ICME Design of High Performance Turbine Alloys

James Saal
Materials Design Engineer
Background - QuesTek Innovations LLC

A global leader in integrated computational materials design:

- Our *Materials by Design®* technology and expertise applies Integrated Computational Materials Engineering (ICME) tools and methods to design improved alloys faster and at less cost than traditional empirical methods.

- Start-up company in 1997, as a technology spinoff from Northwestern University in Evanston, Illinois.

- 15 U.S. patents awarded or pending; four computationally-designed, commercially-available steels.

- Chief Executive Officer: Aziz Asphahani, Ph.D., Former ASM President, NACE Fellow, ASM Fellow.

- Chief Science Officer: Greg Olson, Sc.D., member of NAE, AAAS, RSAES, Fellow of ASM and TMS.

- **Table of Elemental Symbols and Atoms:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Mass (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>13</td>
<td>26.982</td>
</tr>
<tr>
<td>Ti</td>
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<tr>
<td>Fe</td>
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<tr>
<td>W</td>
<td>74</td>
<td>183.84</td>
</tr>
</tbody>
</table>
Phased R&D based on ICME Approach

2015 University Turbine Systems Research Workshop
November 4, 2015
QuesTek Innovations - Commercial successes

- Recipient of >70 SBIR/STTR awards
  - $22 Million in government funding from DOD, DOE, etc. since 2002
  - $48 Million in cumulative commercialization value (top 5% of all SBIR awardees)
- Four computationally-designed, commercially-sold high performance Ferrium® steels licensed to Carpenter Technology
- >$750,000 in alloy licensing fees and royalties on material sales & $80,000 in software royalties
- Growing number of alloy development and modeling projects with industry (producers, OEMs, end-users) for next generation oil and gas pipelines, specialty alloys for aerospace, etc.

Proven success in developing novel alloys to meet specific performance requirements, commercializing, qualifying for aerospace usage, and transitioning into demanding applications.
Applications of QuesTek aerospace-qualified alloys

**Ferrium M54 steel**
Qualified for T-45 hook shanks with >2x life vs. incumbent alloy. QuesTek serving as prime to deliver 60 in 2017.

![Ferrium M54 steel hook shank for T-45](image)

**Ferrium S53 steel**
Cadmium-free landing gear in flight service on U.S. Air Force platforms A-10, C-5, KC-135 and T-38 to replace corrosion-prone 4340 and 300M steel.

![Ferrium S53 steel roll pins for C-5 aircraft](image)

**Ferrium C61 and C64 steel**
Being qualified for next generation helicopter transmission shaft and gears for U.S. Navy and U.S. Army to replace 9310 and Alloy X 53 to allow for greater power density / lightweighting.

![Ferrium C61 steel forward rotor shaft for Boeing's Chinook platform](image)

NAVIR Public Release #2014-712
Distribution Statement A: "Approved for public release; distribution is unlimited"
ICME-designed alloys for Additive Manufacturing (AM)

AM alloy design considerations
- Rapid heating / cooling / solidification
- Oxygen tolerance ("gettering")
- Novel precipitation strengthening concepts (e.g., elements with limited solid-state solubility)

QuesTek computational models
- Process-structure-property of AM processes
- Rapid solidification
- Multiple heating/cooling cycles
- Designing innovative new compositions (powders) specifically for Additive Manufacturing to enhance materials performance

Current projects
- Subcontract under Honeywell DARPA “Open Manufacturing” project (Nickel 718+ superalloys)
- Navy-funded project to design a new powder tailored for AM processes (Aluminum)
- Lockheed Martin funded project to apply QuesTek’s castable Ti alloy for AM

QuesTek sees tremendous opportunity in the design and development of new alloys for Additive Manufacturing
QuesTek Turbine DOE SBIR Programs

- Castable Single Crystal Ni-based Superalloys for IGT Blades – Phase II SBIR
- Exploration of High-Entropy Alloys for Turbine Applications – Phase I SBIR
Castable Single Crystal Ni-based Superalloys for IGT Blades

Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number(s) DE-SC0009592.”
SBIR Program PHASE II, DOE PM: Steve Richardson

SIEMENS
ICME-designed castable single crystal (SX) Ni Superalloy for industrial gas turbines

