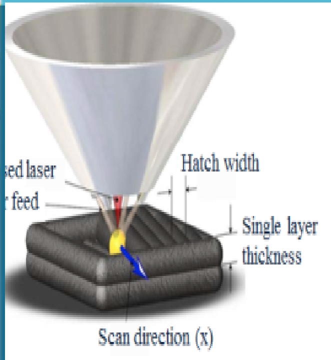
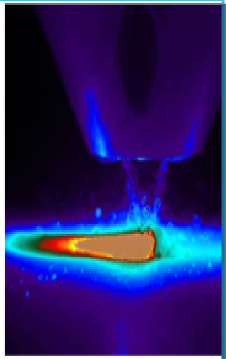
SAND2022-11912C

Sandia National Laboratories

Towards More Ductile Refractory High-Entropy Alloys at Room Temperature





Sal Rodriguez, Principal Investigator

sbrodri@sandia.gov

(505) 720-8668

Collaborators: Rob Sharpe, Erin Barrick, Darryn Fleming, Andrew Kustas, Nima Fathi, Eric Lang, Levi Van Bastian, and Graham Monroe

Presented at NENE, Portoroz, Slovenia

September 15, 2022.

U.S. DEPARTMENT OF ENERGY NNSA

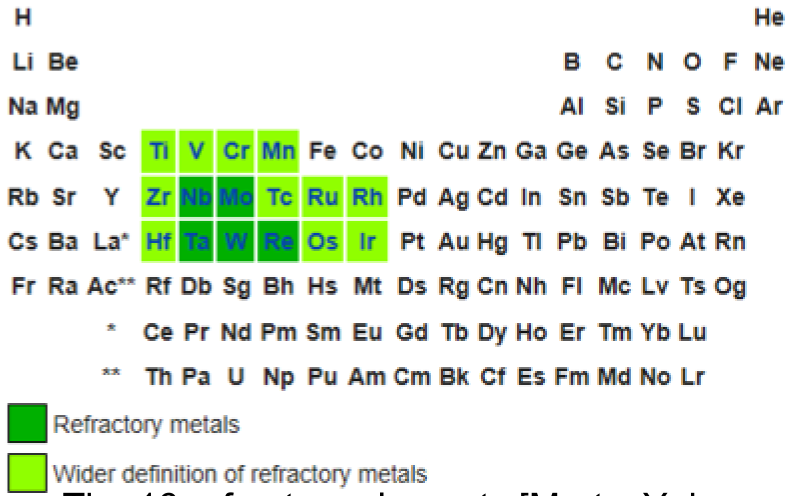
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND2022-zzz, Unclassified Unlimited Release, UUR

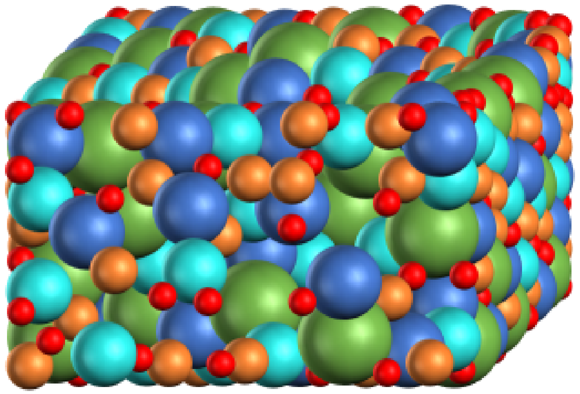
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

What are RHEAs?

- Refractory high-entropy alloys (RHEAs) are alloy combinations with four to six refractory elements in near -equiatomic proportions.
- But there are exceptions to this definition...
  - ✓ Can also include Ni, Al, Si to refine the alloy properties; deviations from equiatomic.
- "Refractory" refers to high-temperature elements.
- "Entropy" means the high mixing tendency of these combinations—larger entropy lowers Gibbs formation.
  - ✓ $\Delta G = \Delta H - T\Delta S$
- Want ΔH to be low and ΔS to be high, so that ΔG → small.
- First manufactured in 2010 as a solution for high-temperature aerospace applications [Senkov *et al.*, 2010; Miracle and Senkov, 2017; Senkov *et al.*, 2018; Murty, Yeh, Ranganathan, and Bhattacharjee, 2019].
- Most often ordered alphabetically; great suggestion from Miracle and Senkov, i.e., WHfTaZrNb = HfNbTaWZr, etc.



The 16 refractory elements [Murty, Yeh, Ranganathan, and Bhattacharjee, 2019; Wikipedia, 2022].

