Exploration of High-Entropy Alloys for Turbine Applications

Ricardo Komai, Materials Design Engineer
rkomai@questek.com

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

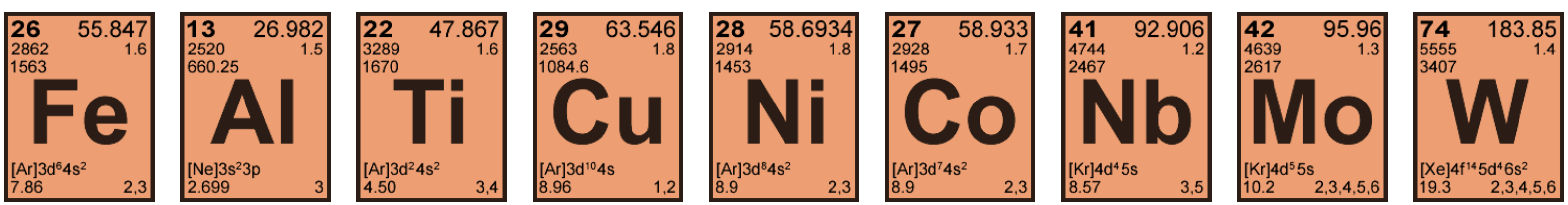
Background - QuesTek Innovations LLC

- Global leader in Integrated Computational Materials Engineering (ICME)
- Founded in 1997 by Greg Olson & Ray Genellie / Northwestern University "spin-off"
- 24 full-time employees (13 with PhDs)
- 7 member Board of Directors (4 in the National Academy of Engineering; 3 in the American Academy of Arts and Sciences)

- Business model: design, develop and patent new materials; license to Producers/OEMs/End-users; formation of strategic partnerships
- In-house software, databases and models work across a range of alloy systems

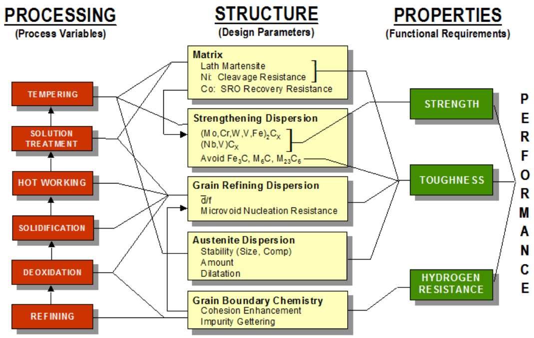
- 12 US patents awarded; 18 US patents pending (>50 Foreign Patents filed)
- 2016 recipient of prestigious SBA Tibbetts Award for excellence in commercializing new technologies

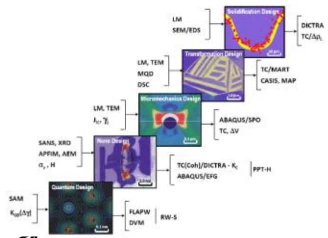
- Formed JV in Europe (Stockholm) in 2016, planning for JV in Japan in 2018

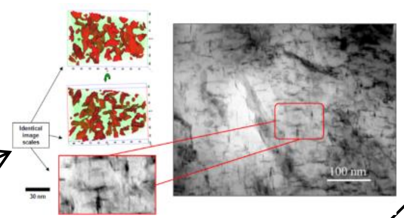


QuesTek's ***Integrated Computational Materials Engineering*** approach

"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."



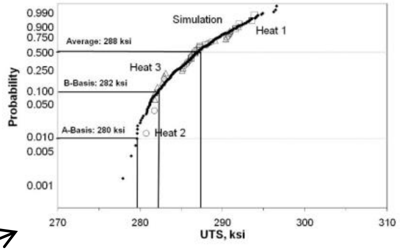


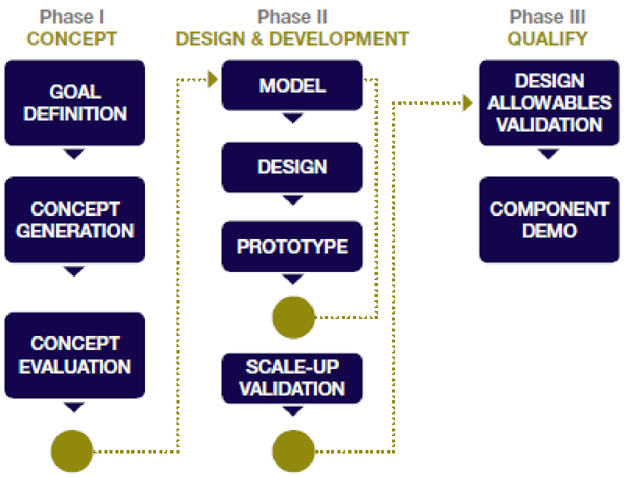


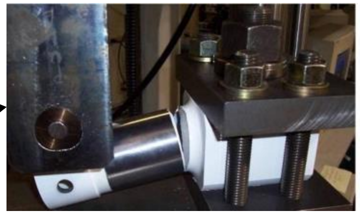
SAE Aerospace An SAE International Group	AEROSPACE MATERIAL SPECIFICATION	SAE AMS5922	REV. A
		Issued 2008-01 Revised 2010-05 Superseding AMS5922	

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







Commercial successes

<u>Ferrium® S53® steel</u>

Ultra high strength, corrosion resistant steel Used as landing gear on U.S. Air Force jets and **numerous flight-critical SpaceX components**

From materials design to flight in 10 years

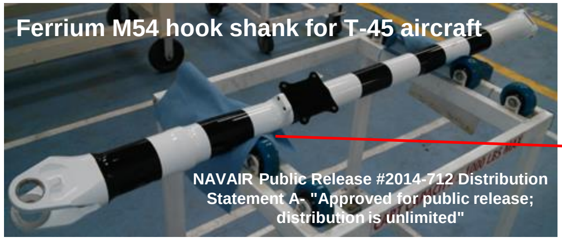
Dragon manned capsule flight test, photo courtesy of SpaceX

<u>Ferrium M54® steel</u>

Ultra high strength steel, SCC resistant

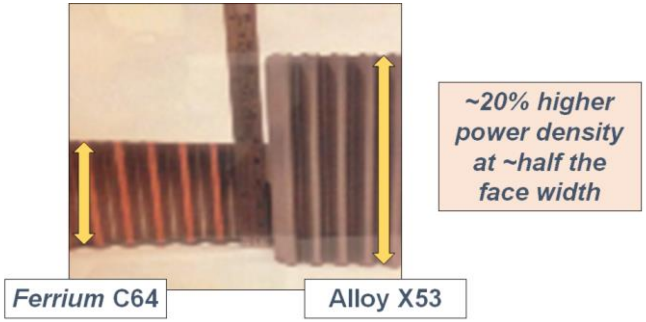
Flying as hook shank on Navy T-45 jets

From materials design to flight in 7 years



<u>Ferrium C64® steel</u>

High surface hardness, tough core steel q**ualified by Sikorsky (Lockheed Martin) and Bell Helicopter as next generation helicopter gear material**



