Refractory Complex Concentrated Alloys (RCCAs): A New Class of High-Temperature Structural Materials

Enabling Technologies for Improving Fusion Power Plant Performance and Availability Workshop

New Orleans, LA | 7, 8 March 2023

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Case Number: AFRL-2023-1764

Outline

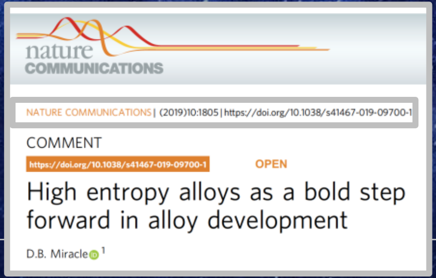
Introduction

- *History of Alloy Development & High-Entropy Alloys (HEAs)*
- *HEAs and Complex, Concentrated Alloys (CCAs)*

Refractory CCAs (RCCAs)

- *Overview*
- *Challenges and Opportunities*

Closing


nature COMMUNICATIONS

NATURE COMMUNICATIONS | (2019)10:1805 | https://doi.org/10.1038/s41467-019-09700-1

COMMENT

https://doi.org/10.1038/s41467-019-09700-1 OPEN

High entropy alloys as a bold step forward in alloy development

D.B. Miracle[1]


C. R. Physique 19 (2018) 721–736

Contents lists available at ScienceDirect

Comptes Rendus Physique

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ELSEVIER

New trends in metallic alloys / Alliages métalliques : nouvelles tendances

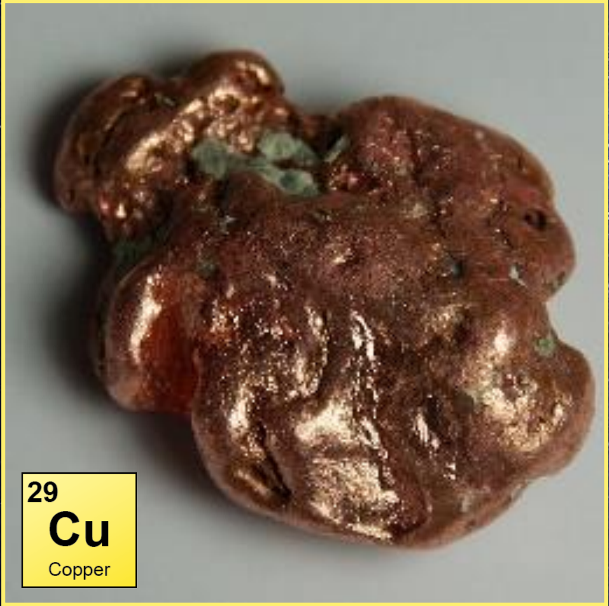
From high-entropy alloys to complex concentrated alloys

Des alliages à haute entropie aux alliages concentrés complexes

Stéphane Gorsse[a,b,*], Jean-Philippe Couzinié[c], Daniel B. Miracle[d]