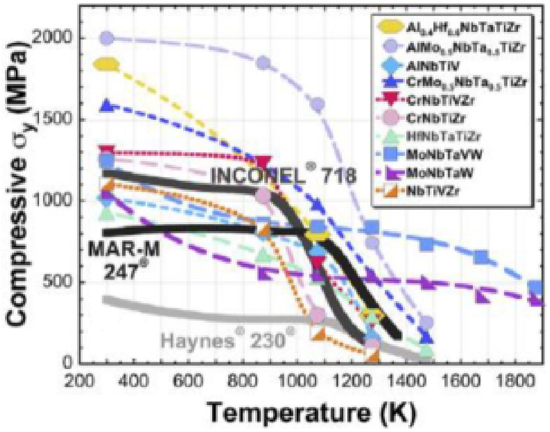

Conceptual arrangement of five-element equiatomic RHEA with diverse atomic radii [Moisés Beato Nuñez, SNL].

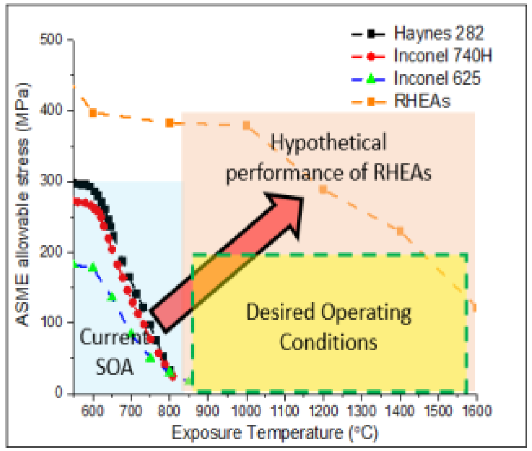
Extraordinary Properties of Some RHEAs

- High yield stress at high Temp.[1]
- Corrosion/Erosion Resistance[2]
- Self-Healing[3]
- Creep Resistance[4]

1. Compressive yield stress ~2X higher than Inconel 718 and ~10X stronger than stainless steel (SS) from room temperature to 1,000 °C. Can reach yield stress > 735 MPa at 1,200 °C and 300 MPa at 1,600 °C [Miracle and Senkov, 2017].
2. Corrosion resistance to boiling nitric acid (HfNbTaTiZr), sCO_2, and NaCl (HfNbTaZr).
3. Radiation self-healing: up to 20 times fewer displacements per atom (DPA) than SS.
4. Creep strength resistance > 35 MPa for 30,000 hours operation at 1,200 °C.

Compressive yield stress: RHEAs vs. Inconel 718 and other superalloys [Miracle and Senkov, 2017].

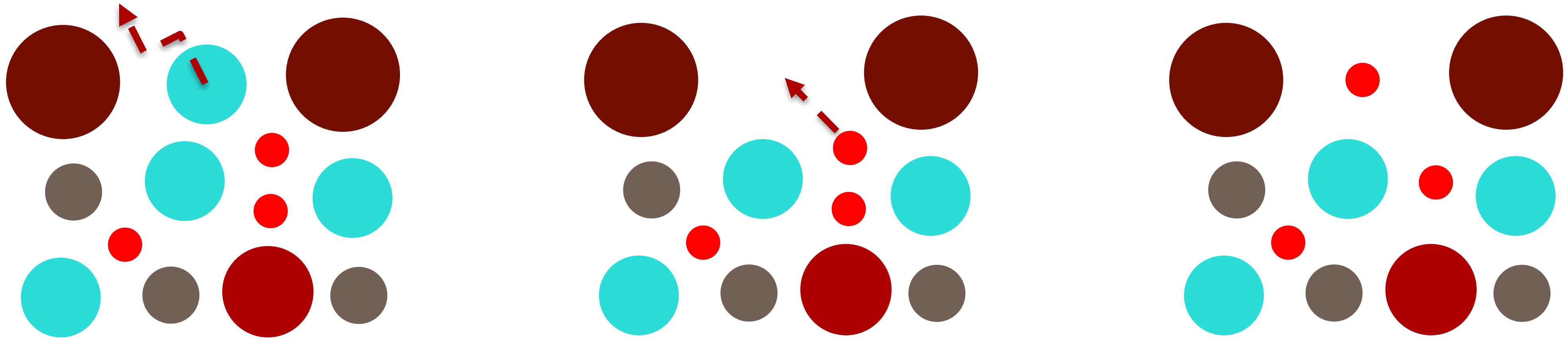




Super alloys vs. RHEAs.

