

Cost-Competitive Super Alloys for High Radiation, Temperature, Pressure, and Corrosive Environments

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Refractory High Entropy Alloys (RHEAs)



Five Awesome RHEA Properties

$T > 1,600 \text{ } ^\circ\text{C}$

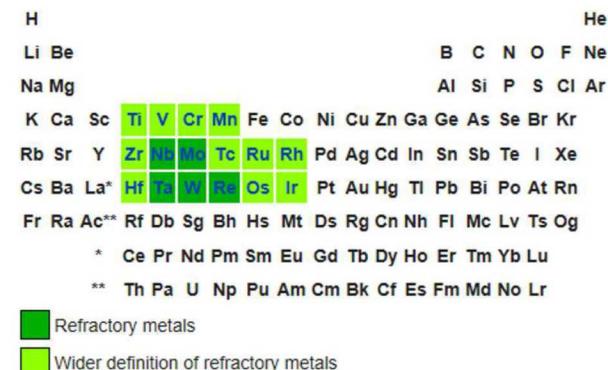
$P > 300 \text{ MPa}^1$

Corrosion Resistance²

Radiation Resistance³

Self-Healing⁴

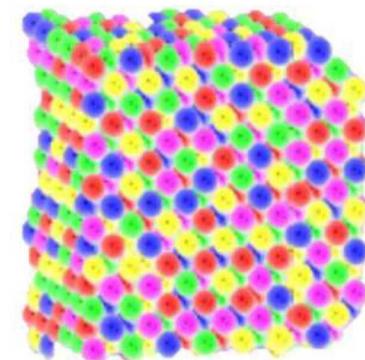
1. Compressive yield stress is two times larger than Inconel 718 at 1,000 °C; ~10X stronger than SS.
2. Negligible degradation after 240 hours exposure to nitric acid at the boiling point (e.g., HfNbTaTiZr).
3. No issues for proto-RHEA with up to 10 displacements per atom from a high-energy electron beam.
4. Self-healing associated with high entropy and atomic stress.



The 16 refractory elements.

Refractory High Entropy Alloys (RHEAs)

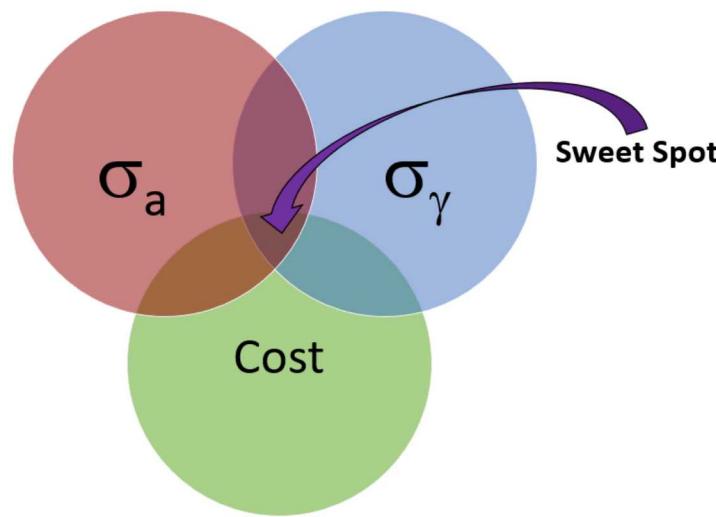
- RHEAs typically consist of five refractory elements that form alloys in near-equiautomic proportions.
- “Refractory” means high-temperature; “entropy” means high mixing tendency—larger entropy lowers Gibbs formation.
- Atomic ordering means the lattice is under larger stress than regular metallic lattice configurations.
 - ✓ This gives RHEAs self-healing properties, meaning that radiative or structural damage is reduced **automatically** as the high-stress atoms reorient and repair the damage.
- ***But the number of possible RHEA permutations is 4,368, so it is very expensive to research all RHEAs.***
- ***We developed an algorithm to cherry-pick RHEAs with the highest temperature, structural strength, and corrosion/radiation resistance, while remaining cost-competitive.***



The
CoCrFeMnNi
HEA.

