Concentrated Solid Solution Alloys: Computational Modeling and Experimental Validation

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NETL 2017 Project Review Meeting

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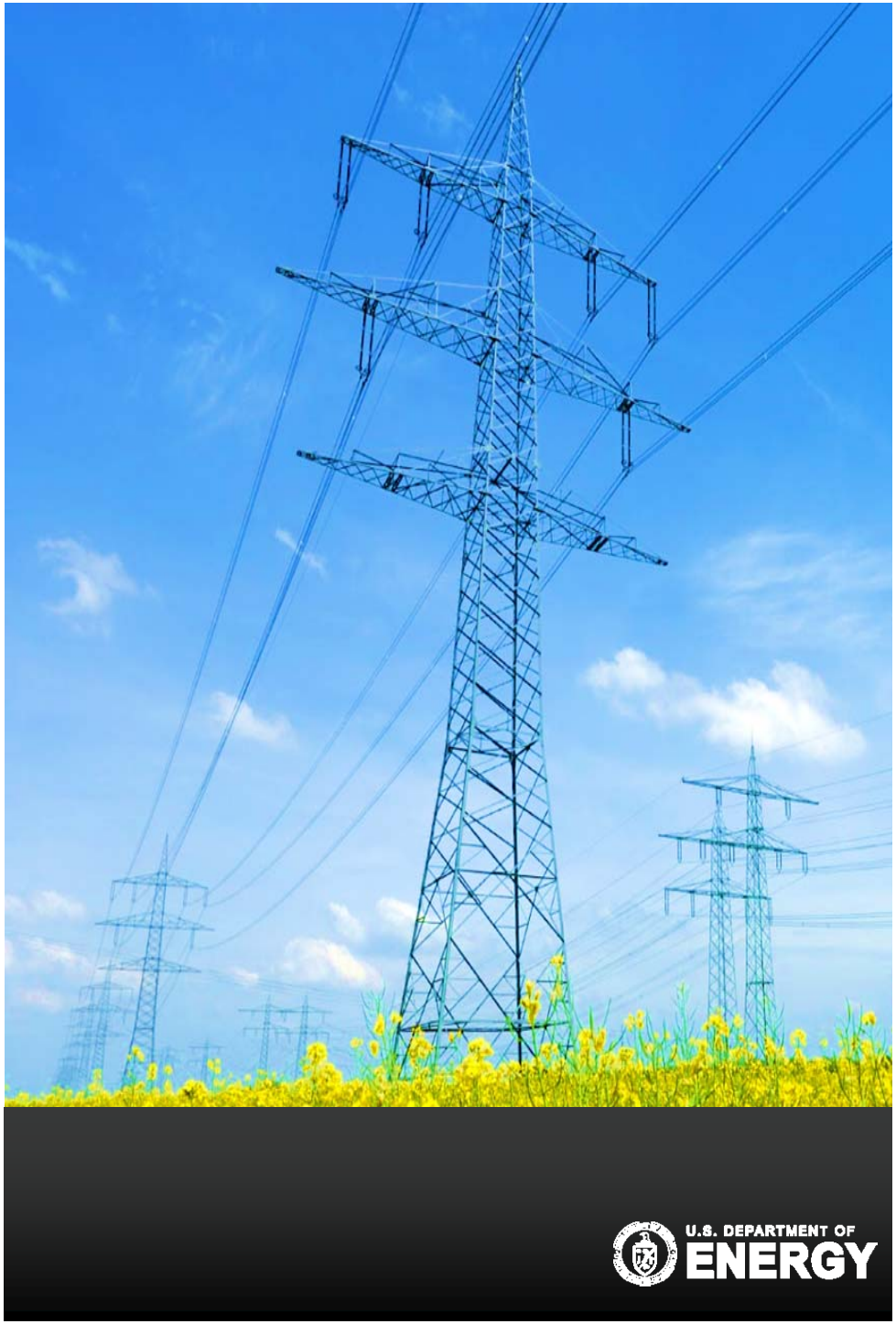
NATIONAL ENERGY TECHNOLOGY LABORATORY



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- Collaborators: Mike Widom (CMU), Peter K. Liaw (UT), Yong Zhang (USTB), Shengmin Guo (LSU), Junwei Qiao (TIT), Chuan Zhang (CompuTherm), Chao Jiang (INL), Karin A. Dahmen (UIUC)

NETL R&IC Advanced Alloy Development

Heat Resistant Alloy Development

Importance

Perfect design methodology and manufacturing practice to shorten the time needed to develop advanced heat resistance alloys for transformational FE energy systems.

Scope

Increase the operational temperature of martensitic steels, austenitic stainless steels, and nickel superalloys for transformational FE energy systems.

Expected Accomplishments

FY2017: Second γ' strengthened nickel superalloy (IN740H) for use as thick wall cast components in AUSC power cycles.

Beyond: Assessment of the potential for new alloy candidate classes (e.g., HEA's, γ' strengthened Co superalloys, high yield stress SS, etc.) & process technologies (i.e., FSW, high shear materials processing, etc.) to significantly impact performance in transformational energy cycles.

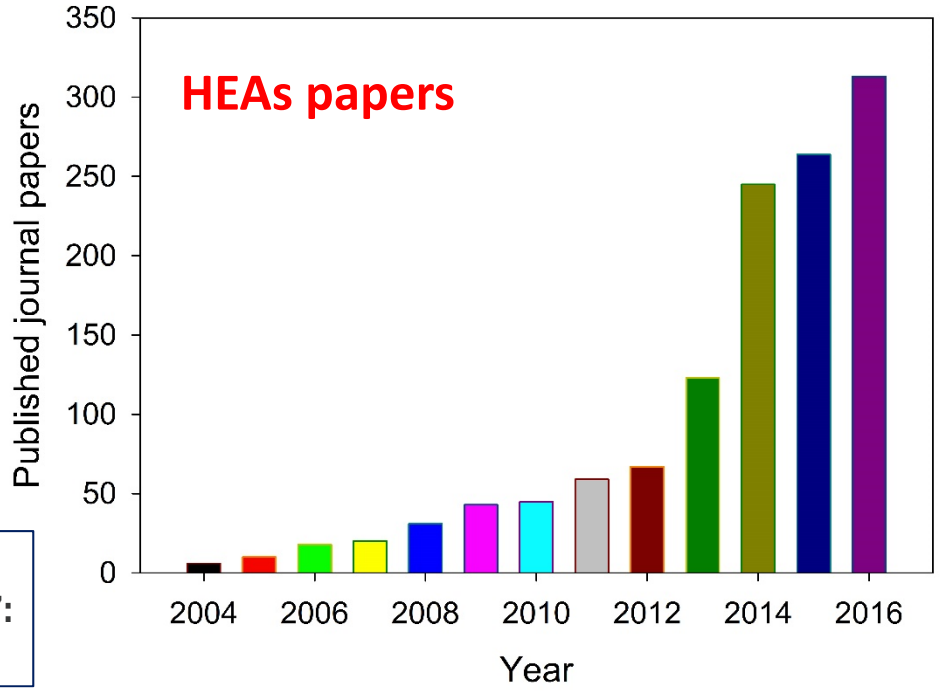
HEA Definitions

Two definitions by Professor Jien-Wei Yeh:

- One is based on composition. HEAs are preferentially defined as alloys containing at least five principal elements, each with an atomic percentage between 5% and 35%.
- The other is based on configurational entropy. HEAs are defined as alloys having configurational entropies at a random state larger than 1.5R, regardless if they are single phase or multi-phase at room temperature.

Other names that are used:

- Equiatomic multicomponent alloys
- Multi-principal-component alloys
- Compositionally complex alloys
- Solid-solution alloys
- Concentrated solid solution alloys



1. Yeh et al. (2004) Adv. Eng. Mater. 6: 299-303.
2. Cantor et al. (2004) Mater. Sci. Eng. A 375-377: 213-218.

Total, Mixing, and Excess Entropies

Total properties

$$G = \sum_i^N x_i G_i + \Delta G_{mix}$$

$$H = \sum_i^N x_i H_i + \Delta H_{mix}$$

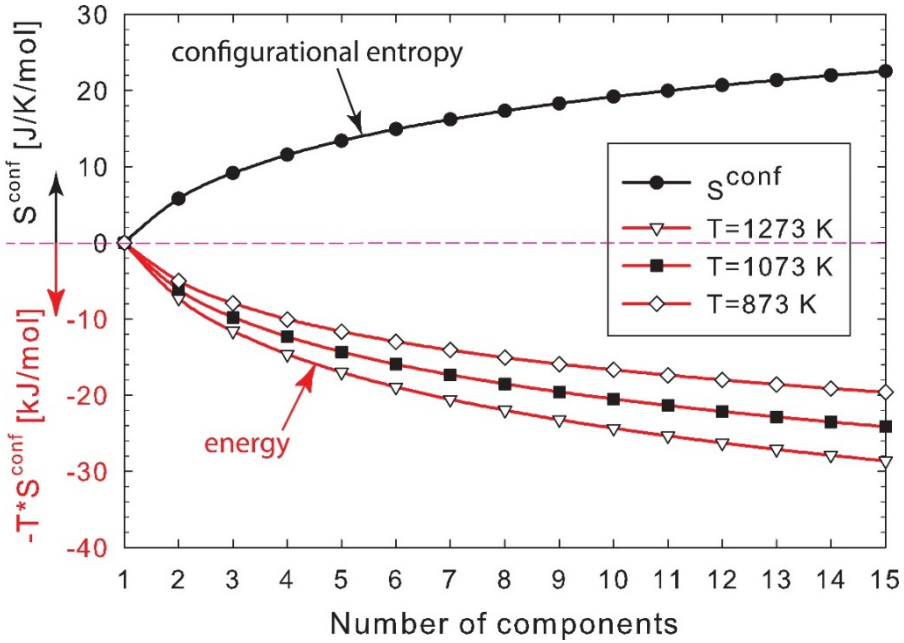
$$S = \sum_i^N x_i S_i + \Delta S_{mix}$$

Mixing properties

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S_{mix}^{conf}\Big|_{ideal} = -R\sum_{i=1}^{N} x_i \ln x_i$$

$$\Delta S_{mix}^{conf}\Big|_{\max} = R \ln N$$



Total mixing entropy:

$$\Delta S_{mix} = \Delta S_{mix}^{conf} + \Delta S_{mix}^{el} + \Delta S_{mix}^{ph} + \Delta S_{mix}^{mag}$$

Excess entropy: (CALPHAD)

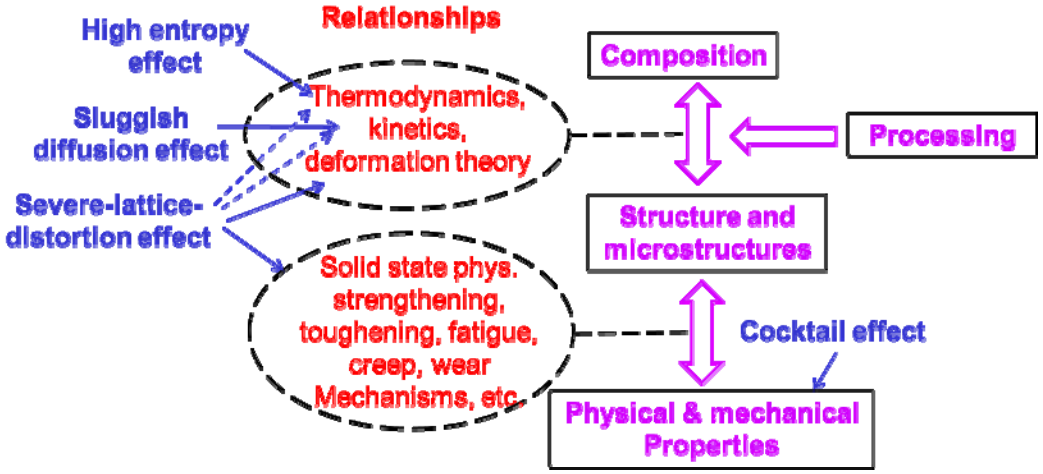
$${}^{ex}S^{\varphi} = {}^{total}S^{\varphi} - {}^{conf}S^{\varphi}_{ideal} = {}^{total}S^{\varphi} + R\sum_{i=1}^{N} x_i \ln x_i$$

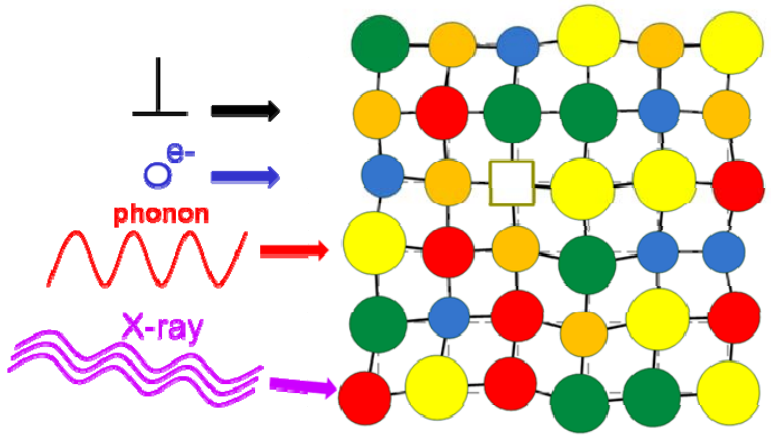
Proposed Four Core Effects

J.W. Yeh, Ann. Chimie Sci. Materiaux 31 (2006) 633.

