Exploration of High-Entropy Alloys for Turbine Applications

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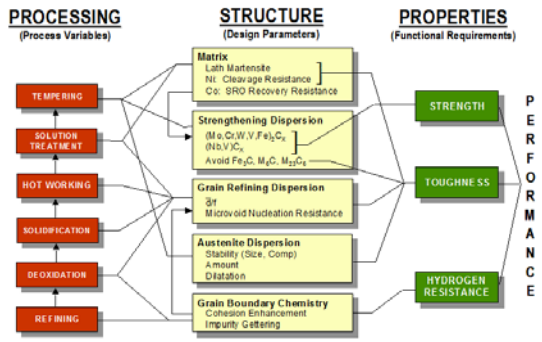
This material is based upon work supported by the Department of Energy under Award Number(s) DE-SC0013220.
Phase II DOE NETL SBIR Program, TPOC Mark Freeman

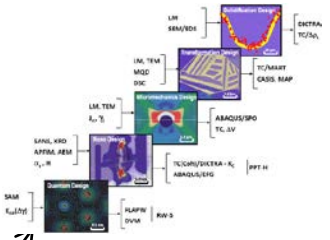
Background—QuesTek Innovations LLC

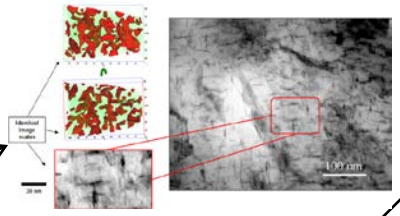
- Founded 1997 (Prof. Greg Olson, cofounder)
- 23 employees (13 with PhD, 6 with MS, 4 with BS)
- A global leader in computational materials design:
  - Our ***Materials by Design***® expertise applies the ***Integrated Computational Materials Engineering* (ICME)** technologies and ***Accelerated Insertion of Materials*** (AIM) methodologies to design an 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

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."







SAE Aerospace
An SAE International Group

AEROSPACE MATERIAL SPECIFICATION

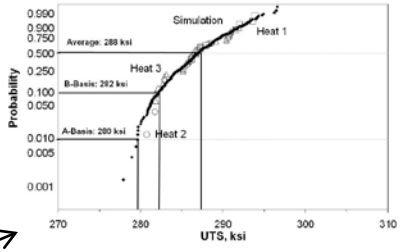
SAE AMS5922 REV. A

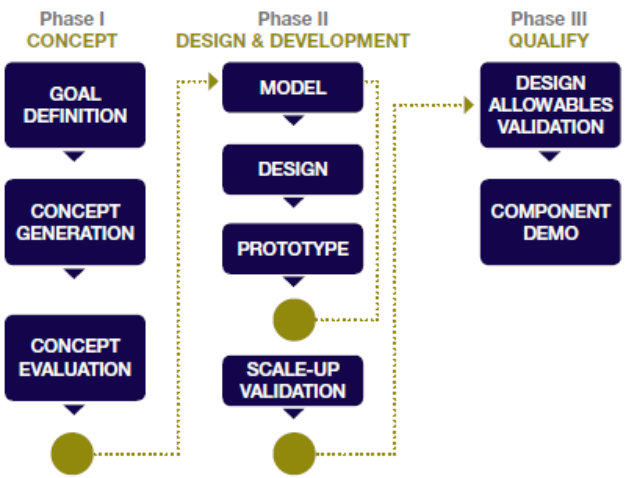
Issued 2008-01
Revised 2010-05

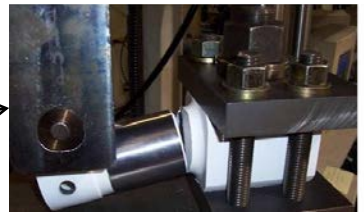
Superseding AMS5922

Steel, Corrosion-Resistant, Bars, and Forgings
10Cr - 5.5Ni - 14Co - 2Mo - 1W (0.19-0.23C)
Vacuum Induction Melted, Vacuum Arc Remelted, Normalized, Annealed

UNS S10500







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

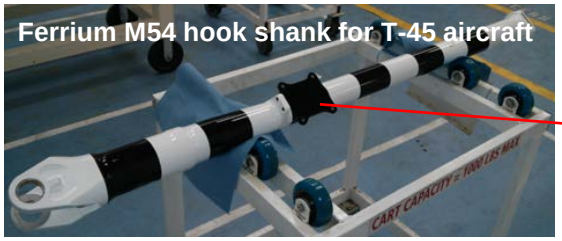
Ferrium S53 roll pin for C-5 aircraft

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

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

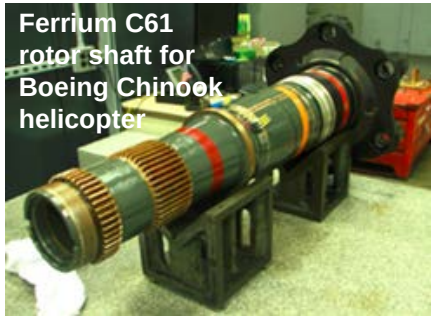


Ferrium M54 hook shank for T-45 aircraft

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

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



Ferrium C61 rotor shaft for Boeing Chinook helicopter

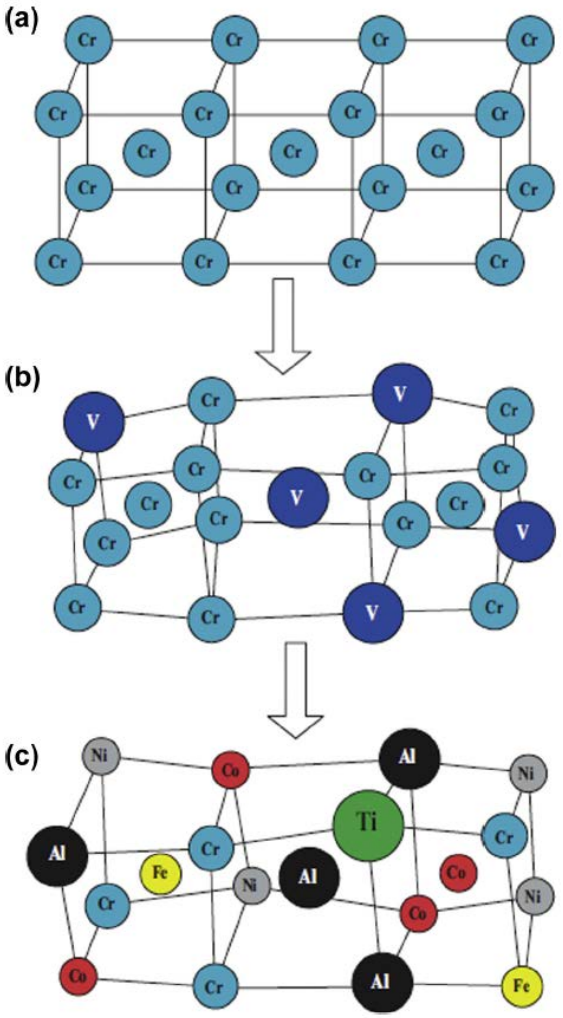
20% increase in power density (power to weight ratio) vs. incumbent steel

