Exploration of High-Entropy Alloys for Turbine Applications
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Phase II DOE NETL SBIR Program, TPOC Mark Freeman
Background—QuesTek Innovations LLC

- Founded 1997 (Prof. Greg Olson, cofounder)
- 23 employees (13 with PhD, 6 with MS, 4 with BS)
- A global leader in computational materials design:
  - Our Materials by Design® expertise applies the Integrated Computational Materials Engineering (ICME) technologies and Accelerated Insertion of Materials (AIM) methodologies to design and deploy innovative, novel materials faster and at less cost than traditional methods
  - Aligned with the Materials Genome Initiative
- 12 US patents awarded (and 18 US patents pending)
- 25 foreign (and 21 foreign pending)
- Create IP and license it to producers, processors, OEMs, end-users
- 4 commercially available steels
- Designing novel Fe, Al, Ti, Cu, Ni, Co, Nb, Mo and W based alloys for government and industrial sectors

Fe  Al  Ti  Cu  Ni  Co  Nb  Mo  W

26  13  22  29  28  27  41  42  74
55.847 2520 47.867 63.546 58.6934 58.933 92.906 95.96 183.85
2662 650.25 3289 2553 2514 2526 4744 4639 5555
1953 1670 1670 1084.6 1453 1495 2407 2817 3407
6.86 1.5 1.6 1.8 1.8 1.7 1.2 1.3 1.4
2.3 4.50 3.4 1.2 2.3 2.3 3.5 2.3 19.3
3 8.56 8.9 8.9 8.9 8.9 8.67 10.2 10.2
2.3 2.3 2.3 2.3 2.3 2.3 2.3 2.3 2.3
QuesTek’s **Integrated Computational Materials Engineering** approach

“Integrated Computational Materials Engineering (ICME) methods involve the holistic application of different computational models across various length scales to the design, development, and rapid qualification of advanced materials.”
Leading applications of QuesTek alloys

**Ferrium S53 steel**
In flight service on U.S. Air Force platforms A-10, C-5 and T-38 to replace existing corrosion-prone steels.
*From materials design to flight in 10 years*

**Ferrium M54 steel**
Navy qualified landing gear “hook shank” with >2x life vs. incumbent alloy; cost savings of $3 Million to fleet.
*From materials design to flight in 7 years*

**Ferrium C61 and C64 steel**
Being qualified for next generation helicopter transmission shaft and gears for U.S. Navy and U.S. Army, replacing existing steels used for 50 years

Meets strength and corrosion resistance requirements without need for toxic cadmium coating

NAVAIR Public Release #2014-712
Distribution Statement A- “Approved for public release; distribution is unlimited”

20% increase in power density (power to weight ratio) vs. incumbent steel
DoE SBIR HEA Program Overview

- **Program goal**: Test the feasibility of HEAs for industrial gas turbine (IGT) blade applications
- **QuesTek’s approach**: Use ICME tools to design and prototype HEA blade alloys
- **Phase I**: Build foundational ICME thermodynamic database (CALPHAD)
- **Phase II Year 1**: Use database and other ICME tools to design HEA and produce prototype heat
- **Phase II Year 2**: Characterize performance and iterate design, Peter Liaw as collaborator
**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

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HEAs as an Industrial Gas Turbine Alloy

- Consider HEAs as a 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


Path to HEA ICME Design

- Develop structure-property models
  1. Predict **high-temperature stability** from CALPHAD databases
  2. Model solid solution, grain size, and (possibly) precipitation strengthening
  3. Utilize creep metrics to predict relative **creep resistance**
  4. Predict **resistance to high-temperature oxidation**

- Produce lab-scale prototype buttons
- Characterize critical properties
- Recalibrate models as needed
Current empirical models for predicting HEA stability are overly simplistic

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

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

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

CALPHAD takes into account both enthalpy and entropy of all phases, enabling full phase equilibria prediction.

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
Density Functional Theory for HEA Thermodynamics

- Physics-based first-principles predictions of 408 ternary enthalpies of mixing in **FCC** and **BCC** solid solutions
  - Use the special quasi-random structure (SQS) approach
  - Elements considered: Al Co Cr Cu Fe Mn Mo Nb Ni Ti V W
  - To add in follow-up work: Hf Mg Pd Ru Ta Zr...

Performed on the iForge high-performance computing cluster at the National Center for Supercomputing Applications (UIUC)
Sparsity of ternary interaction parameters reduced after CALPHAD database update

**Attractive / Repulsive / No value**

- **FCC Fe-X-Y**
- **BCC Fe-X-Y**
- **FCC Ni-X-Y**
- **BCC Ni-X-Y**

**Exploration of High-Entropy Alloys for Turbine Applications**

**UTSR Program Review Meeting**

**November 2, 2016**
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>
</tr>
</thead>
<tbody>
<tr>
<td>TCFE6</td>
<td>24%</td>
</tr>
<tr>
<td>TTNI7</td>
<td>24%</td>
</tr>
<tr>
<td>QT-HEA</td>
<td>55%</td>
</tr>
</tbody>
</table>

Effect of CALPHAD + DFT
High-temperature Stability of HEA Compositions (#1)