DOE NETL Projects

- "Exploration of High-Entropy Alloy (HEAs) for Turbine Applications"
  - Phase I and Phase II SBIR
  - Contract # DE-SC0013220
  - TPOC Mark Freeman
- "Castable Single Crystal Ni-based Superalloys for IGT Blades"
  - Phase I, Phase II, Phase II.A SBIR
  - Contract # DE-SC0009592
  - TPOC Mark Freeman
- "Improved Models of Long Term Creep Behavior for Fossil Energy Power Plants"
  - Phase I and Phase II SBIR
  - Contract # DE-SC0015922
  - TPOC Omer Bakshi

High-Entropy Alloys at QuesTek

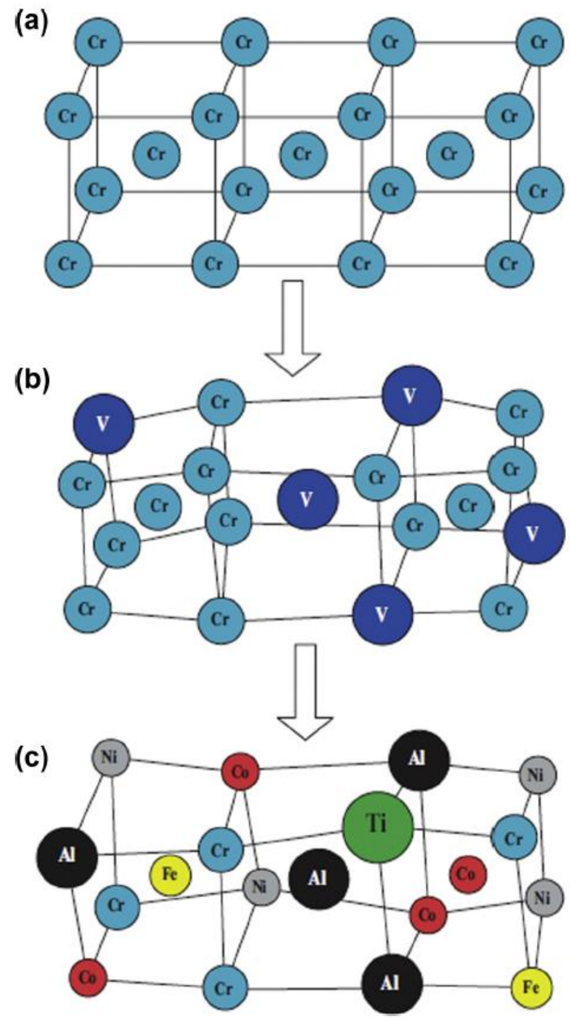
- DOE
  - "Exploration of High-Entropy Alloy (HEAs) for Turbine Applications"
    - Phase I and Phase II SBIR
    - Contract #DE-SC0013220
  - WastePD-EFRC (The Ohio State University)
    - Highly corrosion resistant transition metal HEA (FCC) developed
- DOD NAVAIR
  - "An Integrated Computational Materials Engineering (ICME) Tool for the Streamlined Development of High-Entropy Alloys for Advanced Propulsion Systems"
    - Phase I STTR with University of Tennessee, Knoxville
    - Contract # N68335-17-C-0618

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**:
  - Use database and other ICME tools to design HEA and produce prototype heat
  - Characterize performance and iterate design, Peter Liaw as collaborator

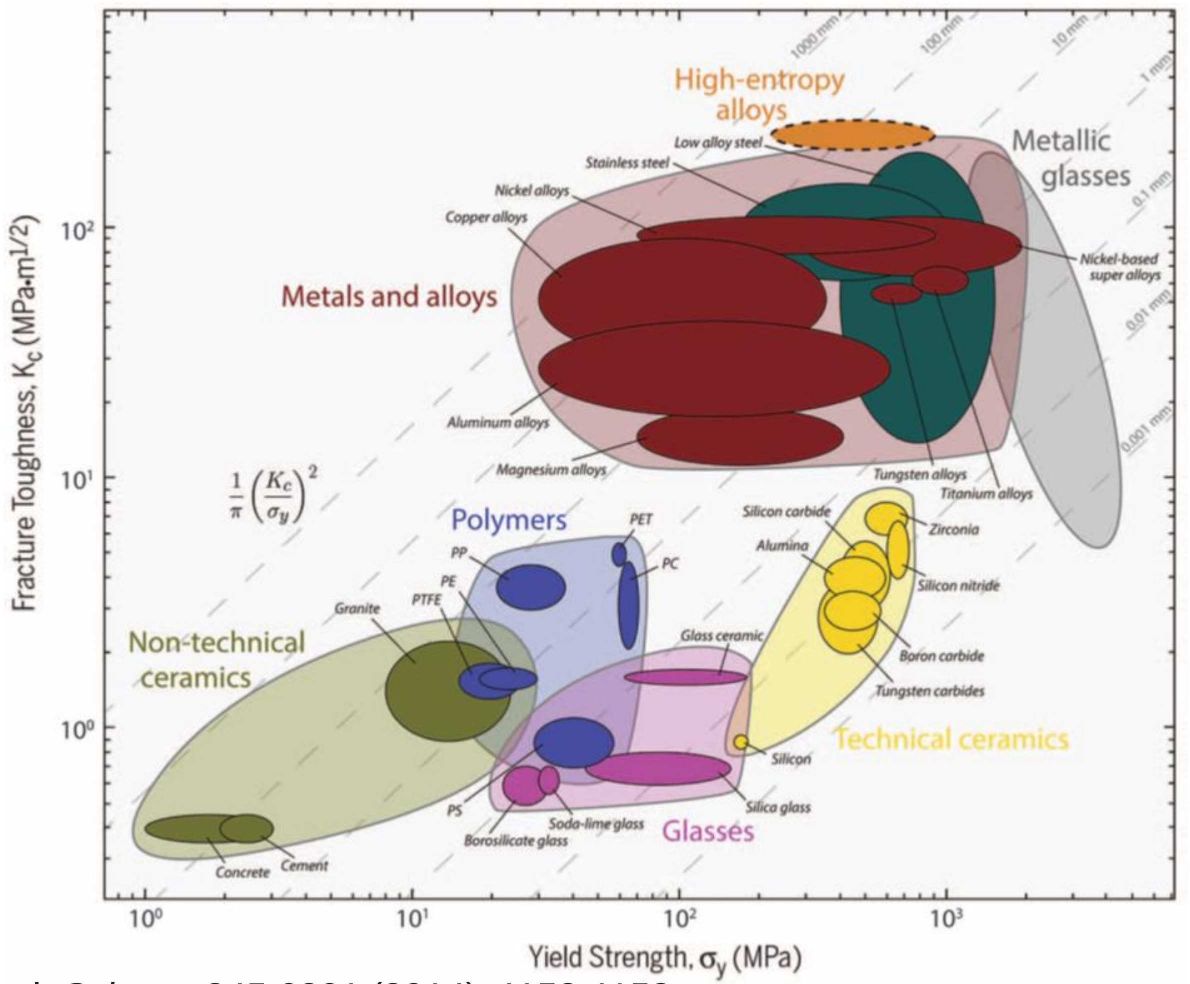
High Entropy Alloys (HEAs)