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

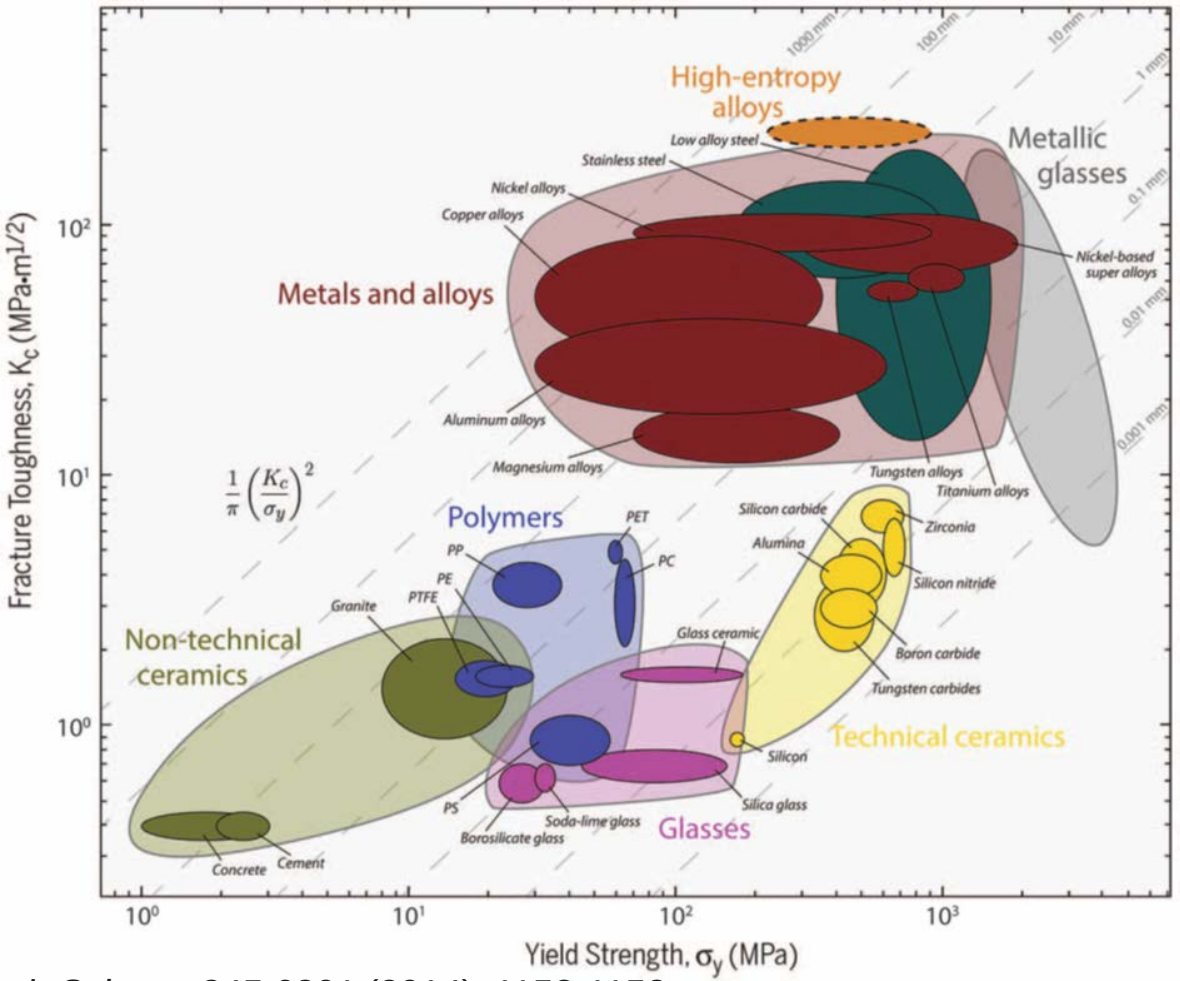
High Entropy Alloys (HEAs)

- 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



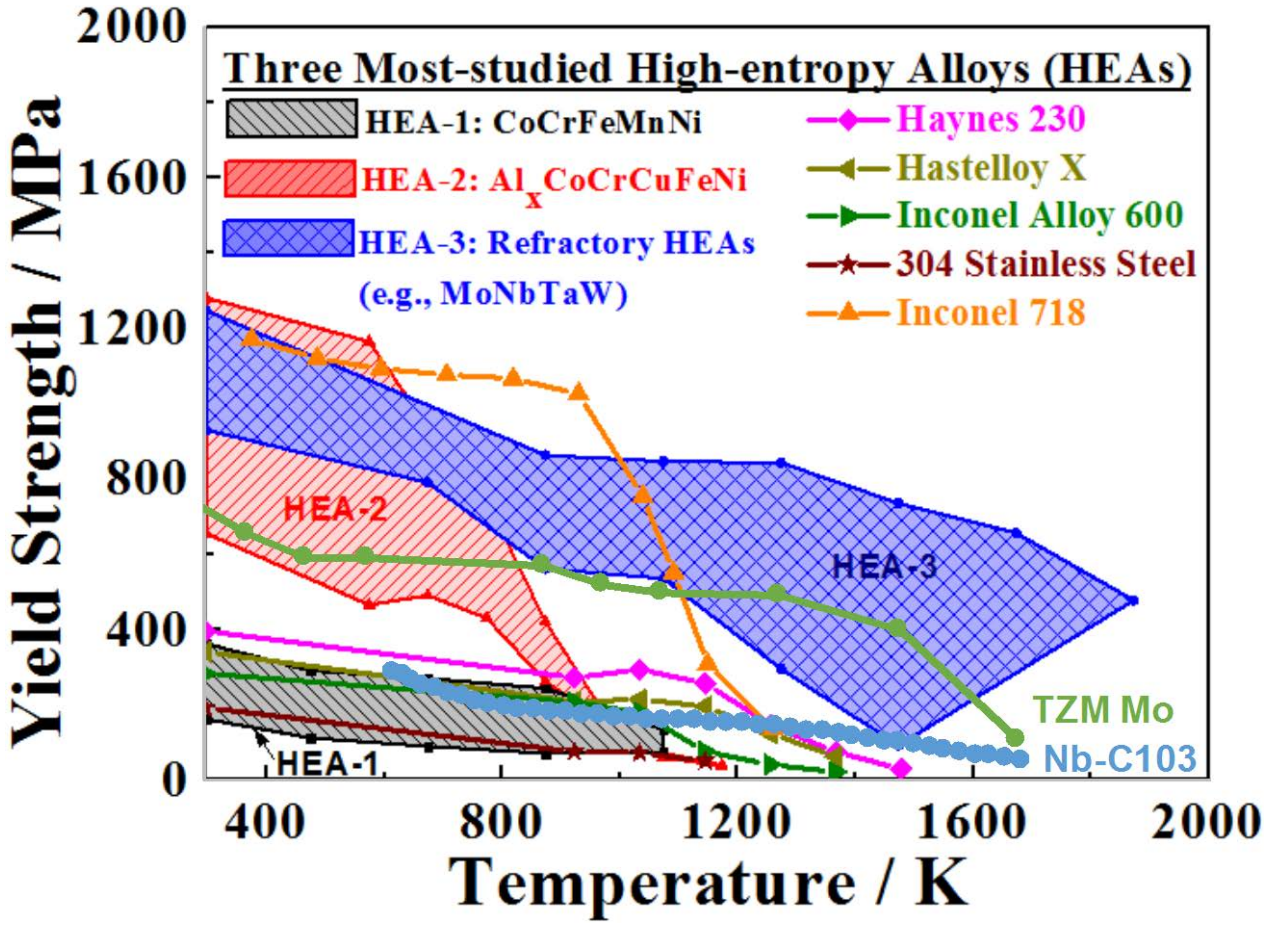
Zhang, Yong, et al. "Microstructures and properties of high-entropy alloys. "*Progress in Materials Science* 61 (2014): 1-93.

HEA Properties Relative to Other Materials



Gludovatz, Bernd, et al. *Science* 345.6201 (2014): 1153-1158.

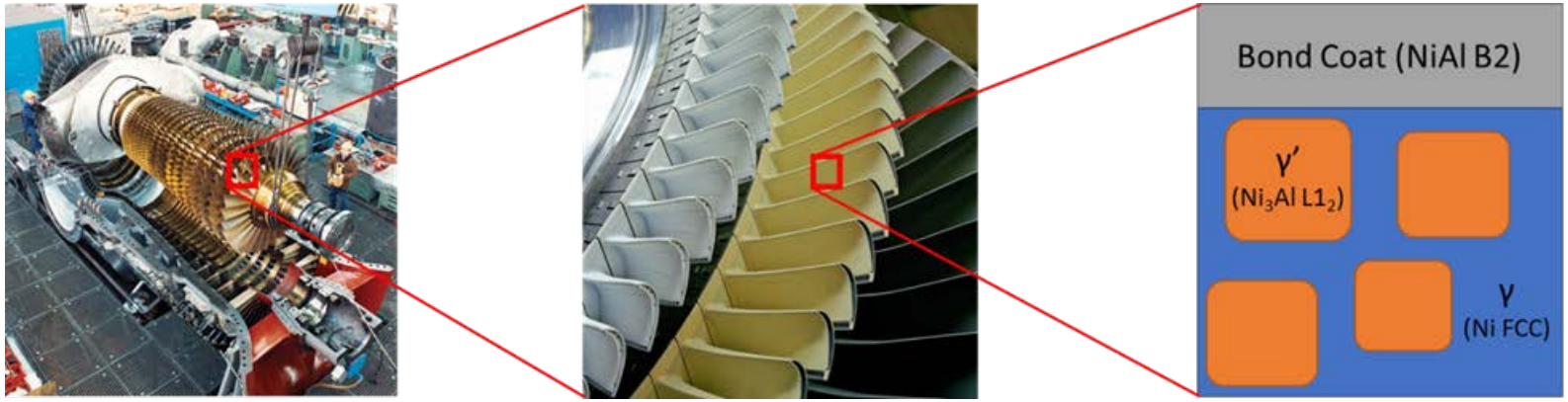
HEA Properties Relative to Other Materials



Modified, from H. Diao, X. Xie, R. Feng, B. Chen, C. Zhang, F. Zhang, K. A. Dahmen, and P. K. Liaw, "Mechanical Behavior of Single-phase High-entropy Alloys (HEAs): An overview", in preparation.

