ICME Design of High Performance Turbine Alloys

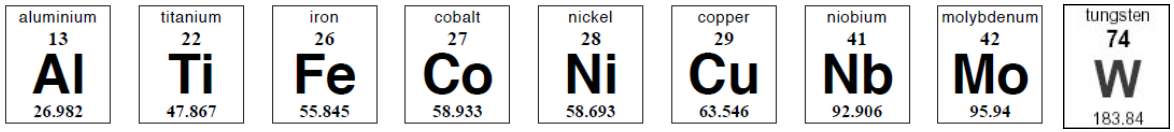
James Saal

Materials Design Engineer

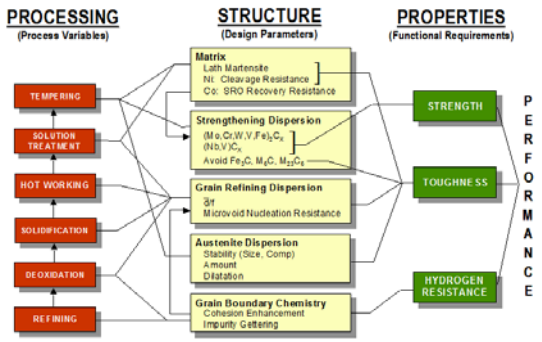
Background - QuesTek Innovations LLC

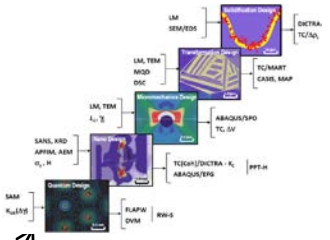
A global leader in integrated computational materials design:

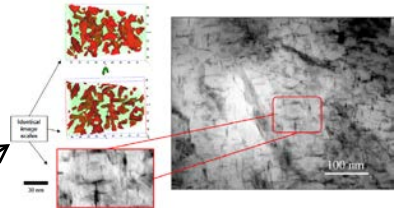
- Our ***Materials by Design***® technology and expertise applies **Integrated Computational Materials Engineering** (ICME) tools and methods to design improved alloys faster and at less cost than traditional empirical methods
- Start-up company in 1997, as a technology spinoff from **Northwestern University** 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.



Phased R&D based on ICME Approach







SAE Aerospace
An SAE International Group

AEROSPACE MATERIAL SPECIFICATION

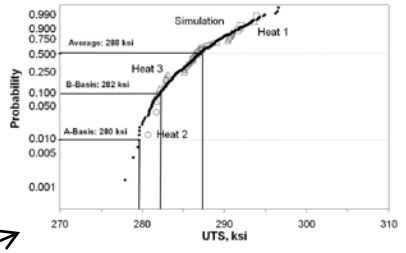
SAE AMS5922 REV. A

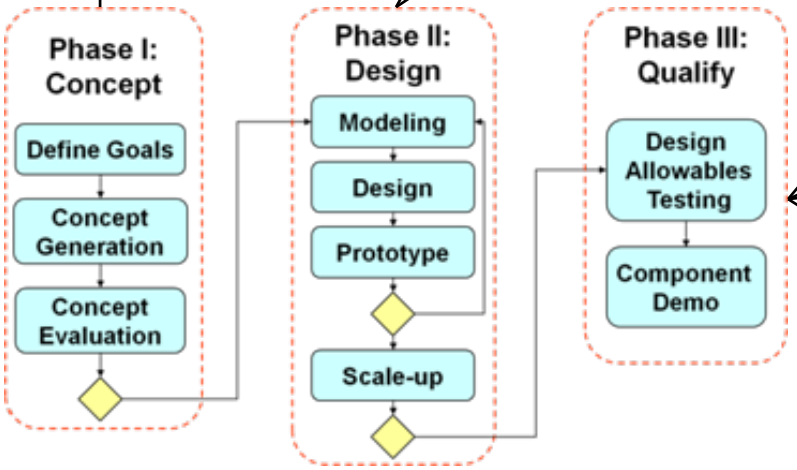
Issued 2008-01
Revised 2010-05

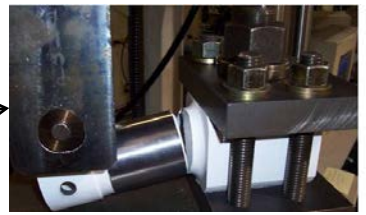
Superseding AMS5922

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







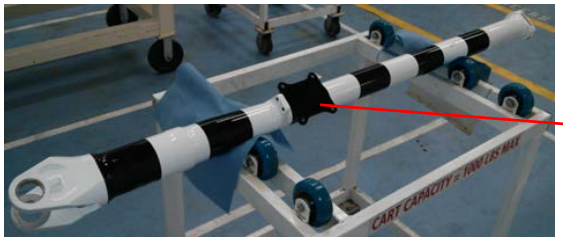
QuesTek Innovations - Commercial successes

- 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

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

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

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, 20% increase in power at same geometry vs. 9310.

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."

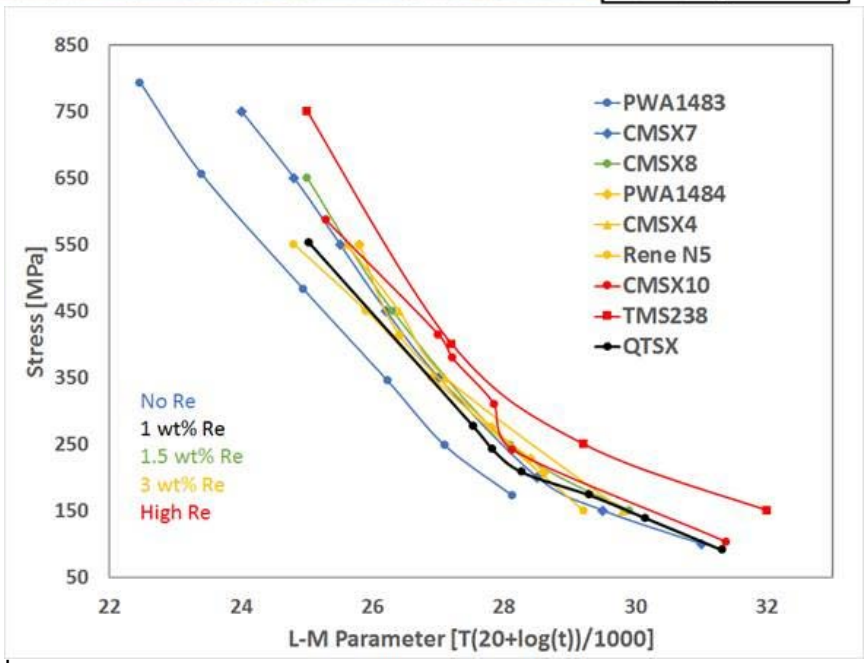
SBIR Program PHASE II, DOE PM: Steve Richardson

PCC Airfoils, LLC
A Division of Precision Castparts Corp.

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)



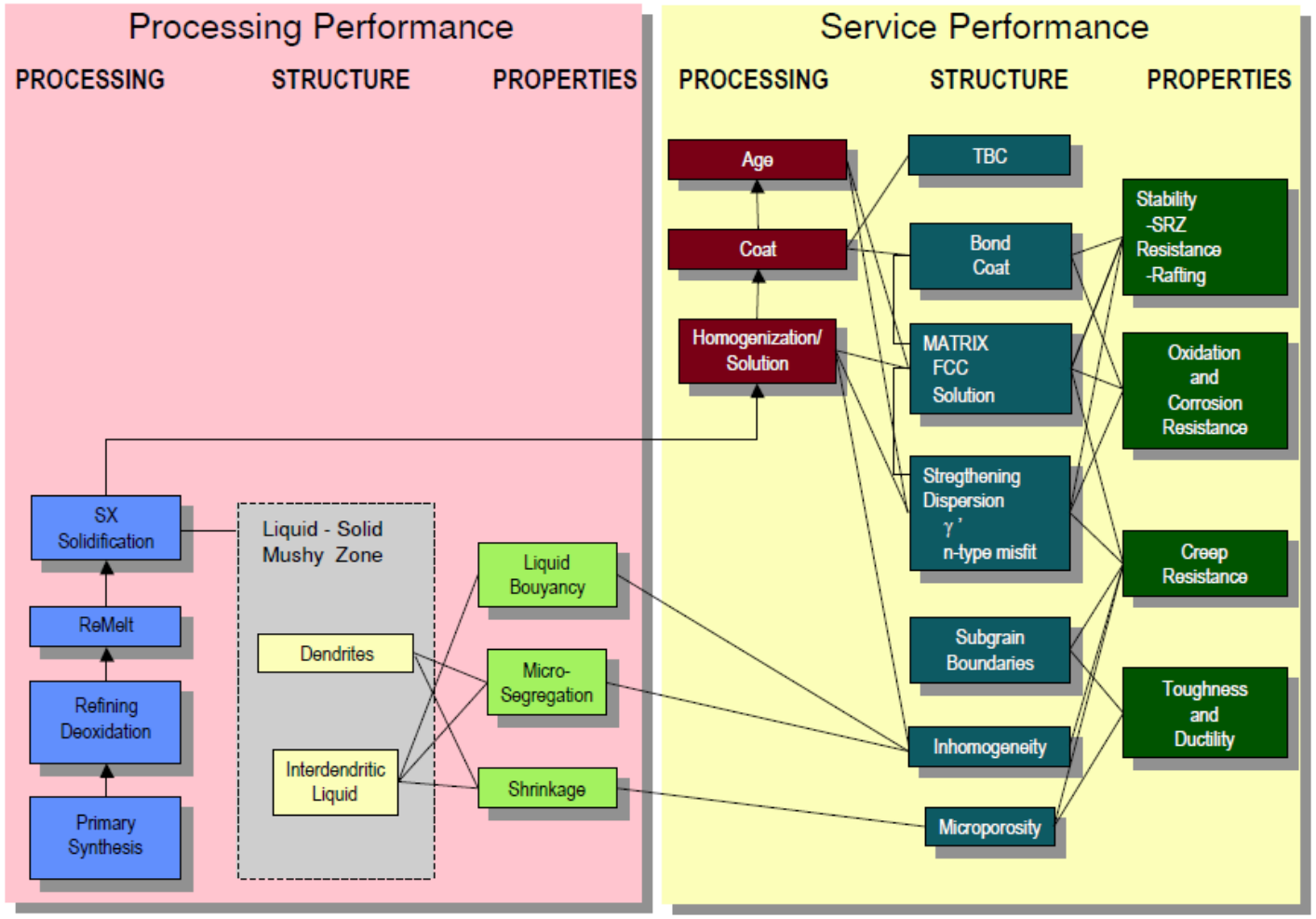
* From Desiree Polyak, “Rhenium.” March 2014, USGS Minerals Yearbook

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

ID	**Re**	Al	Co	Cr	Hf	Mo	Ta	Ti	W	other
PWA1480	-	5	5	10	-	-	12	1.5	4	
PWA1483	-	3.6	9	12.2	-	1.9	5	4.1	3.8	0.07C
GTD444	-	4.2	7.5	9.8	0.15	1.5	4.8	3.5	6	0.08C
CMSX7	-	5.7	10	6	0.2	0.6	9	0.8	9	
CMSX8	1.5	5.7	10	5.4	0.2	0.6	8	0.7	8	
PWA1484	3	5.6	10	5	0.1	2	9	-	6	
CMSX4	3	5.6	9	6.5	0.1	0.6	6.5	1	6	
Rene N5	3	6.2	7.5	7	0.15	1.5	6.5	-	5	0.01Y
CMSX10	6	5.7	3	2	0.03	0.4	8	0.2	5	0.1Nb
TMS238	6.4	5.9	6.5	4.6	0.1	1.1	7.6	-	4	5.0Ru

Re-free alloys

Recently-developed

2nd Gen alloys

High-Re alloys

QuesTek's design ("QT-SX") contains these same elemental constituents, but with 1% Re

QuesTek Creep Modeling

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

Alloy	Creep merit index (m^{-2} s *10^{15})	Coarsen K_{MP}*10^{20}
CMSX-10	6.93	4.59
PWA1484	5.68	5.97
CMSX-4	4.51	6.00
TMS-75	4.49	
QTSX	**3.97**	**6.59**
René N5	3.82	7.17
TMS238	3.47	4.94
PWA1483	2.77	12.2

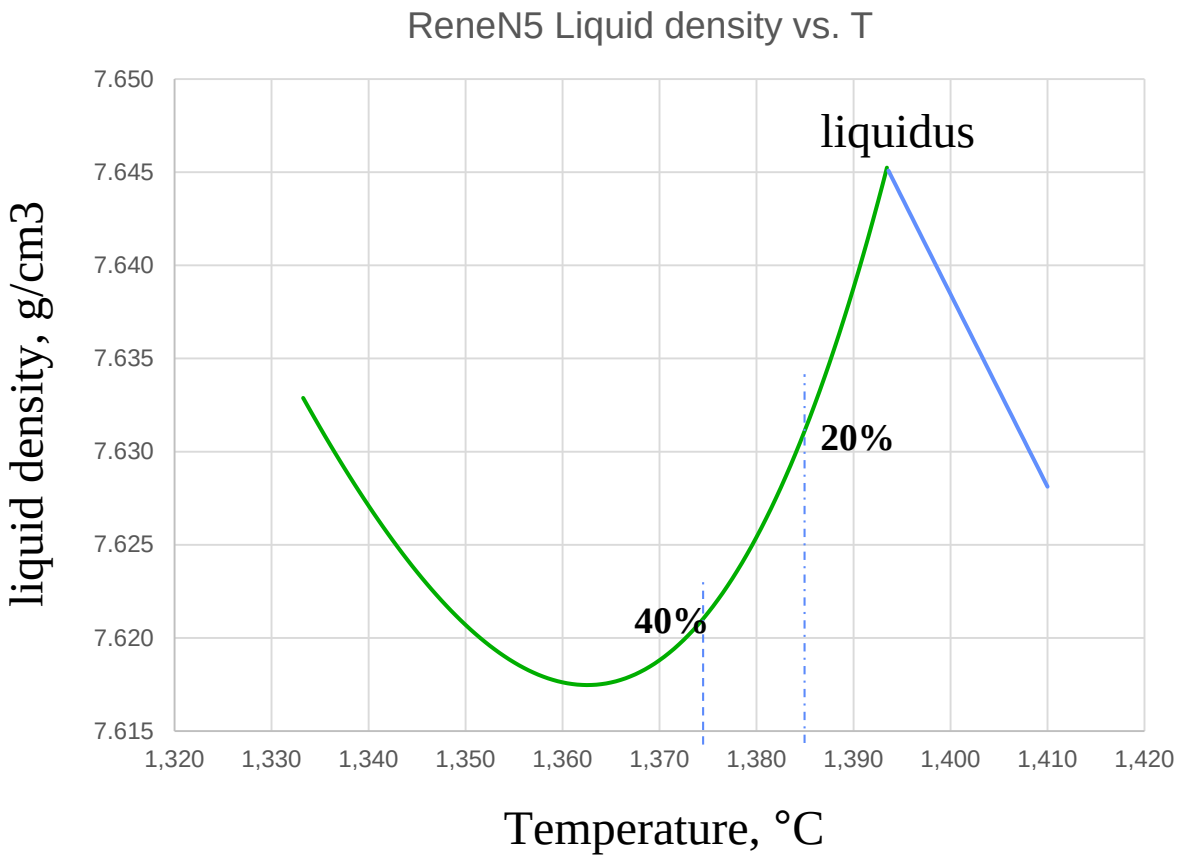
$$M_{\text{creep}} = \sum_i x_i / \tilde{D}_i$$

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

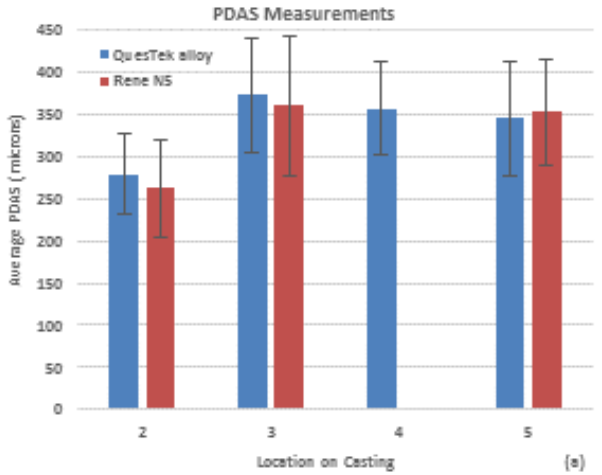
Modeling of liquid density during solidification

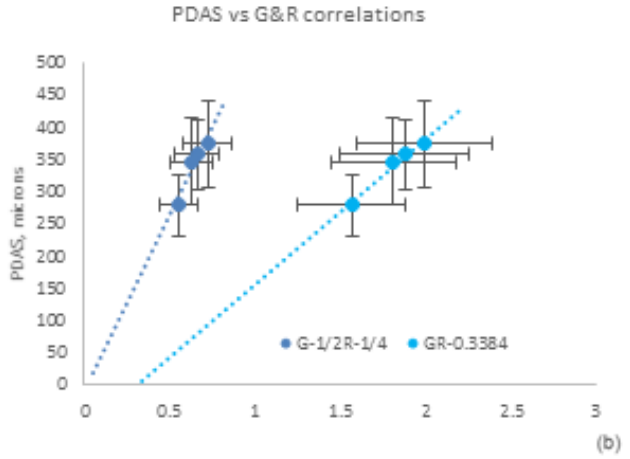
Freckle-resistance is related to the modeling of the liquid density during solidification based on a critical Rayleigh number: $\overline{Ra} = C\Delta\rho^{0.4}\Delta T^{0.4}\dfrac{\lambda_1^2(G,R)}{G}$