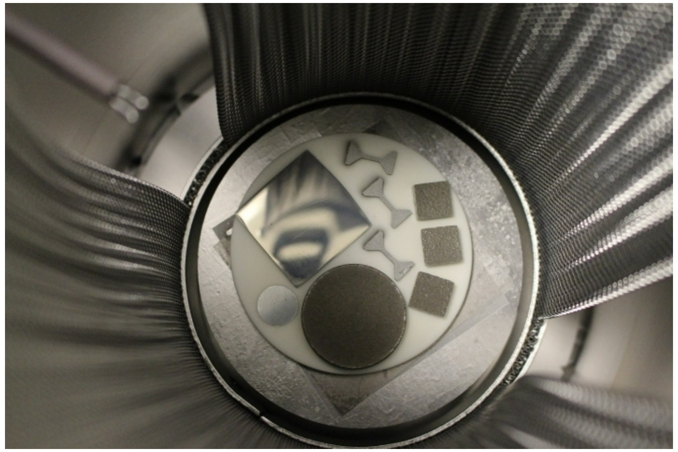
Self-Healing RHEAs

- The RHEA lattice is under larger stress than regular metallic lattice configurations.
  - ✓ Higher ΔS,
  - ✓ Force generated from Δr atomic radius differences, etc.
- This gives RHEAs **self-healing** properties, whereby radiative or structural damage is reduced ***automatically, without external stimuli,*** as the high-stress atoms reorient, thereby repairing the damage [Egami, Guo, Rack, and Nagase, 2013; Liaw, 2014].
- We recently observed experimental evidence that certain RHEA combinations are self-healing.
  - ✓ Up to 20 times fewer displacements per atom (DPA) than SS.
  - ✓ DPA is minimized and micro damage is reverted as the strong interatomic forces reposition the crystalline structure.
- RHEA configurations with a high degree of self-healing can be selected for harsh environment applications.
  - ✓ Reduce microcracks
  - ✓ Mitigate radiation damage, pitting, and corrosion
  - ✓ Extending the durability and reliability of turbomachinery components
  - ✓ Ideal for materials under harsh environments (e.g., nuclear reactors, concentrated solar, high-temperature turbines)

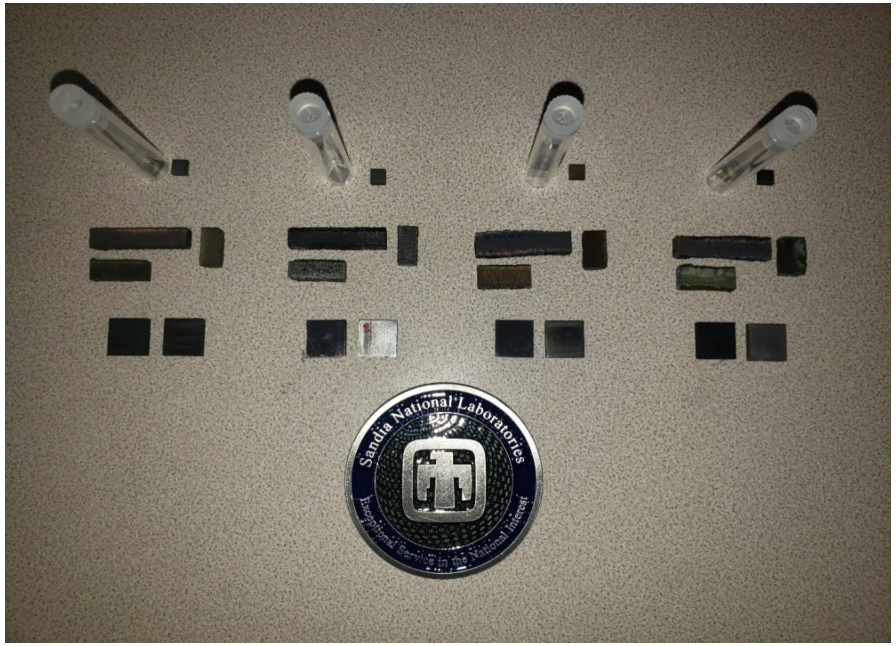


Some RHEA Samples Across Sandia National Laboratories (sample sizes are ~ 0.5 to 3 cm)

Polished RHEA sample.



Annealing of NbTaVW, HfNbTaZr and MoNbTaVW RHEAs.



Multiple RHEA composition pieces printed using the Laser Engineered Net Shaping (LENS) approach [Smith, 2016].

HfNbTaZr 1-inch Spark Plasma Sintered (SPS) tube in collaboration with Calnano.

NbTaVW RHEA Type A dogbone specimens printed via the LENS machine.