The history of metallic alloys

Stone Age



Bronze Age

Iron Age

29 Cu Copper

82 Pb Lead

79 Au Gold

47 Ag Silver

50 Sn Tin

80 Hg Mercury

26 Fe Iron

13 Al Aluminum

27 Co Cobalt

12 Mg Magnesium

42 Mo Molybdenum

41 Nb Niobium

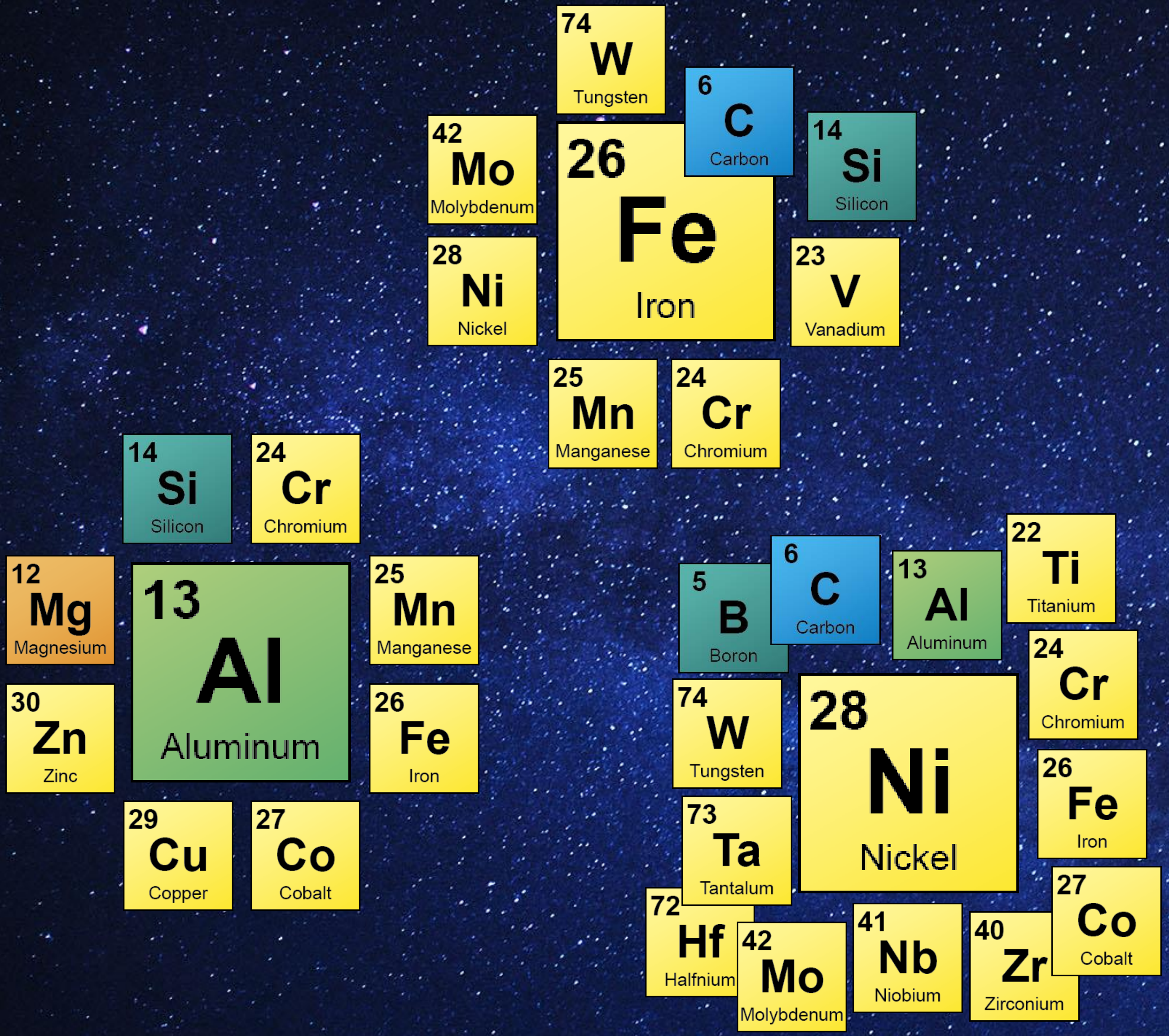
28 Ni Nickel

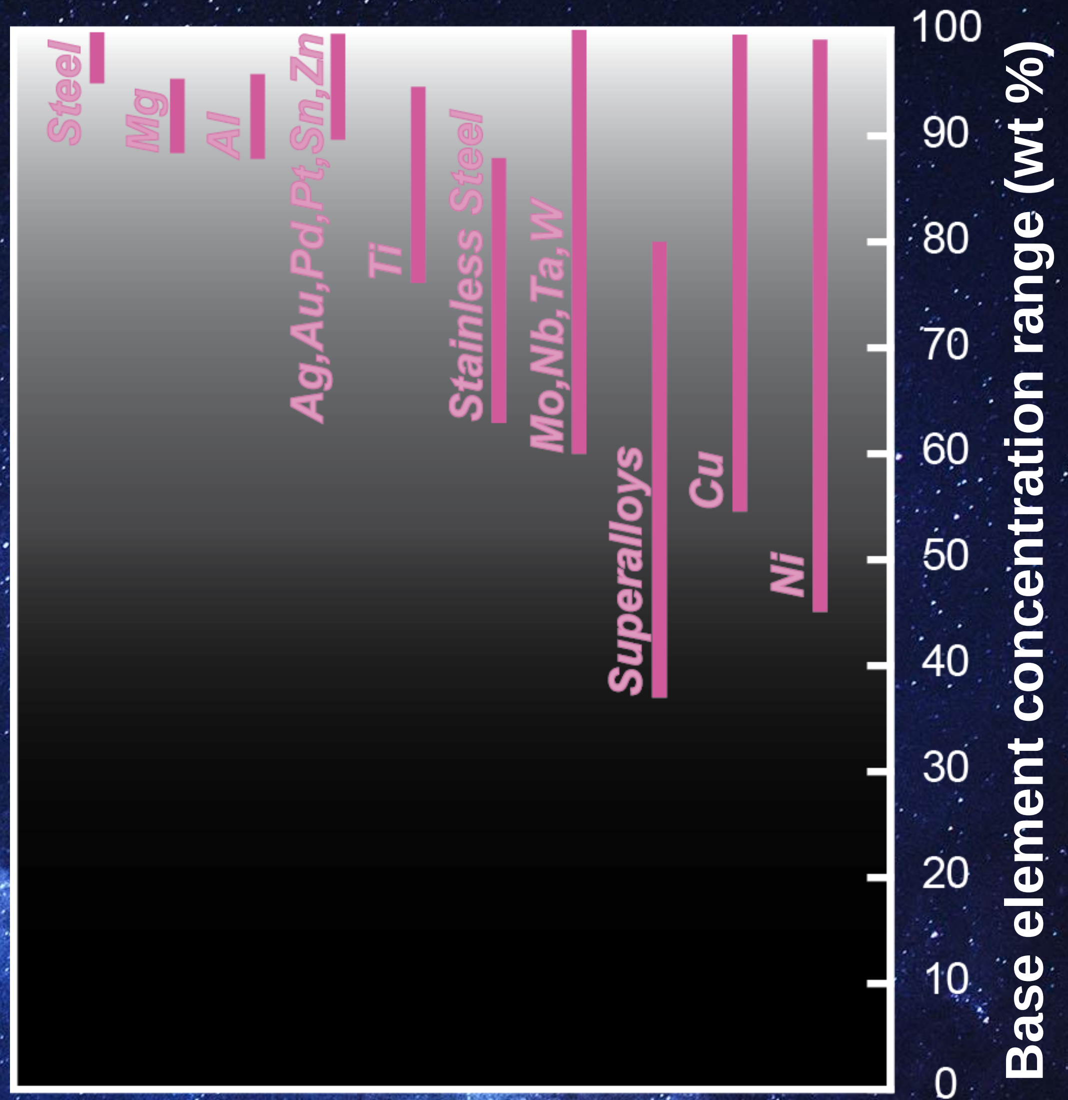
22 Ti Titanium

30 Zn Zinc

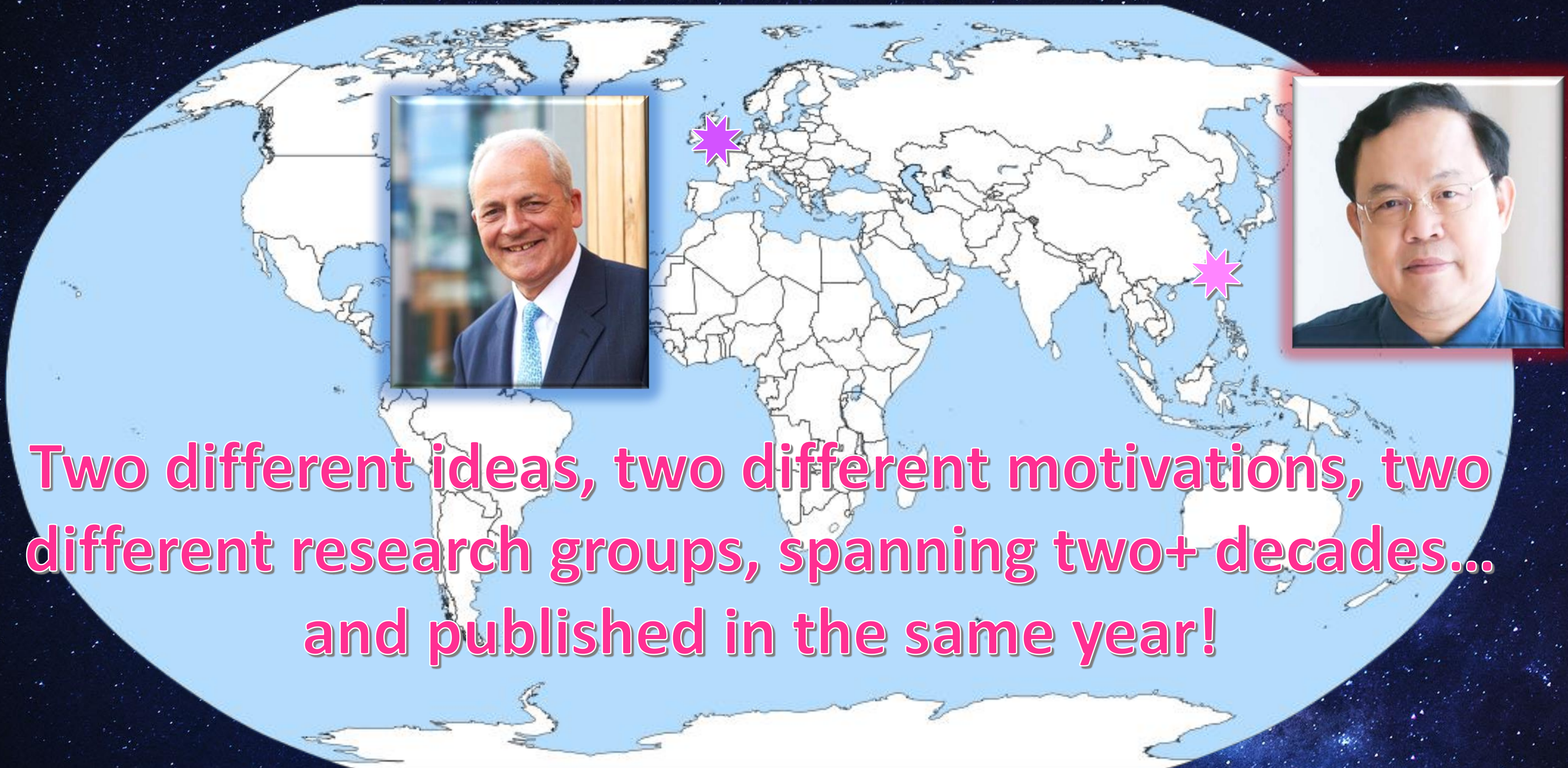
-9000 -8000 -7000 -6000 -5000 -4000 -3000 -2000 -1000 0 1000 2000

Are Materials a Mature Technology?





The art of lightly alloyed base elements has become increasingly sophisticated



Two different ideas, two different motivations, two different research groups, spanning two+ decades… and published in the same year!

Two Big Ideas

"…to investigate the unexplored central region of multicomponent alloy phase space."

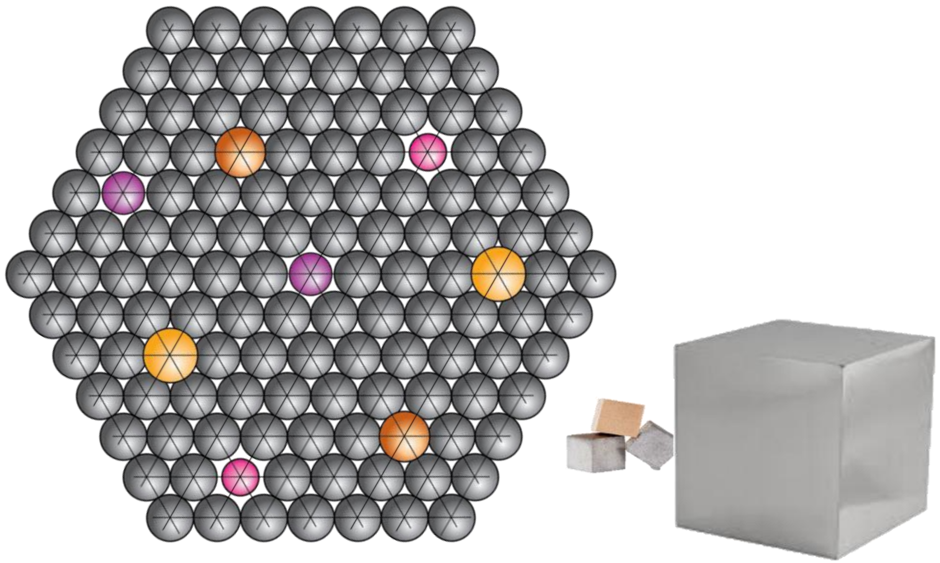
Cantor *et al.*, *Mat. Sci. Eng. A*, **375-377**, 213 (2004).

