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RAPID DESIGN OF COST-EFFECTIVE REFRACTORY HIGH ENTROPY ALLOYS STRENGTHENED BY PRECIPITATION

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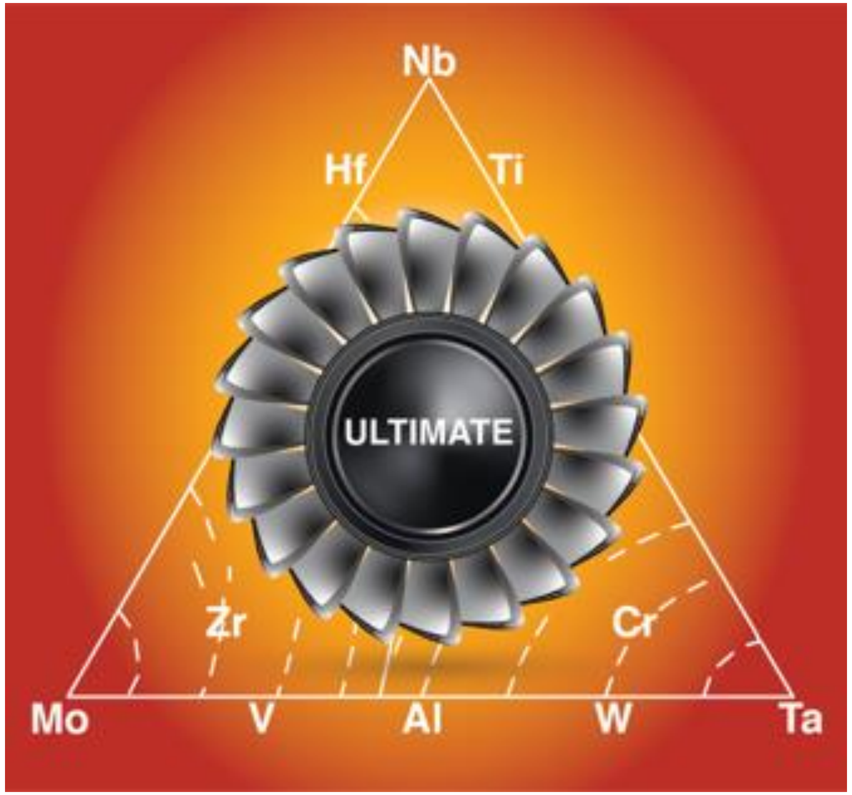

Project Overview: Target Properties

Phase I	
Properties	Project target
Creep	Creep strain <2% at 200 MPa after 100 hours
Ductility	RT elongation >1.5%
Fracture toughness	>10 MPa·$m^{1/2}$ at RT
Manufacturability	with <0.1mm in variation among five tensile bars manufactured specified to the appropriate ASTM E8/E8M standard.
Phase II	
Yield stress at 1300℃	>400 MPa
Solidus Temperature	≥1500℃
Density	≤9.0 g/cm^3
Thermal conductivity	9-12 W/mK at RT; >24 W/mK at 1300℃;
CTE from RT to 1300℃	<2%
Thermo-mechanical fatigue	>1000 cycles at 0.45% strain and R=-1 between 100-1300℃
Creep	Coated samples retain creep strength (at 1300℃ under 200MPa for 100 hours) after exposure to air at 1700℃ for 100 hours
Manufacturability	A generic turbine with dimensions between 3 and 6 inches with internal cool channels with critical dimensional variation < 1% among three samples.

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Technical Approach

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- Computationally interrogate key parameters
- Specify compositional **range** for alloy(s)

Thermo-physical

- liquidus and solidus temperatures
- phase composition and mole fraction
- density
- materials cost

CALPHAD

Intrinsic ductility

- shear instability
- VEC
- ΔE_B
- Phase transformation
- Grain boundary cohesion

DFT, ML

Yield strength

- solid solution
- precipitation
- grain refinement
- short range order
- temperature effect

MCMD, DFT, validated models

Oxidation resistance

- oxygen diffusivity
- oxygen solubility
- composition gradient to promote forming □-Al_2O_3 scale

AIMD, DFT, CALPHAD, FEM

Manufacturing ability

- minimize cracking
- reduce solidification range
- suppress ductile to brittle transition

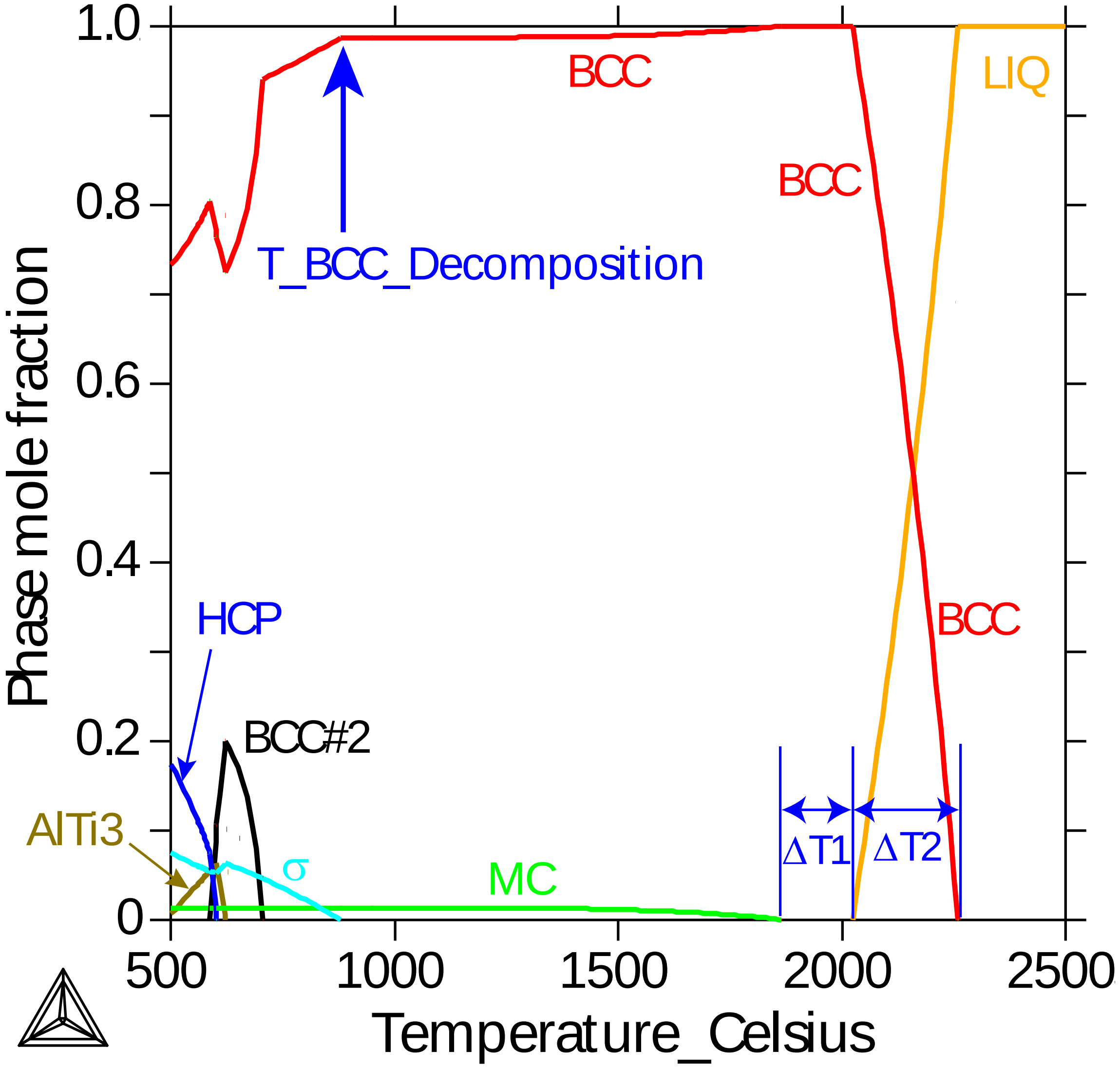
Validated models, CALPHAD

- Arc melted buttons (250g)
- Structure & property assessment
- ***Simulate AM build.*** *Single & multi-pass beam scanning of the surface to assess effect of solidification rate on cracking, segregation and precipitate formation*

- Direct Energy Deposition DED-AM
- Design of Experiments to **interrogate processing parameters** (laser power, powder flow & velocity) on the build.

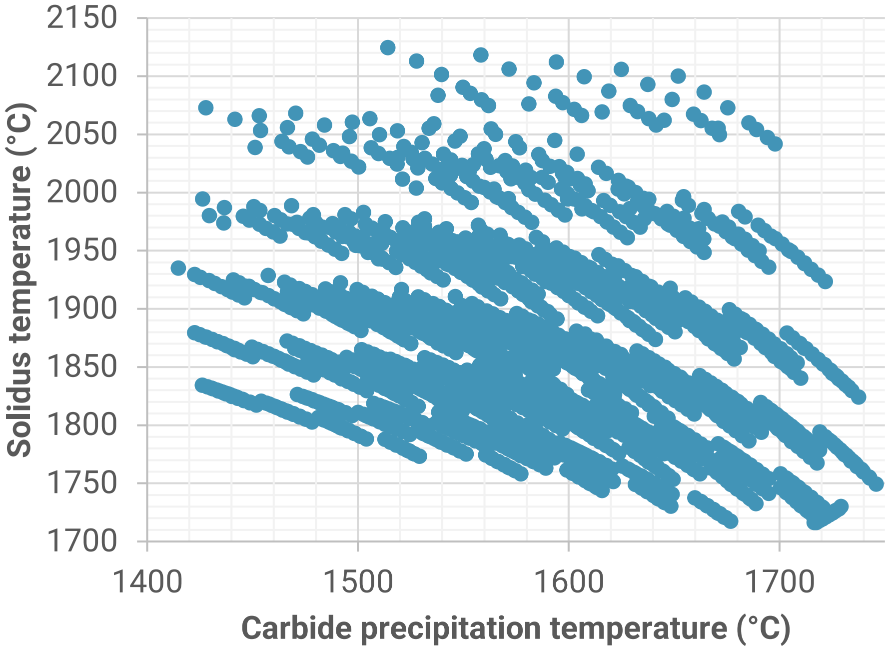
Technical Approach

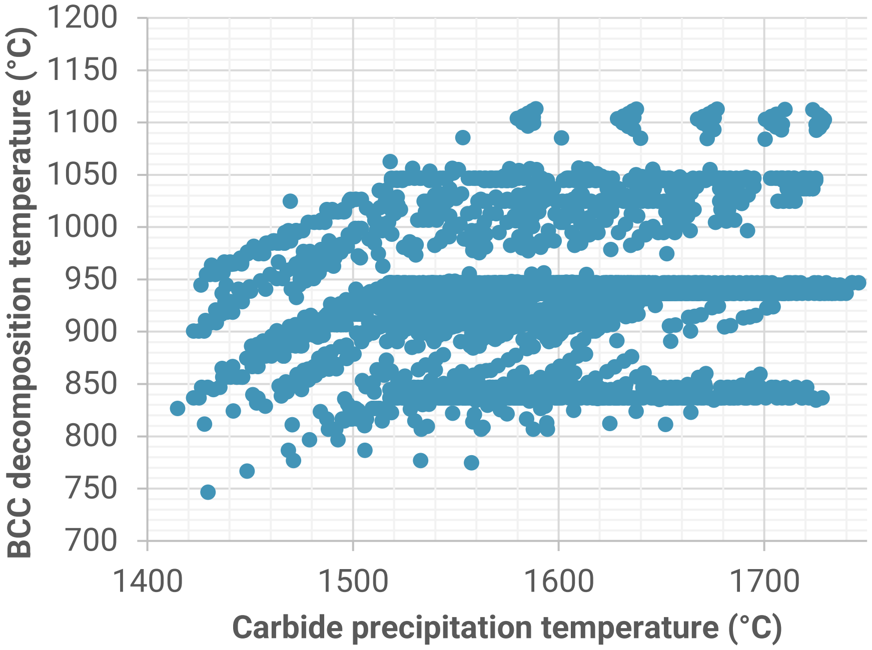
Element	Function
Nb, V, Ti	Provide for low density and high ductility
Nb, Ta, Zr, Hf, Ti, C	MC carbide formers for precipitation strengthening at elevated temperatures
Ta, Mo, V, W	Provide for solid solution strengthening. Increase melting temperature. BCC stabilizers
Ti, Zr, Hf	Increase intrinsic alloy ductility & solid solution strengthening Promote toughness through phase transformation induced ductility
Al, Cr	Increase oxidation resistance Enhance bulk alloy environmental resistance and compatibility with environmental barrier systems.