HEAs as an Industrial Gas Turbine Alloy

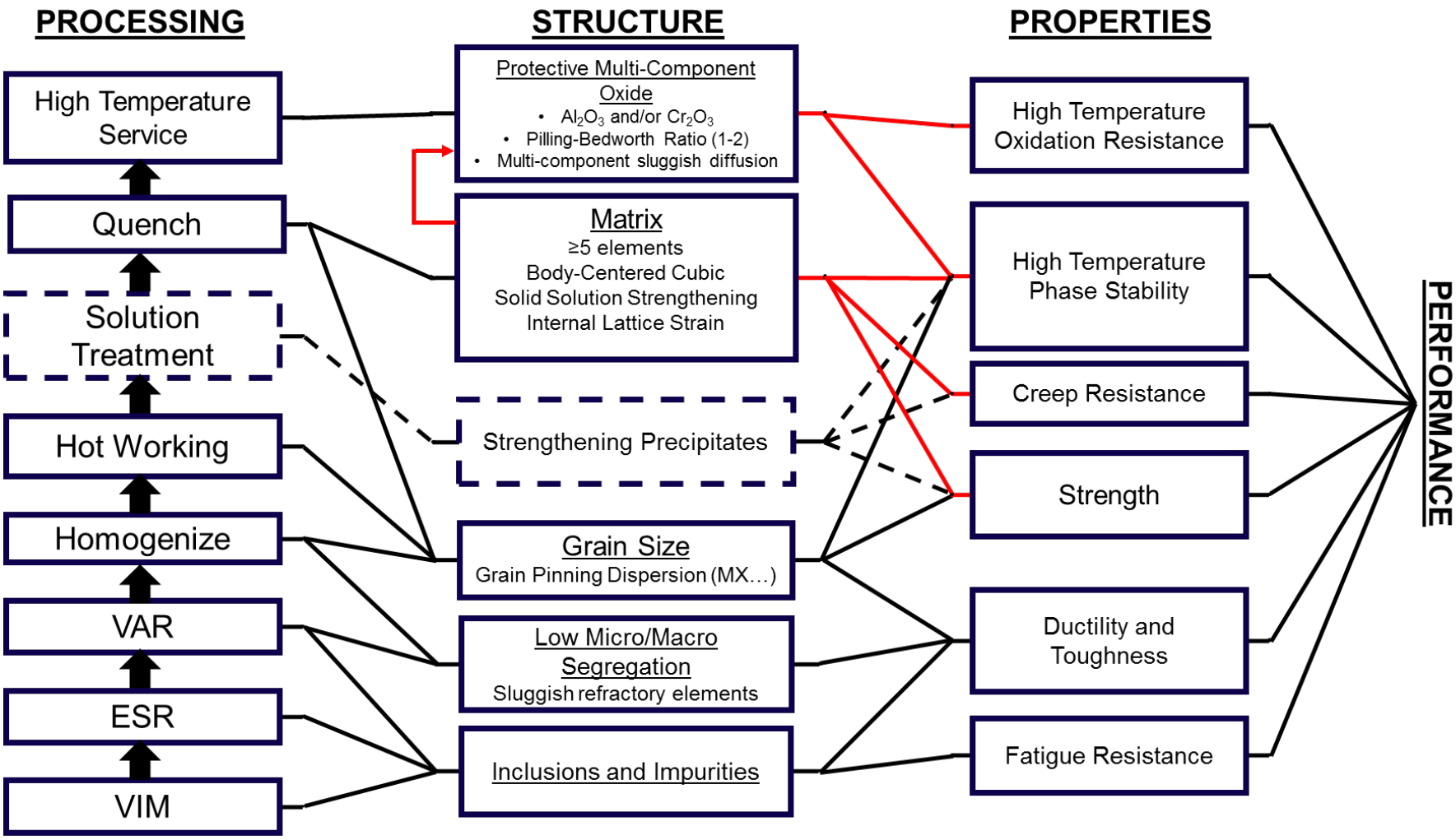
- Consider HEAs as a component in an IGT blade or vane alloy
  - Stability at higher temperatures than Ni/Ni_3Al
  - Higher strength
  - Better thermodynamic compatibility with bond coat
- HEAs have been demonstrated to be made as a single crystal (Bridgman solidification) and an FCC HEA in equilibrium with an $L1_2$



Tsai, Ming-Hung, et al. "Morphology, structure and composition of precipitates in $Al_{0.3}CoCrCu_{0.5}FeNi$ high-entropy alloy." Intermetallics 32 (2013): 329-336.

Ma, S. G., et al. "A successful synthesis of the $CoCrFeNiAl_{0.3}$ single-crystal, high-entropy alloy by bridgman solidification." JOM 65.12 (2013): 1751-1758.

IGT HEA System Design Chart



Path to HEA ICME Design

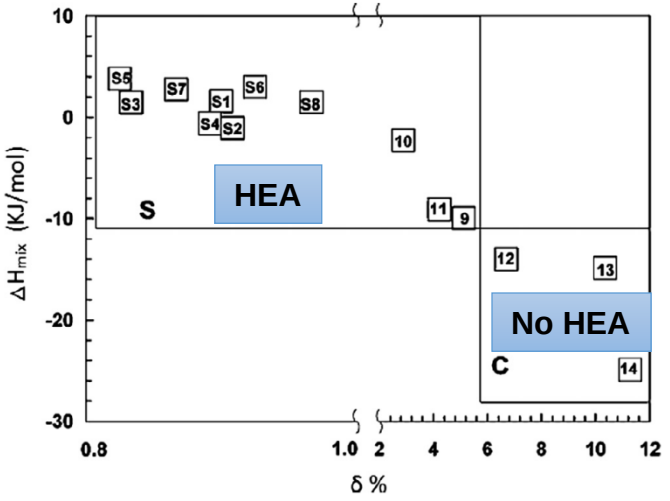
- Develop structure-property models
  1. Predict **high-temperature stability** from CALPHAD databases
  2. Model solid solution, grain size, and (possibly) precipitation **strengthening**
  3. Utilize creep metrics to predict relative **creep resistance**
  4. Predict **resistance to high-temperature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

- **Fundamentally a competition between Gibbs energy of formation and driving force for ordering/phase separation**

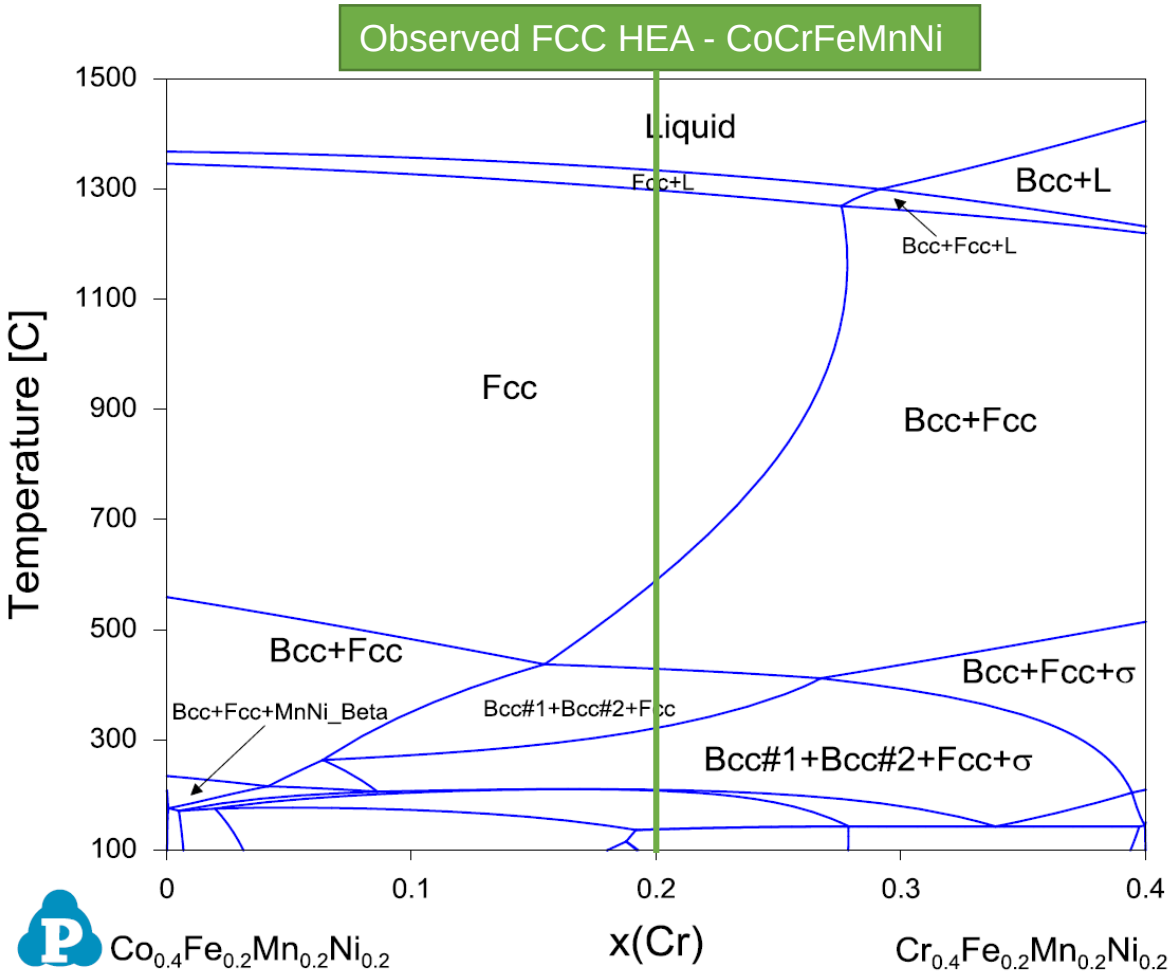


$$\Delta H_{\text{mix}} = \sum_{i=1, i\neq j}^{N} 4\Delta H_{\text{AB}}^{\text{mix}} c_i c_j$$

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

Zhang, Yong, et al. "Microstructures and properties of high-entropy alloys. "*Progress in Materials Science* 61 (2014): 1-93.