- Ongoing Department of Energy-funded project
- Existing best in class SX alloys have issues that limit their use:
  - Casting defects (“freckles” or multi-grains)
  - High levels (3-6%) of expensive rhenium (~$2,000 / lb*)
- Demonstrated on laboratory scale freckle-free castings w/ reduced Re content of ~1%
- Each 100 lb casting would use 2-5 less pounds of Re, saving $4-10K in raw material cost
- Has comparable high temperature tensile performance vs. Rene N5, CMSX4, 7 & 8, and creep (at right)

Goal: Single Crystal Ni Superalloy for IGT

- **SX castings – High Temperature Performance**
  - Desirable from a creep standpoint – no grain boundaries
- **IGT blade castings are large > 8 inches**
  - Slower solidification / cooling rates exacerbate processing issues (below)
- **Primary casting (processing) constraints:**
  - Freckle formation
  - Formation of high angle boundaries (HAB) and low-angle boundaries (LAB)
  - Hot-tearing
  - Shrinkage porosity
- **3rd generation blade alloys are especially difficult to cast as SX due to their high refractory content**
  - Increased tendency for hot tearing
  - Increased tendency for **freckle formation**

**QuesTek’s approach: ICME-based design of a new processable, high-performance single crystal alloy for IGT applications**
Systems design chart for SX castings
List of benchmark alloys

<table>
<thead>
<tr>
<th>ID</th>
<th>Re</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Hf</th>
<th>Mo</th>
<th>Ta</th>
<th>Ti</th>
<th>W</th>
<th>other</th>
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<td>-</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>1.5</td>
<td>4</td>
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<td>3.6</td>
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<tr>
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<td>0.8</td>
<td>9</td>
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<td>CMSX8</td>
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<td>0.6</td>
<td>8</td>
<td>0.7</td>
<td>8</td>
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<td>PWA1484</td>
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<td>9</td>
<td>-</td>
<td>6</td>
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<td>6</td>
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<tr>
<td>Rene N5</td>
<td>3</td>
<td>6.2</td>
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<td>0.15</td>
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<td>-</td>
<td>5</td>
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<td>TMS238</td>
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<td>1.1</td>
<td>7.6</td>
<td>-</td>
<td>4</td>
<td>5.0Ru</td>
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</table>

QuesTek’s design (“QT-SX”) contains these same elemental constituents, but with 1% Re
QuesTek Creep Modeling

- $\gamma'$ Coarsening Rate Constant
- Reed creep merit index: Assumes that the diffusivity at the $\gamma/\gamma'$ interface controls the climb process = rate controlling mechanism during creep

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Creep merit index (m$^{-2}$ s $\times 10^{15}$)</th>
<th>Coarse $K_{MP} \times 10^{20}$</th>
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<tbody>
<tr>
<td>CMSX-10</td>
<td>6.93</td>
<td>4.59</td>
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<tr>
<td>PWA1484</td>
<td>5.68</td>
<td>5.97</td>
</tr>
<tr>
<td>CMSX-4</td>
<td>4.51</td>
<td>6.00</td>
</tr>
<tr>
<td>TMS-75</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>QTSX</td>
<td>3.97</td>
<td>6.59</td>
</tr>
<tr>
<td>René N5</td>
<td>3.82</td>
<td>7.17</td>
</tr>
<tr>
<td>TMS238</td>
<td>3.47</td>
<td>4.94</td>
</tr>
<tr>
<td>PWA1483</td>
<td>2.77</td>
<td>12.2</td>
</tr>
</tbody>
</table>

$M_{creep} = \sum x_i/\bar{D}_i$

Re free
Re 1 wt.%
Re 3 wt.%
Re 5 ≥ wt.%

QTSX is predicted to have creep behavior similar to alloys containing higher amounts of Re, like the 2nd generation alloys
Modeling of liquid density during solidification

Freckle-resistance is related to the modeling of the liquid density during solidification based on a critical Rayleigh number: 

$$\overline{Ra} = C\Delta\rho^{0.4} \Delta T^{0.4} \frac{\lambda_1^2(G, R)}{G}$$

Actual modeling output is a combined use of various databases and software.
Modeling freckling behavior in N5 and QT-SX castings

Target this range (>B, <A)
Coarsening rate and liquid density comparisons

(lower is better)

(a): Coarsening Rate Constant

(b): Liquid density difference at 20% solidification

Comparable coarsening rate to CMSX-8 (1.5% Re) alloy

Reduced buoyancy differences (less than non-Re CMSX-7)
1st round of casting results

Simulation of chosen casting scenario with N5: (a) R contour (b) G contour (c) location designations

One “tree” (four castings) produced by PCC from both N5 and QT-SX

(left) Setup of the small scale test slab cluster (right) Picture of actual casting with N5 showing a bi-grain formation
As-cast Microstructures
(Phase I Castings)

Along growth direction

Transverse

QT-SX

ReneN5
2nd round of casting results

Freckles typically started here.
2nd round of casting results

Freckles typically started here.