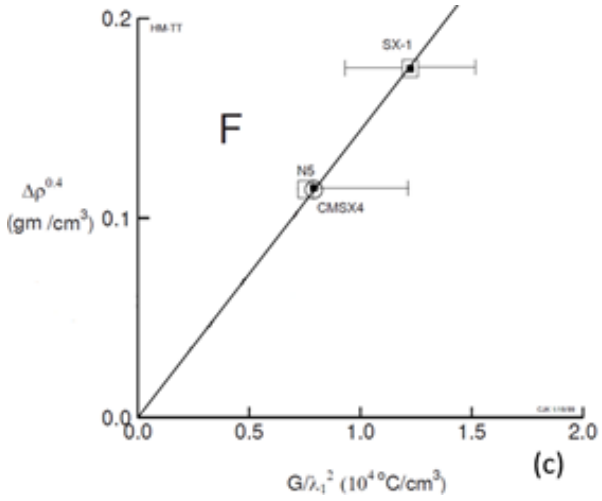


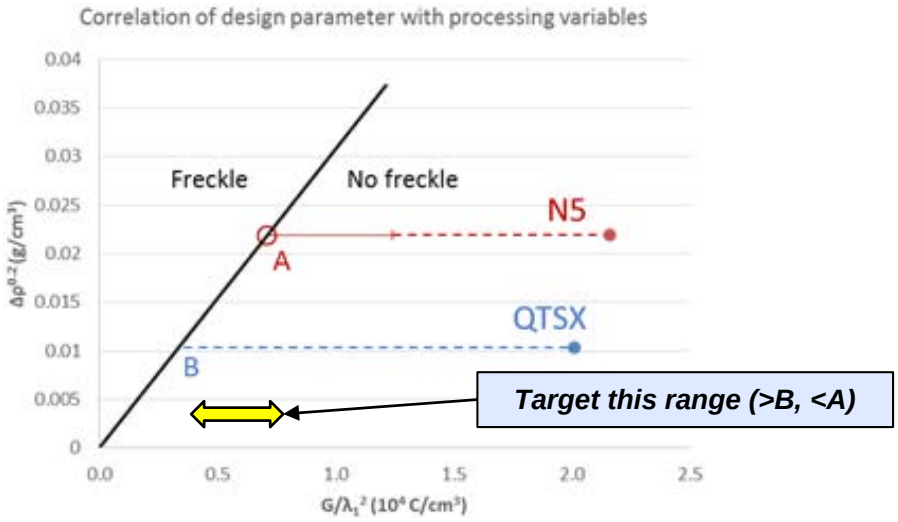
Actual modeling output is a combined use of various databases and software

Modeling freckling behavior in N5 and QT-SX castings



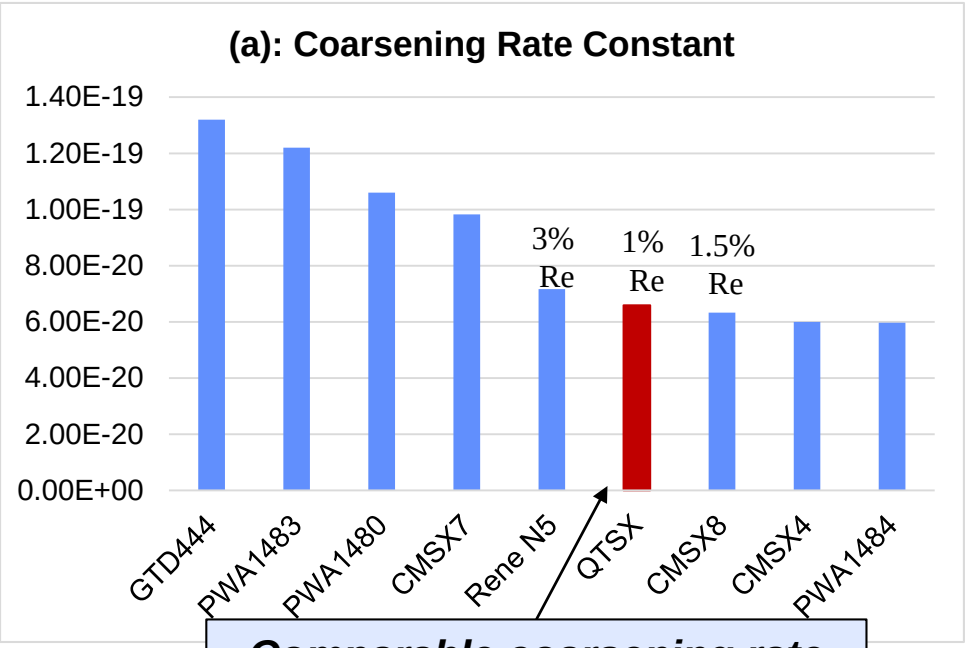




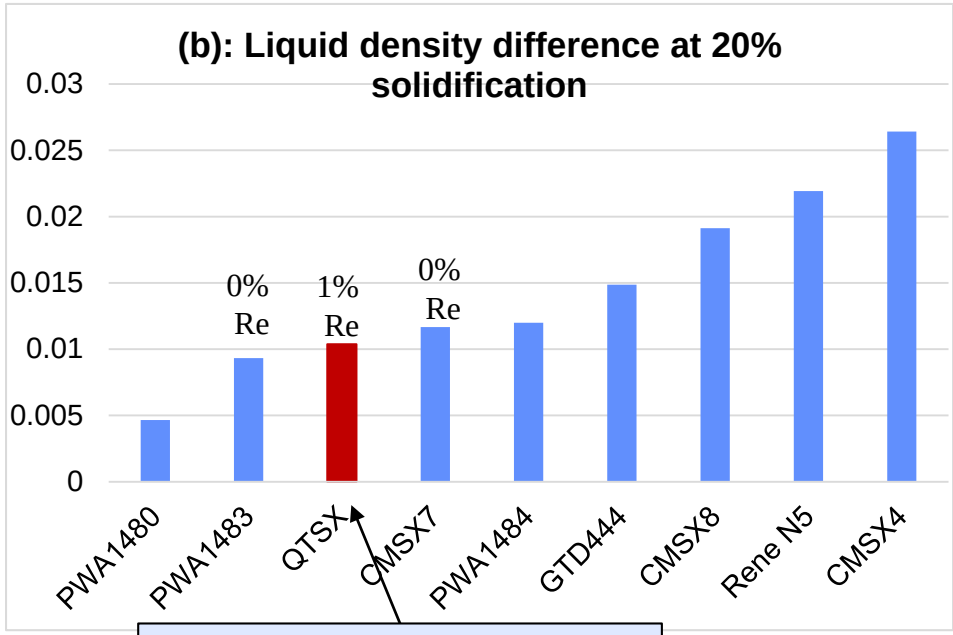


Coarsening rate and liquid density comparisons

(lower is better)



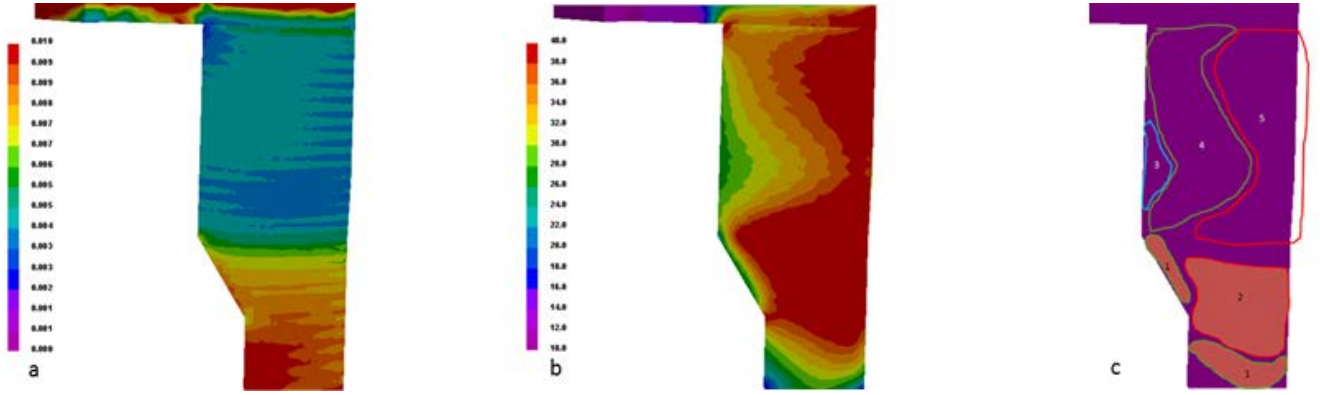
Comparable coarsening rate to CMSX-8 (1.5% Re) alloy

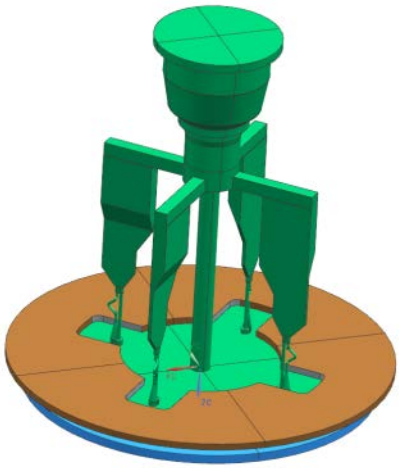


Reduced buoyancy differences (less than non-Re CMSX-7)

1st round of casting results

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

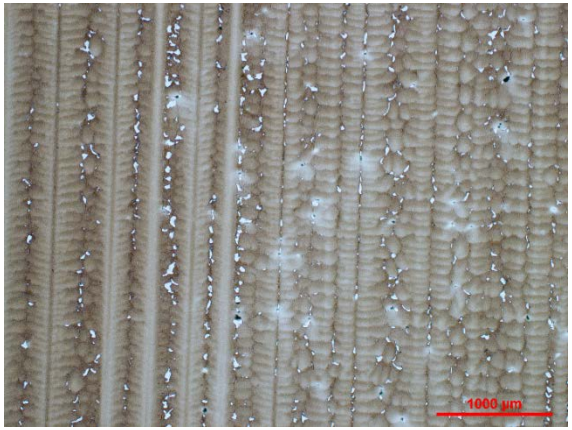
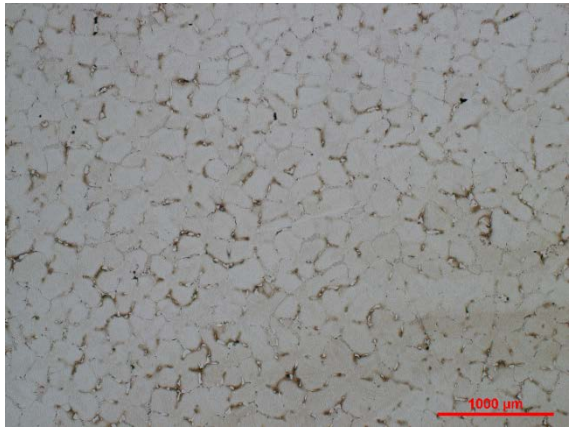
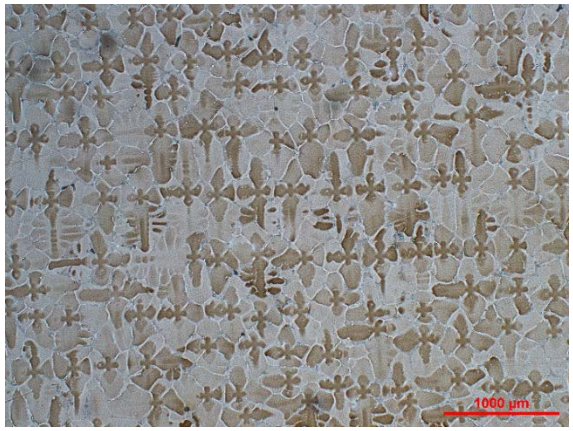




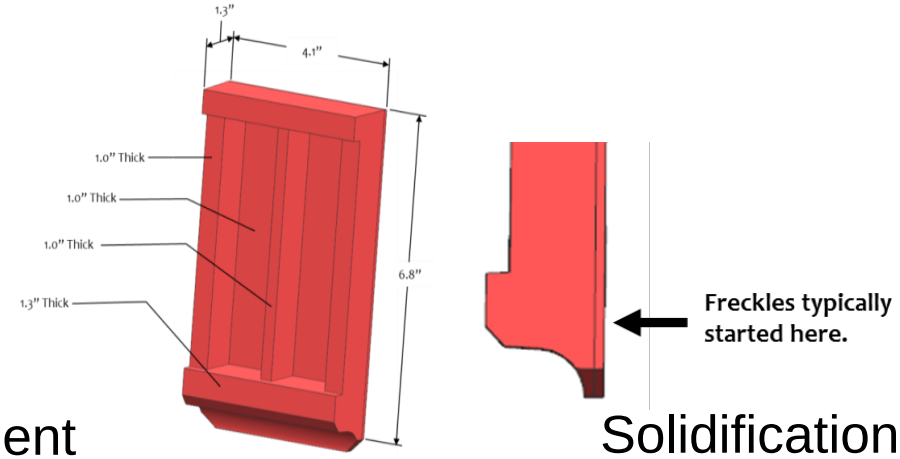
One "tree" (four castings) produced by PCC from both N5 and QT-SX

(left) Setup of the small scale test slab cluster (right) Picture of actual casting with N5 showing a bi-grain formation

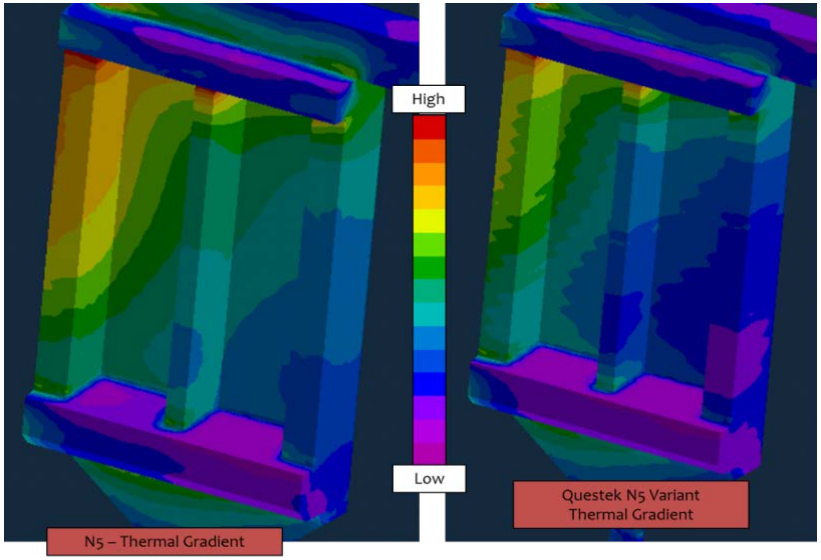
As-cast Microstructures
(Phase I Castings)