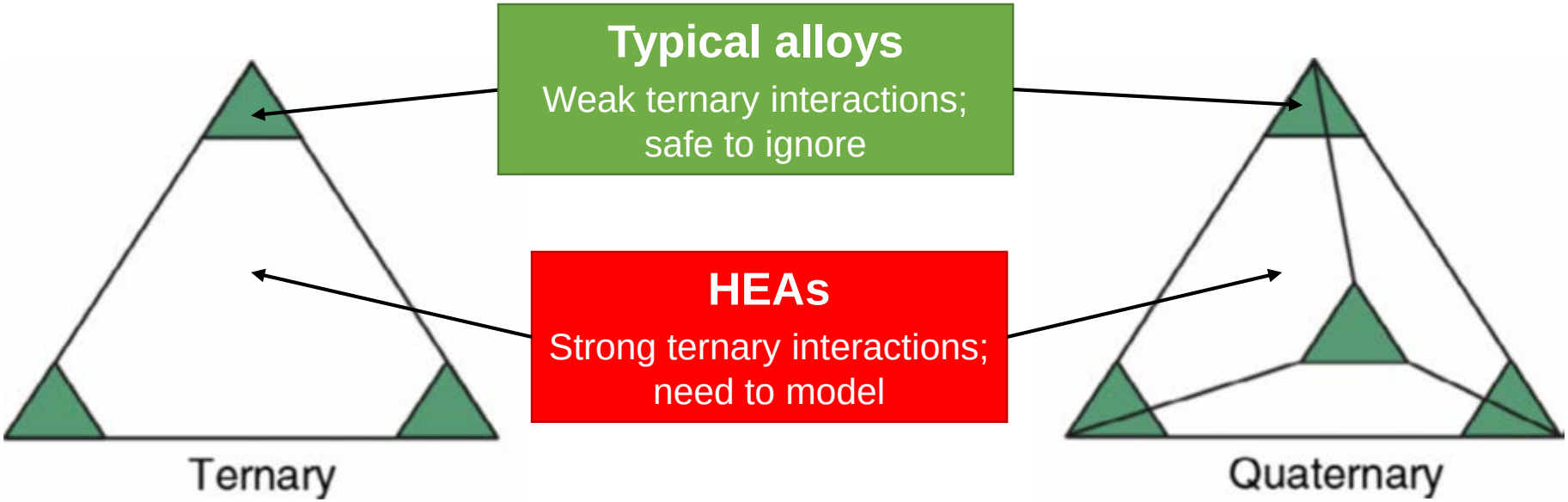
CALPHAD takes into account both enthalpy and entropy of all phases, enabling full phase equilibria prediction



Zhang, F., et al. "An understanding of high entropy alloys from phase diagram calculations." Calphad 45 (2014): 1-10.

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**



Density Functional Theory for HEA Thermodynamics

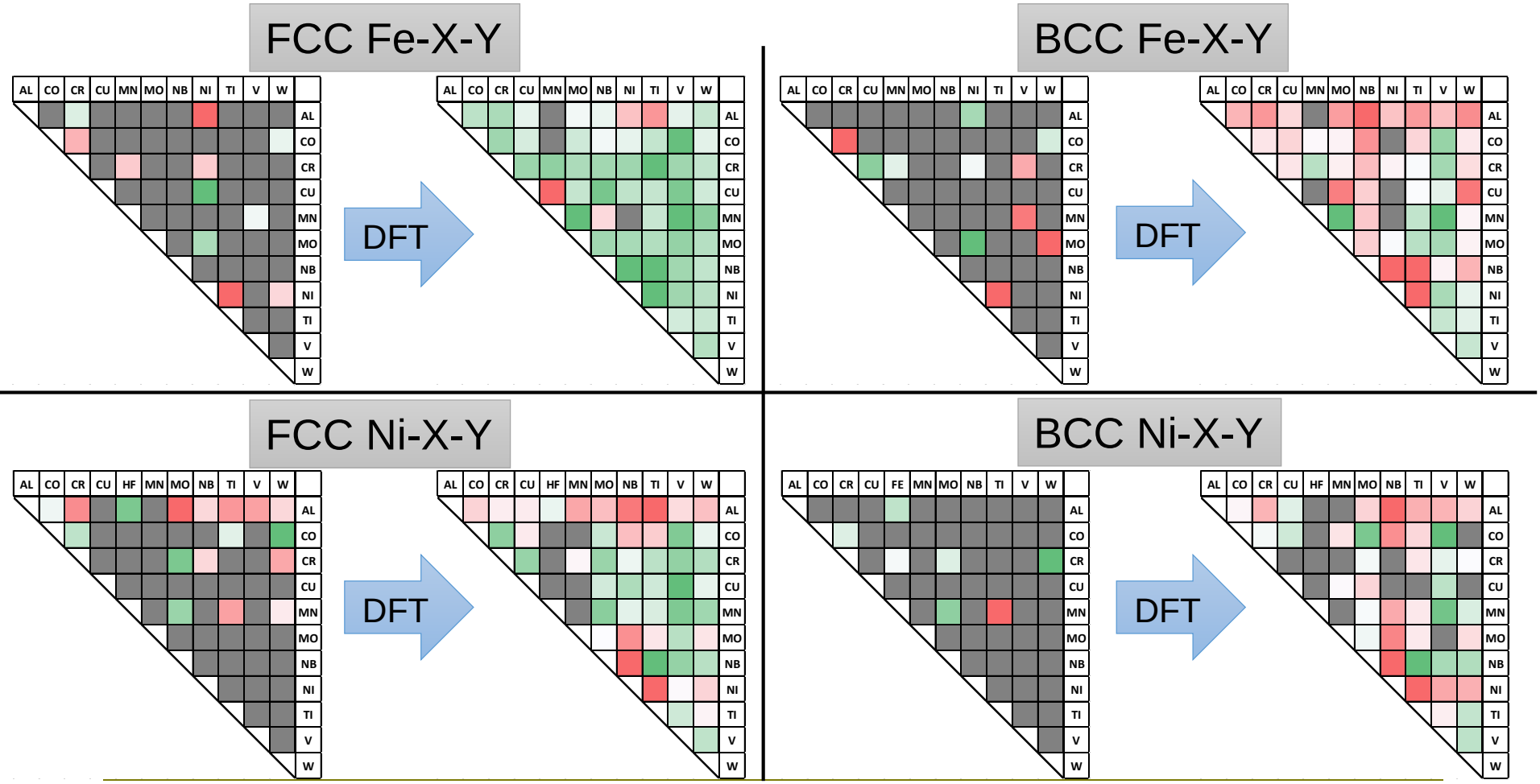
- Physics-based first-principles predictions of 408 ternary enthalpies of mixing in **FCC** and **BCC** solid solutions
  - Use the special quasi-random structure (SQS) approach
  - Elements considered: Al Co Cr Cu Fe Mn Mo Nb Ni Ti V W
  - To add in follow-up work: Hf Mg Pd Ru Ta Zr…

