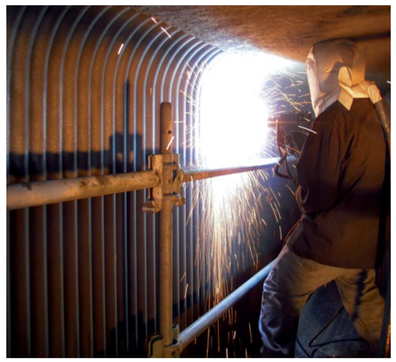
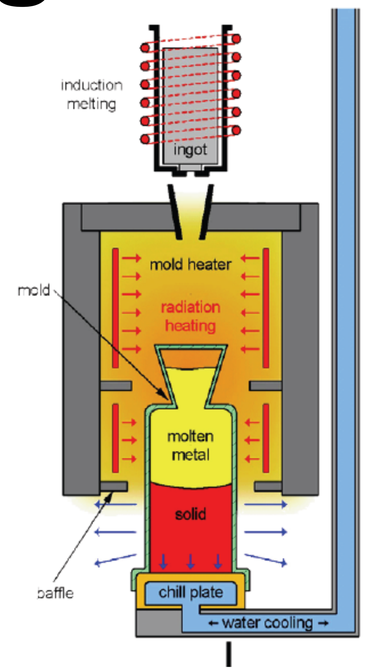
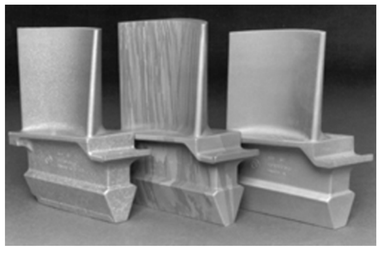
ICME Based Computational Design of Advanced Alloys




Siemens SGT5-8000H 375MW Gas Turbine

NETL 2015 CCR Project Review Meeting

Jiadong Gong,
David Snyder,
Jason Sebastian,
Gregory B. Olson

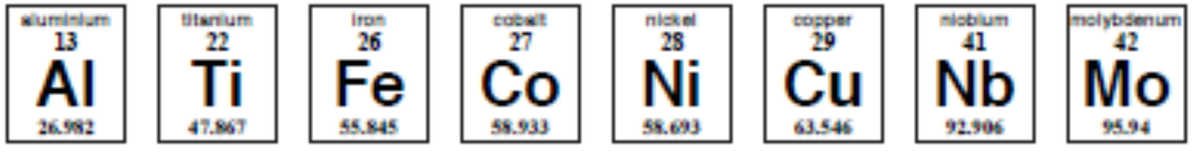
QuesTek Innovations LLC

Agenda

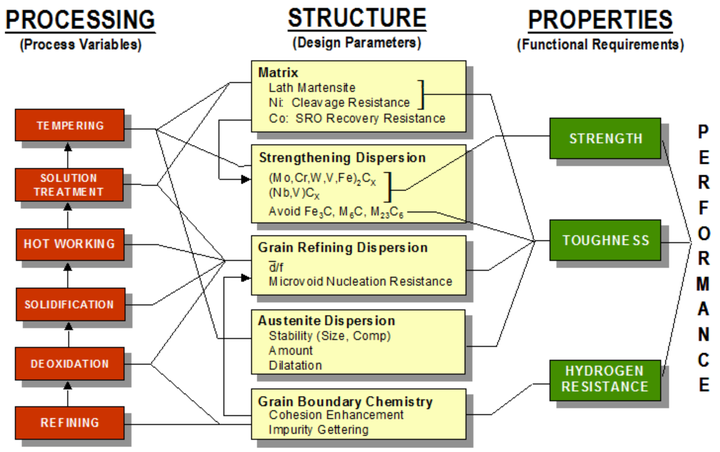
- QuesTek background
- SBIR project case studies
  - Computational Design of Weldable, High-Cr Ferritic Steel
  - Design of Castable SX Ni-based Superalloys for IGT Blade
  - Computational High Entropy Alloy Design
- Closing

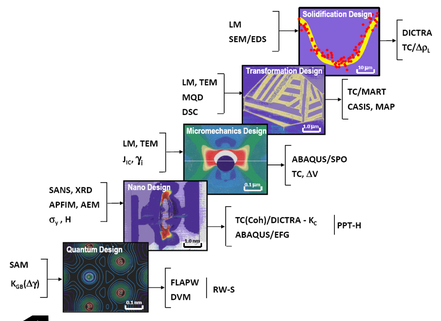
Background on QuesTek

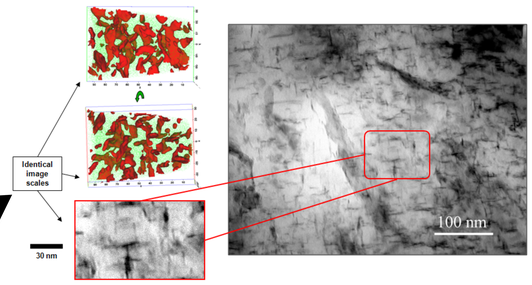
- Founded in 1997(Prof. Greg Olson, cofounder)
- A global leader in computational materials design:
  - Our ***Materials by Design***® technology and expertise applies Integrated Computational Materials Engineering (ICME) tools and methods to design new alloys 50% faster and at 70% less cost than traditional empirical methods
  - Aligned with President Obama's Materials Genome Initiative
- Creates IP and licenses it to alloy producers, processors or OEMs
- 30+ patents awarded or pending worldwide
- 4 computationally-designed, commercially-sold alloys
- Designing 10+ new Fe, Al, Cu, Ni, Co, Nb, Ti, Mo and W based alloys for government and industry



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







SAE Aerospace
An SAE International Group

AEROSPACE MATERIAL SPECIFICATION

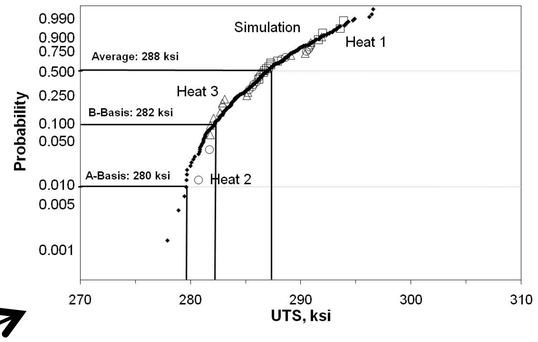
SAE AMS5922 REV. A

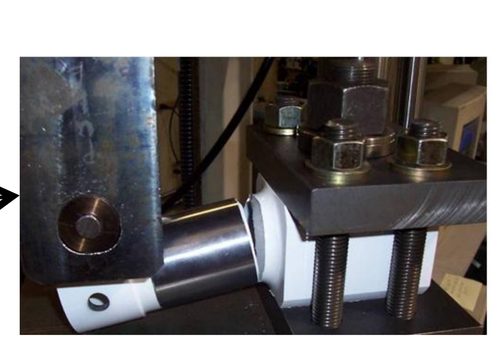
Issued 2008-01
Revised 2010-05

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

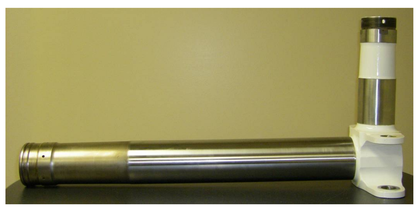
UNS S10500

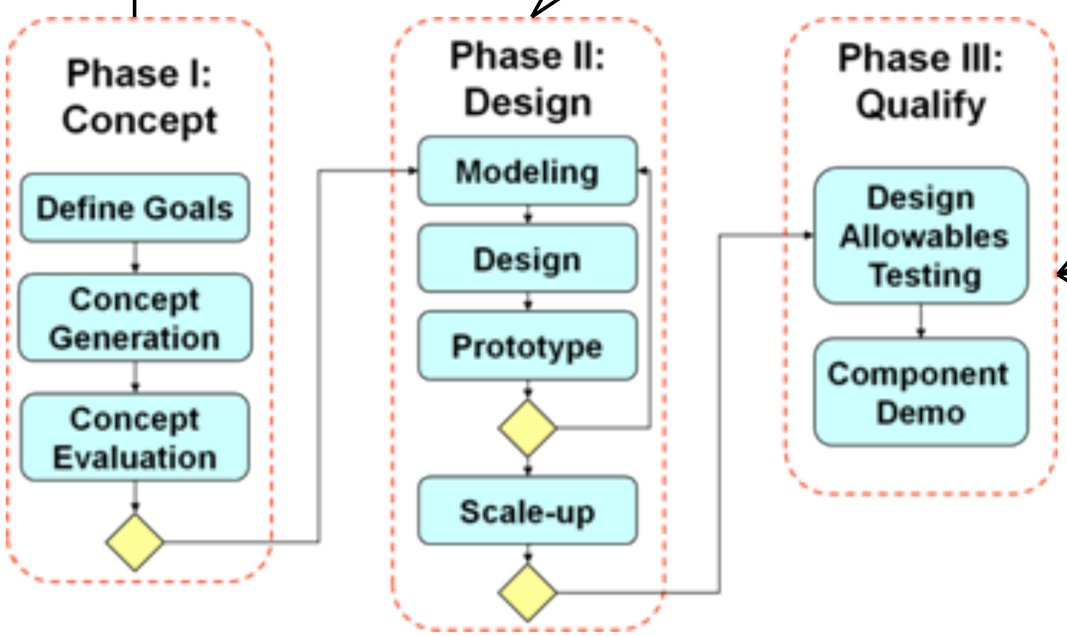




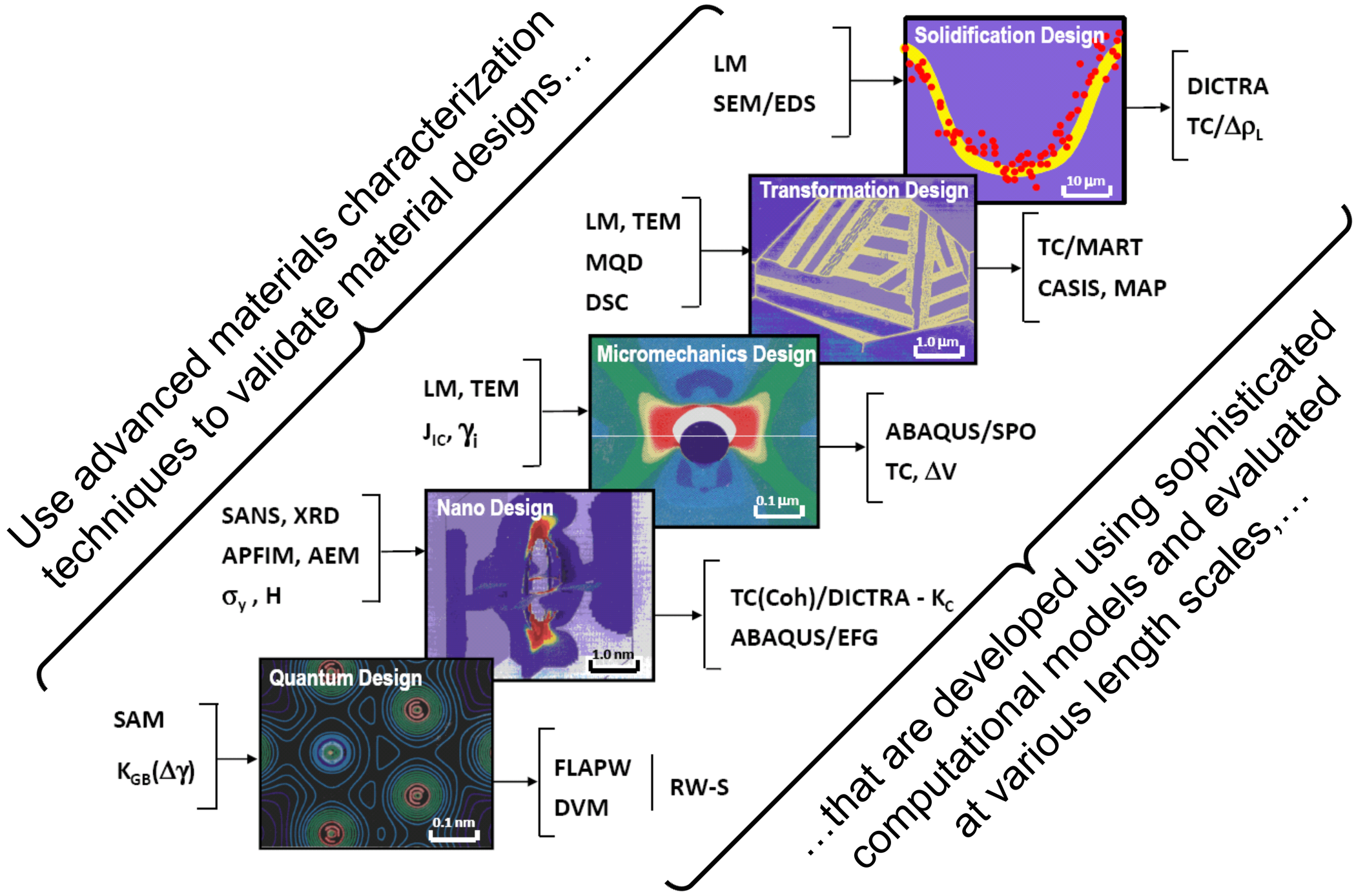




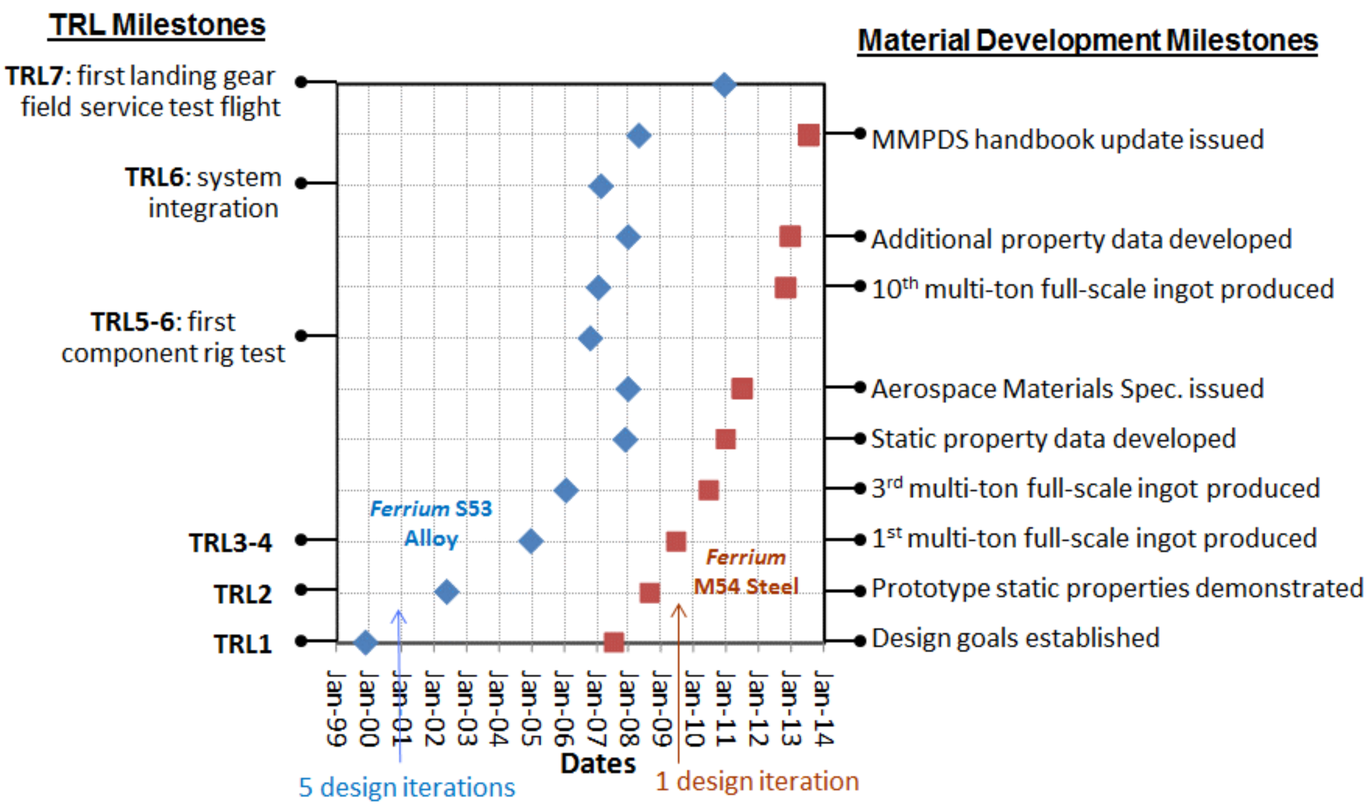




Computational materials design overview



Computational materials qualification acceleration of QuesTek's *Ferrium*® S53® and M54™ steels



Milestone	*Ferrium* S53	*Ferrium* M54
Created System Design Chart (Design Goals)	Dec. 1999	Aug. 2007
Number of design iteration(s)	5	1
Feasibility to meet static property requirements	Jun. 2002	Sep. 2008
1st Multi-ton full-scale ingot production	Jan. 2005	Jul. 2009
3rd Multi-ton full-scale ingot production	Feb. 2006	Jul. 2010
Static property data development	Dec. 2007	Jan. 2011
Aerospace Materials Specification (AMS 6516)	Jan. 2008	Jul. 2011
Metallic Materials Development and Standardization (MMPDS)	May. 2008	Dec. 2013
Material Qualification Time	**8.5 Years**	**6 Years**

Ferrium M54 for T-45 hookshanks



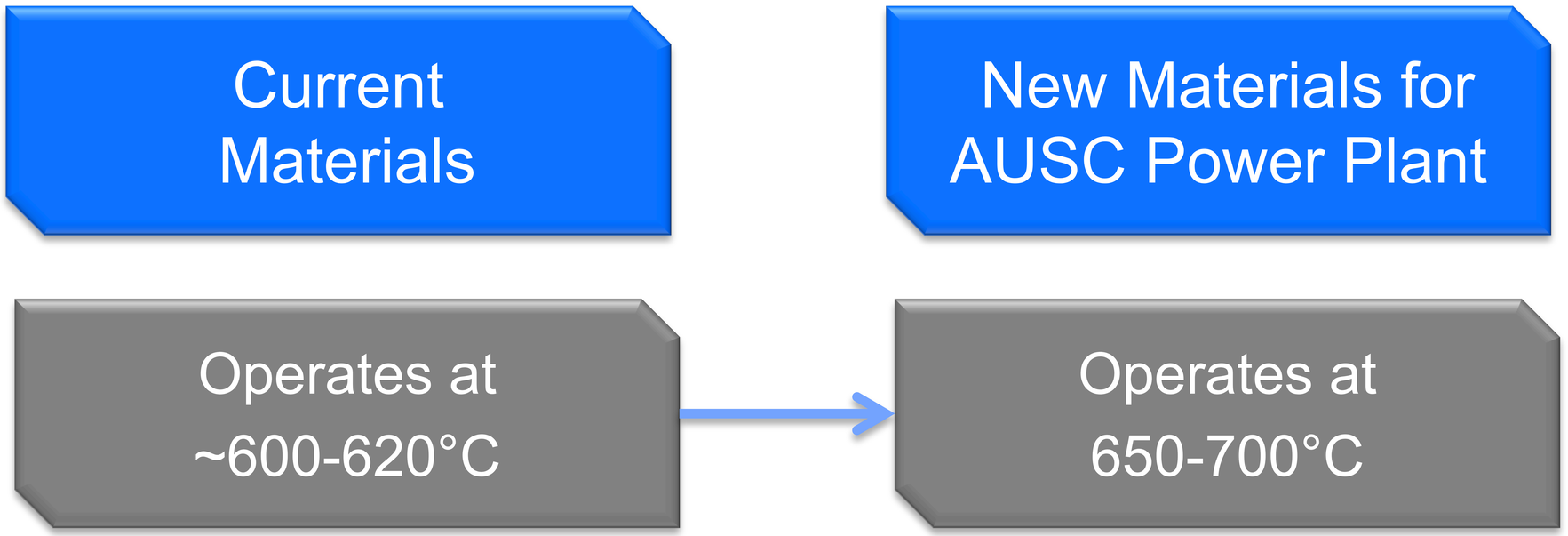


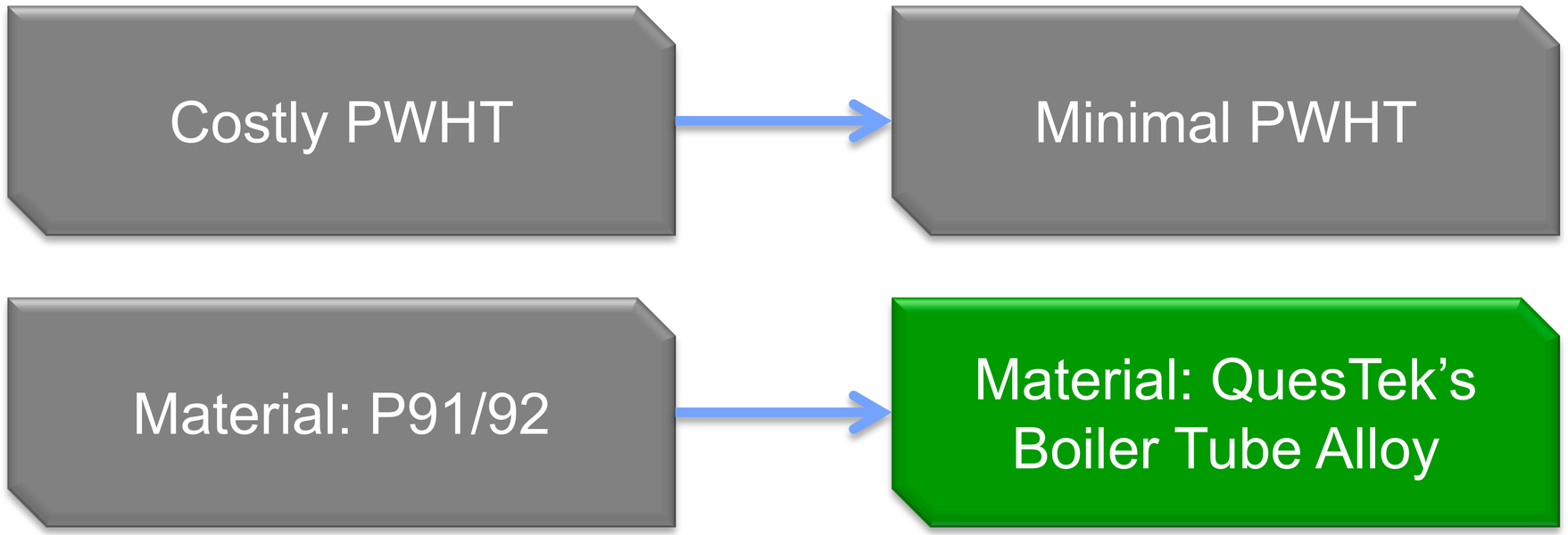
- Incumbent alloy (Hy-Tuf) was underperforming in service
- New *Ferrium* M54 selected for evaluation under SBIR Ph II
- Full-scale rig testing completed in 2014, inserted into field service evaluation in Oct. 2014
- Project Recipient of NAWCAD Commander's Award
- Currently producing replacement flight assets using M54