Alloy Design: High Throughput CALPHAD

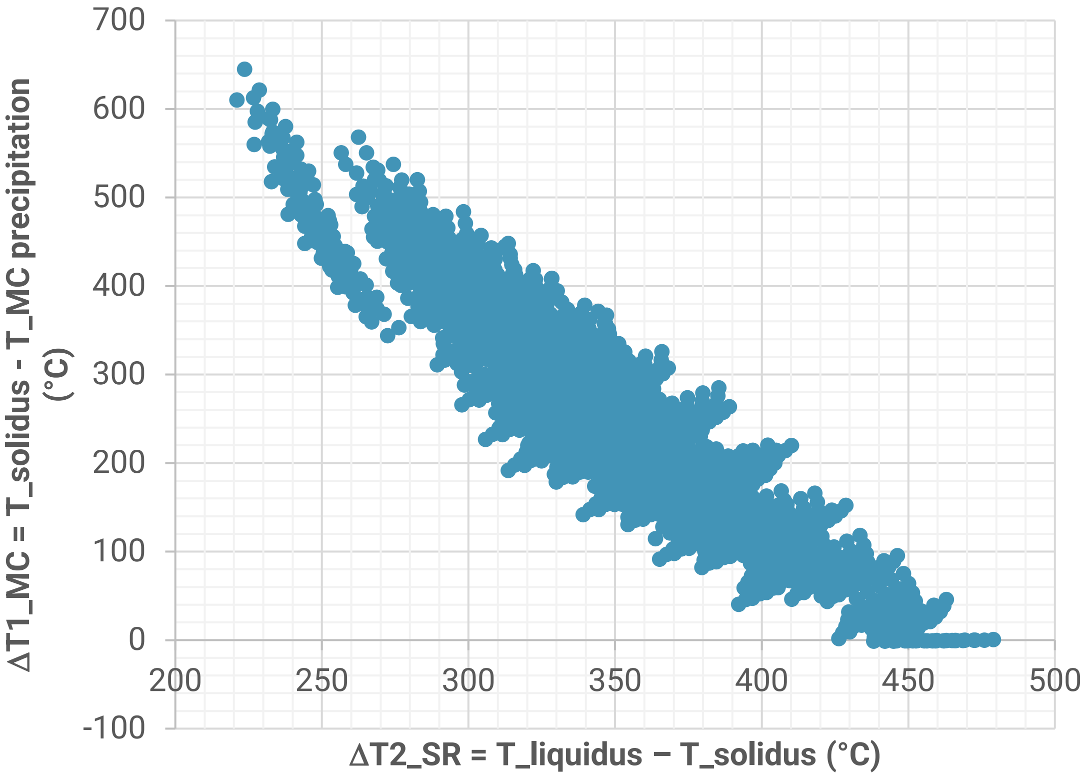
- Alloys: Nb-Ti-Ta-Mo-V-Zr-Hf-Cr-W-Al-C system
- HT CALPHAD: ThermoCalc TCNI8 database
  - Screening criteria: T_solidus ≥ 1800C, T_MC precipitation ≥ 1400C, T_decomposition ≤ 1000C, density ≤ 9.5 g/cm^3, price ≤ $115/kg (C103).



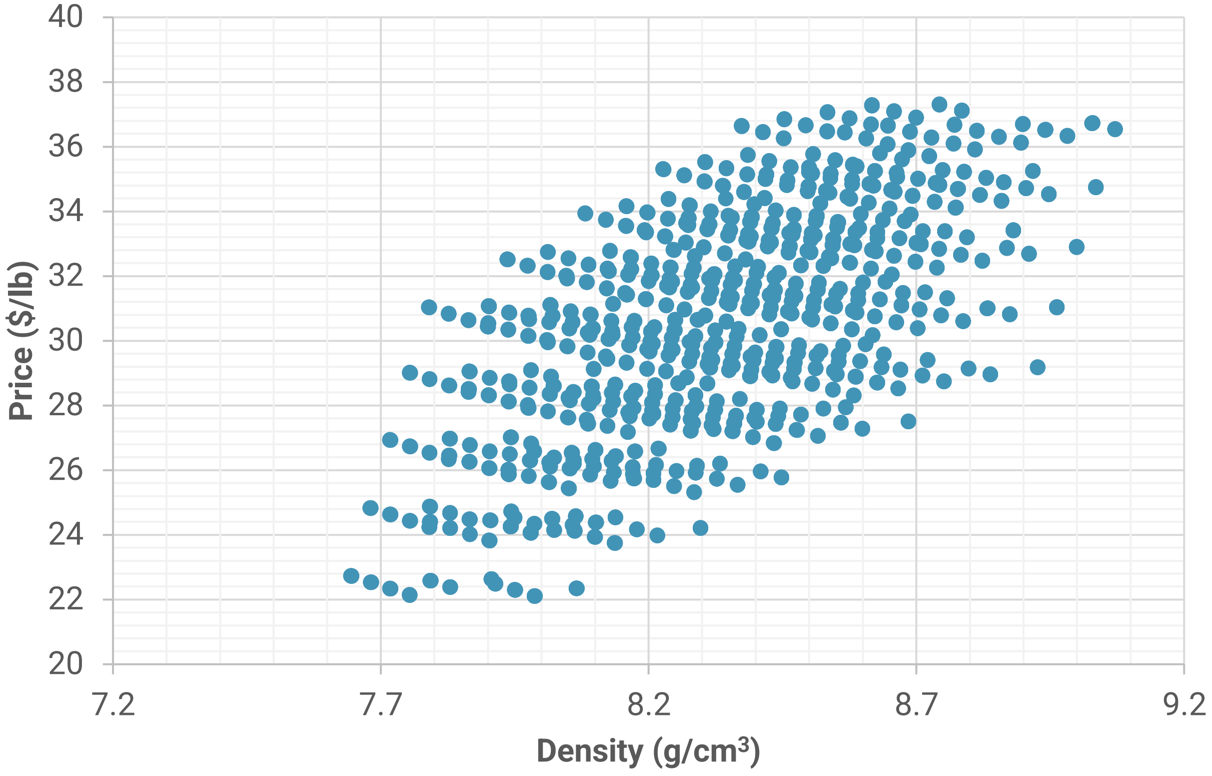


Alloy Design Details: HT CALPHAD

- ΔT2= T_liquidus – T_solidus; ΔT1 = T_solidus - T_MC precipitation



Solidification range vs BCC stability range



Materials cost vs density

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High Throughput Materials Design

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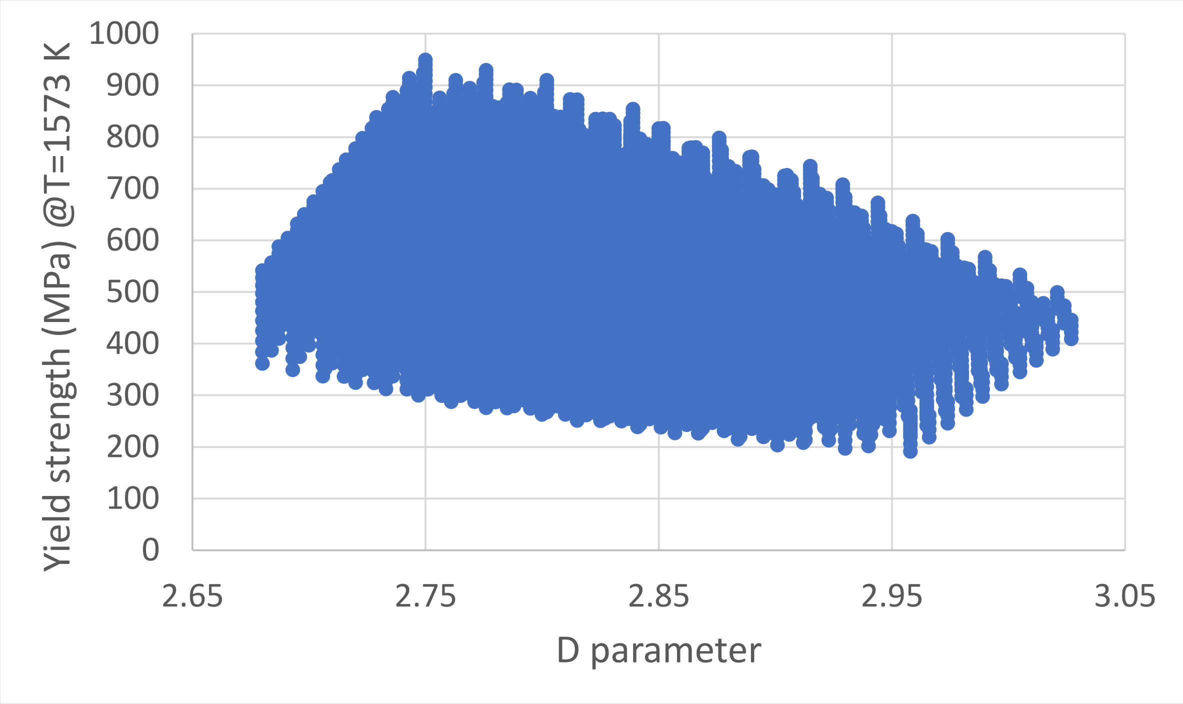

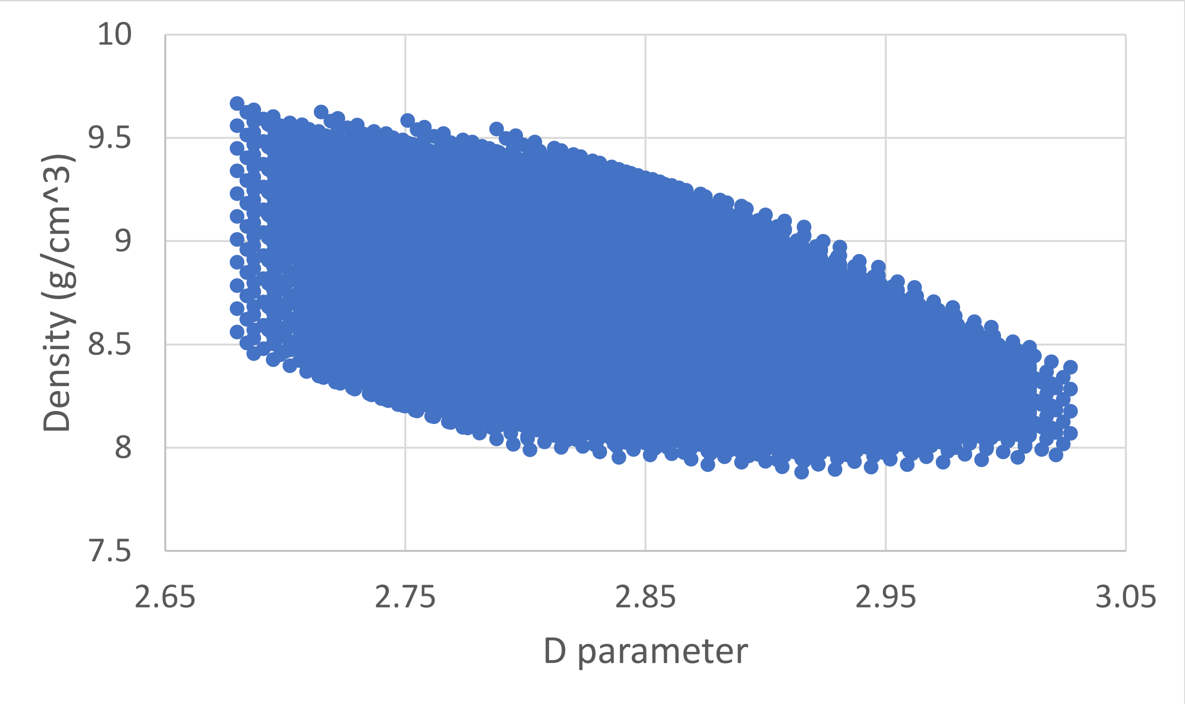

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High Throughput Materials Design

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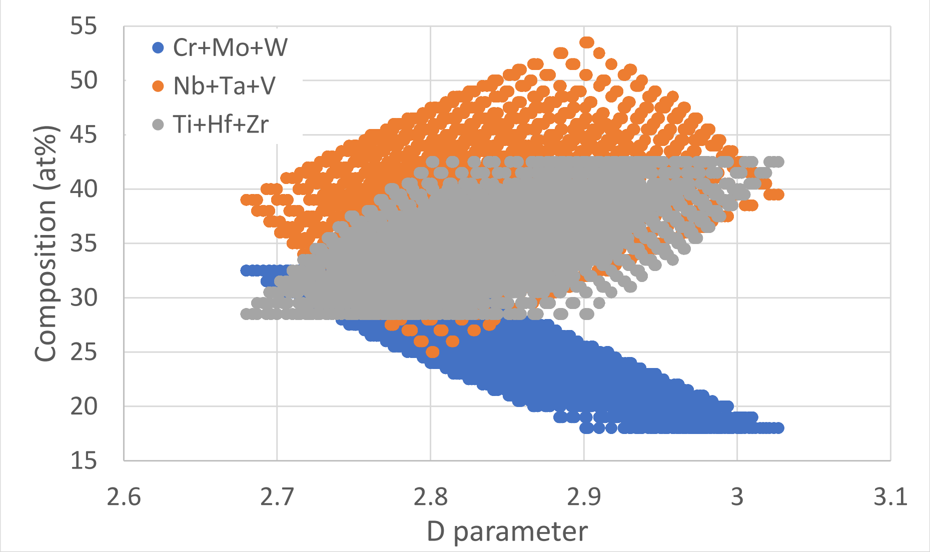