	Along growth direction	Transverse
QT-SX		
ReneN5		

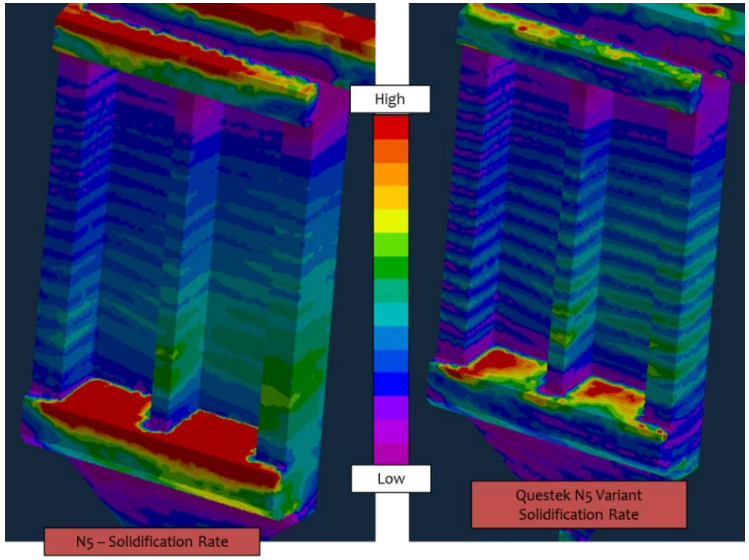
2nd round of casting results



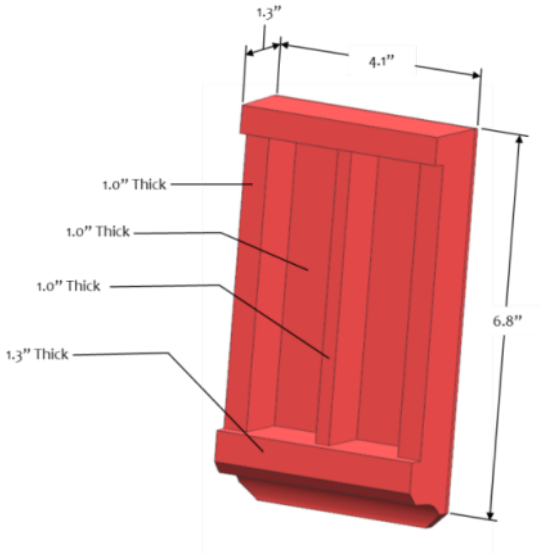
Thermal Gradient

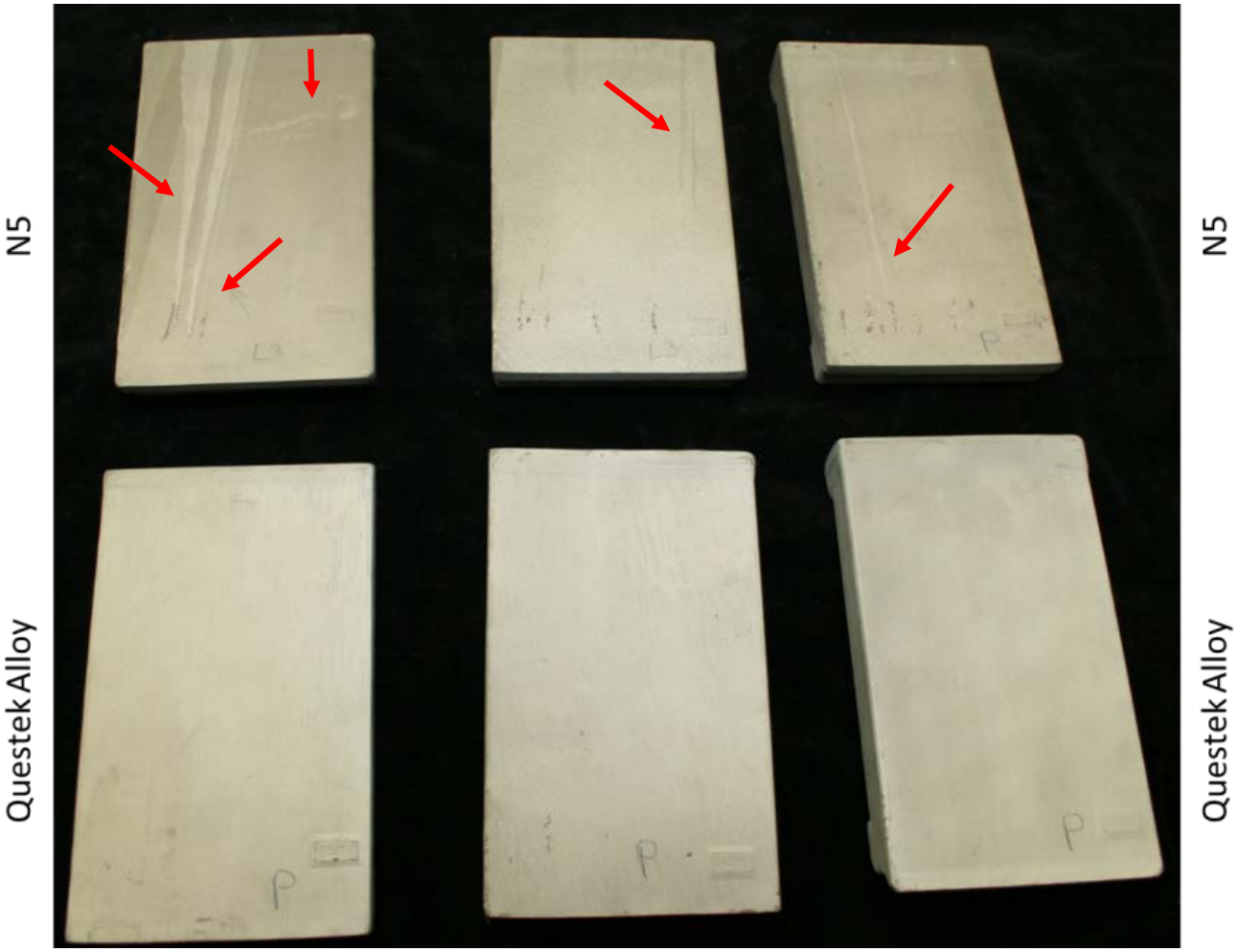


Solidification Rate



2nd round of casting results





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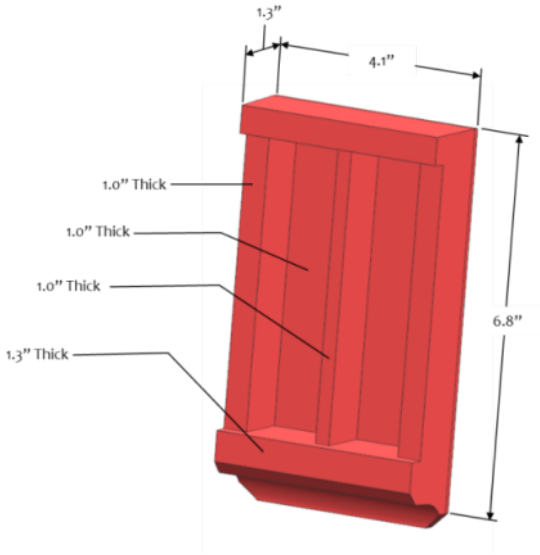
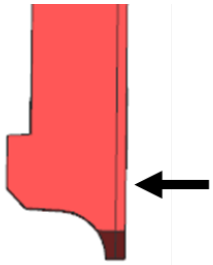
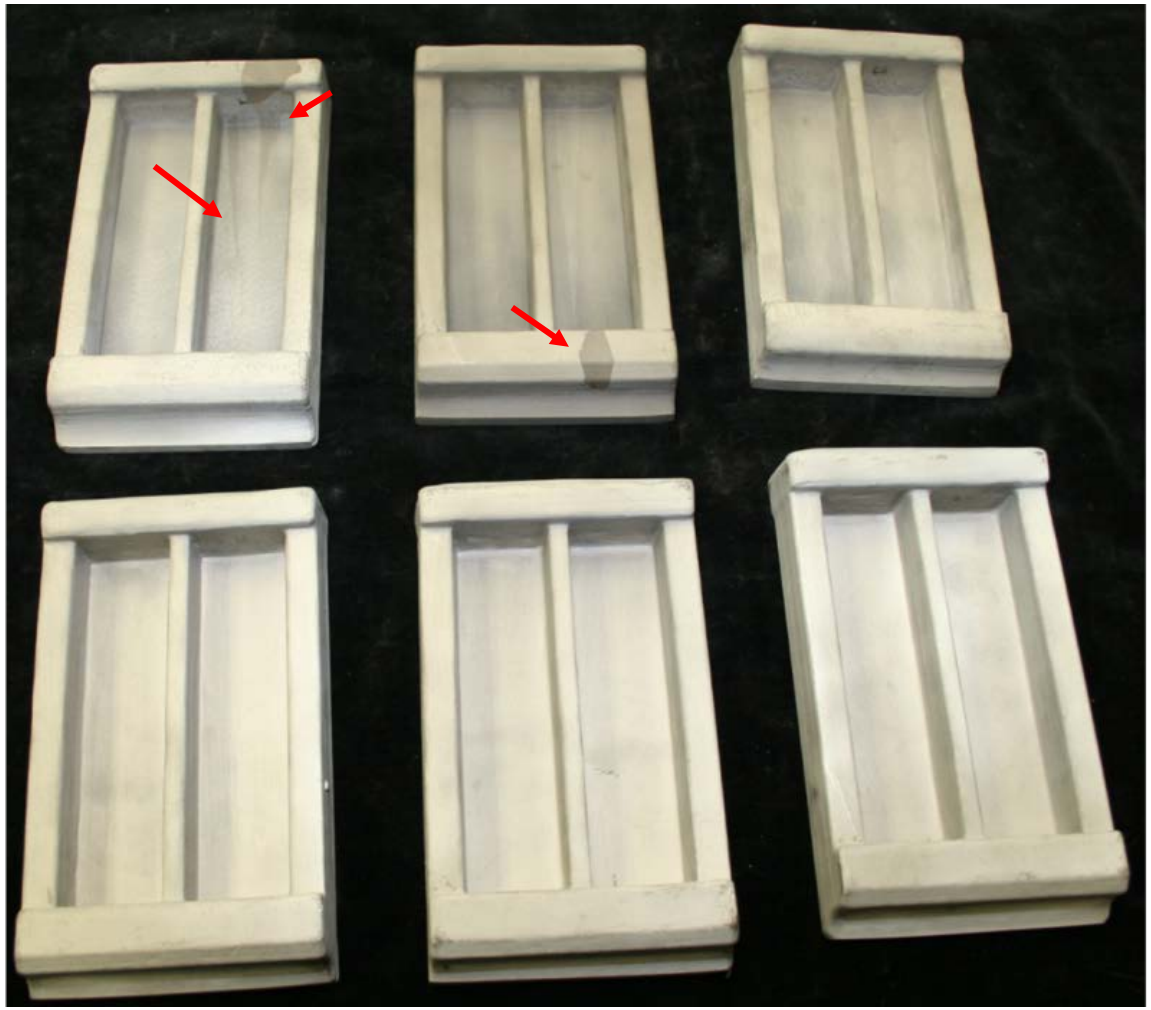




Freckles typically started here.

N5

Questek Alloy



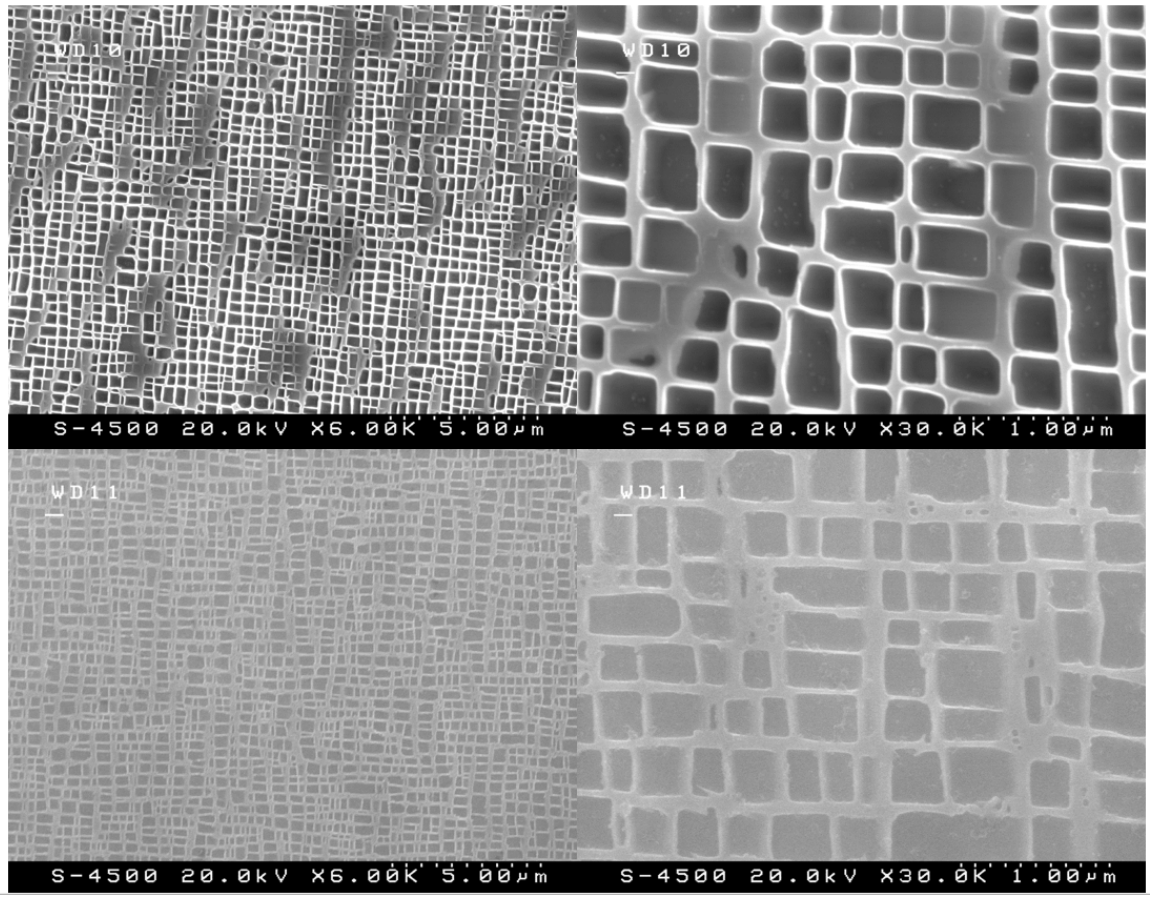
N5

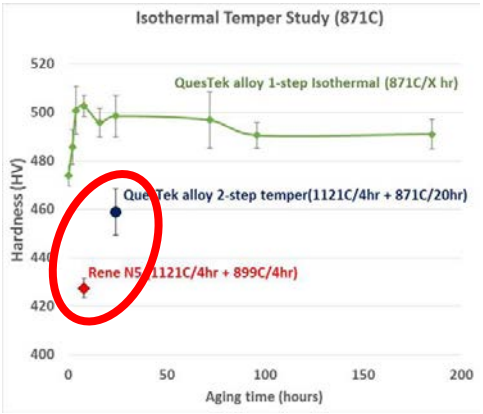
Questek Alloy

Microstructure after double-step aging

QTSX:

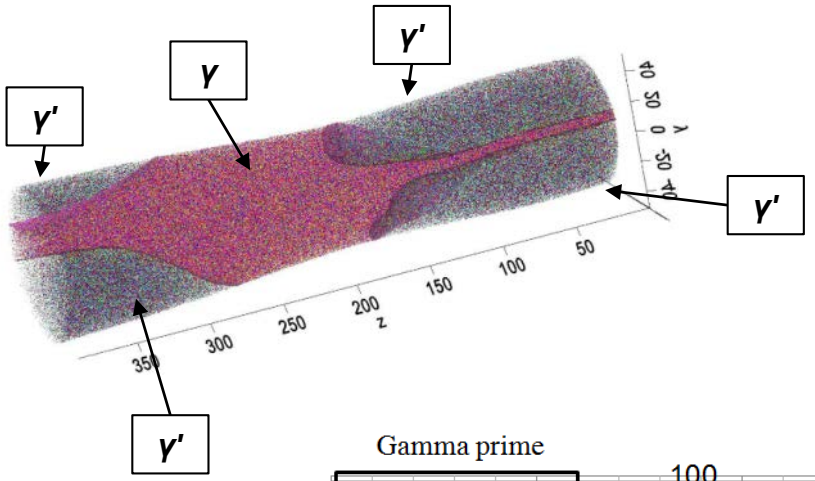
Rene N5:

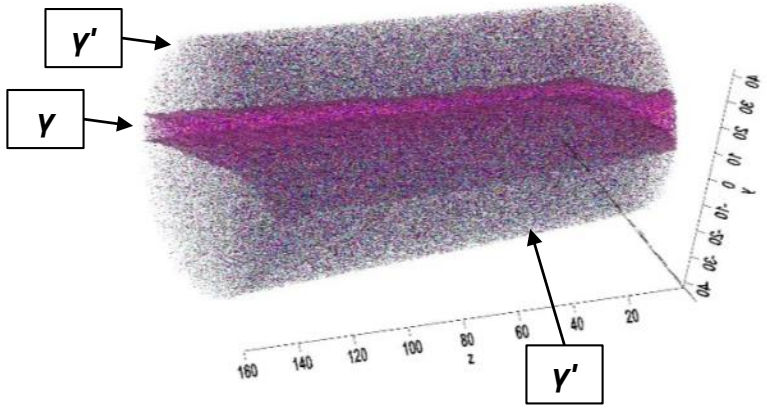


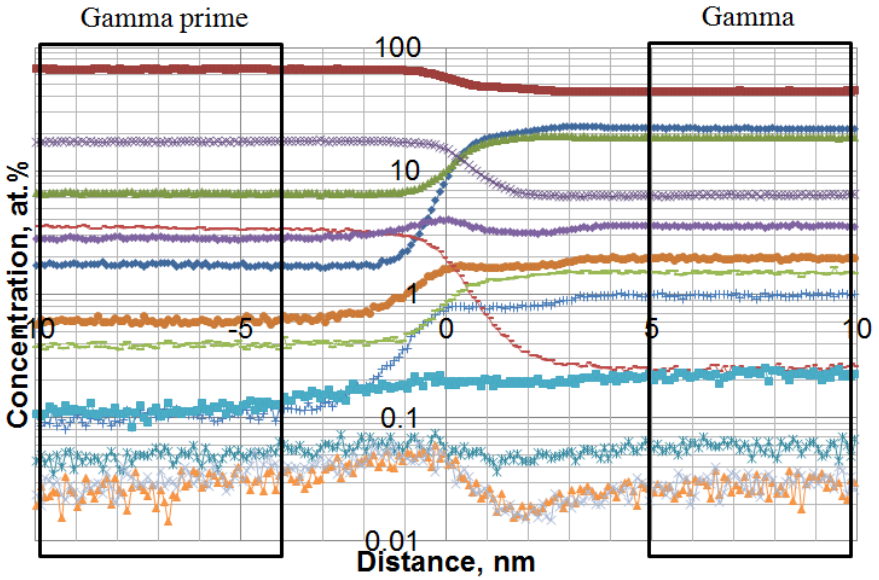


Characterization and microstructure analysis confirm the achievement of the design goal of γ' phase fraction and lattice misfit (no evidence of TCP phases were found during all heat treatments)