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Characterization and microstructure analysis confirm the achievement of the design goal of γ’ phase fraction and lattice misfit (no evidence of TCP phases were found during all heat treatments)
 Atom-probe (LEAP) analysis of the QT-SX nanostructure

Excellent agreement with ICME predicted compositions
Oxidation modeling

- Continuous $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ formation
- Wahl applied Wagner’s model to multicomponent systems

Oxygen concentration computed at FCC/Oxide boundary* assumed to be the content in FCC when the spinel forms

\[ y_M^0 \geq y_{MC1}^0 = \left( \frac{\pi g}{2 v} \frac{D_0 V_{\text{Alloy}}}{D_M V_{\text{MO}}} \right)^{1/2} \]

Model agrees well with experimental data for benchmark alloys

- Both $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ expected to form at high $T$
- Internal $\text{Al}_2\text{O}_3$ expected to form below 850°C
Oxide characterization

QTSX oxidized in air for 100h at 900°C, 1000°C and 1100°C

EDS mapping of continuous oxide in QTSX alloy heat treated for 100h at 1000°C.

Continuous Al-rich oxide observed in all samples
Evolution of microstructures during long-term exposure at elevated temperature

<table>
<thead>
<tr>
<th>Time at 1150°C (hours)</th>
<th>QTSX</th>
<th>Rene N5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg γ' particle area (sq µm)</td>
<td>Avg γ' particle size (µm)</td>
</tr>
<tr>
<td>0 (as-aged)</td>
<td>0.09</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>0.17</td>
<td>0.41</td>
</tr>
<tr>
<td>30</td>
<td>0.32</td>
<td>0.57</td>
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</table>
Tensile Test Results (ASTM E8 and E21)

Comparison to Select Incumbent SX alloys*

*Baseline data taken from respective patent filings
Stress Rupture Test Results (ASTM E139)

Comparison to Select Incumbent SX alloys*
*Baseline data taken from respective patent filings, literature

![Graph showing L-M Parameter at 150MPa](image)

- PWA1483
- CMSX7
- CMSX8
- PWA1484
- CMSX4
- Rene N5
- CMSX10
- TMS238
- QTSX

L-M Parameter [T(20+log(t))/1000] vs Stress [MPa]

- No Re
- 1 wt% Re
- 1.5 wt% Re
- 3 wt% Re
- High Re
Ongoing Work

- Post-cast heat treatment optimization (complete)
  - Homogenization optimization
  - Double-step aging (simulated TBC cycle)
- Extended characterization
  - Long-term thermal stability (~1000hr)
  - Stress-rupture life
  - Oxidation testing
- Final casting trials
  - Demonstration of castability with full-scale IGT blade geometry
  - Assemble final technical data package for new alloy
  - Using actual blade geometry
- Phase IIA
  - Planning for continuation
Exploration of High-Entropy Alloys for Turbine Applications

Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number(s) DE-SC0013220."
SBIR Program PHASE II, DOE PM: Mark Freeman
High Entropy Alloys (HEAs)

• HEAs are **stable** single phase FCC, BCC, or HCP solid solutions at or near equiatomic compositions in multicomponent systems (n>=5)
  – BCC or FCC: AlCoCrCuFeNi and its derivatives (add Ti,Mo,V,Mn,Nb etc.)
  – Refractory BCC (MoNbTaTiVW)
  – HCP (AlLiMgScTi, DyGdHoTbY)

• HEAs are disordered solid solutions

HEA Properties Relative to Other Materials

Potential for HEA Property Design

- Large variation in properties with composition/processing

**Effect of Al**

**Effect of Nb**

![Graphs showing yield stress vs. temperature and engineering stress vs. engineering strain for different AlCoCrCuFeNi compositions.]