- high entropy effect for thermodynamics
- sluggish diffusion effect for kinetics
- severe lattice distortion effect for structure
- cocktail effect for properties

$$G = H - TS$$

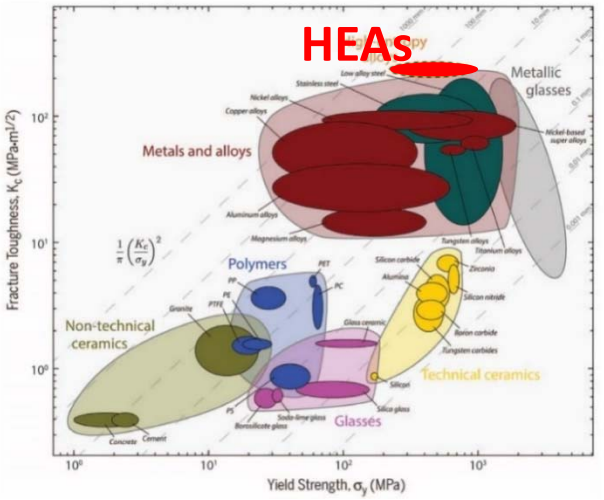




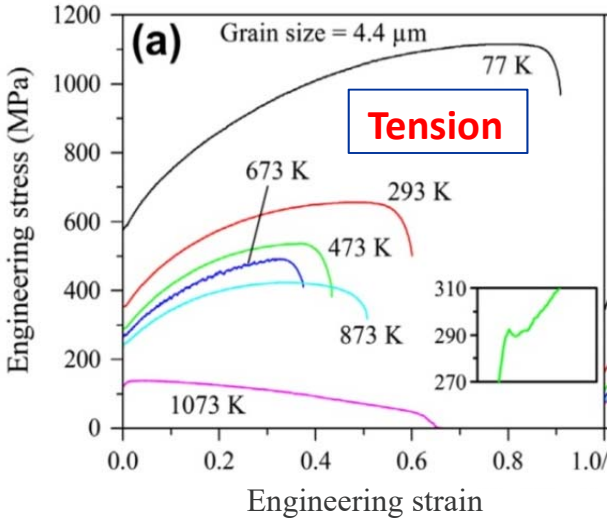
Yeh, Chapter 3, "Physical Metallurgy," High-Entropy Alloys: Fundamentals and Applications, eds. Gao, Yeh, Liaw, and Zhang, Springer, 2016.

Materials Properties

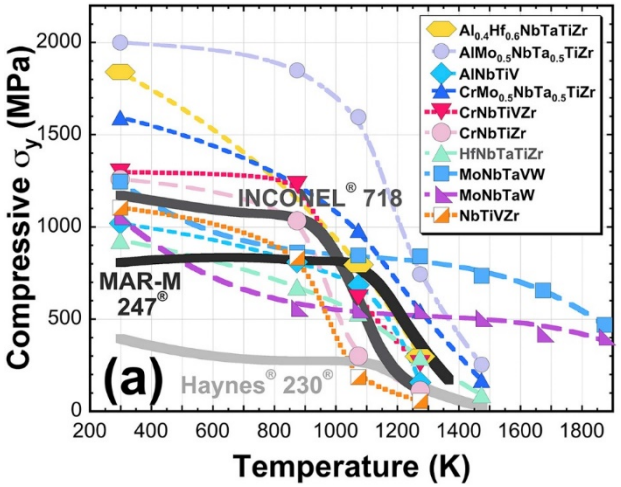
Gludovatz: *Science*, **345** (2014) 1153.



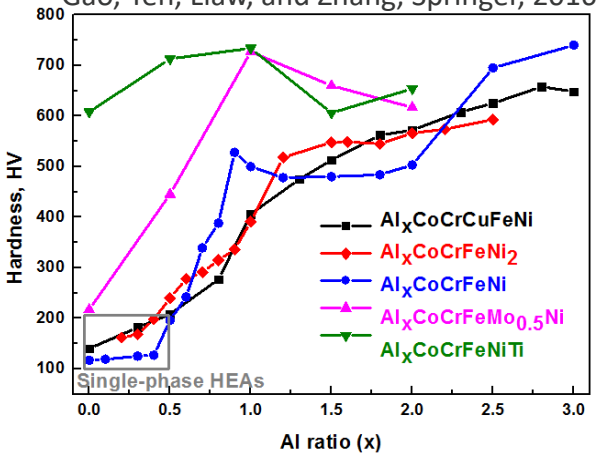
Otto: *Acta Mater.*, **61** (2013) 5743.



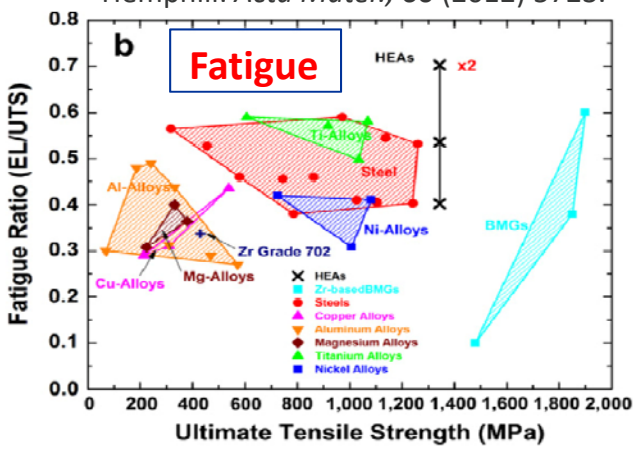
Miracle: *Acta Mater.*, **122** (2017) 448.



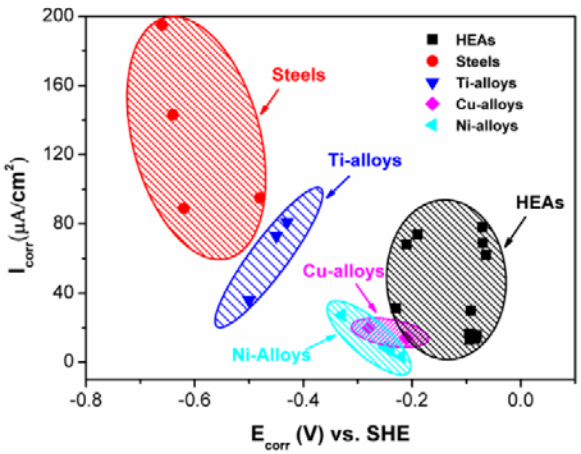
Diao: Chapter 6, High Entropy Alloys, eds. Gao, Yeh, Liaw, and Zhang, Springer, 2016.



Hemphill: *Acta Mater.*, **60** (2012) 5723.



Shi: *Metals*, **7** (2017) 43.



Current DOE-FE Alloy Prospectus

Many existing conventional heat resistant alloys are vulnerable to environmental degradation at high temperatures, which causes significant oxidation, loss of strength, and undesirable phase transformation & coarsening, leading to accelerated creep and shorter creep life.

Many existing Al-, Mg- and Ti-base alloys are lightweight but lack sustained high strength at fossil energy temperatures. Lost strength at intermediate temperatures also limits their usefulness in a variety of applications.

Higher strength alloys are more expensive and heavier, making them less desirable for transportation/defense industries, e.g., Ni-alloys. Oxidation needs to be improved for both steels and Ni-alloys.

Current refractory metal alloys (mostly Nb- and Mo-based) are heavy and lack adequate oxidation resistance.

General DOE-FE Material Objectives

Enhanced strength at room temperature AND high temperatures.

Enhanced chemical stability against oxidation and other forms of corrosion in harsh environment.

Low atomic diffusion to slow down microstructure coarsening and degradation.

Enhanced thermal stability at high temperatures.

Economically competitive against existing materials.

Reduced weight (lower density).

NETL HEA Research Objectives

Provide fundamental understanding of HEA formation and intrinsic thermodynamic, electronic and magnetic properties.

Design and develop high-performance HEAs that are superior to commercial Ni-base superalloys , or use HEA concepts to improve upon existing nickel superalloys.

Design and develop high-performance HEAs that are superior to stainless steels.

Design and develop high-performance light-weight HEAs that are superior to commercial Ti alloys.

Design and develop high-performance refractory BCC HEAs.

Design and develop tough corrosion-resistant oxidation-resistant coatings based on HE concepts.

Explore high-entropy compounds.

Computational Details

- Model disordered atomic structure of HEAs
  - Hybrid Monte Carlo / Molecular Dynamics (MC/MD): Total simulation time is up to 100 ps.
    - NVT (constant number of substance, volume, and temperature)
    - NPT (constant number of substance, pressure, and temperature)
    - MC: swapping atomic positions to reach equilibrium
  - Special Quasi-random Structure (SQS): use ATAT developed by van de Walle and collaborators.
- Ab initio molecular dynamics simulations
  - Liquid structure and diffusion
- Density functional theory (DFT) calculations
  - Structural, elastic, electronic, magnetic and vibrational properties.
- CALPHAD modeling
  - ThermoCalc software with TCNI7 and TTNI8 thermodynamic databases
  - CompuTherm Pandat software with PanHEA database
  - Reliability of the database

Widom, "Hybrid Monte Carlo/Molecular Dynamics Simulation of a Refractory Metal High Entropy Alloy," Metall. Mater. Trans. A, 45 (2014) 196-200.

Reported Single-phase HEA Compositions

Gao, Chapter 11, "Design of High Entropy Alloys," High-Entropy Alloys: Fundamentals & Applications, eds. Gao, Yeh, Liaw, and Zhang, Springer, 2016.

FCC	Refs.
CoCrFeNi	1
CoFeMnNi	2,3
CoCrMnNi	3
CoFeNiPd	4
CoCrFeMnNi	5
CoCrFeNiPd	6
$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$	7

HCP	Refs.
CoFeReRu	22
MoPdRhRu	23
DyGdHoTbY	24
DyGdLuTbTm	24
DyGdLuTbY	25
$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$	7

BCC	Refs.
AlNbTiV	8
HfNbTiZr	9
MoNbTaW	10,11
NbTaTiV	12
NbTiVZr	13
AlCrMoTiW	14
AlNbTaTiV	12
HfNbTaTiZr	15
HfNbTiVZr	16
MoNbTaVW	10,11
MoNbTaTiV	17
MoNbTiVZr	18
NbReTaTiV	17
MoNbReTaW	17
CrMoNbTaVW	19
HfNbTaTiVZr	20
MoNbTaTiVW	21
MoNbReTaVW	17
MoNbReTaTiVW	17

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[12]X. Yang et al. Iumrs Int. Conf. 2011 **36**, 292 (2012).
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[17]H. Bei et al. US20130108502 A1.
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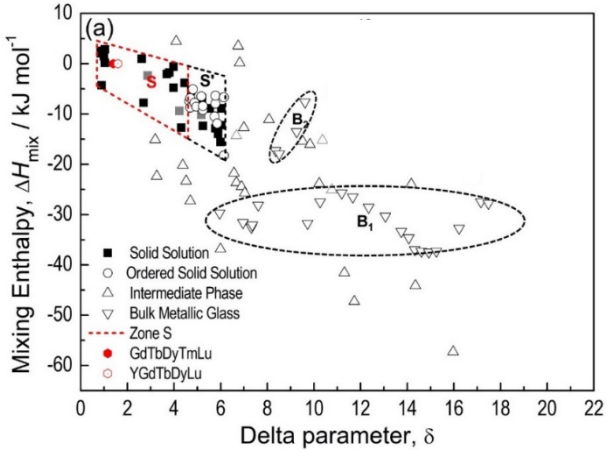
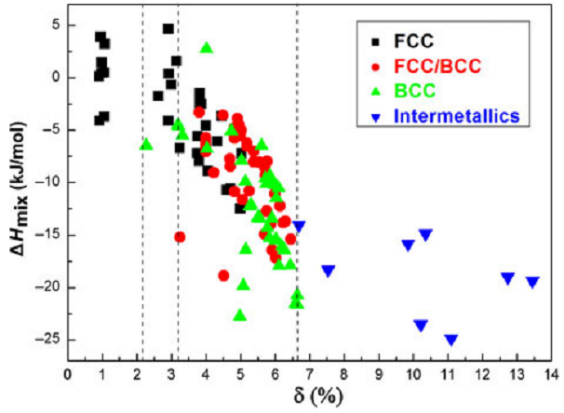
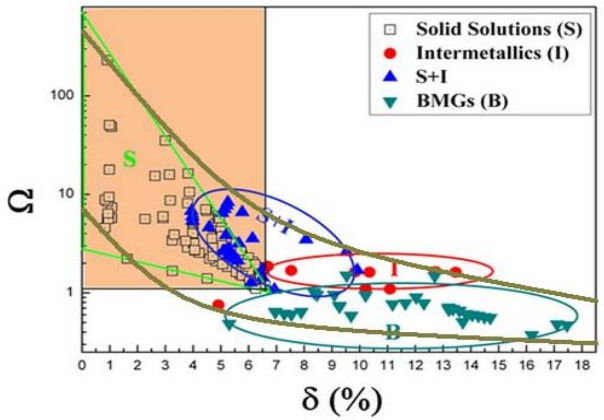
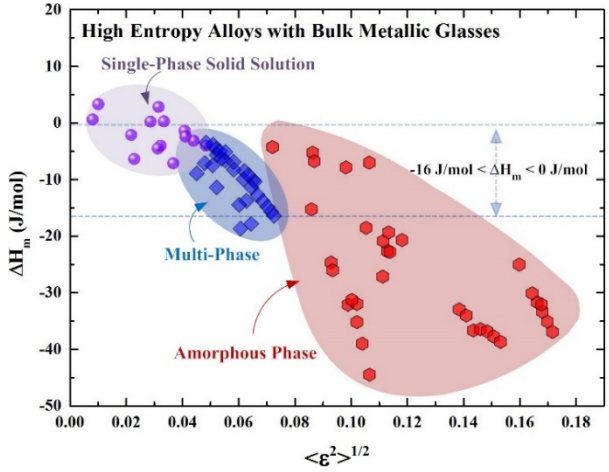
Disordered HEA Formation Rules