- The solidus is the highest temperature before melting begins
- Calculated solidus temperatures for all 5-component equiatomic compositions (3003) with CALPHAD
  - ~100 are single phase BCC HEAs (phase fraction > 0.8)
- Histogram of all compositions and BCC HEA compositions
- BCC HEAs demonstrate higher average solidus temperatures
Experimental validation currently underway

<table>
<thead>
<tr>
<th>Al</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Cr</td>
<td>Fe</td>
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</tbody>
</table>

Use CALPHAD to predict processing temperatures

- Vacuum encapsulated and homogenized at 1100°C

AlCrMoTiV, as-homogenized, single phase with minor Al oxides
Develop Structure-Property Models for Further Screening of Compositions (#2-3-4)

- **Strength**: Solid solution, grain size, (and precipitate strengthening)
- **Creep**: Vacancy diffusivity
- **Oxidation**: Alumina and chromia formation

*Build upon QuesTek’s experience with Ni Superalloy design and modeling*

DE-SC0009592 SBIR Program PHASE II.A, DOE PM: Steve Richardson
HEA Strength Modeling (#2)

General alloy strength model framework:

$$\sigma_{tot} = \sigma_{ss} + \sigma_{gb} + \sigma_{ppt}$$

- **Solid solution strengthening**
  $$\sigma_{ss} = \left( \sum_i B_i^{3/2} X_i \right)^{2/3}$$
  Fleisher/Labush

- **Grain boundary strengthening**
  $$\Delta \sigma_g = k_y d^{-1/2}$$
  Hall-Petch

- **Precipitation strengthening**

- **Shear modulus**
  $$\mu_{HEA} = \sum_i^n X_i \mu_i$$

- **Atomic misfit**
  $$\epsilon_i = \frac{d \alpha}{dX_i \alpha}$$

- **Z = another fitting constant (T-dep, etc.)

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$$B_i = 3 \mu_{HEA} \epsilon_i^{4/3} Z$$

Obtain from DFT

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**Which functional form to use?**
- No host atom = no “base” strength
- Mechanistic uncertainty

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Vacancy Diffusivity in Matrix as Creep Metric (#3)

- Reed creep merit index, $M_{\text{creep}}$:
  - Large amount of slow diffusing elements is better for creep resistance, slows dislocation motion
  - Assume constant and chemistry independent dislocation density
  - Good for ranking materials

\[
M_{\text{creep}} = \sum_i \frac{x_i}{\bar{D}_i}
\]

- Take reciprocal for the effective vacancy diffusivity, $D_{\text{eff}}$:

\[
D_{\text{eff}} = \frac{1}{M_{\text{creep}}}
\]

- $\bar{D}_i$ taken from CALPHAD mobility database
- Will confirm HEA creep mechanism in collaboration with Peter Liaw at U.Tenn.
Surface Oxidation Modeling (#4)

- Criteria for continuous protective oxide formation (e.g. Al$_2$O$_3$ and Cr$_2$O$_3$)
- All input parameters derived from CALPHAD databases

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

\[
y_M^0 \geq y_{MC1}^0 = \left( \frac{\pi g}{2N_o} \frac{D_OV_{Alloy}}{D_MV_{MO}} \right)^{1/2}
\]

Model agrees well with experimental data for benchmark alloys

- Both Al$_2$O$_3$ and Cr$_2$O$_3$ expected to form at high T
- Internal Al$_2$O$_3$ expected to form below 850°C


R. Rapp, – 21st conference National Association of corrosion engineers, 1965
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.A, DOE PM: Steve Richardson
Optimize alloy composition and processing using ICME models to predict critical properties.
Alloy performance proven in prototype castings and creep characterization

Freckle-free castability

Equivalent creep performance to high-Re alloys
WastePD: Center for Performance and Design of Nuclear Waste Forms and Containers

A DOE Energy Frontier Research Center

Program Manager: Gerald S. Frankel
Fontana Corrosion Center
The Ohio State University

Design Synergy Lead: Greg Olson
QuesTek Innovations LLC
Understand the fundamental mechanisms of waste form performance, and apply that understanding to develop tools for design of waste forms with improved performance.

- Containers are metallic: steel underground tanks, SS dry storage casks, CRA canisters for final disposal. Containers also must be stable for long periods of time.

https://efrc.engineering.osu.edu
Summary and Next Steps

QuesTek Innovations is using ICME tools and technologies to develop HEAs for high-performance applications.

QuesTek employed high-performance computing to accelerate development of an HEA CALPHAD database.

Modeling and experimental work will continue (with Peter Liaw at U.Tenn.), culminating in a preliminary HEA design for industrial gas turbine applications.

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HEA Properties Relative to Other Materials

Poor CALPHAD description for solid solutions at equiatomic compositions due to lack of ternary parameters

\[ G^\alpha = \sum_{i}^c x_i G_i^\alpha - T S_{mix}^{ideal} + x^s G_m \]

Redlich-Kister polynomial for solid solution mixing energy in CALPHAD

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

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

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.

(a) SQS-24 when \( x_A = x_B = x_C = \frac{1}{3} \)

(b) SQS-32 when \( x_A = \frac{1}{2}, x_B = x_C = \frac{1}{4} \)