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A critical review of high entropy alloys (HEAs) and related concepts

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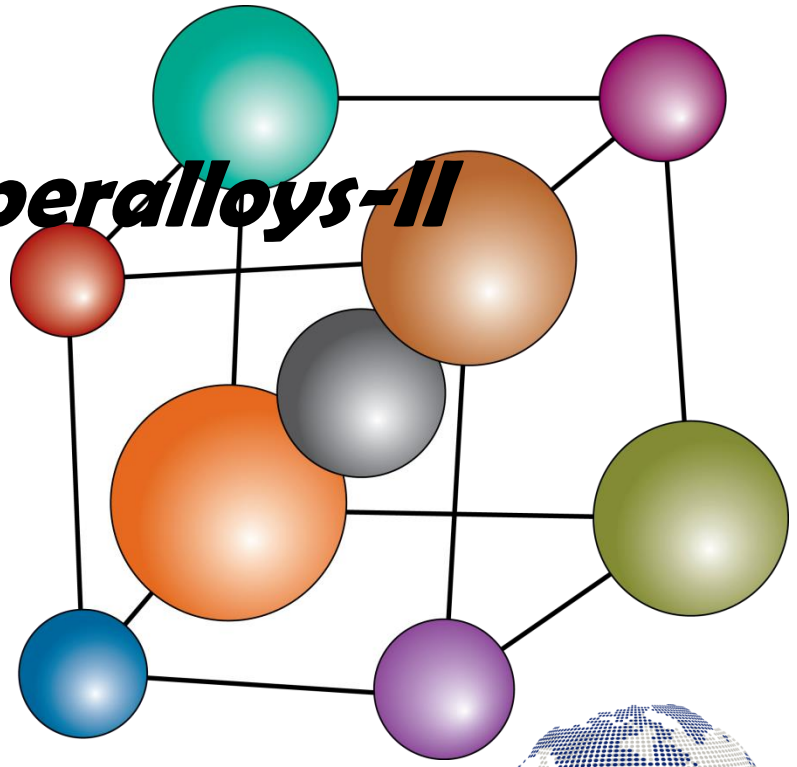
A CRITICAL REVIEW OF HIGH ENTROPY ALLOYS AND RELATED CONCEPTS

Beyond Nickel-Based Superalloys-II

Cambridge, UK

20 July 2016



A Critical Review of High Entropy Alloys and Related Concepts
DBM and O.N. Senkov, *Acta Mater.*, OVERVIEW, In Review.

New Strategies and Tests to Accelerate Discovery and Development of Multi-Principal Element Structural Alloys DBM, B.S. Majumdar, K. Wertz and S. Gorsse, *Scripta Mater.*, Accepted.

D.B. Miracle[1] and O.N. Senkov[1,2]

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OUTLINE

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INTRODUCTION
History, Definitions, Hypotheses, Visualizations

THERMODYNAMICS
Enthalpy and Entropy of Solid Solution and Intermetallic Phases

TAXONOMY
Elemental Constituents, Alloy Families

MICROSTRUCTURES
Definitions, Observed and Calculated Phases, Assessment

PROPERTIES
Functional, Mechanical, Assessment

APPLICATIONS & DESIGN
Functional, Structural

FUTURE WORK
Basic and Applied

MAJOR ACCOMPLISHMENTS
Ideas, Achievements, Closing Remarks

MANUSCRIPT APPROACH

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Each section is written in an independent style
- Extensively cross-referenced to other sections, separate summaries

Only major results are shown here
- Emphasize *Mechanical Properties* and *Major Accomplishments*

Critical review of main hypotheses recently published
- Scope is different but conclusions are the same

EARLY HEA HYPOTHESES

It's Time to Learn and Move Ahead!

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If it's published often enough, it's accepted as fact, even if there are no data to support it!

- ✓ *…more than expected 1-phase, solid solution microstructures with 'simple' crystal structures…*
- ✓ *…unusually strong and ductile…*
- ✓ *…sluggish diffusion…*
- ✓ *…violates Gibbs phase rule…*

NONE OF THESE STATEMENTS ARE CORRECT

THERE ARE GREAT REASONS TO STUDY HEAS, BUT NOT THESE

The problem lies not with the new ideas, but in letting go of the old ones. John Maynard Keynes

INTRODUCTION
Definitions and Use of Terms

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Intended or not, HEAs are associated with controlling configurational entropy to produce 1-phase solid solutions

- This stirs unproductive controversy that distracts from the major objective of exploring vast composition space by placing limits on possibilities

We apply a careful use of terms to avoid these implications

- We use the term, “HEA” when configurational entropy or the intent to produce 1-phase, solid solution microstructures are important
- We use multi-principle element alloys (MPEAs) or complex concentrated alloys (CCAs) to evoke vast composition space with no restrictions concerning entropy or the phases present
- *This is a practical approach to clarify discussion, to focus efforts, and to avoid an unproductive controversy, and is not intended to detract from contributions of pioneers in the field*

(CCA,MPEA) = HEA w/o (SS, 1-phase, entropy)

THERMODYNAMICS
All Terms Can Be Important

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Four primary thermodynamic terms must be considered in the competition between SS and IM phases

– Each of these four terms can be significant

The competition between phases is controlled by relatively small differences between these four larger values

– Usually (*but not always!*), (H^{SS}–H^{IM}) > 0 and (S^{SS}–S^{IM}) > 0

No single value or pair of values consistently dominate phase selection

These considerations make it difficult to accurately predict phases by focusing on a single thermodynamic term

$$\Delta G^{SS\text{-}IM} = G^{SS} - G^{IM} = (H^{SS} - H^{IM}) - T(S^{SS} - S^{IM})$$