RHEA Search and Validation

- The number of RHEAs with ductile properties at room temperature (RT) is less than 1%.
- Ductility is a key goal for widespread commercial RHEA manufacturing.
  - ✓ Intricately associated with component machinability.
- High-strength ductile (HSD) RHEAs are of much interest to the nuclear industry, other energy sectors, aerospace, and transportation.
- We conducted a literature search for HSD RHEAs at RT.
- 17 such combinations were identified.
- We manufactured 11 via Spark Plasma Sintering (SPS) and Laser Engineered Net Shaping (LENS):
  - ✓ $AlNbTiVZr_{1/2}$, CrMoNbTaV, CrMoVW, HfMoNbTiZr, HfNbTiV, HfNbTiVZr, $Hf_{1/2}Nb_{1/2}Ta_{1/2}Ti_{2/3}Zr$, MoNbTiVZr, $Mo_{1/2}NbTiW_{1/2}$, NbTaTiV, and $NbTiV_2Zr$.
- The 11 underwent a series of tests to assess their relative strength, ductility, and machinability.
- The following seven had the highest degree of machinability:
  - ✓ CrMoNbTaV, CrMoVW, HfNbTiV, MoNbTiVZr, $Mo_{1/2}NbTiW_{1/2}$, NbTaTiV, and $NbTiV_2Zr$.
- A synthesis of the experimental data, elemental combinations, material properties, and machinability provided insights regarding HSD RHEA compositions and pathways for improving ductility at RT.

RHEA Search and Validation

The 11 RHEAs of interest that were manufactured for this research include:

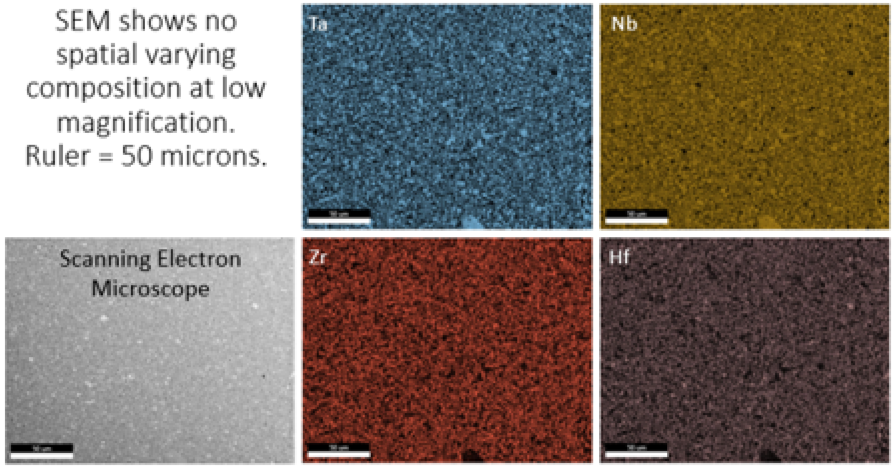
- $AlNbTiVZr_{1/2}$
- CrMoNbTaV
- CrMoVW
- HfMoNbTiZr
- HfNbTiV
- HfNbTiVZr
- $Hf_{1/2}Nb_{1/2}Ta_{1/2}Ti_{3/2}Zr$
- MoNbTiVZr
- $Mo_{1/2}NbTiW_{1/2}$
- NbTaTiV
- $NbTiV_2Zr$

Other potential HSD RHEAs of interest that will be manufactured soon by our team include:

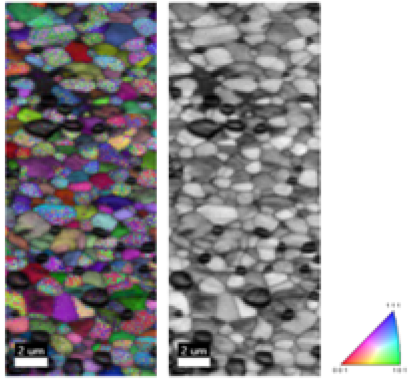
- NbTiVZr [8]
- HfNbTaTiZr [9, 10]
- HfNbTiZr [11, 12]
- MoNbTiV [13]
- $Mo_{1/3}NbTiV_{1/3}Zr$ [14]
- HfNbTaTiV [15]

RHEA Characterization

- Scanning Electron Microscope (SEM) with a 50-microns scale bar shows RHEA homogeneity.
- A granular homogeneous pattern is observed for the Electron BackScatter Diffraction (EBSD), with scale bars at 2-microns.
- A high degree of mixing of the principal elements is important to reach the RHEA's optimum strength and ductile properties.



SEM images for HfNbTaZr.



EBSD images for HfNbTaZr.