NCSA

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



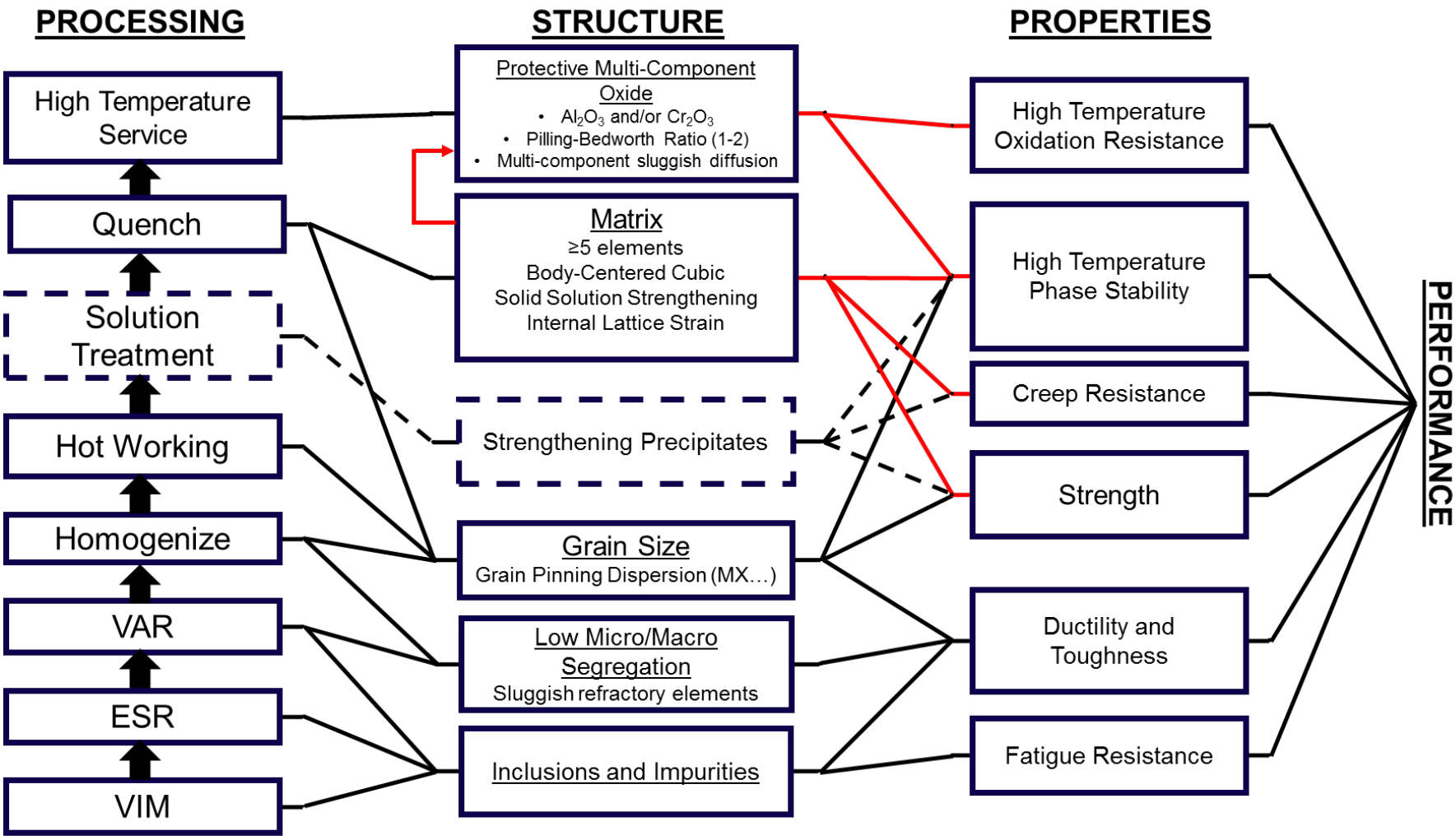
How well do CALPHAD databases predict known HEAs?

- 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

Database	Agreement with Exp.
TCFE6	24%
TTNI7	24%
QT-HEA	55%

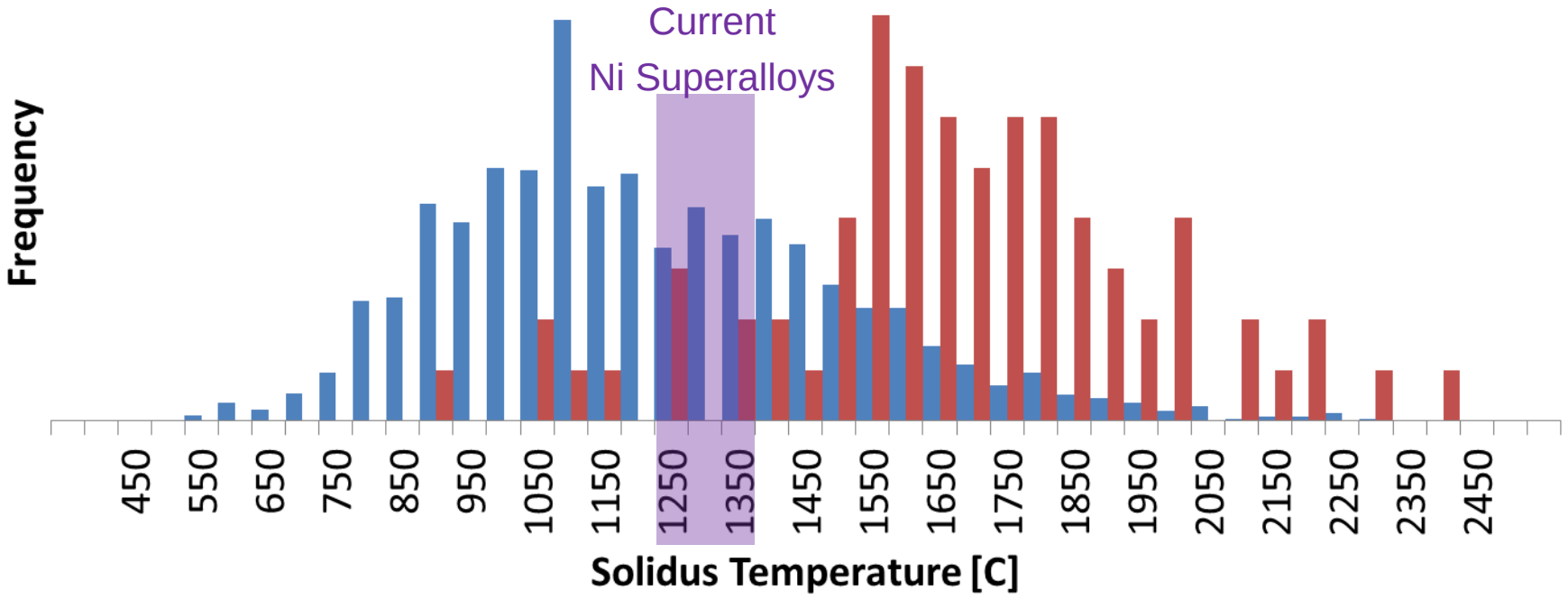
Effect of CALPHAD + DFT

IGT HEA System Design Chart



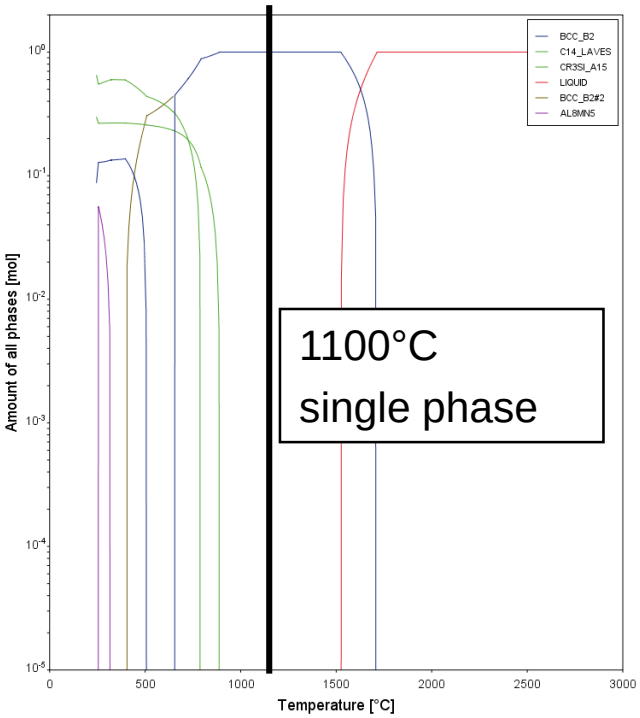
High-temperature Stability of HEA Compositions (#1)

- 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



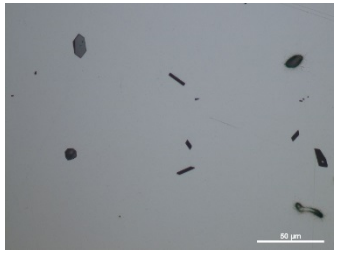
Experimental validation currently underway

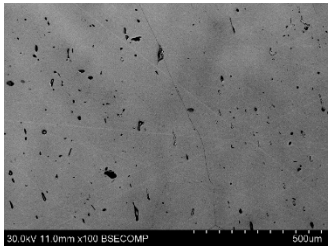
Al	Cr	Mo	Ti	V
Al	Cr	Fe	Mo	V
Al	Cr	Mn	Mo	V
Al	Cr	Fe	Mn	V
Al	Cr	Mn	Ti	V
Al	Cr	Mn	Mo	Ti
Al	Cr	Mn	V	W



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

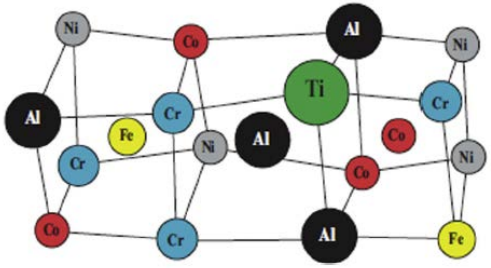
Grain boundary strengthening

$$\Delta\sigma_g = k_y d^{-\frac{1}{2}}$$

Hall-Petch

Precipitation strengthening

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



σ_{ss} example model:

Toda-Caraballo et al. *Acta Materialia* 85 (**2015**)

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

- **Shear modulus** $\mu_{HEA} = \sum_i^n X_i \mu_i$
- **Atomic misfit** $\epsilon_i = \frac{da}{dX_i}\frac{1}{a}$

Obtain from DFT

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

Fleischer, R. L. *Acta metallurgica* 11.3 (1963): 203-209
Labusch, Rea. physica status solidi (b) 41.2 (1970): 659-669
Toda-Caraballo, Isaac, and Pedro EJ Rivera-Díaz-del-Castillo." Acta Materialia 85 (2015): 14-23.