Case Study:
Computational Design of Weldable, High-Cr Ferritic Steel

Target and background





SBIR program status

- **Department of Energy SBIR**
  - Phase I (2012)
  - Phase II (2013 to present)
  - TPOCs: Patricia Rawls, Sydni Credle, Vito Cedro
- **Phase I**
  - Define requirements
  - Initial alloy design (two prototypes) and production (~5 lb. each)
  - Validation and testing
    - Tensile
    - Microstructure
- **Phase II**
  - Alloy redesign (five additional prototype)
  - Production (~30 lb. each)
  - Validation and testing
    - Tensile
    - Microstructure / nanostructure
    - Corrosion (fireside, steamside)
    - Creep
  - Redesign
  - Intermediate-scale production (~500 – 1,000 lb.)
  - Final validation and testing

Alloy design concepts / descriptions

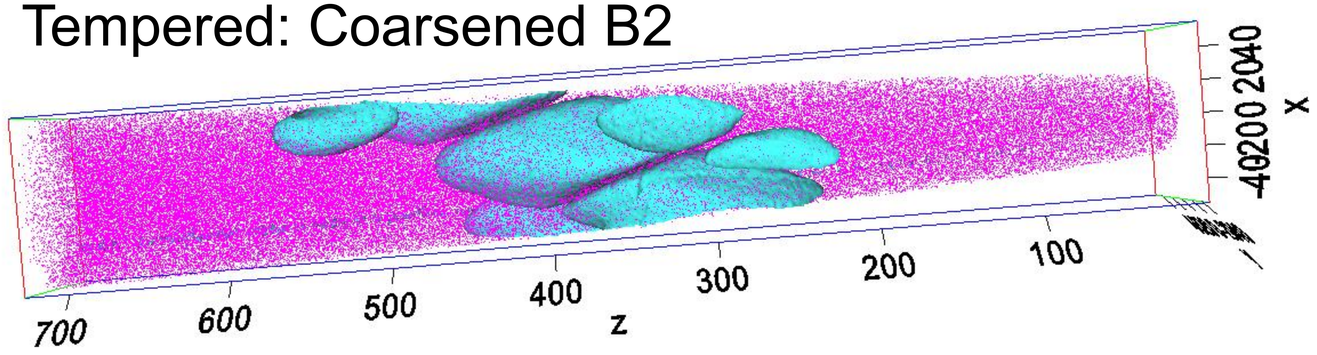
	Description
Concept	Fully-ferritic
Strengthening phases	B2,L21 and MX
Grain-Pinning	(Ti,Ta)C
Improvement	• Robust as-weld microstructure • Higher Cr content
Challenges	• B2/L21 coarsening mechanism • Toughness

Intermetallic phase for strengthening

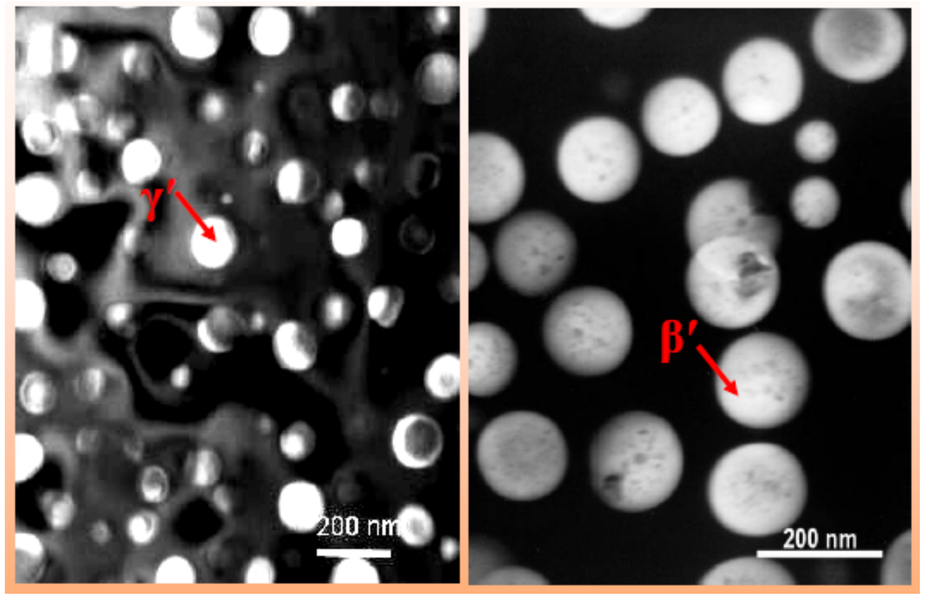
1120°C/48hr homogenized + extrusion+ 1000°C/2hr SHT AC + temper at 675°C

The 1st run alloys show coarsened B2 phase but no L21 phase.

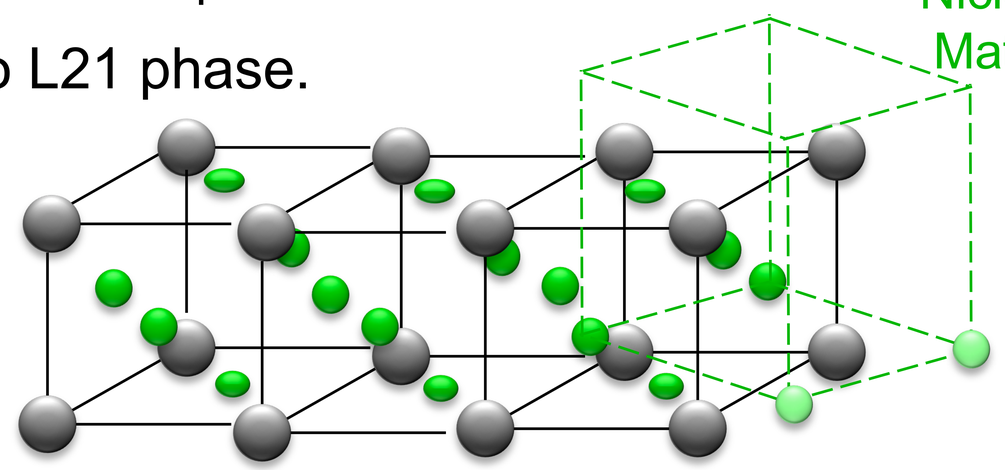
Tempered: Coarsened B2



L21 suppressed, BT-1B

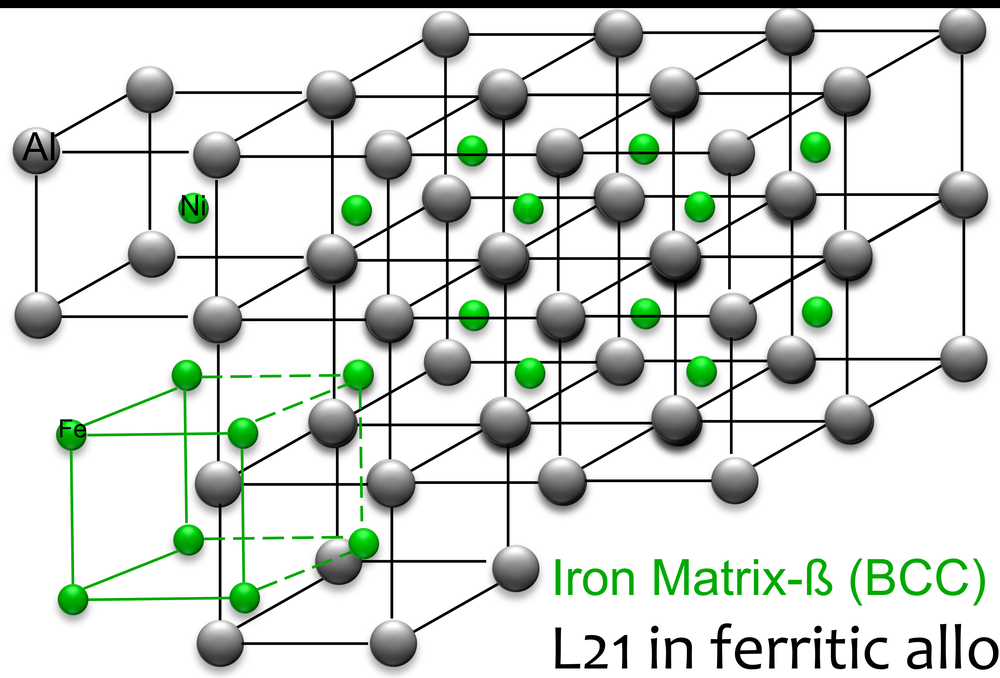


FCC Ni BCC Fe



L12 phase in Ni alloys

Small lattice mismatch for coherent and finer precipitation for better strength



Iron Matrix-ß (BCC)

L21 in ferritic alloys

System Design Chart

Processing

- Melting & solidification
- Homogenization & hot rolling
- Heat treatment
- In-field welding / post weld treatment
- Heating & cooling cycles

Fully ferritic alloys

Structure

Stable oxide layer
- High Cr and Al
- No primary carbides
- Film stress

Matrix structure
- Ferritic
- Ni content
- δ - ferrite
- No TCP phases and $Cr_{23}C_6$

Precip. structure
- PSD of Ni-Ti (B2) and/or Ni-Ti-Al (Heusler)
- Thermal stability
- Coarsening rate

Grain size
- Grain refinement for smaller grains

Properties

- Creep strength
- Microstructural stability
- Fatigue strength
- Fracture toughness
- Coefficient of thermal expansion
- Oxidation resistance

Performance

- Creep resistance
- Thermal fatigue resistance
- Steam-side corrosion resistance
- Resistance to type IV fracture

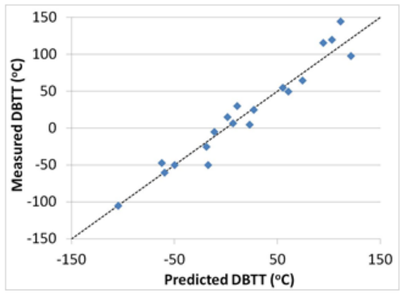
Alloy design highlights

$$DBTT = DBTT_0 + K_{GS}GS + K_{Ti+Al}(Ti + Al) + K_{Ni}Ni + K_{Mn}Mn + K_{Cr}Cr + K_{Mo}Mo + K_{Al}Al$$

$DBTT_0$	Grain Size	Ti+Al*	Ni	Mn	Cr	Mo	Al
14.2	0.4	-482	-18.6	221	-1.5	0	10

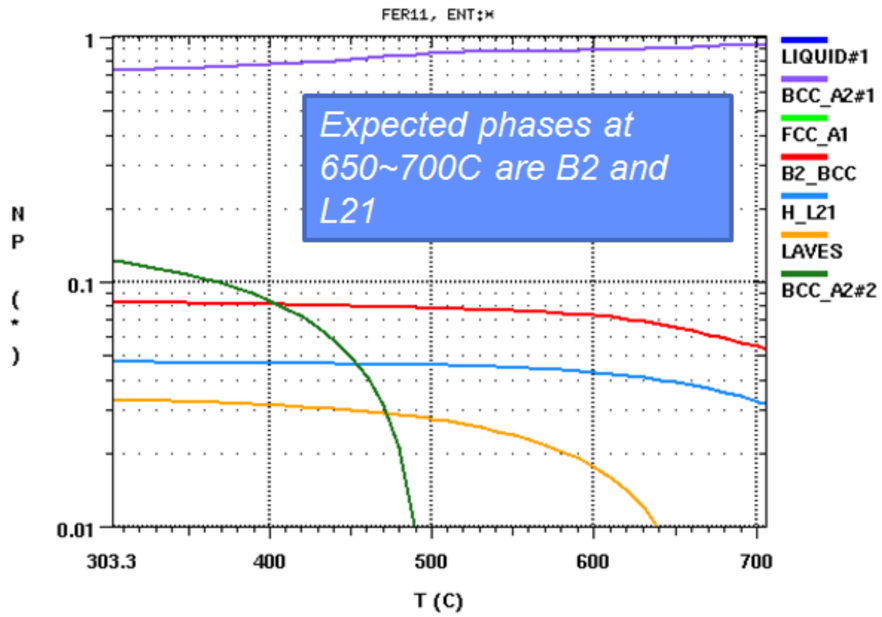
$$DBTT = 14.2 + GrainSize \cdot 0.4 - 482.0 \cdot 0.2 - 1860 \cdot W_{Ni} - 150 \cdot W_{Cr} + 1000 \cdot W_{Al}$$

* For small Ti and Al amounts. They act as O and N getters. Anything more than 0.6 Ti and 0.1 Al should be dealt with as individual element.

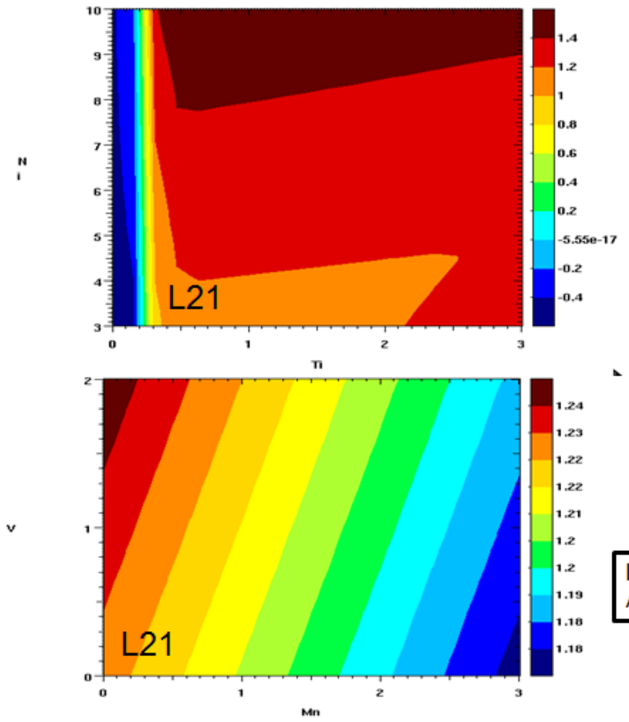


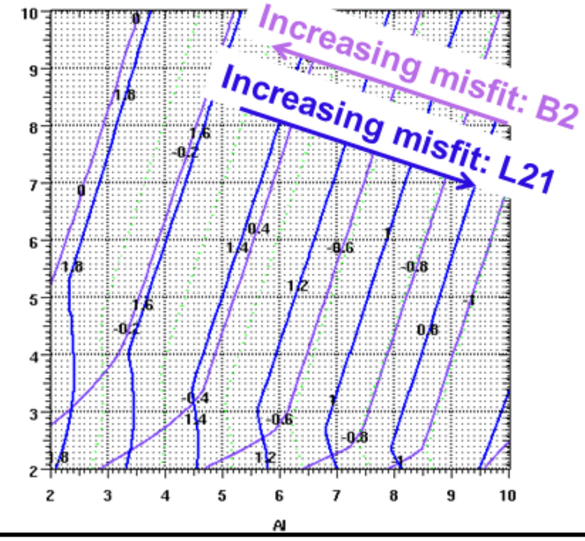
Alloy	DBTT/ °C
BT1B	48.136
BT1C1	61.796

DBTT modeling



Thermodynamic step diagrams





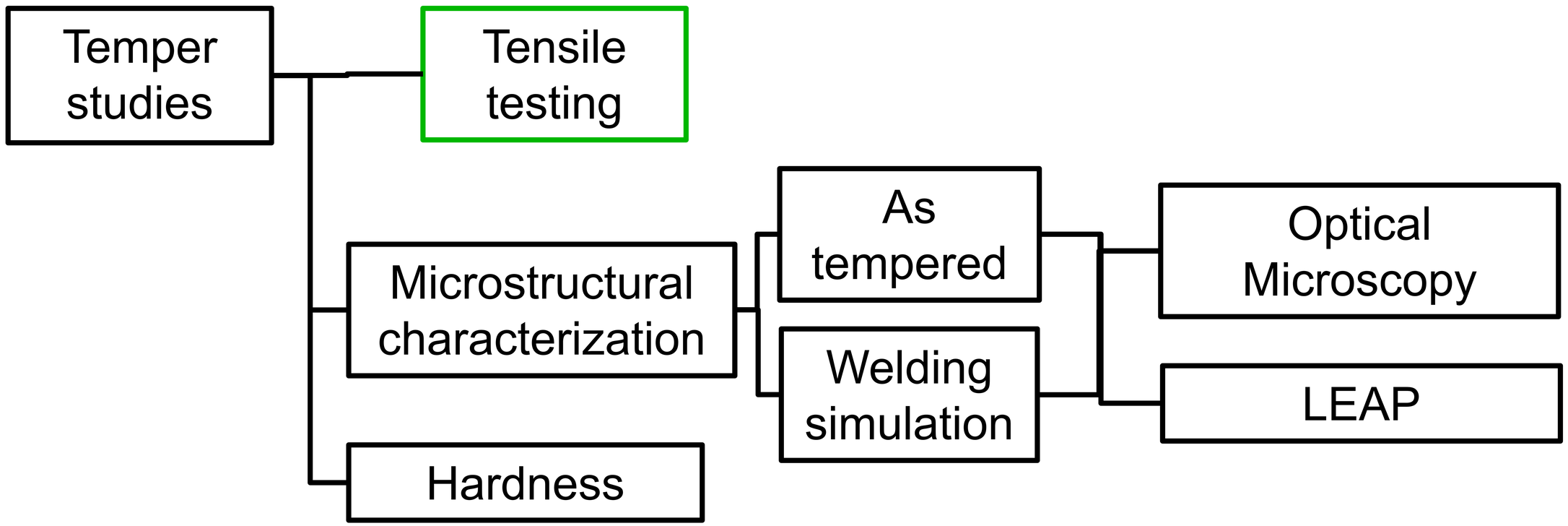
Increasing Ti and Ni increases L21/BCC mismatch
Al is the main ingredient that can reduces L21/BCC lattice mismatch