- Non-deformed tensile sample
- As-cast tensile sample ($\delta=77\%$)
- Forged sample ($\delta=864\%$)

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HEAs as an Industrial Gas Turbine Alloy

• Consider HEAs as a matrix component in an IGT blade or vane alloy
  – Stability at higher temperatures than Ni/Ni₃Al
  – Higher strength
  – Better thermodynamic compatibility with bond coat
• HEAs have been demonstrated to be made as a single crystal (Bridgman solidification) and an FCC HEA in equilibrium with an L1₂

Primary Design Challenge: Limited CALPHAD Databases

- CALPHAD databases have been built with a focus on specific corners of composition space (e.g. Fe, Ni, Al), shown in green.
- HEAs are in the center of composition space, and extrapolations of CALPHAD models to these regions are likely limited, due to lack of data.

Typical alloys
Weak ternary interactions; safe to ignore

HEAs
Strong ternary interactions; need to model
Phase I Goal: Improve current CALPHAD databases with DFT thermodynamics tailored to find HEAs

Phase I Result: With the new CALPHAD database, accuracy in predicting HEA formation has dramatically improved.
Poor CALPHAD description for solid solutions at equiatomic compositions due to lack of ternary parameters

\[ G^\alpha = \sum_{i}^{c} x_i G_i^\alpha - TS_{mix}^{ideal} + x_s G_m \]

Redlich-Kister polynomial for solid solution mixing energy in CALPHAD

\[ x_s G_m = \sum_{i=1}^{c-1} \sum_{j>i}^{c} x_i x_j \sum_{n=0}^{\infty} L_{ij}^{\nu} (x_i - x_j)^\nu + \sum_{i=1}^{c-2} \sum_{j>i}^{c-1} \sum_{k>j}^{c} x_i x_j x_k^0 L_{ijk} \]

Ternary interaction parameters typically ignored due to lack of data, but can have a large effect in HEA systems


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Special Quasi-random Structure (SQS)

- SQSs are specially constructed supercells designed to mimic a chemically disordered solid solution locally around each atom
- Can be used to simulate ternary solid solutions in DFT
High-throughput DFT for HEA Thermodynamics

• Physics-based first-principles predictions of 408 ternary enthalpies of mixing in FCC and BCC solid solutions
  – Phase I elements considered: Al Co Cr Cu Fe Mn Mo Nb Ni Ti V W
  – To add in Phase II: Hf Mg Pd Ru Ta Zr...

Performed on the iForge high-performance computing cluster at the National Center for Supercomputing Applications (UIUC)
Comparison of DFT-predicted ternary solid solution mixing enthalpies to changes in volume

- Consistent with notion that favorable interatomic interactions lead to smaller volumes (i.e. strong bonds are short bonds)
- Use the ternary mixing enthalpies as foundation for HEA-specific CALPHAD database
Sparsity of ternary interaction parameters reduced after CALPHAD database update

<table>
<thead>
<tr>
<th>FCC Fe-X-Y</th>
<th>BCC Fe-X-Y</th>
<th>FCC Ni-X-Y</th>
<th>BCC Ni-X-Y</th>
</tr>
</thead>
</table>

- **Attractive / Repulsive / No value**

- **DFT**

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How well do CALPHAD databases predict known HEAs?

- In the Al-Co-Cr-Cu-Fe-Ni-Ti-V-Nb-Mo-Mn-W system, 31 BCC and 36 FCC single-phase HEA-forming compositions (of ≥5 components) reported in the literature.
- Assume any phase fraction ≥ 0.9 predicted by CALPHAD is a prediction of HEA formation.

<table>
<thead>
<tr>
<th>Database</th>
<th>Agreement with Exp.</th>
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<tbody>
<tr>
<td>TCFE6</td>
<td>24%</td>
</tr>
<tr>
<td>TTN17</td>
<td>24%</td>
</tr>
<tr>
<td>QT-HEA</td>
<td>55%</td>
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</tbody>
</table>

Effect of CALPHAD + DFT
Use New Database to Predict Novel HEA Compositions

• Consider all equi-atomic 5-component compositions in Al-Co-Cr-Cu-Fe-Ni-Ti-V-Nb-Mo-Mn system
  – 462 compositions
• 104 compositions are predicted to have HEA phase fraction \( \geq 0.9 \)

<table>
<thead>
<tr>
<th></th>
<th>Stable Phase</th>
<th>Phase Fraction</th>
<th>( H_{\text{mix}} ) BCC [J/mol]</th>
<th>( H_{\text{mix}} ) FCC [J/mol]</th>
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<tbody>
<tr>
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<td>-42049.9</td>
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<td></td>
<td></td>
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</table>