Nuclear RHEA Cherry-Picking

- Thus, our algorithm reduces the number of alloys by choosing elements with properties favorable for use in high radiation fields, at an acceptable cost.
- *Therefore, the initial set of 4,368 RHEA combinations is now reduced to the six most promising RHEAs.*
- *A TA was submitted a month ago, specifying the unique composition of the six RHEAs, SD# 15012.*



Venn Diagram for RHEA Down-Selection.

$$n_{tot} = \frac{n!}{k!(n-k)!} = \frac{16!}{5!(16-5)!} = 4,368$$



$$n_{tot} = \frac{n!}{k!(n-k)!} = \frac{6!}{5!(6-5)!} = 6$$

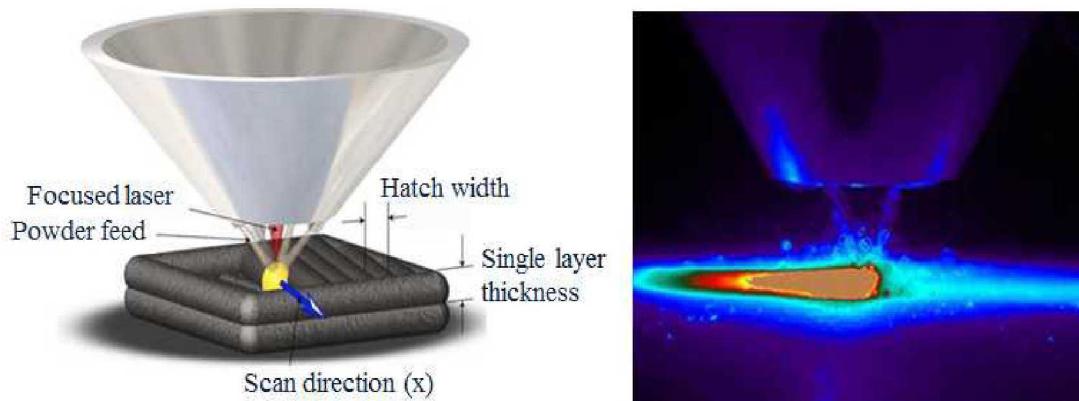
Self-Healing RHEAs



- We recently found that RHEAs can be **self-healing**.
- This means that radiative or structural damage is reduced **automatically (up to 10 DPA vs. 0.5 DPA for steel)**.
- We did not know this when we submitted our concept LDRD proposal, “Engineering of Refractory High Entropy Alloys for Advanced High Temperature Nuclear Reactors”, Idea 20-0214.
- ☹

Refractory High Entropy Alloys (RHEAs)

- Furthermore, Advanced Manufacturing of RHEAs can
 - ✓ more than double strength and hardness [Waseem and Ryu, 2017].
 - ✓ SNL showed a 250% increase in strength and order-of-magnitude increase in ductility [Kustas, 2018].
 - ✓ SNL extended structural properties in advanced alloys through rapid cooling rates [Kustas et al., 2018; Agribay, Kustas, et al., 2018].
 - A patent is currently being sought [Kustas, Rodriguez, et al., 2018].
 - ✓ SNL's microstructure control can further increase RHEA high-temperature, corrosion, creep, and thermal-fatigue resistance.



Hybrid laser engineered net shaping (LENS) AM system, where fluidized powder consolidates onto multi-material layers [Smith, 2016].

We See Many Technical & Business Opportunities...