Atom-probe (LEAP) analysis of the QT-SX nanostructure



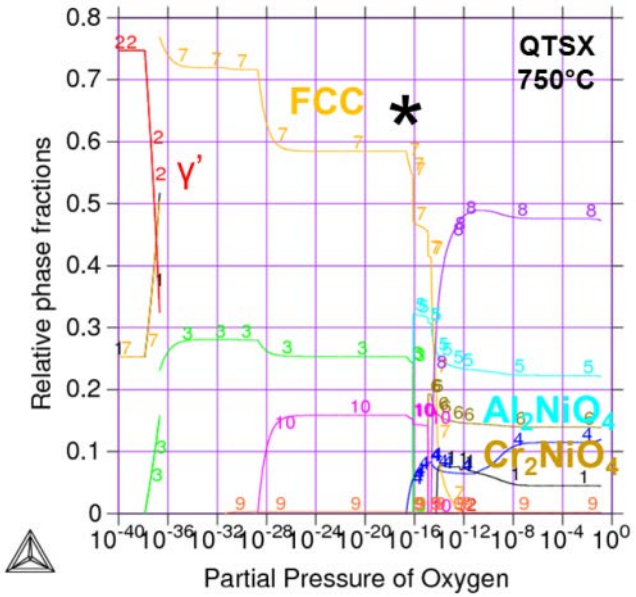




Excellent agreement with ICME predicted compositions

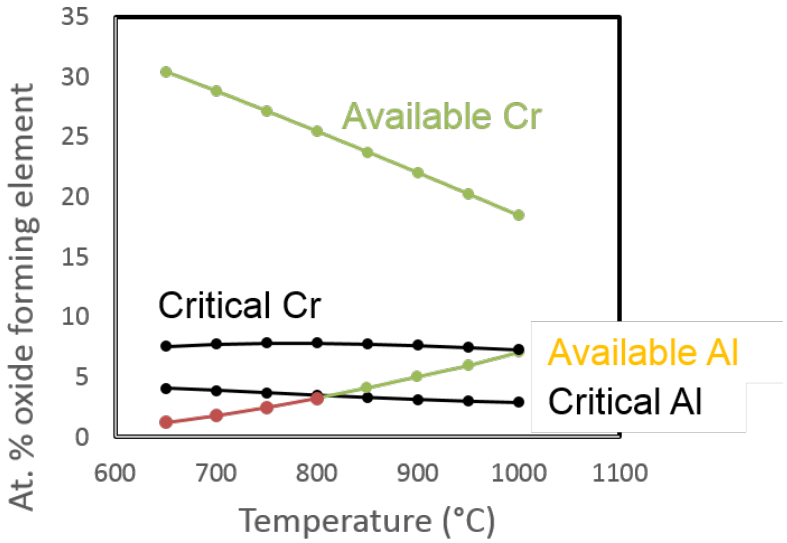
Oxidation modeling

- **Continuous Al_2O_3 and Cr_2O_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

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

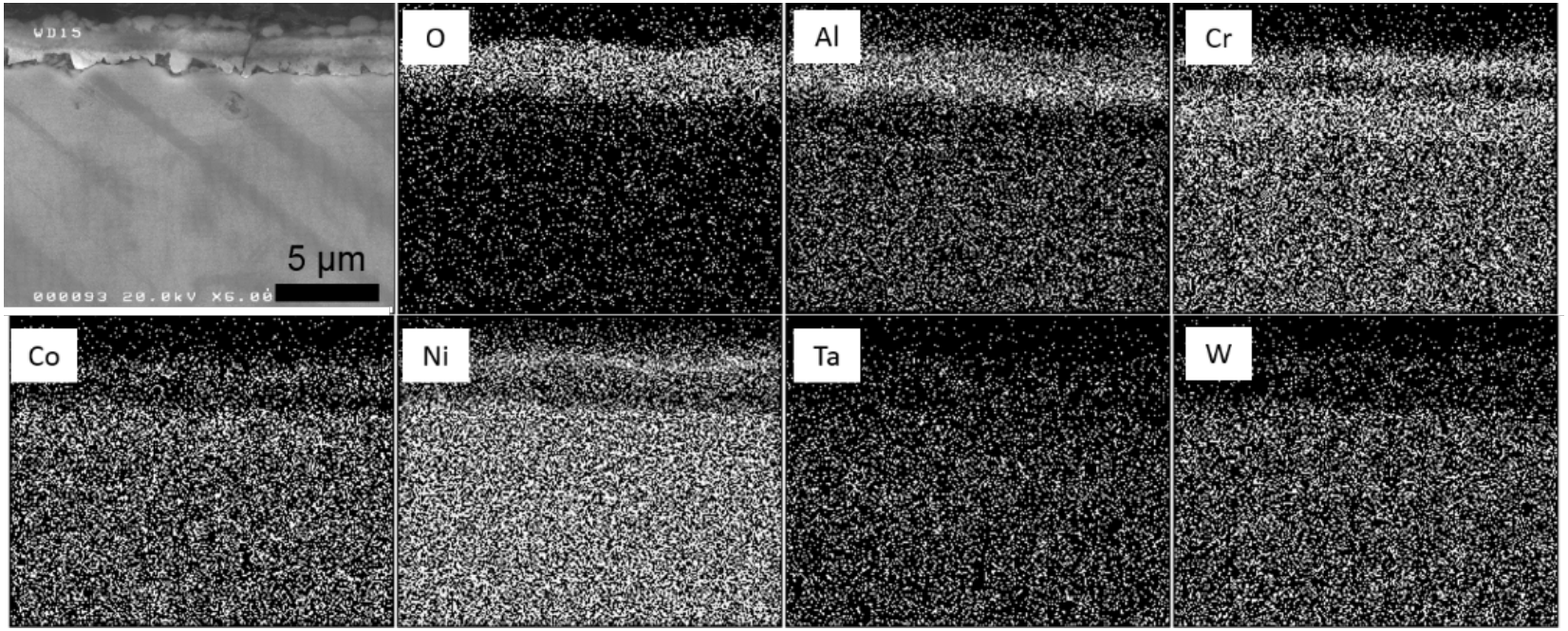


- Both Al_2O_3 and Cr_2O_3 expected to form at high T
- Internal Al_2O_3 expected to form below 850°C

Model agrees well with experimental data for benchmark alloys

Oxide characterization

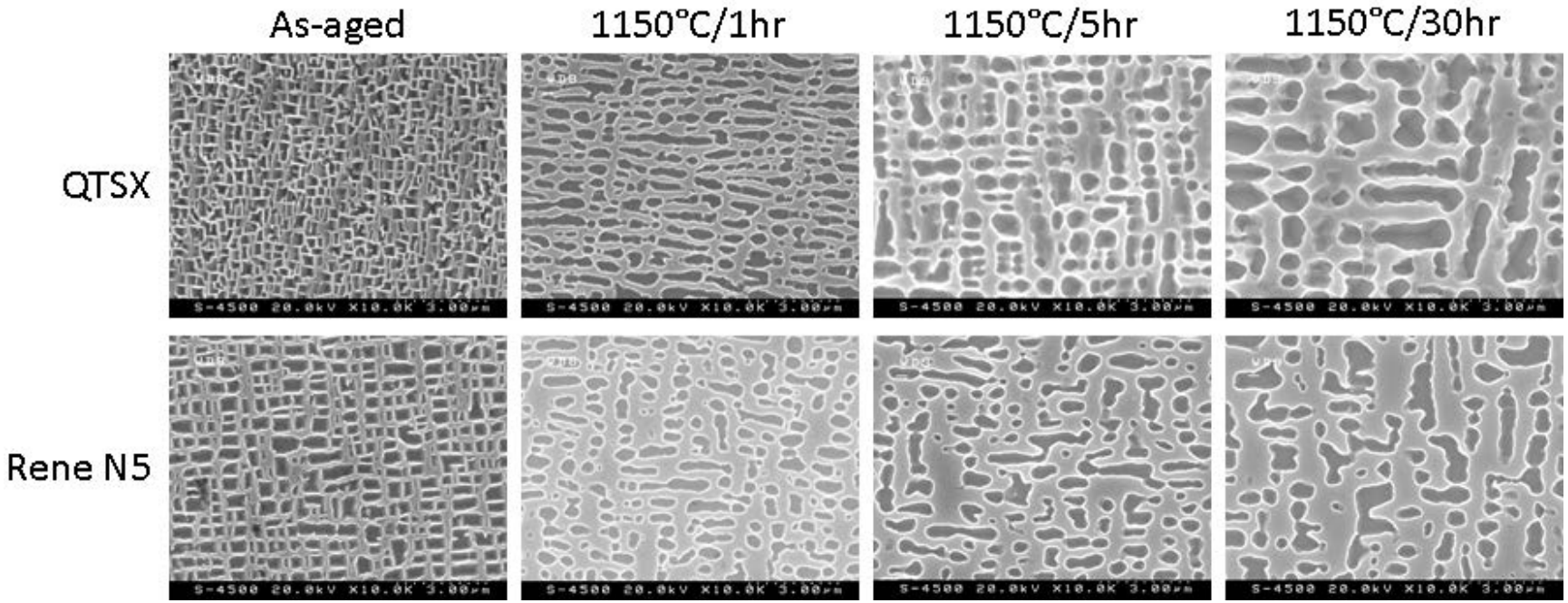
QTSX oxidized in air for 100h at 900°C, 1000°C and 1100°C



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

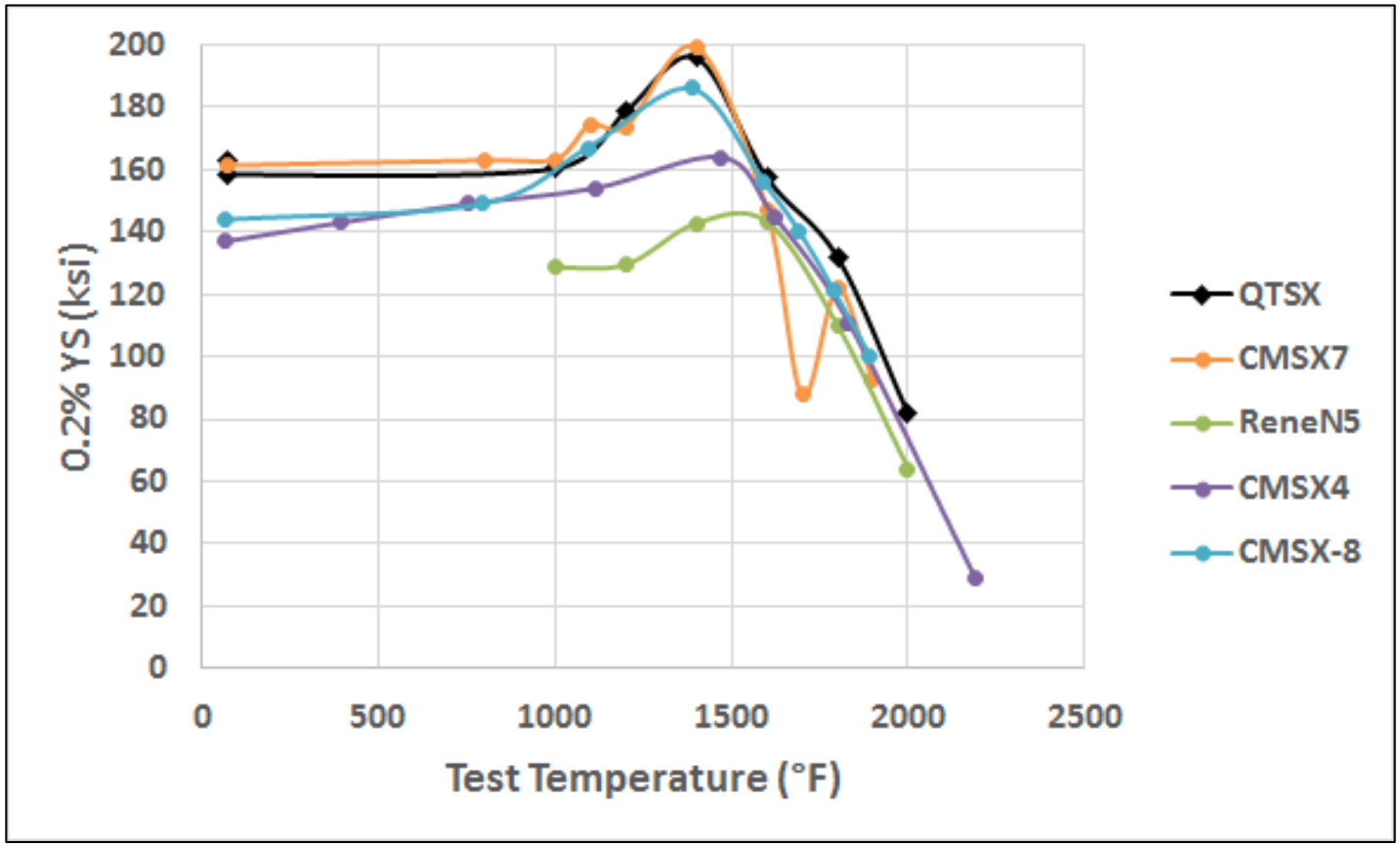


	QTSX			Rene N5		
Time at 1150C (hours)	Avg γ' particle area (sq μm)	Avg γ' particle size (μm)	γ' area fraction	Avg γ' particle area (sq μm)	Avg γ' particle size (μm)	γ' area fraction
0 (as-aged)	0.09	0.3	69%	0.13	0.36	67.2%
1	0.17	0.41	48.5%	0.19	0.44	40%
30	0.32	0.57	46.7%	0.28	0.53	40%

Tensile Test Results (ASTM E8 and E21)

Comparison to Select Incumbent SX alloys*

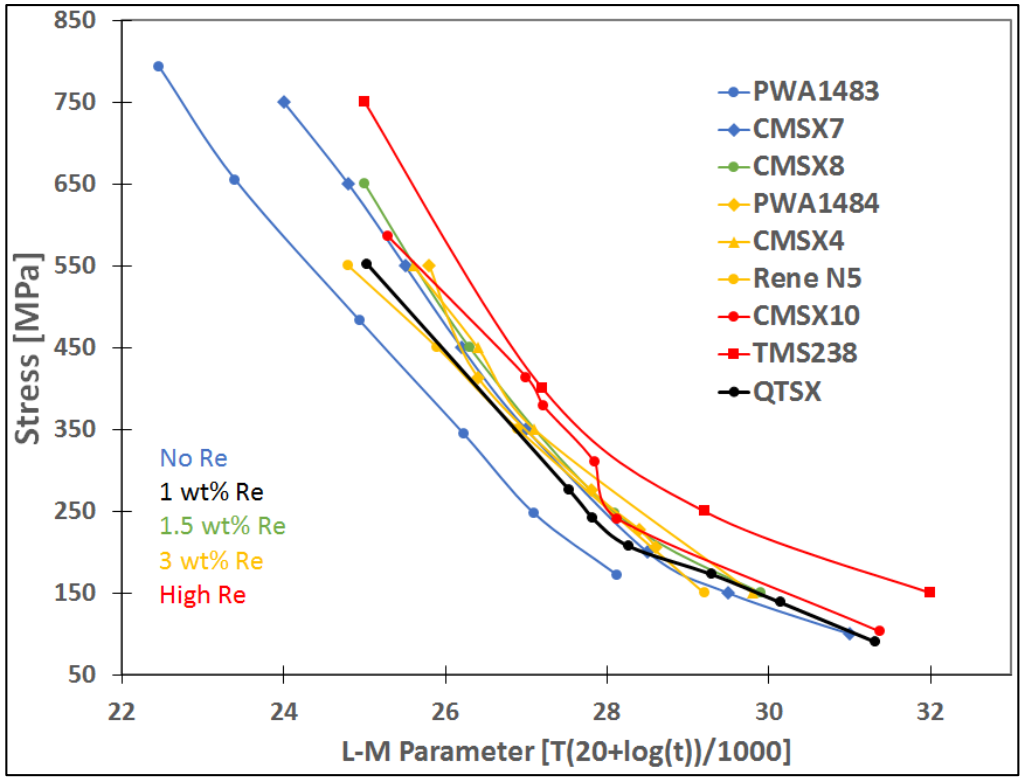
**Baseline data taken from respective patent filings*

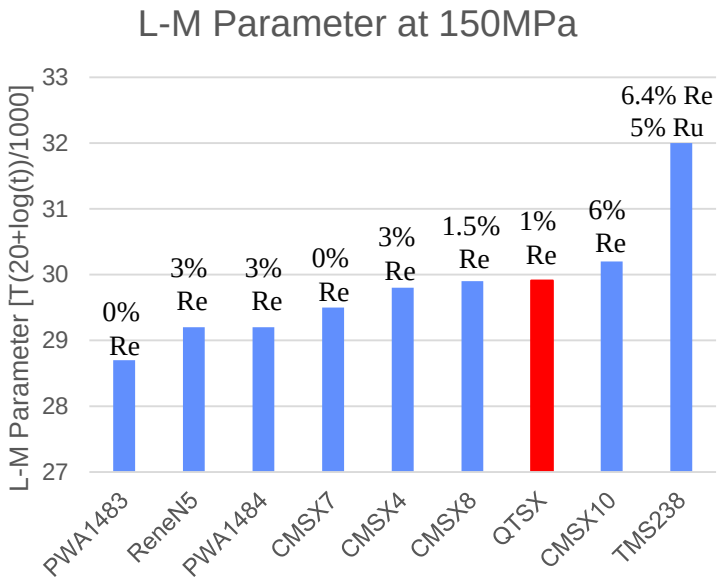


Stress Rupture Test Results (ASTM E139)