L21/bcc lattice misfit modeling

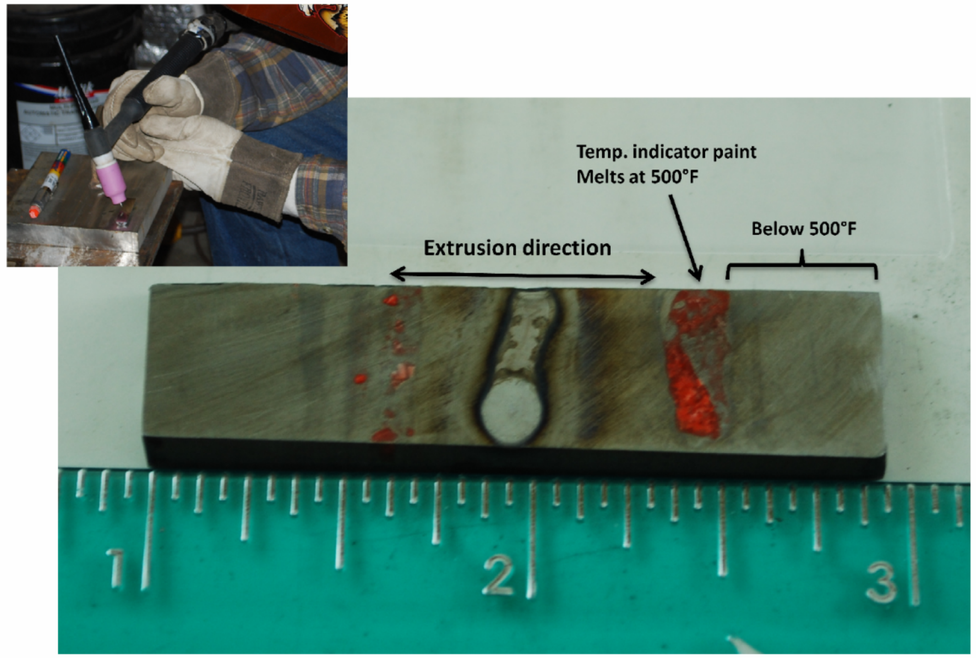
Two prototype alloys (BT-1B and BT-1C) were computationally designed

Production and processing

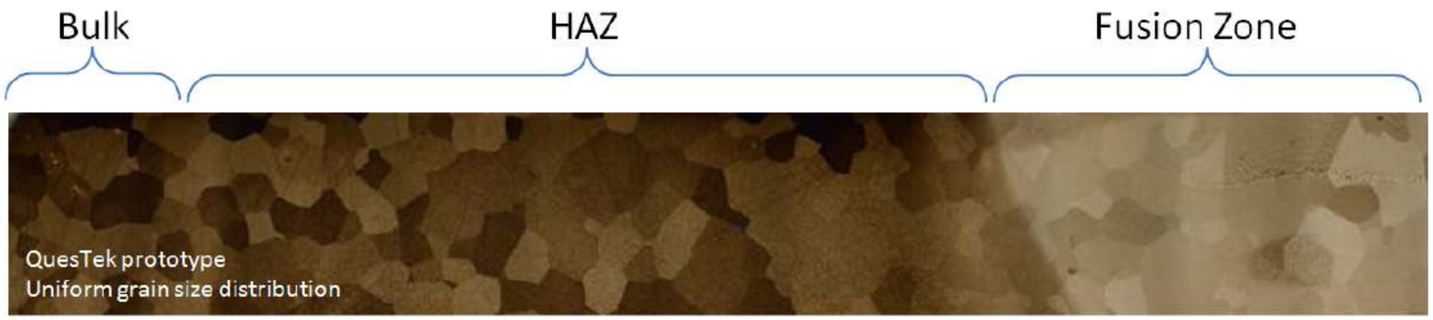
- Vacuum melted (30 lb scale)
- Homogenized and extruded/rolled
- Solution treated, air cooled and tempered (optimized with hardness response studies)

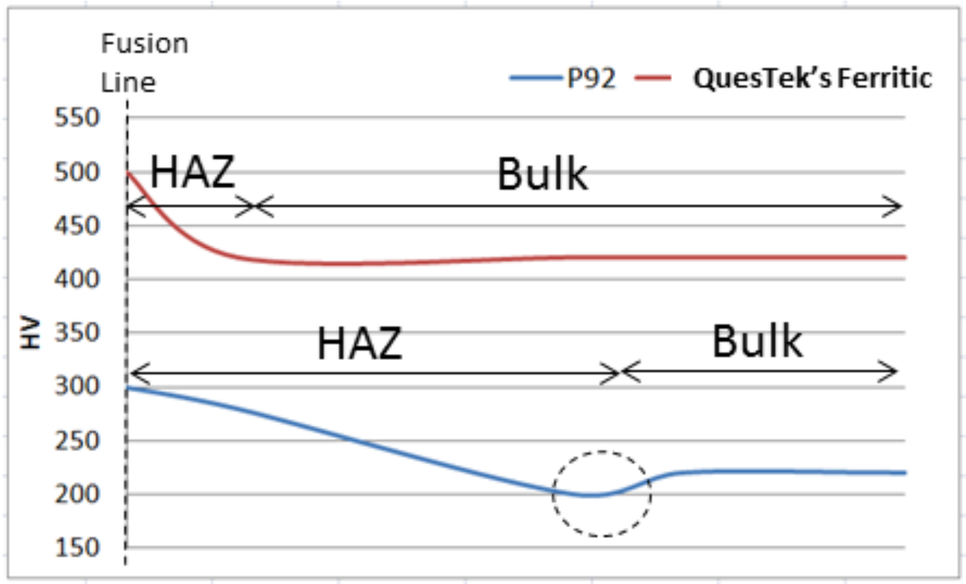


Weldability of prototype alloys



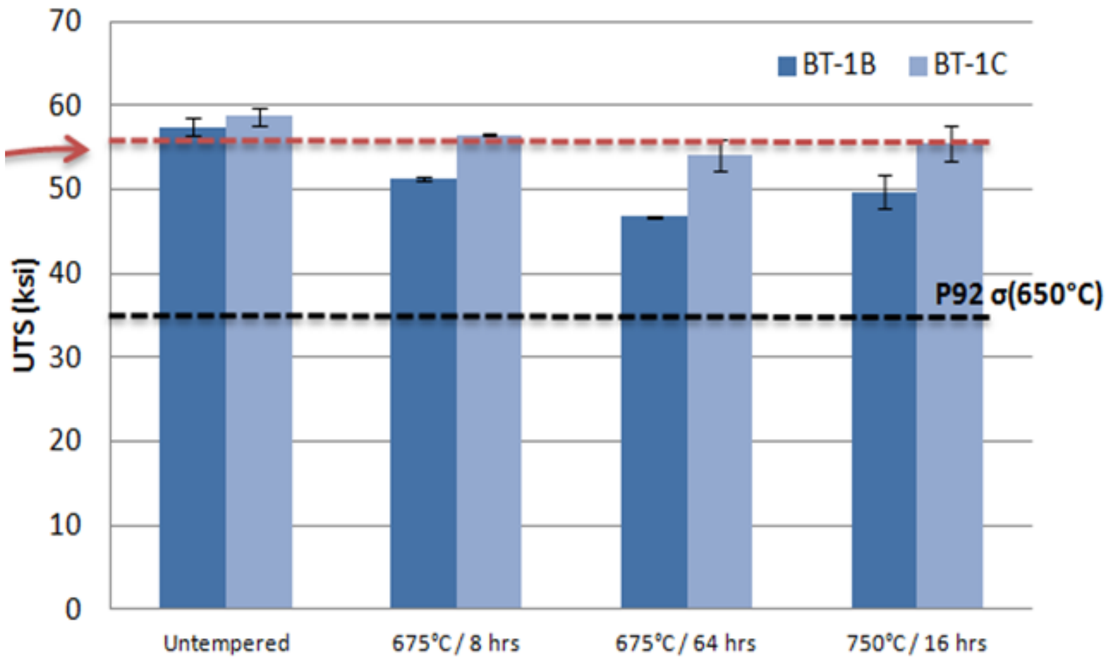
- *Fully ferritic structure achieved*
- *Uniform grain structure through weld*
- *No softening in HAZ (Type IV cracking)*



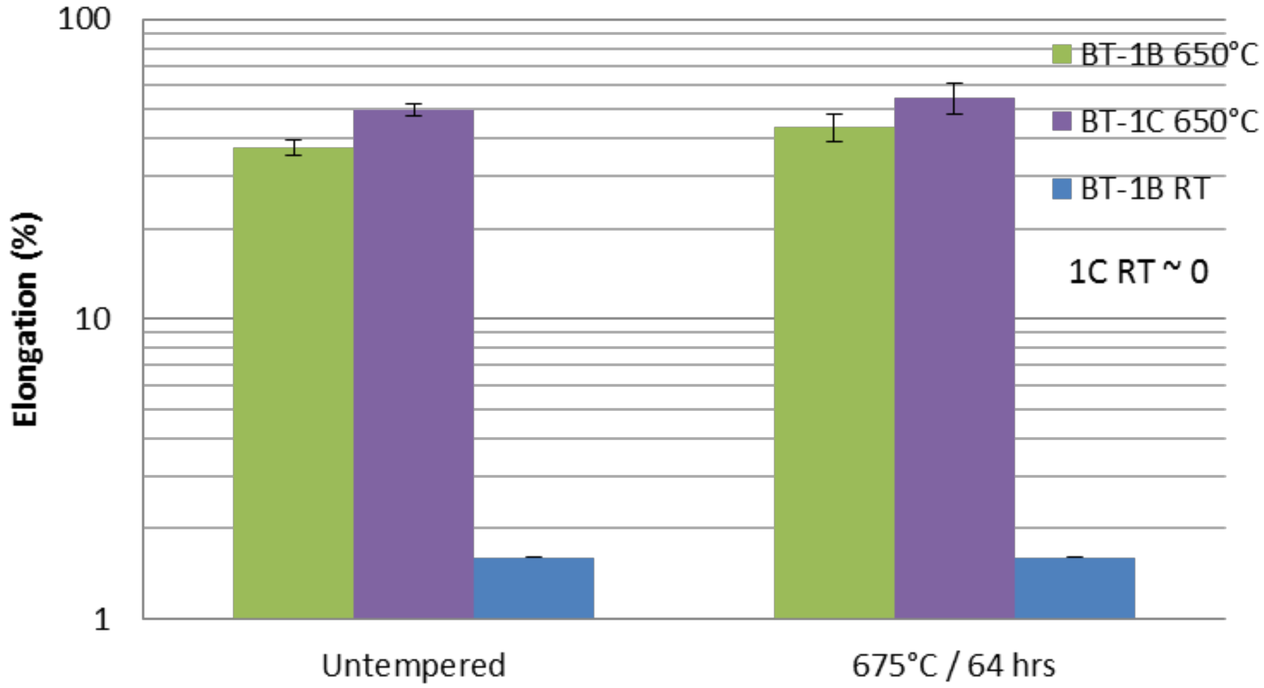


Phase I, Elongation and UTS

Prototypes – BT1B and BT1C, failed due to lack of ductility(high DBTT)



UTS at 650C



Ductility at RT and 650C

Phase II design refinement highlights

$$DBTT = 14.2 + GrainSize \cdot 0.4 - 482.0 \cdot 0.2 - 1860 \cdot W_{Ni} - 150 \cdot W_{Cr} + 1000 \cdot W_{Al}$$

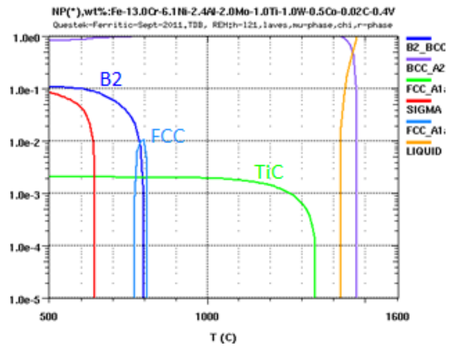
We target the matrix grain size will be 100 micron

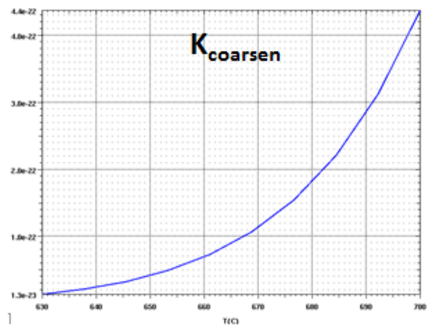
$$DBTT = 14.2 + 100 \cdot 0.4 - 482.0 \cdot 0.2 - 1860 \cdot W_{Ni} - 150 \cdot W_{Cr} + 1000 \cdot W_{Al}$$
$$+0.75 \cdot 86.8 \cdot \sqrt{100\,(np(L2_1) + np(B2))}$$

Sample	DBTT 1st version	DBTT 2nd version	DT / °C
BT1B	8.1	116.2	108.1
BT1C2	21.8	180.0	158.2
BT2A	-155.3	47.0	202.3
BT2B	-152.3	64.4	216.7
BT2C	-151.2	68.7	219.9
BT2D	-151.2	62.5	213.7
BT2E	-139.7	42.0	181.69

Revisions to the DBTT model

Assuming matrix grain is 100 micron





Age at 700 °C:
NP(B2)@Tage = 6.2 (%)
B2/BCC Misfit = -0.09 (%)
NP(TiC) = 0.2 (%)
Driving Force,L21 = 1899 J/mol
BCC(Ni:Al) = 2.25 ratio
DBTT(solute) = -105 (C)
DBTT = 57.4 (C)

Revised thermodynamic step diagram calculations (and precipitate coarsening rate predictions)

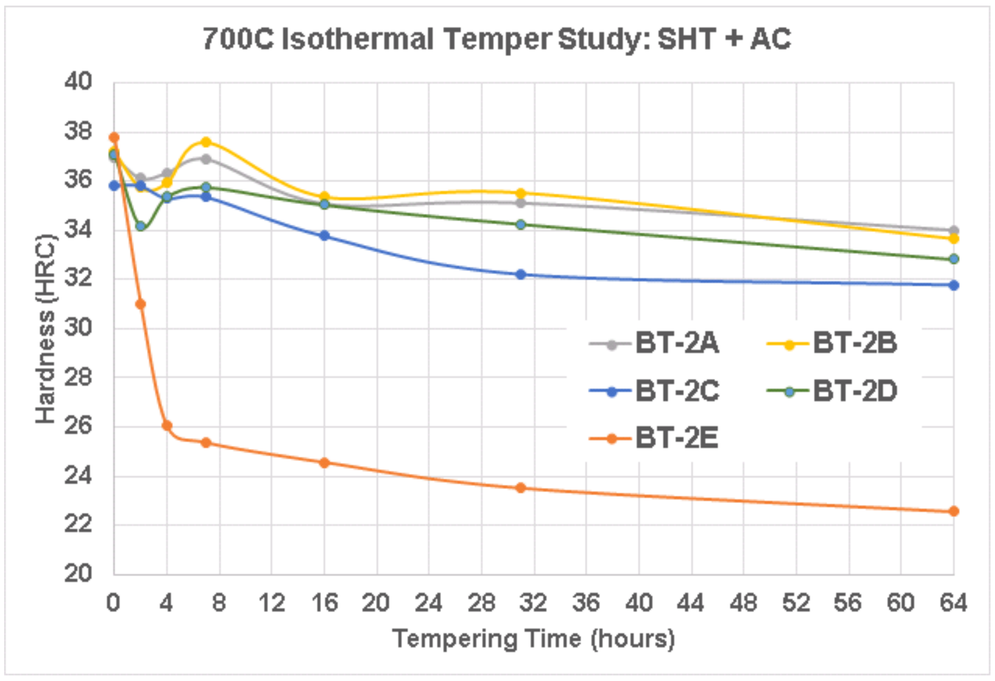
	$\%V_{ppt}$	BCC Ni/Al	DF L21 700	DF laves 650	DBTT (solute)	DBTT	10^{-22} Kcoars
Mod 1B	6.4 B2	2.32	579	1045	-109	51.5	4.45
B2 only	6.4 B2	2.25	701	1176	-104	60.6	3.95
	6.2 B2	2.25	1407	1138	-104	58.6	4.68
	6.3 B2	2.25	467	1110	-104	60	4.19
L21 only	5.0 L21	2.16	2157	715	-103	42	3.2 L21

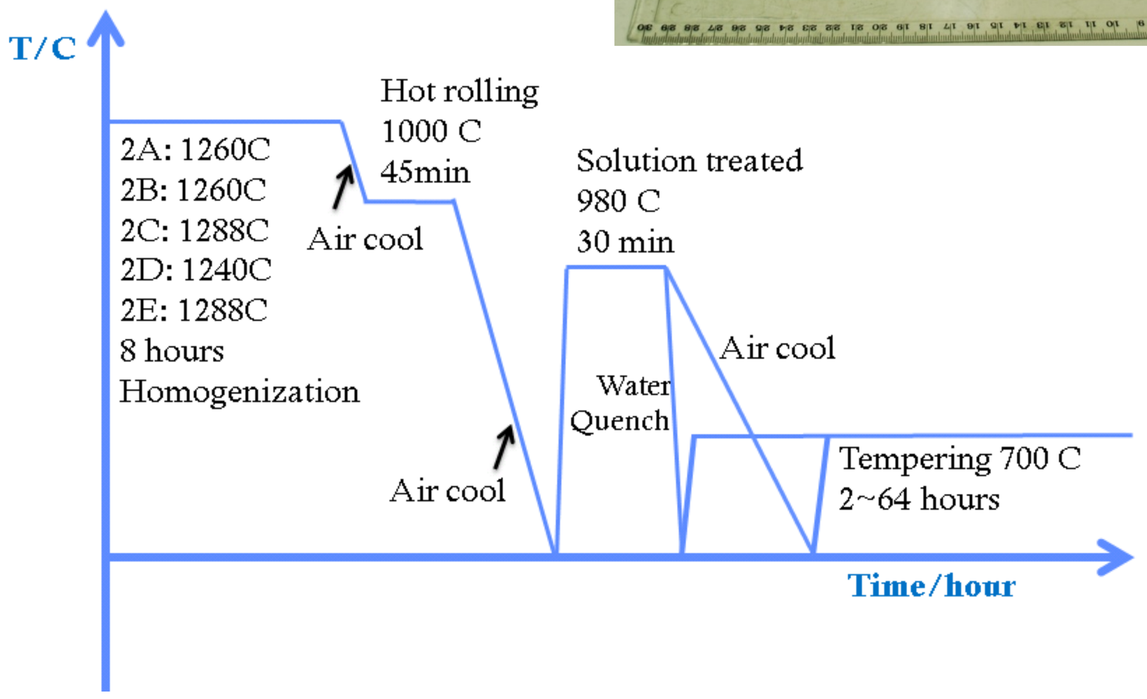
Five Phase II prototype alloys (BT-2A, 2B, 2C, 2D, and 2E) were computationally designed

Phase II prototype production

- Double-vacuum melted (VIM/VAR) at 30-lb scale (SAES)
- Homogenized and hot rolled into plate (Special Metals)
- Test coupons solution treated, air cooled and tempered at 700°C
  - Optimized with hardness response study