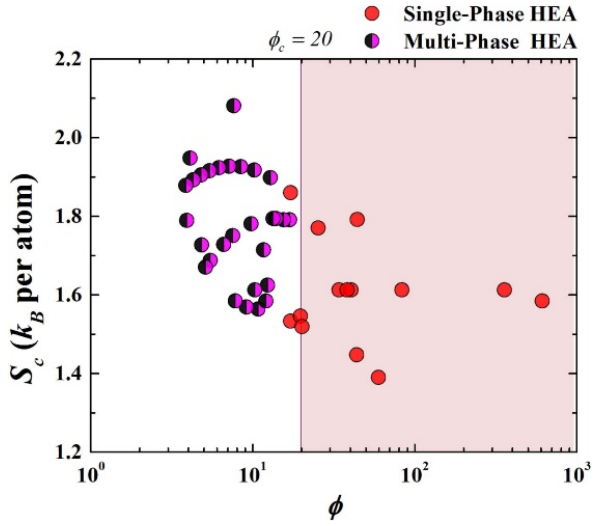
Literature review

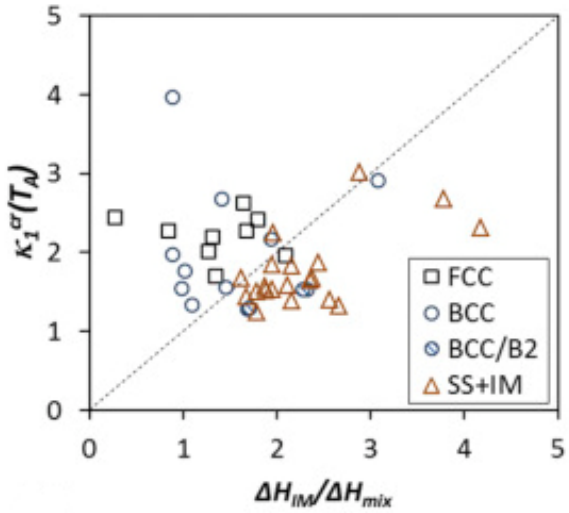










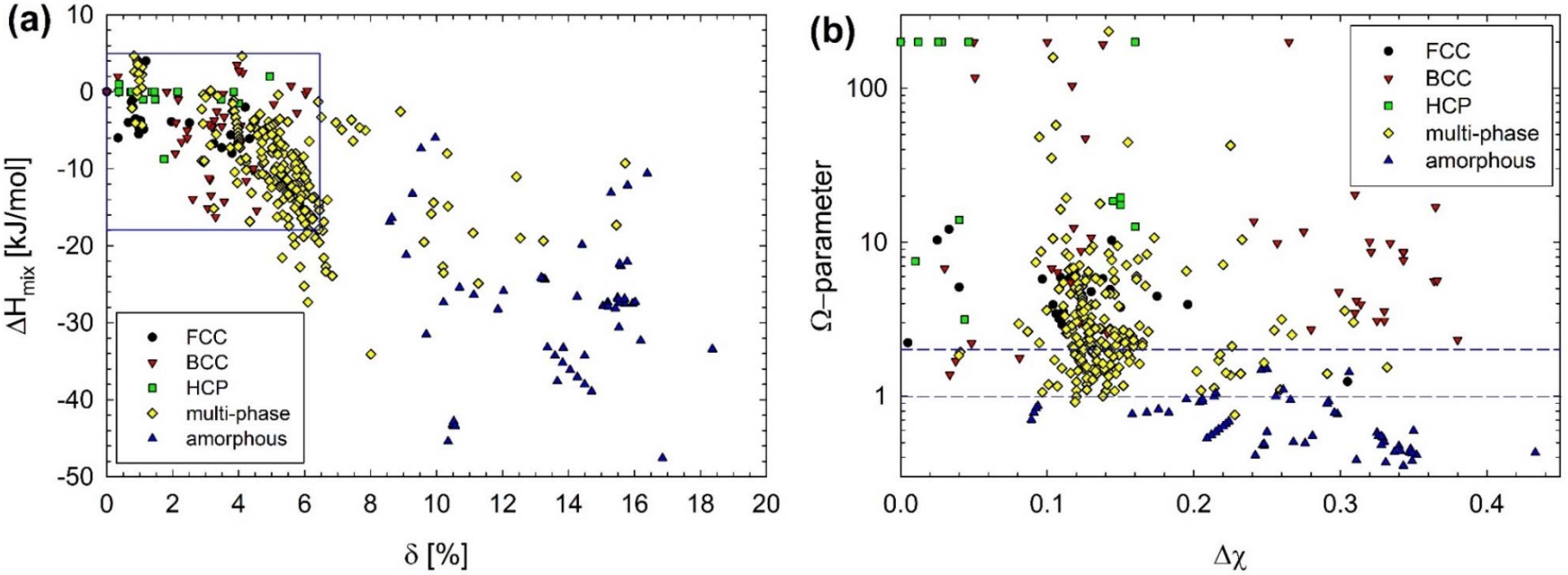


Empirical Rules for Disordered HEA Formation

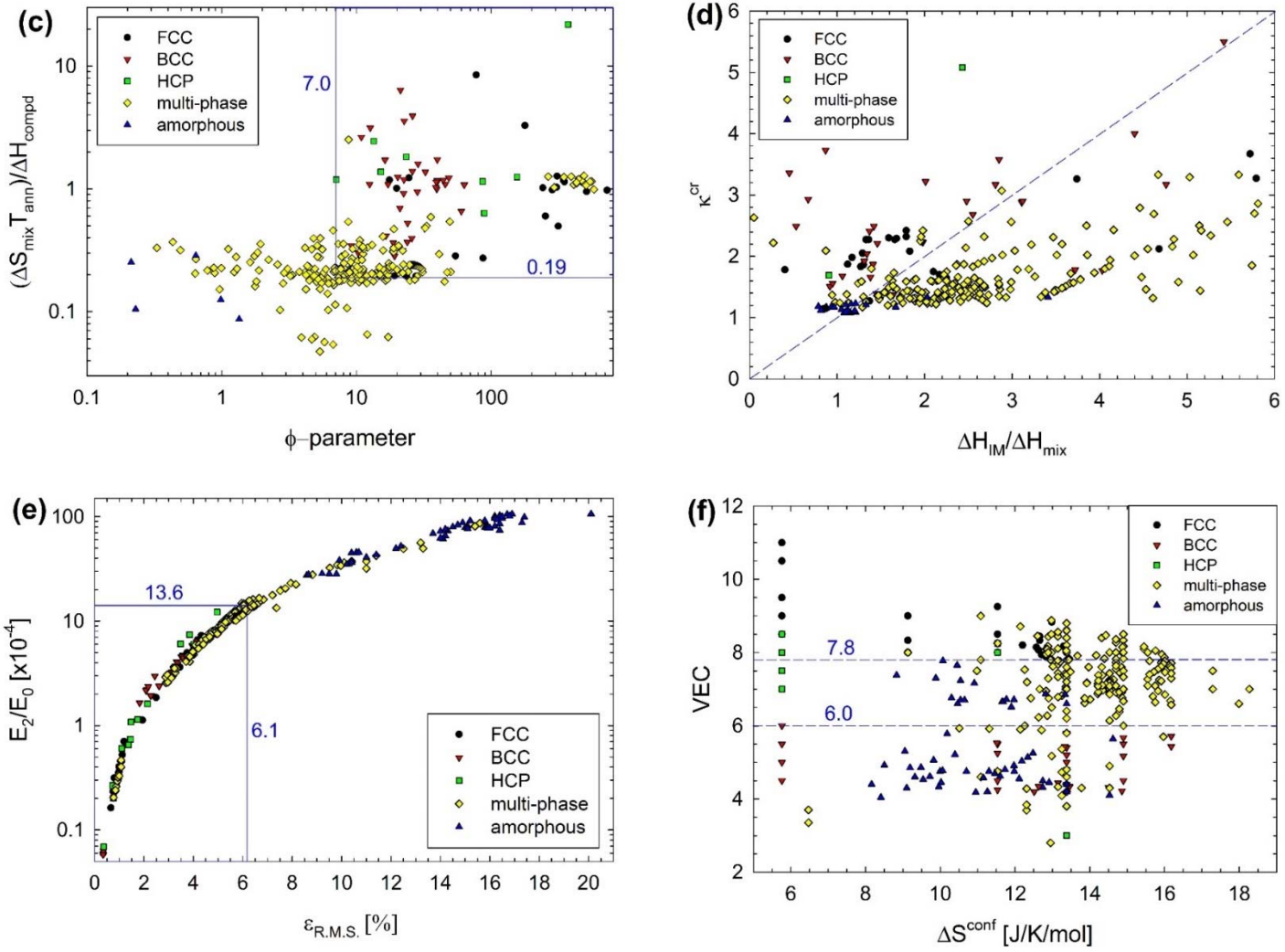
$$\Delta H_{mix} = 4\sum_{i=1,i\neq j}^{N}\Delta H_{ij}^{mix}c_i c_j \qquad \Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \qquad \phi = \frac{-R\sum_{i=1}^{N} c_i \ln c_i - |\sum_{i\neq j} 4H_{ij}c_i c_j| / T_m}{|S_E|}$$

$$\kappa_1^{cr}(T) = 1 + \frac{T\Delta S_{mix}}{|\Delta H_{mix}|}(1-\kappa_2) > \Delta H_{IM}/\Delta H_{mix} \qquad \Delta\chi = \sqrt{\sum_{i=1}^{N} c_i\left(\chi_i - \sum_{j=1}^{N} c_j\chi_j\right)} \qquad VEC = \sum_{i=1}^{N} c_i VEC_i$$

$$\delta = \sqrt{\sum_{i=1}^{N} c_i\left(1 - c_i / \sum_{j=1}^{N} c_j r_j\right)^2} \qquad <\varepsilon^2>^{1/2} \qquad E_2/E_0 = \sum_{j\geq i}^{N} \frac{c_i c_j \left|r_i + r_j - 2\bar{r}\right|^2}{4(\bar{r})^2}$$



Empirical Rules for Disordered HEA Formation



Gao et al. "Thermodynamics of Concentrated Solid Solution Alloys," Current Opinion of Solid State & Materials Science, under review, 2017.

Choose Chemically Similar Elements

H																	He
453.69 Li bcc	1560 Be hcp											B	C	N	O	F	Ne
370.87 Na bcc	923 Mg hcp											933.47 Al fcc	Si	P	S	Cl	Ar
336.53 K bcc	1115 Ca fcc	1814 Sc hcp	1941 Ti hcp	2183 V bcc	2180 Cr bcc	1519 Mn	1811 Fe bcc	1768 Co hcp	1728 Ni fcc	1357.8 Cu fcc	692.68 Zn hcp	302.91 Ga	Ge	As	Se	Br	Kr
312.46 Rb bcc	1050 Sr fcc	1799 Y hcp	2128 Zr hcp	2750 Nb bcc	2896 Mo bcc	2430 Tc hcp	2607 Ru hcp	2237 Rh fcc	1828 Pd fcc	1235 Ag fcc	594 Cd	430 In	505 Sn	904 Sb	Te	I	Xe
301.59 Cs bcc	1000 Ba bcc	*	2506 Hf hcp	3290 Ta bcc	3695 W bcc	3459 Re hcp	3306 Os hcp	2719 Ir fcc	2041.4 Pt fcc	1337.33 Au fcc	234.32 Hg	577 Tl hcp	600.61 Pb fcc	544.7 Bi	527 Po	At	Rn
Fr	973 Ra bcc	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
	*	1193 La dhcp	1068 Ce fcc	1208 Pr dhcp	1297 Nd dhcp	1315 Pm dhcp	1345 Sm	1099 Eu bcc	1585 Gd hcp	1629 Tb hcp	1680 Dy hcp	1734 Ho hcp	1802 Er hcp	1818 Tm hcp	1097 Yb fcc	1925 Lu hcp	
	**	1323 Ac fcc	2115 Th fcc	1841 Pa	1405.3 U	917 Np	912.5 Pu	1449 Am dhcp	1613 Cm dhcp	1323 Bk dhcp	1173 Cf dhcp	1133 Es fcc	Fm	Md	No	Lr	

Number on top is the melting point in Kelvin

bcc
fcc
hcp
dhcp
unusual structure
nonmetal
unknown or uncertain

http://www.theochem.kth.se/people/murugan/course/periodic_table_crystal_structure.pdf

Original source: http://en.wikipedia.org/w/index.php?oldid=595779889

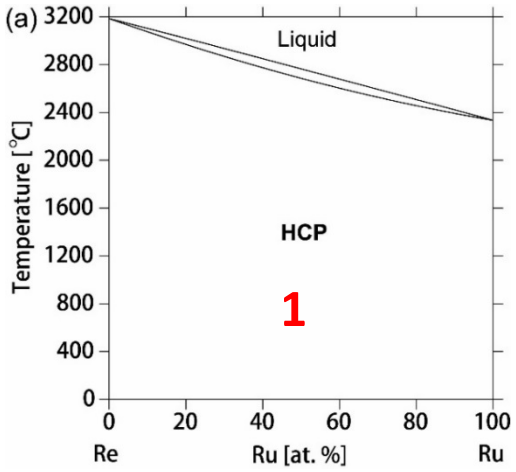
Search Strategies

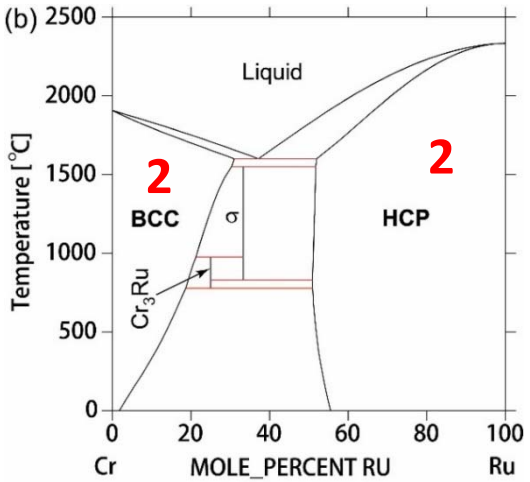
Gao, Chapter 11, "Design of High Entropy Alloys," High-Entropy Alloys: Fundamentals & Applications, eds., Gao, Yeh, Liaw, and Zhang, Springer, 2016.