*Comparison to Select Incumbent SX alloys**

**Baseline data taken from respective patent filings, literature*



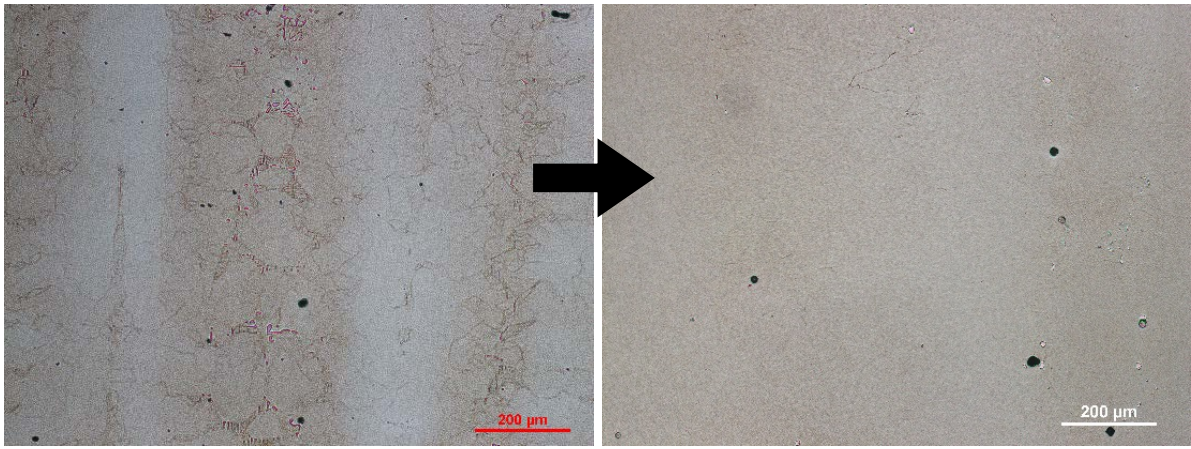


Ongoing Work

- 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

Homogenization Optimization

Round 1 (4-step cycle) ***Round 2 (new 3-step cycle)***



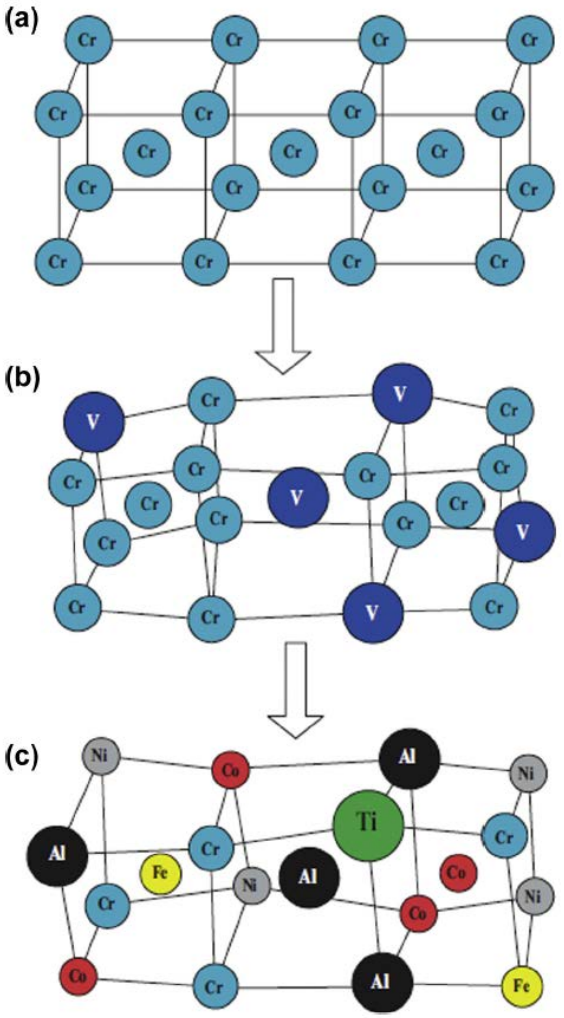
Exploration of High-Entropy Alloys for Turbine Applications

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

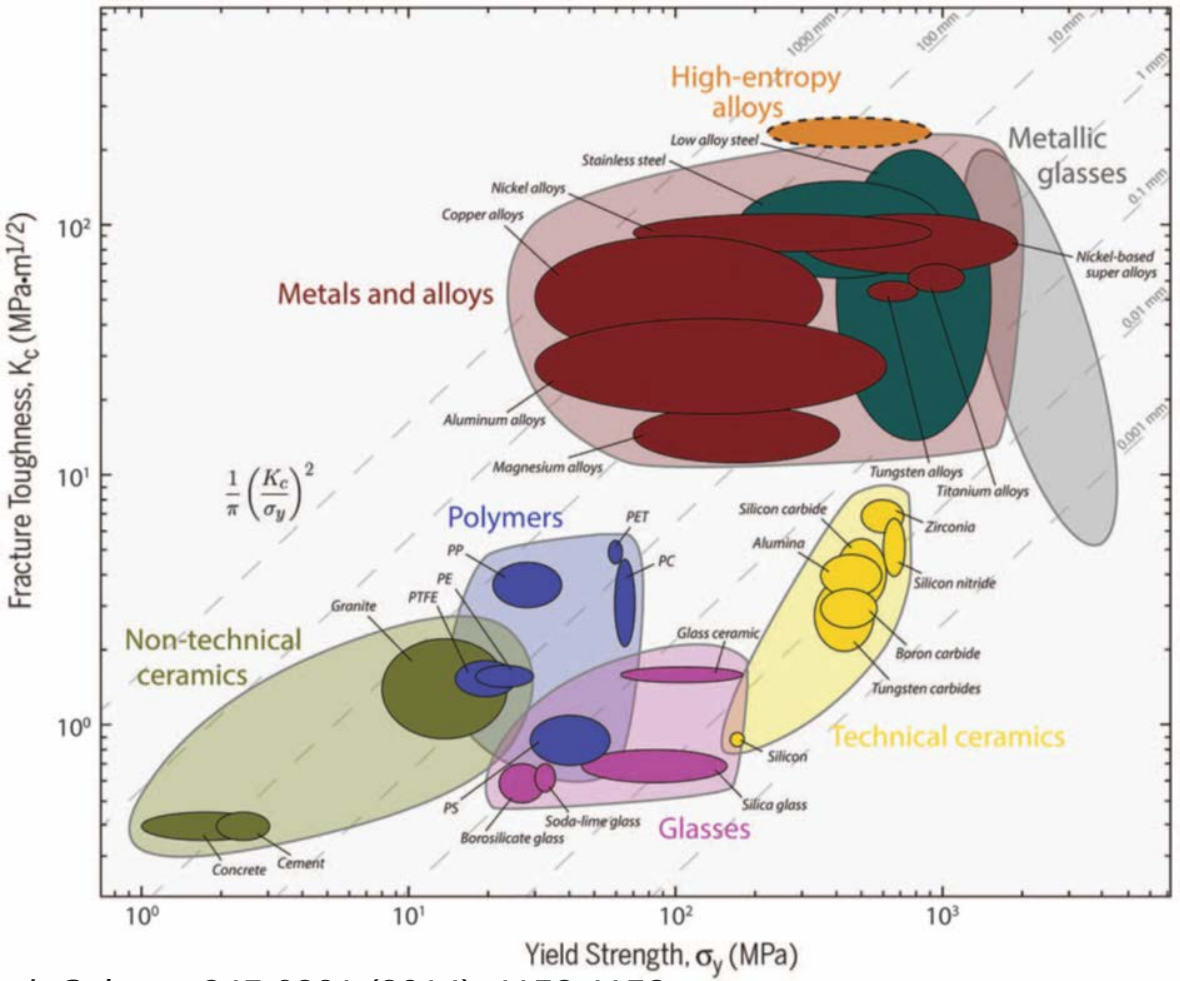
High Entropy Alloys (HEAs)

- 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



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

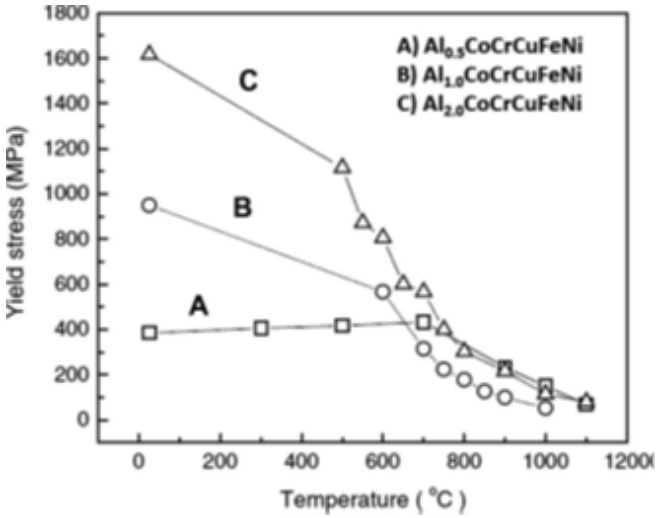


Gludovatz, Bernd, et al. *Science* 345.6201 (2014): 1153-1158.

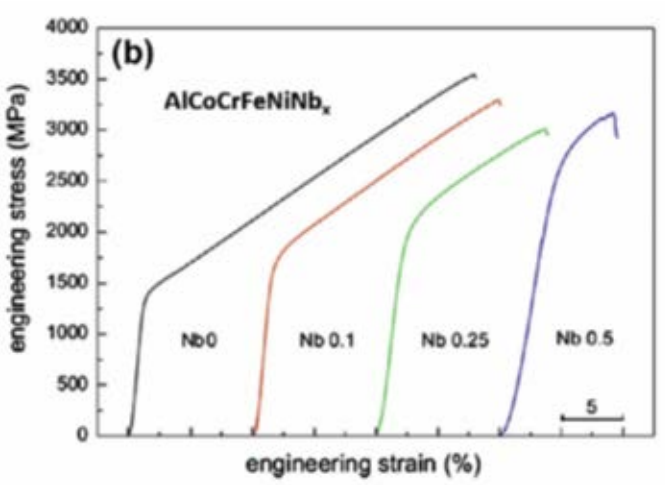
Potential for HEA Property Design

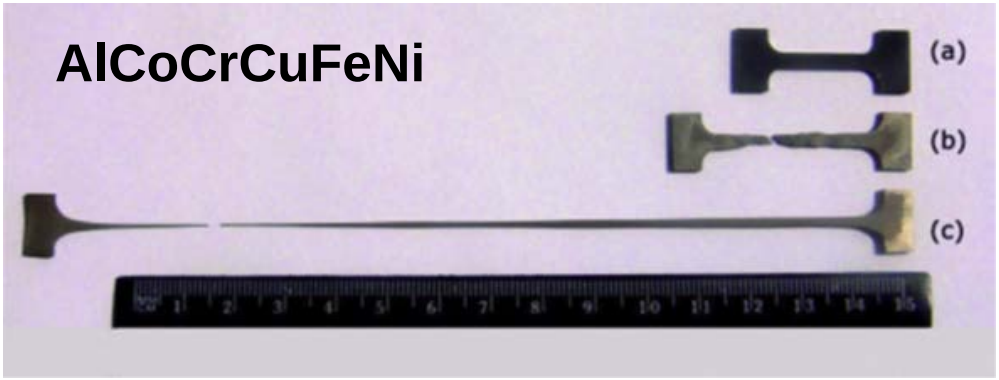
- Large variation in properties with composition/processing

Effect of Al



Effect of Nb





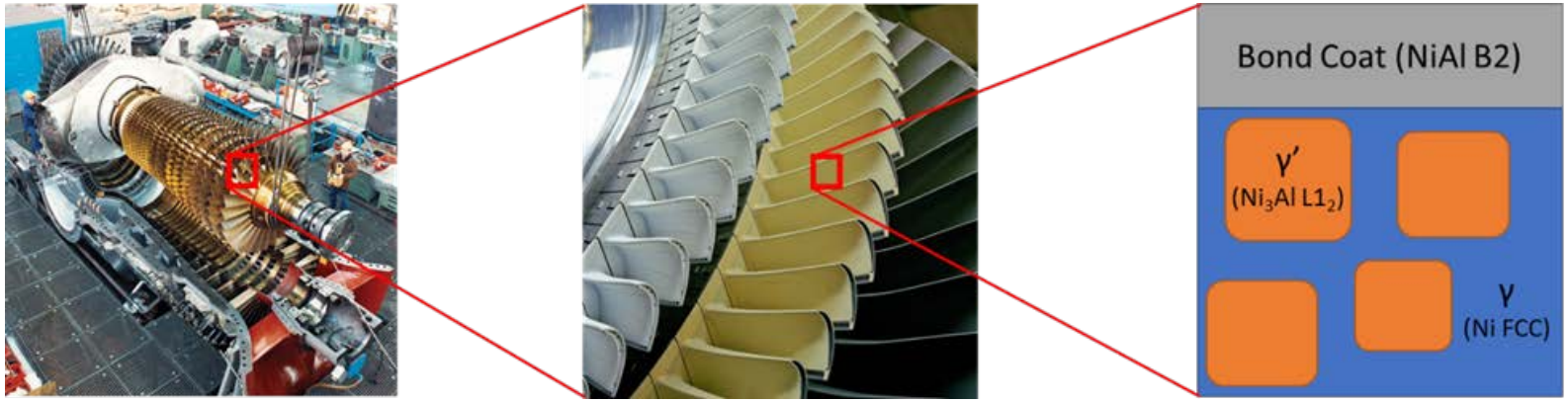
Non-deformed tensile sample

As-cast tensile sample (δ=77%)

Forged sample (δ=864%)

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/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 $L1_2$

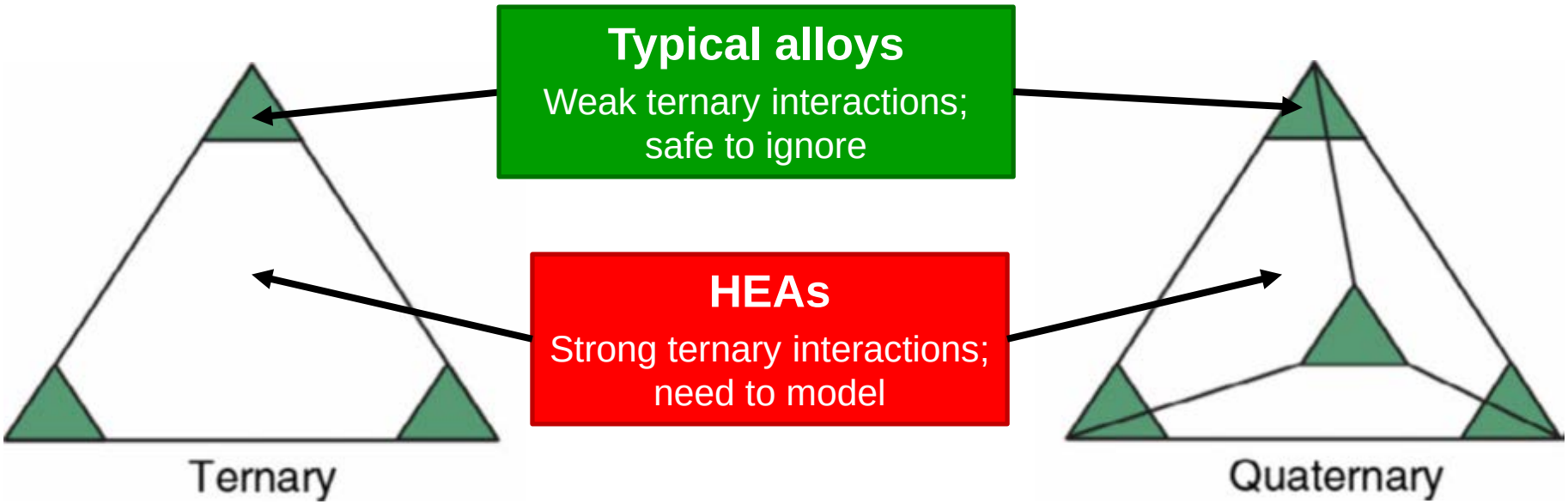


Tsai, Ming-Hung, et al. "Morphology, structure and composition of precipitates in $Al_{0.3}CoCrCu_{0.5}FeNi$ high-entropy alloy." Intermetallics 32 (2013): 329-336.

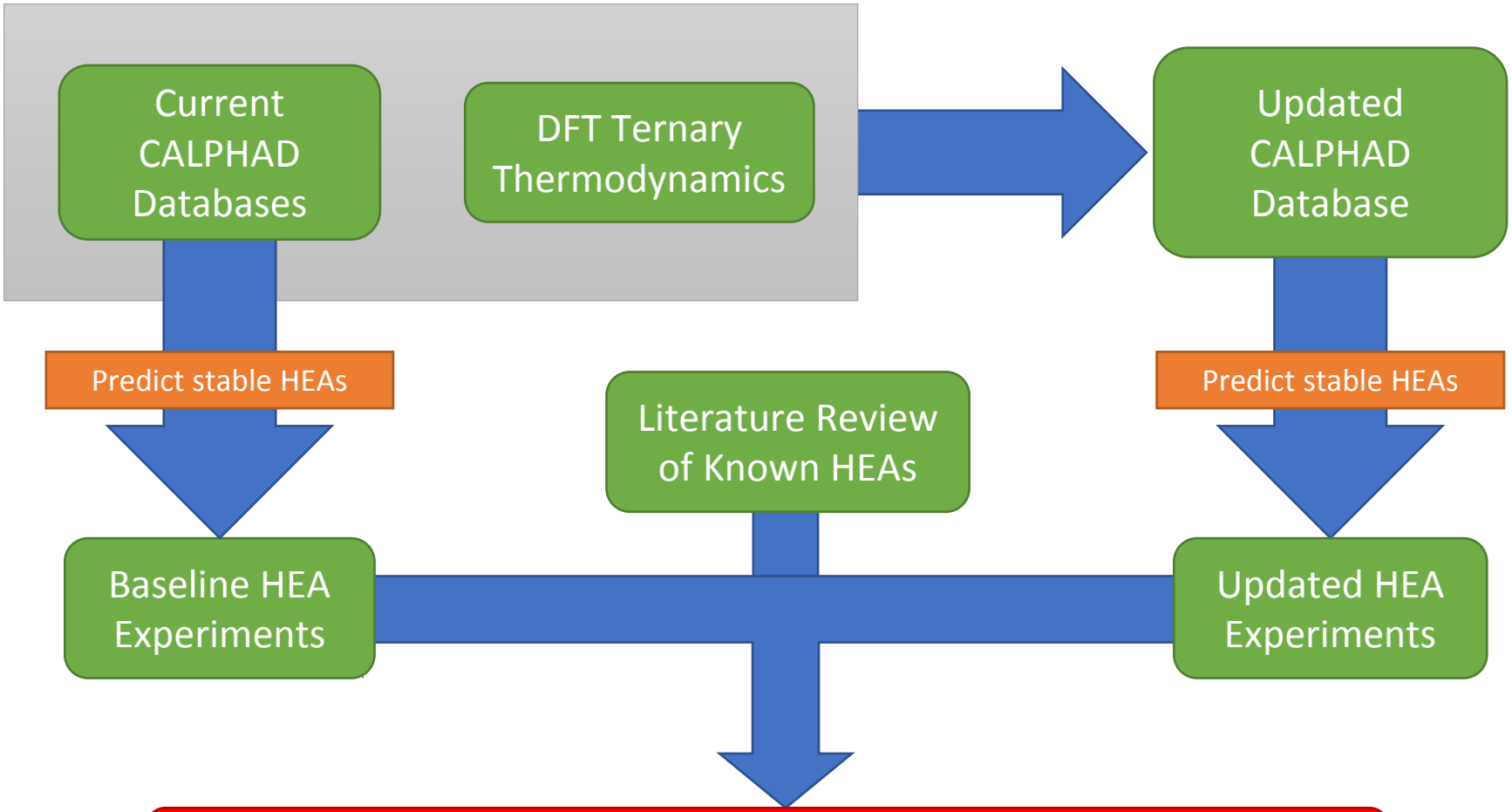
Ma, S. G., et al. "A successful synthesis of the $CoCrFeNiAl_{0.3}$ single-crystal, high-entropy alloy by bridgman solidification." JOM 65.12 (2013): 1751-1758.