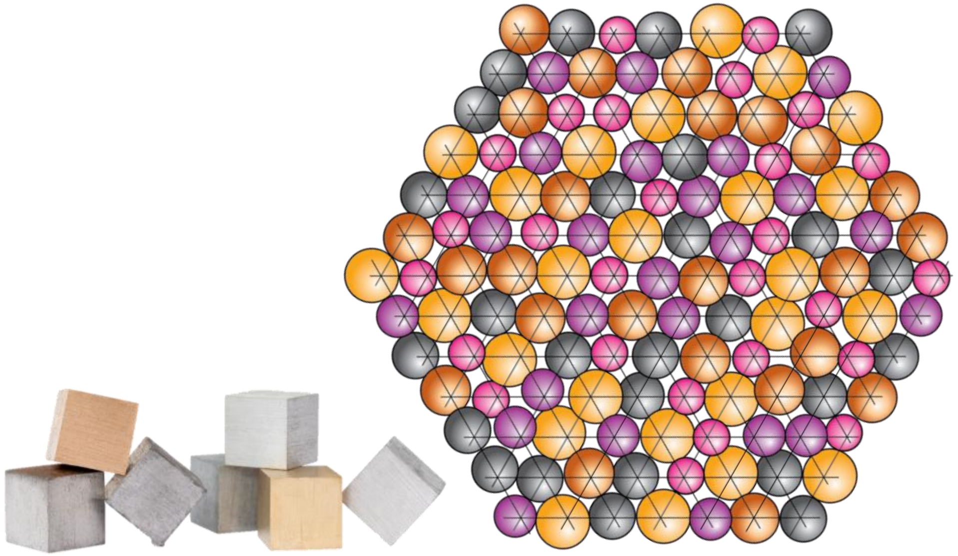
- Vast opportunity to discover new alloys of scientific and practical benefit

Favor solid solution over intermetallic phases thru configurational entropy

- Vary entropy thru the number and concentrations of principal elements ($N \geq 5$)

Yeh *et al.*, *Adv. Eng. Mat.*, **6**, 299 (2004).
Plus many others…






592,000,000,000

What is a high-entropy alloy (HEA)?

An alloy with 5 or more elements with atomic concentrations between 5-35%

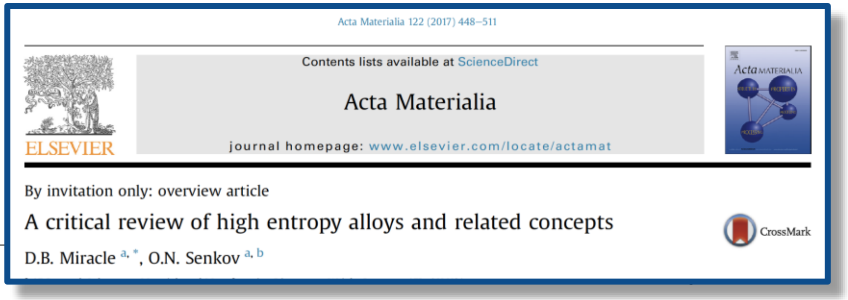
Later definitions specify a magnitude for configurational entropy

- *How do we know the actual configurational entropy of a composition?*
- *Ideal configurational entropy is assumed*

A single-phase, disordered solid solution is not specified in any of the early definitions, but this seems to be accepted as a common requirement

- *Conflation of definition and motivation*
- *This confusion leads to an unproductive controversy*

Neither phase stability nor the attractive properties shown by HEAs are related to the magnitude of configurational entropy


Acta Materialia 122 (2017) 448–511

Contents lists available at ScienceDirect

Acta Materialia

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

ELSEVIER

By invitation only: overview article

A critical review of high entropy alloys and related concepts

D.B. Miracle [a,*], O.N. Senkov [a,b]

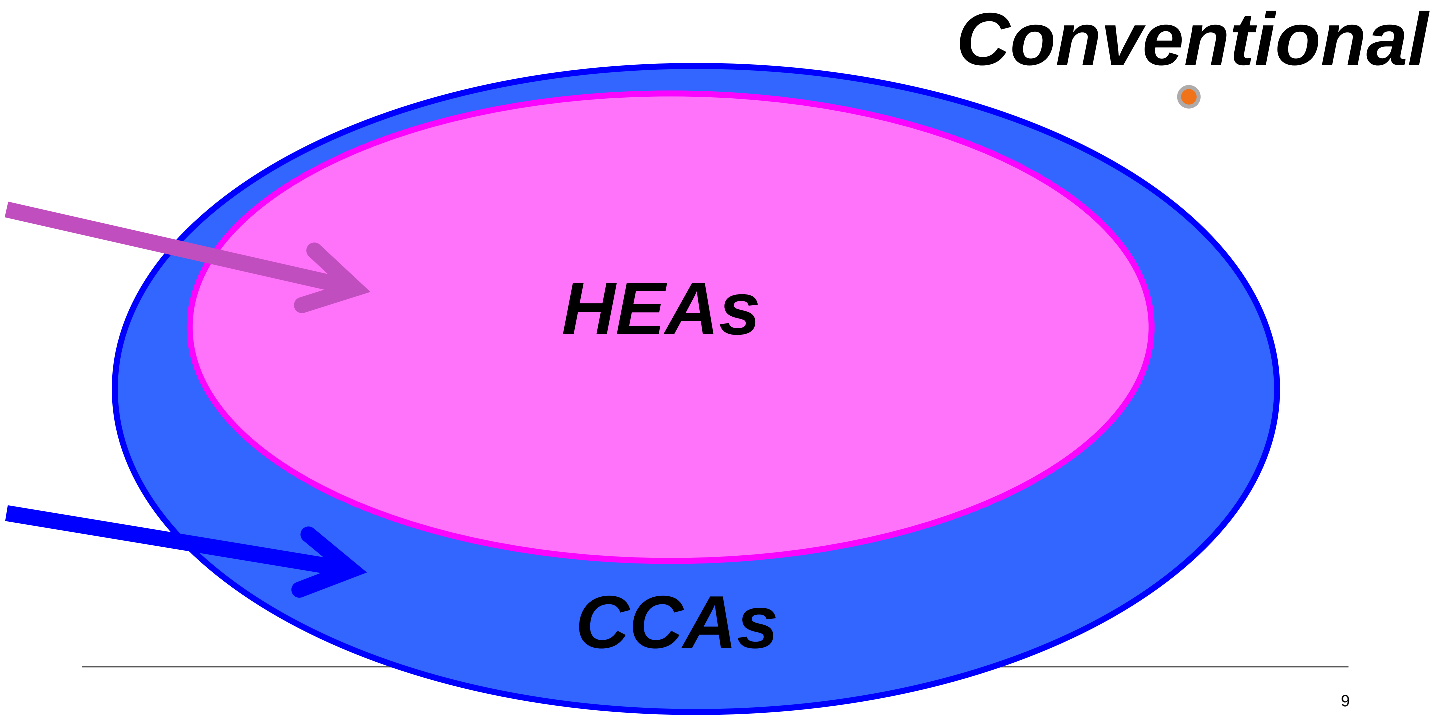
HEAs and Complex, Concentrated Alloys (CCAs)

Attractive properties are found in alloys with *N* < 5, with concentrations >35% and in microstructures with more than a single solid solution metallic phase

Terms such as CCAs and multi-principal element alloys (MPEAs) are introduced to include these possibilities

- *5 or more elements*
- *Nominally single-phase*
- *High configurational entropy*

- *May have <5 elements*
- *Can have >35% of elements*
- *Can have multiple phases*
- *Entropy doesn't matter*