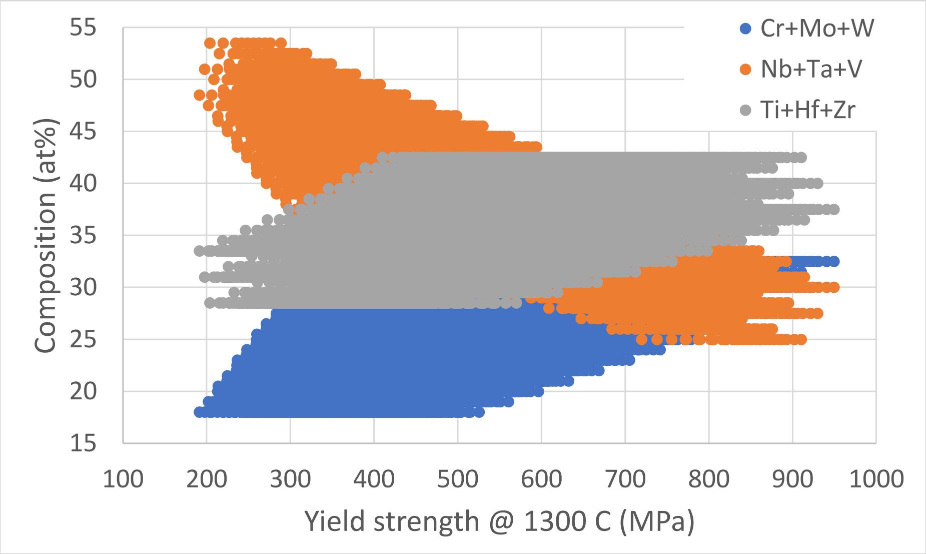

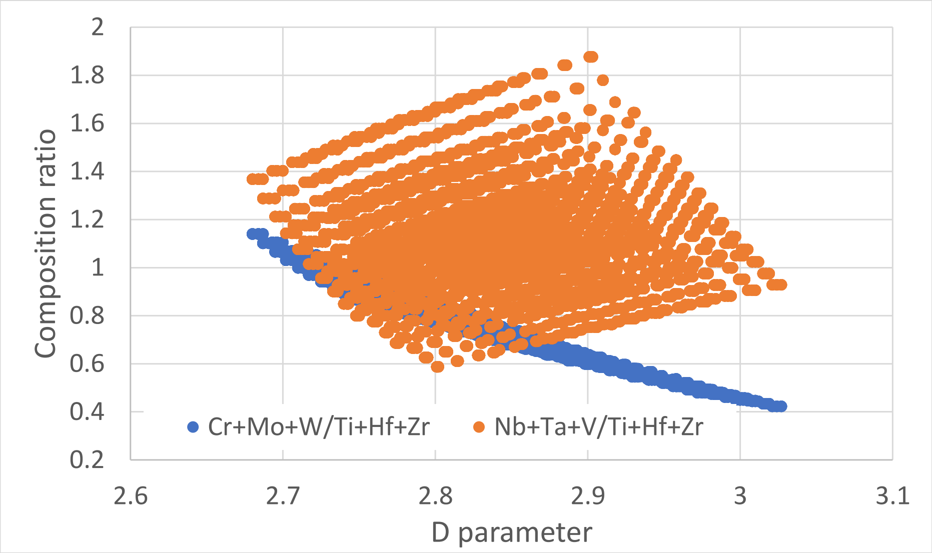

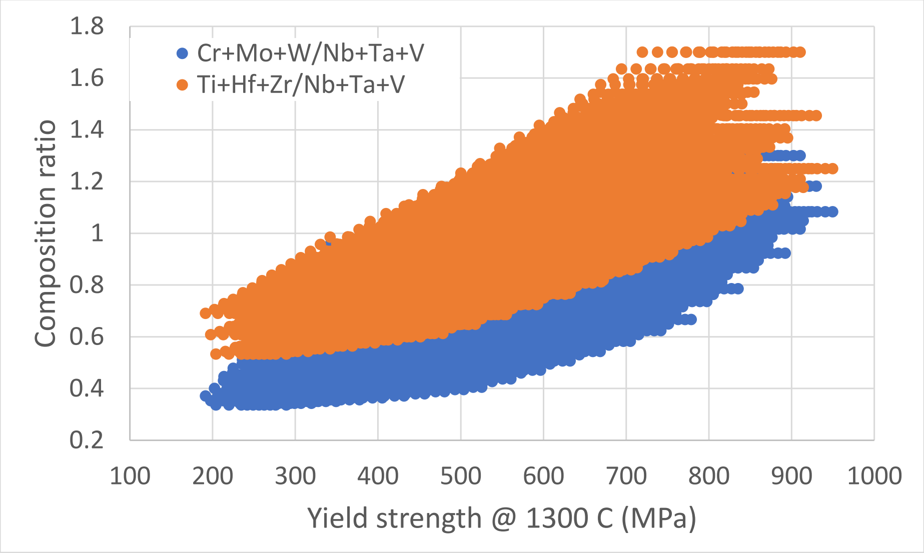

Quasi-Harmonic Approach: Helmholtz Energy

$$F(V,T) = E_c(V) + F_{vib}(V,T) + F_{el}(V,T)$$

$$F_{vib}(V,T) = \frac{9}{8}k_B\Theta_D(V) + k_BT\left\{3\,ln\left[1 - exp\left(-\frac{\Theta_D(V)}{T}\right)\right] - D\left(\frac{\Theta_D(V)}{T}\right)\right\}$$

- V - volume
- T - temperature
- V_{eq} - can be obtained by solving V from $\left(\frac{\partial F}{\partial V}\right)_T$=0
- E_c - 0 K static total energy
- F_{vib} - vibrational contribution
- F_{el} - thermal electronic contribution

Moruzzi et al., PRB (1988); Wang et al., IJQC 96 (2004).

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Existing Approaches to Calculate Debye Temperature from Energy-Volume Curve

- Debye temperature by Moruzzi model

$$\Theta_D = \Theta_0 \left(\frac{V_0}{V}\right)^{\gamma} \; with \; \Theta_0 = 67.48 \left(\frac{r_0 B_0}{M}\right) \text{ and } V_0 = \frac{4\pi}{3} r_0^3$$

- Grüneisen parameter

$$\gamma = \frac{1}{2}(1 + B_0') - \lambda$$

$$\lambda = \begin{cases} 2/3, & \text{Slater expression for high temperature} \\ 1, & \text{Dugdale} - \text{MacDonald for low temperature} \\ 4/3, & \text{Vashchenko} - \text{Zubarev due to free} - \text{volume theory} \end{cases}$$

Moruzzi et al., PRB (1988); Wang et al., Int. J. Quantum Chem. 96(2004);
Slater, J. C. Introduction to Chemical Physics; McGraw-Hill: New York, 1939;
Dugdale & MacDonald, Phys. Rev. 89(1953);
Vashchenko & ZubarevSov Phys. Solid. State 5(1963).

Solution for Thermodynamic Calculations for HEAs with Arbitrary Compositions

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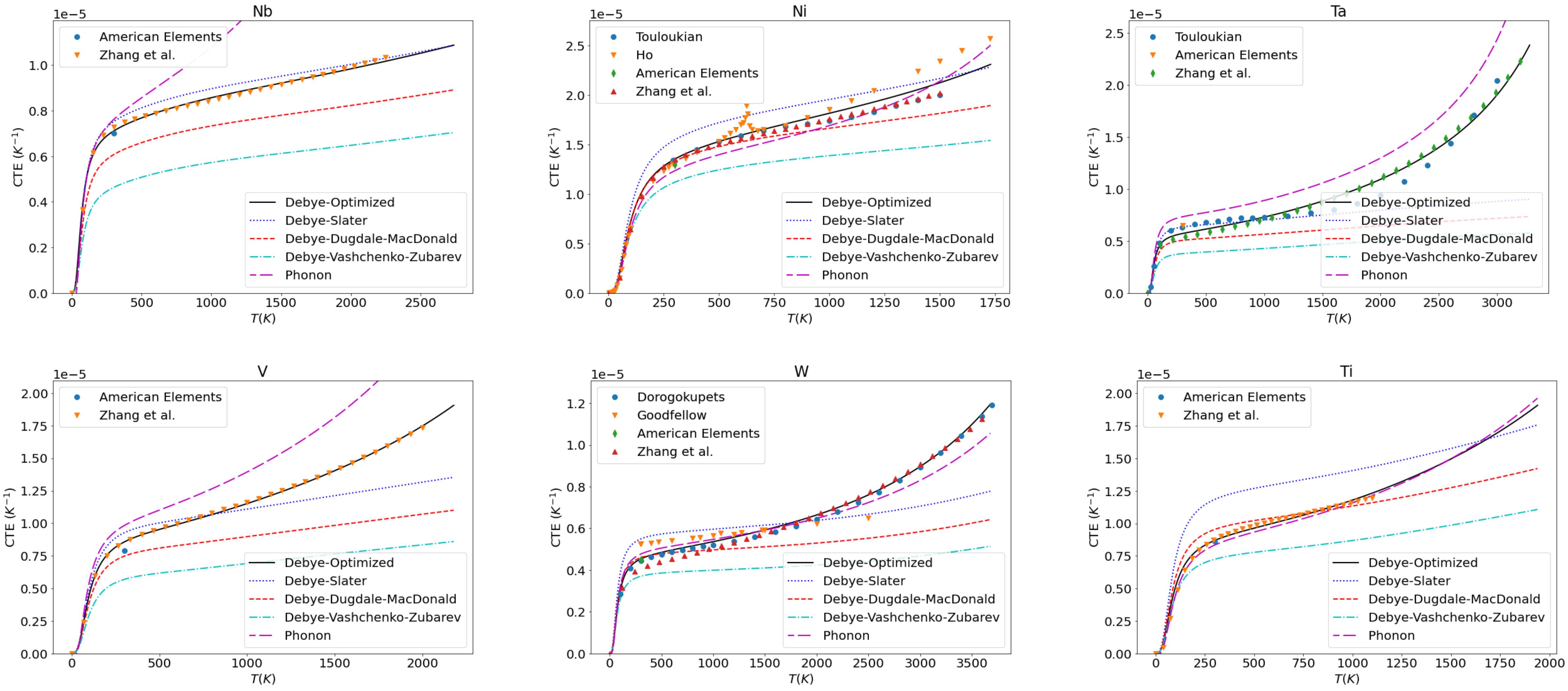
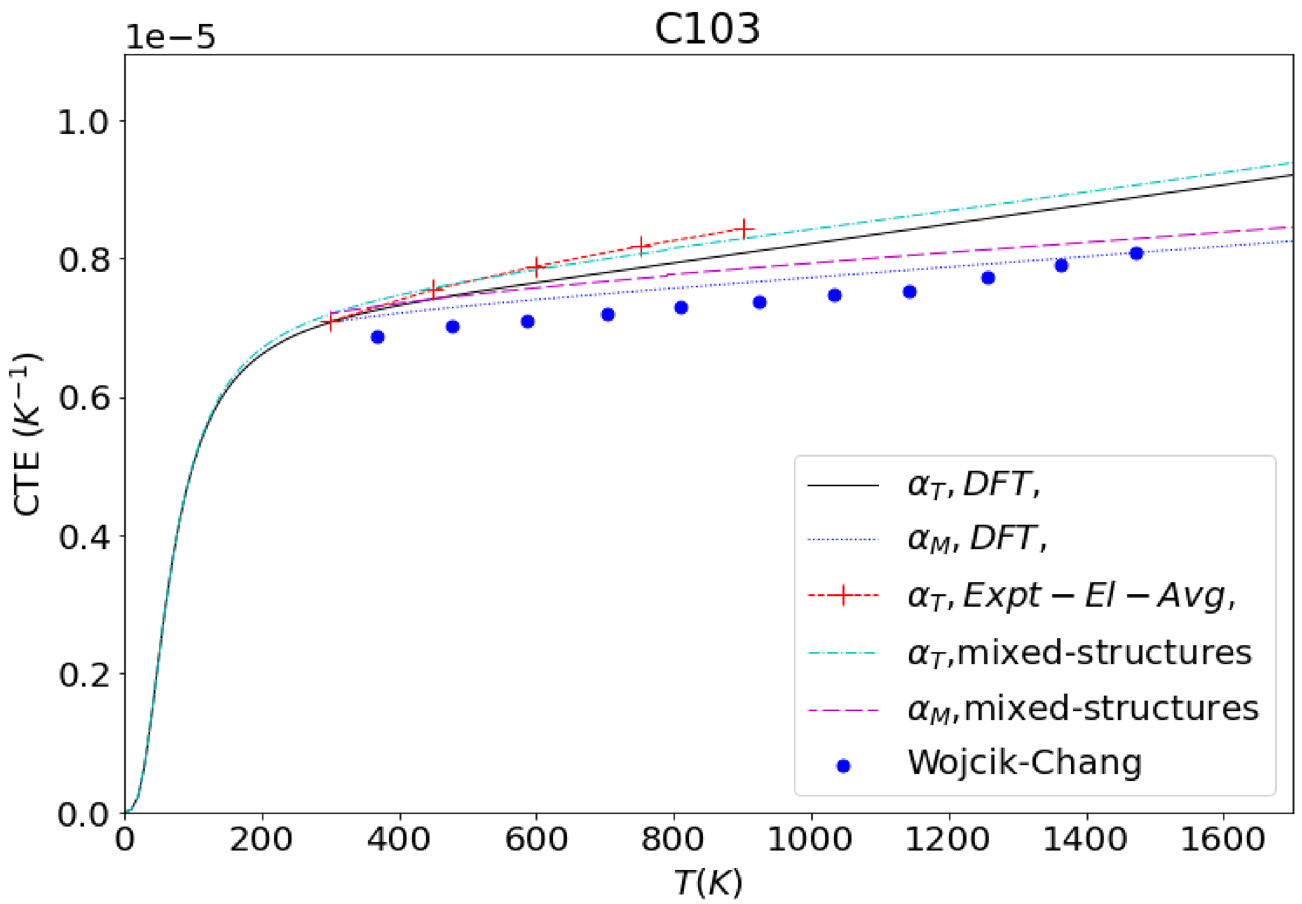
- In this work, we propose:
  - $\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^{\delta}$
- For reference pure elements/species:
  - Calibrate the parameters to reproduce the experimental CTE, heat capacity, and entropy
- For compounds with arbitrary composition:
  - The parameters are determined by arithmetic/geometric average over pure elements/species by composition
- Implemented in DFTTK (density functional theory toolkit) package:
  - Welcome to dfttk's documentation! — dfttk 0.3.4 documentation