- 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



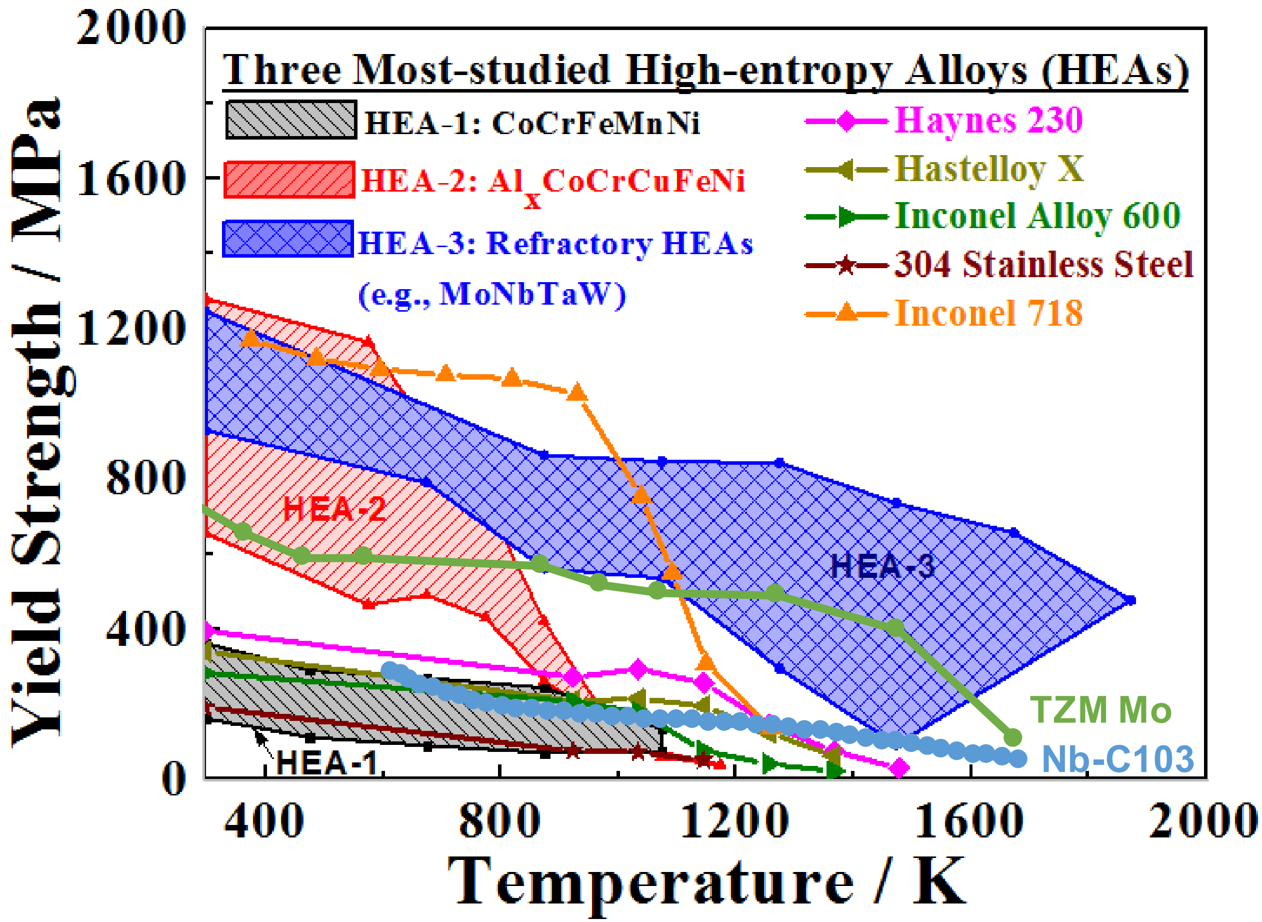
Zhang, Yong, et al. "Microstructures and properties of high-entropy alloys. "*Progress in Materials Science* 61 (2014): 1-93.

HEA Properties Relative to Other Materials



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

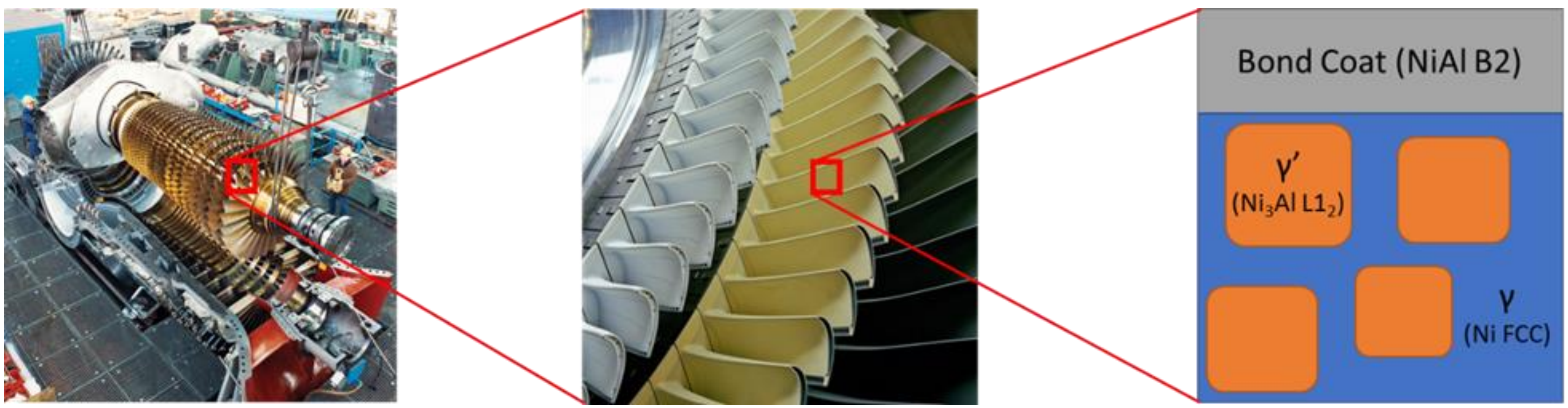
HEA Properties Relative to Other Materials