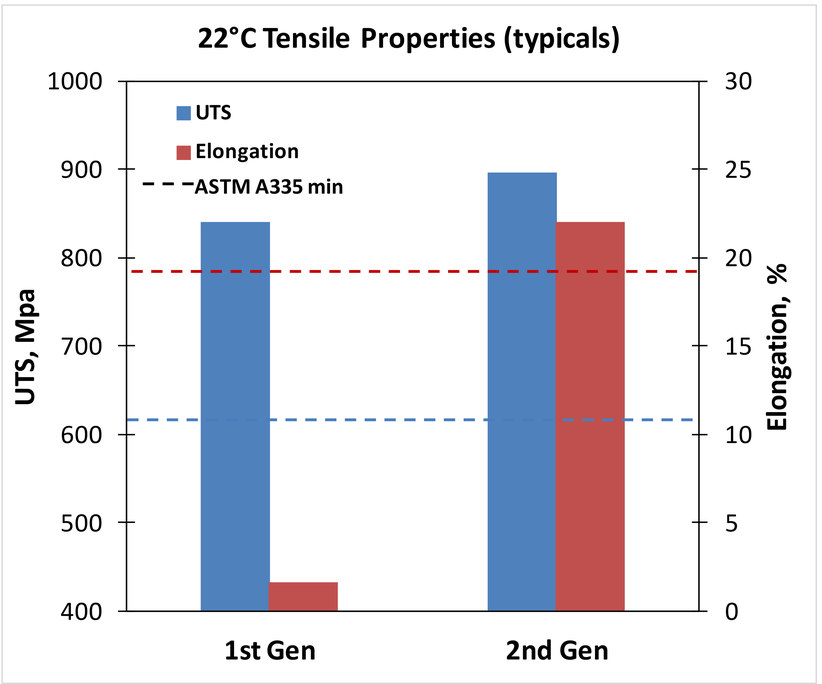




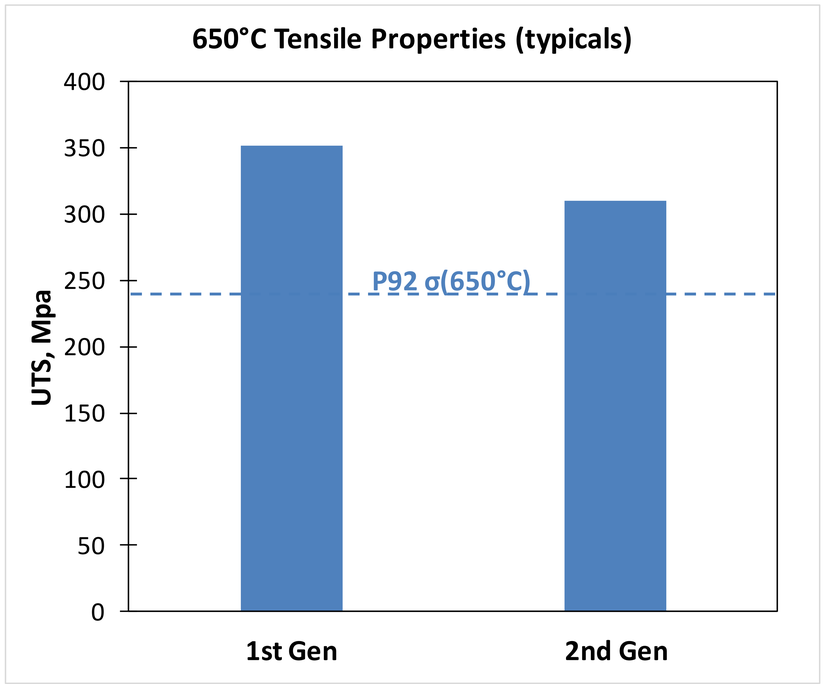
Phase II prototype results

- Properties after long term exposure at 675°C

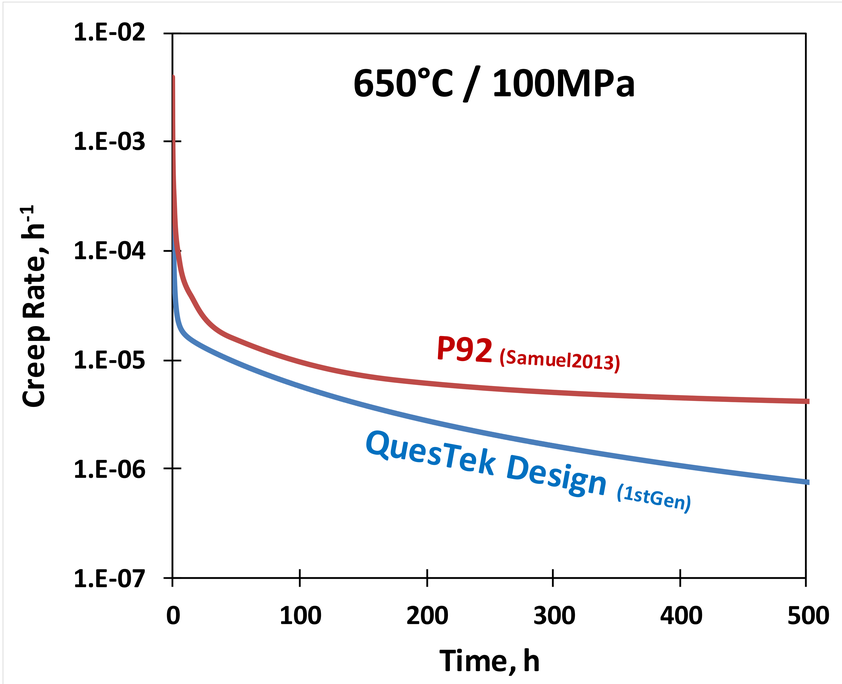
RT Tensile



650°C Tensile



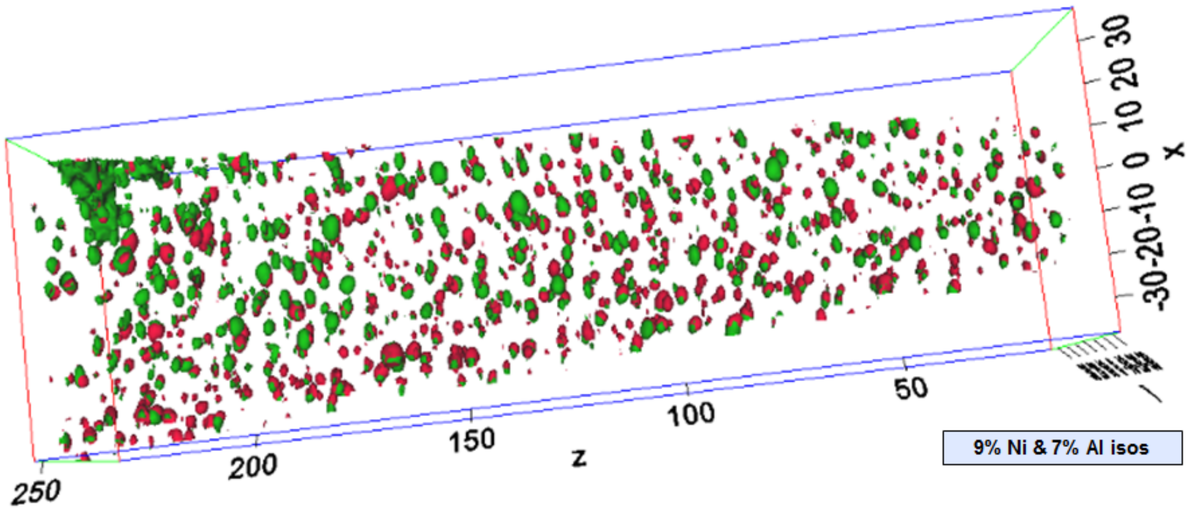
Preliminary Creep Rupture



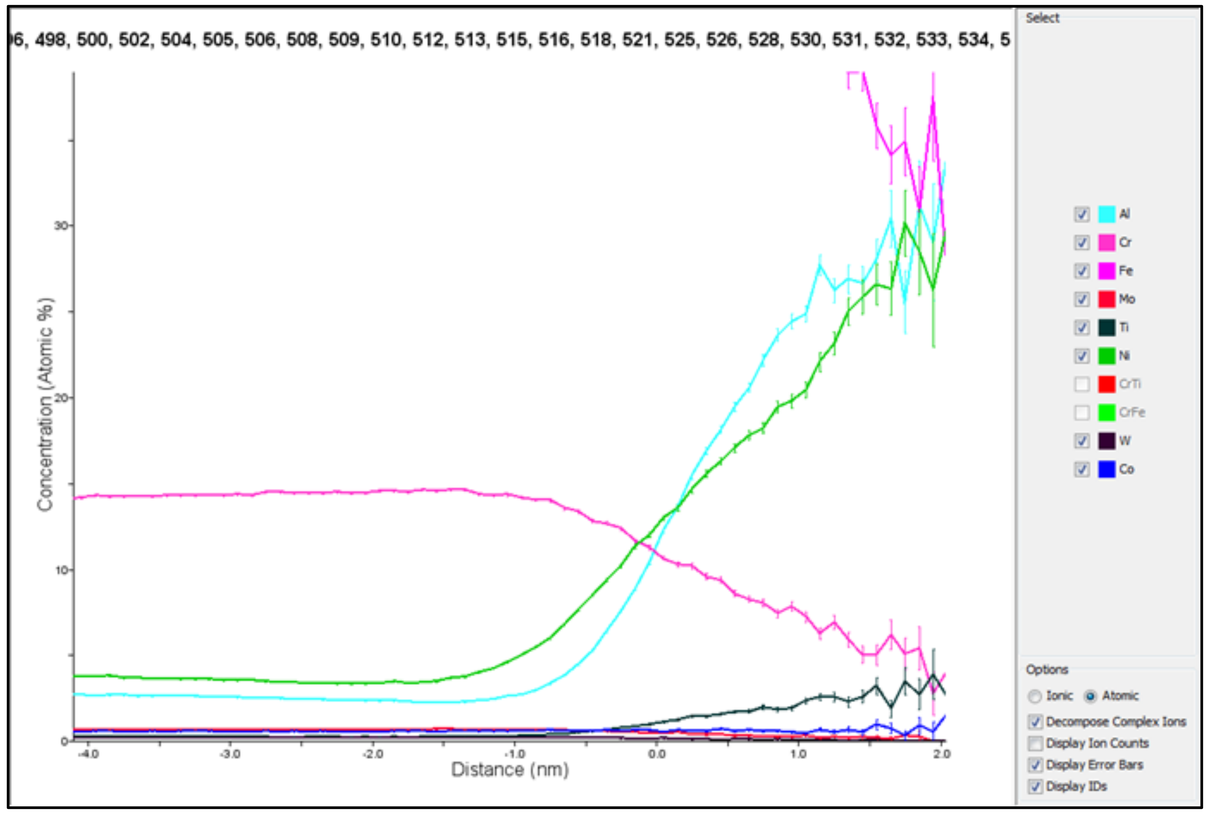
Prototype alloys possess excellent strength, ductility and secondary creep rate compared with baseline P92

Phase II prototype results

- BT-2C preliminary LEAP analysis
- Fine nano-scale B2 strengthening precipitates



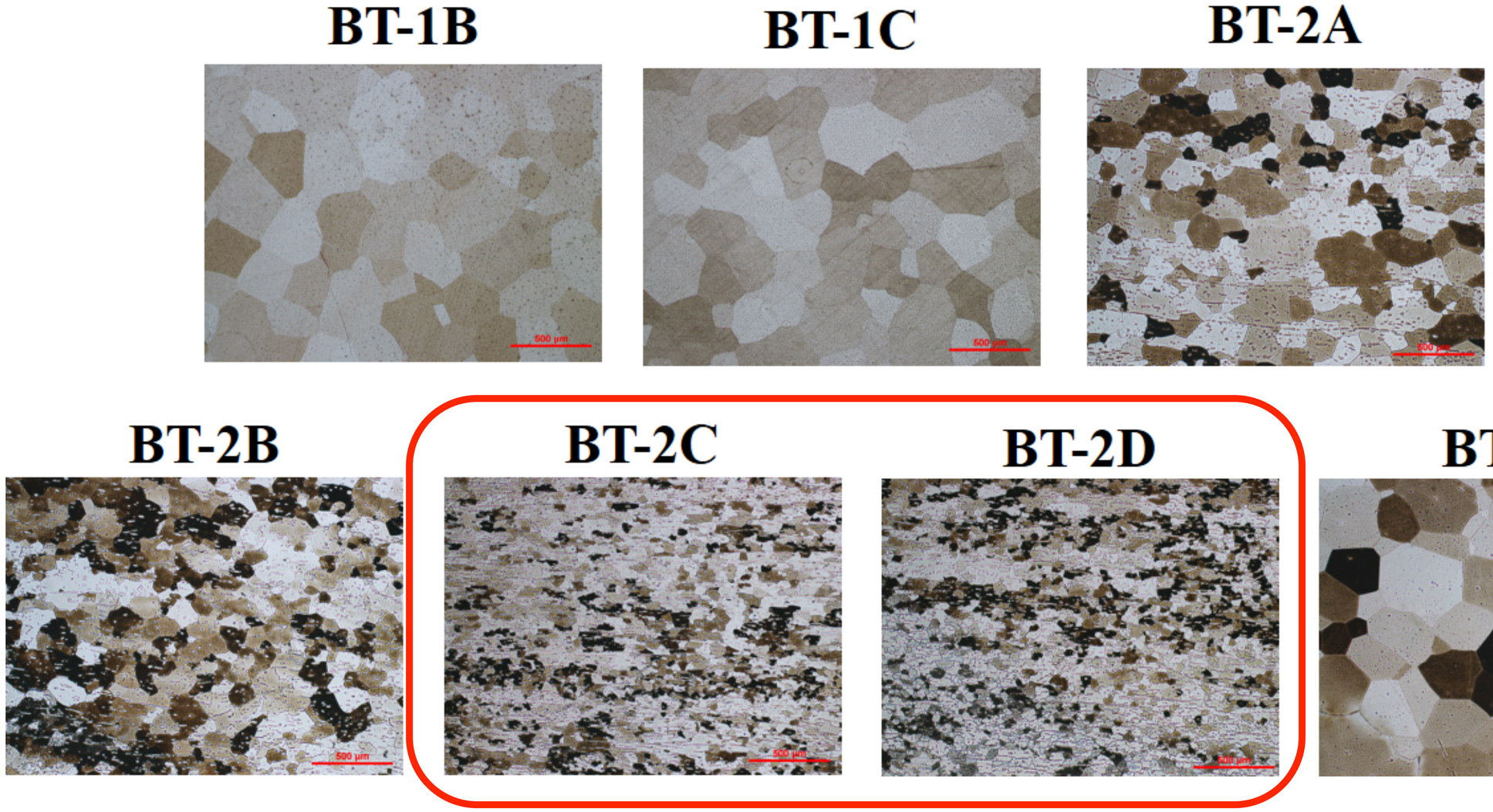
Average ***diameter*** = 2.6 nm
(based on 7%Al isosurfaces)



B2-type composition

Phase II prototype results

- Grain size analysis
  - *Homogenized, forged and solution treated*



Grain refined alloys demonstrate best RT ductility!

In-Process / Next steps

- Prototype characterization
  - Preliminary evaluations complete
  - Extended evaluation in process, including:
  - Corrosion (fireside, steamside)
    - 1000 hour tests nearing completion at B&W
  - Creep
    - Base and welded plate
    - <1000 hour tests in-process
- Final alloy design
- Larger-scale alloy production
  - Alloy production
  - Alloy processing / specification development
  - Extended characterization (>1000 hour)

QuesTek is seeking commercialization partners for their new ferritic alloy technologies (alloy producers, tube producers, boiler designer OEMs, etc.)

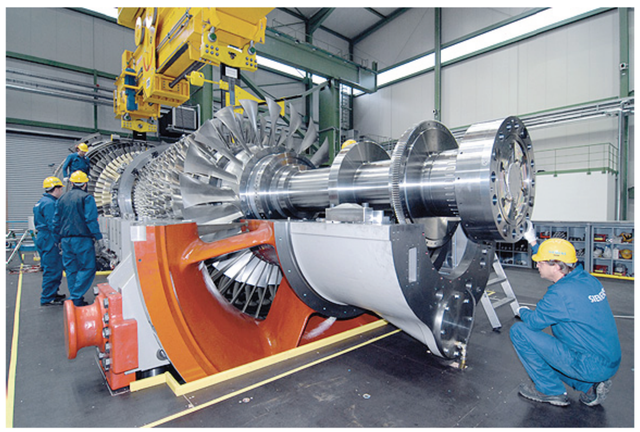
Case Study:
Design of Castable SX Ni-based Superalloys for IGT Blade

Case Study: 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**

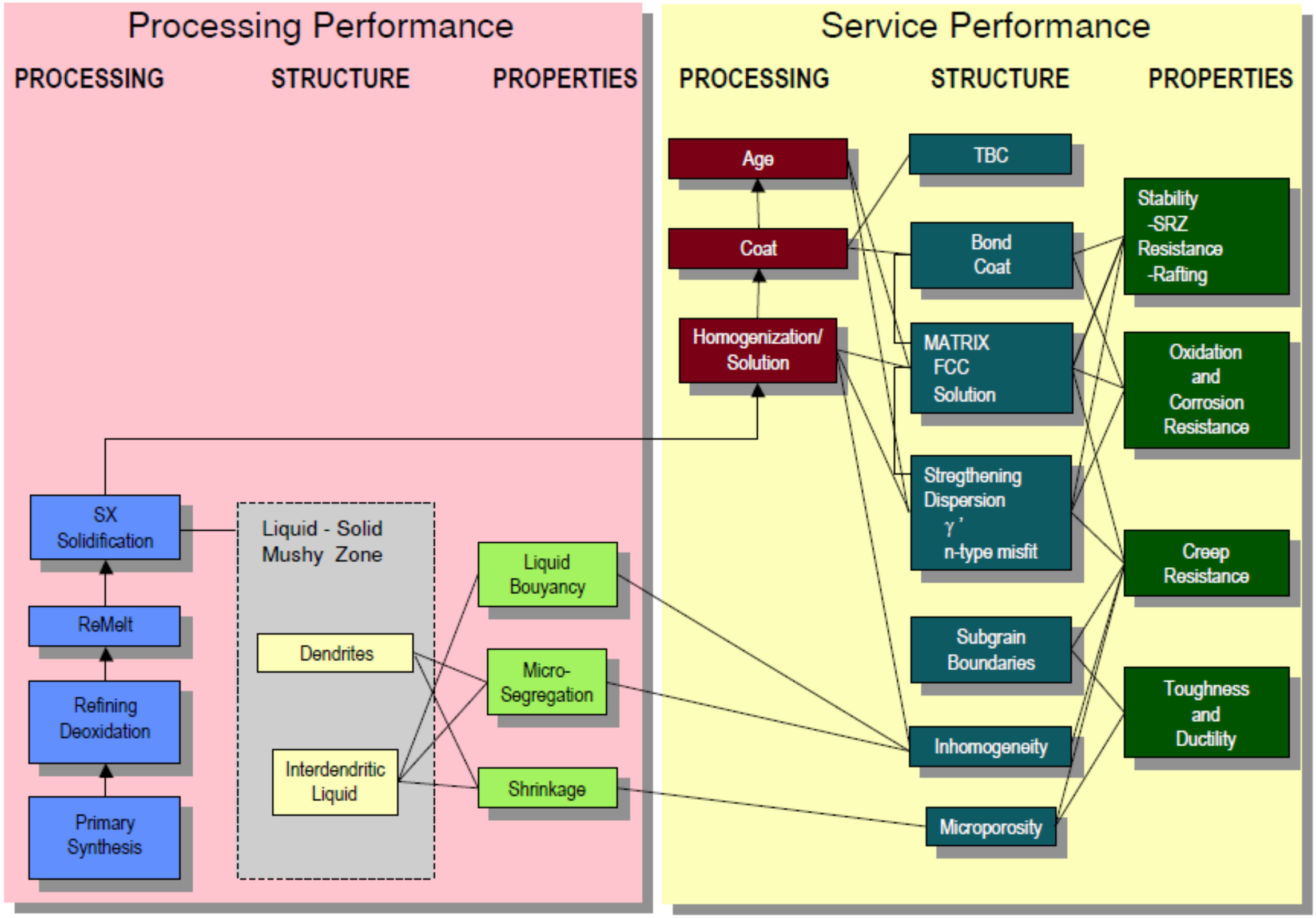
PCC Airfoils, LLC
A Division of Precision Castparts Corp.