TAXONOMY
Summary

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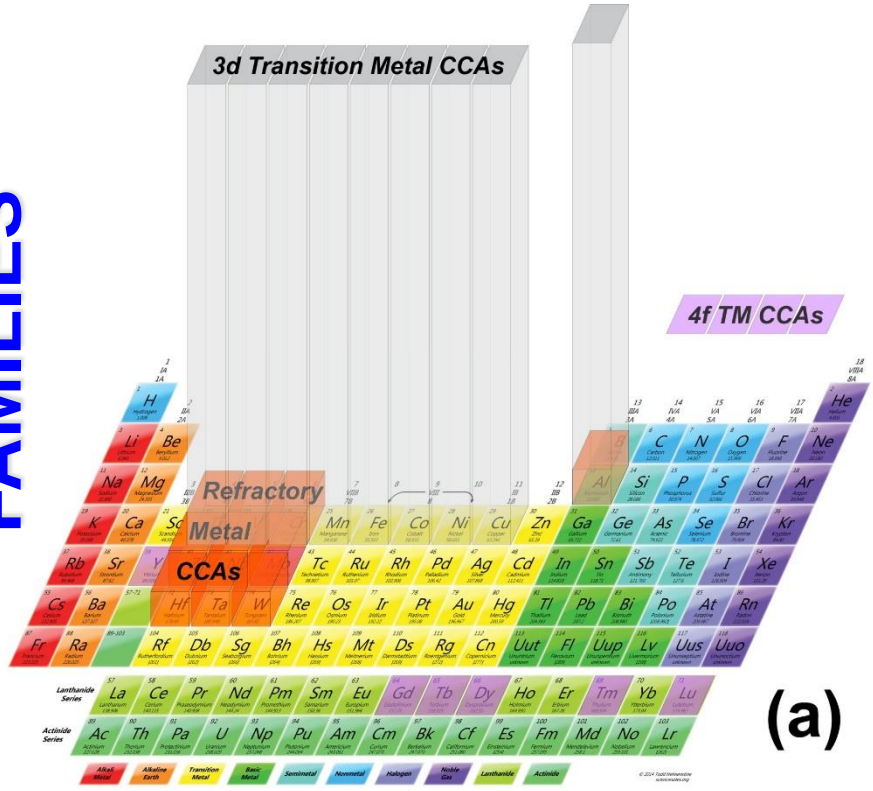
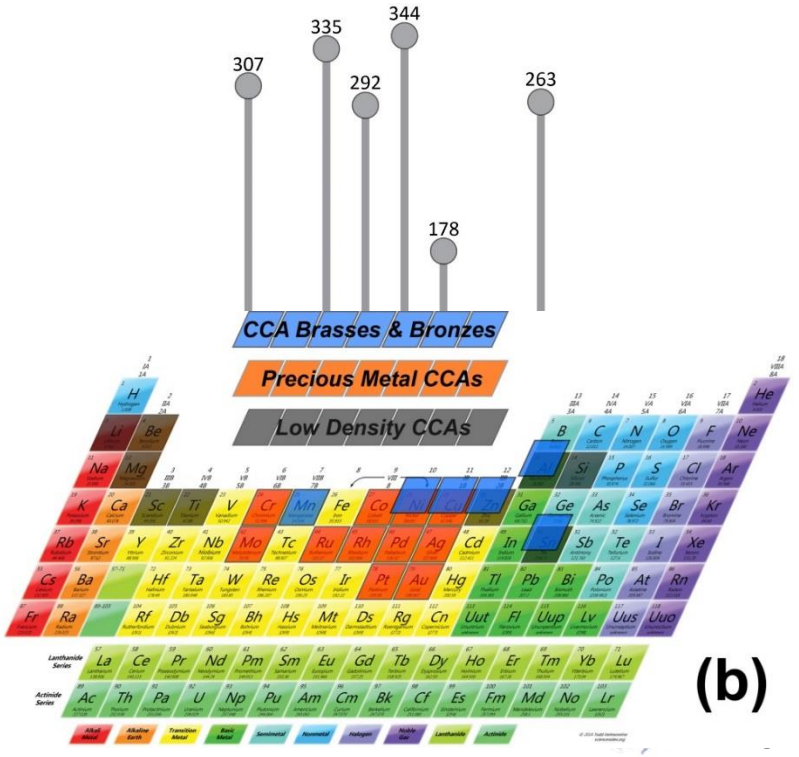
A remarkable focus is found on elements used in MPEAs, and in groupings of elements

A broader use of element groupings is now underway

MPEA ALLOY FAMILIES





MECHANICAL PROPERTIES
3d Transition Metal MPEAs

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MPEAs are often claimed to be unusually strong and ductile, but available data don't support these claims

3d transition metal MPEAs have essentially the same properties as austenitic stainless steels and nickel alloys

- Generally have RT σ_y below 300 MPa and σ_{uts} below 700 MPa
- Significant strengthening from work-hardening and grain refinement are not expected to be effective above about $T_m/2$ (about 500C)

Austenitic stainless steels and nickel alloys are 3d transition metal CCAs

- All austenitic stainless steels and nickel alloys have Cr-Fe-Ni as principal elements and can also have significant additions of Co, Cu, Mn, Mo

3d TM MPEA strengths do not compete with precipitation hardened stainless steels or nickel superalloys

- σ_y <100 MPa at about 1100 K, but superalloy sheet requires σ_y >200 MPa and blades require σ_y >600 MPa

MECHANICAL PROPERTIES

3d Transition Metal CCAs (Tension)

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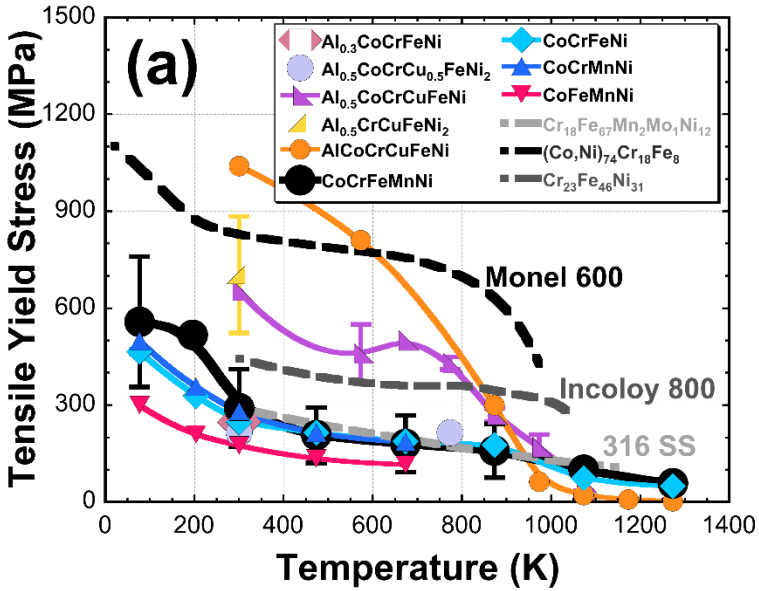