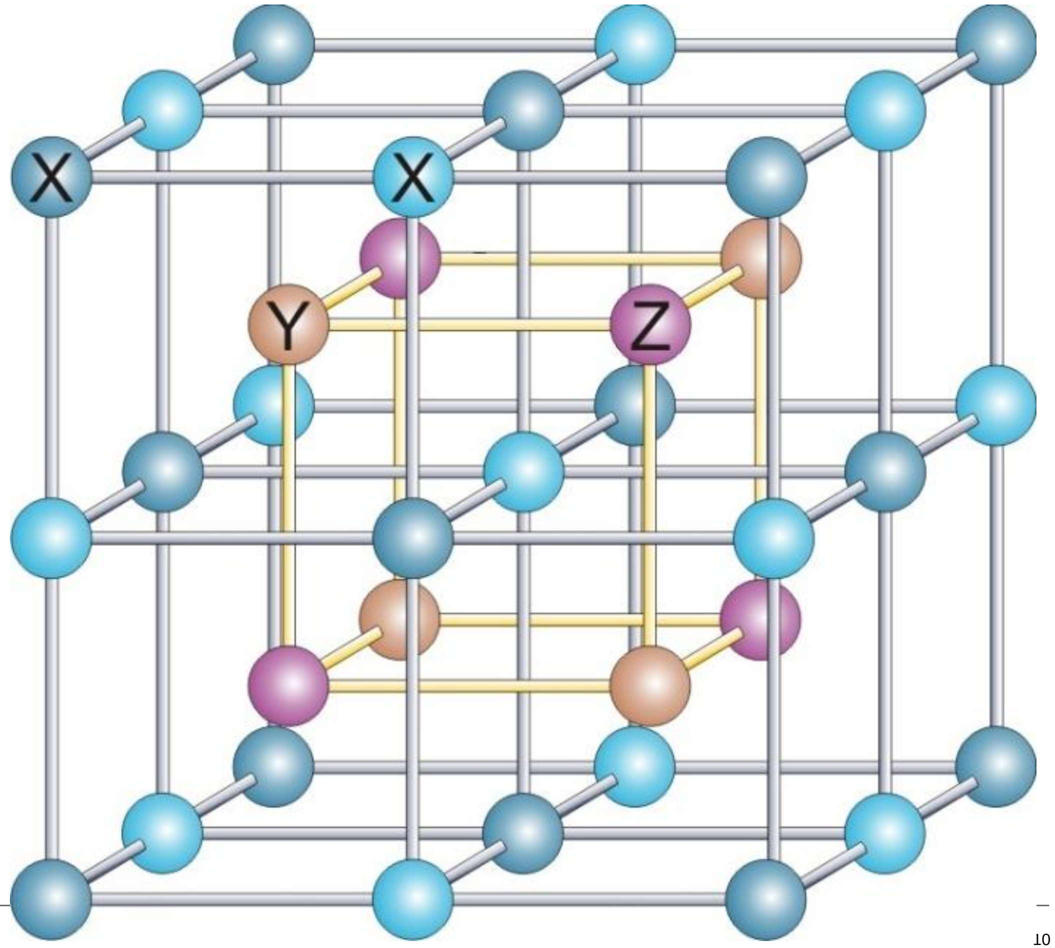


High Entropy Intermetallics

Ordered compounds with metallic/covalent bonding

Iso-electronic or iso-structural substitution are common strategies to design new functional compounds

- Consider the half-Heusler structure (XYZ) for thermo-electric materials
- **X** = Au, Co, Fe, Ir, Ni, Pd, Pt, Rh, Ru; **Y** = Hf, Mn, Ti, Zr; **Z** = Bi, Ga, Sb, Sn
- Complex half-Heusler phases already exist, such as $Ni(Hf_{1-x}Zr_x)Sb_ySn_{1-y}$, $Co(Hf_{0.5}Zr_{0.5})Sb_{0.8}Sn_{0.2}$, and $Co_{1-x}Ni_x(Hf_{0.25}Ti_{0.5}Zr_{0.25})Sb$
- Designing with >2 elements per sublattice and including other principal elements can significantly increase the number of possibilities



High Entropy Ceramics

Ordered compounds with ionic/covalent bonding

MPEAs are an alloying approach, not a family of alloys, so CCAs include other inorganic materials

The MPEA field includes ceramic materials such as oxides/ borides/ nitrides/ carbides

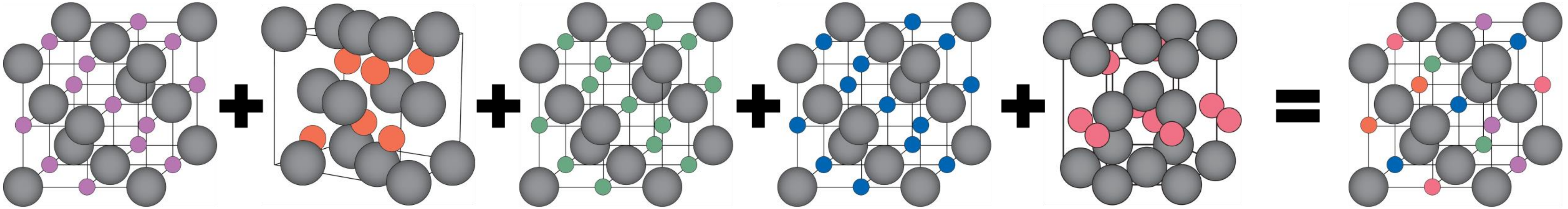

nature COMMUNICATIONS

ARTICLE

Received 8 Apr 2015 | Accepted 25 Aug 2015 | Published 29 Sep 2015 DOI: 10.1038/ncomms9485 OPEN

Entropy-stabilized oxides

Christina M. Rost[1], Edward Sachet[1], Trent Borman[1], Ali Moballegh[1], Elizabeth C. Dickey[1], Dong Hou[1], Jacob L. Jones[1], Stefano Curtarolo[2] & Jon-Paul Maria[1]



Rocksalt (CoO) + Tenorite (CuO) + Rocksalt (MgO) + Rocksalt (NiO) + Wurtzite (ZnO) = Rocksalt (CoCuMgNiZn)O

Distinguishing Features

Edge – *to* – center (dilute – *to* – concentrated)

- Explore beyond the well-lit edges and corners of phase diagrams.
- What is concentrated?

Base element – *to* – multi-principal element (complex)

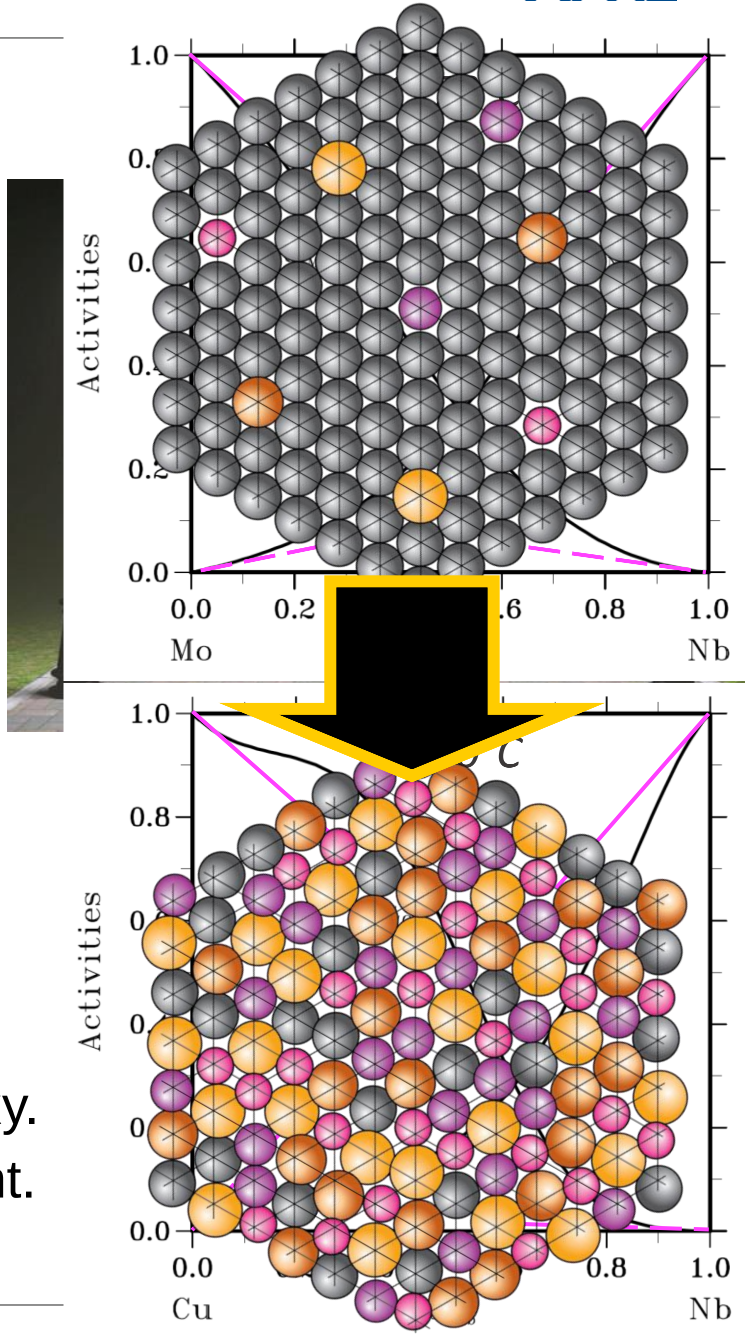
- There is no obvious, dominant base element.

Locally disrupted – *to* – jumbled atomic structures

- From well-ordered with local accents to diverse & eclectic.
- Not just spatial distortion, but also more ruffled energy landscape.
- Rather than a local nuisance, may change intrinsic behaviors.
- Dislocation motion and catalytic activity are two examples.