• Use predictions for experimental verification
Benchmark Compositions

Current work shows good agreement with literature data.
## CALPHAD-predicted HEA Compositions

<table>
<thead>
<tr>
<th>Predicted Phase</th>
<th>Observed Phase</th>
</tr>
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<tbody>
<tr>
<td>HEA</td>
<td>HEA</td>
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<tr>
<td><strong>Co3CrCu0.5FeNi</strong></td>
<td></td>
</tr>
<tr>
<td>HEA</td>
<td>Multi-phase</td>
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<tr>
<td><strong>Al2CoCrCu0.5Fe3Ni</strong></td>
<td></td>
</tr>
<tr>
<td>HEA</td>
<td>HEA</td>
</tr>
<tr>
<td><strong>Co2.5CrCuFeNi</strong></td>
<td></td>
</tr>
</tbody>
</table>

- Results generally agree with CALPHAD predictions
- There is some phase separation with an ordered BCC phase, as also seen in literature
CALPHAD-predicted HEA Compositions w/ Refractories

- Preliminary results show alignment with CALPHAD predictions
- Alloys include refractory metals requiring significantly more power while arc melting which changes the cooling process
- *Investigations into homogenization and quenching ongoing
Phase II Plans

• Extend HEA CALPHAD database with additional elements

• Integration of Process-Structure and Structure-Property predictions into a preliminary HEA IGT design (in collaboration with OEM)

• Prototype production at a scaled-up level (in collaboration with alloy producer)

• Application development
Summary

QuesTek Innovations has used ICME tools and technologies to develop alloys for high-performance applications.

QTSX is an ICME-design single crystal superalloy with the castability of earlier alloys, creep properties of new alloys, and low Re content.

High-performance computing accelerated development of ICME CALPHAD database for high entropy alloys, enabling HEA design for IGT applications.
Modeling and design tasks

- Thermodynamic and kinetic database
- Freckling model
- Processing design (HT windows, incipient melting)
- $\gamma + \gamma'$
  - Including $\gamma'$ coarsening model
- TCP, HAB and LAB

Models used in Phase I design

- Creep modeling (intermediate temperature)
  - Calculation of "Reed-D" for existing alloys (climb-controlled creep)
  - Develop explicit vacancy diffusivity model
- Oxidation/alumina formation

“Indirect consideration” during Phase I design (for further expansion in potential Phase II)

Alloy design in Phase I

- Alloy design

Alloy design in Phase I
Atom-probe (LEAP) analysis of the QT-SX nanostructure

Excellent agreement with predicted compositions (\(\gamma'\) comparisons below)

<table>
<thead>
<tr>
<th></th>
<th>Ion, at.%</th>
<th>Cr %</th>
<th>Ni %</th>
<th>Co %</th>
<th>Al %</th>
<th>Hf %</th>
<th>Mo %</th>
<th>Re %</th>
<th>Ta %</th>
<th>Ti %</th>
<th>W %</th>
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<tr>
<td>LEAP1</td>
<td>1.74</td>
<td>66.76</td>
<td>6.63</td>
<td>17.28</td>
<td>0.05</td>
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</table>
High Entropy Alloys (HEAs)

- Still some uncertainty as to particular mechanism for formation
- **Fundamentally a competition between configurational entropy and driving force for ordering/phase separation**
- Hume-Rothery parameters often used as indicators: atomic mismatch ($\delta$) and enthalpy of mixing ($\Delta H_{\text{mix}}$)

\[
\delta = \sqrt{\sum_{i=1}^{N} c_i \left( 1 - r_i \right) \left( \sum_{i=1}^{N} c_i r_i \right)^2}
\]

\[
\Delta H_{\text{mix}} = \sum_{i=1,i \neq j}^{N} 4 \Delta H_{AB}^{\text{mix}} c_i c_j
\]

Four Primary Tasks

- Literature review of known HEAs
- DFT calculations of BCC/FCC ternary mixing enthalpies
- HEA CALPHAD database development and predictions
- Experimental synthesis/characterization of HEA buttons
Literature Review

• Compiled a comprehensive list of known HEAs with detailed compositions and phase stability information

• Three major HEA categories in the literature:
  – BCC or FCC: AlCoCrCuFeNi and its derivatives (add Ti, Mo, V, Mn, Nb etc.)
  – Refractory BCC (MoNbTaTiVW)
  – HCP (AlLiMgScTi, DyGdHoTbY)