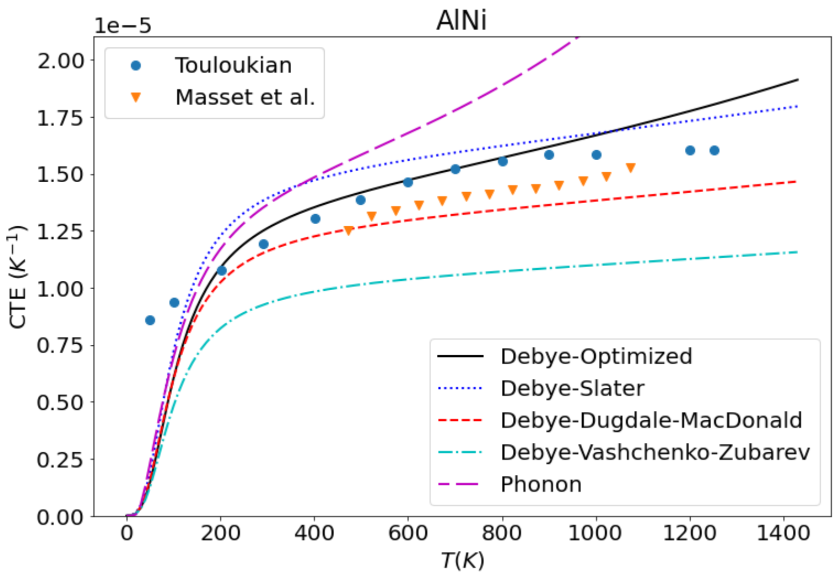
CTEs for Pure Elements

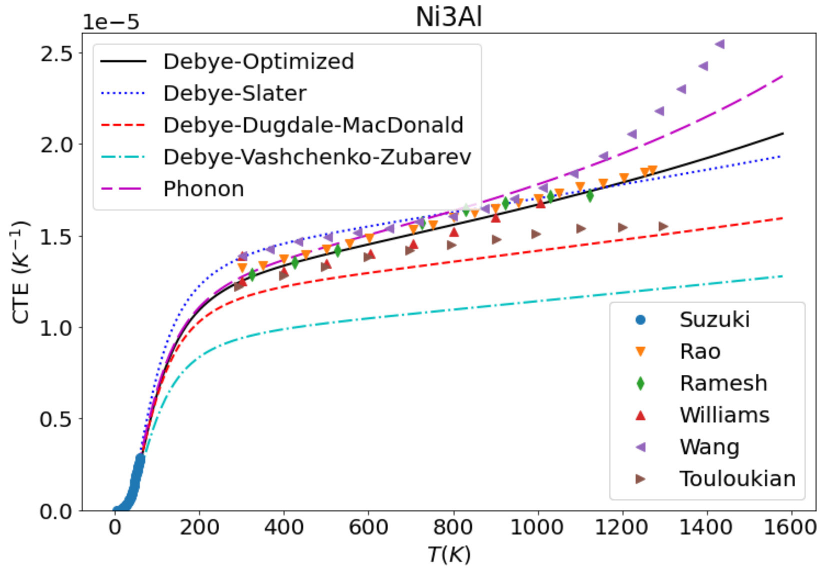


Lines: theoretical; **Other symbols:** experimental or critical evaluations

Predictions for C103, NiAl and Ni_3Al







Lines: theoretical results
Symbols: experimental data

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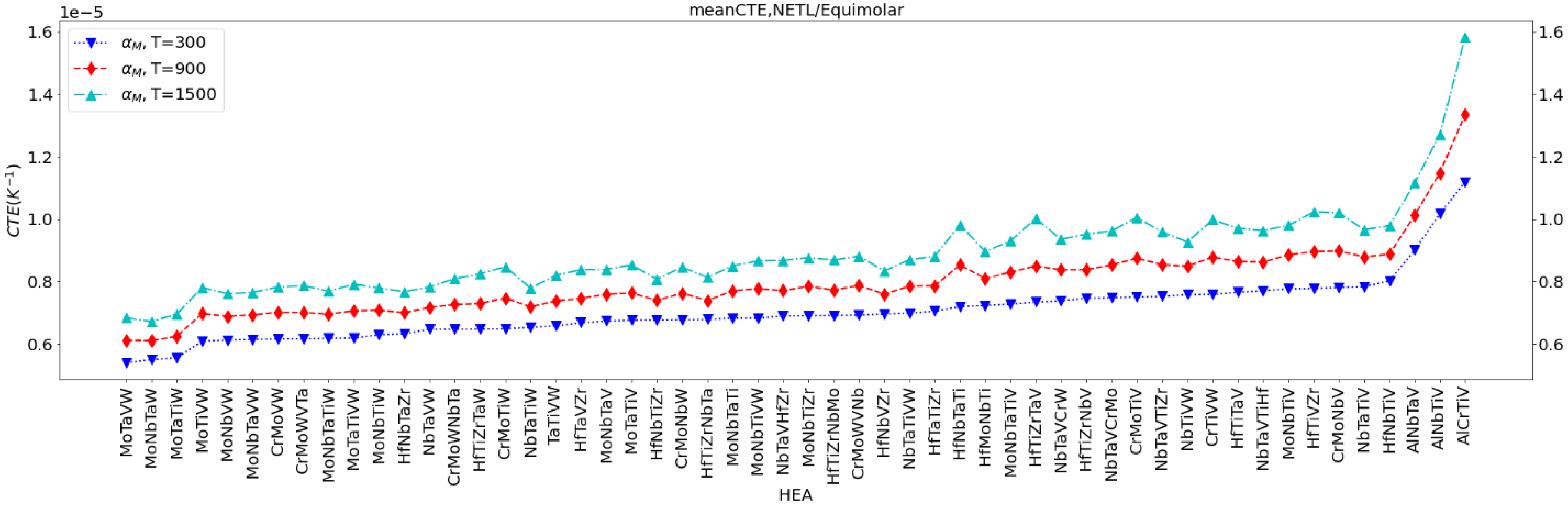
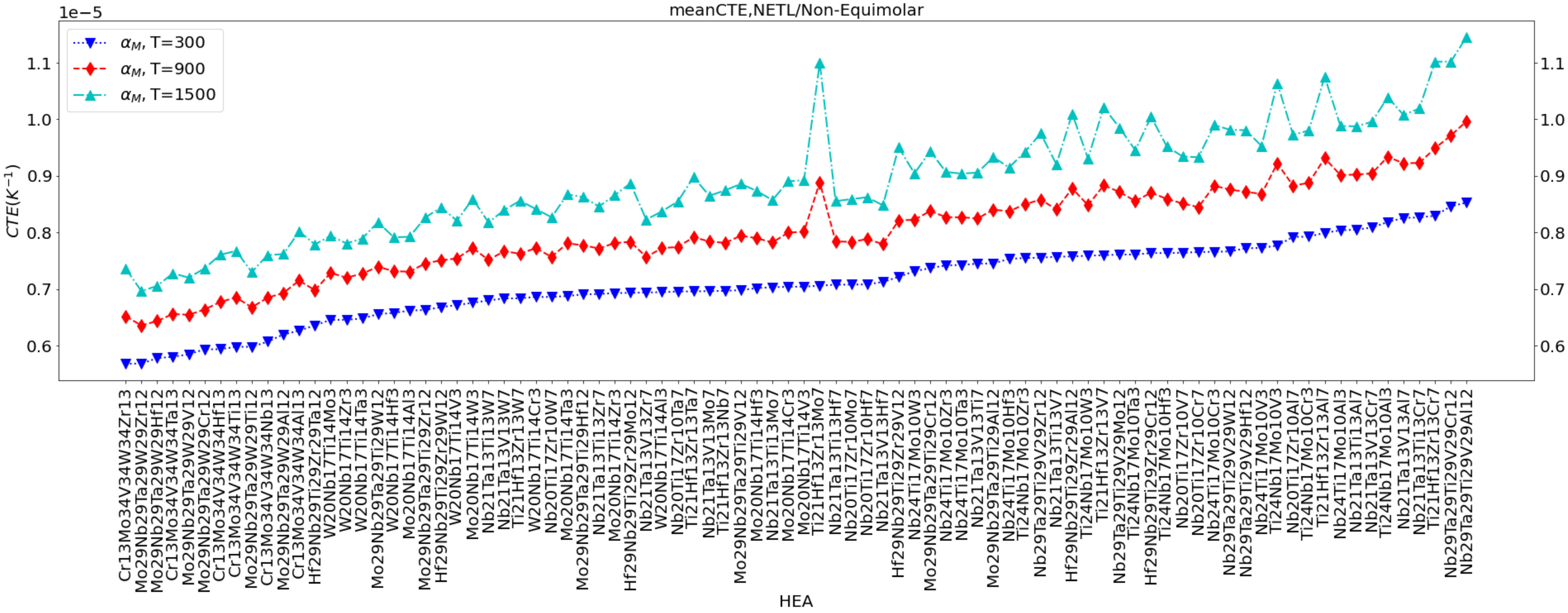
Predictions for equimolar RHEAs



Predicted mean CTE (10^{-6} K^{-1}) for equal molar system at the temperature 300, 900, and 1500 K.

Predictions for non-equimolar RHEAs



Predicted mean CTE (10^{-6} K^{-1}) for non-equimolar system at the temperature 300, 900, and 1500 K.

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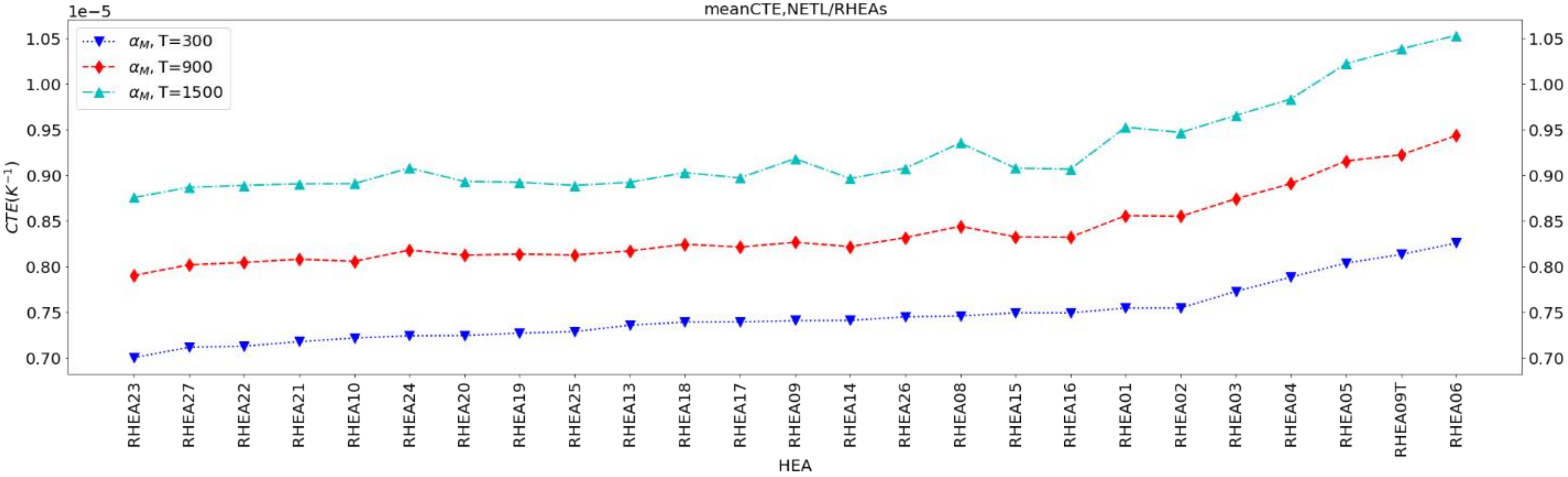
Predictions for NETL RHEAs



Predicted mean CTE (10^{-6} K^{-1}) for new RHEAs system at the temperature 300, 900, and 1500 K.

Coefficient of Thermal Expansion (CTE)

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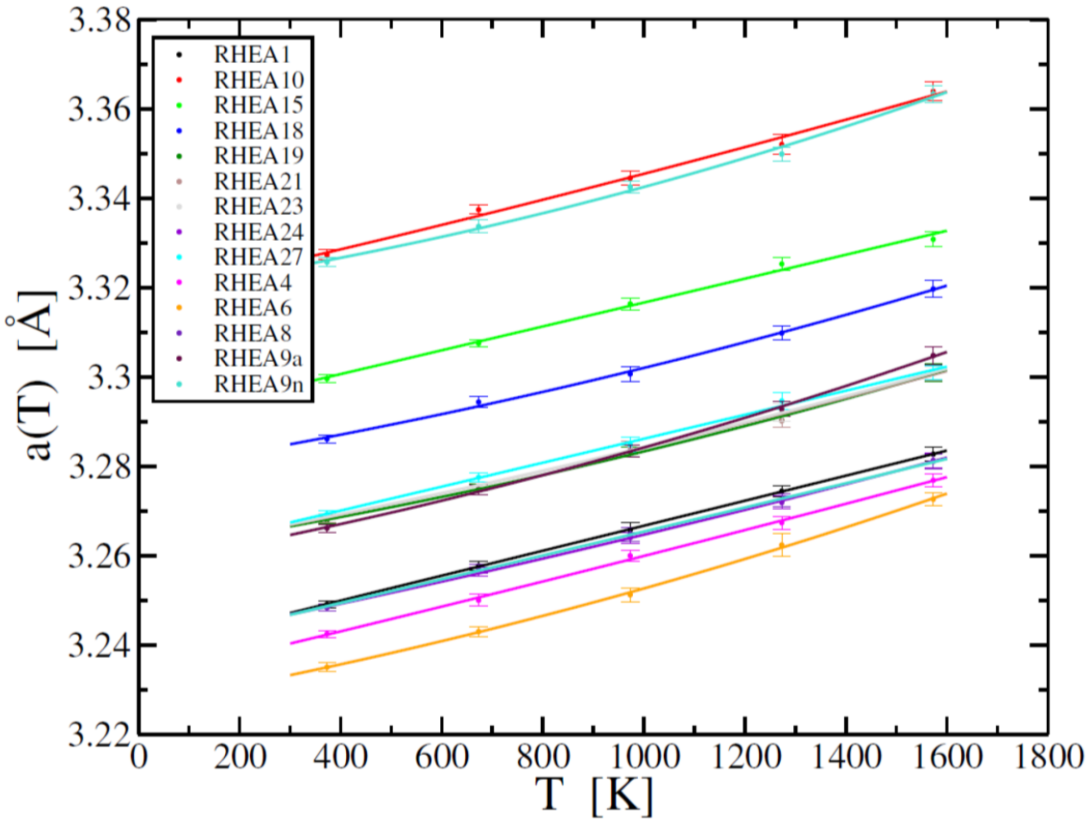
Ab initio molecular dynamics (AIMD) simulations



*NET (%) is the net expansion from RT-1200C.