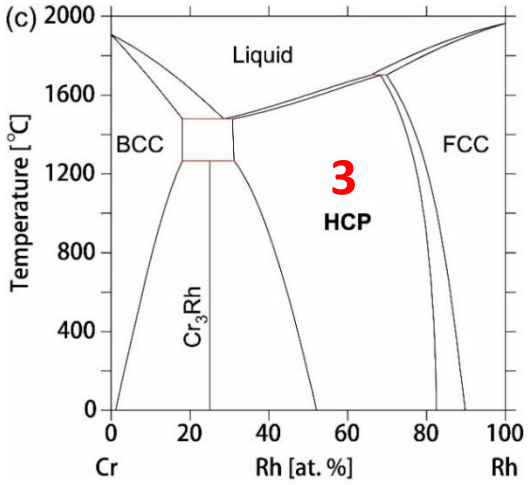
- **Inspection from existing binary/ternary phase diagrams**
  - Look for isomorphous or large solubility
- **Prediction from CALPHAD modeling**
  - The key is the database
- **Phase stability from density functional theory (DFT)**
- **Ab initio molecular dynamics (AIMD) simulations**
  - Avoid potent short-range order in the liquid
- **Experimental validations: casting and characterization**

Searching results

1. **Dy-Er-Gd-Ho-Lu-Sc-Sm-Tb-Tm-Y**
2. **Mo-Nb-Ta-Ti-V-W**
3. **Co-Os-Re-Ru**
4. **Ba-Ca-Eu-Sr-Yb**
5. **Co-Cr-Fe-Mn-Ni**
6. **Mo-Nb-Re-Ta-Ti-V-W**

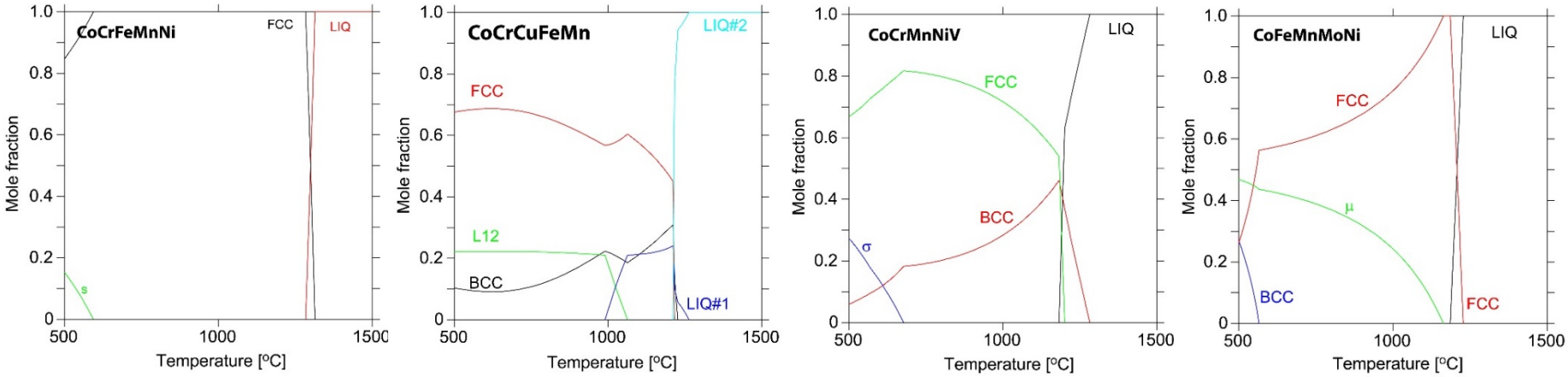






CALPHAD Modeling vs. Experiments

Equilibrium Mole Fractions vs. Temperature



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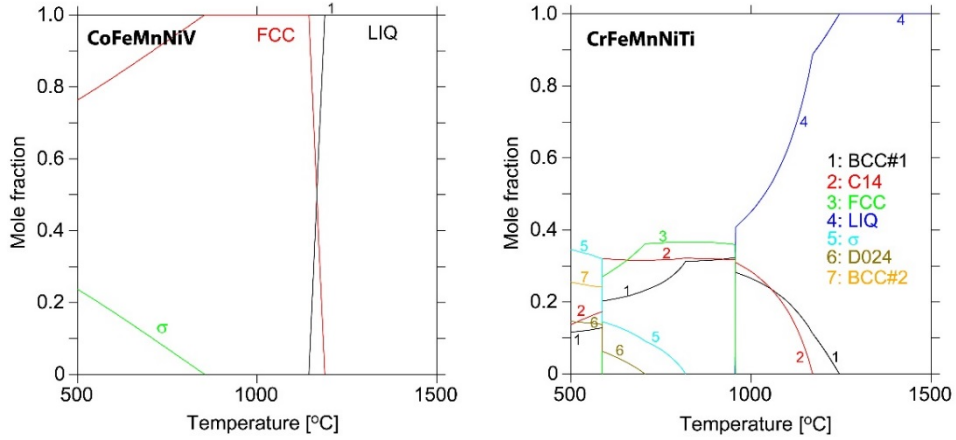
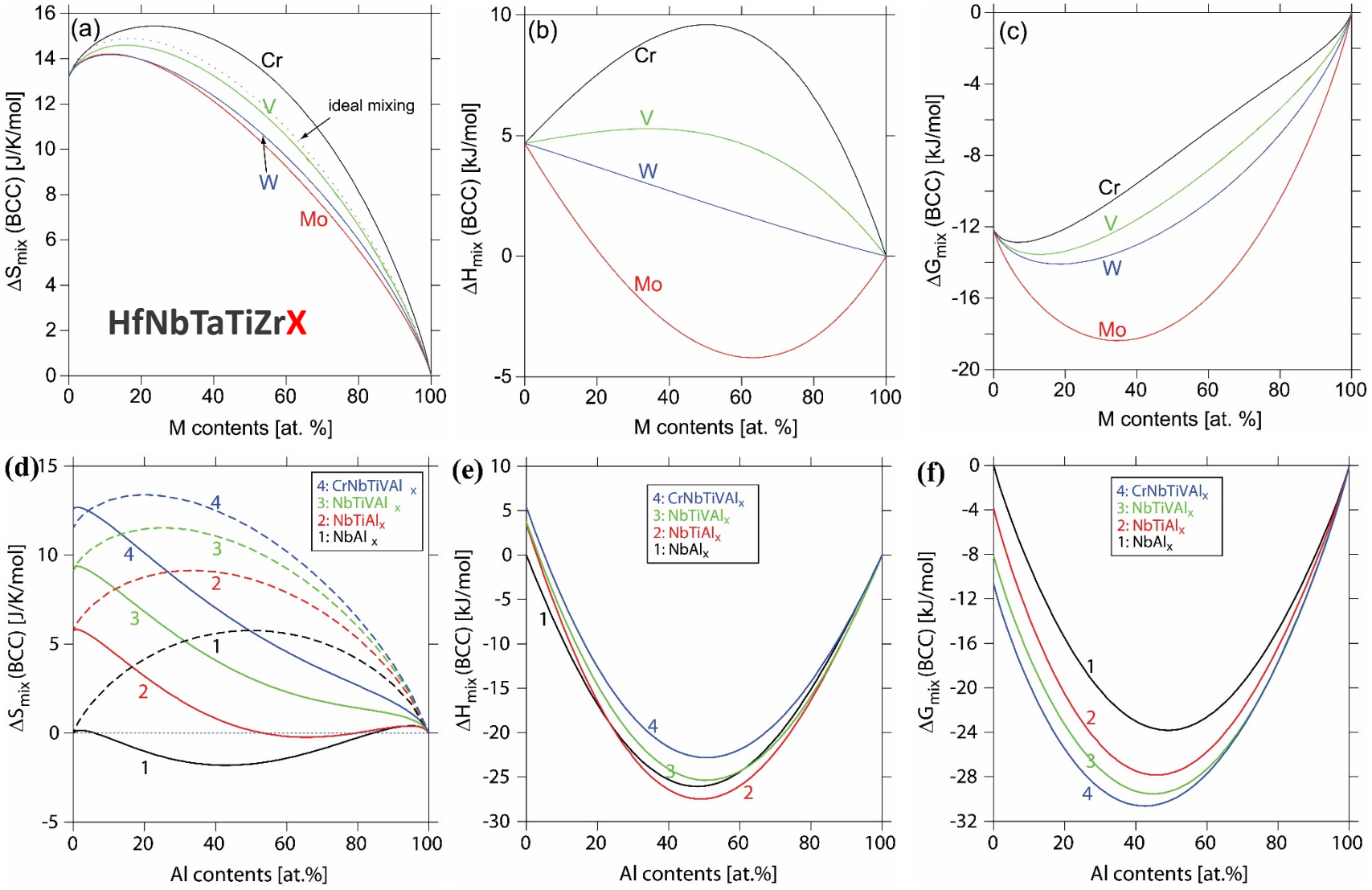


Otto: *Acta Mater.*, **61** (2013) 2628.

Only FCC was observed in CoCrFeMnNi while composite forms in other 5 alloys.

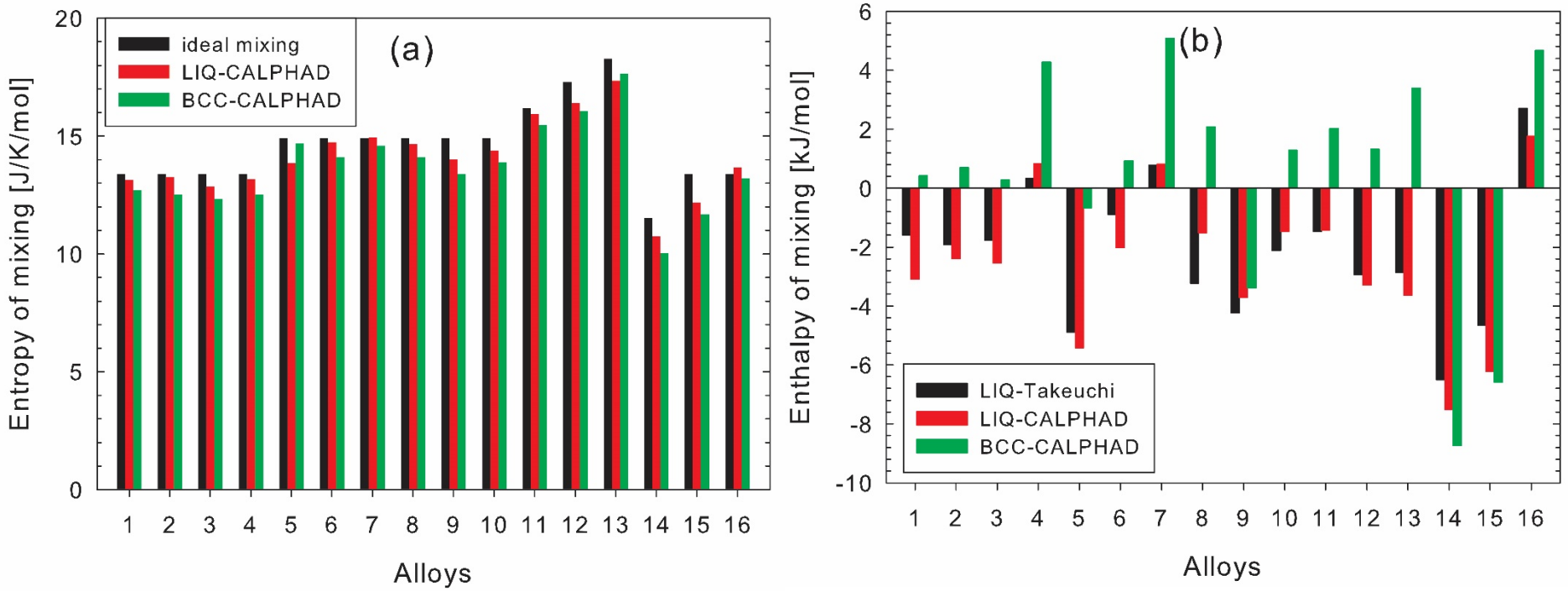
CALPHAD reasonably reproduced their observation.