<table>
<thead>
<tr>
<th>Q12013</th>
<th>Exp. Phases</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
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</table>

AI is a BCC stabilizer in AlCoCrCuFeNi alloys
the amount of Al in the AlCoCrCuFeNi system can tune the crystal from fcc to fct/bcc and to fully bcc
spinal-ordered structure of disordered bcc and ordered bcc phases
arc melt at current 500A in cold Cu hearth
spatial-ordered at cooling rate of 10^2-10^3 K/s
arc melt at current 500A in cold Cu hearth
cooling rate 1 to 10K/s
The experimental results indicate that Co is not necessarily required in obtaining
the solid solution structure in HEAs, which is good for
Entropic stabilization of superalloy phases

\[ x^S G_m = \sum_{i=1}^{c-1} \sum_{j>i}^c x_i x_j \sum_{v=0}^n v L(x_i - x_j)^v + \sum_{i=1}^{c-2} \sum_{j>i}^{c-1} \sum_{k>j}^c x_i x_j x_k L_{ijk}^0 \]

- **FCC/BCC** \( (X_i) \)
  - \( S_{\text{config}} = \sum_{i=1}^N x_i \ln x_i \)

- **L12** \( (X_i)_3 (Y_i) \)
  - \( S_{\text{config}} = 0.75 \sum_{i=1}^N y_i^I \ln y_i^I + 0.25 \sum_{i=N+1}^N y_i^{II} \ln y_i^{II} \)

- **Heusler** \( (X_i)_2 (Y_i) (Z_i) \)
  - \( S_{\text{config}} = 0.5 \sum_{i=1}^N y_i^I \ln y_i^I + 0.25 \sum_{i=N+1}^N y_i^{II} \ln y_i^{II} + 0.25 \sum_{i=\frac{N}{3}+1}^\frac{2N}{3} y_i^{III} \ln y_i^{III} \)

Hmm, so can either compare individual terms:

- \( x_A x_B > x_A x_B x_C \)

...or can compare sum of terms:

- \( \sum_{i=1}^{c-1} \sum_{j>i}^c x_i x_j > \sum_{i=1}^{c-2} \sum_{j>i}^{c-1} \sum_{k>j}^c x_i x_j x_k \)
Assessment of CALPHAD HEA phase stability

- “High-throughput” CALPHAD:
  - Script to derive data for all combinatorially possible systems
  - ['Al', 'Co', 'Cr', 'Cu', 'Fe', 'Hf', 'Mg', 'Mn', 'Mo', 'Nb', 'Ni', 'Pd', 'Ru', 'Ta', 'Ti', 'V', 'W', 'Zr']

- Checked several QuesTek and commercial databases
  - TCNI6, TCFE6, SSOL4, QT2015, qt2-al-04062015, ni-data7

- Ternary mixing enthalpies for BCC and FCC
- Phase stability for 5-component equiatomic HEA compositions
CALPHAD/DFT Ternary Mixing Enthalpy Comparisons
FCC and BCC ternary mixing enthalpies [kJ/mol]

Only slight variation between traditional CALPHAD databases as they are likely based on the same input data.

Larger variation between DFT and CALPHAD, due to lack of extensive data in these ternary systems.
HEAs in Current CALPHAD Databases

- 5-component, equiatomic compositions at 300K
- Highest phase fraction is typically 0.8, indicative of a single element demixed from the solid solution
  - E.g. AlCoCrFeNi consists of 80% BCC AlCoFeNi and 20% BCC Co in TCNI6
- SSOL4 has largest breadth of elements, but TCNI6/Ni-data7 have most HEA-like compositions and best agreement with DFT

<table>
<thead>
<tr>
<th>Database</th>
<th>Highest NP Count</th>
<th>Phase(s)</th>
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<tbody>
<tr>
<td>TTTNI7</td>
<td>~0.8 9</td>
<td>B2</td>
</tr>
<tr>
<td>QT-FE</td>
<td>0.85 1</td>
<td>BCC</td>
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<tr>
<td>QT-AI</td>
<td>~0.8 4</td>
<td>BCC</td>
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<tr>
<td>SSOL4</td>
<td>~0.8 1</td>
<td>BCC</td>
</tr>
<tr>
<td>TCFE6</td>
<td>0.75 1</td>
<td>BCC</td>
</tr>
<tr>
<td>TCNI6</td>
<td>~0.8 14</td>
<td>BCC/FCC</td>
</tr>
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</table>
Status of current CALPHAD databases – cont’d

• Did single point equilibrium calculations at T=1000 °C for transition metal-based systems using available databases and compared with experimental HEA-forming systems.