SIEMENS



QuesTek's proposed 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

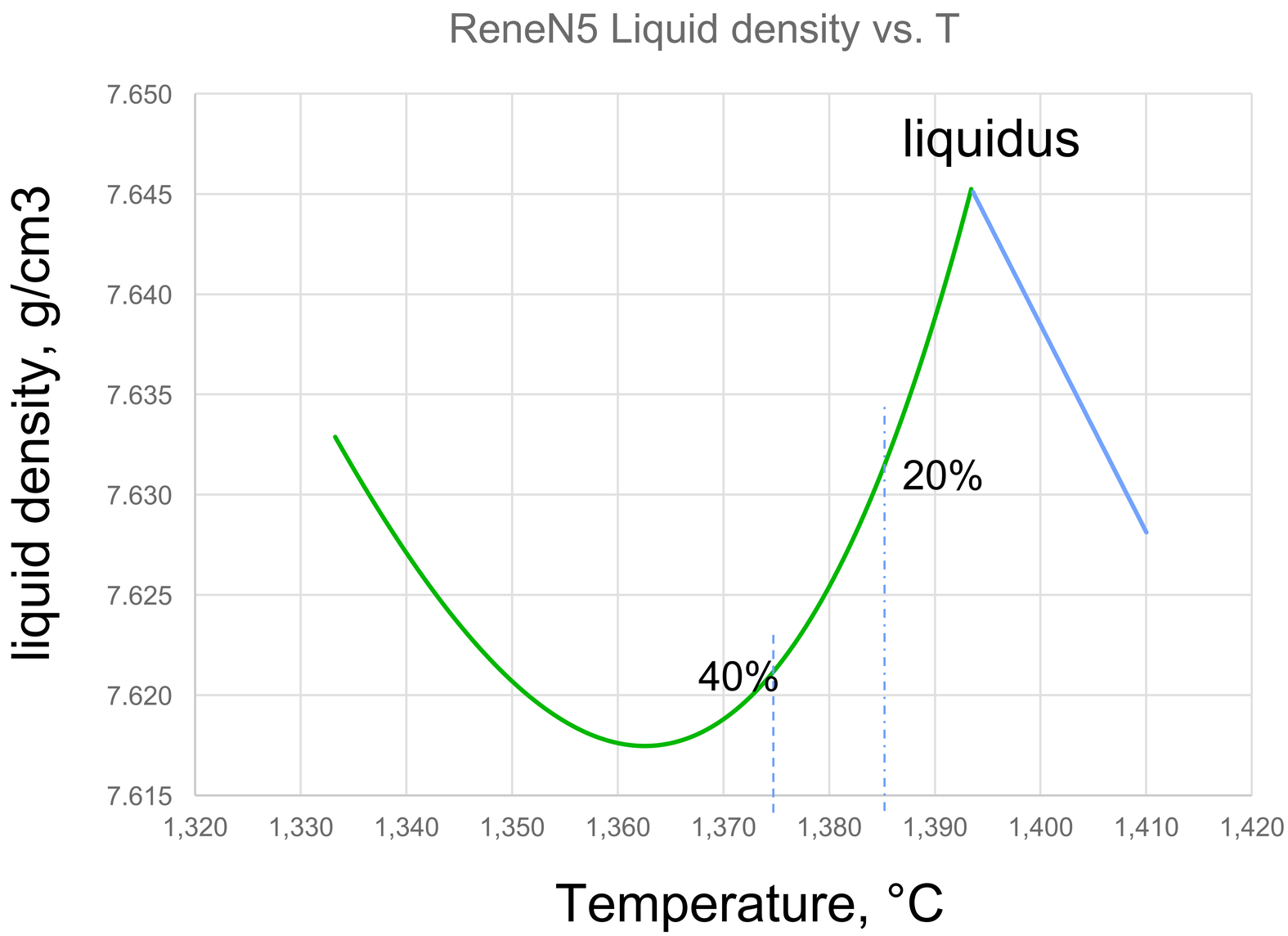
High-Re alloys

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

Modeling of liquid density during solidification

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

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

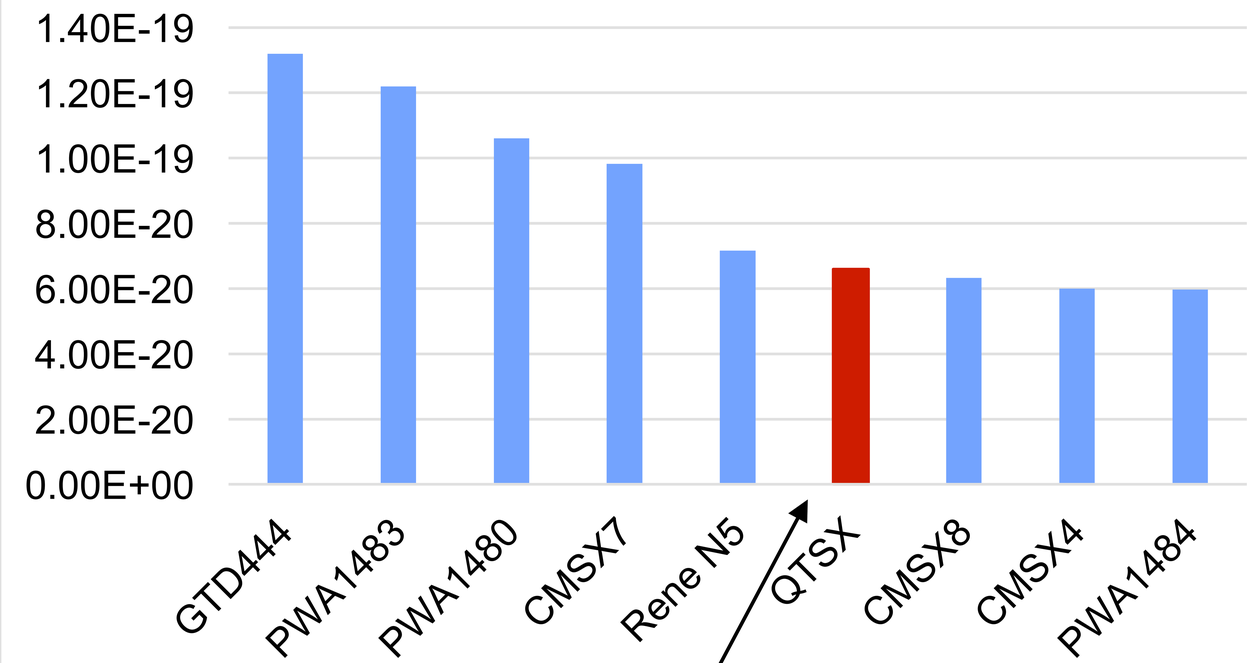


Actual modeling output is a combined use of various databases and software

Coarsen rate and liquid density difference comparisons

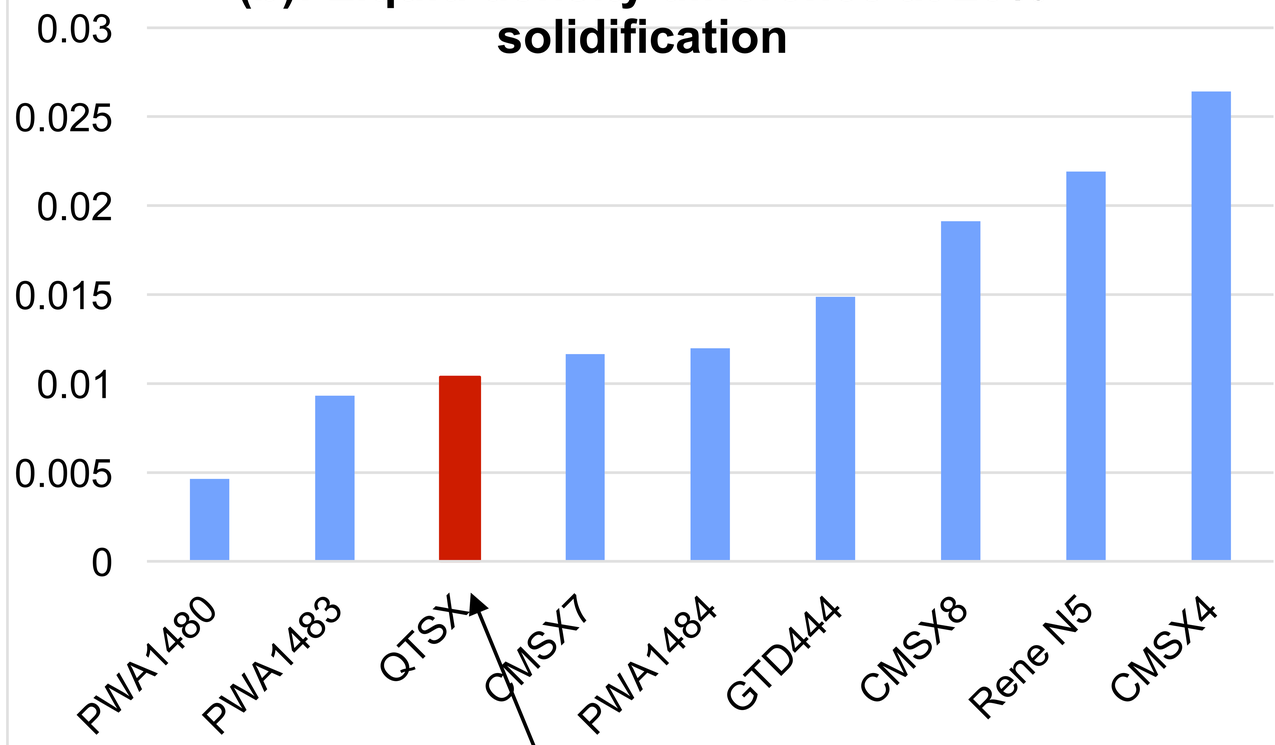
(lower is better)

(a): Coarsening Rate Constant for different alloys



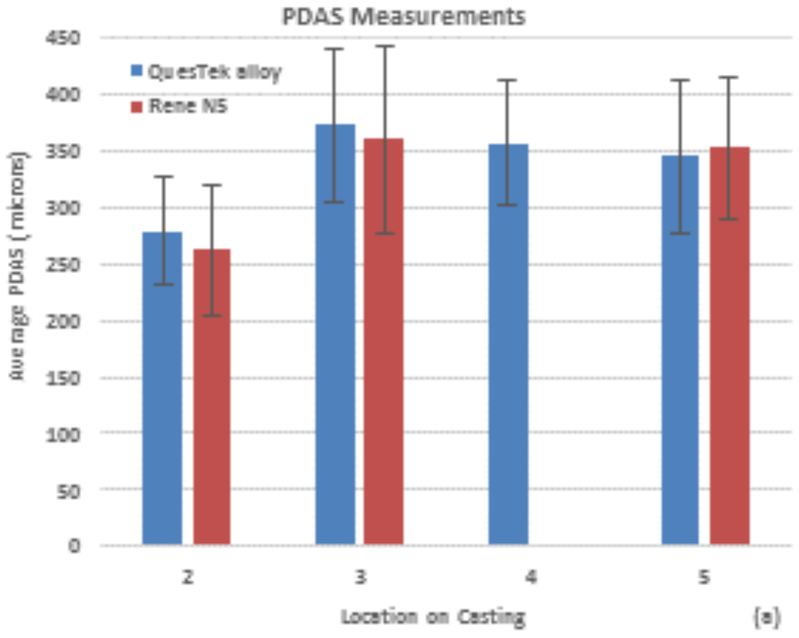
Comparable coarsening rate to CMSX-8 (1.5% Re) alloy

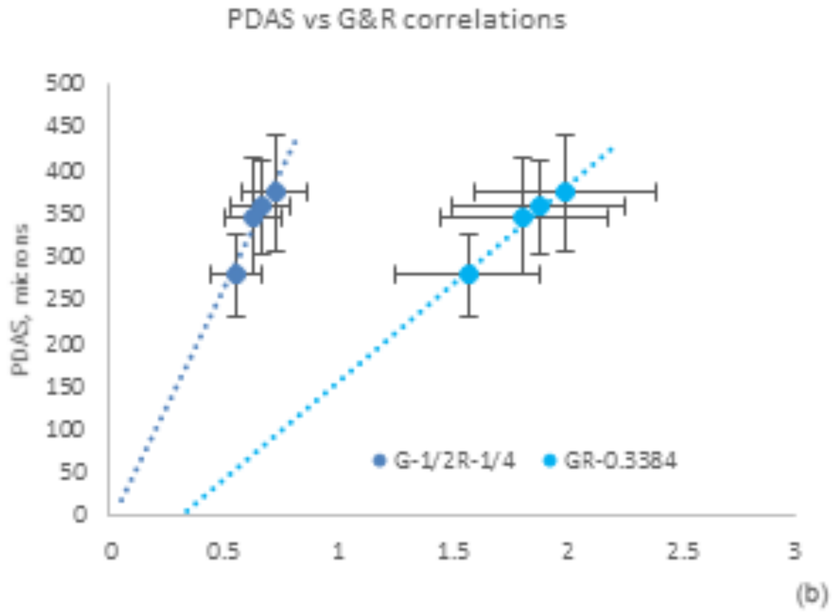
(b): Liquid density difference at 20% solidification

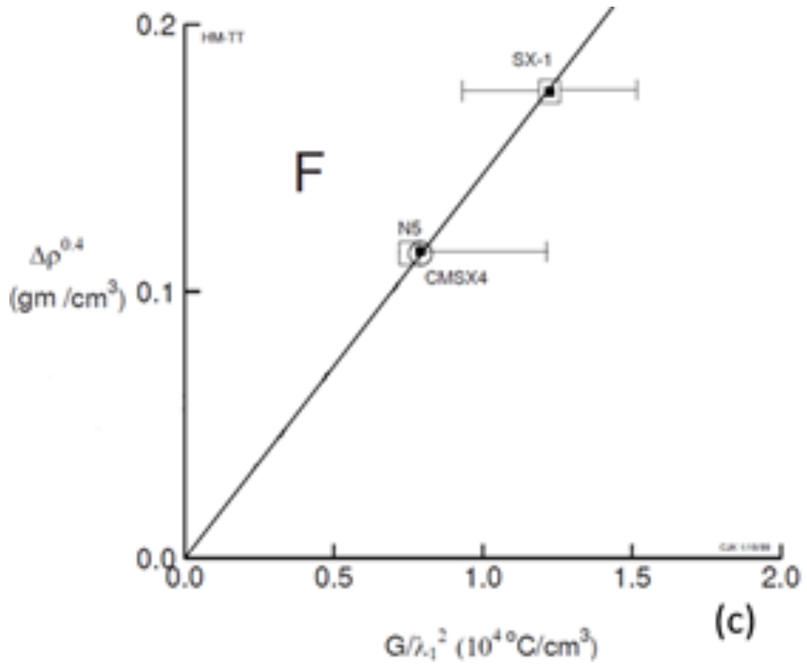


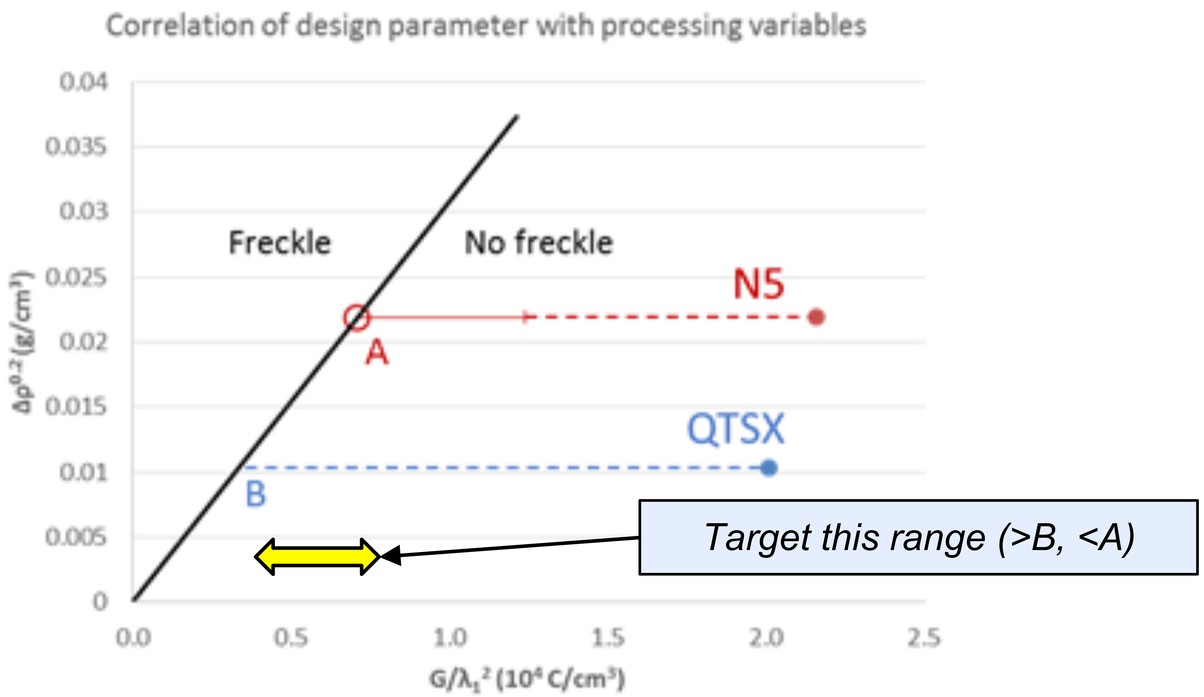
Reduced buoyancy differences (less than non-Re CMSX-7)