CALPHAD: Entropy vs Enthalpy



CALPHAD vs Miedema Model

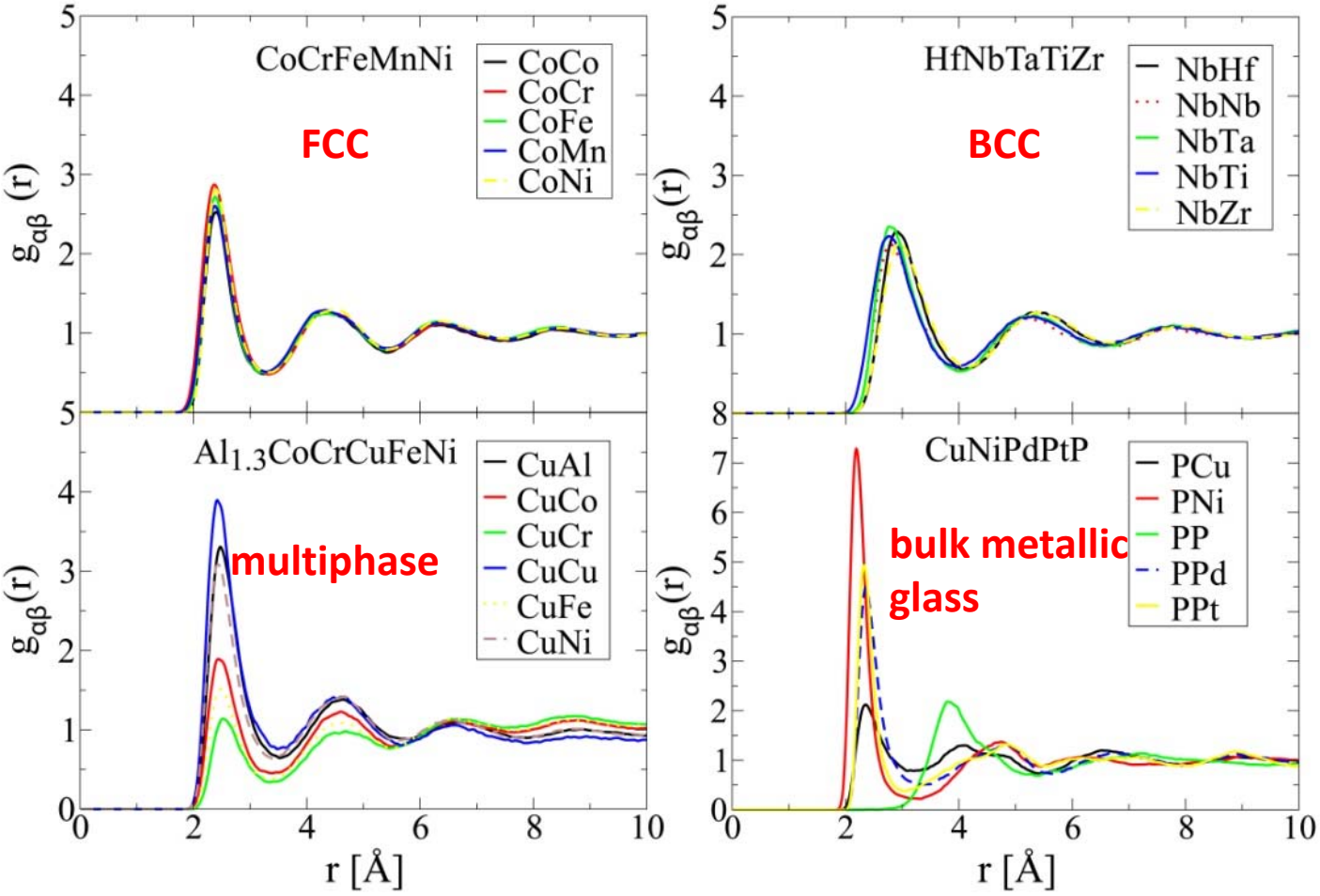
Gao, Carney, Dogan, Jablonski, Hawk, and Alman, "Design of Refractory High-Entropy Alloys", JOM, 67 (2015) 2653



1. Entropy of mixing is fairly close for BCC and liquid phases using CALPHAD and Miedema model.
2. Enthalpy of mixing shows significant discrepancy in terms of the sign and value between CALPHAD and Miedema model.

AIMD Simulations

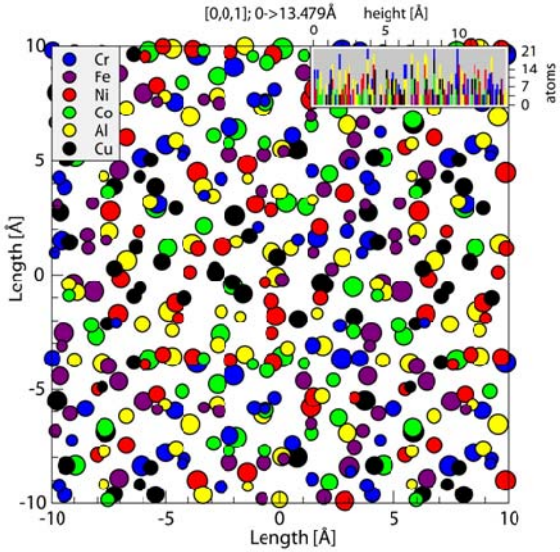
Partial Pair Distribution Function (PDF)

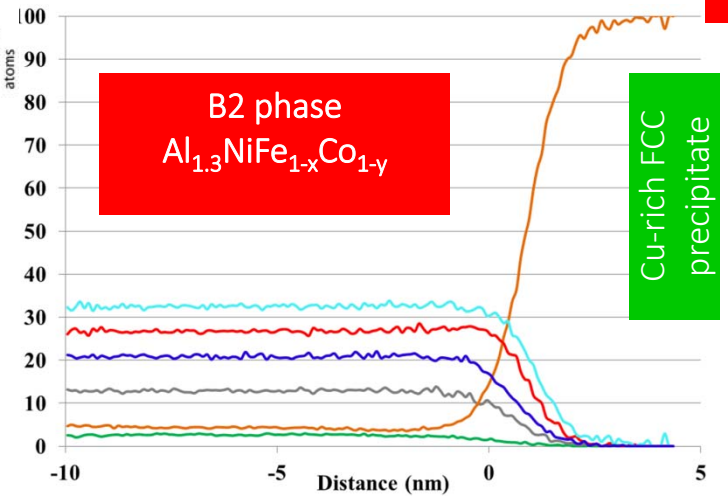


Calculated PDF in single-phase HEAs (CoCrFeMnNi and HfNbTaTiZr), multi-phase alloy ($Al_{1.25}$CoCrCuFeNi), and amorphous alloy (CuNiPdPtP).

Liquid Structure and Diffusion

Al1.3CoCrCuFeNi at 1400°C

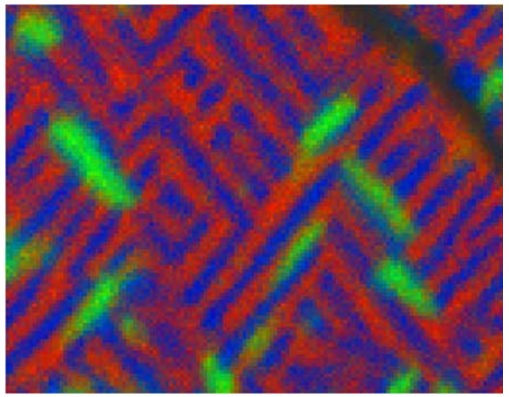


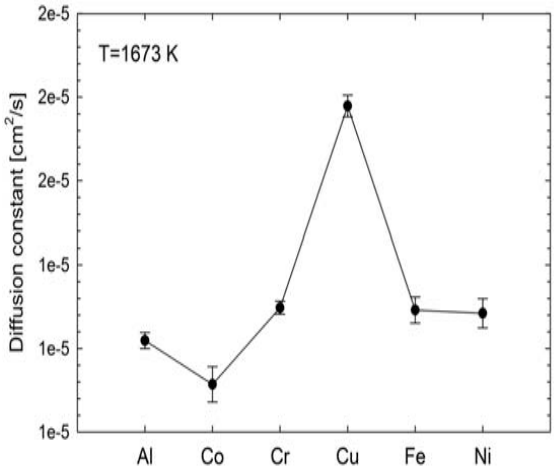


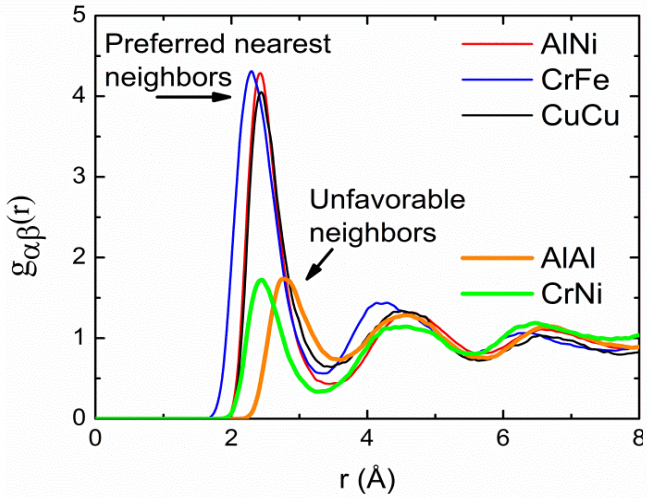
B2 phase
$Al_{1.3}NiFe_{1-x}Co_{1-y}$

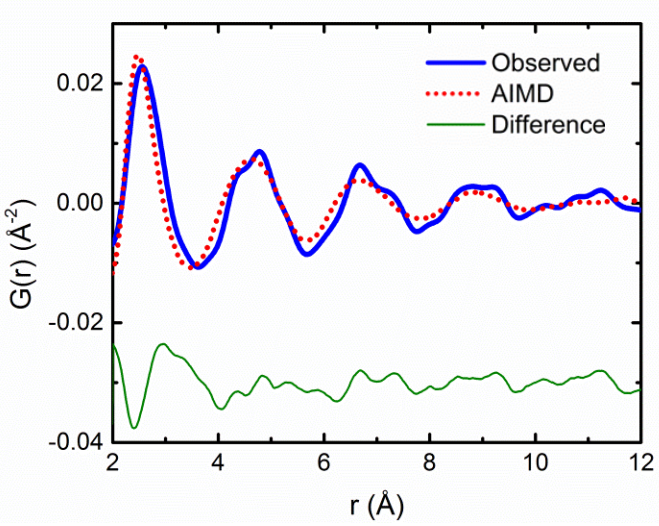
Cu-rich FCC precipitate

Al-Ni-enriched | Cr-Fe-enriched | Cu-rich



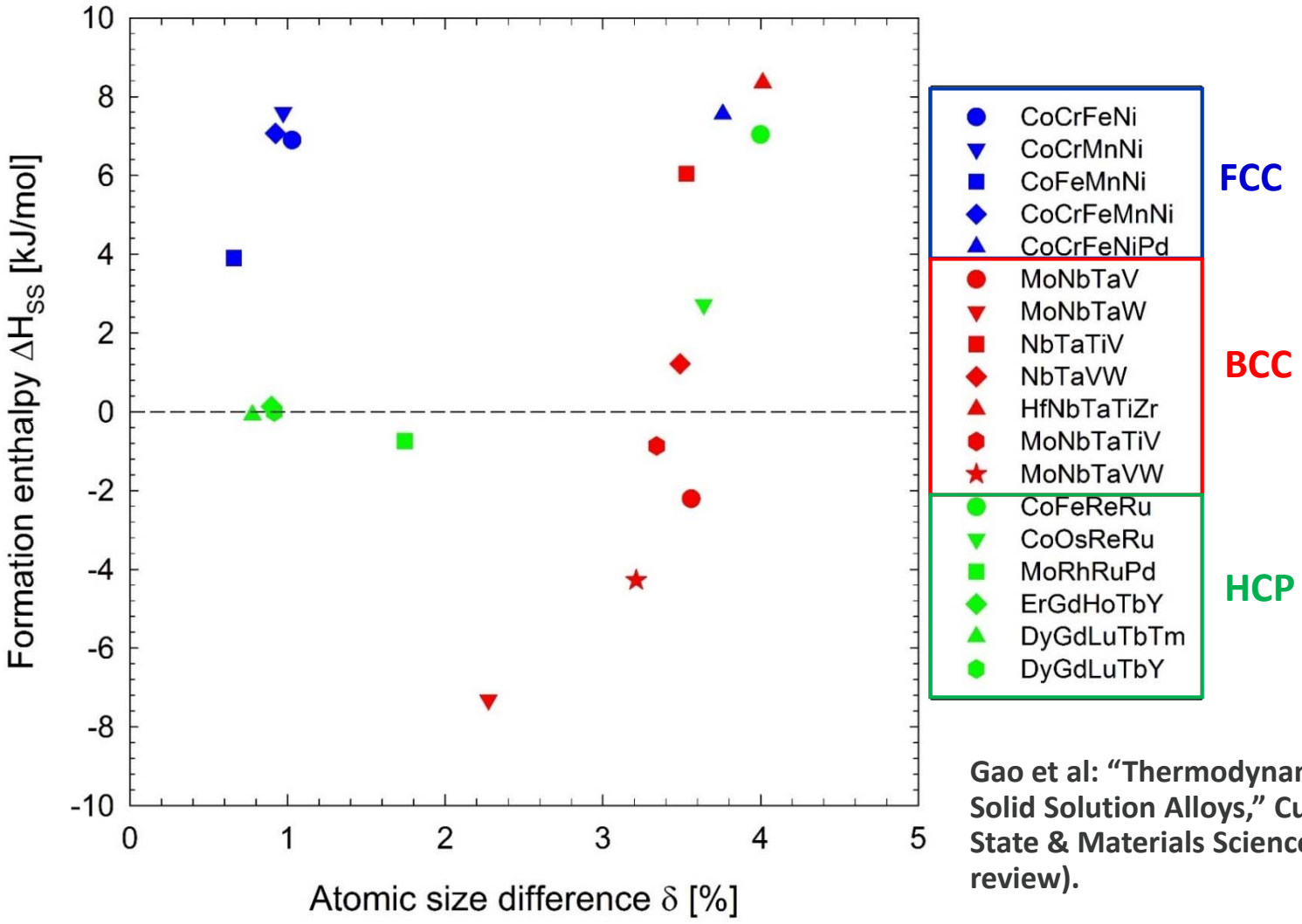






Santodonato, Zhang, Feygenson, Parish, Gao, Weber, Neuefeind, Tang, and Liaw, Nature Communication, 6 (2015) 5964.