• Comparison to compilation of experimental data:

<table>
<thead>
<tr>
<th>Database</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ni-data7</td>
<td>Decent agreement compared with exps.</td>
</tr>
<tr>
<td>QT-2015</td>
<td>Close to Ni-data7, BCC phase generally more stable</td>
</tr>
<tr>
<td>QT2-Al-04062015</td>
<td>Lacks Co</td>
</tr>
<tr>
<td>SSOL4</td>
<td>Intermetallic phases too stable</td>
</tr>
<tr>
<td>TCFE6</td>
<td>Liquid phase too stable</td>
</tr>
<tr>
<td>TCNI6</td>
<td>Lacks Cu</td>
</tr>
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</table>
Benchmark HEA formation

- Two benchmarks based on experimentally observed HEA-forming compositions
  - FCC: $\text{Al}_{0.5}\text{CoCrCuFeNi}$
  - BCC: $\text{AlCoCrCu}_{0.5}\text{FeNi}$
- Chemically measured compositions close to target
- Published SEM compared to QT optical: FCC $\text{Al}_{0.5}\text{CoCrCuFeNi}$

Round One – Pre-DFT CALPHAD

<table>
<thead>
<tr>
<th>Predicted Phase</th>
<th>Observed Phase</th>
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<tbody>
<tr>
<td>Co3CrCu0.5FeNi</td>
<td>HEA</td>
</tr>
<tr>
<td>Al2CoCrCu0.5Fe3Ni</td>
<td>HEA</td>
</tr>
<tr>
<td>Co2.5CrCuFeNi</td>
<td>HEA</td>
</tr>
</tbody>
</table>

- Results generally agree with CALPHAD predictions
- There is some phase separation with an ordered BCC phase, as also seen in literature
Round Two – Post-DFT CALPHAD

- Preliminary results show alignment with CALPHAD predictions
- Alloys include refractory metals requiring significantly more power while arc melting which changes the cooling process
- Investigations into homogenization and quenching ongoing
Experimental Investigation

- 15-20 gram buttons arc melted under argon
- Sectioned for chemical and XRD analysis
- Chemical analysis provides confirmation of HEA composition
- XRD analysis provides phase identification through the Bragg Law
  - XRD pattern allows identification of phases and their respective lattice constants

\[
\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]

- FCC and BCC peaks appear at regular, expected intervals based on the \( hkl \) values
  \[
s^2 = h^2 + k^2 + l^2
\]

<table>
<thead>
<tr>
<th>( s^2 )</th>
<th>FCC</th>
<th>BCC</th>
<th>ordered phase</th>
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</tr>
<tr>
<td>12</td>
<td>222</td>
<td>222</td>
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</tr>
</tbody>
</table>
Investigated Compositions

• Benchmark compositions
  – Compositions from literature, one FCC, one BCC, one FCC + BCC
    • $\text{Al}_{0.5}\text{CoCrCuFeNi}$  $\text{AlCoCrCu}_{0.5}\text{FeNi}$  $\text{AlCoCrCuFeNi}_{0.5}$

• Round One
  – Compositions created using the pre-DFT CALPHAD database
    • $\text{Co}_3\text{CrCu}_{0.5}\text{FeNi}$  $\text{Al}_2\text{CoCrCu}_{0.5}\text{Fe}_3\text{Ni}$  $\text{Co}_{2.5}\text{CrCuFeNi}$
    • $\text{CoCuFeNi}$  $\text{Al}_{0.5}\text{Co}_{2.5}\text{CrCuFeNi}$  $\text{Al}_{0.5}\text{Co}_3\text{CrCuFeNi}$
    • $\text{Al}_{1.5}\text{CoCr}_3\text{Cu}_{0.5}\text{FeNi}$

• Round Two
  – Compositions created using the post-DFT CALPHAD database
    • $\text{AlCrNbTiV}$  $\text{CoCrMnNiV}$  $\text{CrCuFeMoNi}$
    • $\text{CoCrFeTiV}$  $\text{CrMoNbTiV}$
Experiment Summary

- New HEA compositions require more effort to produce as they include more reactive and higher melting temperature elements
  - Refractories likely of interest for IGT applications in Phase II
- Homogenization steps are required to validate new compositions, currently underway