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**



Phase I Goal: Improve current CALPHAD databases with DFT thermodynamics tailored to find HEAs



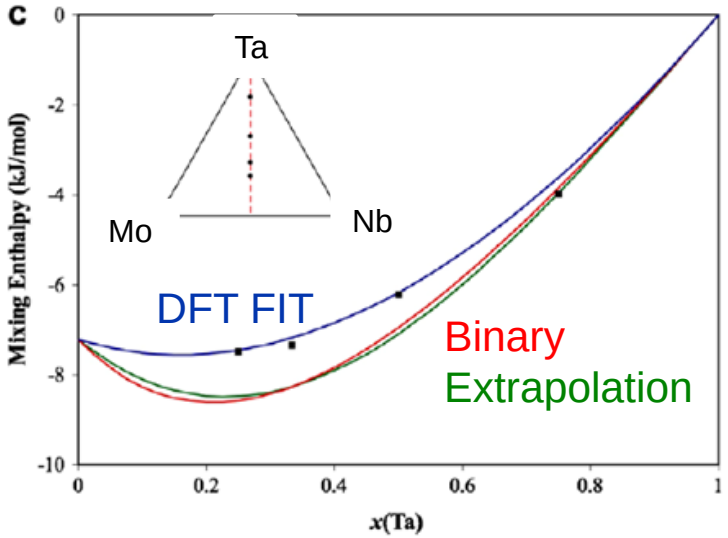
Phase I Result: With the new CALPHAD database, accuracy in predicting HEA formation has dramatically improved.

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

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

Redlich-Kister polynomial for solid solution mixing energy in CALPHAD

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

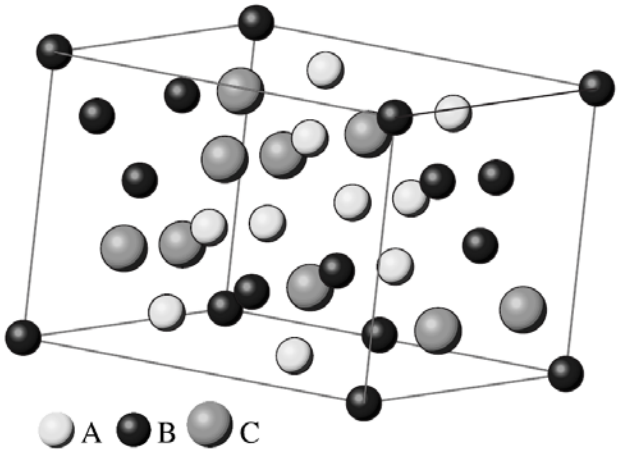


Ternary interaction parameters typically ignored due to lack of data, but can have a large effect in HEA systems

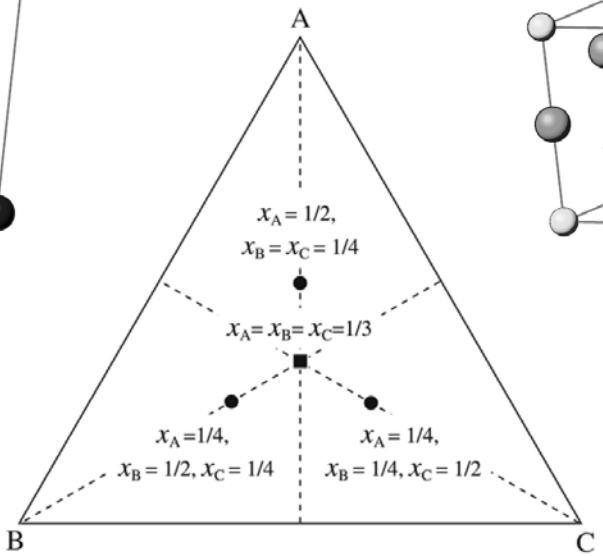
Jiang, Chao. "First-principles study of ternary bcc alloys using special quasi-random structures." Acta materialia 57.16 (2009): 4716-4726.

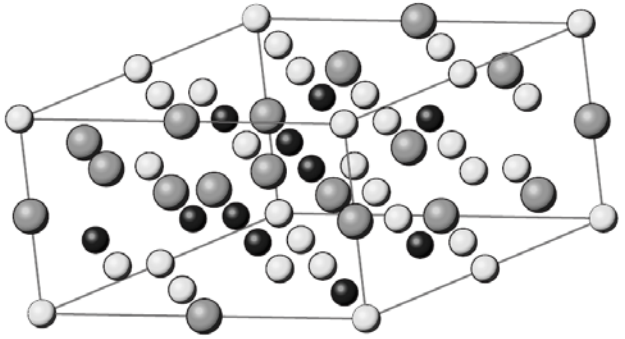
Special Quasi-random Structure (SQS)

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

High-throughput DFT for HEA Thermodynamics

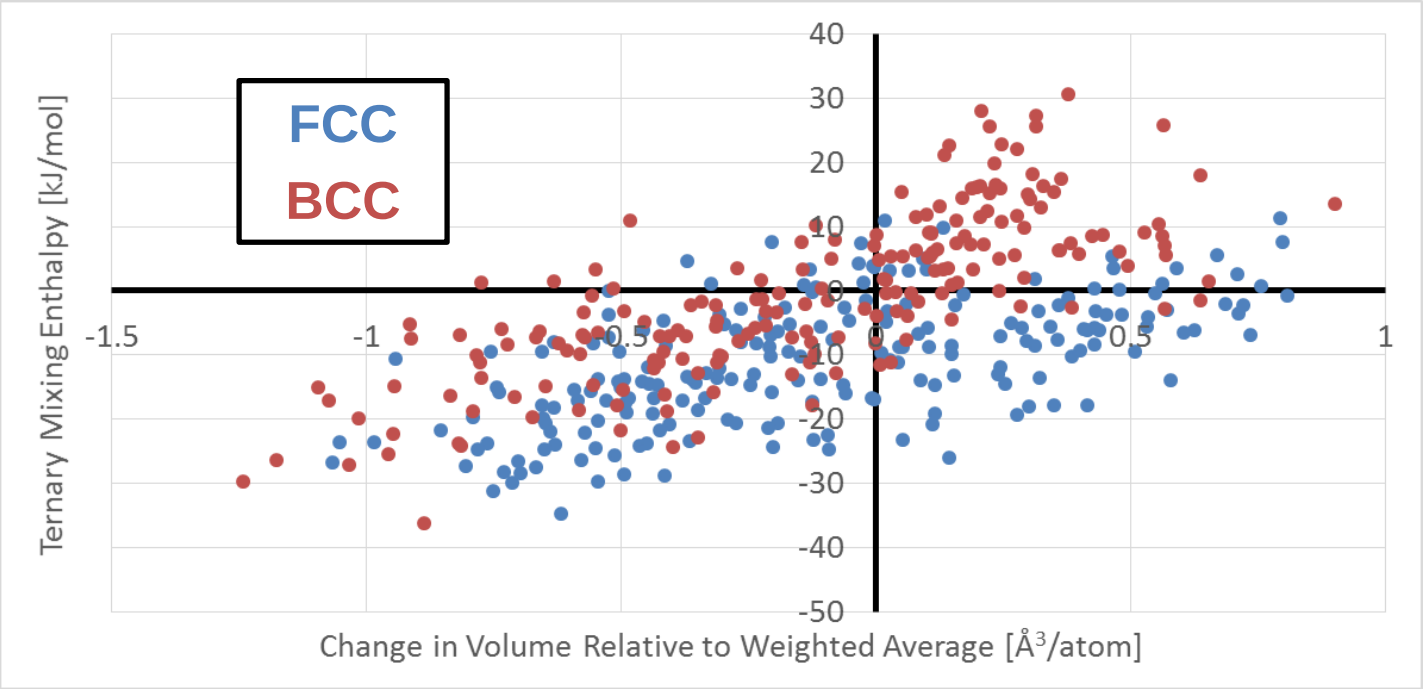
- Physics-based first-principles predictions of 408 ternary enthalpies of mixing in **FCC** and **BCC** solid solutions
  - Phase I elements considered: Al Co Cr Cu Fe Mn Mo Nb Ni Ti V W
  - To add in Phase II: Hf Mg Pd Ru Ta Zr…

NCSA

Performed on the iForge **high-performance computing** cluster at the National Center for Supercomputing Applications (UIUC)

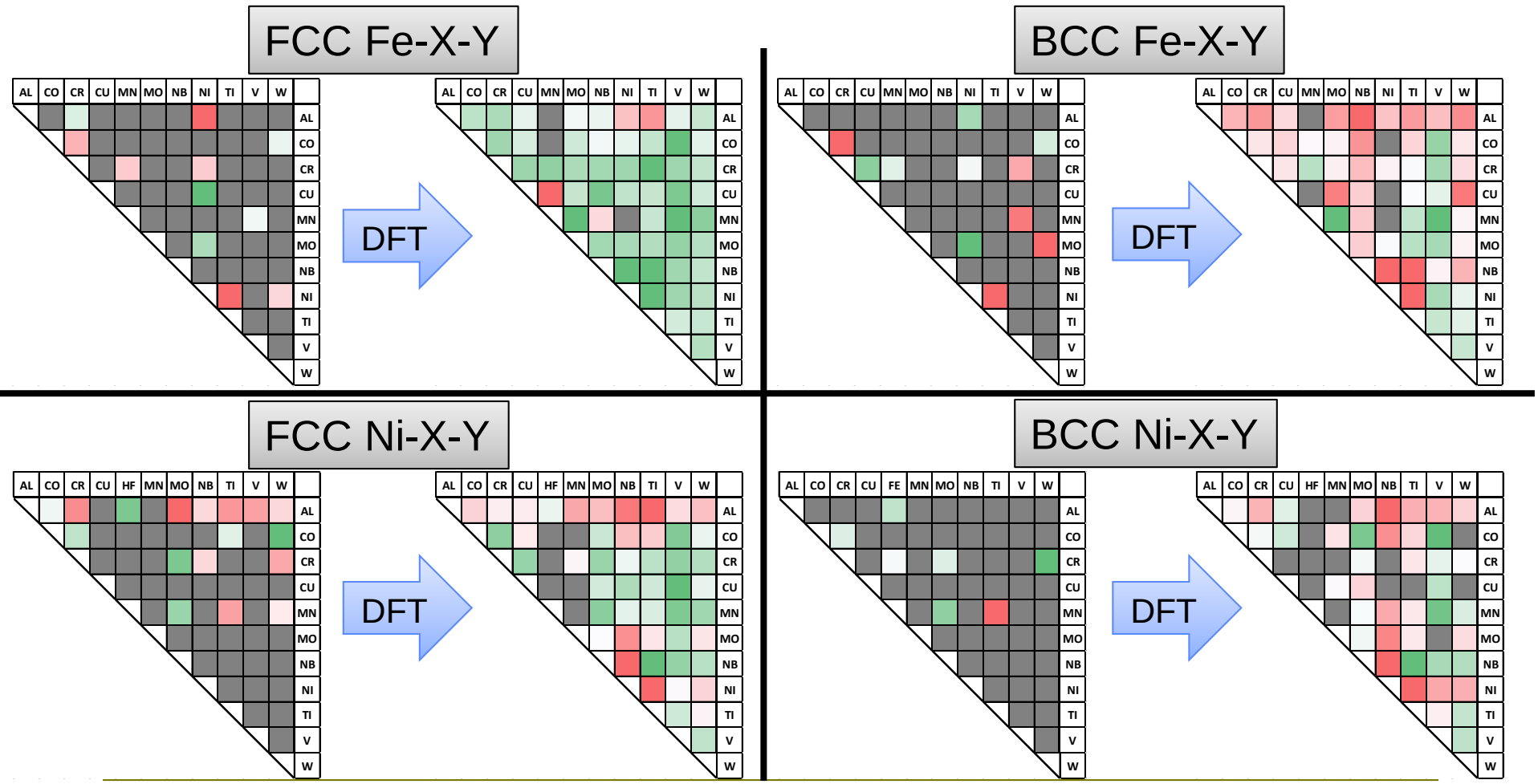
Comparison of DFT-predicted ternary solid solution mixing enthalpies to changes in volume

- 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

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

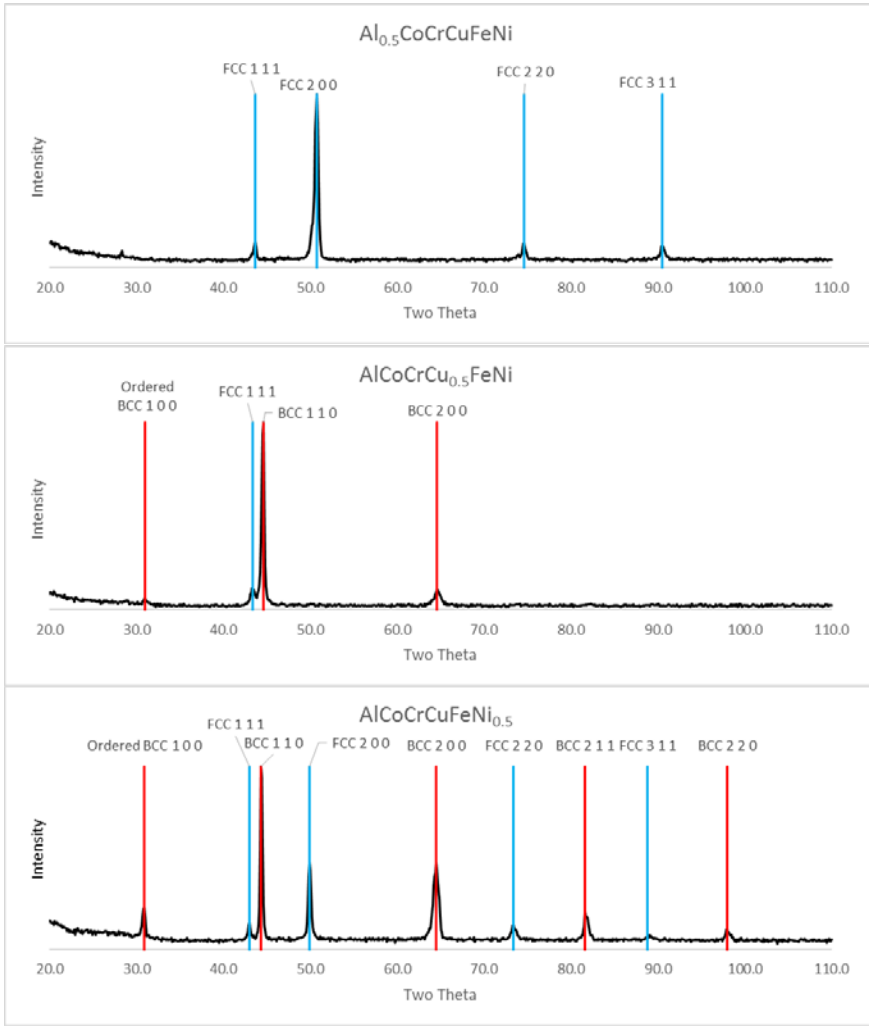
Use New Database to Predict Novel HEA Compositions

- 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 ≥ 0.9

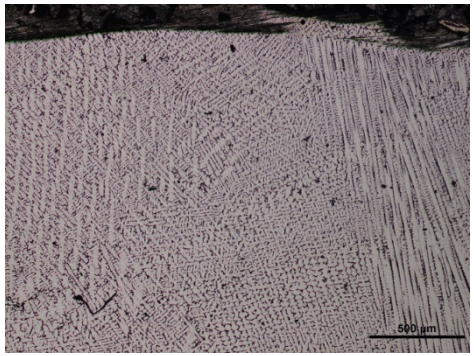
	Stable Phase	Phase Fraction	H^{mix} BCC [J/mol]	H^{mix} FCC [J/mol]
MoNbTiVW	FCC	1	-11009.7	-42049.9
AlMoNbTiV	FCC	1	-13591.2	-39585.2
AlCrMoNbTi	FCC	1	-6244.67	-39055.7
AlCrFeMnTi	FCC	1	-11221.8	-37813.5
CrMoNbTiV	FCC	1	-2000.57	-36628.9
AlNbTiVW	FCC	1	-7775.46	-36256.3
...				