Enthalpy of Formation: DFT



Gao et al: "Thermodynamics of Concentrated Solid Solution Alloys," Current opinion of Solid State & Materials Science, 2017 (under review).

Vibrational Entropies: DFT

Vibrational density of states

$$S_{ph}(V,T) = 3k_B \int_0^\infty n_{ph}\left[(f_{BE}+1)\ln(f_{BE}+1) - f_{BE}\ln f_{BE}\right]d\varepsilon$$

$$f_{vib}(T) = k_B T \int g(\omega) ln\left[2sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right]d\omega$$

$$S_{el}(V,T) = -2k_B \int_{-\infty}^\infty n_{el}(\varepsilon,V)\left[f_{FD} lnf_{FD} + (1-f_{FD})ln(1-f_{FD})\right]d\varepsilon$$

f_{BE}: Bose-Einstein distribution function

f_{FD}: Fermi-Dirac distribution functions

n_{ph}: phonon density of states

n_{el}: electron density of states

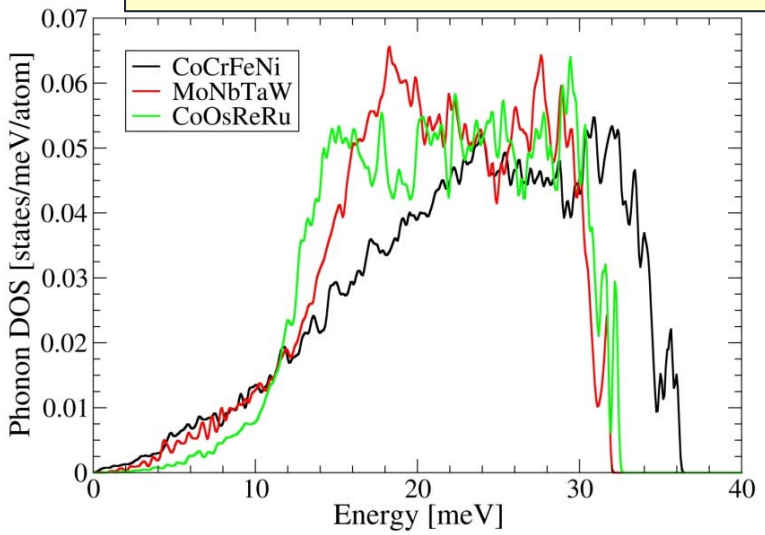
w: vibrational frequency

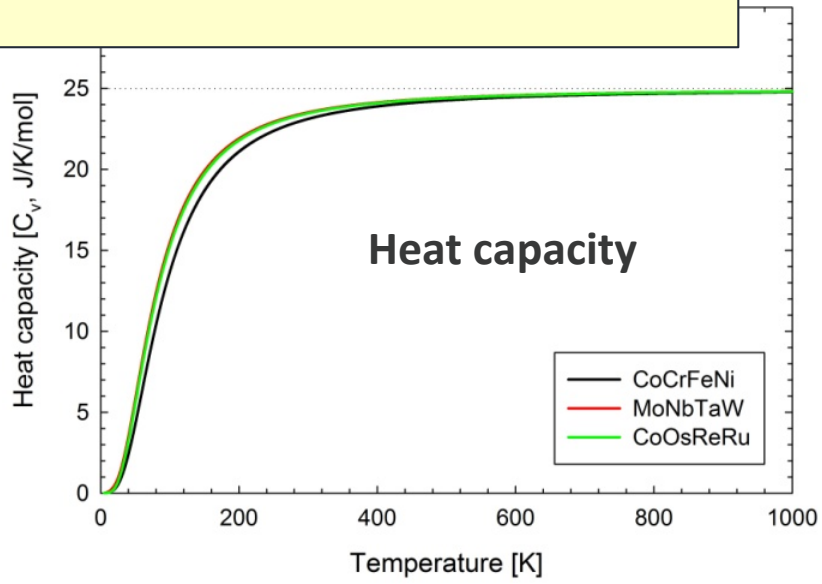
k_B: Boltzmann constant

ħ: reduced Planck constant

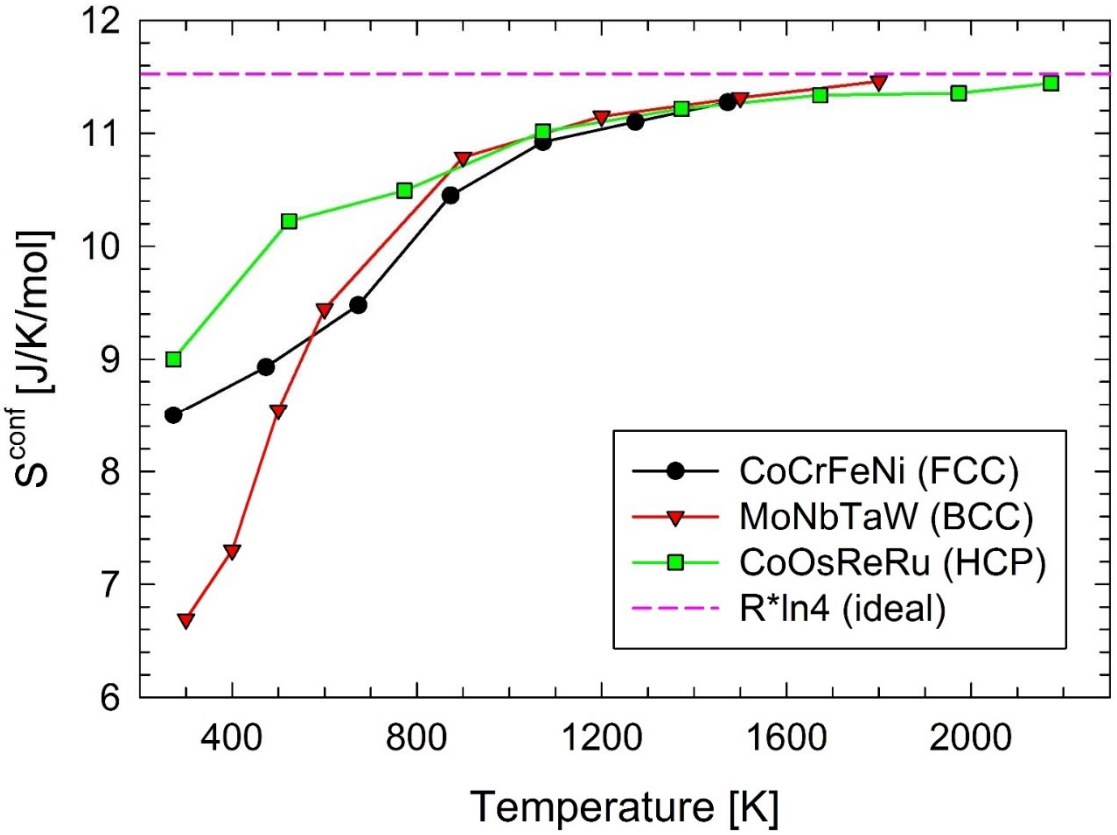
T: absolute temperature

Gao, Niu, Jiang, & Irving, Chapter 10, "Applications of Special Quasi-random Structures to High-Entropy Alloys," High-Entropy Alloys: Fundamentals & Applications, eds., Gao, Yeh, Liaw, and Zhang, Springer, 2016.



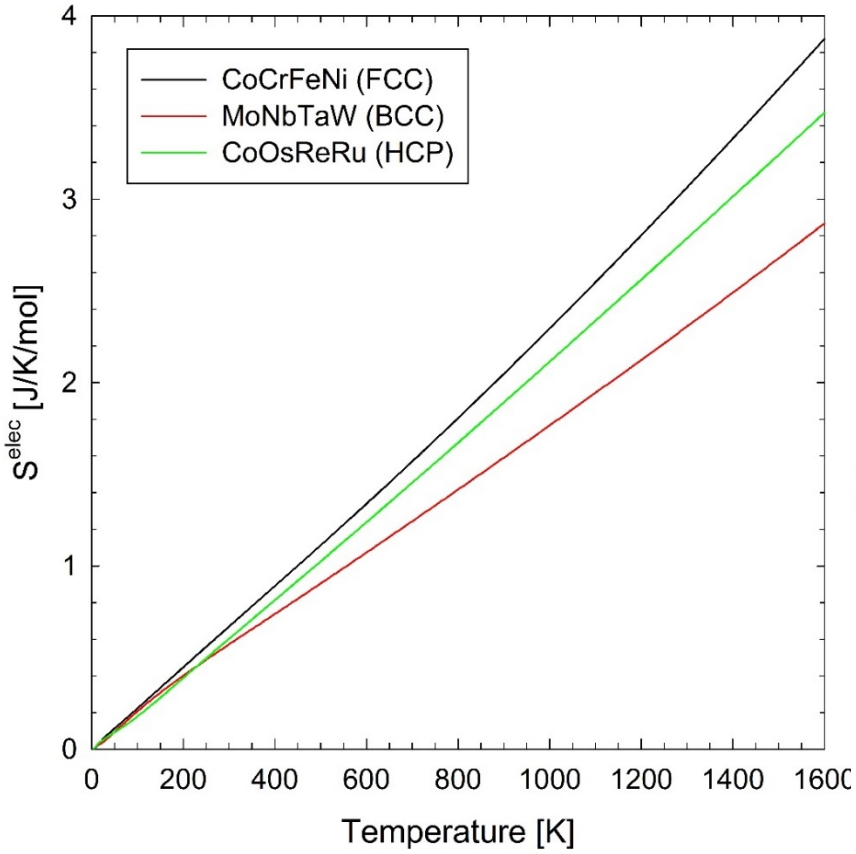


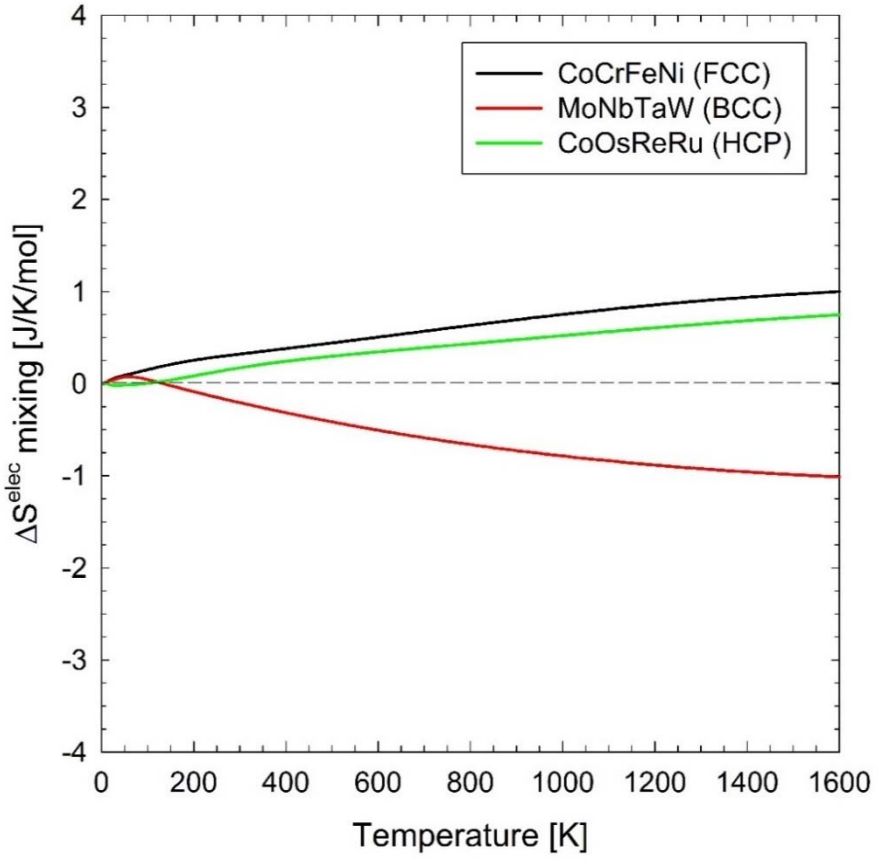
Configurational Entropy



Gao et al: "Thermodynamics of Concentrated Solid Solution Alloys," Current opinion of Solid State & Materials Science, under review, 2017.