Modeling freckling behavior in N5 and QT-SX castings

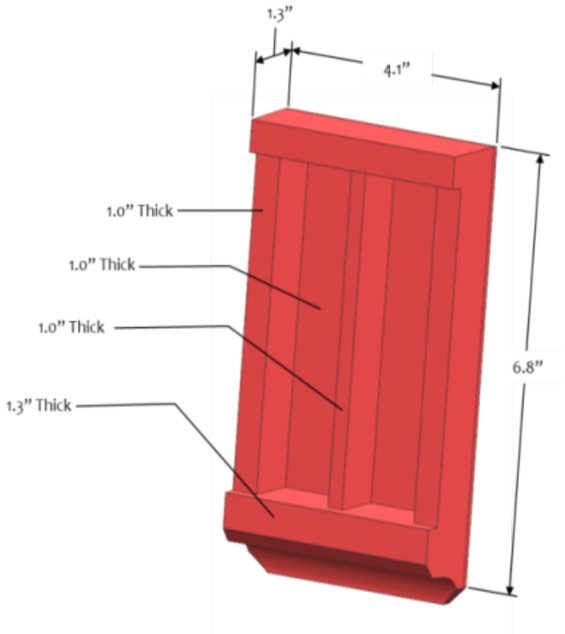


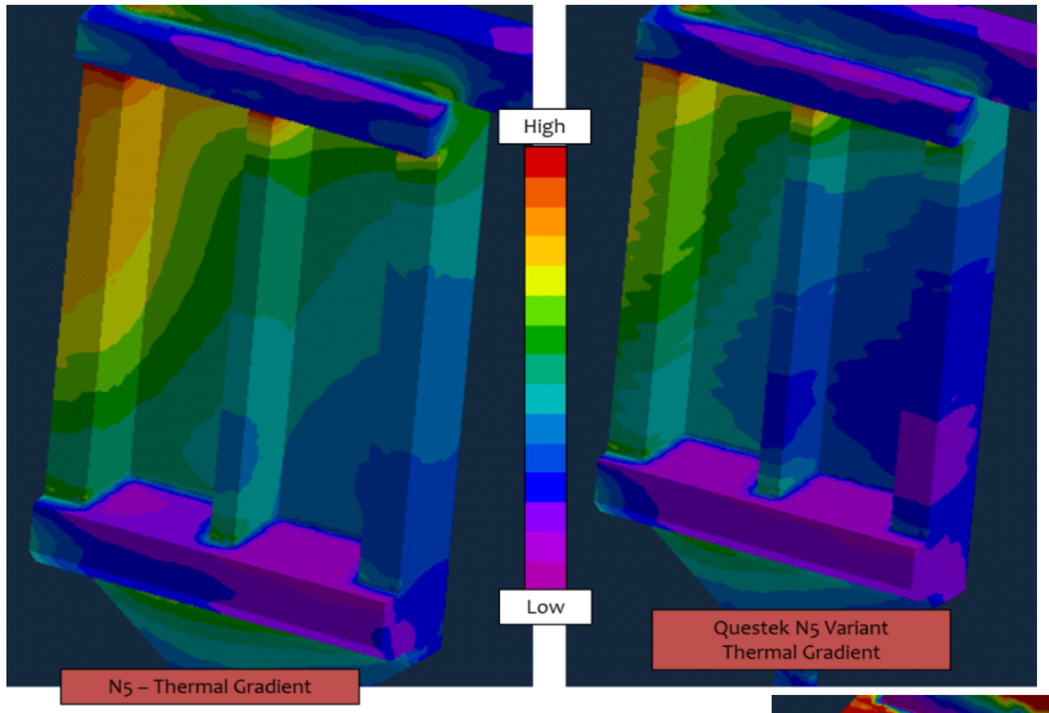


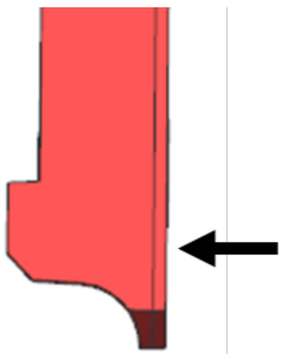




2nd round of casting results

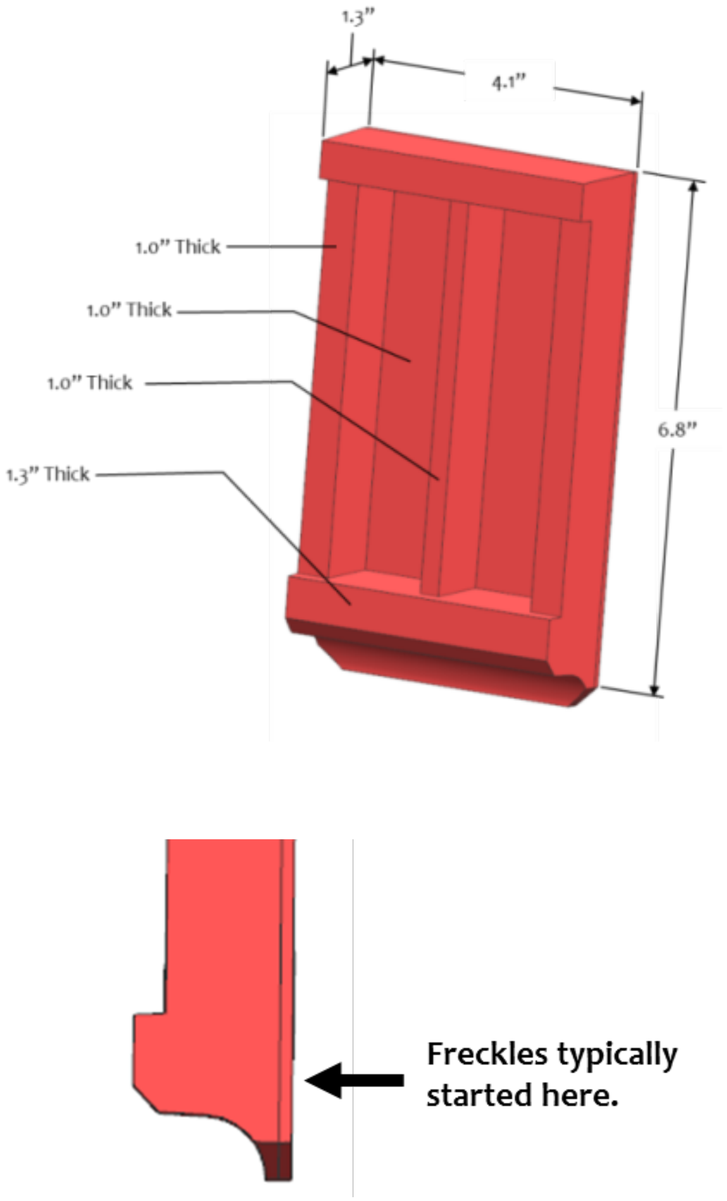


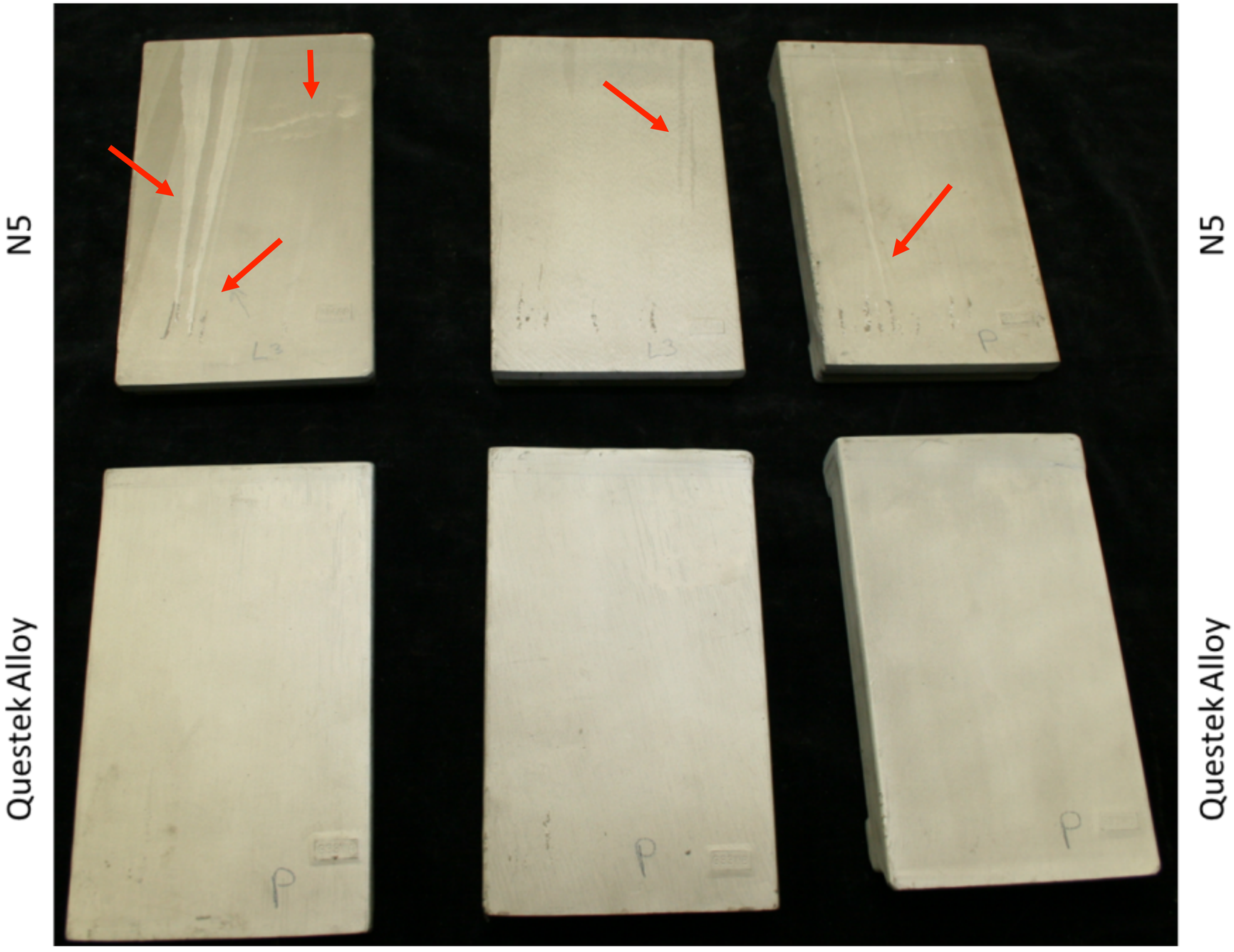




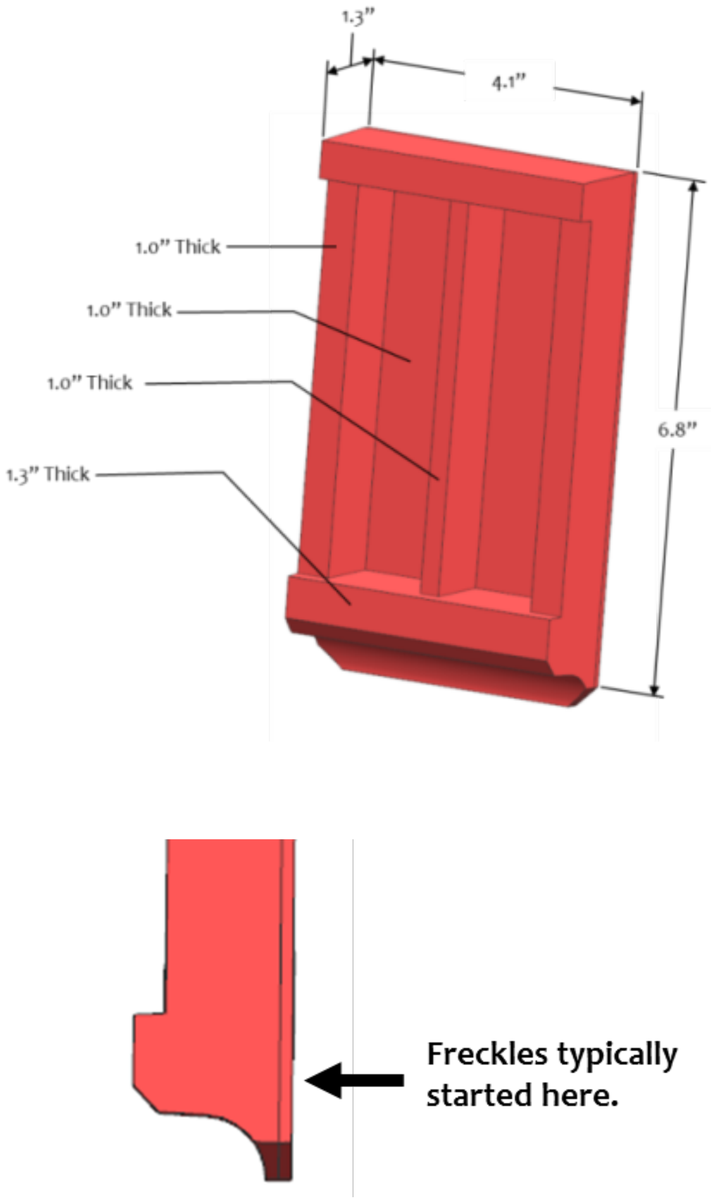
Freckles typically started here.

2nd round of casting results



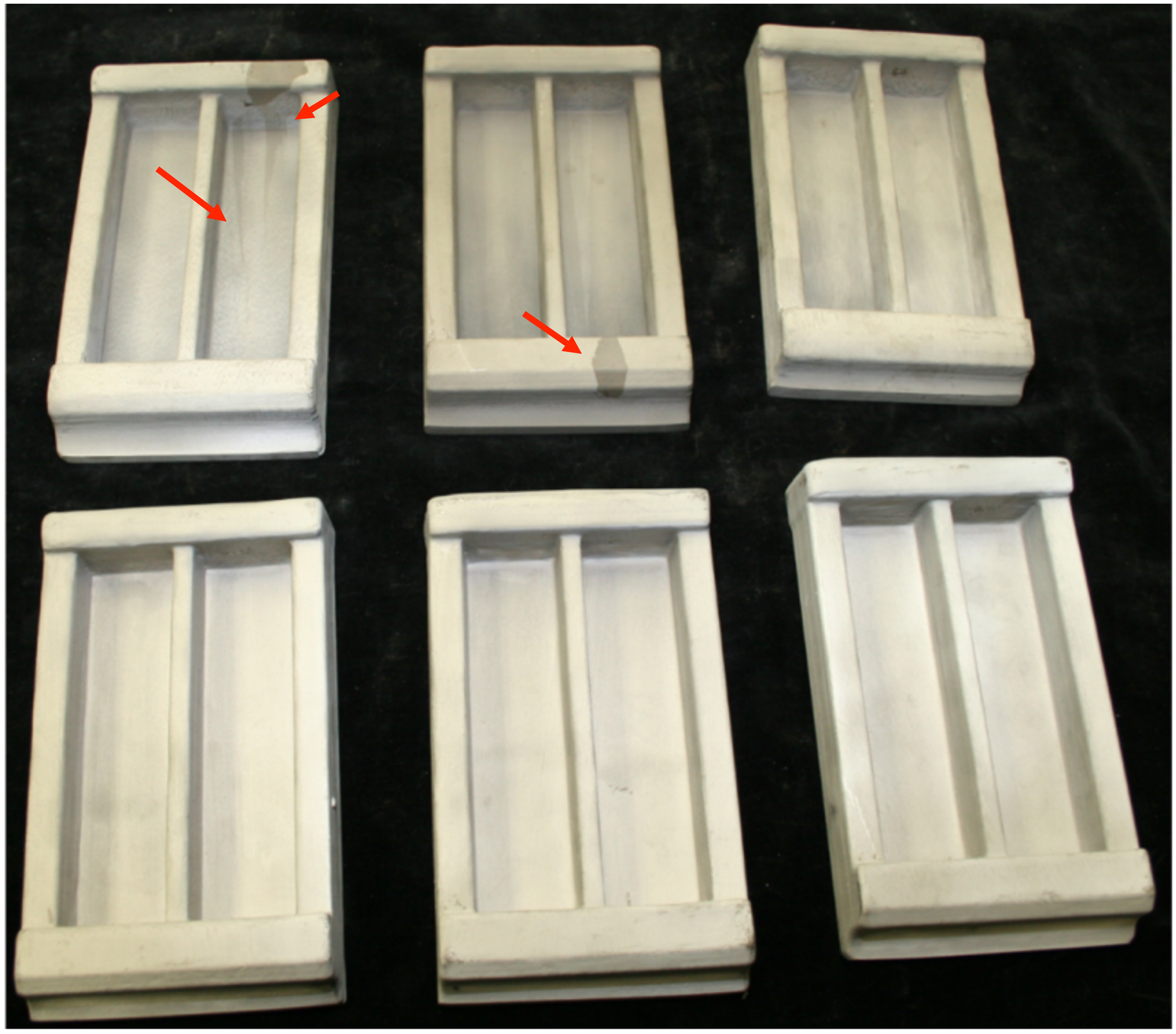


2nd round of casting results



N5

Questek Alloy



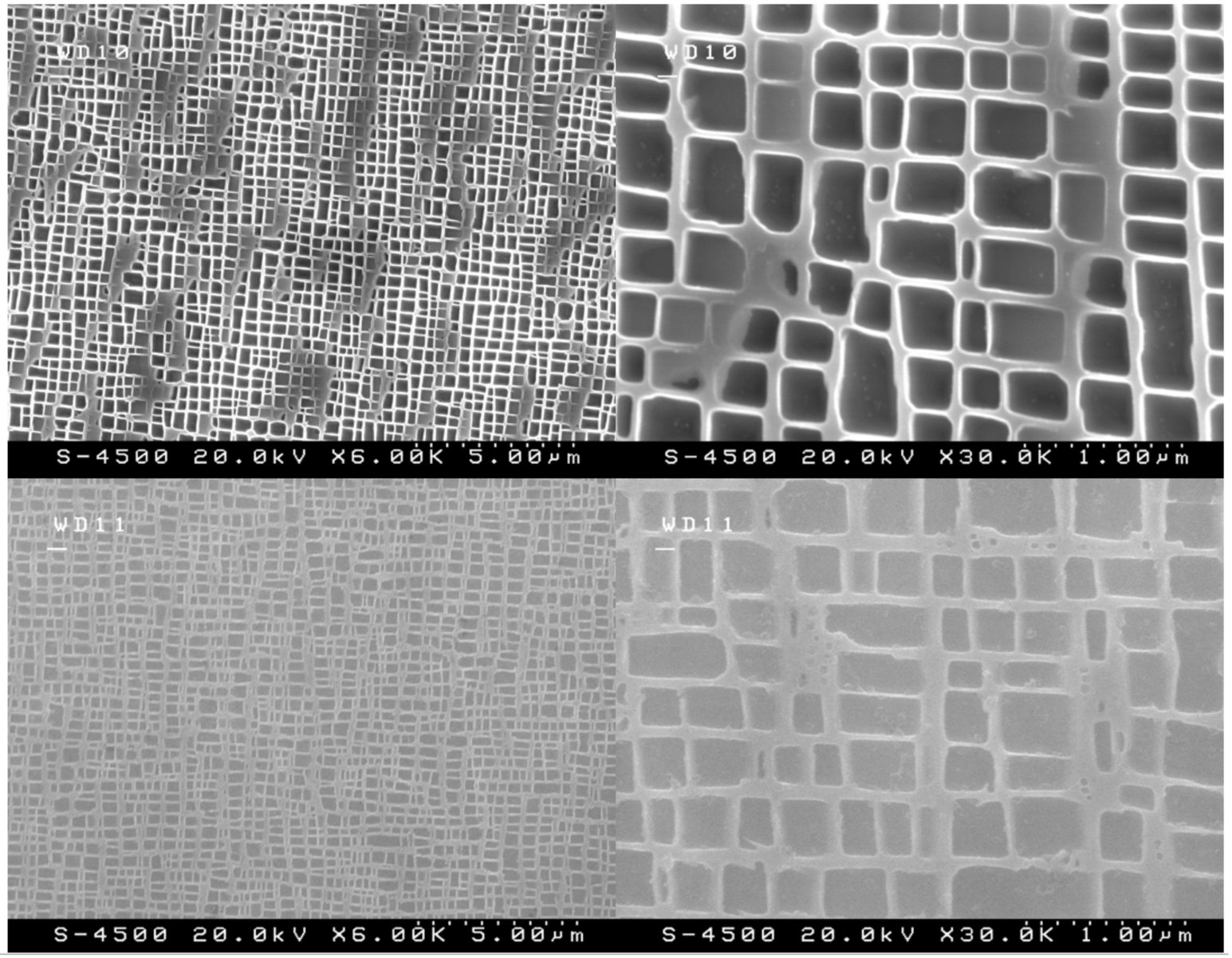
N5

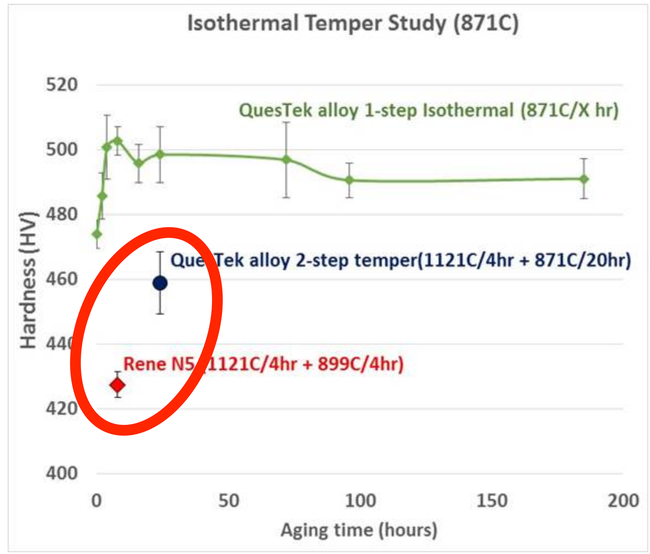
Questek Alloy

Microstructure after double-step aging

QTSX:

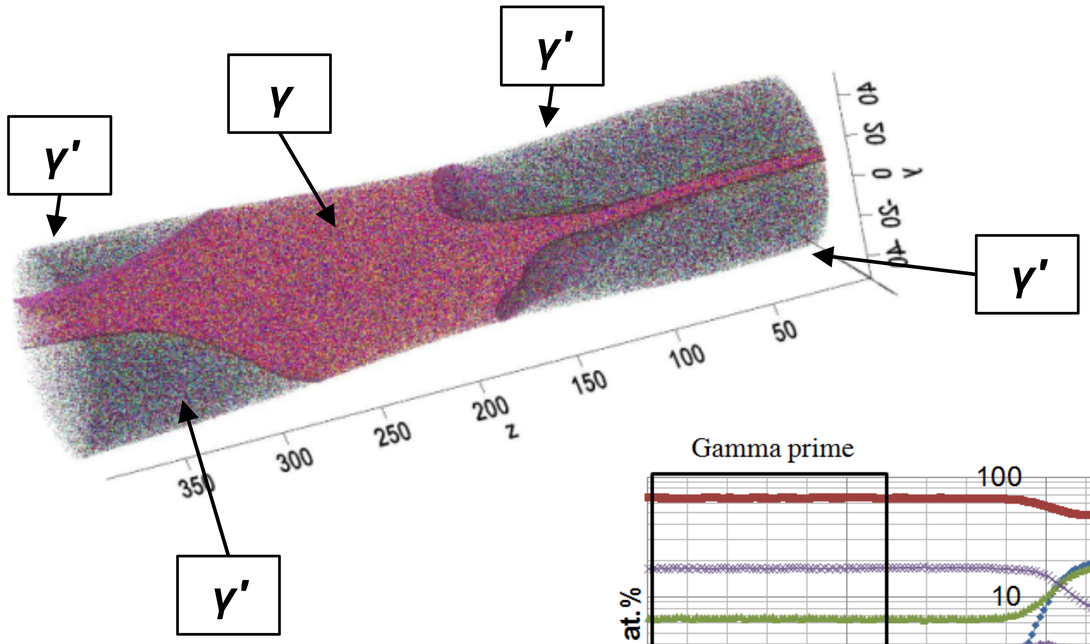
Rene N5:

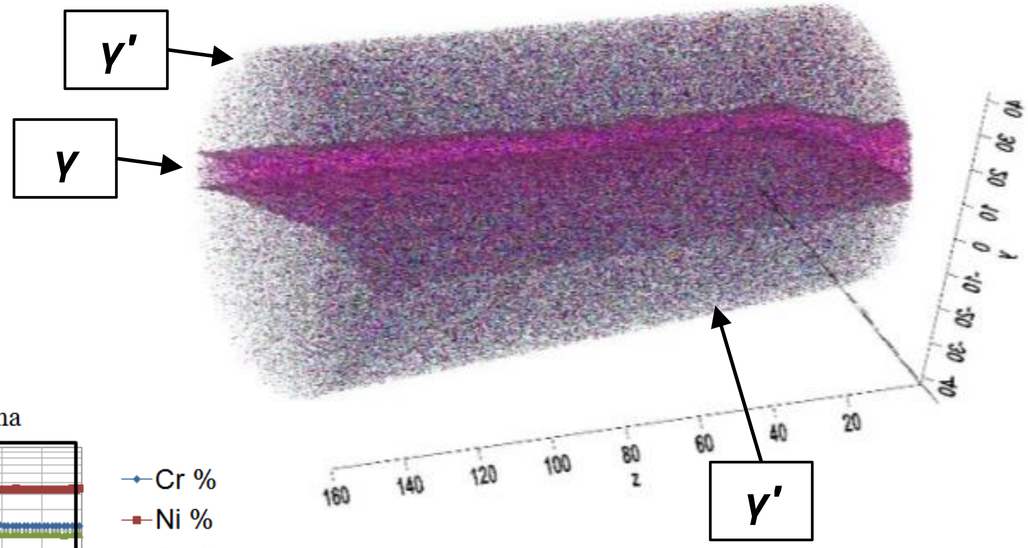


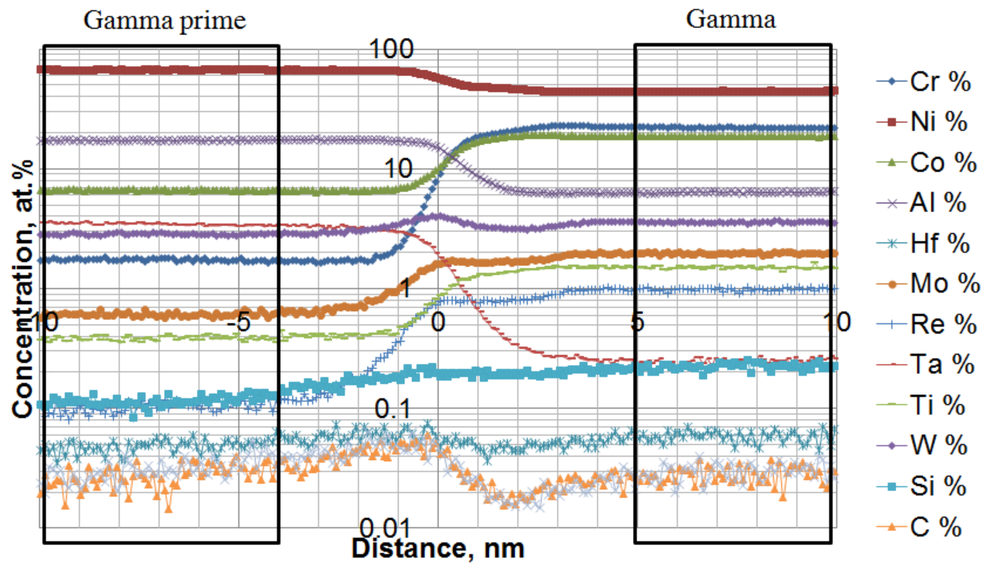


Characterization and microstructure analysis confirm the achievement of the design goal of γ' phase fraction and lattice misfit (no evidence of TCP phases were found during all heat treatments)