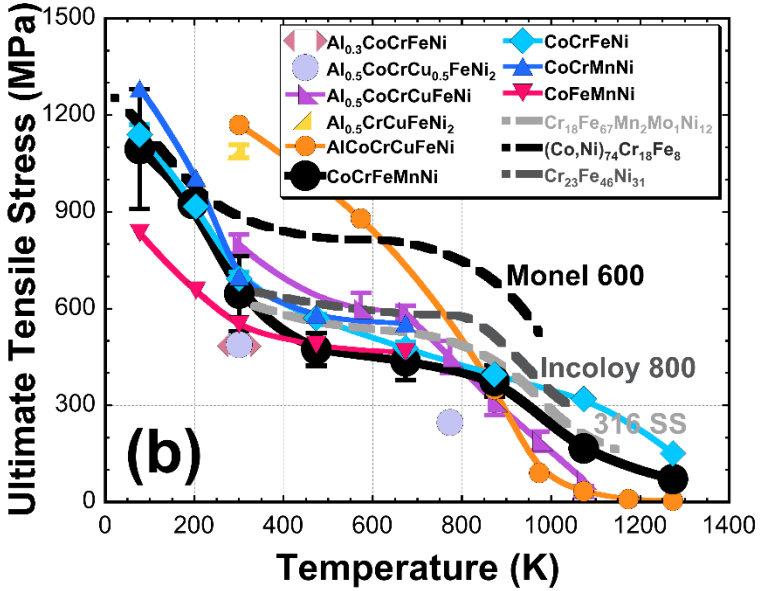

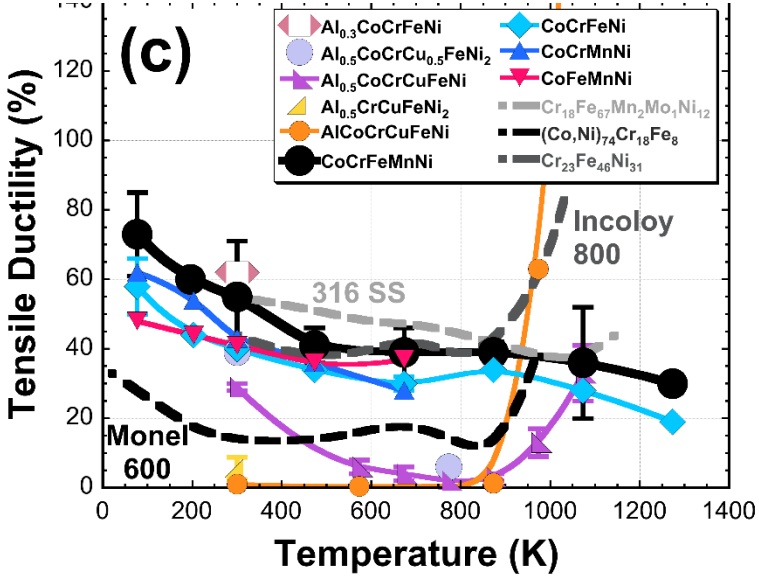

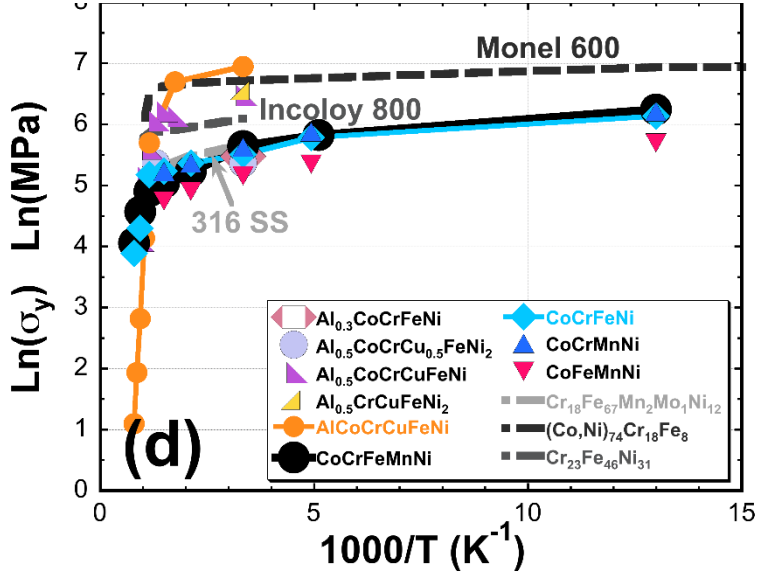

REFRACTORY METAL CCAs
Structural Properties Summary

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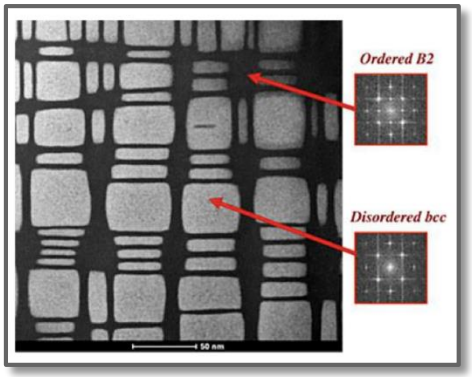
Refractory metal CCAs were created to compete with nickel superalloys