Overall RHEA Machining Tests

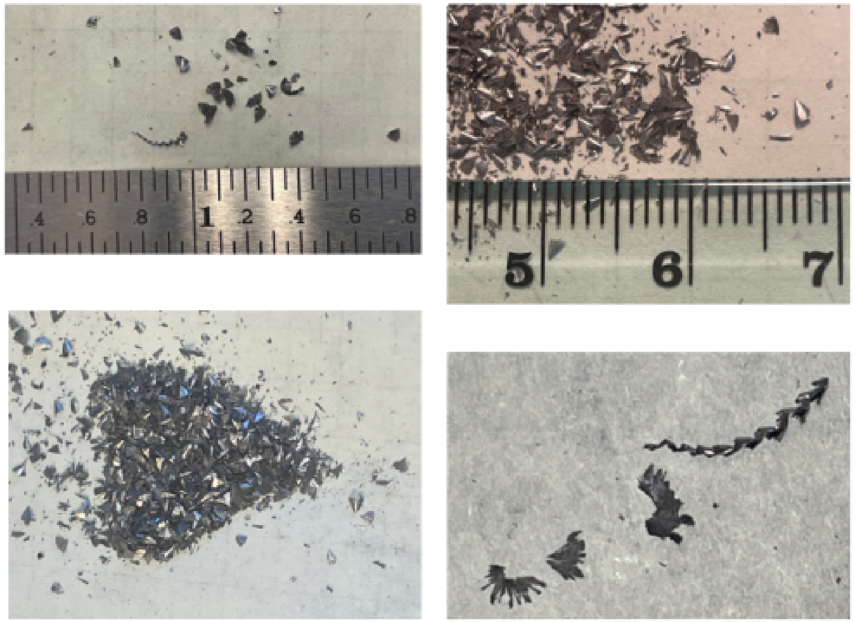
- The machining performed to date includes drilling, lathing, slicing, welding, and filing.
- Some examples are shown below, and in the next slide.

A. Rotational lathing of a RHEA tube. B. Drilled and lathed RHEA. C. RHEA-to-RHEA welding. D. RHEA drilling.

RHEA Drill Tests

- The ability of RHEAs to withstand drilling represents a significant step towards demonstrating machinability.
- Machinability is generally a property of ductile materials, because the machined surface tends to have a smooth finish over a range of machining tasks.
- Drilling was conducted with a 3.18 mm (1/8th inch) drill at 550 RPM.
- The drill was coated with cobalt carbide, with a hardness of 75 HRC on the Rockwell scale.
- Because of the hardness of the RHEAs, it was determined that the drill bits should be replaced right after each drill test.

Drilled NbTaTiV with two fully-completed drill holes. A partial hole on the left was stopped to show the smooth, drilled surface.



Drilling RHEA curls (the ruler at the left is in inches, while the one on the right is in cm).

HSD RHEA Validation

Green = Machinable
Yellow = Minimal machining capacity
Red = Little to no machining capacity

RHEA / References	Manufacturing Method	Poisson's Ratio	Yield Strength at RT (MPa)	Machinable? / Visual results
$AlNbTiVZr_{1/2}$ [14, 22]	SPS	0.36	1,430	Minimal. Generated curls in the range of 0.5 to 2 mm; the opposite surface popped.
CrMoNbTaV [26]	LENS	0.33	1,909	Machinable. Generated smooth drill hole with curls in the range of 0.1 to 1 mm.
CrMoVW [27]	LENS	0.29	1,972	Machinable. Generated smooth drill hole with curls in the range of 0.2 to 1 mm.
HfMoNbTiZr [1, 28]	SPS	0.35	1,719	Minimal. Generated dust and curls in the range 0.1 to 0.2 mm; the opposite surface popped.
$Hf_{1/2}Nb_{1/2}Ta_{1/2}Ti_{3/2}Zr$ [16]	SPS	0.35	903	No. Generated dust; the opposite surface popped. The sample fractured into several pieces.
HfNbTiV [15]	SPS	0.37	1,100	Machinable. Generated smooth drill hole with curls in the range of 0.5 to 2 mm. Top two in terms of machinability.
HfNbTiVZr [1]	SPS	0.37	1,737	No. Generated dust and a few curls up to 0.2 mm; the opposite surface popped. The sample fractured into several pieces.
MoNbTiVZr [14]	SPS	0.33	1,779	Machinable. Generated smooth drill hole with curls in the range of 0.1 to 0.2 mm.
$Mo_{1/2}NbTiW_{1/2}$ [2]	SPS	0.33	1,440	Machinable. Generated smooth drill hole with curls in the range of 0.5 to 0.2 mm.
NbTaTiV [29]	LENS	0.36	1,273	Machinable. Generated smooth drill hole with curls in the range of 0.25 to 2 mm. Top two in terms of machinability.
$NbTiV_2Zr$ [1]	SPS	0.36	918	Machinable. Generated smooth drill hole with curls in the range of 0.5 to 2 mm.