Vacancy Diffusivity in Matrix as Creep Metric (#3)

- Reed creep merit index, M_{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

$$\boldsymbol{M_{creep} = \sum_i \frac{x_i}{\widetilde{D}_i}}$$

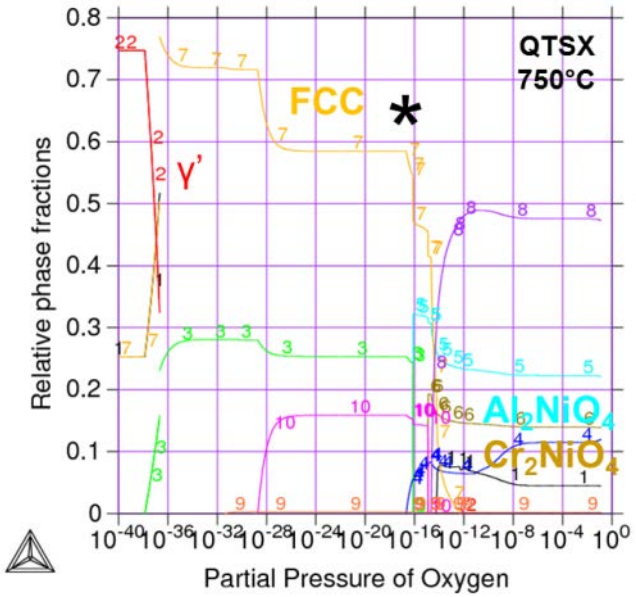
- Take reciprocal for the effective vacancy diffusivity, D_{eff}:

$$\boldsymbol{D_{eff} = \frac{1}{M_{creep}}}$$

- $\widetilde{D}_i$ taken from CALPHAD mobility database
- Will confirm HEA creep mechanism in collaboration with Peter Liaw at U.Tenn.

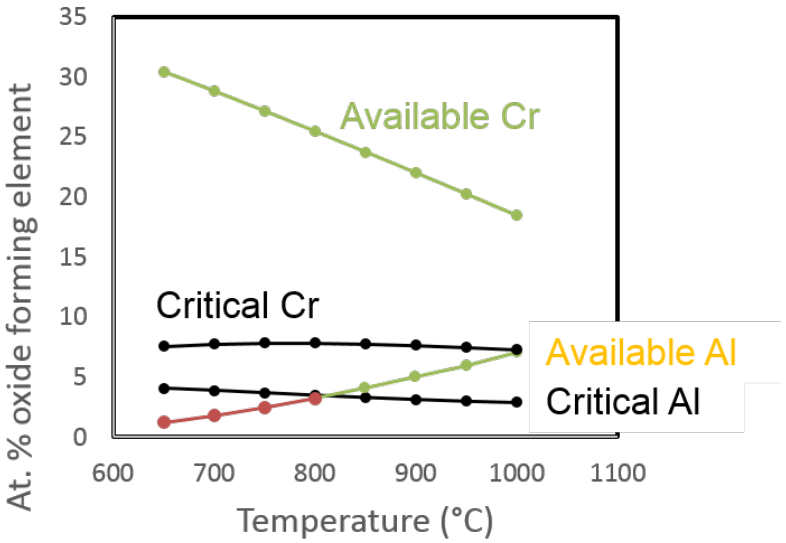
Surface Oxidation Modeling (#4)

- Criteria for continuous protective oxide formation (e.g. Al_2O_3 and Cr_2O_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

$$y_M^0 \geq y_{MC1}^0 = \left(\frac{\pi g}{2\nu} N_o \frac{D_O V_{Alloy}}{D_M V_{MO}}\right)^{1/2}$$



- Both Al_2O_3 and Cr_2O_3 expected to form at high T
- Internal Al_2O_3 expected to form below 850°C

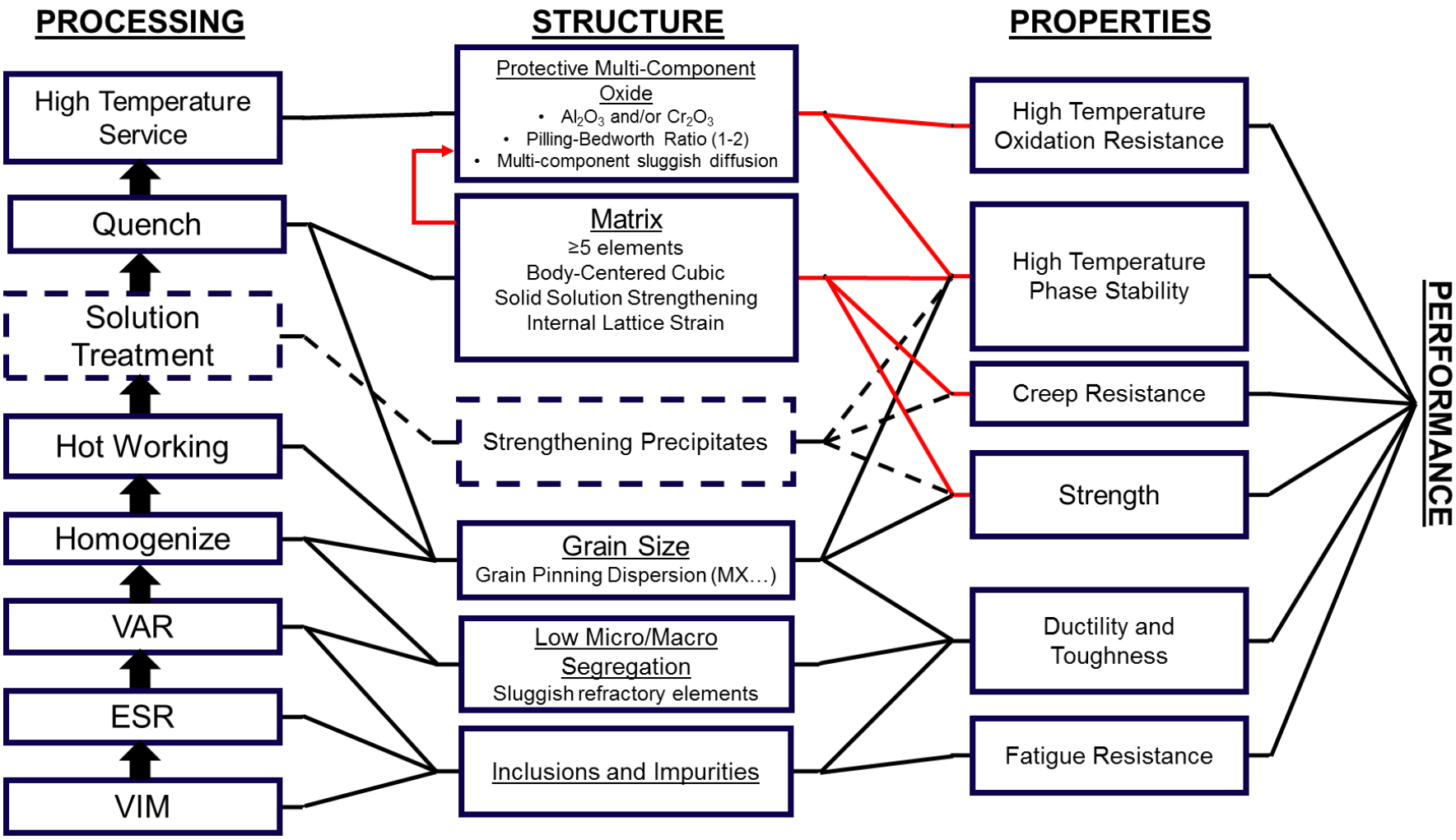
Model agrees well with experimental data for benchmark alloys