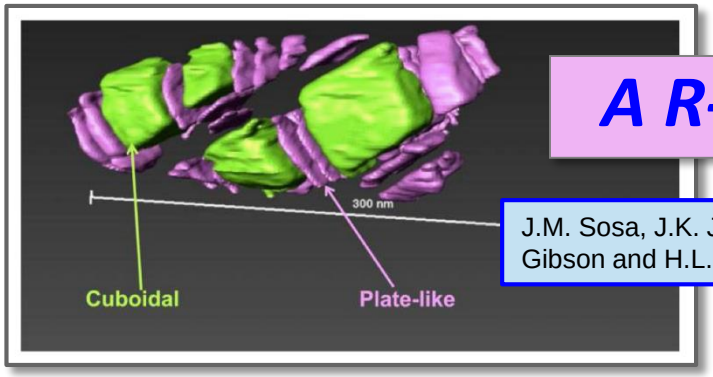
- Refractory metal CCAs are still in relatively early stages of exploration (only 26 alloys in this assessment)
- A wide range in elemental properties (density, modulus, environmental resistance) suggest a wide range in alloy properties

Densities range from 5.59 to 13.75 g cm^{-3}

Most alloys have one or two BCC phases, one or more Laves phases, and one alloy reports a B2 phase

- The full extent of the BCC solid solution phase field has not been explored





A R-CCA Superalloy!

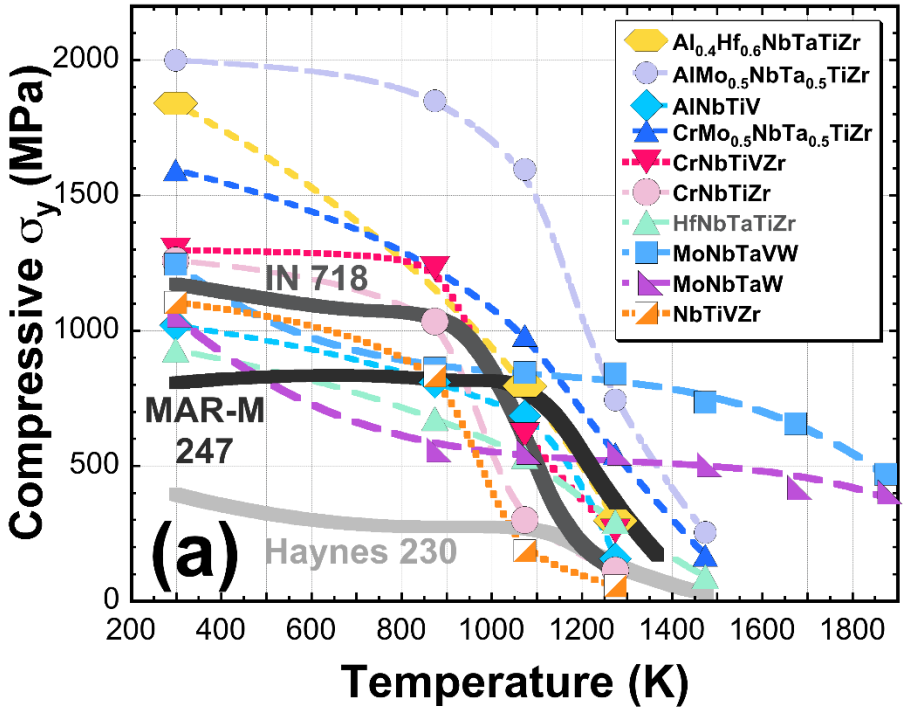
J.M. Sosa, J.K. Jensen, D.E. Huber, G.B. Viswanathan, M.A. Gibson and H.L. Fraser; *Mat. Sci. Tech.*, **31**, 1250 (2015).

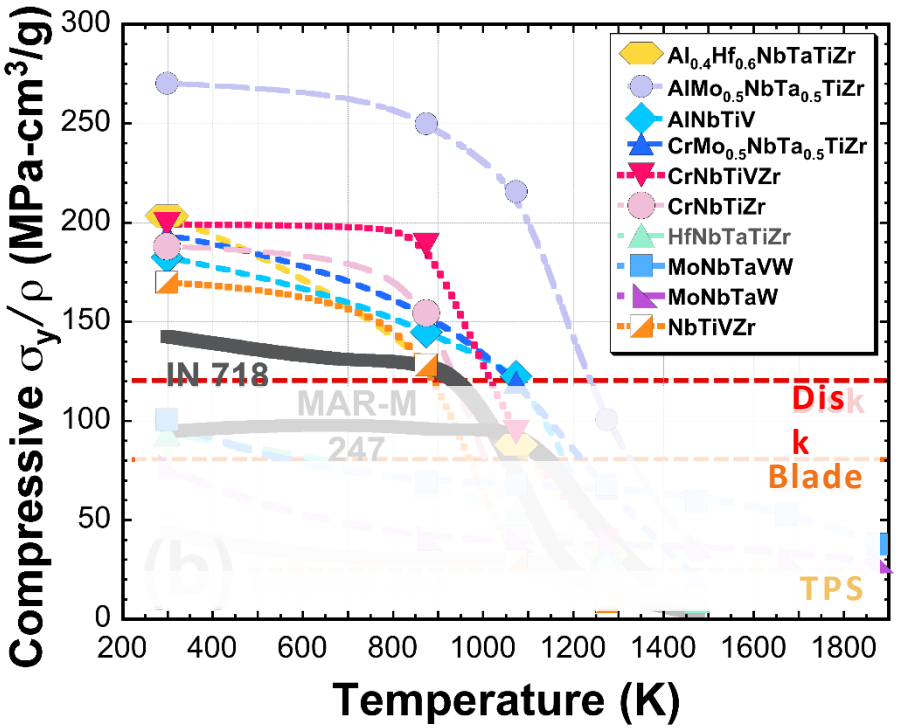
REFRACTORY METAL CCAs
Structural Properties Summary

A Century of Scientific Excellence

Most mechanical properties are measured in compression with only a few tensile studies

- Several alloys have yield and specific yield strengths that show potential to increase stresses and/or temperatures compared to superalloys
- The strongest alloys have ≥10% RT compressive ductility, offering the possibility of useful tensile ductility





REFRACTORY METAL CCAs
Suggested Future Work

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Continued exploration of principal element combinations

- New alloy bases
- Control the type, volume fraction, size, morphology and distribution of second phases to design precipitation strengthened microstructures
- Extent of solid solution phases

Tensile properties of alloys with compressive ductility ≥10%

Characterize oxidation behavior and explore alloying to improve environmental stability

- Simple, hi-throughput oxidation screening tests are recommended

Effect of deformation processing on microstructure, properties

- Cold-rolling has been demonstrated in one alloy

A NEW STRATEGY TO RAPIDLY CHARACTERIZE ALLOYS

New Strategies and Tests to Accelerate Discovery and Development of Multi-Principal Element Structural Alloys
DBM, B.S. Majumdar, K. Wertz and S. Gorsse, *Scripta Mater.*, Accepted.