Analysis of the Data, Part 1

- The seven machinable RHEAs generally had Mo, Nb, V, and Ti, with the top two RHEAs involving primarily Nb, Ti, and V.

- That is not surprising, as Nb, Ti, and V are intrinsically ductile, so adding them to the RHEA cocktail helps induce ductility.

- By contrast, the top seven RHEAs rarely had Cr, Hf, Ta, W, or Zr; this is confirmed via contrast with the minimal and non-machinable RHEAs, which tended to use Hf and Zr.

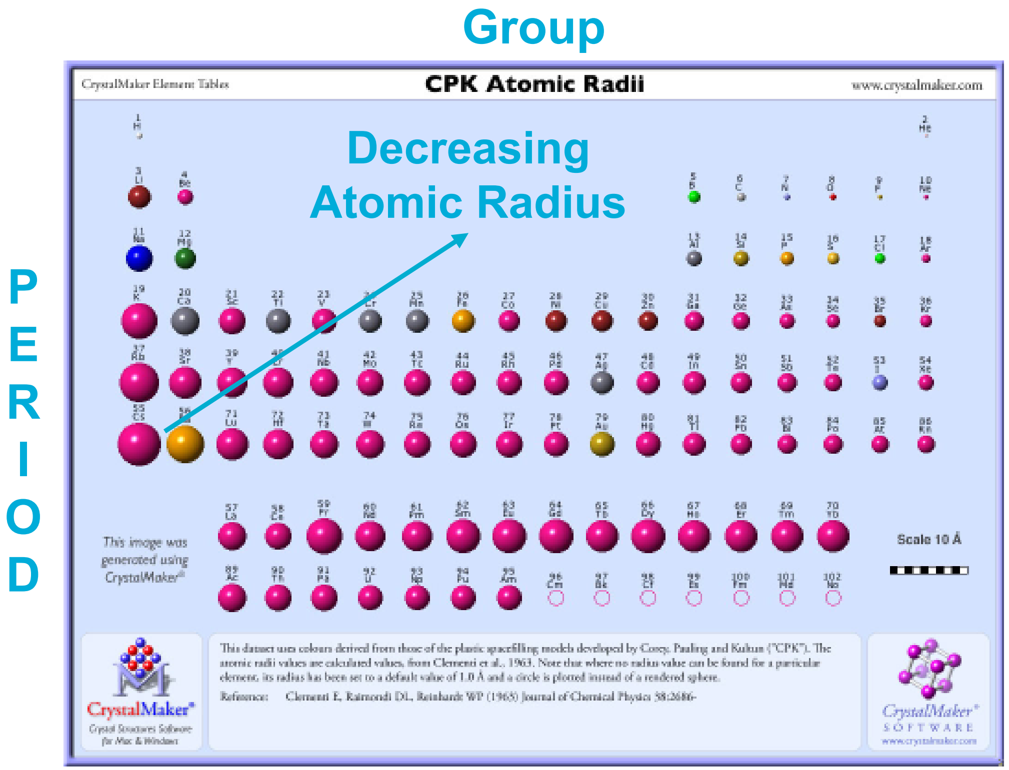
- However, it is noted that relatively pure Hf and Zr are considered ductile.

- More generally, Group IV (e.g., Ti, Zr, and Hf) and Group V (e.g., V, Nb, and Ta) are intrinsically ductile, while Group VI (e.g., Cr, Mo, and W) is brittle.

- Thus, additional mechanisms are likely exerting a stronger influence on ductility…

Analysis of the Data, Part 2

- Refractory element combinations with a wide range in radii promote interatomic mixing (AKA “atomic size mismatch”).
- Period 6 elements have a larger radius than those in Period 5, which in turn are larger than those in Period 4.
- Moreover, as the elements move from left to right, the radius becomes smaller.
- Hence the smallest refractory atoms are those on the right hand side of Period 4 (e.g., Ti, V, Cr, and Mn).
- Ti is included because its radius is almost the same as that of V).
- The largest refractory atoms are those on the left hand side of Period 6 (e.g., Hf, Ta, and W).



Periodic table of elements showing relative atomic size.
(Source: www.crystalmaker.com.)

Analysis of the Data, Part 3

- By applying a Venn diagram for ductility vs. radius range, Ti, V, Hf, and Ta achieve this desirable metric.
  - ✓ *That is, RHEAs with intrinsic ductility + high entropy can now be obtained.*

- Thus, RHEA hybrids that use Hf, Ta, Ti, V combinations have a reasonable chance of being ductile, with Nb and Zr being good replacements for Hf and Ta, respectively (given their comparable radius and intrinsic ductility).