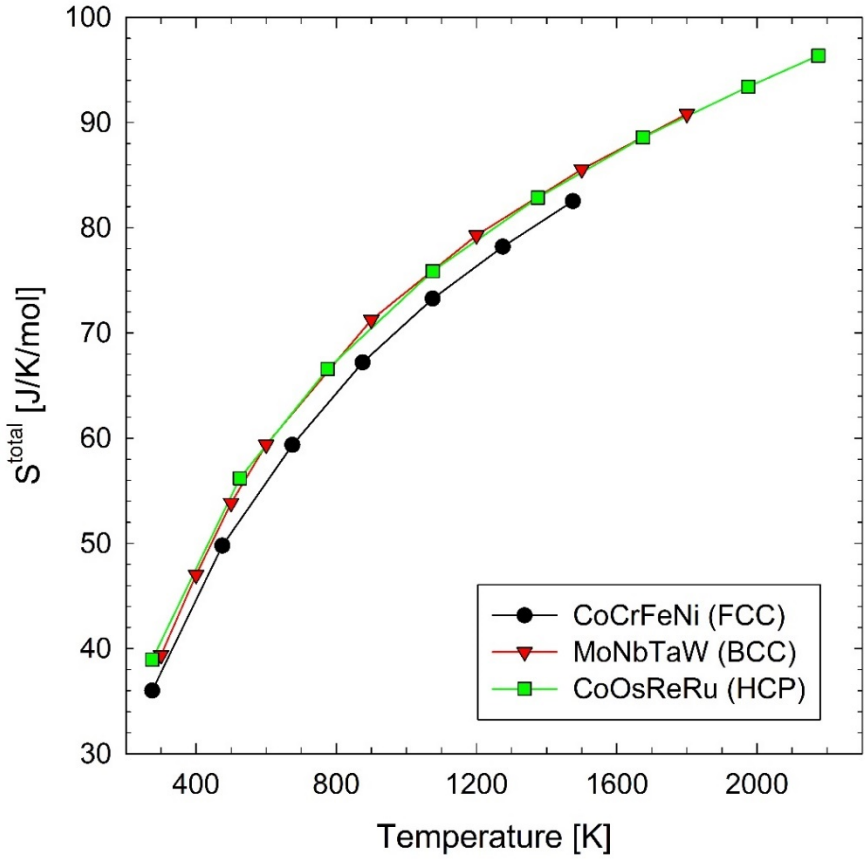
Electronic Entropy

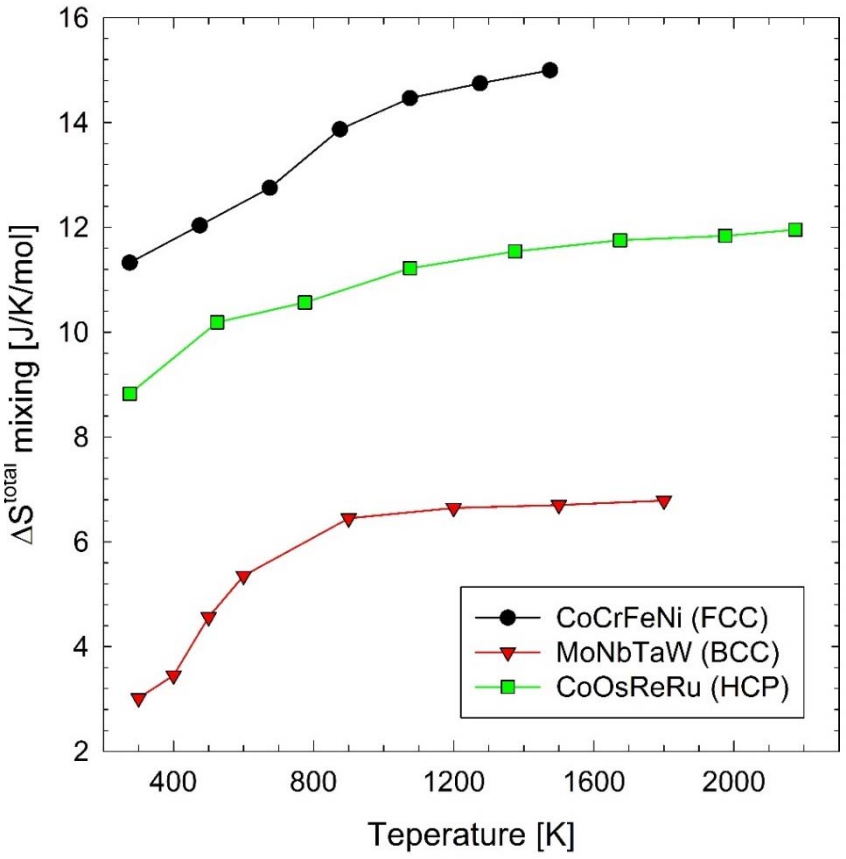




Gao et al: "Thermodynamics of Concentrated Solid Solution Alloys," Current opinion of Solid State & Materials Science, under review, 2017.

Total Entropy Properties

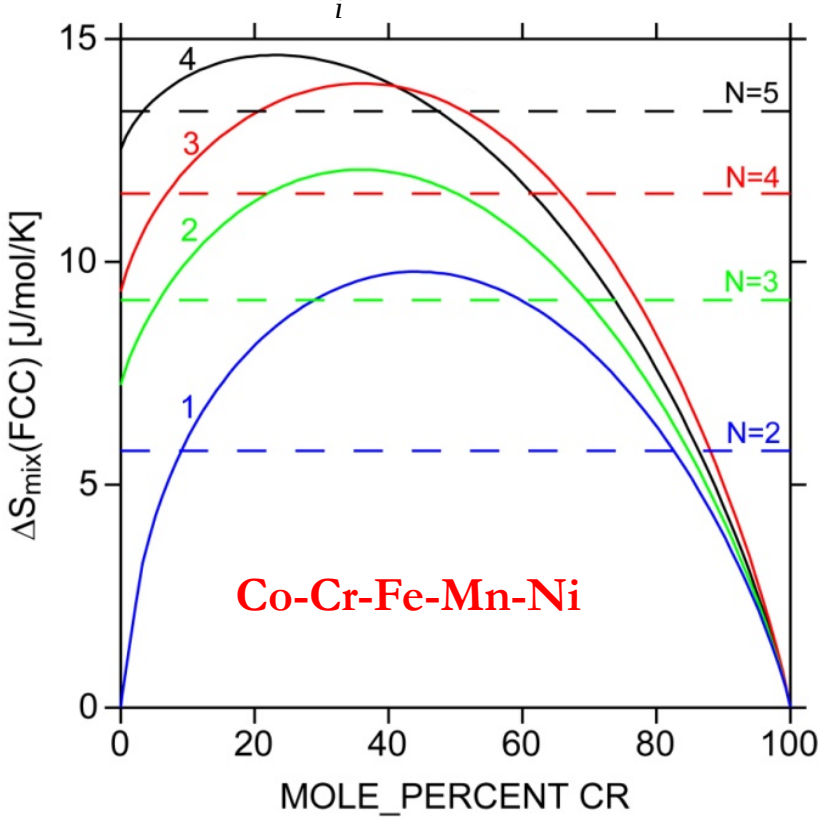


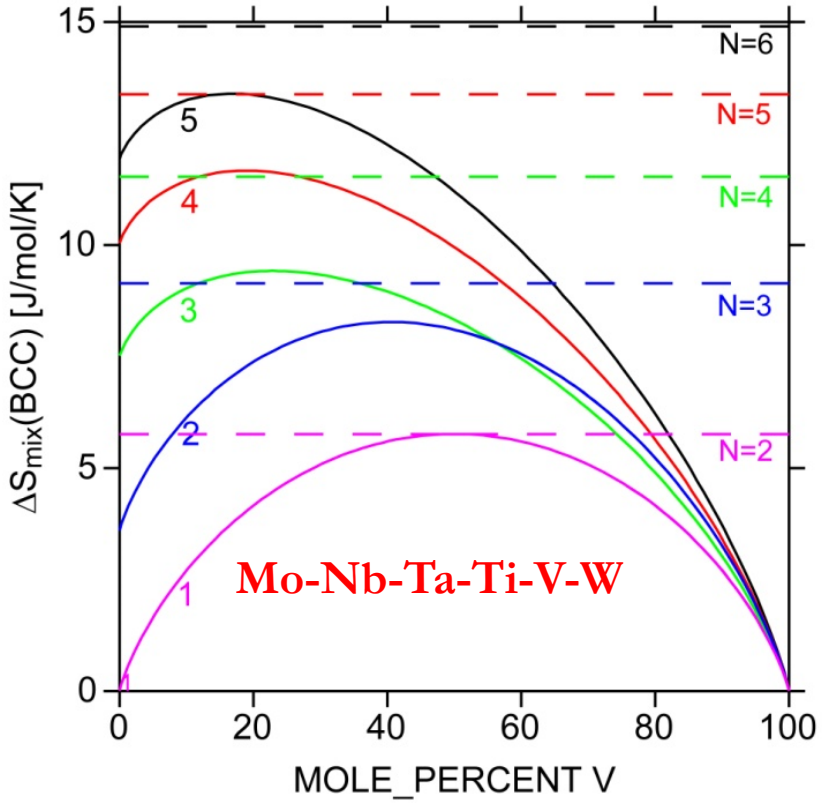


Gao et al: "Thermodynamics of Concentrated Solid Solution Alloys," Current opinion of Solid State & Materials Science, under review, 2017.

Excess Entropy: CALPHAD

$$^{ex}S^{\varphi} = {}^{total}S^{\varphi} + R\sum_i x_i \ln x_i$$





- Positive excess entropy in FCC phase is predicted in Co-Cr-Fe-Mn-Ni system.
- Negative excess entropy in BCC phase is predicted in Mo-Nb-Ta-Ti-V-W system.
- Maximum entropy of mixing may deviate from equimolar compositions.

Manufacturing Large-Scale HEAs

Mechanical & Physical Behavior

Initially, eight (8) heats of materials based on High Entropy Alloy (HEA) concept were produced.

- HEA materials have low yield strength (YS) but work harden substantially.
- HEA material behavior similar to 300 series stainless steels.
- Uniform elongation at elevated temperatures suggest SP behavior potential for selected HEA materials.

Nominal Compositions of HEA Materials

ID Name	Co	Cr	Fe	Mn	Ni	Nb	C
HEA1	26.0	22.7	24.9	---	25.9	---	---
HEA2	21.7	19.1	17.4	20.3	21.5	---	---
HEA3B	21.5	19.2	17.2	19.9	22.2	0.11	0.02
HEA4	17.6	17.2	31.0	16.3	17.9	0.09	0.02
HEA5B	17.0	20.9	29.3	15.2	17.6	0.09	0.02
HEA6B	14.9	16.1	39.8	13.6	15.4	0.17	0.03
HEA7B	12.5	15.8	46.9	11.7	12.9	0.16	0.03
HEA8B	26.8	---	22.6	24.5	26.1	---	---

Homogenization + Thermo-Mechanical Processing

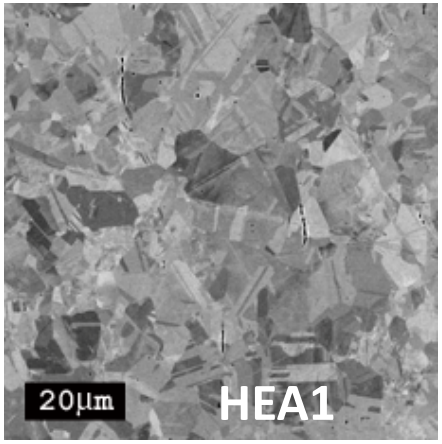
2016 R&D 100 Awards
"Computationally Optimized Heat Treatment of Metal Alloys"
NETL / P.D Jablonski and J.A. Hawk

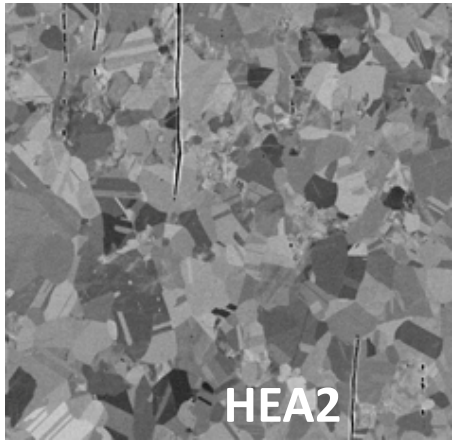
- Use computational thermodynamics and kinetics to design and optimize homogenization treatments.
- Homogenized HEAs to +/- 5%, or better, (i.e., largest allowable variation would be 95-105% of nominal).

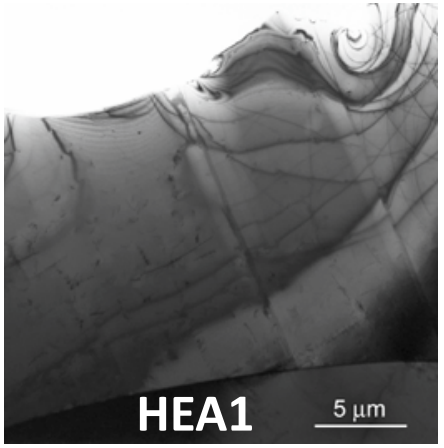
- Thermo-Mechanical processing accomplishes two things
  - Breaks up and refines the cast structure
  - Changes the size/shape of the material for further testing
- Hot working temperatures chosen so that:
  - Materials soften adequately without grain boundary failure.
  - In-process recrystallization is promoted.
  - Oxidation is minimized.