RHEA ALLOY	NET (%)*	α (10^{-6})
1	1.10	8.6
4	1.12	9.1
6	1.22	11.6
8	1.05	8.3
9	1.14	11.5
10	1.12	11.6
15	1.03	9.4
18	1.05	8.1
19	1.04	9.9
23	1.12	9.0
23	1.04	9.4
24	1.06	9.1
27	1.05	8.2

Alloy Design Details: Yield Stress Modeling

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY · OAK RIDGE National Laboratory · Carnegie Mellon University

- Our approach is to sum Peierls stress and solid solution strengthening for single BCC phase
  - $\sigma = \tau_p + \sigma_y\ (T, \dot{\epsilon})$
- As a simple approximation, the Peierls stress is calculated using the following analytical formula (Joos et al., Phys. Rev. Lett. 78(1997)2)
  - $\tau_p = G_{alloy} \frac{2\pi}{1-\nu_{alloy}} \exp\left(-\frac{2\pi}{1-\nu_{alloy}} \frac{h}{b}\right)$

ν_{alloy}=Poisson's ration

G_{alloy}=the shear modulus

- The solid solution strengthening is calculated by the theoretical model developed by Maresca and Curtin (Acta Mater. 182(2020)235-249). The main equations for the model are for the calculations of zero temperature yield stress σ_{y0}, the energy barrier for dislocation motion E_b and the yield stress at finite temperature $\sigma_y(T, \epsilon)$.
  - $\sigma_{y0} = 0.0915 G_{alloy} \left(\frac{1+\nu_{alloy}}{1-\nu_{alloy}}\right)^{4/3} \left[\frac{\sum_i c_i \Delta V_i^2}{b^6}\right]^{2/3}$
  - $E_b = 0.874 G_{alloy} b^3 \left(\frac{1+\nu_{alloy}}{1-\nu_{alloy}}\right)^{2/3} \left[\frac{\sum_i c_i \Delta V_i^2}{b^6}\right]^{1/3}$
  - $\sigma_y(T, \dot{\epsilon}) = \sigma_{y0}[1 - \left\{\frac{k_B T}{\Delta E_b} \ln(\frac{\dot{\epsilon}_0}{\dot{\epsilon}})\right\}^{2/3}]$

σ_{y0} = yield stress at T=0K

ΔV = volume misfit

E_b=the energy barrier for dislocation motion

c_i = the alloy concentration for element *i*

$\sigma_y(T, \dot{\epsilon})$ =yield stress at finite temperature

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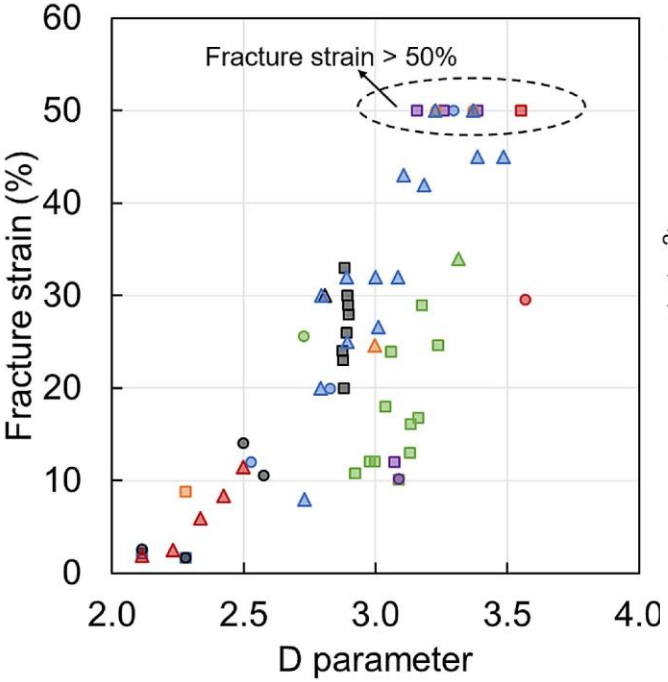
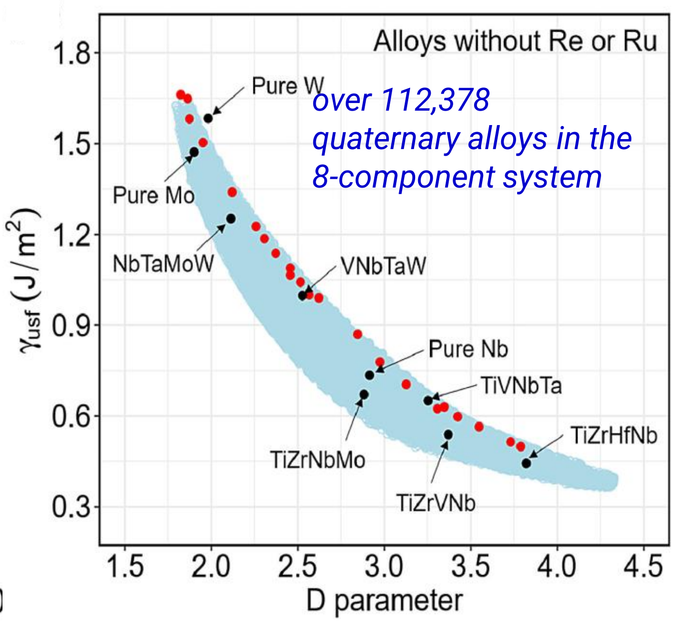
[1] F. Maresca et al., Acta Materialia 182 (2020) 235. [2] C.H. Lee et al., Nature Communications 12(1) (2021).

Intrinsic Ductility: D-Parameter

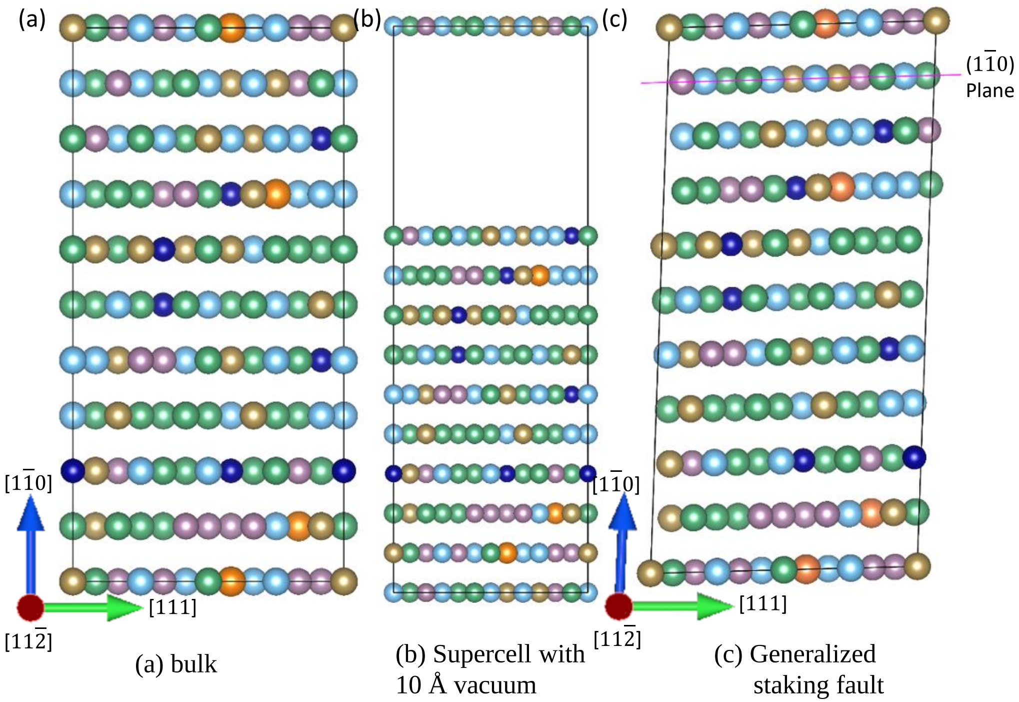
$$D = \frac{\gamma_{suf}}{\gamma_{usf}}$$

γ_{suf}=(1-10) surface energy; γ_{usf}=(1-10)[111] unstable stacking fault energy