- Finally, the 17 selected RHEAs have much in common with the selection of HfTaTiV and NbZr, i.e., they are hybrid RHEAs stemming from the senary HfNbTaTiVZr RHEA, which is comparable to the CrMnFeCoNi Cantor high-entropy alloy.

Summary & Conclusions, Part 1

- Eleven RHEAs from the literature were manufactured and tested to evaluate their ductility, machinability, and strength.

- Seven were found to be highly machinable:
  - ✓ CrMoNbTaV, CrMoVW, HfNbTiV, MoNbTiVZr, $Mo_{1/2}NbTiW_{1/2}$, NbTaTiV, and $NbTiV_2Zr$ RHEAs, **of which the most machinable were HfNbTiV and NbTaTiV.**

- Such RHEAs predominantly had Nb, Ti, and V, which are very ductile intrinsically.

- The atomic size is also found relevant towards the degree of ductility, with a wider range of atomic radii being the most favorable.

- This includes Ti, V, Cr, and Mn from Period 4, and Hf, Ta, and W from Period 6.

- Refractory elements that have both intrinsic ductility and the widest radii range include Ti, V, Hf, and Ta.

- RHEA hybrid combinations that employ some or all of the following elements (Hf, Ta, Ti, and V), have a high likelihood of being ductile.

Summary & Conclusions, Part 1

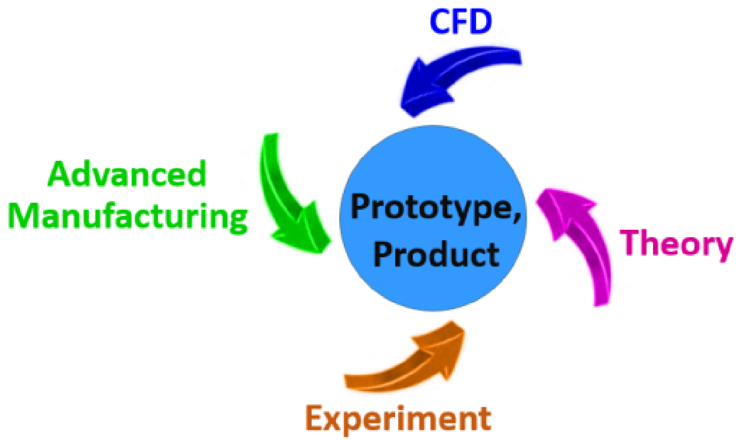
- Moreover, Nb and Zr can replace Hf and Ta, respectively, given their comparable radius and intrinsic ductility.

- Relying solely on intrinsically-ductile elements to form HSD RHEAs is not sufficient, as such combinations can yet experience brittle failure.
  - ✓ It is also necessary to use a wide radii range.

- The data also indicates that the Poisson's ratio is not a reliable indicator of ductility.

- The application of advanced manufacturing, experiment, theory, and computational modeling is recommended for fast-prototyping optimization and validation [Rodriguez, 2019] to tap the vast potential offered by RHEAs.

- Finally, only a small fraction of RHEAs has been explored [Miracle and Senkov, 2017; Senkov et al., 2018].



The technology quad: theory, computation, advanced manufacturing, and experiments [Rodriguez, 2019].