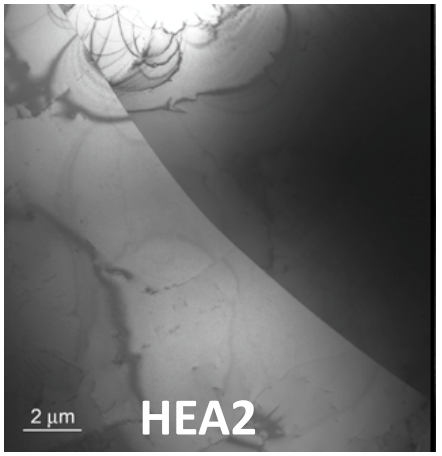
HEA Tensile Mechanical Behavior

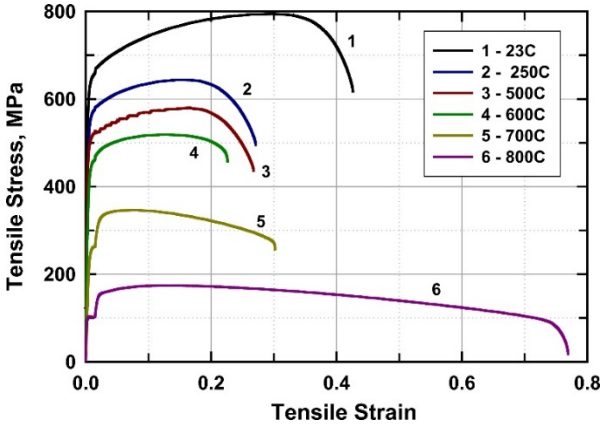
HEA1&2 materials exhibit many of same characteristics as do stainless steel.

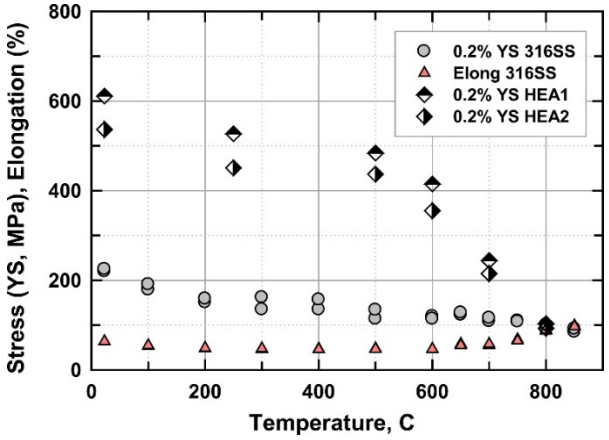


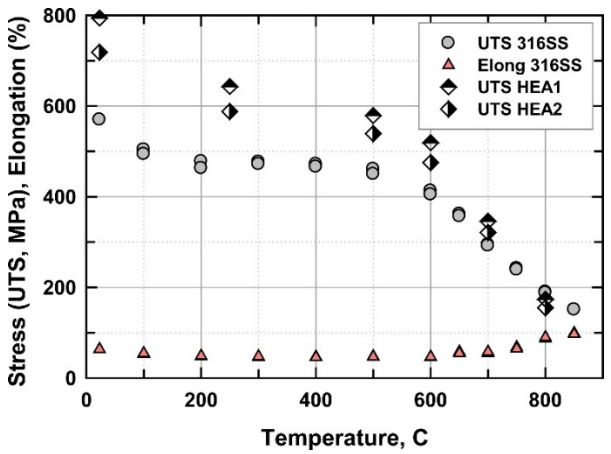








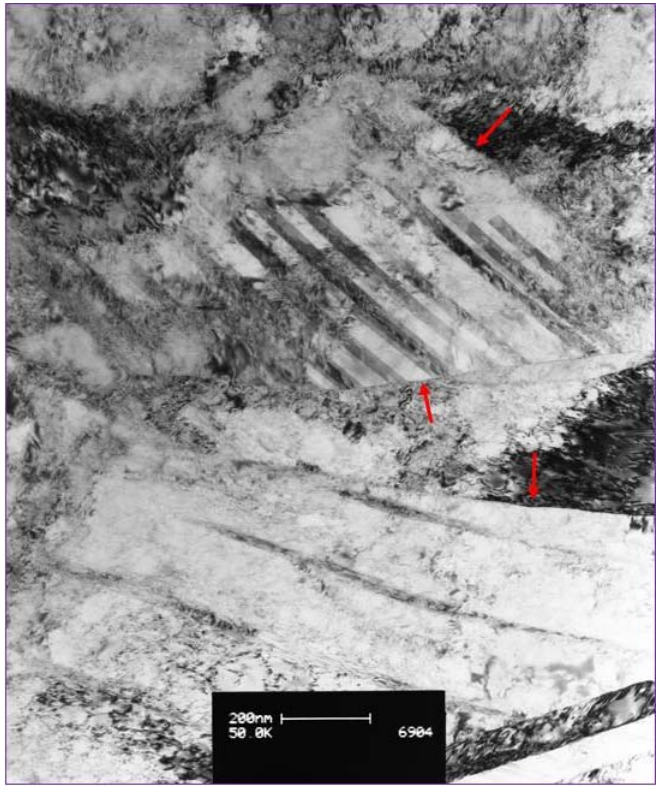


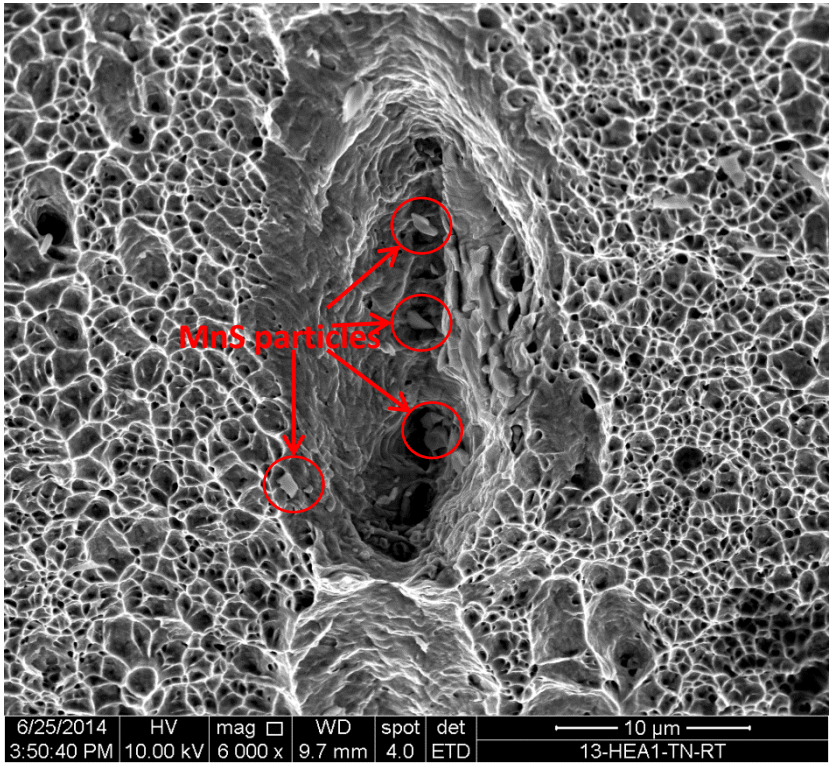


Licavoli JJ, Gao MC, Sears JS, Jablonski PD and Hawk JA, "Microstructure and Mechanical Behavior of High Entropy Alloys," J. Mater. Eng. Perf. 24 (2015), 3685-3698

HEA-1, CoCrFeNi

Tensile Tested at RT



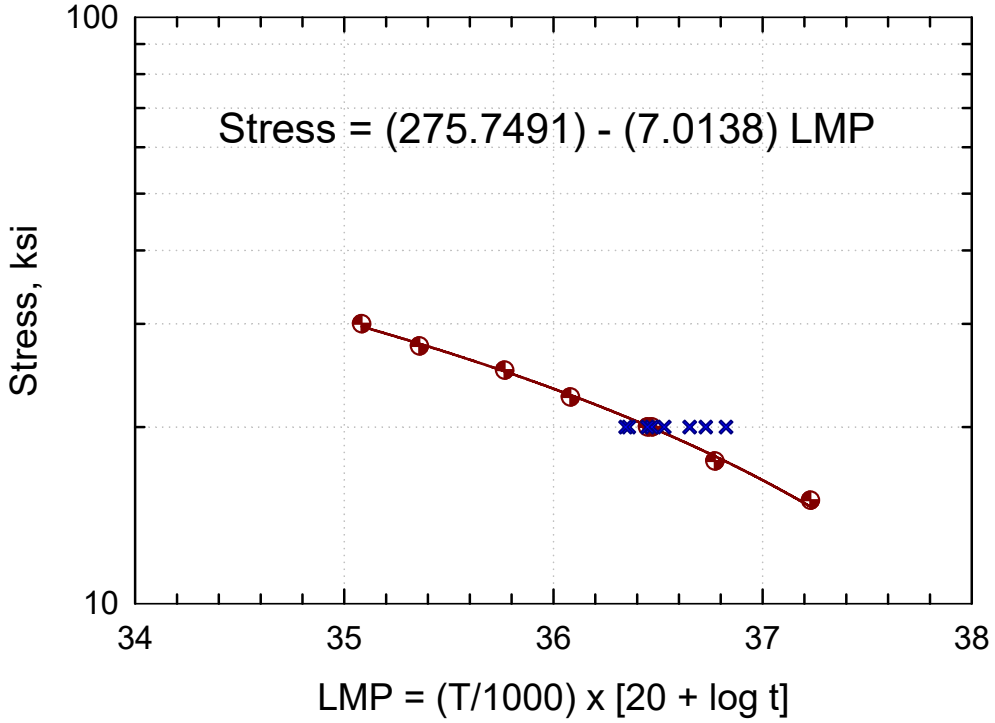


A lot of fine twinning is present in this sample – the twinning width/spacing often being in the 50-100 nm range.

Presence of high-density micro-voids on the fracture surface, suggesting excellent ductility. MnS particles are also identified.

Plot of Stress vs. LMP for HEA3B

20 ksi from 1067°F (575°C) to 1202°F (650°C)



LMP = Larson-Miller Parameter

Temperature (°C)	LMP	Time to Failure (hours)
650	36.8249	145
637.5	36.7281	255
625	36.6518	469
612.5	36.5302	822
600	36.4709	1,604
600	36.4502	1,556
587.5	36.3608	2,959
575	36.3450	6,408

- At a constant stress, the LMP value should be roughly the same no matter what the temperature of the test.
- For HEA3B the LMP value decreases from a high at the shortest creep life to a low at the longest creep life.
- This suggests continuous evolution of the microstructure during the test.

Summary of Research

- Formation of single-phase HEAs
  - Empirical rules cannot separate single-phase solid solution from multi-phase compositions effectively. More effective to combine phase diagram inspection, CALPHAD modeling, AIMD simulation, DFT enthalpy calculations, and empirical rules screening.
- Entropy calculations using DFT / MC/MD methods and CALPHAD
  - Positive vibrational entropy of mixing for FCC CoCrFeNi agrees with positive excess entropy calculated from CALPHAD. Negative vibrational entropy of mixing for BCC MoNbTaW agrees with negative excess entropy calculated from CALPHAD.
  - The true configurational entropy is close to ideal at high temperatures, but decreases with lowering temperatures. Presence of short range order lowers the configurational entropy.
  - Maximum entropy of mixing may deviate from equimolar compositions.
- DFT calculations predict:
  - Elastic properties of rare-earth HCP HEAs and BCC MoNbTaTiV HEA obey the rule of mixture for rare earth HCP HEAs.

Summary of Research

- Solid solution strengthening modeling
  - Consider differences in atomic size and shear modulus among constituents
  - Calculated yield strength agrees well with experiments for single-phase BCC HEAs
- Manufacturing large-scale ingots and Mechanical Properties
  - Research on new alloys, especially HEA's, requires particular attention to detail in how to design & prepare materials.
  - From alloy design research, melt stock, melting methodology, and subsequent thermo-mechanical processing / heat treatment, is very important and must be carefully considered.
  - Paying attention to detail in manufacturing process results in desired microstructures and consistency in mechanical – physical properties.
  - Alloy design methodology using HEA concepts on nickel superalloys resulted in several feasible/fabricable compositions.

Future Research and Follow-up Activities

- Understand the role of TMP in mechanical behavior on FCC-based HEA's (reformulate HEA1 & HEA2)
- Determine grain boundary embrittlement mechanisms and remediate in precipitation strengthened FCC-based HEA's (HEASA alloys)
- Apply alloy design philosophy to other alloy systems to hybridize them with the HE concepts
- Design philosophy improvement
  - Use ICME toolset to design "gradient" type behavior
  - Develop holistic view of microstructure design aside from entropy enhancement
- Continue corrosion / oxidations studies to understand potential

Future Research and Follow-up Activities

- Creep evaluation on modified alloys (ongoing with HEA 3B in determining activation energy for creep and creep stress exponent).
- Gain fundamental understanding of the extent of physical and mechanical performance (hardness, tensile, creep, etc.) of HEAs. Explore manufacturing options such as melt-solidification.
- Perform high-throughput screening of single-phase HEAs with face-centered cubic, body-centered cubic, and hexagonal closed-packed structures.
- Design and develop high-performance light-weight HEA's.
- Design and develop HEA oxidation and corrosion resistant coatings with outstanding fracture toughness.
- Design and develop high-entropy compounds.