- Use predictions for experimental verification

Benchmark Compositions

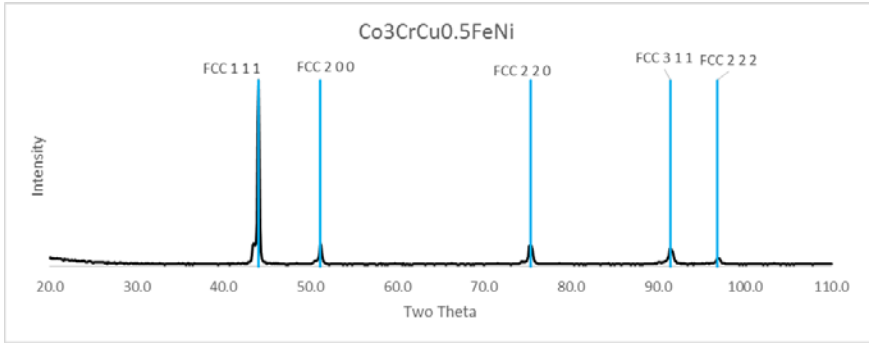


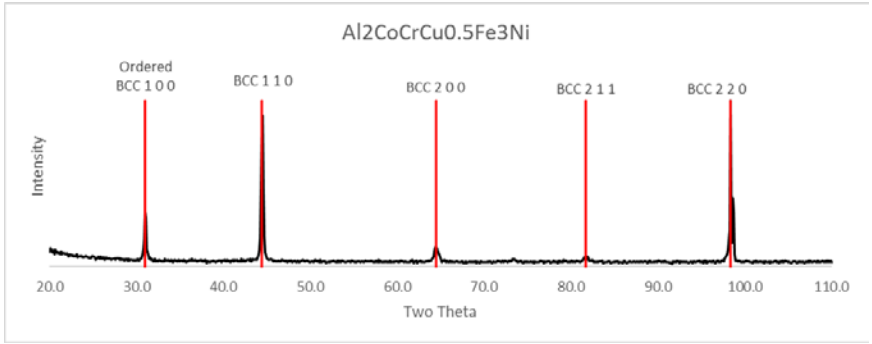
Expected Phase	Observed Phase
HEA	HEA
HEA	HEA
Multi-phase	Multi-phase

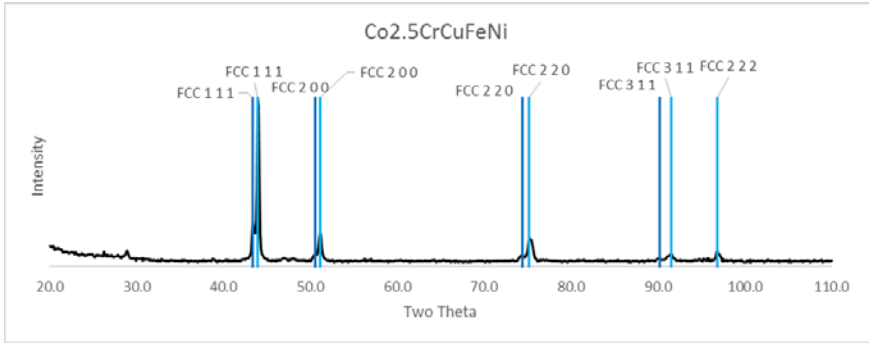


Current work shows good agreement with literature data

CALPHAD-predicted HEA Compositions



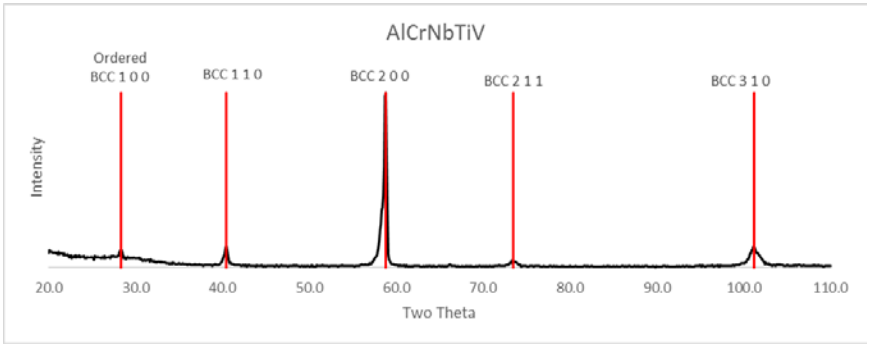


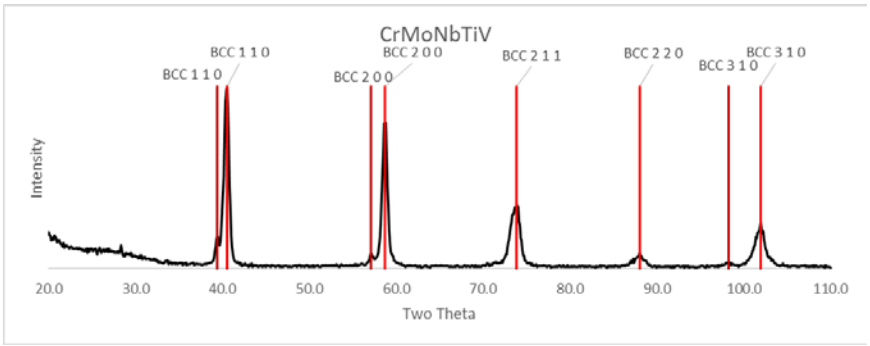


Predicted Phase	Observed Phase
HEA	HEA
HEA	HEA
HEA	Multi-phase

- 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





Predicted Phase	Observed Phase
HEA	HEA
HEA	Multi-phase*

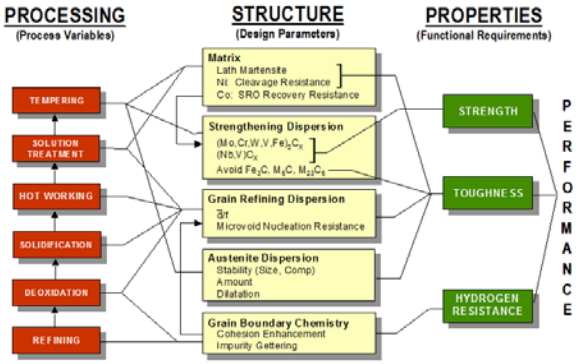
- Preliminary results show alignment with CALPHAD predictions
- Alloys include refractory metals requiring significantly more power while arc melting which changes the cooling process
- *Investigations into homogenization and quenching ongoing

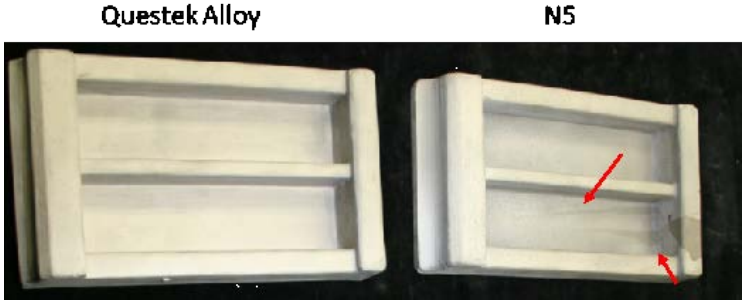
Phase II Plans

- 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

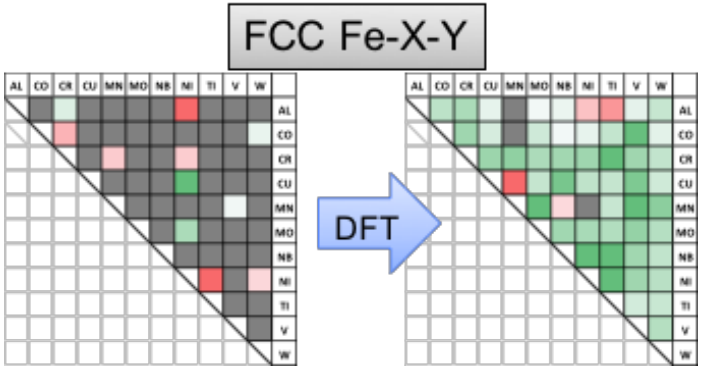
QuesTek Innovations has used ICME tools and technologies to develop alloys for high-performance applications





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)
- γ + γ'
  - Including γ' coarsening model
- TCP, HAB and LAB

Models used in Phase I design

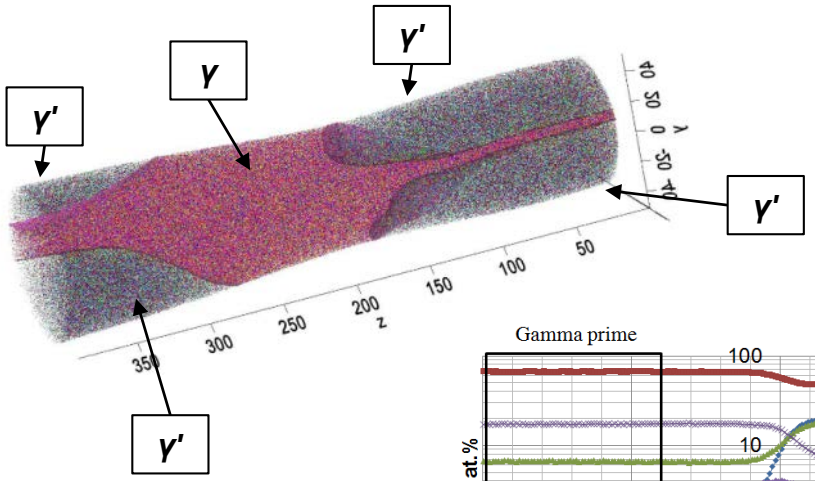
- *Creep modeling (intermediate temperature)*
  - *Calculation of "Reed-D" for existing alloys (climb-controlled creep)*
  - *Develop explicit vacancy diffusivity model*
- *Oxidation/alumina formation*

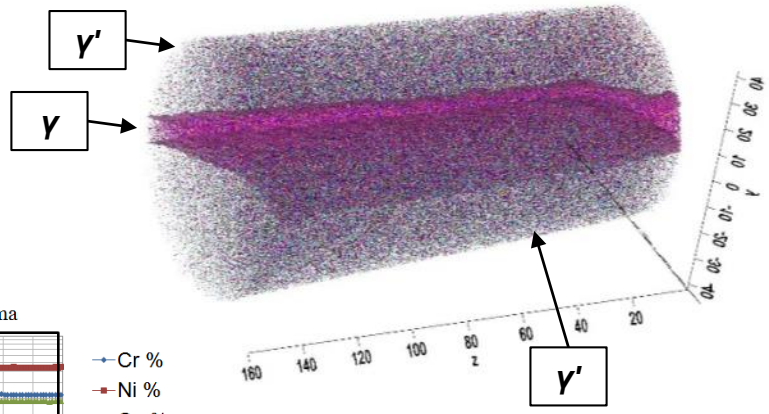
"Indirect consideration" during Phase I design (for further expansion in potential Phase II)

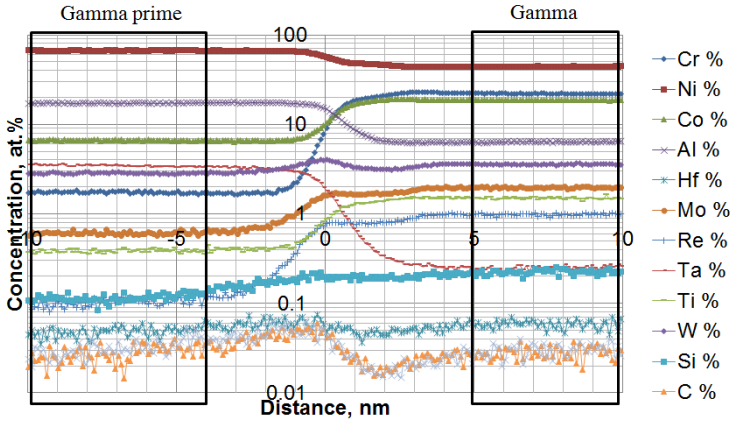
- **Alloy design**

Alloy design in Phase I

Atom-probe (LEAP) analysis of the QT-SX nanostructure





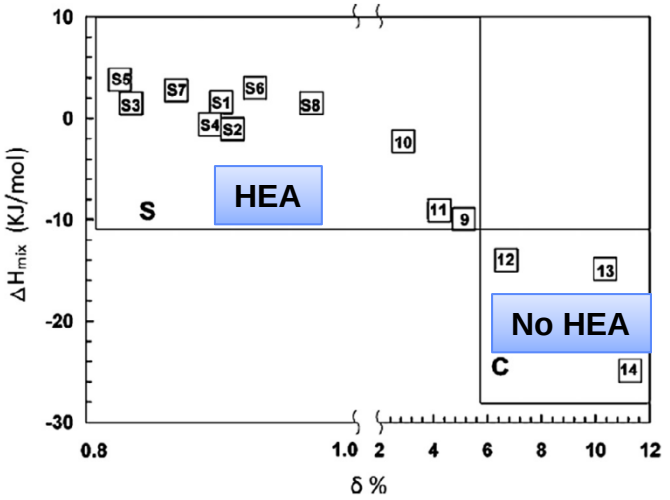


Excellent agreement with predicted compositions (γ' comparisons below)

Ion, at.%	Cr %	Ni %	Co %	Al %	Hf %	Mo %	Re %	Ta %	Ti %	W %
LEAP1	1.74	66.76	6.63	17.28	0.05	0.61	0.10	3.43	0.38	2.84
LEAP2	1.92	70.34	6.64	16.97	0.08	0.85	0.07	0.72	0.42	1.79
Prediction	2.1	69.0	6.0	16.9	0.05	0.23	<0.01	4.0	0.19	1.6

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 (δ) and enthalpy of mixing (ΔH_{mix})



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

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

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

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)

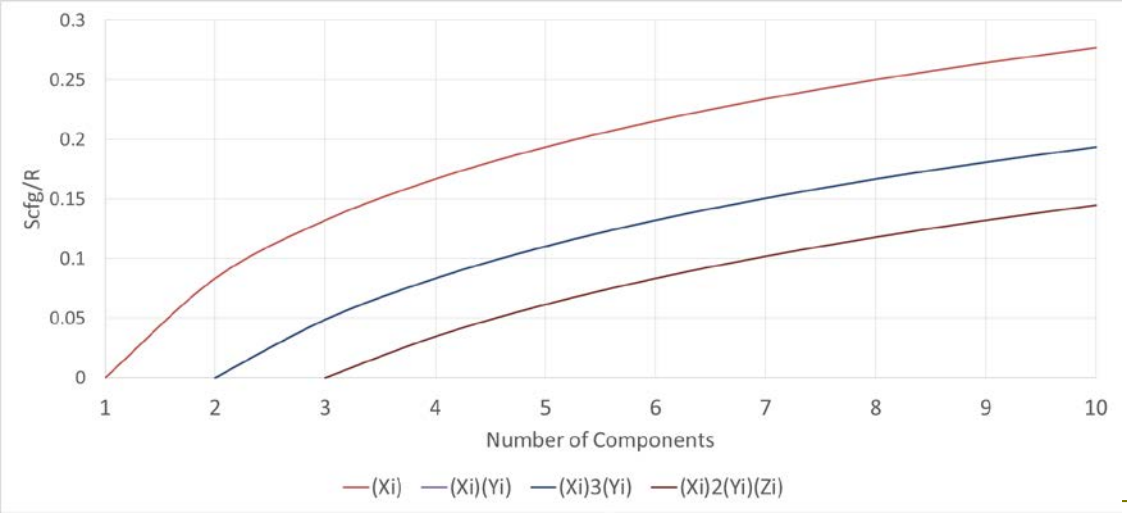
QT2015	Exp. Phases	Al	Co	Cr	Cu	Fe	Ni	Ref	Note
FCC_A1#2 FCC_A1#1	fcc	0	1	1	1	1	1	1	Al is a BCC stabilizer in AlxCoCrFeNi alloys
FCC_A1#2 FCC_A1#1 B2_BCC	fcc	0.3	1	1	1	1	1	1	the amount of Al in the AlxCoCrCuFeNi system can tune the cryst
FCC_A1#2 FCC_A1#1 B2_BCC	fcc	0.5	1	1	1	1	1	1	from fcc to fcc+bcc and to fully bcc
FCC_A1#2 B2_BCC FCC_A1#1	bcc+fcc	0.8	1	1	1	1	1	1	
FCC_A1#2 B2_BCC FCC_A1#1 BCC_A2	B2+bcc+fcc	1	1	1	1	1	1	1	spinodal structure of disordered bcc and ordered bcc phases(B2)
B2_BCC BCC_A2 FCC_A1	B2+bcc+fcc	2	1	1	1	1	1	1	
B2_BCC FCC_A1 BCC_A2#1	B2+bcc+fcc	2.5	1	1	1	1	1	1	arc melt at current 500A in cold Cu hearth
B2_BCC#1 BCC_A2#2 BCC_A2#1	bcc	2.8	1	1	1	1	1	1	spalt-quenced at cooling rate of 10^3-10^4K/s
B2_BCC#1 BCC_A2#1 BCC_A2#2	bcc	3	1	1	1	1	1	1	
FCC_A1#2 FCC_A1#1	fcc	0	1	1	1	1	1	4	arc melt at current 500A in cold Cu hearth
FCC_A1#2 FCC_A1#1 B2_BCC	fcc	0.5	1	1	1	1	1	4	cooling rate 1 to 10K/s
FCC_A1#2 B2_BCC FCC_A1#1 BCC_A2	bcc+fcc	1	1	1	1	1	1	4	
B2_BCC FCC_A1#3 BCC_A2 FCC_A1#1	bcc+fcc	1.3	1	1	1	1	1	4	
B2_BCC BCC_A2 FCC_A1#1	bcc+fcc	1.5	1	1	1	1	1	4	
B2_BCC BCC_A2 FCC_A1	bcc+fcc	2	1	1	1	1	1	4	
B2_BCC FCC_A1 BCC_A2	bcc	2.3	1	1	1	1	1	4	
B2_BCC#1 BCC_A2#1 BCC_A2#2	bcc	3	1	1	1	1	1	4	
FCC_A1#2 FCC_A1#1	fcc	0.2	0	1	1	1	2	6	The experimental
FCC_A1#2 FCC_A1#1	fcc	0.4	0	1	1	1	2	6	results indicate that Co is not necessarily required in obtaining
FCC_A1#2 FCC_A1#1	fcc	0.6	0	1	1	1	2	6	the solid solution structure in HEAs, which is good for