Conventional Characterization

1st Tier
- Tensile strength, ductility

2nd Tier
- Fracture toughness
- Fatigue
- Creep

Final Characterizations
- Environmental resistance
- '…ilities'

Strengths
- Enables intuitive 'pre-selection' when a knowledge base already exists for a small number of candidate alloy systems.

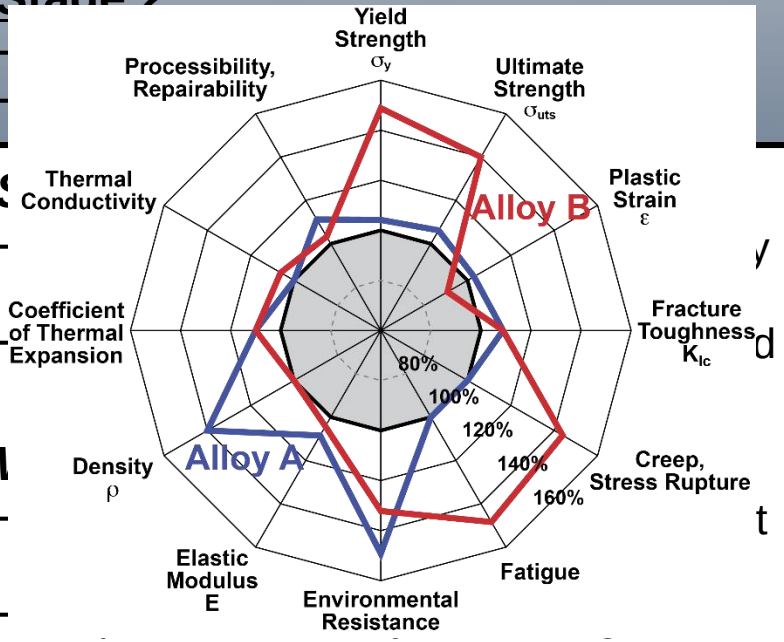
Weaknesses
- Starts with difficult-to-measure properties that depend on both composition and microstructure, making it hard to reject alloys quickly.

New Characterization Strategy

Stage 0
- Hi throughput phase diagram calculations

Stage 1
- Microstructure-independent properties
- Environmental resistance
- Modulus, density, thermal properties

Stage 2



PHASE DIAGRAM CALCULATIONS

A Quick Head Start to Alloy Discovery

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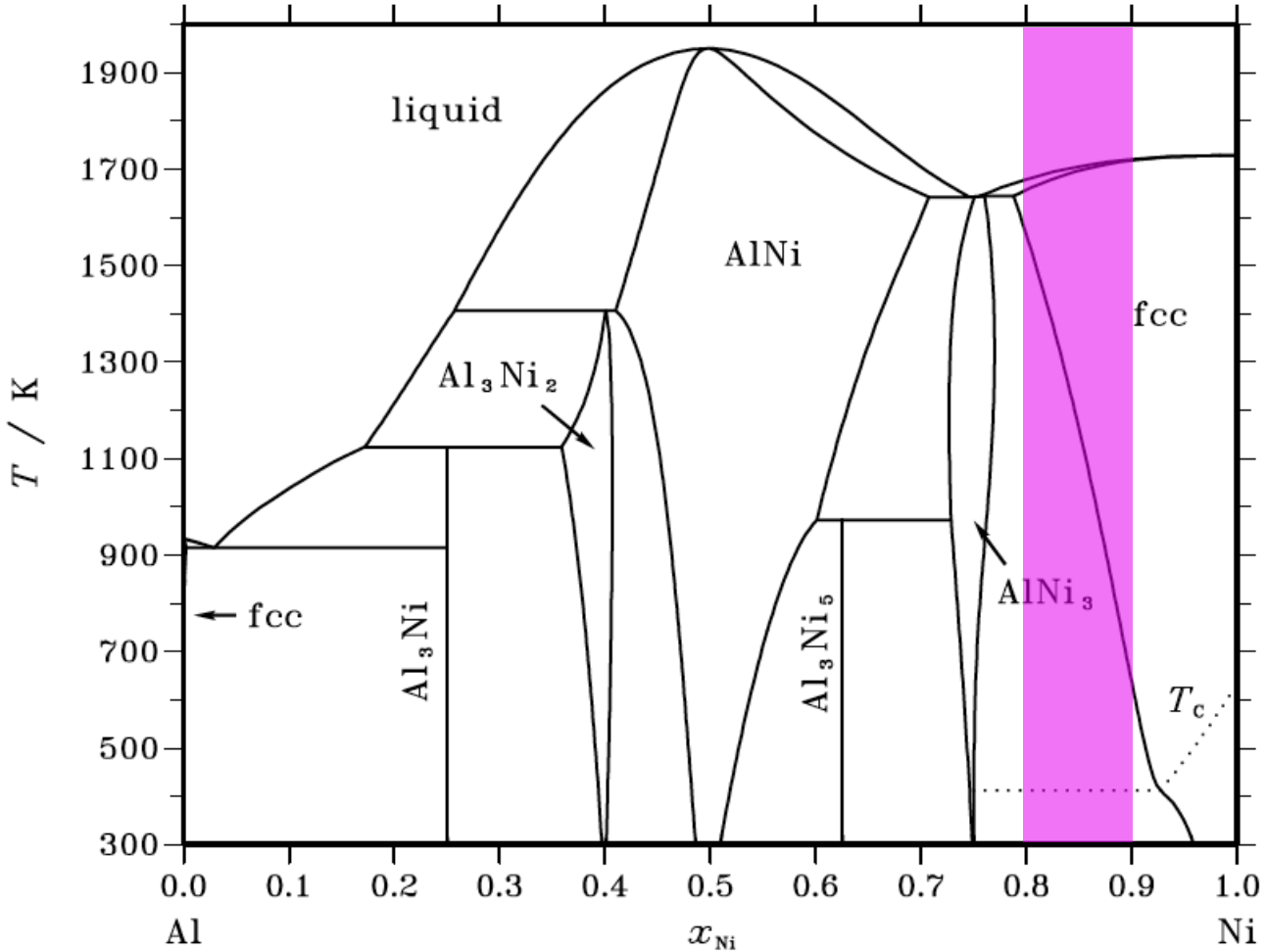
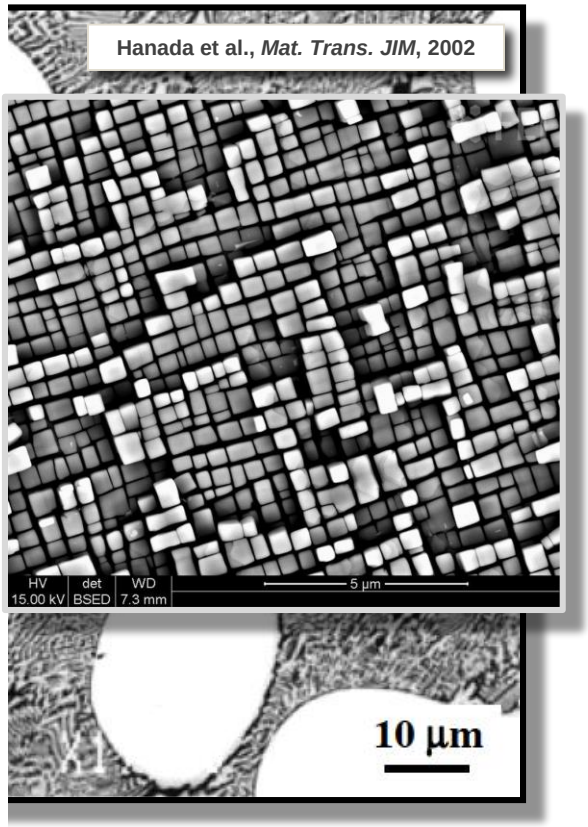
Specific phase diagram features enable two-phase microstructures that may give a good balance of properties