Modified, from Diao, et. al, "Fundamental deformation behavior in high-entropy alloys: An overview", Curr. Opin. Solid State Mater.Sci. (2017), http://dx.doi.org/10.1016/j.cossms.2017.08.003

HEAs as an Industrial Gas Turbine Alloy

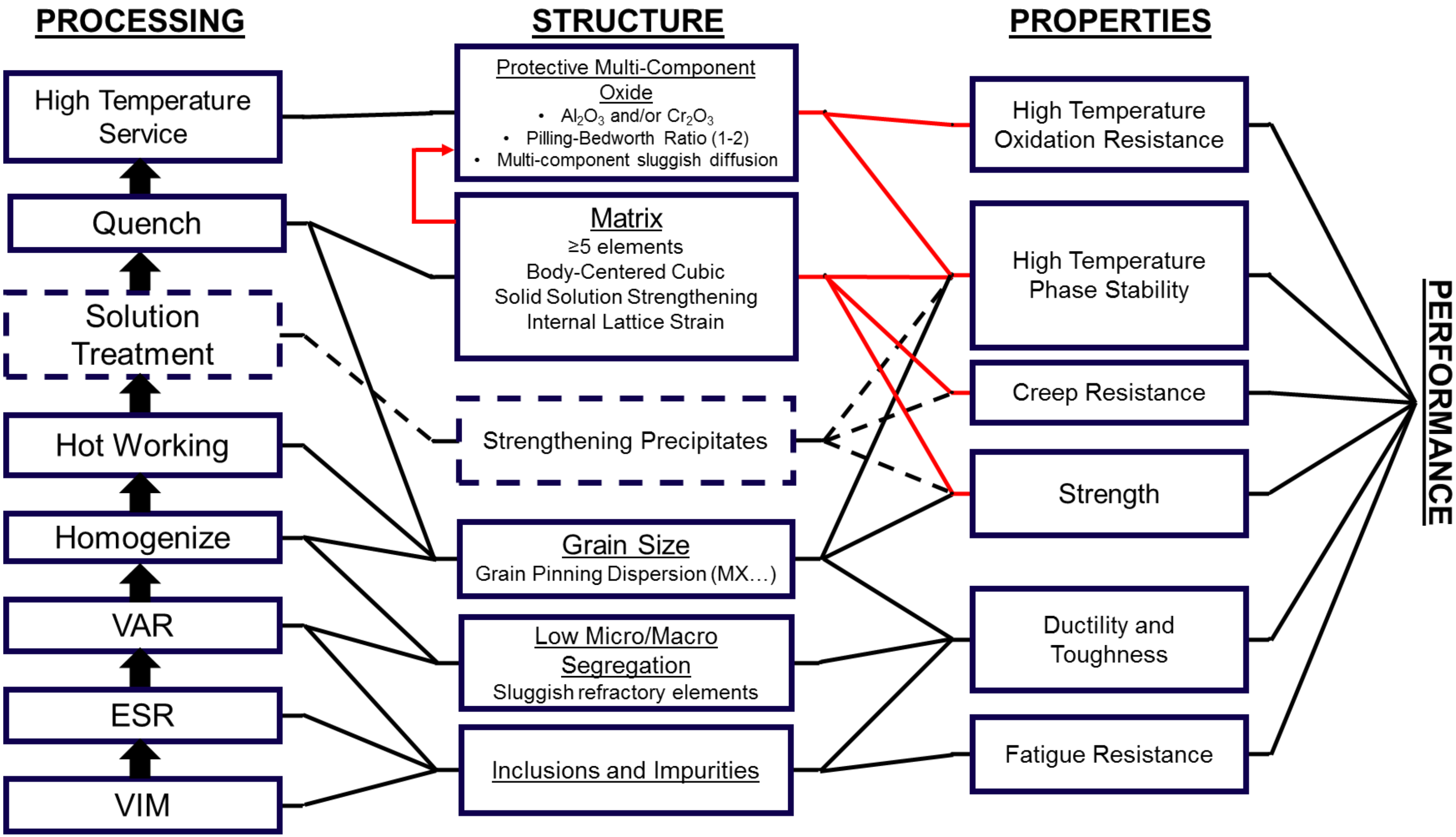
- Consider HEAs as a component in an IGT blade or vane alloy
  - Stability at higher temperatures than Ni/Ni_3Al
  - Higher strength
  - Better thermodynamic compatibility with bond coat
- HEAs have been demonstrated to be made as a single crystal (Bridgman solidification) and an FCC HEA in equilibrium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