Atom-probe (LEAP) analysis of the QTSX nanostructure





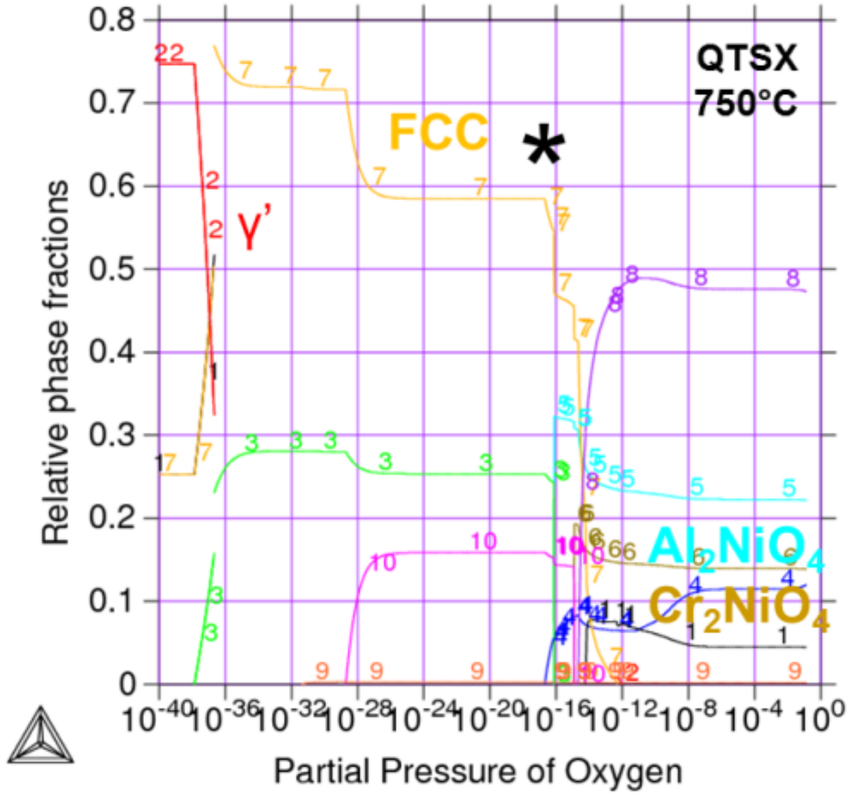


Excellent agreement with predicted compositions (γ' comparisons below)

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

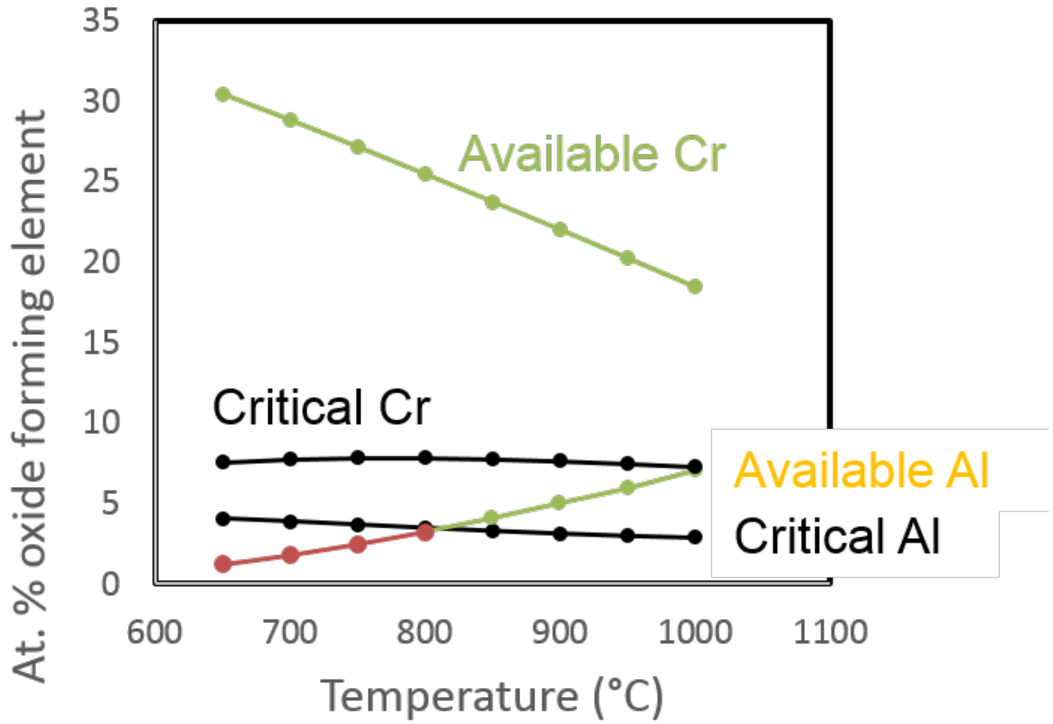
Oxidation modeling

- 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

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

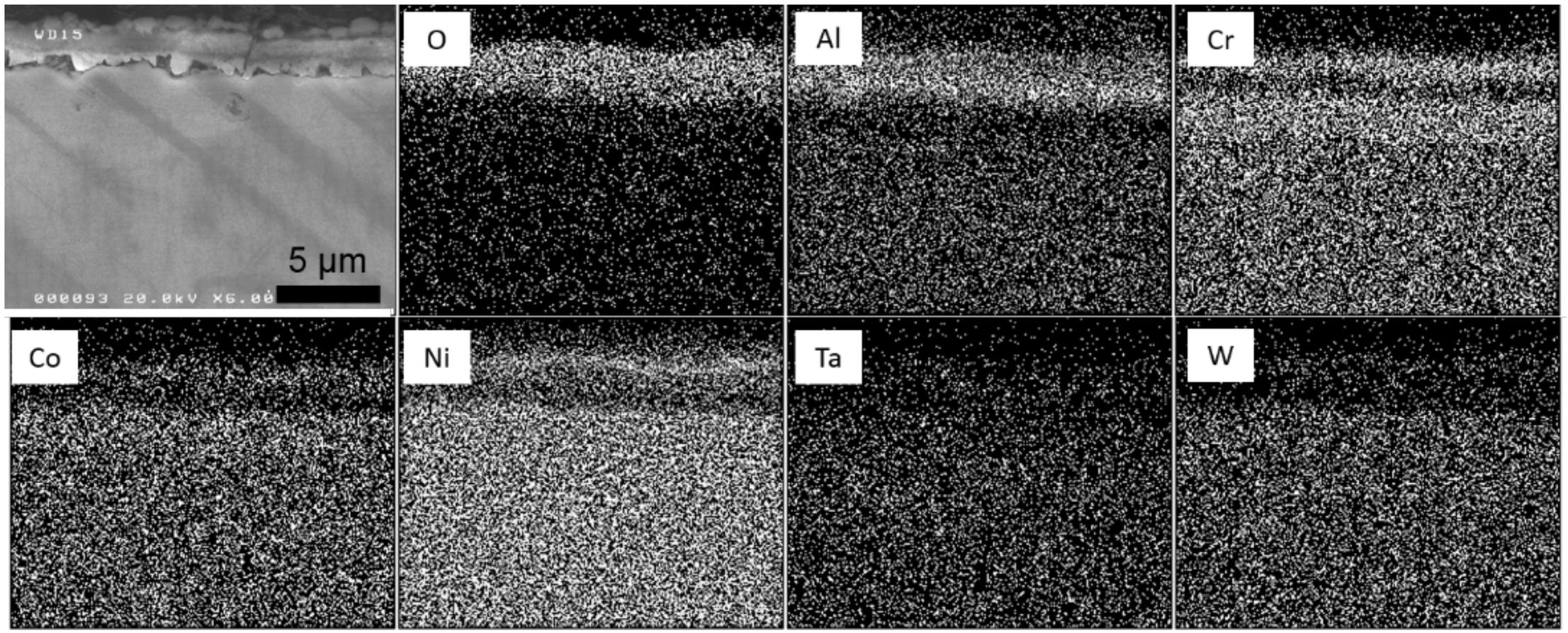


- Both Al_2O_3 and Cr_2O_3 expected to form at high T
- Internal Al_2O_3 expected to form below 850°C

Model agrees well with experimental data for benchmark alloys

Oxide characterization

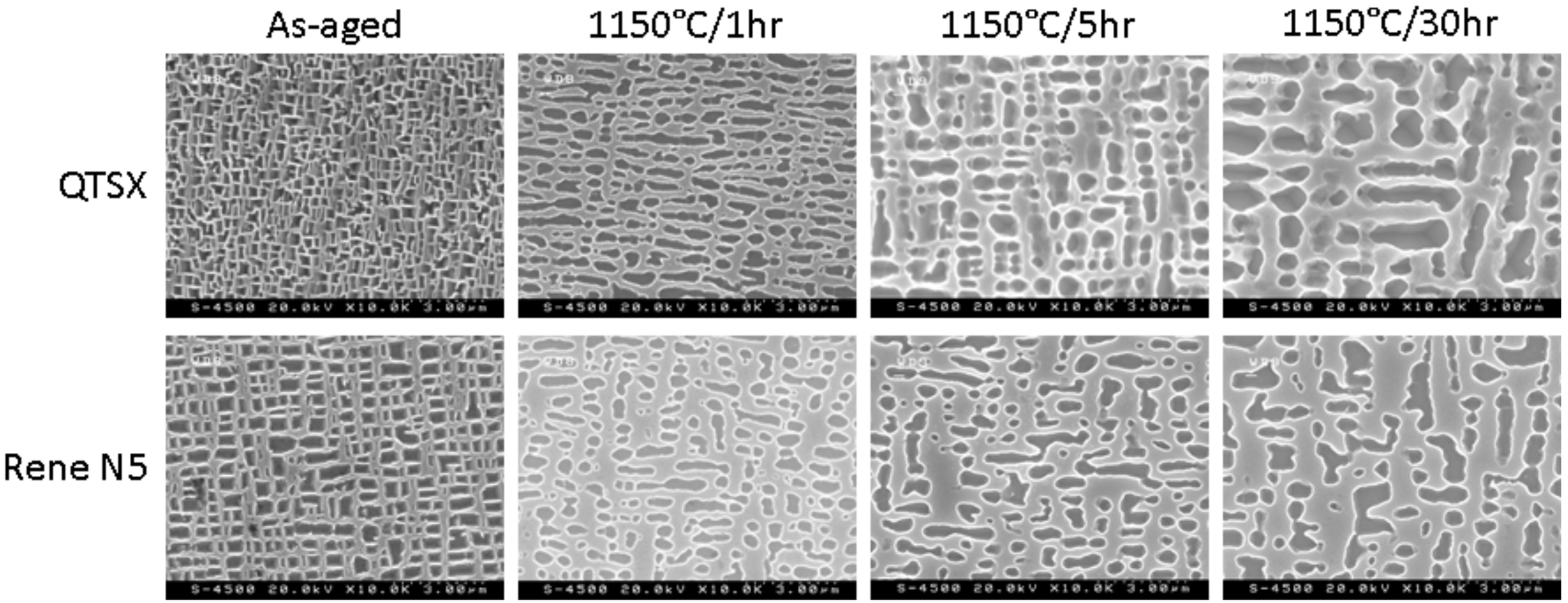
QTSX oxidized in air for 100h at 900°C, 1000°C and 1100°C



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

Continuous Al-rich oxide observed in all samples

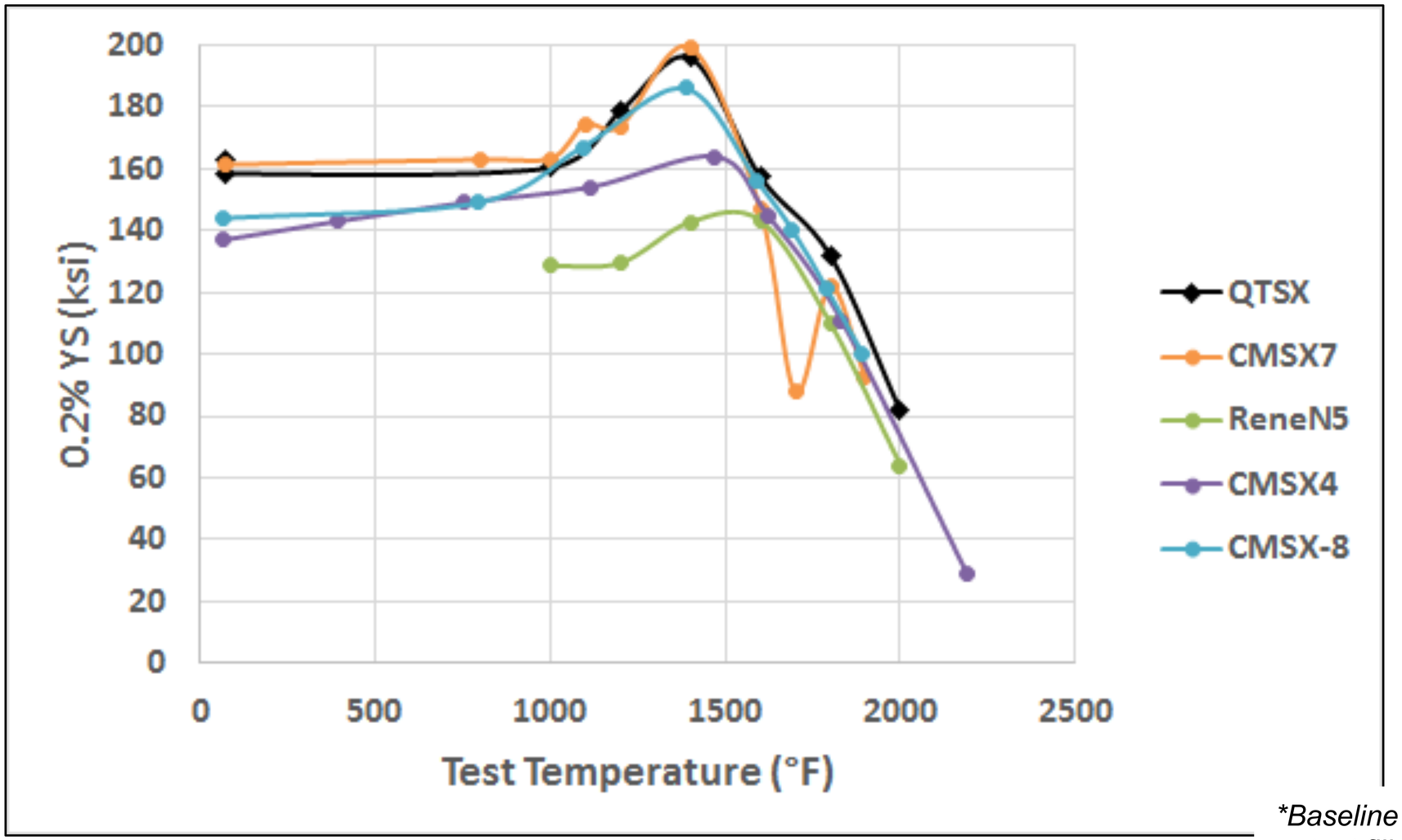
Evolution of <u>microstructures</u> during long-term exposure at elevated temperature



	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**

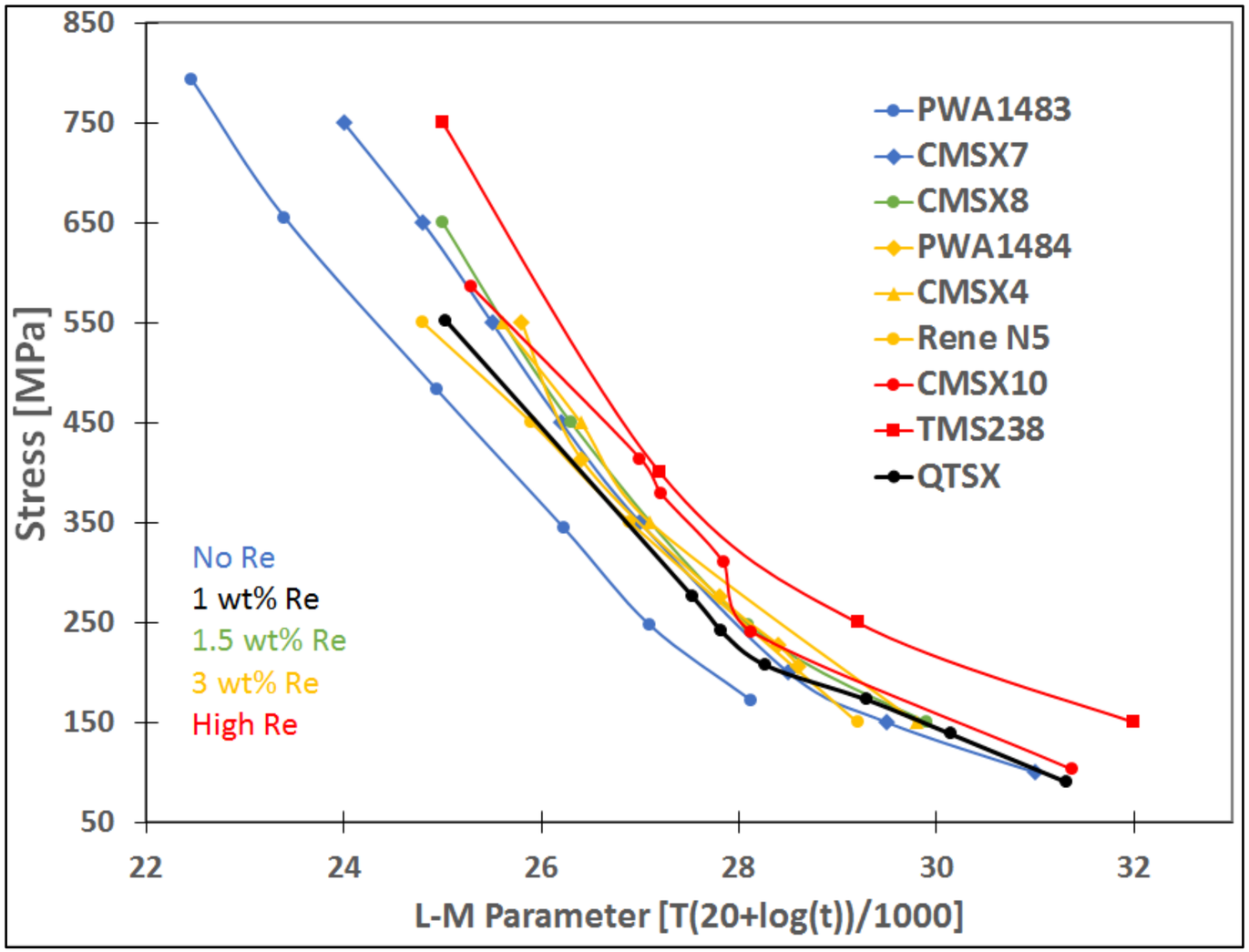


*Baseline data taken from respective patent filings

Stress Rupture Test Results (ASTM E139)

(Phase I Castings)

*Comparison to Select Incumbent SX alloys**



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

Raw Data

ID	Test Temperature (Deg F)	Test Stress (MPa)	Life (hrs)	Elongation (%)
SR1	1600	551.6	76.7	20.6
SR2	1800	275.8	86.6	30
SR3	1800	241.3	147.4	43.8
SR4	1800	206.8	340.6	41.4
SR5	1900	172.4	224.6	43.8
SR6	2000	137.9	119	30.6
SR7	2100	89.6	107.7	24.8