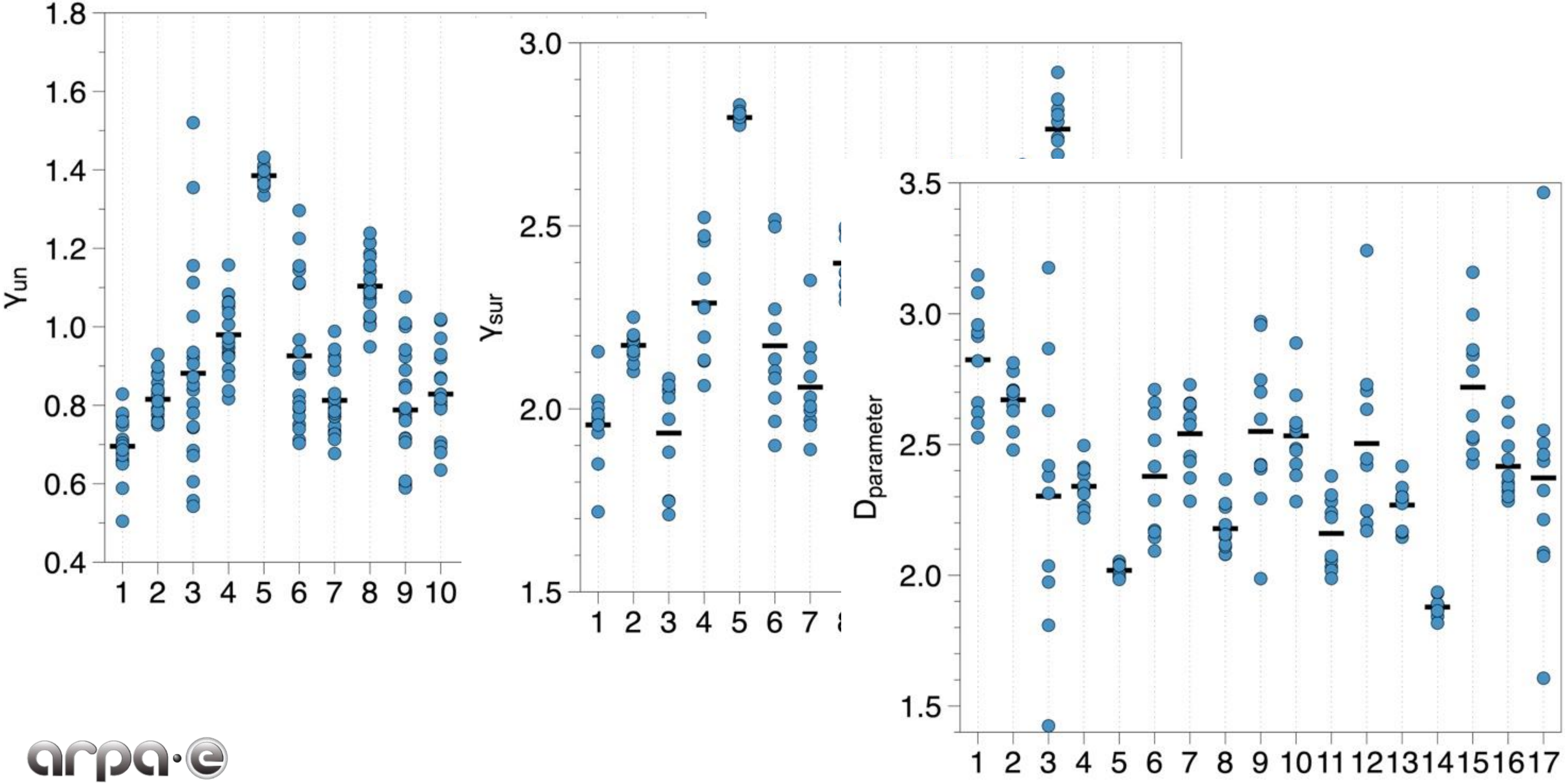


black dots: experiments are available.
Red dots: DFT validations

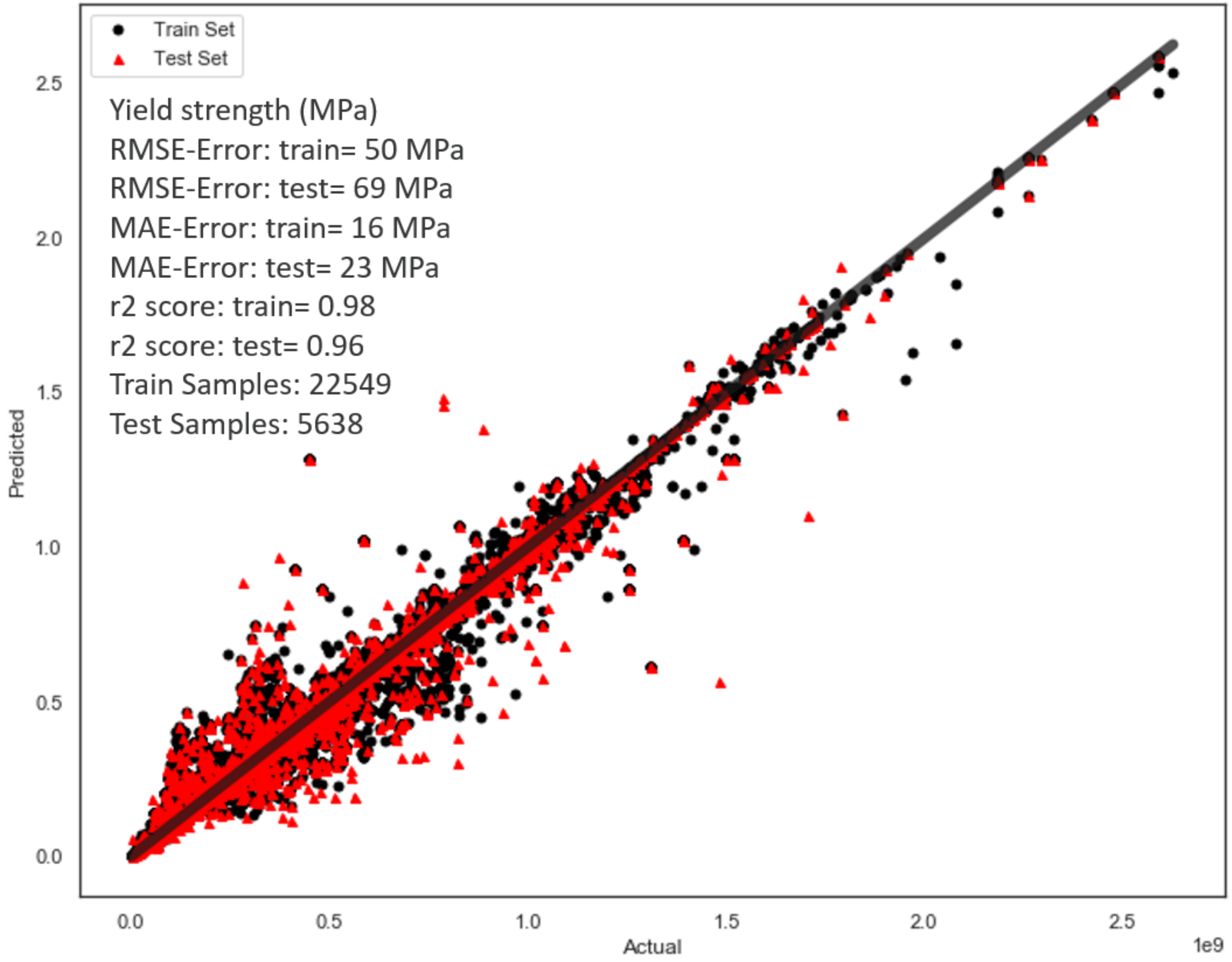


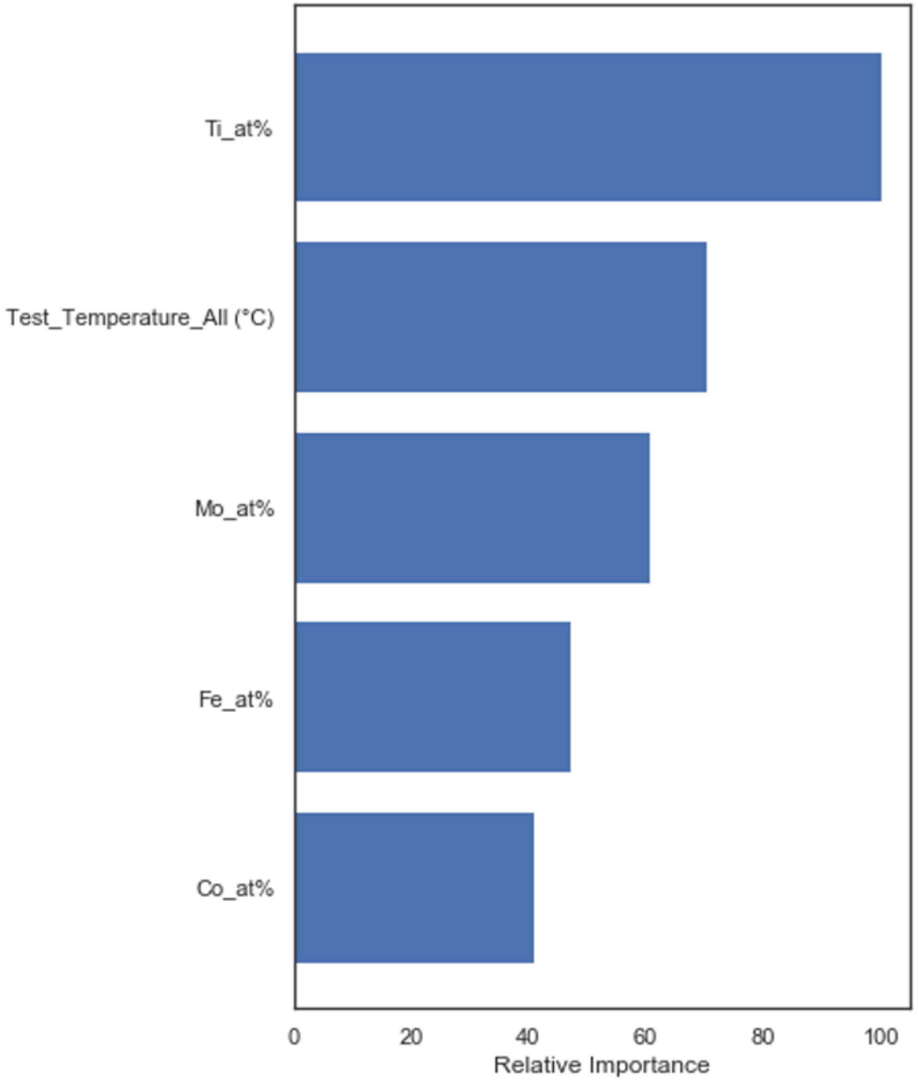
*Y.J. Hu, A. Sundar, S. Ogata, L. Qi, Screening of generalized stacking fault energies, surface energies and intrinsic ductile potency of refractory multicomponent alloys, Acta Materialia **210** (2021) 116800*

Intrinsic Ductility: D-Parameter

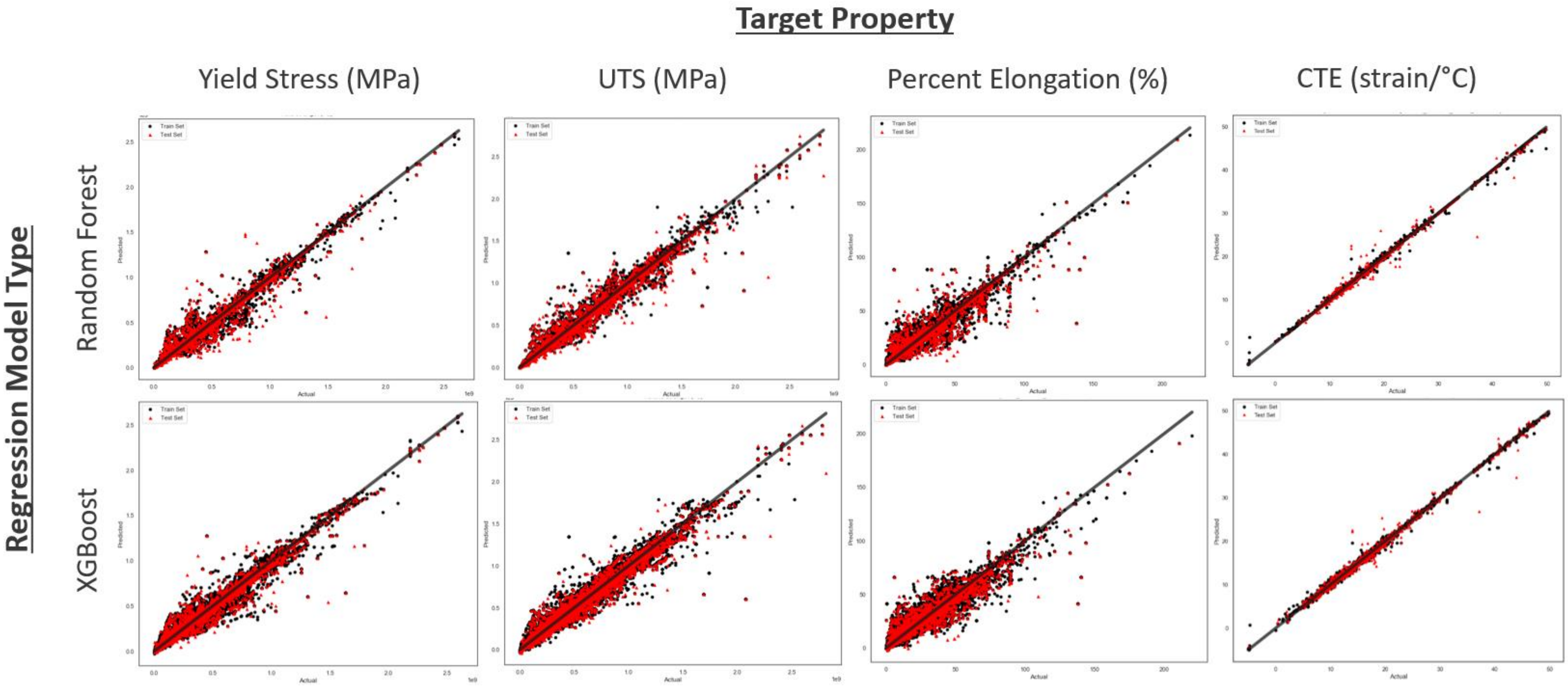


Machine Learning Modeling





Machine Learning Modeling



Alloy Design Results: Round #1

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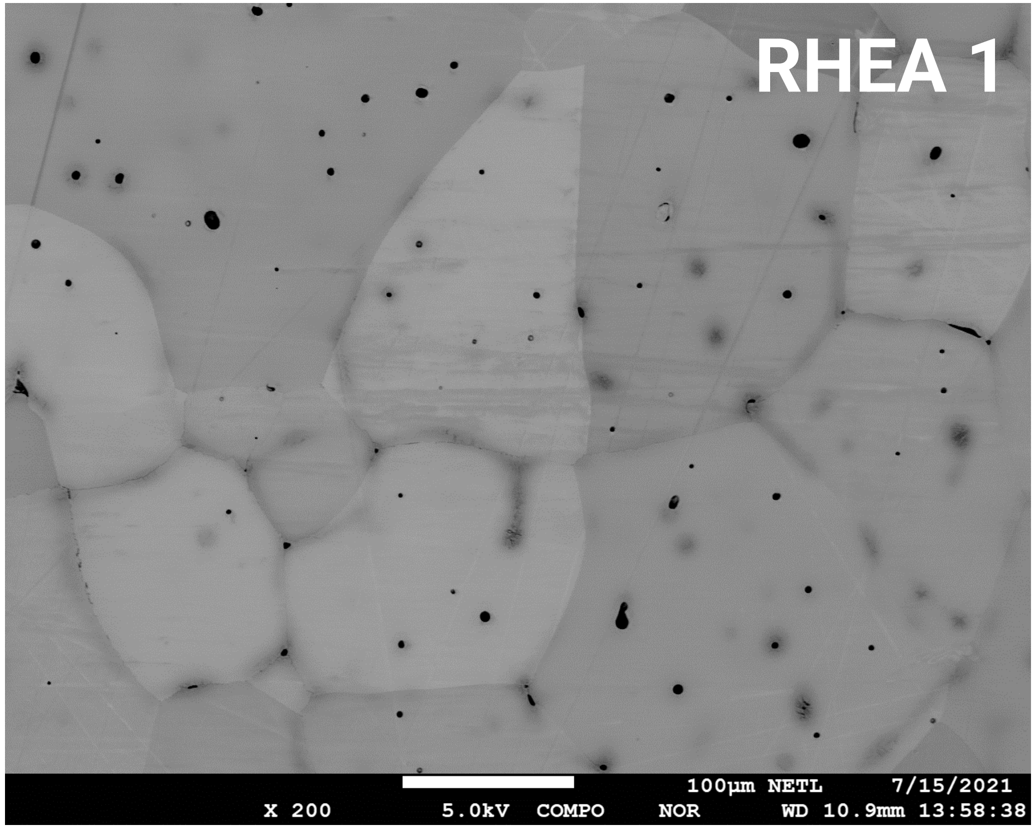

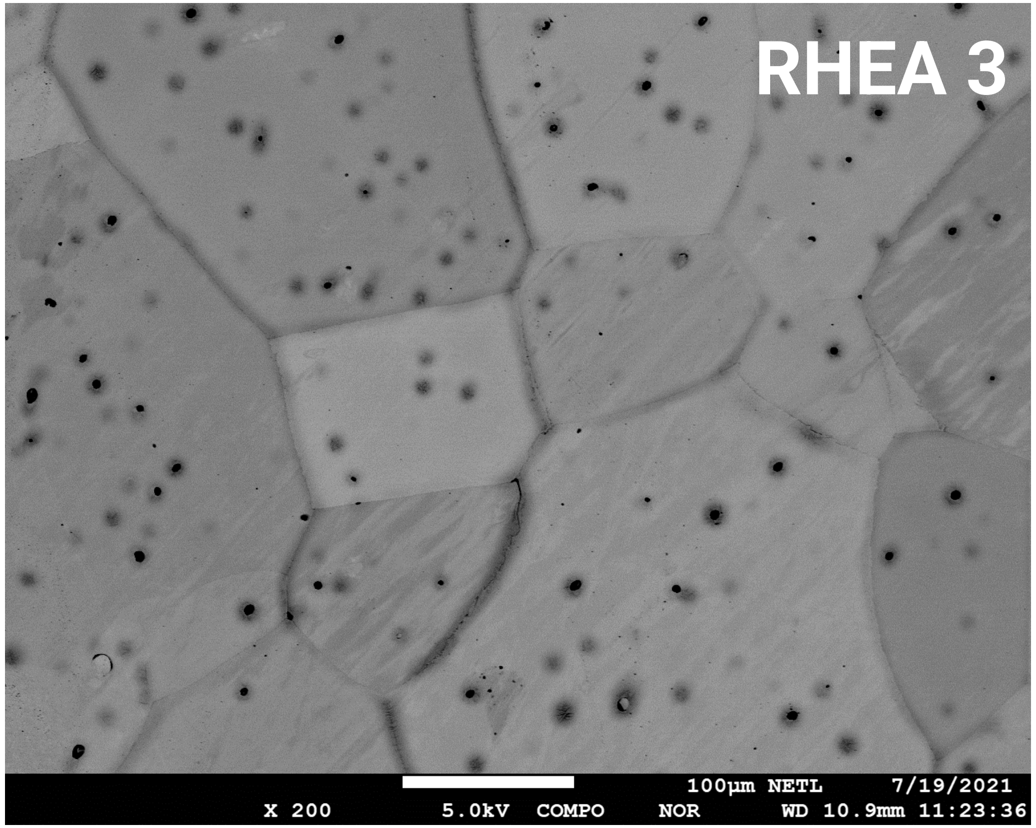

SEM backscattering electron micrographs. Those round, black features are presumably Ti-rich FCC MC carbides, as measured by EDS and WDS. The size is less than 10 µm. They appear to be homogeneously distributed. This demonstrates the concept of MC carbide precipitation in a RHEA.