References, Part 1

[1] O. Senkov et al., “Development and Exploration of Refractory High-entropy Alloys—A Review”, J. Mater. Res., Vol. 1, 2018.
[2] O. Senkov et al., “Ductile Nb alloys with reduced density and cost”, J. of Alloys and Compounds, Vol. 808, 2019.
[3] D. B. Miracle and O. N. Senkov, “A Critical Review of High-entropy Alloys and Related Concepts”, Acta Mater., Vol. 122, 2017, pp. 448-511.
[4] S. Dixit et al., “Refractory High-Entropy Alloy Thin Coatings for High Temperature Aerospace and Energy Applications,” J. of Thermal Spray Technology, Vol. 31, 2021, pp. 1021-1031.
[5] S. Rodriguez et al., “Application of Refractory High-Entropy Alloys for Higher-Reliability and Higher-Efficiency Brayton Cycles and Advanced Nuclear Reactors”, Sandia National Laboratories, SAND2021-1 1377, 2021.
[6] K. Kaufmann and K. S. Vecchio, 2020, “Searching for high entropy alloys: A machine learning approach”, Acta Materialia, Vol. 198, 2020, pp. 178-222.
[7] A. P. Mouritz, Introduction to Aerospace Materials, Woodhead Publishing Limited, Cambridge, 2012, pp. 463-464.
[8] N. Y. Stepanov et al., “Effect of Al on structure and mechanical properties of AlxNbTiVZr (x = 0, 0.5, 1, 1.5) high entropy alloys”, Materials Science and Technology, Institute of Materials, Minerals and Mining, Vol. 31, 2015A, pp. 1184-1193.
[9] C. Juan et al., “Solution strengthening of ductile refractory HfMoxNbTaTiZr high-entropy alloys”, Materials Letters, Vol. 175, 2016, pp. 284-287.
[10] L. Dirras et al., “Elastic and plastic properties of as-cast equimolar TiHfZrTaNb high-entropy alloy”, Mater. Sci. Eng. A, Vol. 654, No. 30, 2016.
[11] Y. D. Wu et al., “A refractory Hf25Nb25Ti25Zr25 high-entropy alloy with excellent structural stability and tensile properties”, Materials Letters, Vol. 130, 2014, pp. 277-280.
[12] X. Li et al., “Ductile and Brittle Crack-Tip Response in Equimolar High-Entropy Alloys”, Acta Materialia, Vol. 189, 2020, pp. 174-187.
[13] P. Cao et al., “Ab Initio Study of AlxMoNbTiV High Entropy Alloys”, J. of Physics Condensed Matter, Vol. 27, 2015, pp. 1-6.
[14] Y. D. Wu et al., “Phase composition and solid solution strengthening effect in TiZrNbMoV high-entropy alloys”, Materials & Design, Vol. 83, 2015, pp. 651-660.
[15] Z. An et al., “Spinodal Modulated Solid Solution Delivers a Strong and Ductile Refractory High-Entropy Alloy”, Materials Horizons, Vol. 8, 2021, pp. 948-955.

References, Part 2

[16] S. Sheikh et al., “Alloy design for intrinsically ductile refractory high-entropy alloys”, J. Appl. Phys., Vol. 120, 2016, pp. 1-5.

[17] U. Bhandari, C. Zhang, and S. Yang, “Mechanical and Thermal Properties of Low-Density Al20+xCr20-xMo20-yTi20V20+y Alloys”, Crystals, Vol. 278, 2020, pp. 1-9.

[18] B. S. Murty, J. W. Yeh, S. Ranganathan, and P. P. Bhattacharjee, High-Entropy Alloys, Elsevier, 2nd Ed., 2019, pp. 71, 73-75, and 93.

[19] T. Egami, W. Guo, P. D. Rack, and T. Nagase, “Irradiation Resistance of Multicomponent Alloys”, The Minerals, Metals & Materials Society, Vol. 45A, 2014, pp. 180-183.

[20] A. Kustas and S. Rodriguez, Non-Provisional Patent, US62810723, “Refractory High Entropy Alloy Compact Heat Exchanger”, 2019.

[21] S. Rodriguez, A. Kustas, and D. Ames, Provisional Patent, US62909901, “High-entropy Alloys, Refractory High-entropy Alloys, Methods of Selecting and Making, and Structures Formed from High-entropy and Refractory High-entropy Alloys”, 2020.

[22] Z. An et al., “A Novel HfNbTaTiV High-Entropy Alloy of Superior Mechanical Properties Designed on the Principle of Maximum Lattice Distortion”, J. of Materials Science & Technology, Vol. 79, 2021, pp. 109-117.

[23] W. Guo et al., “Microstructures and mechanical properties of ductile NbTaTiV refractory high entropy alloy prepared by powder metallurgy”, J. of Alloys and Compounds, Vol. 776, 2019, pp. 428-436.

[24] W. D. Klopp, “Review of Ductilizing of Group VIA Elements by Rhenium and Other Solutes”, NASA, TN D-4955, 1968.

[25] N. Y. Stepanov et al., “An AlNbTiVZr0.5 high-entropy alloy combining high specific strength and good ductility”, Materials Letters, Vol. 161, 2015B, pp. 136-139.

[26] R. A. Romero, Investigation of Refractory High Entropy Alloys for Extreme Environment Applications, University of Texas at El Paso, Ph.D. Diss., Open Access Theses & Dissertations 3540, 2022.

[27] D. Ikeuchi et al., “A New Refractory and Transition Metal High-Entropy Alloy System”, Scripta Materialia, Vol. 158, 2019, pp. 141-145.

[28] W. Guo et al., “Microstructures and mechanical properties of refractory MoNbHfZrTi high-entropy alloy”, Materials & Design, Vol. 81, 2015, pp. 87-94.

[29] C. Lee et al., “Lattice distortion in a strong and ductile refractory high-entropy alloy”, Acta Materialia, Vol. 160, 2018, pp. 158-172.

[30] S. Rodriguez, Applied Computational Fluid Dynamics and Turbulence Modeling: Practical Tools, Tips and Techniques, Springer International Publishing, 1st Ed., 2019, pp. 5-7.