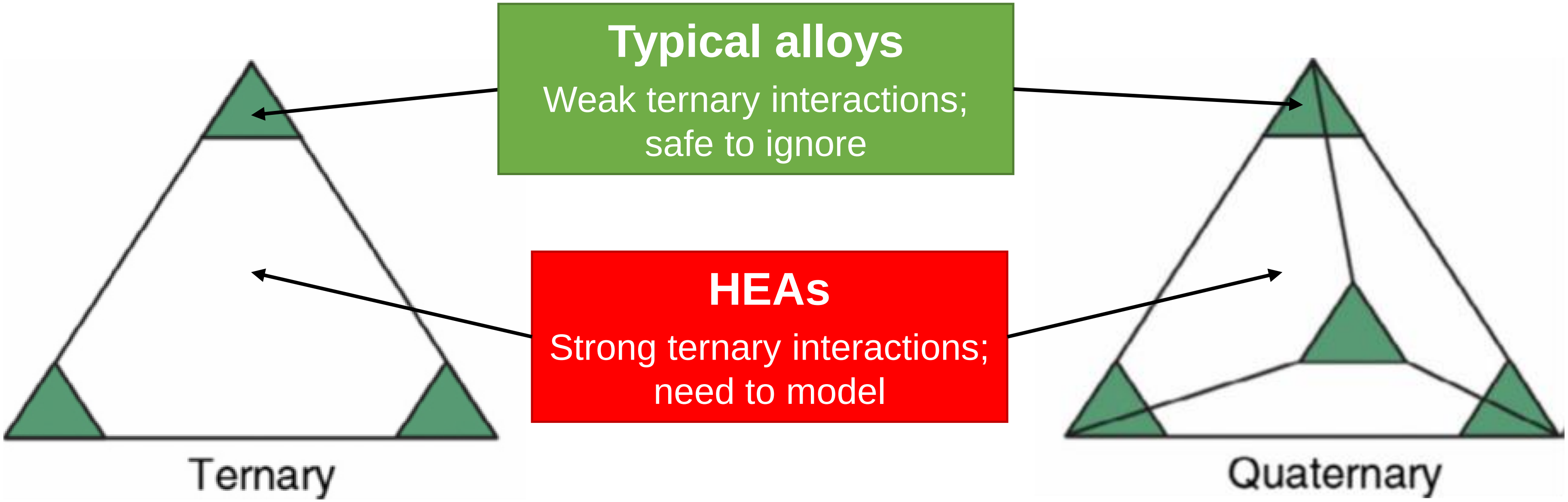
Path to HEA ICME Design

- 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

Initial Design Challenge: Limited CALPHAD Databases

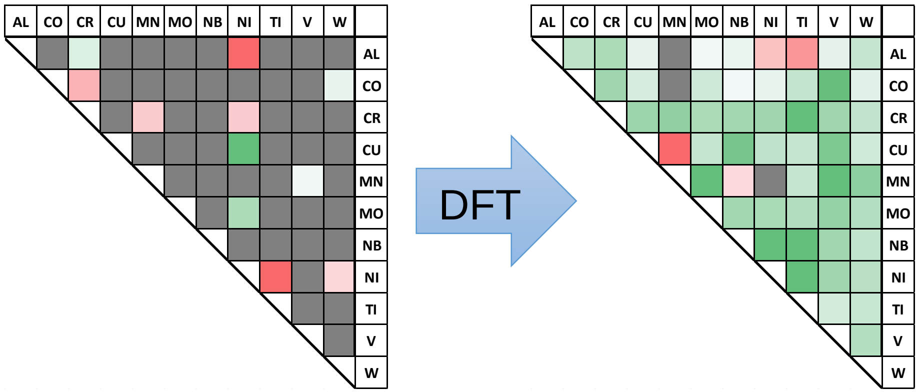
- CALPHAD databases have been built with a focus on specific corners of composition space (e.g. Fe, Ni, Al), shown in green
- HEAs are in the center of composition space, and extrapolations of CALPHAD models to these regions are likely limited, **<u>due to lack of data</u>**



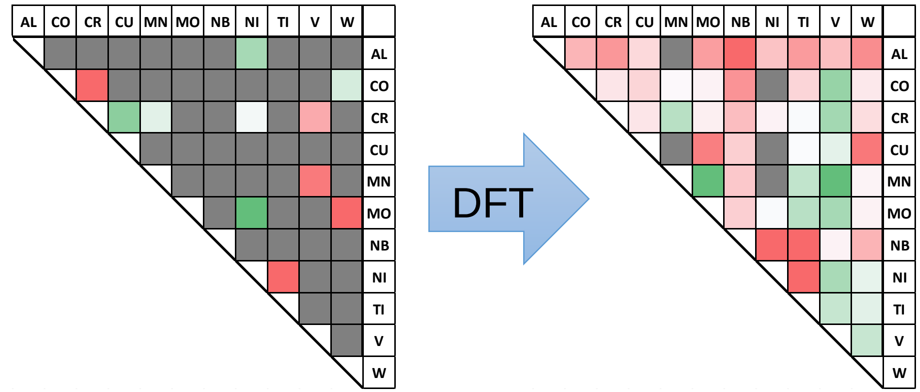
Sparsity of ternary interaction parameters reduced after CALPHAD database update

Attractive / Repulsive / No value

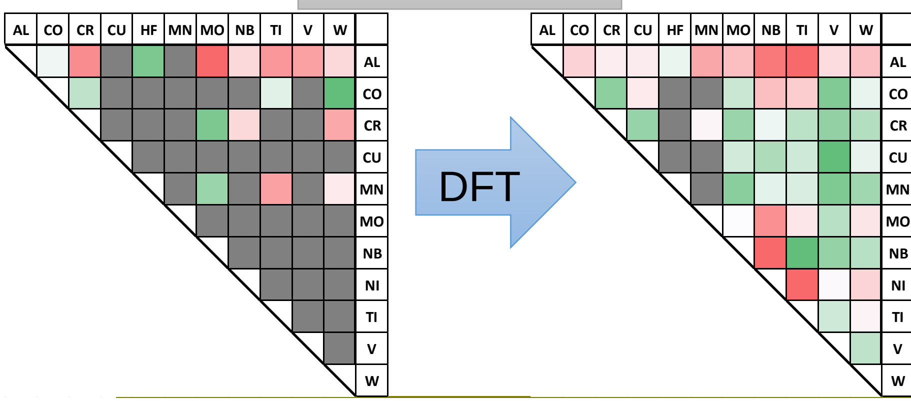
FCC Fe-X-Y



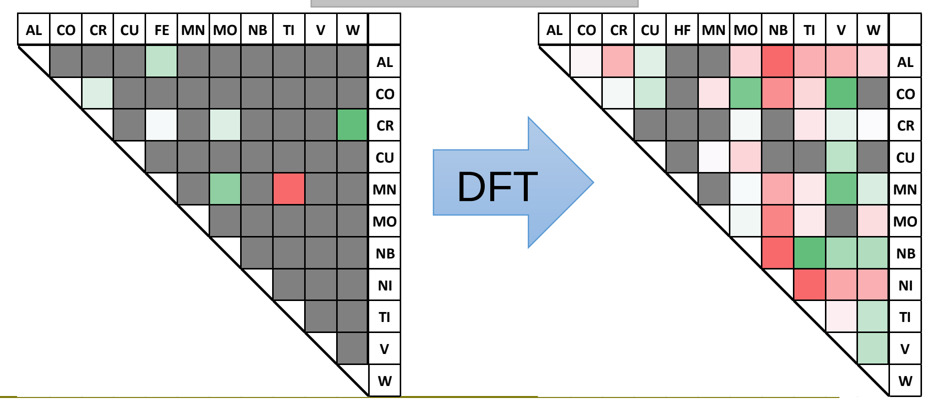
BCC Fe-X-Y



FCC Ni-X-Y



BCC Ni-X-Y



How well do CALPHAD databases predict known HEAs?

