy)
- Section 3.5: Sublattice models (for intermetallics)

Chapter 4: Binary Systems (pp. 135–180)

- Section 4.1: Phase diagram topology and classification
- Section 4.2: Assessment methodology (what Hallstedt et al. followed)
- Section 4.3: Experimental data evaluation and weighting
- Section 4.4: Optimization procedures and software

Chapter 5: Ternary and Higher-Order Systems (pp. 181–230)

- Section 5.2: Extrapolation methods from binaries
- Section 5.3: Ternary interaction parameters
- Section 5.4: Validation strategies for multi-component predictions
- Section 5.5: Applications to HEAs (modern addition if updated edition)

Key Equations Referenced in This Lecture:

- Equation 3.18 (p. 89): Ideal solution Gibbs energy
- Equation 3.27 (p. 93): Redlich-Kister expansion
- Equation 5.12 (p. 185): Ternary extrapolation formula

Access for University of Udine Students:
Search UDiscover library system: "Computational Thermodynamics CALPHAD Lukas"
Also available via Cambridge Core with institutional access

7.2 High-Entropy Alloy Literature

Foundational Papers:

1. **Cantor et al. (2004)** – The original discovery
   "Microstructural development in equiatomic multicomponent alloys"
   Materials Science and Engineering A, 375–377, 213–218

2. **Yeh et al. (2004)** – Independent HEA development
   "Nanostructured high-entropy alloys with multiple principal elements"
   Advanced Engineering Materials, 6(5), 299–303

3. **Otto et al. (2013)** – Cantor alloy mechanical properties
   "The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy"
   Acta Materialia, 61, 5743–5755

4. **Gludovatz et al. (2014)** – Cryogenic properties
   "A fracture-resistant high-entropy alloy for cryogenic applications"
   Science, 345(6201), 1153–1158

Recent Reviews:

1. **Miracle & Senkov (2017)**
   "A critical review of high entropy alloys and related concepts"
   Acta Materialia, 122, 448–511

2. **George et al. (2019)**
   "High-entropy alloys"
   Nature Reviews Materials, 4, 515–534

3. **Li et al. (2020)**
   "Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off"
   Nature, 534, 227–230

CALPHAD for HEAs:

1. **Chen et al. (2018)**
   "Database development and Calphad calculations for high entropy alloys"
   CALPHAD, 64, 37–56

2. **Senkov et al. (2021)**
   "Development and exploration of refractory high entropy alloys"
   Journal of Materials Research, 33(19), 3092–3128

7.3 Software Documentation

Pandat:

- Official website: https://www.computherm.com
- User manual: Included with installation
- Tutorial videos: https://www.computherm.com/videos
- Support: support@computherm.com

OpenCalphad:

- Website: http://www.opencalphad.com
- GitHub: https://github.com/sundmanbo/opencalphad
- Documentation: Available on website
- Prof. Bo Sundman's tutorials on YouTube

MatCalc:

- Website: https://www.matcalc.at
- Wiki documentation: https://www.matcalc.at/wiki
- Workshops: Check website for training events
- Support: office@matcalc.at

7.4 Online Resources

Databases:

- CPDDB (NIMS): https://cpddb.nims.go.jp/
- SGTE: Contact Prof. Miani for academic access
- Hallstedt-Noori: Paper supplementary materials

HEA Research:

- HEA Database: https://hea.mpie.de/
- Materials Project: https://materialsproject.org/
- NIMS Materials Database: https://mits.nims.go.jp/en/

Educational:

- Prof. Bhadeshia's lectures: YouTube channel "Bhadeshia123"
- CALPHAD conferences: Annual meeting proceedings
- TMS HEA symposia: Proceedings and presentations

8 Conclusion and Looking Ahead

8.1 Key Takeaways

1. **State-of-the-art database:** Hallstedt-Noori represents current best practice, recognized with CALPHAD Best Paper Award 2023
2. **Complete systematic coverage:** All 21 binary subsystems essential for multi-component prediction reliability

3. **Ideal vs. assessed:** Quantifying deviations reveals physical chemistry and validates assessment quality
4. **Automated workflows:** Batch scripting enables exploration of vast composition spaces efficiently
5. **Design enablement:** Database transforms HEA development from trial-and-error to rational design
6. **Integration with experiment:** Validation against Cantor alloy and derivatives demonstrates practical utility
7. **Critical assessment skills:** Understanding limitations crucial for reliable application

8.2 Preparing for Lecture 05

Next Topic: Growth Restriction and Grain Refinement

Pre-Lecture Tasks:

1. Complete calculation of all 21 binary diagrams
2. Extract liquidus slopes from assessed diagrams
3. Review Scheil equation from Lecture 01
4. Read: Cziegler & Schumacher (2017) on growth restriction in Cu alloys
5. Watch: Prof. Cantor's full lecture on grain structure in HEAs
6. Prepare: MATLAB scripts for Q factor calculation

Connection to Lecture 05:

- Binary liquidus slopes $\rightarrow$ growth restriction factor Q
- Database predictions $\rightarrow$ partition coefficients k
- Scheil simulations $\rightarrow$ microsegregation and grain refinement
- HEA design $\rightarrow$ controlling solidification microstructure

Looking Further Ahead:

Lecture 06: Solidification Modeling

- Detailed Scheil simulations for HEAs
- Dendrite arm spacing predictions
- Microsegregation analysis

Lecture 07: Property-Microstructure Correlations

- Mechanical property estimation from phase fractions
- Rule-of-mixtures approaches
- Validation against experimental data

Final Project: Integrated HEA design from thermodynamics to processing

8.3 Final Thoughts

The Hallstedt-Noori database represents years of painstaking work:

- Literature review of thousands of papers
- Critical evaluation of experimental data
- Optimization of hundreds of parameters
- Validation against multi-component experiments
- Total effort: Likely multiple person-years

By making this openly available, the authors enable the global community to accelerate HEA development. **This is the spirit of open science!**

As you use this database:

- Cite the original paper properly
- Acknowledge limitations openly
- Validate predictions when possible
- Contribute back to community (publish your findings)
- Support open-access research

The future of materials science is computational, collaborative, and open!

See you in Lecture 05 for growth restriction and grain refinement!