PHASE DIAGRAM CALCULATIONS

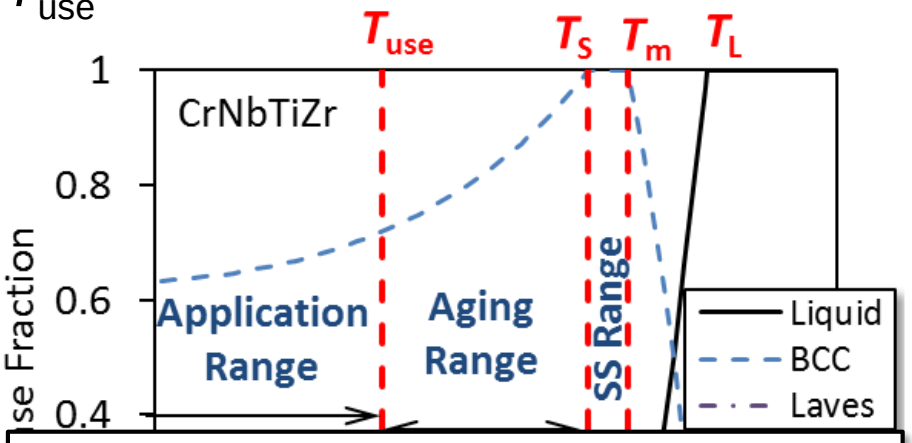
A Quick Head Start to Alloy Discovery

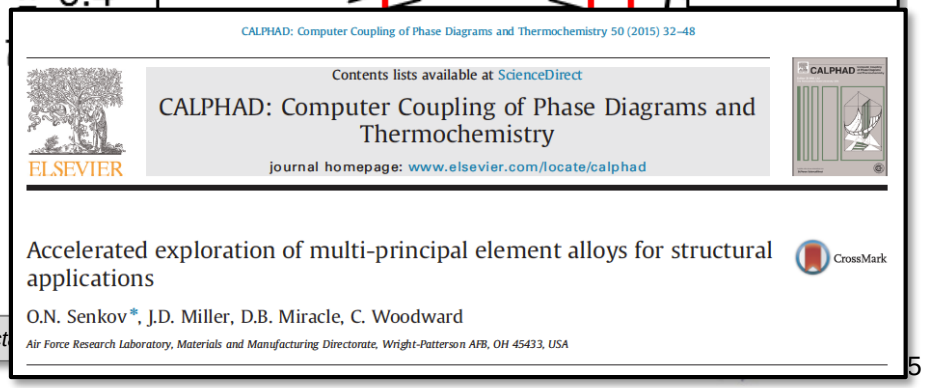
A Century of Scientific Excellence

Specific phase diagram features enable two-phase microstructures that may give a good balance of properties

Phase diagram criteria from CALculated PHAse Diagram (CALPHAD) calculations

- $T_m > T_{use}$, no phase transformation < T_{use}
- At least 1 SS phase and no more than 1 IM phase at T_{use}
- One phase must dissolve above T_{use}
- fcc, bcc, hcp or ordered derivative crystal structures
- *These are selective criteria*




CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 50 (2015) 32–48

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Accelerated exploration of multi-principal element alloys for structural applications