Dozens – *to* – hundreds of billions

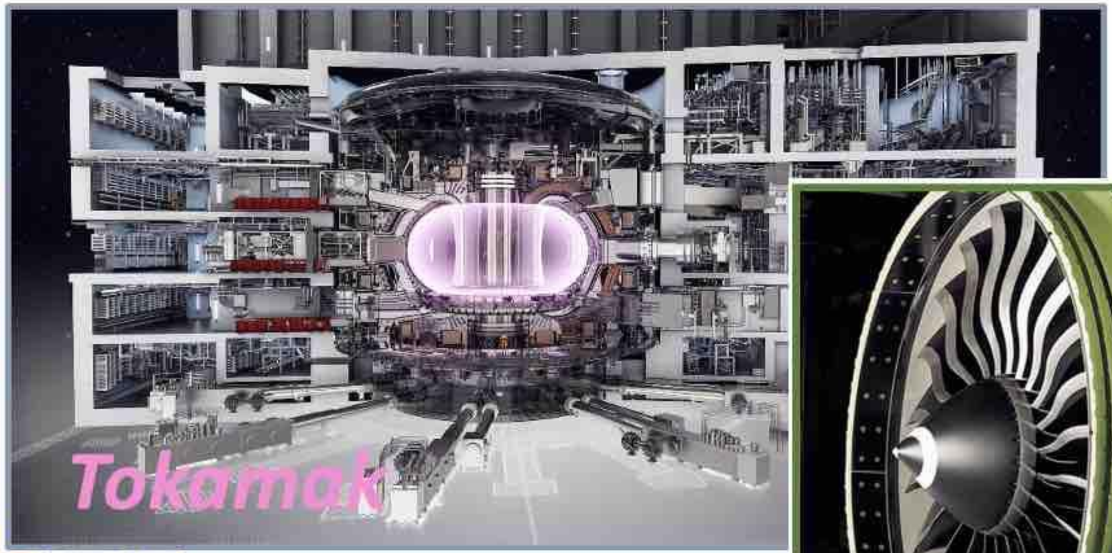
- We must move beyond equimolar compositions as a convenient proxy.
- Fundamentally changes materials research, exploration, development.



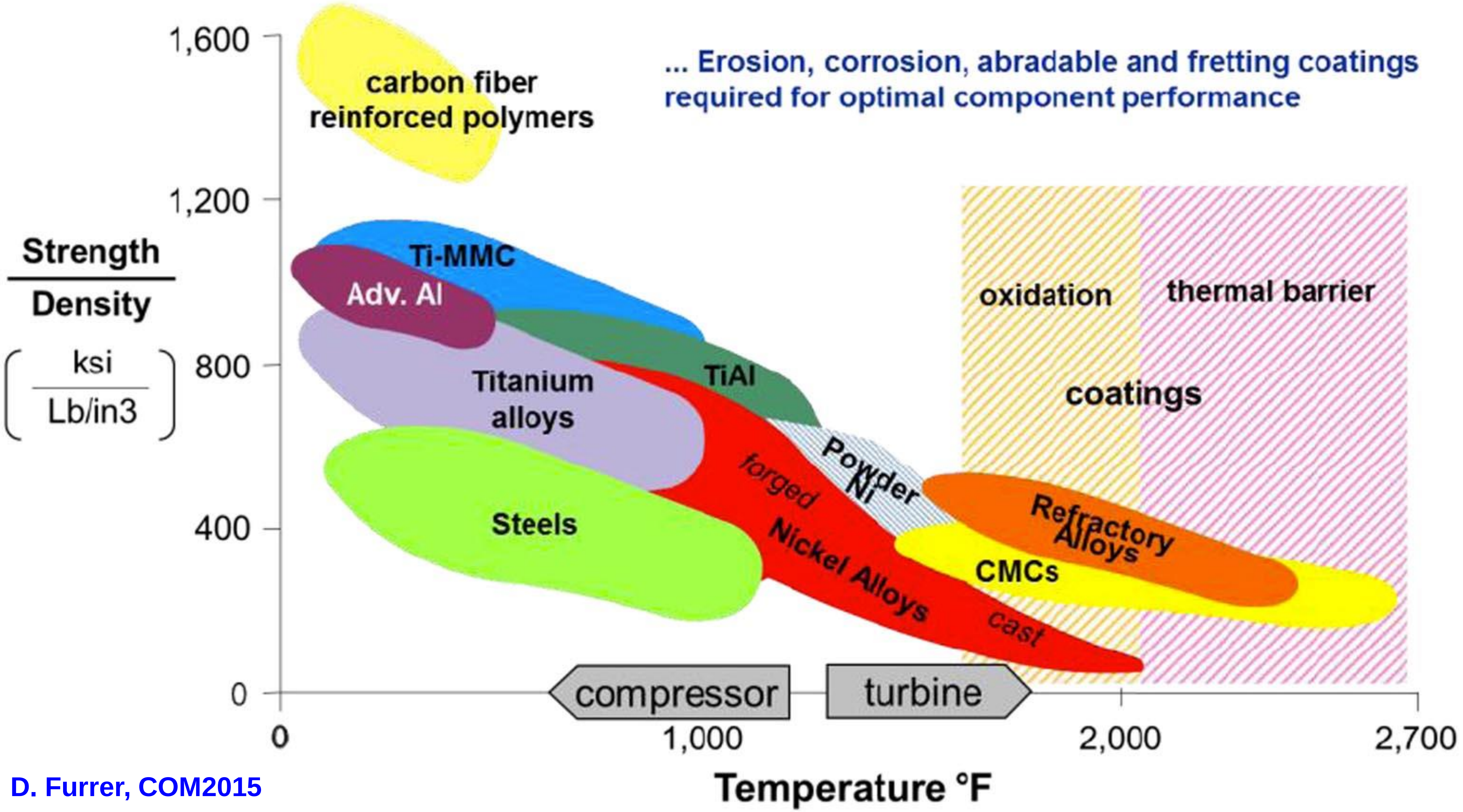
High temperature alloys | *Motivations*

Commercial and societal impacts of high temperature materials

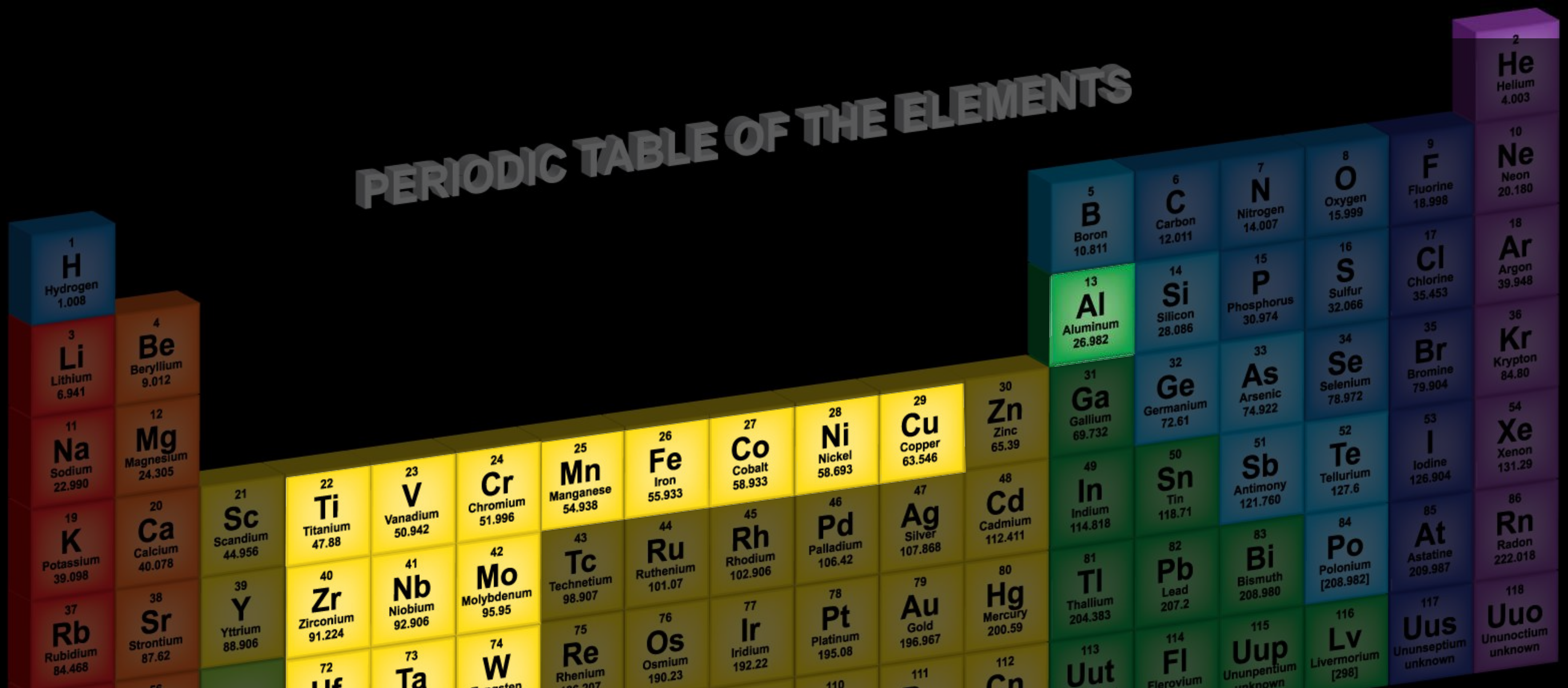
- Improved **energy** conversion, reduced emissions in power generation
- Improved performance and economy in aerospace turbine systems (**transportation**)