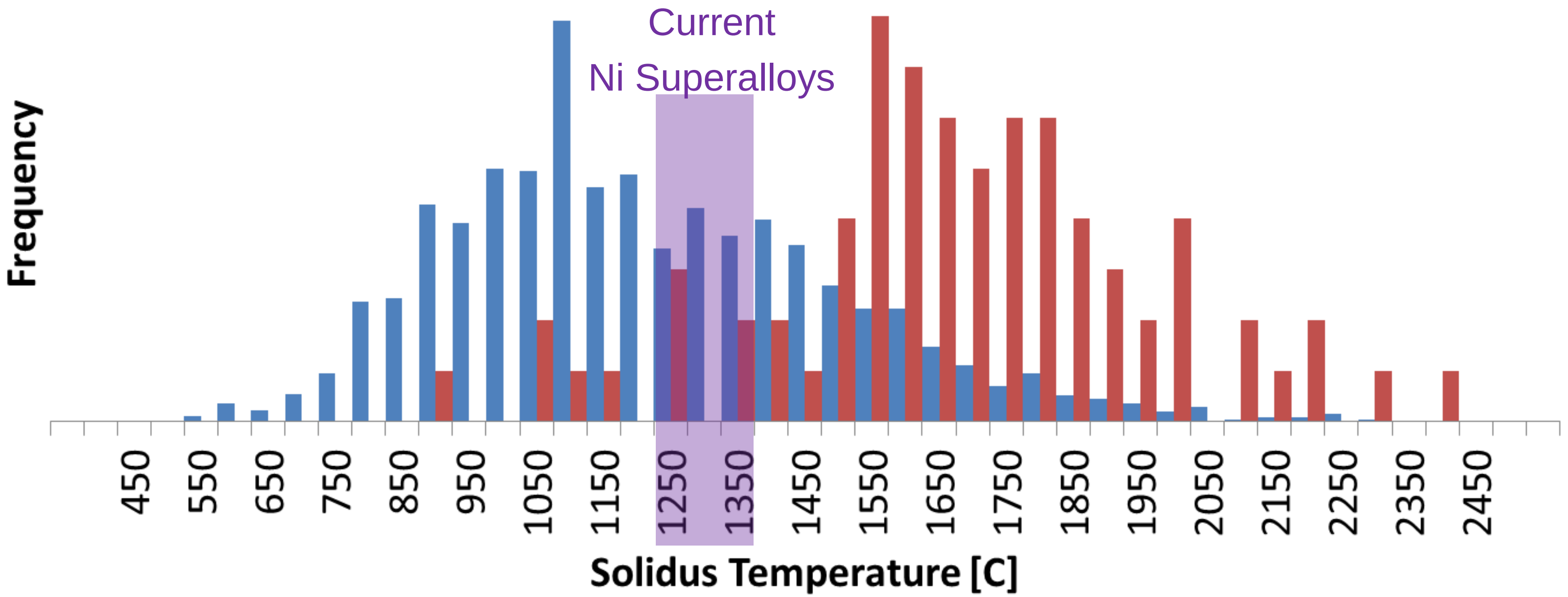
- In the Al-Co-Cr-Cu-Fe-Ni-Ti-V-Nb-Mo-Mn-W system, 31 BCC and 36 FCC single-phase HEA-forming compositions (of ≥5 components) reported in the literature
- Assume any phase fraction ≥ 0.9 predicted by CALPHAD is a prediction of HEA formation

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

Effect of CALPHAD + DFT

High-temperature Stability of HEA Compositions

- 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

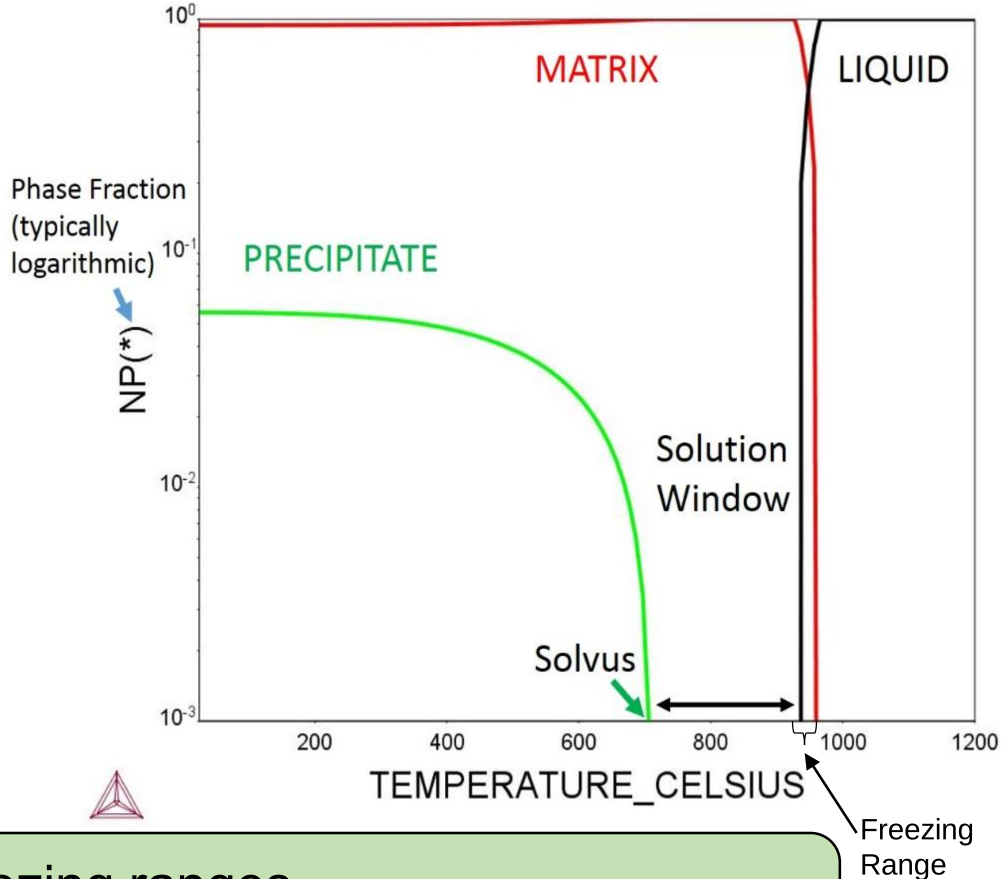


Thermodynamic features of screening

- "Step Diagram"

  A calculation to demonstrate the equilibrium phase balance at each temperature

- Features:
  - Freezing Range
    - Transition from liquid to solid
    - Interdendritic segregation information
    - Can this be compatible with AM?
  - Solution Window
    - Homogenization treatment guidance
    - Is there a single phase?