Next Steps

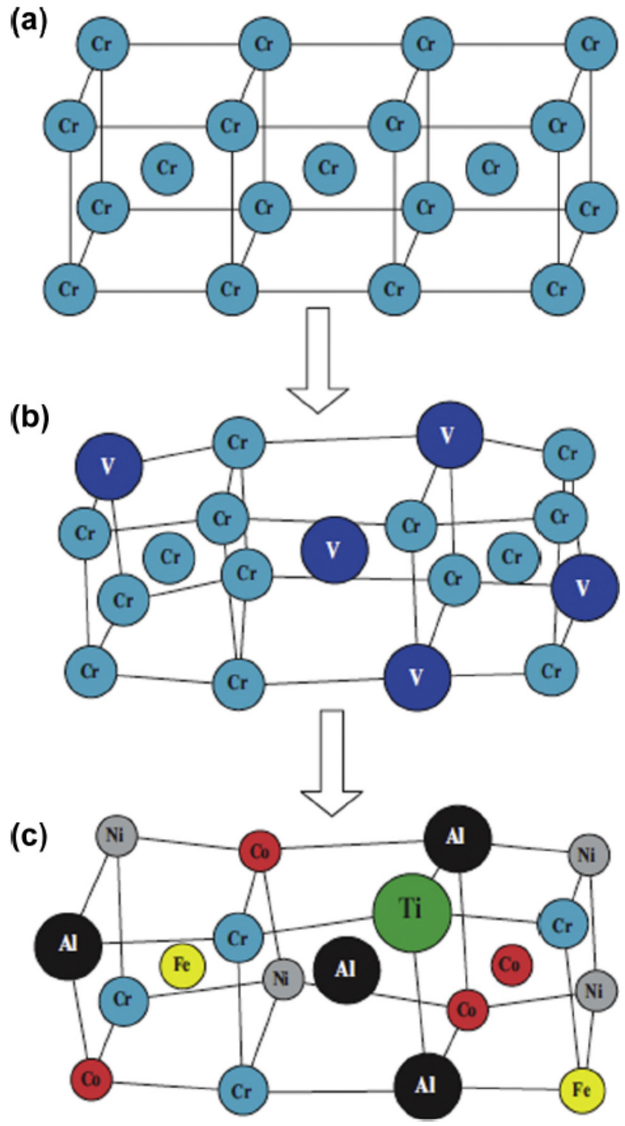
- Second Round of QTSX castings complete
  - Successfully demonstrated improved Freckle resistance over baseline Rene N5

- Extended characterization in progress
  - Detailed heat treatment optimization
  - High temperature tensile
  - Extended stress- and creep-rupture testing
    - *Increase to ~1000hr test duration*
  - Cyclic oxidation testing

Case Study:
Computational High Entropy Alloy Design

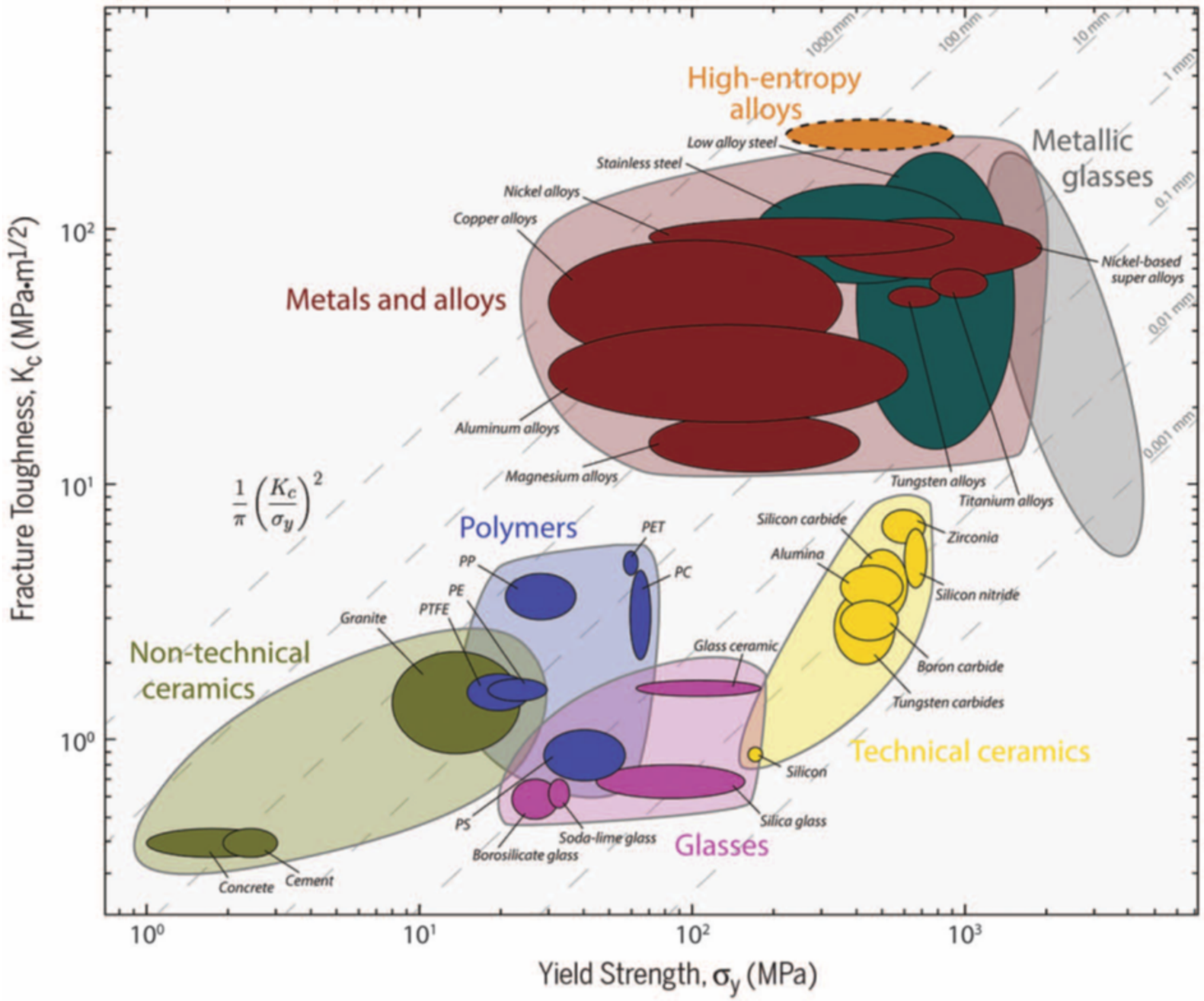
High Entropy Alloys (HEAs)

- High entropy alloys (HEAs) are stable single phase FCC, BCC, or HCP solid solutions at or near equiatomic compositions in multicomponent systems (n>=5)
  - E.g. AlCoCrCuFeNi, CuNiCoZnAlTi, $CoCrFeNiAl_{0.3}$, and YGdTbDyLu
- HEAs are disordered solid solutions



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

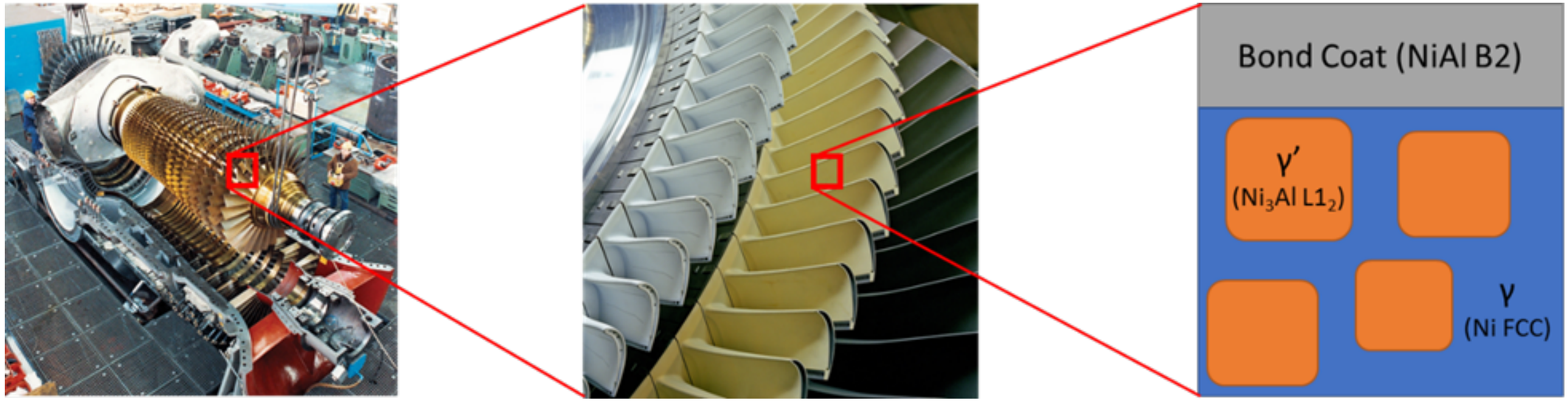
HEA Properties Relative to Other Materials



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

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
- Can also consider entropically stabilized γ' near conventional superalloy compositions
- HEAs have been demonstrated to be made as a single crystal (Bridgman solidification) and an FCC HEA in equilibrium with an $L1_2$

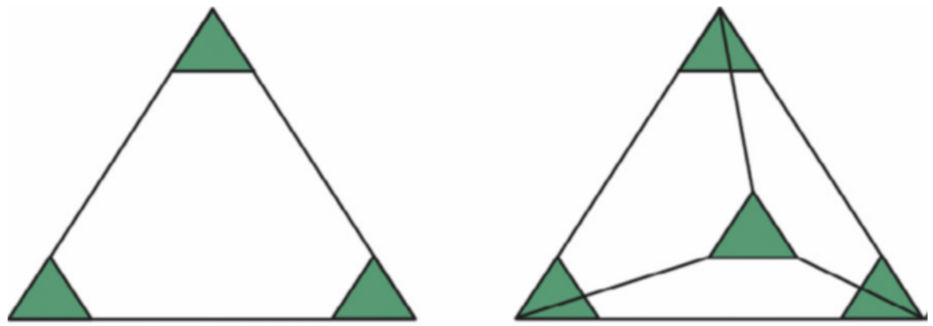


Tsai, Ming-Hung, et al. "Morphology, structure and composition of precipitates in $Al_{0.3}CoCrCu_{0.5}FeNi$ high-entropy alloy." Intermetallics 32 (2013): 329-336.
Ma, S. G., et al. "A successful synthesis of the $CoCrFeNiAl_{0.3}$ single-crystal, high-entropy alloy by bridgman solidification." JOM 65.12 (2013): 1751-1758.

Primary Design Challenge: Poor 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 poor

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

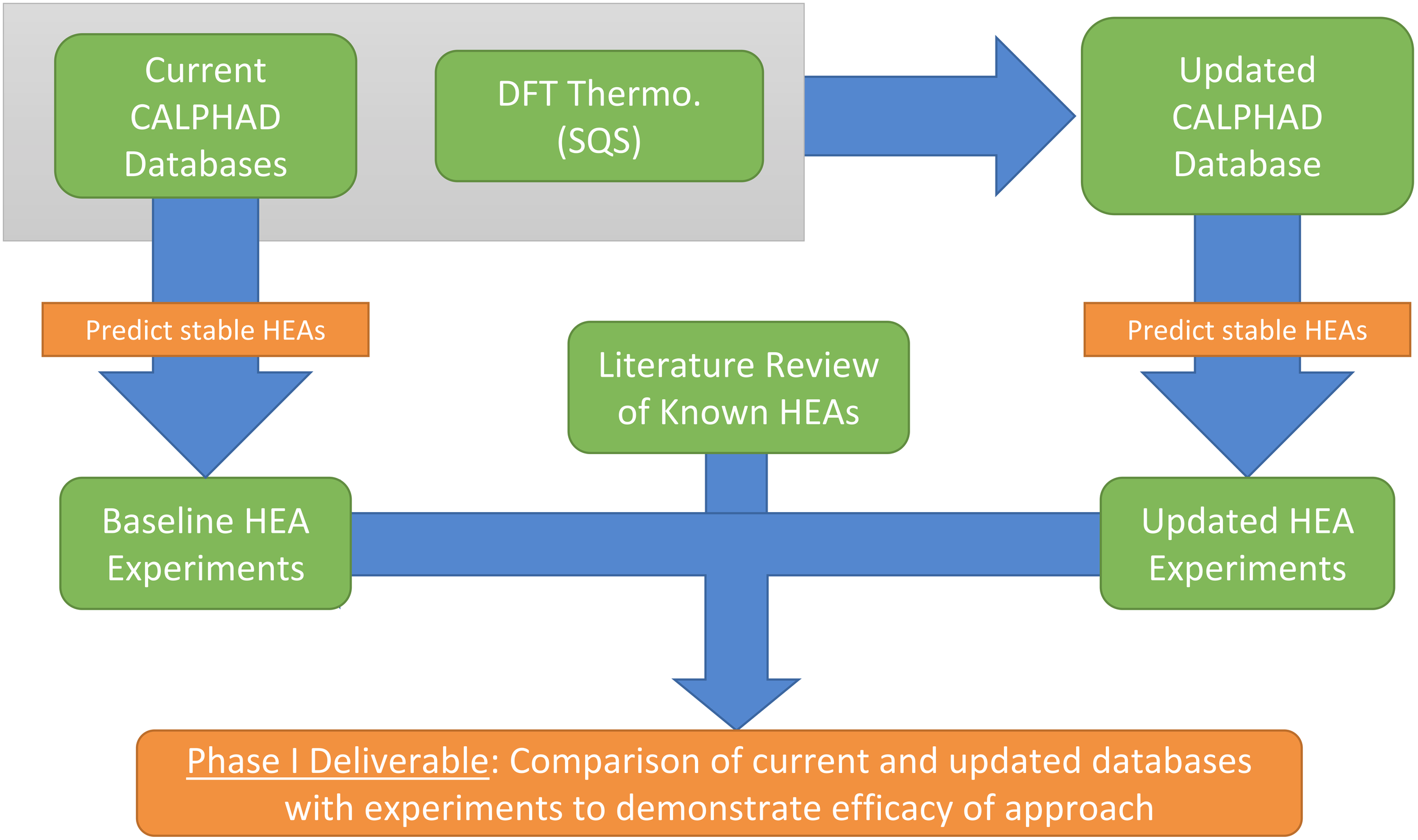


Redlich-Kister polynomial for solid solution mixing energy in CALPHAD

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

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

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



Closing Remarks

- ICME methodologies and tools have been developed and applied to the design of a series of novel alloys for customized properties to meet performance requirement in critical applications in power generation.
- Thermodynamic and kinetic models/databases for multicomponent systems have been developed that enable accelerated materials innovations.
- The successful computational development and implementation of QuesTek's novel alloys validates the ICME approach in genomic data based materials design.
- Recent application of ICME methodologies in the design and development of advanced alloys for energy applications demonstrates improved efficiency and accuracy in optimization and qualification, helping to accelerate the maturation of the novel materials in various systems.

BACKUP

Present alloys: SAVE12 and P92

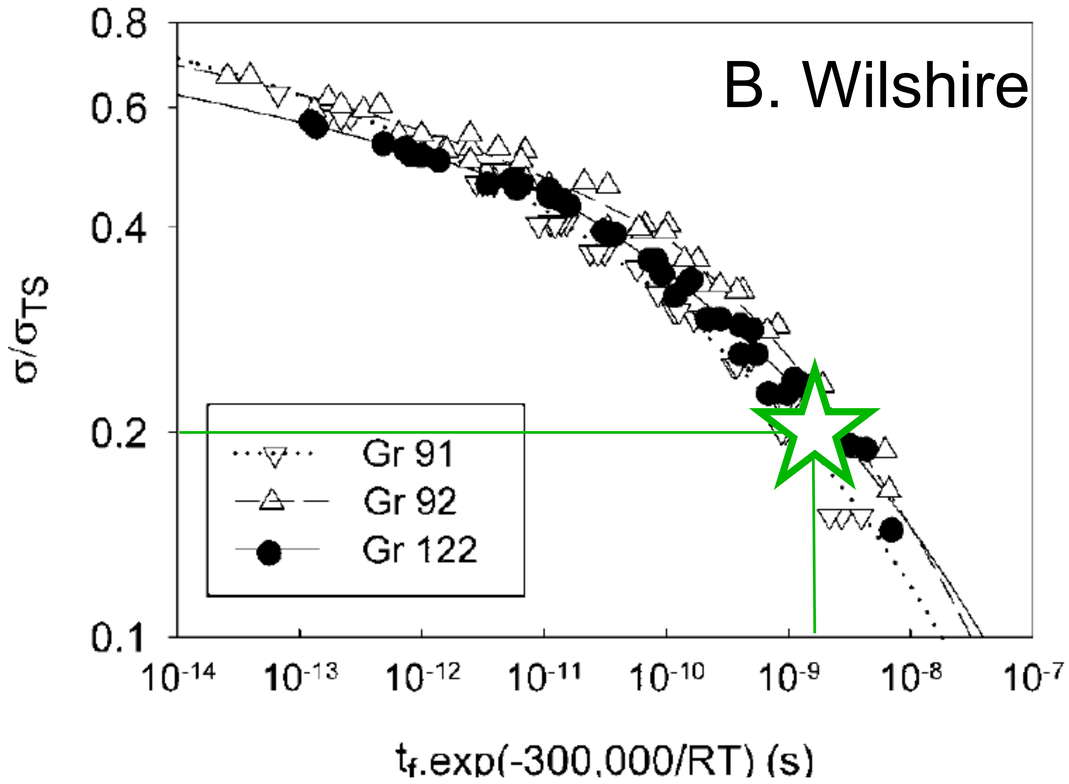
- **Target: 732/760°C**(1350/1400°F) and 35 MPa (5000 psig)
  - This design would be capable of achieving **a net plant efficiency of 45.5% HHV based on US design practice** and as high as **50.5%** when expressed in European format with alternative European boundary conditions
- Current SAVE12 and P92 has operating temperatures to about 620°C

Table 1 - **The typical compositions of SAVE12 and P92 wt%.**

Alloy	Cr	Ni	Mo	W	V	Nb	Mn	Ta	Co	Si	C	N
SAVE12	11	0.6	--	3	0.2	0.07	0.2	0.07	3.0	0.3	0.01	0.04
P92	8.75	0.3	0.45	1.9	0.2	0.06	0.5	--	--	<0.5	0.09	0.06

High temperature tensile strength and creep resistance

- High temperature ultimate tensile strength is shown to be a good predictor for creep behavior beyond t_f<30,000hrs
- To achieve 100,000 hours of creep life at 650°C, **Target σ_{UTS}(650°C) = 400 MPa**
- In comparison, P92 σ_{UTS}(650°C) is measured at 260 MPa.

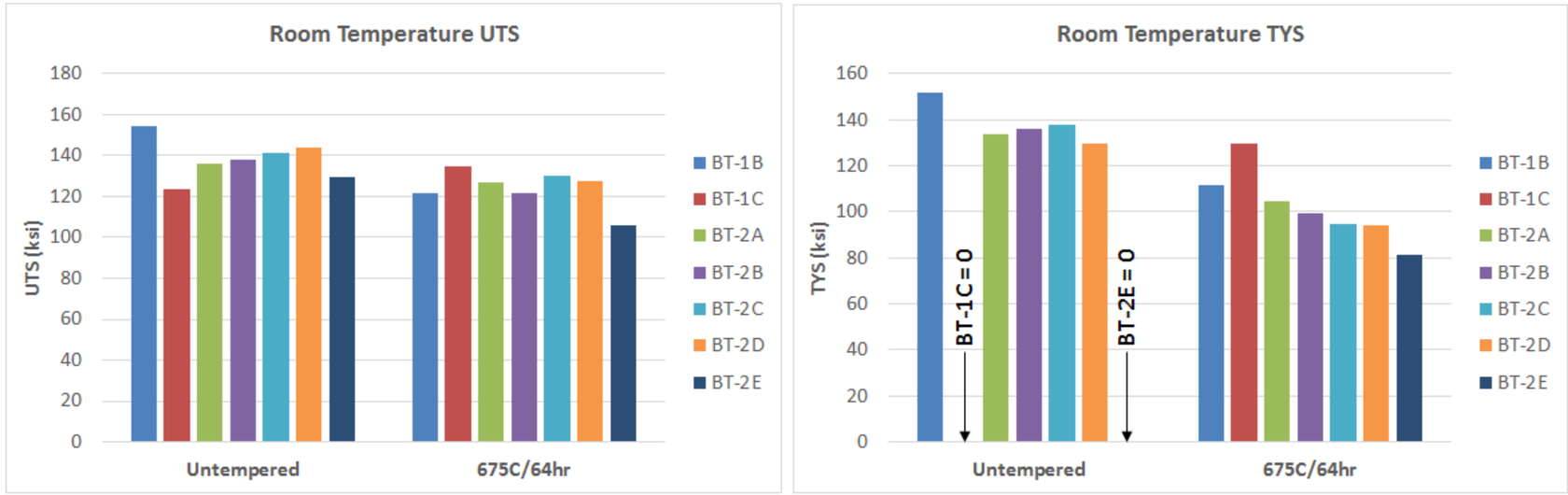


$$\left(\frac{\sigma(T)}{\sigma_{UTS}(T)}\right) = \exp\{-30.62[t_f \exp(\frac{-300{,}000}{RT})]^{0.15}\}$$

QuesTek's prototype achieved σ_{UTS}(650°C) at 360-405 MPa

Phase II prototype results

- Tensile properties in untempered condition and after long term exposure at 675°C



BT-2C and BT-2D possess excellent RT ductility, with minimal sacrifice in strength and strength retention over Phase I alloys