O.N. Senkov*, J.D. Miller, D.B. Miracle, C. Woodward

Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA

Calculation of 135,000 phase diagrams has identified ~100 candidate high temperature structural alloy systems

Senkov et al., *Act*

HI THRU-PUT EXPERIMENTS

Stage 1

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STAGE 0

Calculated Phase Diagrams

STAGE 1

Structure-Insensitive Properties

STAGE 2

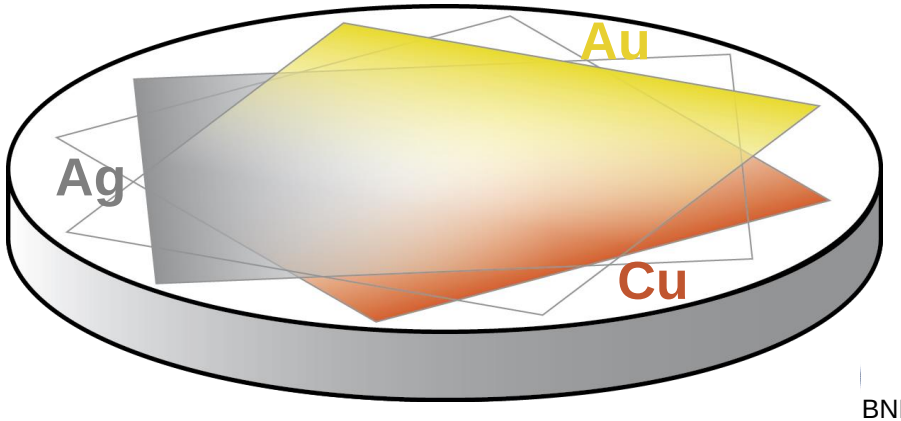
Structure-Sensitive Properties

Materials libraries with controlled composition gradients

- Density, modulus, T_m, environmental resistance

Environmental resistance is probably the most impactful test

- Possibility to reject many candidates early in the evaluation process
- Fast and conceptually straightforward
- Has not yet been demonstrated



HI THRU-PUT EXPERIMENTS

Stage 2

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STAGE 0

Calculated Phase Diagrams

STAGE 1

Structure-Insensitive Properties

STAGE 2

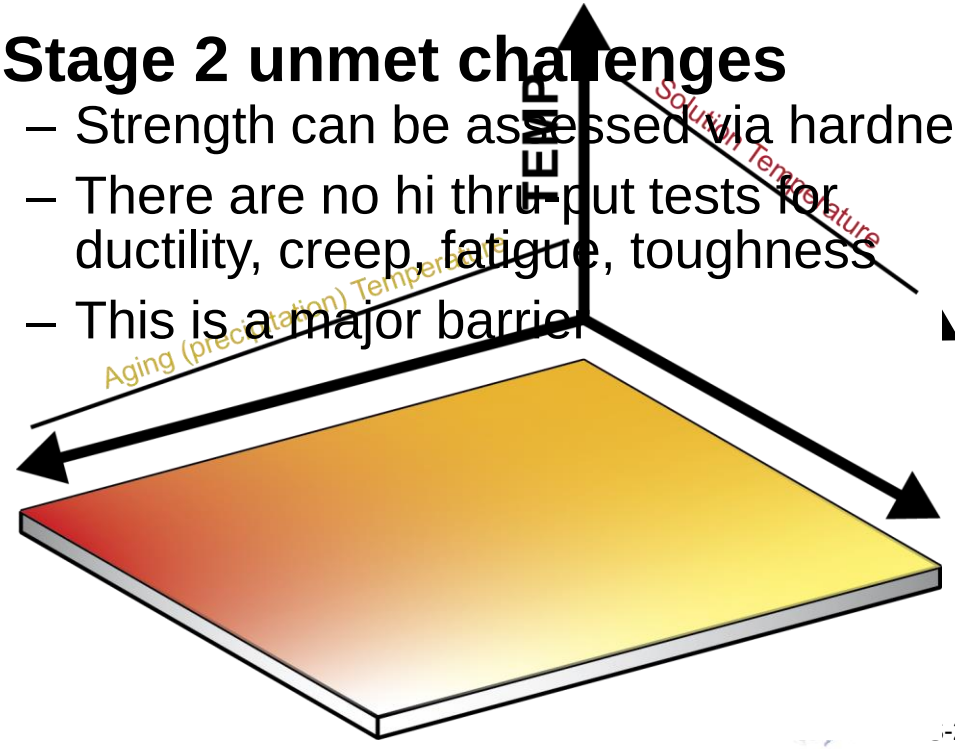
Structure-Sensitive Properties

Fixed-composition materials libraries with controlled microstructure gradients

- Strength, tensile ductility, creep, fracture, fatigue
- Libraries are conceptually simple

Stage 2 unmet challenges

- Strength can be assessed via hardness
- There are no hi thru-put tests for ductility, creep, fatigue, toughness
- This is a major barrier



MAJOR ACCOMPLISHMENTS

Four HEA Core Effects

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Present data & analyses do not support an observable effect of configurational entropy on preferred formation of 1-phase alloys, solid solution phases or simple crystal structures

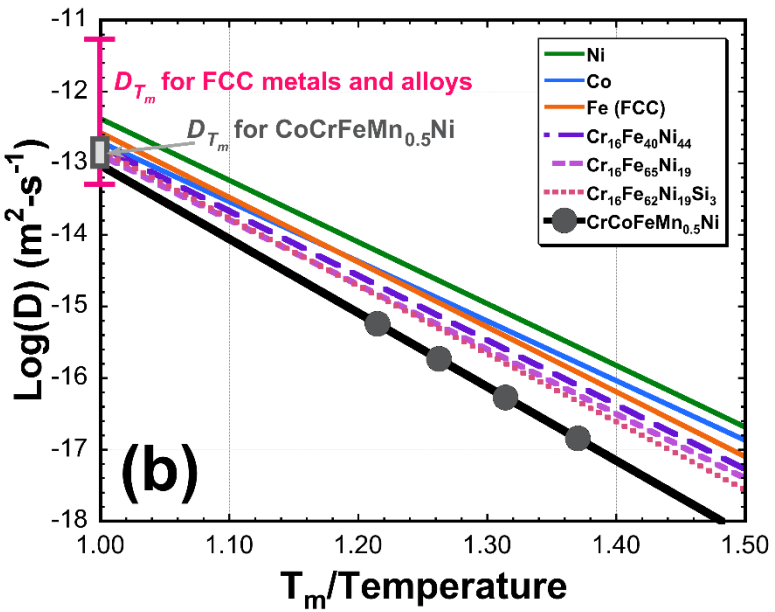
- Two direct experiments and two computational studies do not support the 'high entropy' hypothesis
- Six issues bias observations toward 1-phase/ SS/ 'simple' microstructures
- A simple 'structure in – structure out' (SISO) analysis links observed alloy microstructures to the structures of the constituent elements