Alloy Design Results: High Temperature

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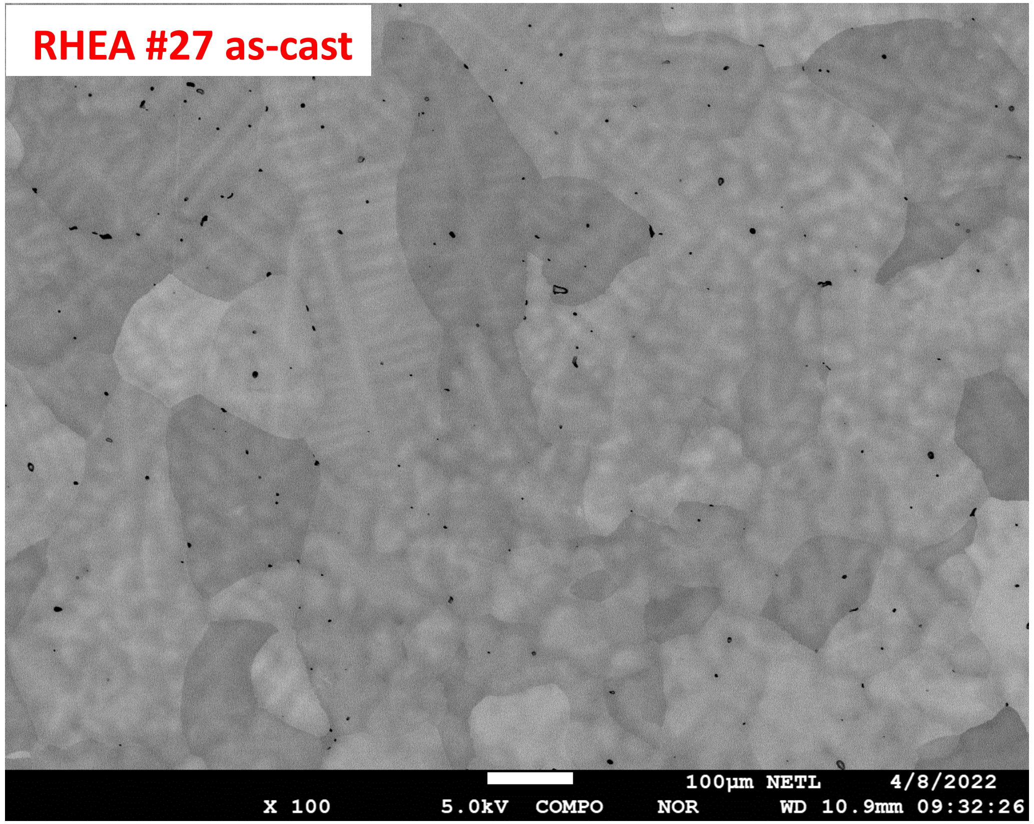

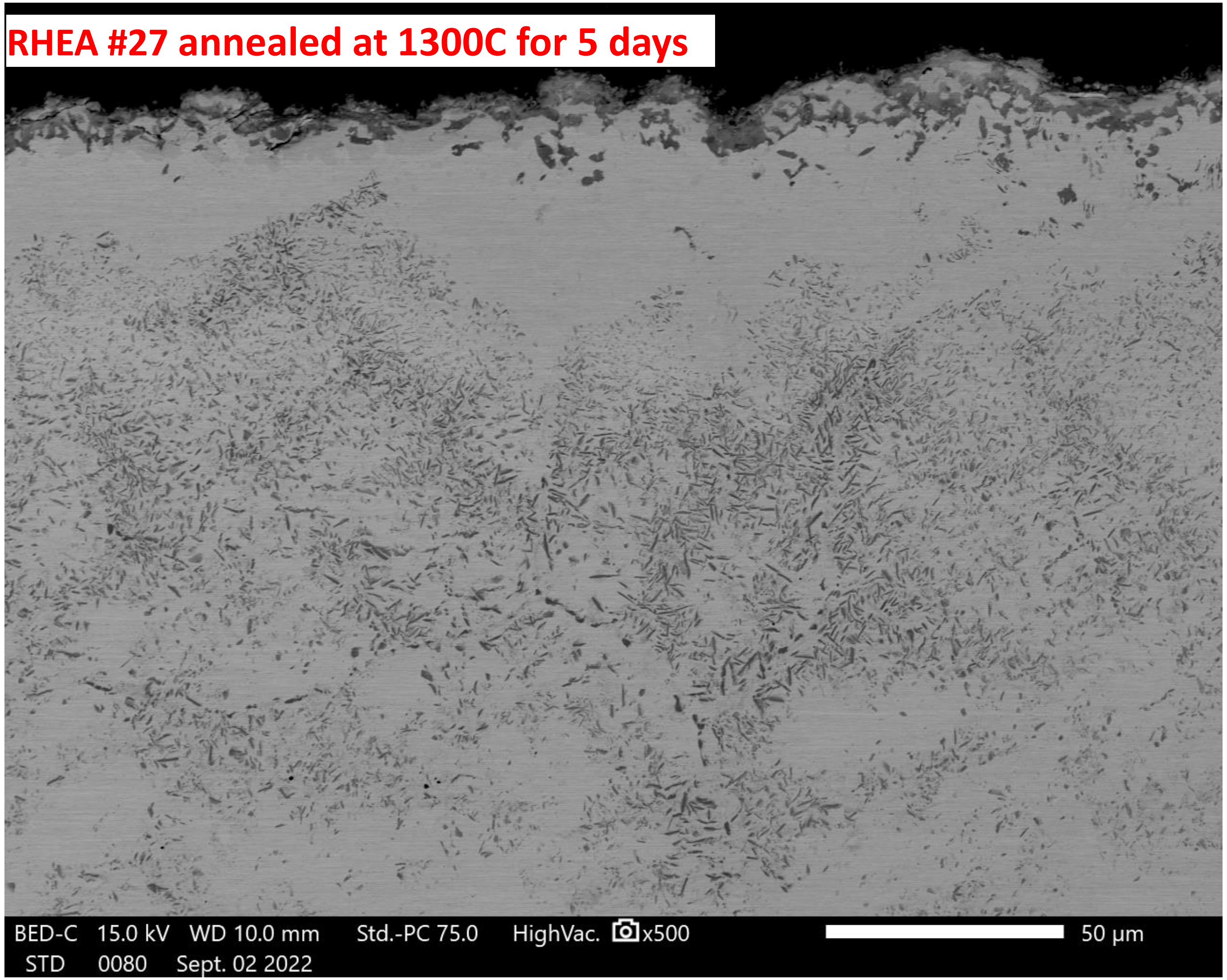

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Alloy Design Results: Mechanical Properties

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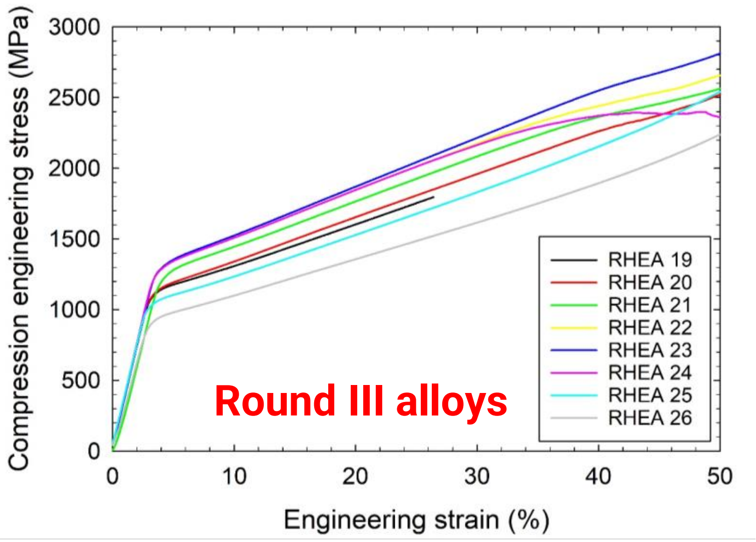
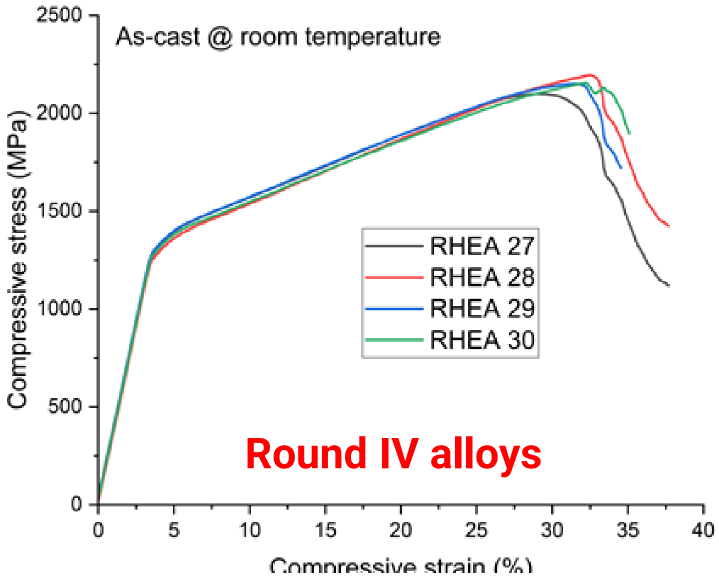
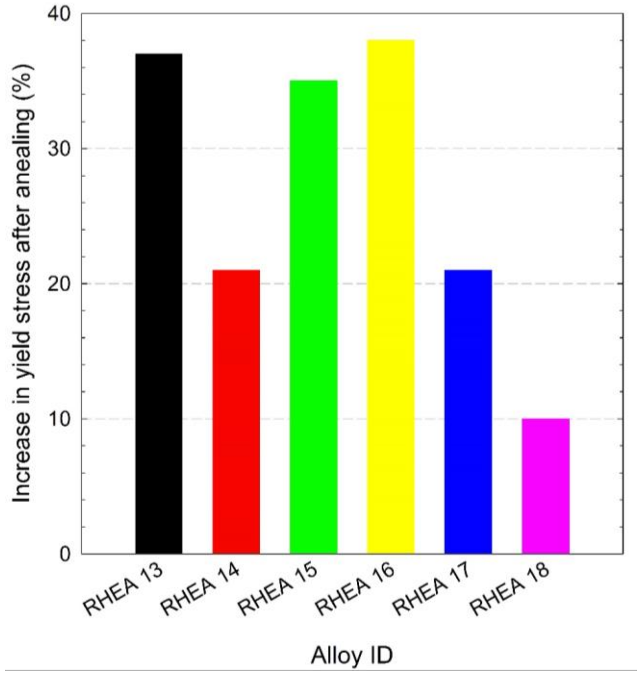
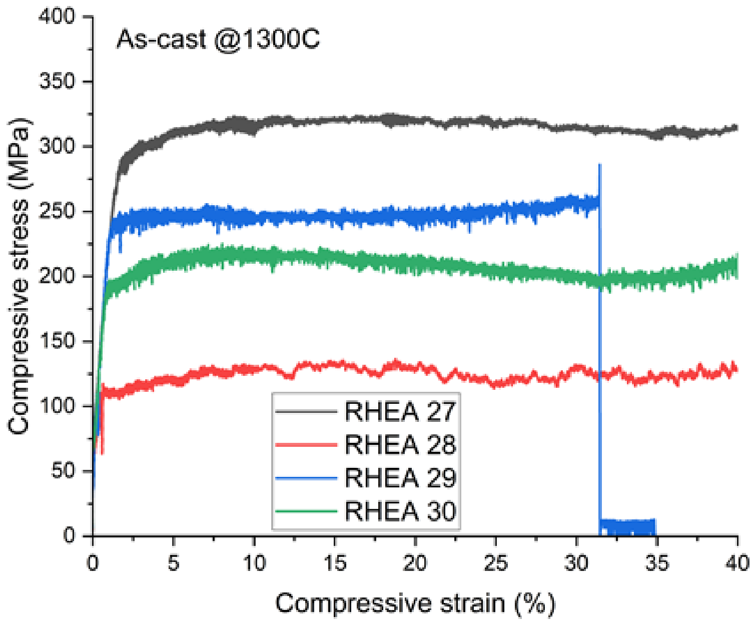
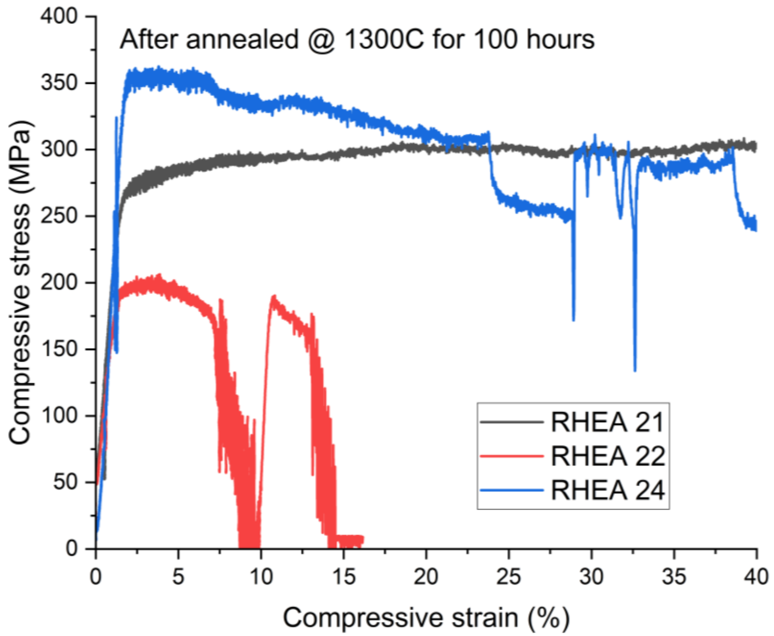




Compression tests at room temperatures before and after annealing at 1300C for 100 hours. The Y axis represents the change in yield stress due to annealing.