FCC HEAs have "reasonable" freezing ranges

BCC refractory containing HEAs tend to have large freezing ranges

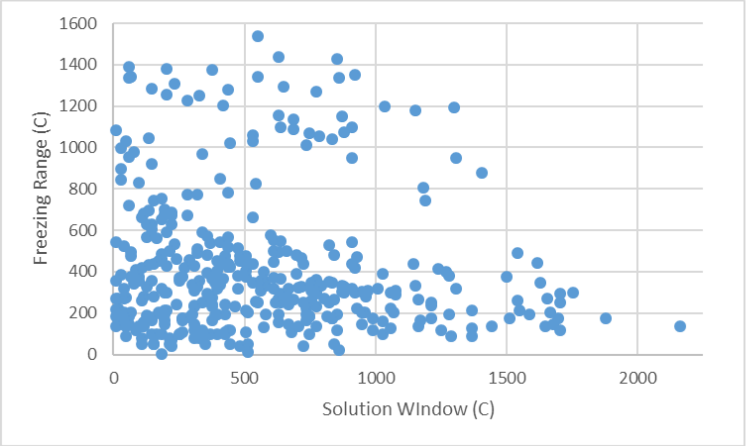
High-Throughput Computational Prediction of HEAs

- **6188 five-element equiatomic combinations of elements from TCHEA2**

- 384 had solution window
- Total Time ~ Two days

TCHEA units(K) or (mole fraction)

index	solidus	liquidus	sss_name	freezing	solution	non_sss_names	solvus
0	1308.90625	1560.78125	None	251.875	None	BCC_B2#2+FCC_L12#1+BCC_B2#1	None
1	1066.71875	1968.125	None	901.40625	None	C14_LAVES+BCC_B2#2+NITI2+BCC_B2#1	None
2	1202.34375	1560.78125	None	358.4375	None	FCC_L12#1+BCC_B2#3+BCC_B2#1	None
3	1299.21875	1961.875	None	662.65625	None	CR3SI_A15+SIGMA+BCC_B2#3+BCC_B2#1	None
4	1289.53125	2205.625	None	916.09375	None	C14_LAVES+BCC_B2#2+BCC_B2#3+BCC_B2#1	None
5	1260.46875	1661.875	None	401.40625	None	SIGMA+BCC_B2#2+FCC_L12#1	None
6	1299.21875	2036.875	None	737.65625	None	BCC_B2#2+SIGMA+FCC_L12#1	None
7	1347.65625	1911.875	None	564.21875	None	SIGMA+BCC_B2#2+FCC_L12#1+HCP_A3#1	None
8	1299.21875	1993.125	None	693.90625	None	C15_LAVES+C14_LAVES+BCC_B2#2+BCC_B2#1	None
9	1231.40625	1522.03125	None	290.625	None	C14_LAVES+BCC_B2#1+BCC_B2#2+H_L21	None
10	1308.90625	1943.125	None	634.21875	None	BCC_B2#2+FCC_L12#1+BCC_B2#1	None
11	1328.28125	3093.125	None	1764.84375	None	MU_PHASE+BCC_B2#1+R_PHASE+BCC_B2#3+FCC_L12#1	None
12	1308.90625	1774.375	None	465.46875	None	C14_LAVES+BCC_B2#2+FCC_L12#1+BCC_B2#1	None
13	1618.90625	1980.625	None	361.71875	None	C14_LAVES#2+C14_LAVES#1+BCC_B2#1	None
14	1696.40625	1793.125	BCC_B2	96.71875	251.875	BCC_B2#2+BCC_B2#1	1444.53125
15	1618.90625	2043.125	None	424.21875	None	BCC_B2#2+SIGMA+BCC_B2#1	None
16	1609.21875	2093.125	None	483.90625	None	C14_LAVES+BCC_B2#1	None
17	1628.59375	1677.03125	None	48.4375	None	BCC_B2#2+BCC_B2#1	None
18	1618.90625	1874.375	None	255.46875	None	BCC_B2#2+SIGMA#2+BCC_B2#1	None
19	1638.28125	1849.375	BCC_B2#2	211.09375	19.375	BCC_B2#2+BCC_B2#3	1618.90625
20	1657.65625	1936.875	None	279.21875	None	C14_LAVES+BCC_B2#1	None
21	1531.71875	1580.15625	BCC_B2	48.4375	213.125	BCC_B2#2+BCC_B2#1	1318.59375
22	1725.46875	1805.625	BCC_B2	80.15625	310	BCC_B2#2+BCC_B2#1	1415.46875
23	1628.59375	2349.375	None	720.78125	None	BCC_B2#2+BCC_B2#1	None
24	1492.96875	1786.875	None	293.90625	None	C14_LAVES+BCC_B2#1	None
25	1647.96875	1924.375	None	276.40625	None	C14_LAVES#2+BCC_B2#1	None
26	1899.84375	2121.875	None	222.03125	None	C14_LAVES+BCC_B2#1	None
27	1609.21875	2274.375	None	665.15625	None	C14_LAVES#2+SIGMA+C14_LAVES#1+BCC_B2#2	None
28	1677.03125	1905.625	None	228.59375	None	C15_LAVES+BCC_B2#1+H_L21	None
29	1909.53125	2161.40625	None	251.875	None	C14_LAVES+SIGMA+BCC_B2#1	None
30	1812.65625	2171.09375	None	358.4375	None	H_L21+BCC_B2#2+BCC_B2#1	None
31	1599.53125	1886.875	None	287.34375	None	C14_LAVES#2+BCC_B2#2+C14_LAVES#1+SIGMA	None
32	1560.78125	1874.375	None	313.59375	None	C14_LAVES#1+BCC_B2#2+BCC_B2#1	None



- **Results still being analyzed for potential prototyping candidates**
  - **Solidus temperature**
  - **Liquidus temperature**
  - **Single solid solution phase name**
  - **Solvus temperature**
  - **Phase names immediately below the single phase region**
  - **Freezing range**
  - **Solution range**
  - **Composition of system**

HEA Prototyping Overview

Goals:

- Produce HEAs by conventional processes (arc melting, VIM, etc.)
- Consider: formability, weldability, compatibility with coatings

Challenges:

- Large ΔT_m between components leads to defects
- Inherent brittleness
- Higher temperature materials have higher temperature detrimental phases (laves, sigma, etc.)
- As-cast inhomogeneity and producing numerous defects