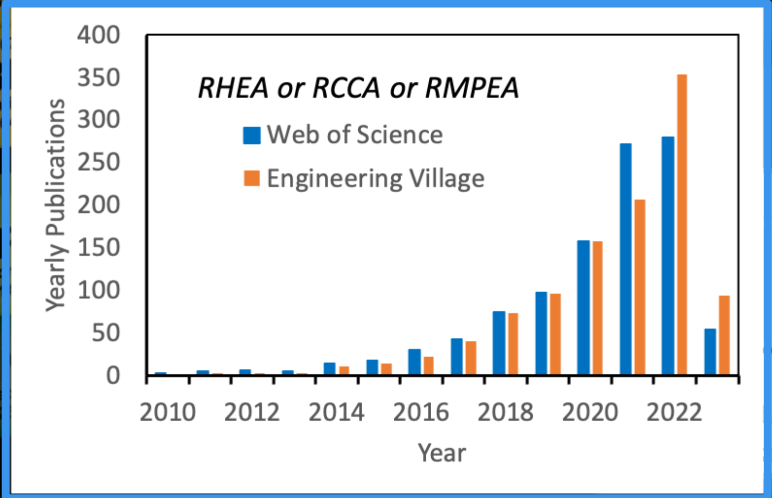


High temperature metallic materials



D. Furrer, COM2015


PERIODIC TABLE OF THE ELEMENTS


RHEA or RCCA or RMPEA
Web of Science
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400
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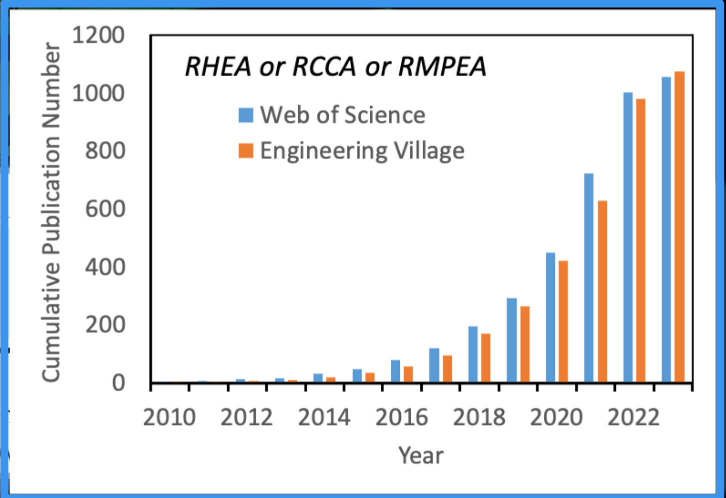
RHEA or RCCA or RMPEA
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Engineering Village
Cumulative Publication Number
1200
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Alloy Families | Refractory metal HEAs

Refractory metal CCAs have at least 3 of the following principal elements: Cr, Hf, Mo, Nb, Re, Ru, Ta, Ti, V, W, and Zr – and may also include Al, Co, Fe, Ni, Si…

- Inspired by motivation to develop high temperature structural alloys
  - *Essentially the first attempt to devise a new family of CCAs for a specific set of requirements by intentional selection of the elements in the palette*
- A wide range in melting temperatures and densities gives design flexibility

Senkov *et al.*, *Intermetallics 18, 1758-1765 (2010)*

RCCAs are generally BCC and many have additional phases

- The temperature dependence of strength is complicated for BCC alloys
- Multi-phase alloys offer broader opportunities to tailor a balance of properties

Development and exploration of refractory high entropy alloys—A review

J. Mater. Res., Vol. 33, No. 19, Oct 14, 2018

Oleg N. Senkov,[a] Daniel B. Miracle,[b] and Kevin J. Chaput
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433, USA

Jean-Philippe Couzinie
Université Paris Est, ICMPE (UMR 7182) CNRS-UPEC, 2-8 rue Henri Dunant, F-94320, Thiais F-94320, France

Refractory CCAs: Risks and Opportunities

Environmental resistance

- Refractory metals and alloys

Balance of RT ductility and high-temperature strength

- BCC metals and alloys

Large number of alloy systems

- CCAs

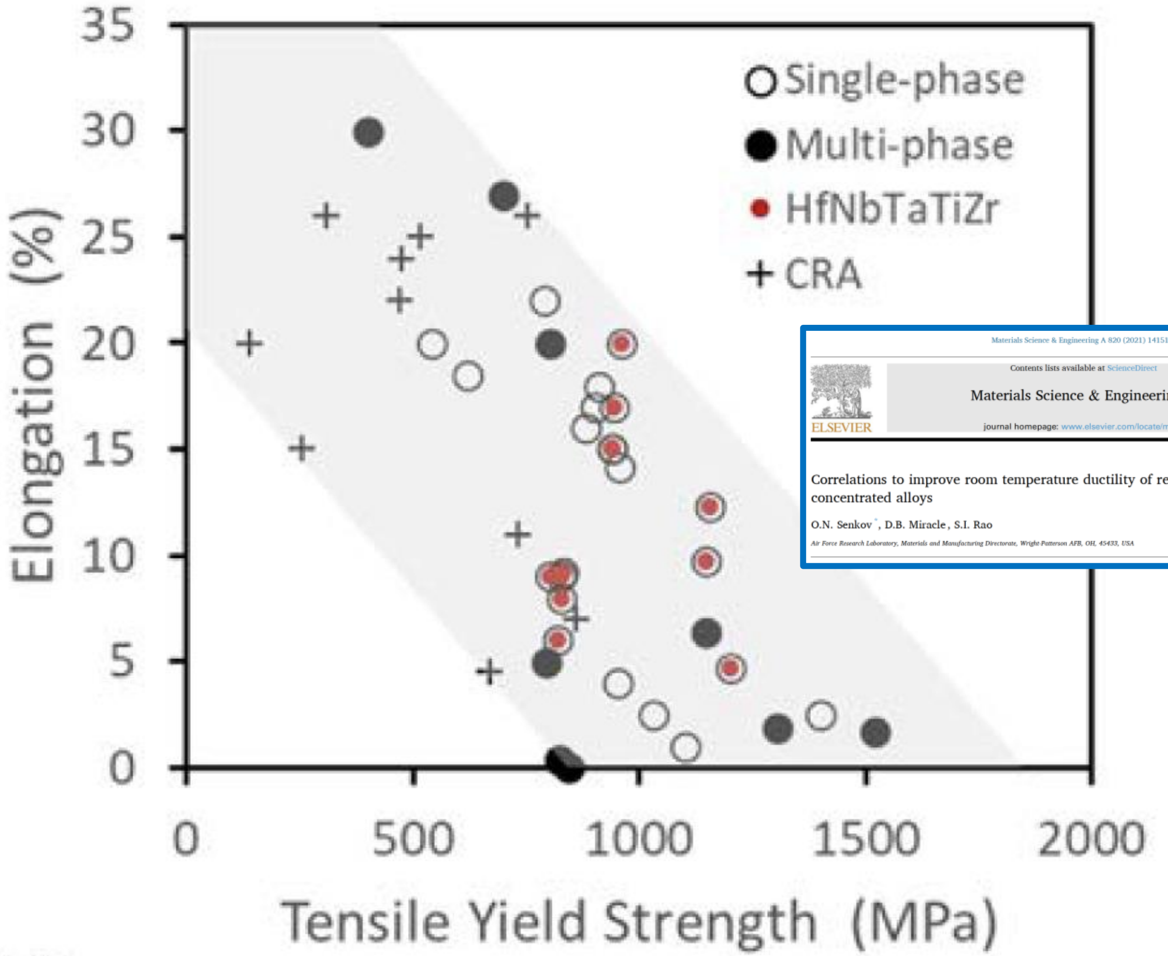
Challenges & opportunities for: accelerated design/modelling (Arroyavé); synthesis (Thoma); testing (Pint); manufacturing (Peter) and T2M (Woodruff) will be discussed