C. Wagner, Electrochemical Society - Journal, v 99, n 10, p 369-380, Oct, 1952

G. Wahl, *Thin Solid Films*, vol 107, pp 417-426, 1983

R. Rapp, – 21st conference National Association of corrosion engineers, 1965

IGT HEA System Design Chart



Castable Single Crystal Ni-based Superalloys for IGT Blades

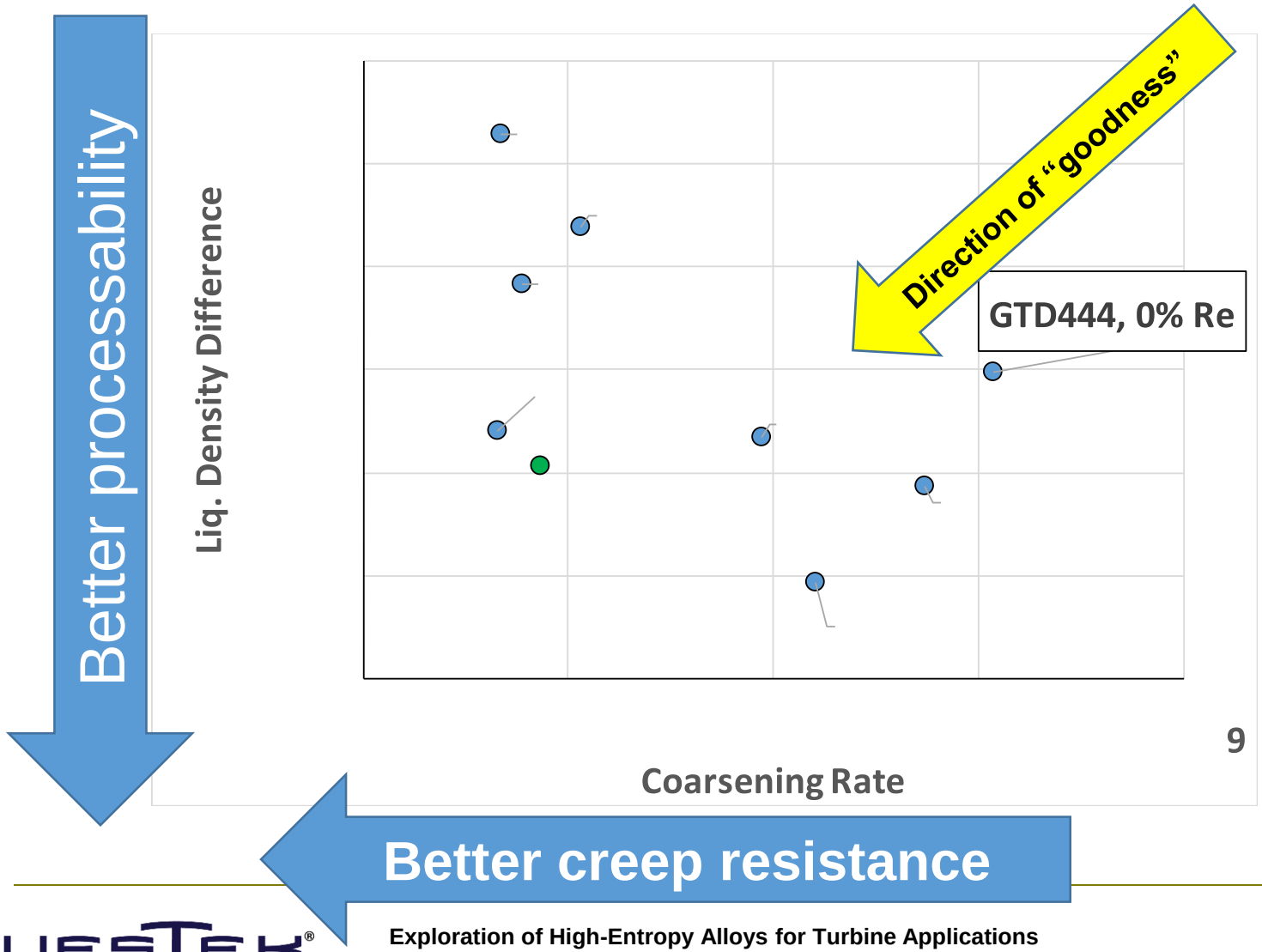
Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number(s) DE-SC0009592."

SBIR Program PHASE II.A, DOE PM: Steve Richardson

PCC Airfoils, LLC
A Division of Precision Castparts Corp.

SIEMENS

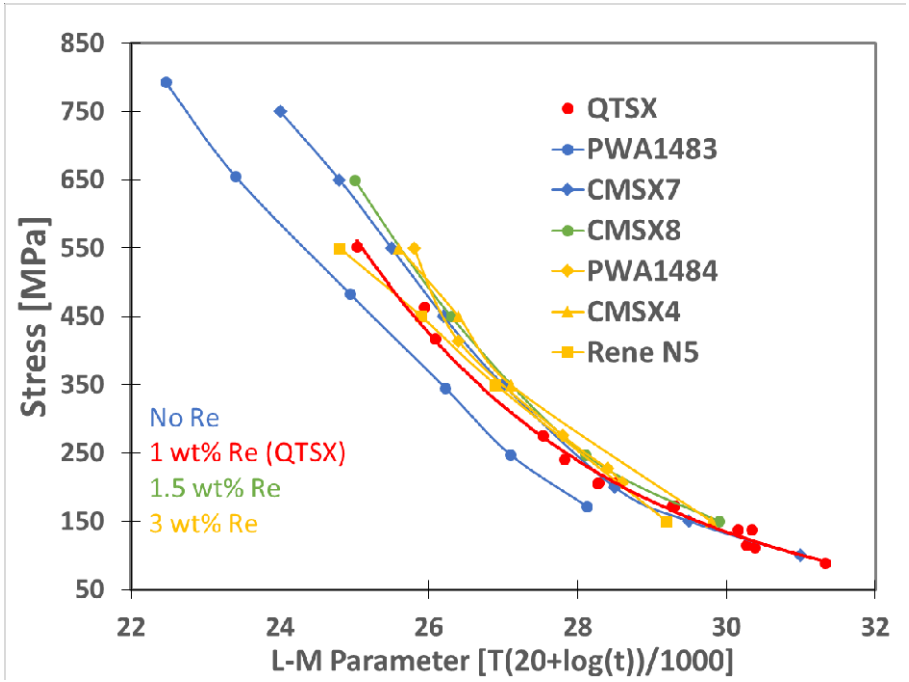
Optimize alloy composition and processing using ICME models to predict critical properties



Alloy performance proven in prototype castings and creep charcterization

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

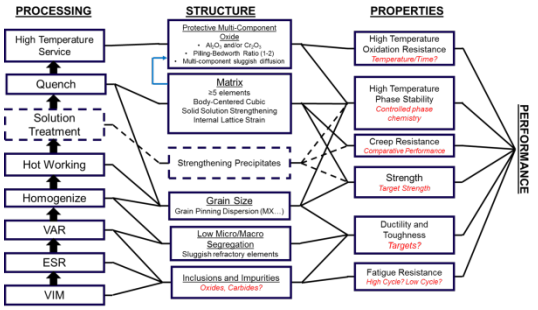
WastePD Mission

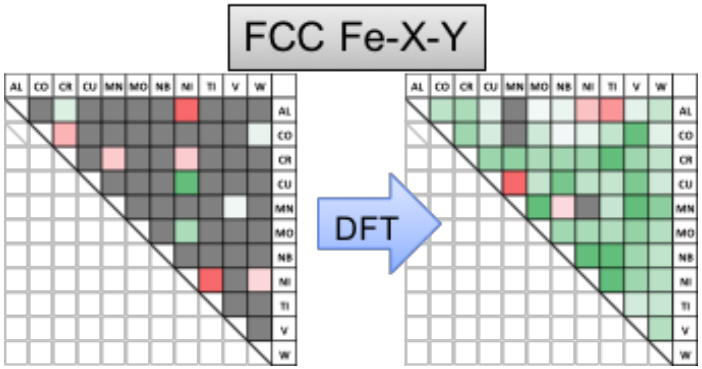
Understand the fundamental mechanisms of waste form performance, and apply that understanding to develop tools for design of waste forms with improved performance.

- 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.