- Lou Qualls, the national technical director for molten salt reactors at ORNL, is very interested in *pro bono* testing our nuclear RHEAs at his test facility.
 - ✓ *He said that if the RHEAs deliver as anticipated, these are the materials he would use in their next-generation, advanced molten salt reactors.*
- LANL is considering our RHEAs:
 - ✓ High-temperature MegaPower micro reactors applications.
 - ✓ *To meet DoD C17 weight constraints (RHEAs can be 10X stronger than SS, so much less mass is needed).*
 - ✓ *For SNL's sCO2 power conversion units (PCUs) (the higher pressure requires RHEAs to reduce weight, increase safety).*
- Dynetics sees the potential for our RHEAs as higher-temperature replacement for Inconel components in hypersonic vehicles.
- *Our RHEAs are of much interest in these areas:*
 - ✓ Usage in radiation-resistant sensors.
 - ✓ Applications that require self-healing.
 - ✓ Very high temperature systems (VHTRs), concentrated solar power, combustors.
 - ✓ Highly corrosive coolants, e.g., molten salts (MS VHTRs, concentrated solar power).
 - ✓ Aerospace.
 - ✓ Harsh environments (T, P, corrosion, radiation).

We See Many Technical & Business Opportunities...



- Issues RHEAs can resolve **NOW**, thereby extending SNL's sCO₂ PCU technology:
 - ✓ The *sCO₂ PCU requires high pressure (>7.4 MPa)*. *RHEAs exceed 300 MPa compressive stress at a reasonable cost.*
 - ✓ RHEAs have 10X the toughness of SS, so much less weight is required (e.g., enables C17 transport).
 - *This permits MICRO reactors to indeed be micro reactor sized!*
 - ✓ With higher RHEA toughness, the pitting of sCO₂ turbomachinery will likely be significantly reduced, if not fully eliminated.
 - ✓ sCO₂ thermal efficiency is ~45% (vs. ~35% for the Rankine cycle). Using RHEAs, the sCO₂ thermal efficiency can increase to 65% or more.
 - ✓ Allow for more durable sCO₂ PCUs due to significantly-reduced corrosion.
 - ✓ RHEA bearings and seals will likely have longer and more reliable operation...
- Advanced Reactor Concepts:
 - ✓ RHEA-based fuel/cladding allow for reactor power cycling (load following).
 - ✓ The stress and radiative self-healing, as well as its high temperature range, make the reactor “hot rock” concept closer to reality.
 - ✓ A RHEA-based fuel is more accident-tolerant.

References

- Agribay, N., A. Kustas, et al., "High Entropy Alloys: A Materials Solution to Metals Additive Manufacturing", Sandia National Laboratories, 2018.
- Kustas, A., "Novel Processes and Materials for Metal Additive Manufacturing", Sandia National Laboratories SAND2018-10799PE, 2018. Kustas, A. B. et al., "Characterization of the Fe-Co-1.5V Soft Ferromagnetic Alloy Processed by Laser Engineered Net Shaping (LENS)", *Addit. Manuf.*, Vol. 21, 2018.
- Kustas, A., S. Rodriguez, et al., "Refractory High Entropy Alloy Compact Heat Exchangers", SD# 14916, Sandia National Laboratories, 2018.
- Kustas, A. B. et al., "Characterization of the Fe-Co-1.5V soft ferromagnetic alloy processed by Laser Engineered Net Shaping (LENS)", *Addit. Manuf.* 21, 41–52. doi:10.1016/j.addma.2018.02.006, 2018.
- Miracle, D. B. and O. N. Senkov, "A Critical Review of High Entropy Alloys and Related Concepts", *Acta Mater.*, Vol. 122, 2017.
- Rodriguez, S., A. Kustas, and D. Ames, "Cost-Competitive RHEAs and HEAs for High Radiation, Temperature, Pressure, and Corrosion Environments", SD# 15012, 2019.
- Senkov, O. N. et al., "Development and Exploration of Refractory High Entropy Alloys—A Review", *J. Mater. Res.*, Vol. 1, 2018.
- Smith, M., "Additive Manufacturing at Sandia", Sandia National Laboratories, 2016.