RCCA Properties

Some commercial refractory alloys meet Fusion P^{3}A mechanical properties goals but severely lack environmental resistance

RCCAs offer improved strength and environmental resistance, but ductility may be a challenge

Property[1]	At Room Temperature (RT)	At 1300C[a]	At 20dpa (14MeV neutron equivalent) and RT	At 20dpa (14MeV neutron equivalent) and 1300C[a]
Yield Strength (MPa)	>200 MPa	>80 MPa	>200 MPa	>100 MPa
Ultimate Tensile Strength (MPa)	>250 MPa	>100 MPa	>300 MPa	>200 MPa
Failure Elongation (%)	>20%	>20%	>5%	>5%
Fracture Toughness (MPa m$^{1/2}$)	>100 MPa√m	>100 MPa√m	>20 MPa√m	>20 MPa√m
Creep Rupture Stress (MPa) @ 1000hr	NA	>80MPa	NA	>80MPa
Thermal Conductivity (W/mK)	>20 W/mK	>20 W/mK	>20 W/mK	>20 W/mK
Volumetric Swelling (%)	NA	NA	<2%	<2%
Neutron Sputtering Rate (μm/yr)	NA	NA	< 100 μm/yr	< 100 μm/yr
Fatigue Failure Cycles (N)	>50,000	>50,000	>10,000	>10,000
Total Activation Dose (on contact after 24hrs) - Rem	NA	NA	<5 Rem	<5 Rem



Materials Science & Engineering A 820 (2021) 141512

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

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Correlations to improve room temperature ductility of refractory complex concentrated alloys

O.N. Senkov *, D.B. Miracle, S.I. Rao

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

Large number of alloy systems

CCAs offer a cosmically vast number of new alloy bases to explore

RCCAs represent a large but more workable subset of new alloy systems

- Palette of ~10-17 elements compared to 72 for metallic alloys

New strategies & tools can accelerate development by synergizing: artificial intelligence; automated materials synthesis; and high throughput computations & experiments

- Calculations can significantly accelerate exploration
- Hi thruput experiments are needed, especially for environmental resistance & tensile ductility

Entropy **2014**, *16*, 494-525; doi:10.3390/e16010494
OPEN ACCESS
entropy
ISSN 1099-4300
www.mdpi.com/journal/entropy

Article

Exploration and Development of High Entropy Alloys for Structural Applications

Daniel B. Miracle *, Jonathan D. Miller, Oleg N. Senkov, Christopher Woodward, Michael D. Uchic and Jaimie Tiley

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

Scripta Materialia 127 (2017) 195–200
Contents lists available at ScienceDirect
Scripta Materialia
journal homepage: www.elsevier.com/locate/scriptamat

Viewpoint Article

New strategies and tests to accelerate discovery and development of multi-principal element structural alloys

Daniel Miracle [a,*], Bhaskar Majumdar [b], Katelun Wertz [a], Stéphane Gorsse [c,d,e]

ANNUAL REVIEWS
Annu. Rev. Mater. Res. 2021. 51:131–64
First published as a Review in Advance on June 3, 2021
The *Annual Review of Materials Research* is online at matsci.annualreviews.org
https://doi.org/10.1146/annurev-matsci-080619-022100

Annual Review of Materials Research

Emerging Capabilities for the High-Throughput Characterization of Structural Materials

Daniel B. Miracle,[1] Mu Li,[2] Zhaohan Zhang,[3] Rohan Mishra,[2,3] and Katharine M. Flores[2,3]

Environmental properties | *Four degradation mechanisms*

Solid solution interstitial hardening and embrittlement

- Rapid bulk diffusion produces thick, brittle surface layers in some refractory metals/alloys (alpha case in titanium alloys)

Pest attack in some refractory metal aluminides, silicides

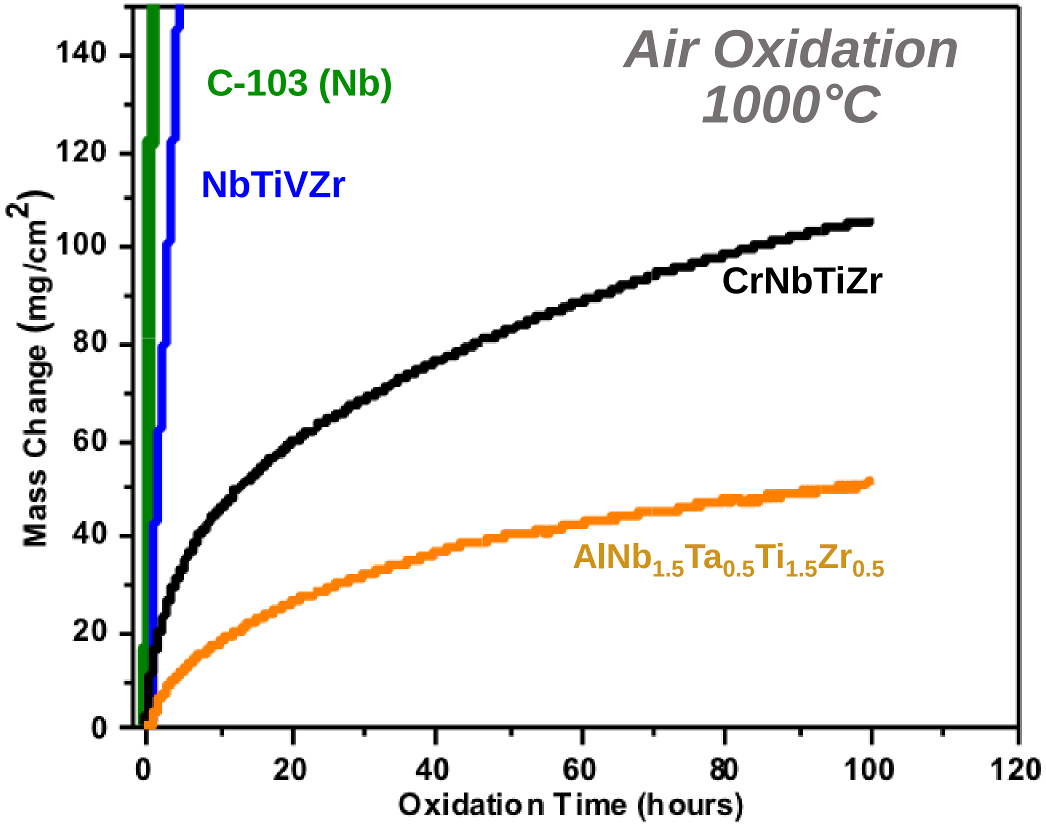
- Grain boundary oxidation near ~700°C produces internal stresses that eject grains