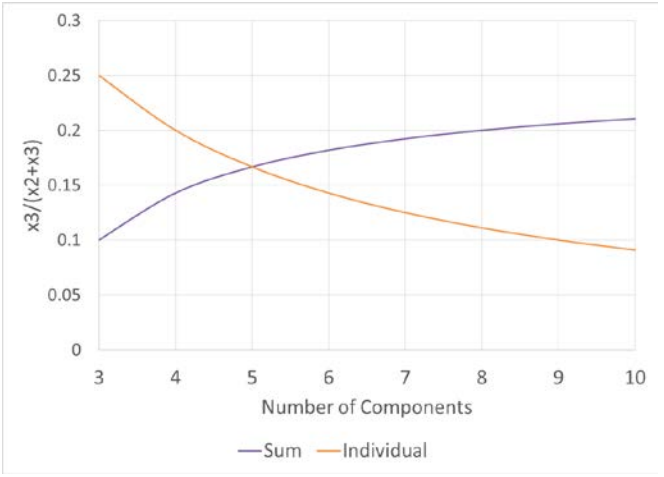
(Config) Entropic stabilization of superalloy phases

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

- **FCC/BCC (X_i)**
- $S_{config} = \sum_{i=1}^{N} x_i \ln x_i$
- **L12 $(X_i)_3(Y_i)$,**
- $S_{config} = 0.75 * \sum_{i=1}^{\frac{N}{2}} y_i^I \ln y_i^I + 0.25 * \sum_{i=\frac{N}{2}+1}^{\frac{N}{2}} y_i^{II} \ln y_i^{II}$
- **Heusler $(X_i)_2(Y_i)(Z_i)$,**
- $S_{config} = 0.5 * \sum_{i=1}^{\frac{N}{3}} y_i^I \ln y_i^I + 0.25 * \sum_{i=\frac{N}{3}+1}^{\frac{N}{3}} y_i^{II} \ln y_i^{II} + 0.25 * \sum_{i=\frac{2N}{3}+1}^{\frac{N}{3}} y_i^{III} \ln y_i^{III}$

- **Hmm, so can either compare individual terms:**
- $x_A x_B > x_A x_B x_C$
- **…or can compare sum of terms:**
- $\sum_{i=1}^{c-1}\sum_{j>i}^{c} x_i x_j > \sum_{i=1}^{c-2}\sum_{j>i}^{c-1}\sum_{k>j}^{c} x_i x_j x_k$



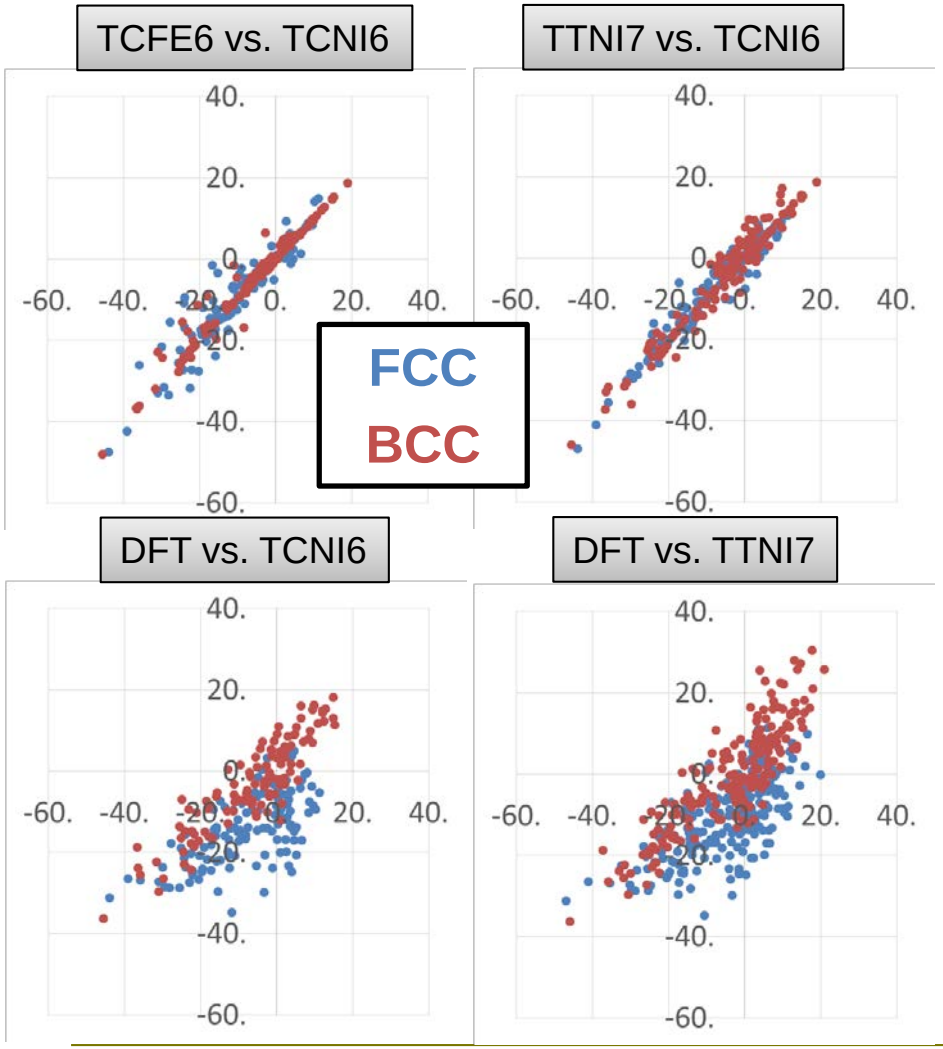


Assessment of CALPHAD HEA phase stability

- "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

Database	Highest NP	Count	Phase(s)
TTNI7	~0.8	9	B2
QT-FE	0.85	1	BCC
QT-Al	~0.8	4	BCC
SSOL4	~0.8	1	BCC
TCFE6	0.75	1	BCC
TCNI6	~0.8	14	BCC/FCC

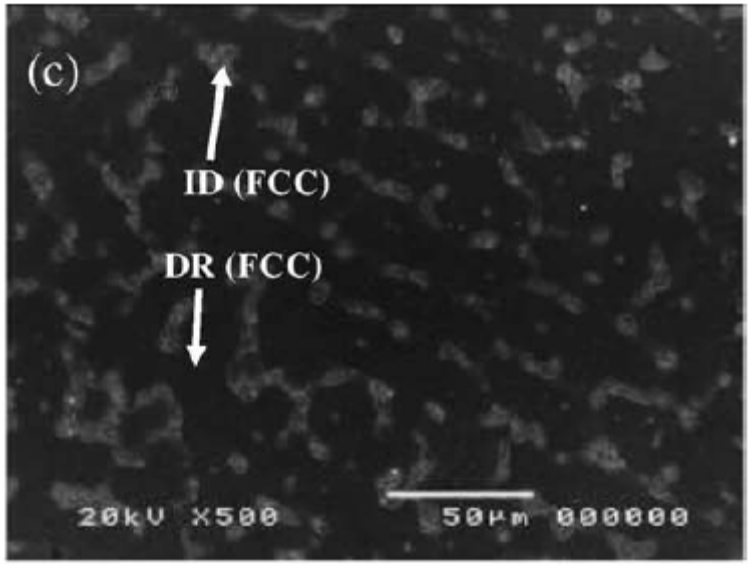
Status of current CALPHAD databases – cont'd

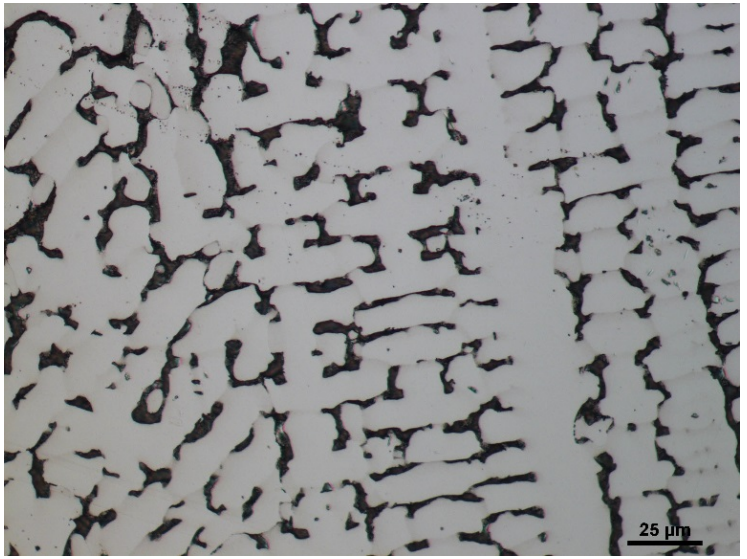
- Did single point equilibrium calculations at T=1000℃ for transition metal-based systems using available databases and compared with experimental HEA-forming systems.
- Comparison to compilation of experimental data:

Database	
Ni-data7	Decent agreement compared with exps.
QT-2015	Close to Ni-data7, BCC phase generally more stable
QT2-AI-04062015	Lacks Co
SSOL4	Intermetallic phases too stable
TCFE6	Liquid phase too stable
TCNI6	Lacks Cu

Benchmark HEA formation

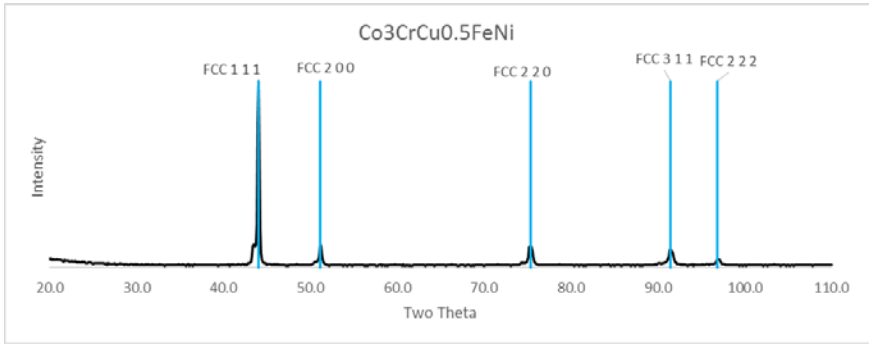
- Two benchmarks based on experimentally observed HEA-forming compositions
  - FCC: $Al_{0.5}CoCrCuFeNi$
  - BCC: $AlCoCrCu_{0.5}FeNi$
- Chemically measured compositions close to target
- Published SEM compared to QT optical: FCC $Al_{0.5}CoCrCuFeNi$

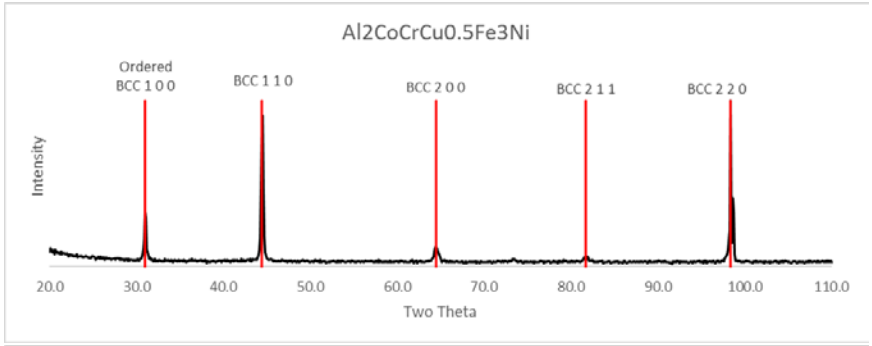


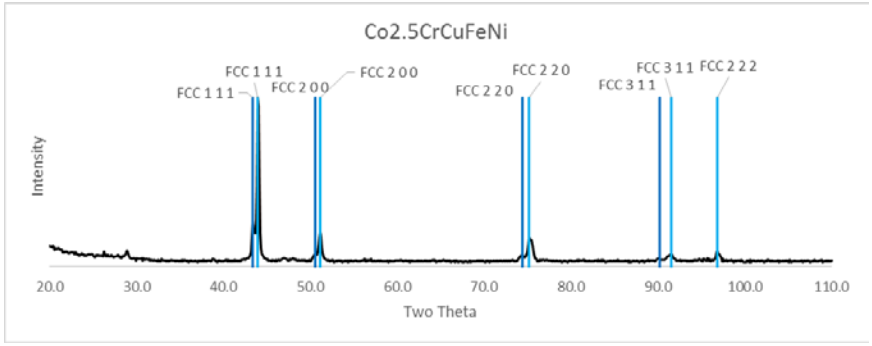


Tung, Chung-Chin, et al. "On the elemental effect of AlCoCrCuFeNi high-entropy alloy system." *Materials letters* 61.1 (2007): 1-5.

Round One – Pre-DFT CALPHAD



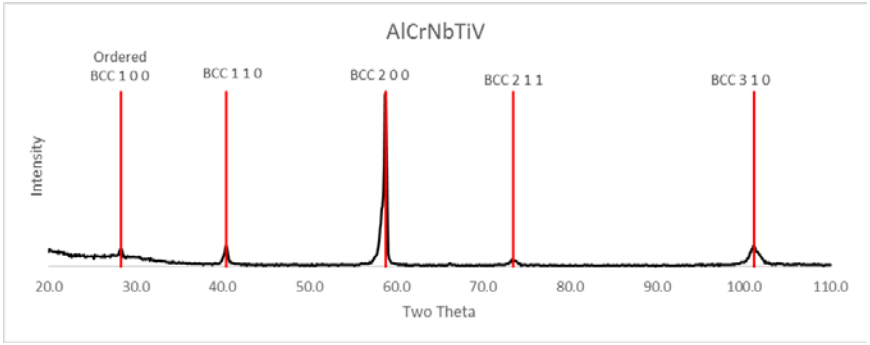


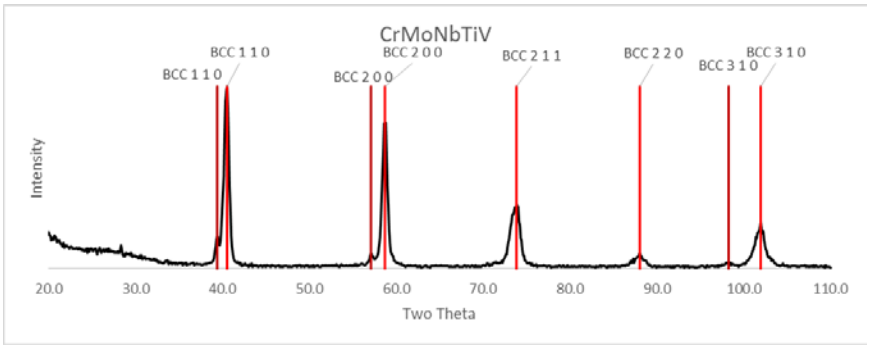


Predicted Phase	Observed Phase
HEA	HEA
HEA	Ordered phase
HEA	Multi-phase

- 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





	Predicted Phase	Observed Phase
AlCrNbTiV	HEA	HEA
CrMoNbTiV	HEA	Preliminary ordered phase

- 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

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2 + k^2 + l^2\right)$$

- FCC and BCC peaks appear at regular, expected intervals based on the *hkl* values

$$s^2 = h^2 + k^2 + l^2$$

s^2	FCC	BCC	ordered phase
1			100
2		110	110
3	111		111
4	200	200	200
5			210
6		211	211
8	220	220	220
10		310	310
11	311		311
12	222	222	222

Investigated Compositions

- Benchmark compositions
  - Compositions from literature, one FCC, one BCC, one FCC + BCC
    - $Al_{0.5}CoCrCuFeNi$ $AlCoCrCu_{0.5}FeNi$ $AlCoCrCuFeNi_{0.5}$

- Round One
  - Compositions created using the pre-DFT CALPHAD database
    - $Co_3CrCu_{0.5}FeNi$ $Al_2CoCrCu_{0.5}Fe_3Ni$ $Co_{2.5}CrCuFeNi$
    - $CoCuFeNi$ $Al_{0.5}Co_{2.5}CrCuFeNi$ $Al_{0.5}Co_3CrCuFeNi$
    - $Al_{1.5}CoCr_3Cu_{0.5}FeNi$

- Round Two
  - Compositions created using the post-DFT CALPHAD database
    - AlCrNbTiV CoCrMnNiV CrCuFeMoNi
    - CoCrFeTiV CrMoNbTiV

Experiment Summary

	Al	Co	Cr	Cu	Fe	Mn	Mo	Nb	Ni	Ti	V	Expected Phase	Phases from XRD
Benchmark Compositions	0.5	1	1	1	1				1			FCC	FCC
	1	1	1	0.5	1				1			BCC	BCC
	1	1	1	1	1				0.5			FCC + BCC	FCC+BCC
Round 1 Pre-DFT		3	1	0.5	1				1			FCC	FCC
	2	1	1	0.5	3				1			BCC	BCC
		2.5	1	1	1				1			FCC	FCC+FCC
		1		1	1				1			FCC	FCC
	0.5	2.5	1	1	1				1			FCC	FCC
	0.5	3	1	1	1				1			FCC	FCC
	1.5	1	3	0.5	1				1			BCC	BCC
Round 2 Post-DFT	1		1					1		1	1	FCC	BCC
		1	1			1			1		1	FCC	?
			1	1	1		1		1			FCC	?
		1	1		1					1	1	FCC	Multi
			1				1	1		1	1	FCC	BCC+BCC

- 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