The increase in yield stress is due to precipitation of fine MC carbides and formation of fine oxides arpa·e CHANGING WHAT'S POSSIBLE

L-DED Processing of RHEA-15

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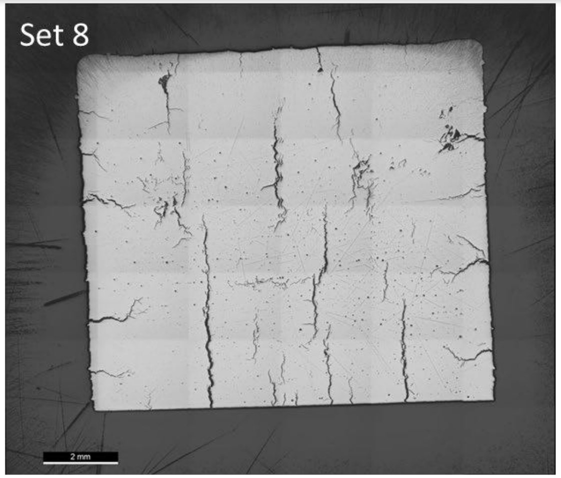
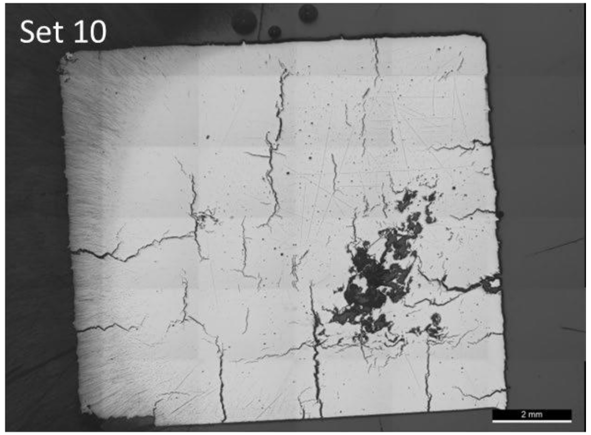
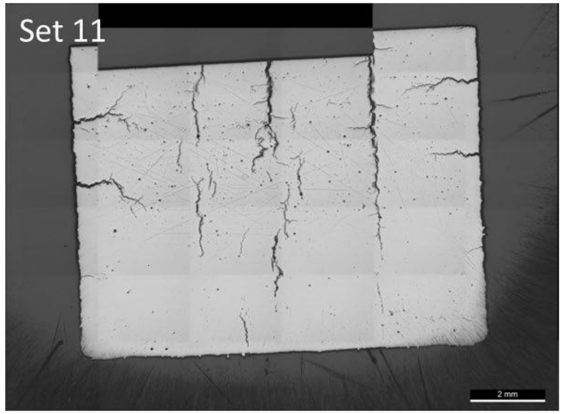
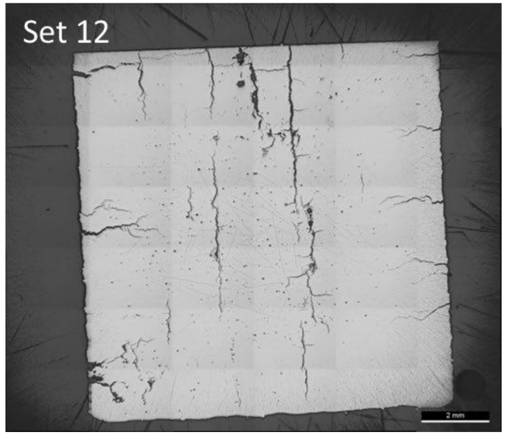




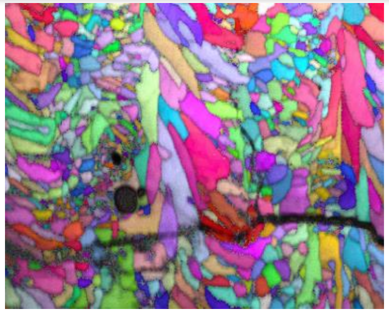




Results from chemical analysis

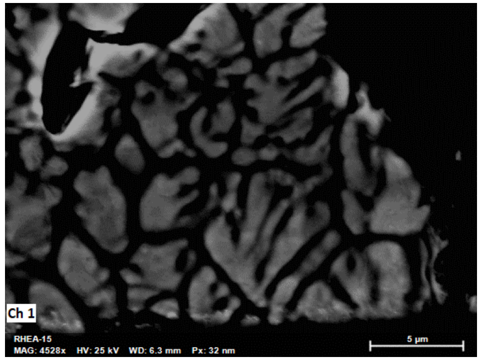
Oxygen-enrichment near the edge- emanating crack/free surface.

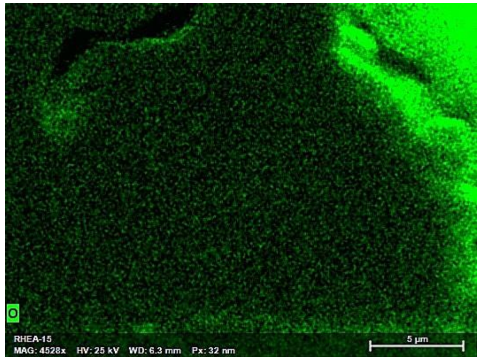
Build direction



100 µm

edge





High oxygen contamination: 0.30 wt%

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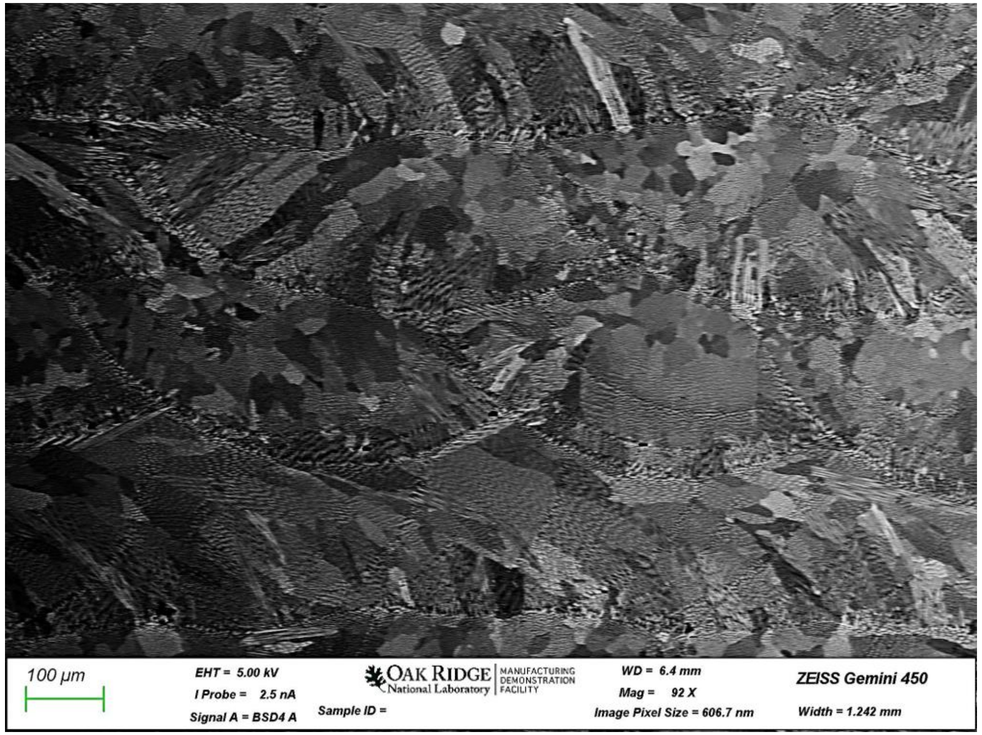
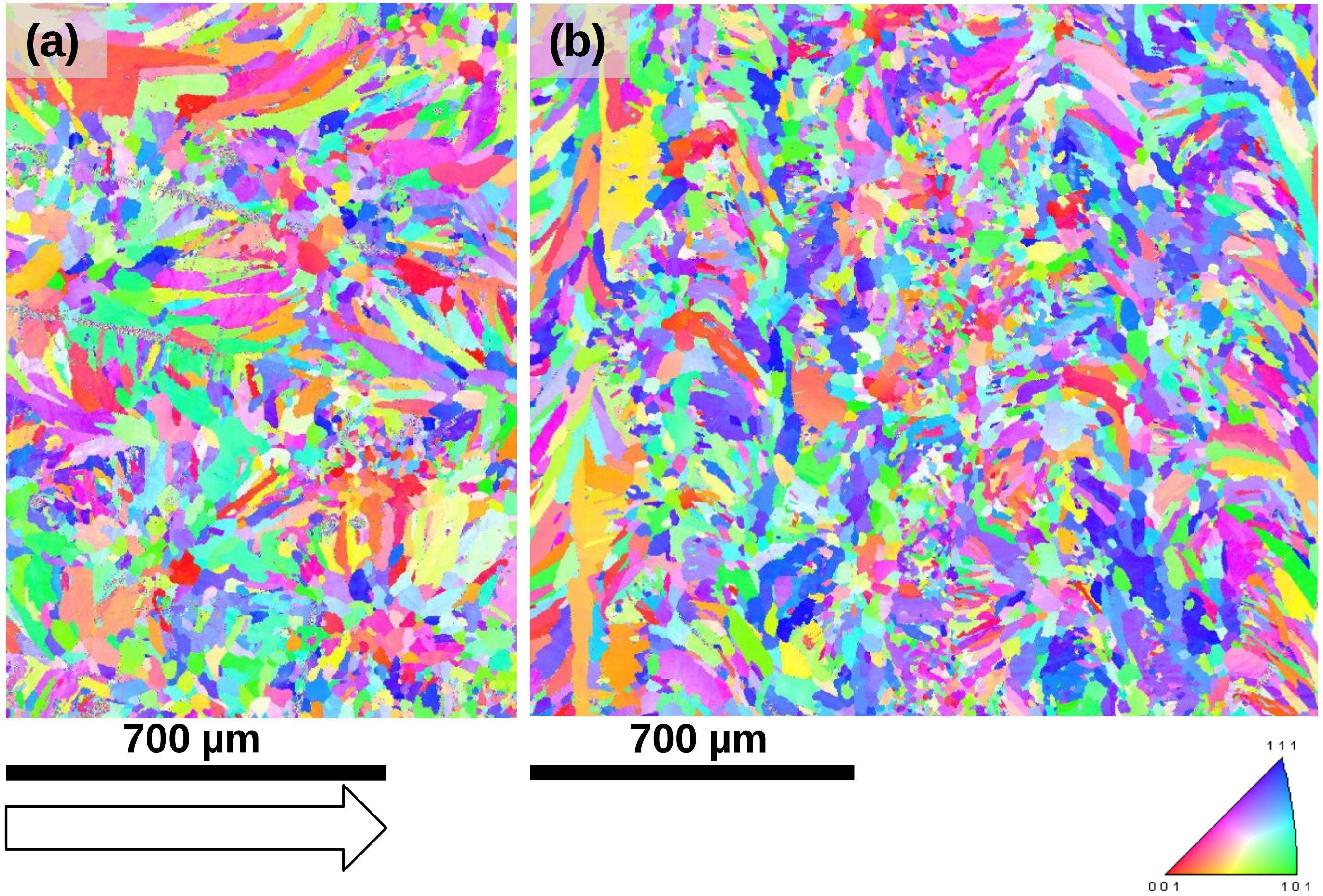
Microstructural Evolution of L-DED Processed RHEA-15 (Round 2 Builds)



67° specimen



Minimal cracking in the internal volume of Round 2 builds and no solidification cracking indicates that RHEA-15 can be processed with L-DED ***if O content is kept minimal****.*

Summaries and Future Work

- High throughput, multiscale modeling are carried out to accelerate alloy design that possess balanced RT ductility & toughness, and high-temperature yield strength and creep performance, while being light weight (≤9 g/cm^3) and low cost.
- Optimzied Debye-Grüneisen approach with volume dependence of the Grüneisen parameter to predict coefficient of thermal expansion (CTE)
- Arc-melt buttons are made to rapidly verify computational design
- Annealing promotes MC carbide precipitation as well as oxide dispersion, contributing about 20% increase in yield strength.
- Plasma arc melted ingots of large size are made. Tensile tests and creep tests are being planned.
- Good progress is made in mitigating thermal cracking in L-DED RHEAs.

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