Summary and Next Steps

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



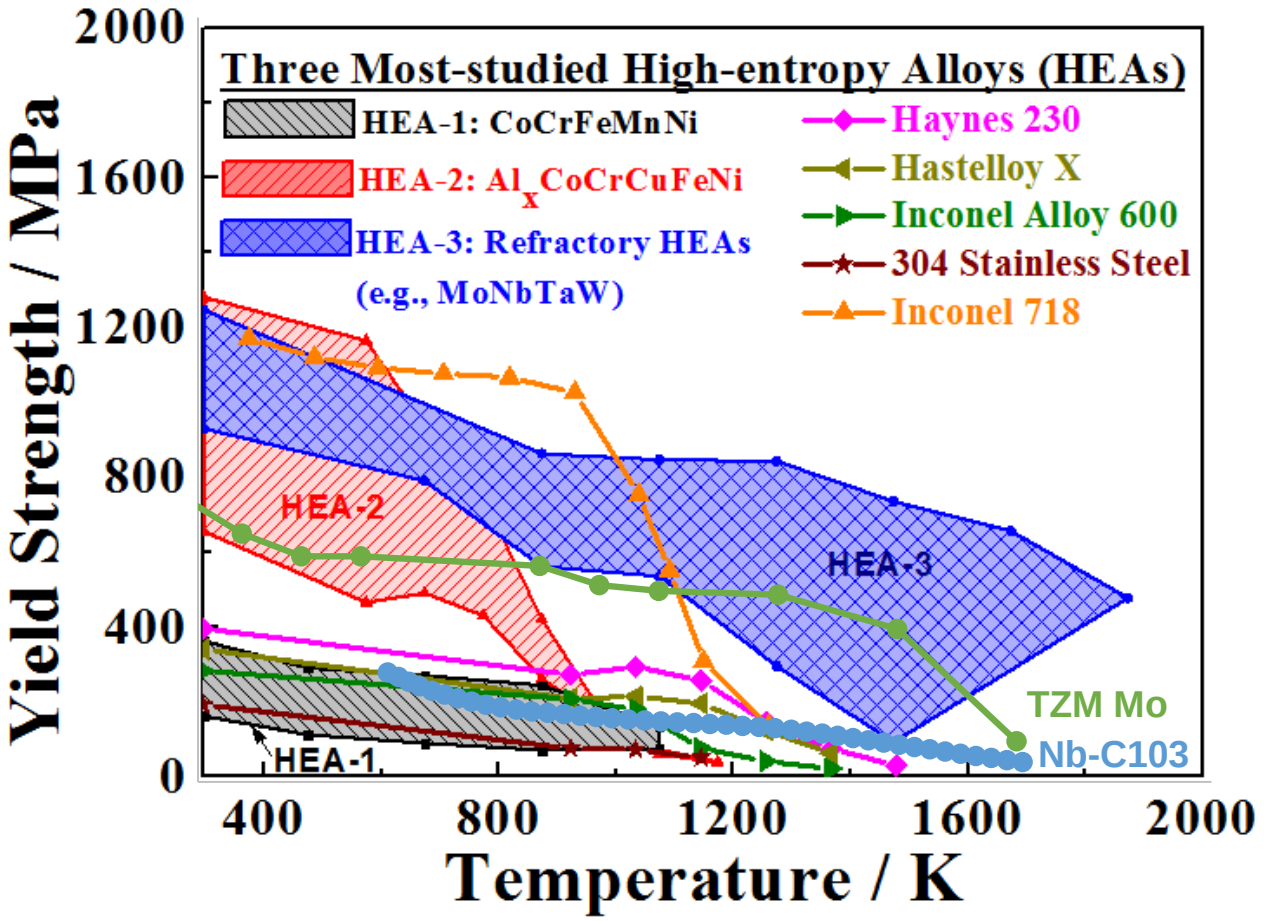


QuesTek employed high-performance computing to accelerate development of an HEA CALPHAD database

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

THE UNIVERSITY OF TENNESSEE KNOXVILLE

HEA Properties Relative to Other Materials



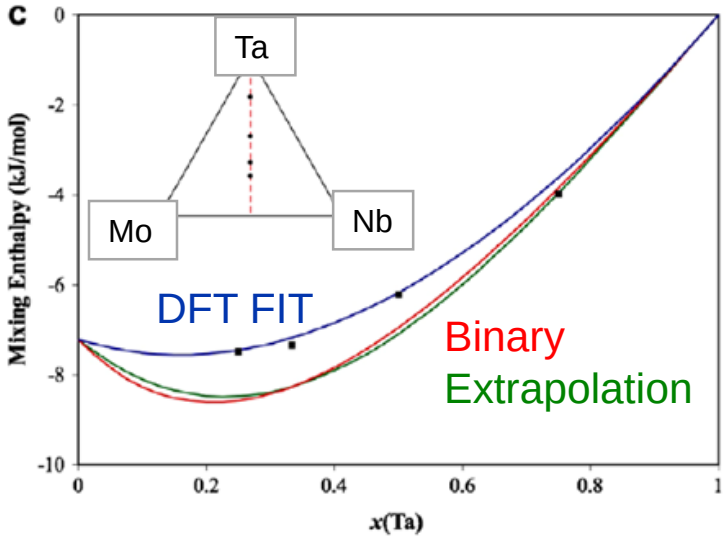
Modified, from H. Diao, X. Xie, R. Feng, B. Chen, C. Zhang, F. Zhang, K. A. Dahmen, and P. K. Liaw, "Mechanical Behavior of Single-phase High-entropy Alloys (HEAs): An overview", in preparation.

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

$$G^{\alpha} = \sum_{i}^{c} x_i G_i^{\alpha} - TS_{mix}^{ideal} + {}^{xs}G_m$$

Redlich-Kister polynomial for solid solution mixing energy in CALPHAD

$$^{xs}G_m = \sum_{i=1}^{c-1}\sum_{j>i}^{c} x_i x_j \sum_{v=0}^{n} {}^{v}L_{ij}\left(x_i - x_j\right)^{v} + \sum_{i=1}^{c-2}\sum_{j>i}^{c-1}\sum_{k>j}^{c} x_i x_j x_k \, {}^{0}L_{ijk}$$

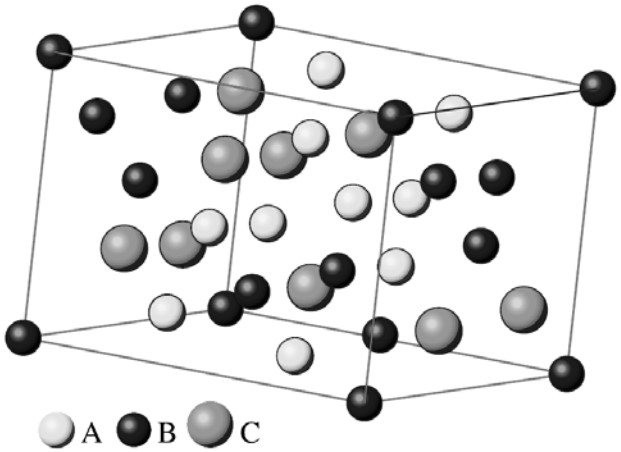


Ternary interaction parameters typically ignored due to lack of data, but can have a large effect in HEA systems

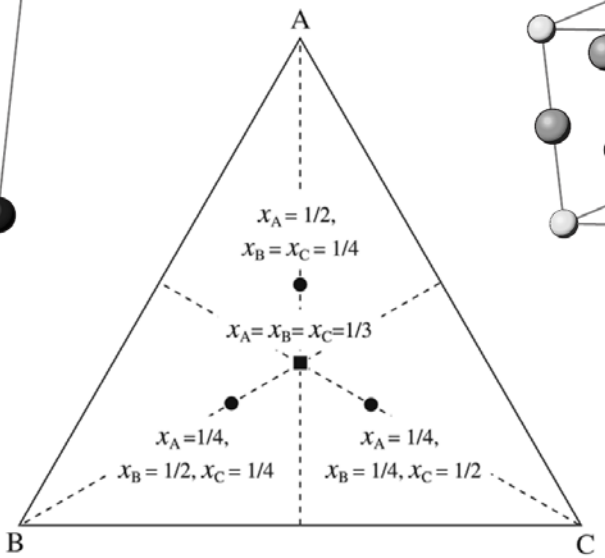
Jiang, Chao. "First-principles study of ternary bcc alloys using special quasi-random structures." Acta materialia 57.16 (2009): 4716-4726.

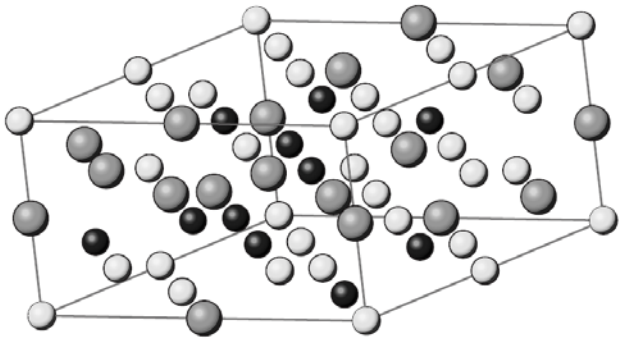
Special Quasi-random Structure (SQS)

- 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 $x_A = \frac{1}{2}$, $x_B = x_C = \frac{1}{4}$