Volatilization

- Elemental Cr and MoO_3 have high vapor pressures

Rapid, non-protective oxide formation

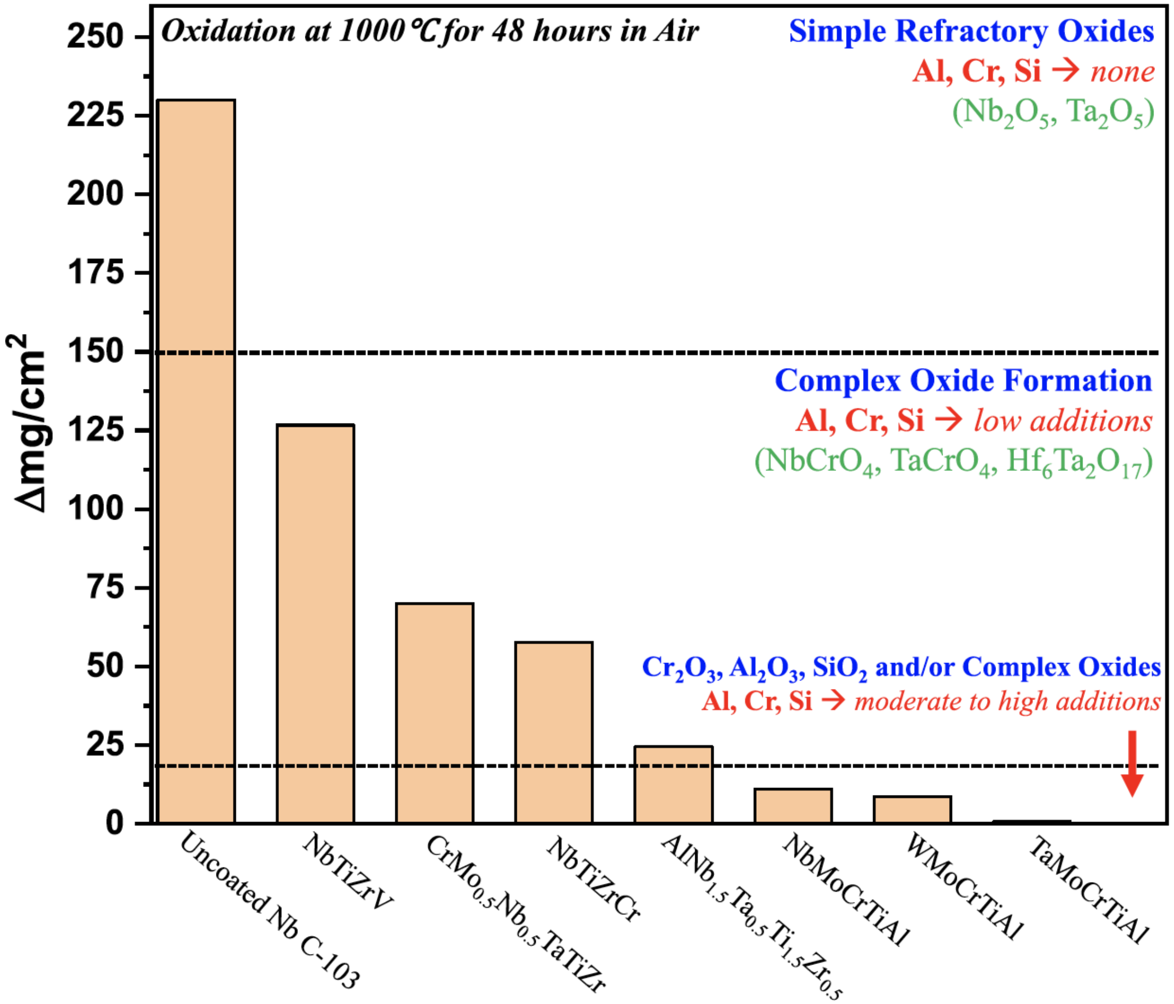
- Includes internal oxidation



Environmental Properties | *RCCAs are much better*

Some RCCAs offer parabolic kinetics that are 100x slower than conventional refractory elements and alloys

ARPA-E ULTIMATE is developing new coating alloys and systems



High Entropy Alloys: Oxidation

Todd M Butler, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, United States

Encyclopedia of Materials: Metals and Alloys doi:10.1016/B978-0-12-803581-8.12126-5

Environmental Properties | *Exceptional irradiation resistance*

Exceptional irradiation resistance with self-healing as a proposed mechanism

Irradiation Resistance of Multicomponent Alloys

T. EGAMI, W. GUO, P.D. RACK, and T. NAGASE

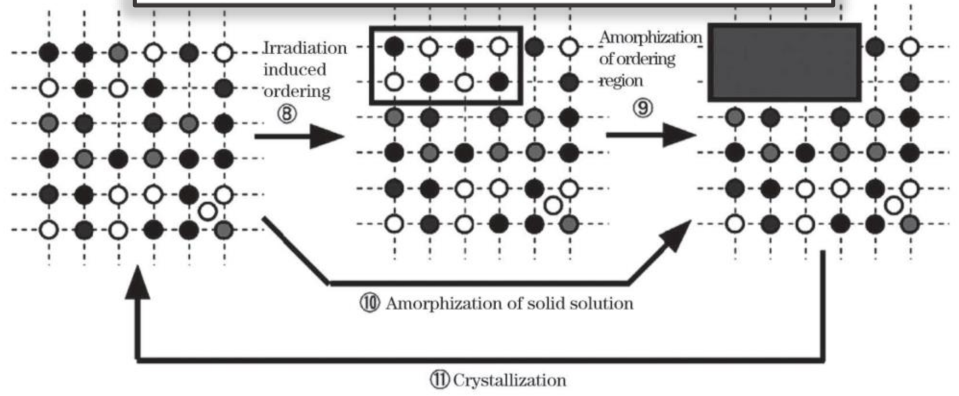
High-entropy alloys (HEAs) are characterized not only by high values of entropy but also by high atomic-level stresses originating from mixing of elements with different atomic sizes. Particle irradiation on solids produces atomic displacements and thermal spikes. The high atomic-level stresses in HEAs facilitate amorphization upon particle irradiation, followed by local melting and re-crystallization due to thermal spikes. We speculate that this process will leave much less defects in HEAs than in conventional alloys. For this reason, they may be excellent candidates as new nuclear materials. We discuss initial results of computer simulation on model binary alloys and an electron microscopy study on Zr-Hf-Nb alloys, which demonstrate extremely high irradiation resistance of these alloys against electron damage to support this speculation.

180–Vol. 45A, JANUARY 2014 METALLURGICAL AND MATERIALS TRANSACTIONS A

Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF IRON AND STEEL RESEARCH, INTERNATIONAL. 2015, 22(10): 879-884

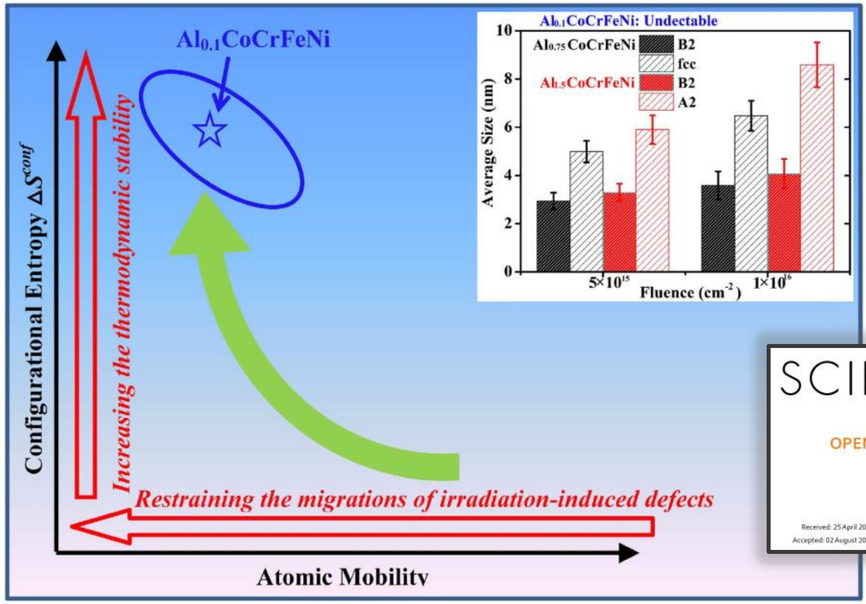
Irradiation Behavior in High Entropy Alloys

Song-qin XIA[1], Zhen WANG[2], Teng-fei YANG[3], Yong ZHANG[1]
(1. State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China; 2. Institute for Science and Technology Information and Strategy, Central Iron and Steel Research Institute, Beijing 100081, China; 3. State Key Laboratory of Nuclear Physics and Technology, Center for Applied Physics and Technology, Peking University, Beijing 100871, China)



(a), (b) Single component crystal; (c), (d), (e) HEAs.

Fig. 5 Schematic illustration of "self-healing" in HEAs



SCIENTIFIC REPORTS

OPEN **Precipitation behavior of $Al_xCoCrFeNi$ high entropy alloys under ion irradiation**

Received: 25 April 2016
Accepted: 02 August 2016

Tengfei Yang[1], Songqin Xia[2], Shi Liu[1], Chenxu Wang[1], Shaoshuai Liu[1], Yuan Fang[1], Yong Zhang[2], Jianming Xue[1], Sha Yan[1] & Yugang Wang[1]

Summary

HEAs and CCAs represent a new approach to materials development

- *CCAs may introduce new mechanisms and a difficult-to-achieve balance of properties*

'High entropy' may be less important than the new behaviors motivated by complex interactions between multiple principal elements

- *ONR MURI is establishing the role of chemical short-range order (SRO) in CCAs*

Significant improvements in oxidation resistance relative to conventional (dilute) refractory alloys are possible

- *Complex oxides have reduced growth kinetics*
- *Al- and Cr-rich B2 alloys can serve as a bond coat for oxidation resistant coating systems*

New concepts for environmental-resistant coating systems are underway

Significant increase in operating temperature (to 1300°C) while still providing RT tensile ductility and fracture toughness is possible

- *Change in deformation mechanisms, tailor mobility of edge and screw dislocations*

THANKS!