Limited data show that MPEA diffusion is not unusually 'sluggish'

- In the same range as FCC elements and conventional alloys

Insufficient data to evaluate the 'lattice distortion' hypothesis

The 'cocktail effect' is a colorful phrase for 'non-linearity' of elemental combinations in general



MAJOR ACCOMPLISHMENTS

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Introduced and established the concept of exploring the vast compositional realm of multi-principle element alloys.

Establish importance – not dominance – of configurational entropy as a control variable in phase selection.

Define/explore 7 new alloy families and 122 new base alloys, emphasizing 3d transition metal and refractory metal alloys.

Expand the known 3d transition metal FCC phase field and discover up to 10 other extended 1-phase fields.

Establish composition/ microstructure/ properties relations for 3d transition metal MPEAs

Expand initial ideas to include multi-phase microstructures, functional materials and high-throughput evaluations.

High throughput calculations identify over 200 alloy bases as potential high temperature structural materials.

RECOMMENDATIONS

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Continue to explore and develop MPEAs for structural use

- Expand the range of alloy families, possibilities have barely been scratched
- Include both SS and precipitation strengthened microstructures
- Expand thermo-mechanical processing efforts to control microstructure

Apply strategy linking high-throughput computations & experiments to develop high temperature MPEAs

- High throughput experiments for structural materials requires new tools

Establish basic scientific concepts

- Strengthening models
- Lattice distortion effects

THANKS!

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Crystal structures at RT and at T_m

All but 2 allotropic transformations convert to BCC at T_m

Table 3

Elemental properties and the number of multi-component alloys that use the indicated elements.

Element	Atomic Number	Used in # of alloys	Structure at RT*	Structure at T_m*		Element	Atomic Number	Used in # of alloys	Structure at RT*	Structure at T_m*
H	1					Rh	45	1	A1 (FCC)	
Li	3	7	A2 (BCC)			Pd	46	3	A1 (FCC)	
Be	4	1	**A3 (HCP)**	**A2 (BCC)**		Ag	47	1	A1 (FCC)	
B	5	3	– (hR105)			Cd	48		A3 (HCP)	
C	6	7	A3 (HCP)			In	49		A6 (tI2)	
N	7					Sn	50	17	A5 (tI4)	
O	8					Sb	51		A7 (hR2)	
Na	11		A2 (BCC)			Te	52		A8 (hP3)	
Mg	12	8	A3 (HCP)			Cs	55		A2 (BCC)	
Al	13	263	A1 (FCC)			Ba	56		A2 (BCC)	
Si	14	15	A4 (cubic)¶			La	57		**A3 (DHCP)**	**A1 (FCC)**
P	15		– (oC8)			Ce	58		**A3 (HCP)**	**A2 (BCC)**
S	16		– (oF128)			Pr	59		**A3 (DHCP)**	**A2 (BCC)**
K	19		A2 (BCC)			Nd	60	1	**A3 (DHCP)**	**A2 (BCC)**
Ca	20		**A1 (FCC)**	**A2 (BCC)**		Sm	62		**C19 (hR3)**	**A2 (BCC)**
Sc	21	1	**A3 (HCP)**	**A2 (BCC)**		Eu	63		A2 (BCC)	
Ti	22	101	**A3 (HCP)**	**A2 (BCC)**		Gd	64	2	**A3 (HCP)**	**A2 (BCC)**
V	23	55	A2 (BCC)			Tb	65	2	**A3 (HCP)**	**A2 (BCC)**
Cr	24	307	A2 (BCC)			Dy	66	2	**A3 (HCP)**	**A2 (BCC)**
Mn	25	79	**A12 (cI58)**	**A2 (BCC)**		Ho	67		A3 (HCP)	
Fe	26	335	**A2 (BCC)**	**A2 (BCC)**		Er	68		A3 (HCP)	
Co	27	292	**A3 (HCP)**	**A1 (FCC)**		Tm	69	1	A3 (HCP)	
Ni	28	344	A1 (FCC)			Yb	70		**A1 (FCC)**	**A2 (BCC)**
Cu	29	178	A1 (FCC)			Lu	71	2	A3 (HCP)	
Zn	30	7	A3 (HCP)			Hf	72	5	**A3 (HCP)**	**A2 (BCC)**
Ga	31		A11 (oC8)			Ta	73	13	A2 (BCC)	
Ge	32	1	A4 (cubic)¶			W	74	2	A2 (BCC)	
As	33		A7 (hR2)			Re	75		A3 (HCP)	
Se	34		A8 (hP3)			Os	76		A3 (HCP)	
Rb	37		A2 (BCC)			Ir	77		A1 (FCC)	
Sr	38		**A1 (FCC)**	**A2 (BCC)**		Pt	78		A1 (FCC)	
Y	39	6	**A3 (HCP)**	**A2 (BCC)**		Au	79	2	A1 (FCC)	
Zr	40	33	**A3 (HCP)**	**A2 (BCC)**		Hg	80		A10 (hR1)	
Nb	41	29	A2 (BCC)			Tl	81		**A3 (HCP)**	**A2 (BCC)**
Mo	42	49	A2 (BCC)			Pb	82		A1 (FCC)	
Ru	44	1	A3 (HCP)			Bi	83		A7 (mC4)	