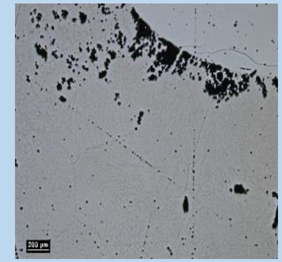
Production by arc melting

CALPHAD Design Approach

- Identify systems with acceptable freezing ranges, and solution windows
- Identify systems that should have the least amount of secondary phase formation
- Identify systems that can alloy possible oxidation protection elements (Cr, Al, etc)

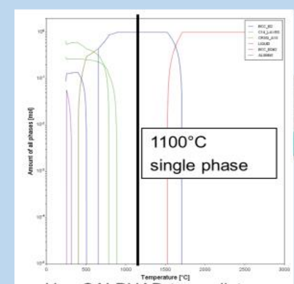
Arc Melting

As-Cast



NbMo-containing HEA, as-cast condition with unincorporated inclusions, pores and material segregation

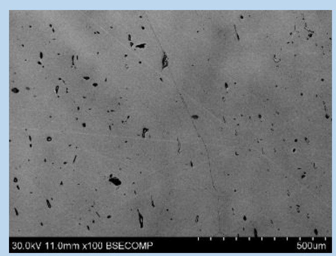
Heat Treatment



Use CALPHAD to predict processing temperatures

Vacuum encapsulated and homogenized at 1100°C

Homogenization



AlCrMoTiV, as-homogenized, single phase with minor Al oxides

Phase and property data for model refinement

Develop Structure-Property Models for Further Screening of Compositions

- **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: Mark Freeman

HEA Strength Modeling

General alloy strength model framework:

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

$$\sigma_{ss} = \left(\sum_i B_i^{3/2} X_i\right)^{2/3}$$

Fleisher/Labush

Solid solution strengthening

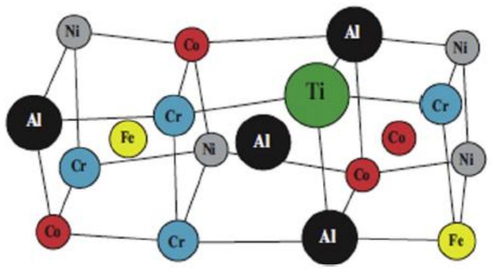
Grain boundary strengthening

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

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

- 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

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

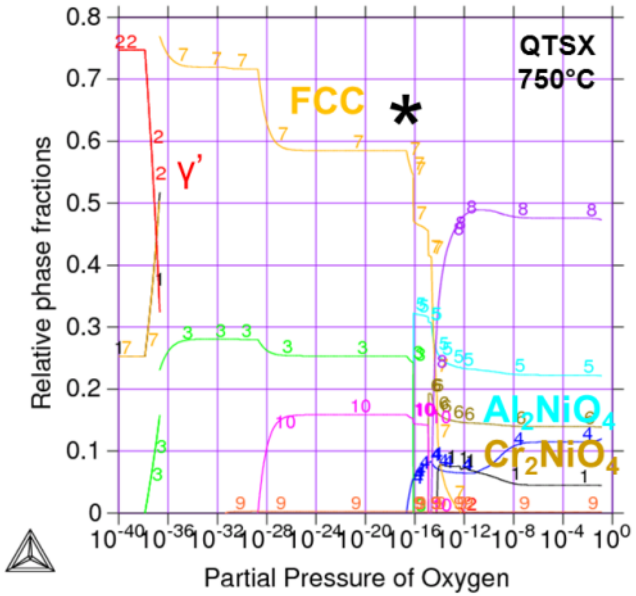
- Take reciprocal for the effective vacancy diffusivity, D_{eff}:

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

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

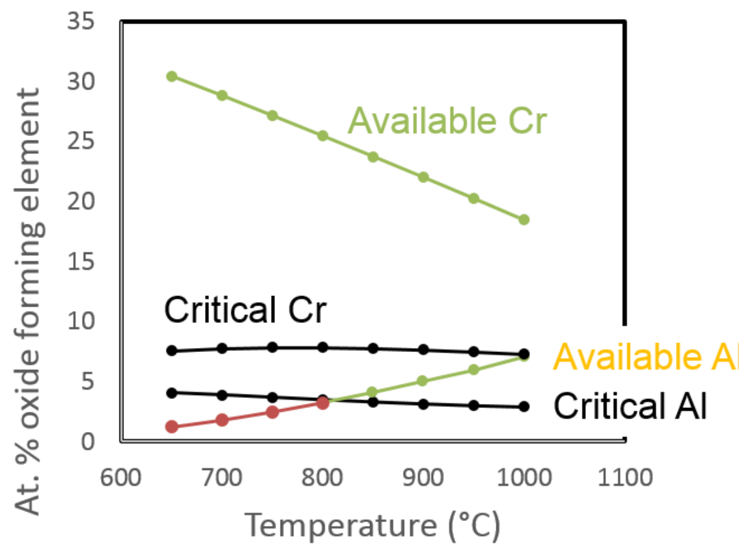
Surface Oxidation Modeling

- 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

QuesTek Innovations LLC

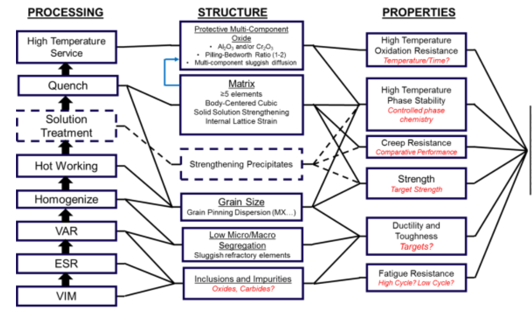
C. Wagner, Electrochemical Society - Journal, v 99, n 10, p 369-380, Oct, 1952

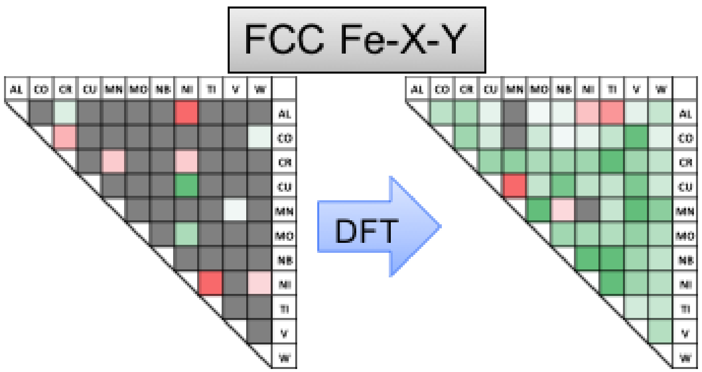
G. Wahl, *Thin Solid Films*, vol 107, pp 417-426, 1983

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

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

Thank you
Questions?

Ricardo Komai
Contact: rkomai@questek.com