A Novel Ceramic Derived Processing Route for Multi-Principal Element Alloys

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What are High Entropy Alloys? HEAs are alloys with 5+ components in near equiatomic amounts. Percentages of each element range from 5-35%. These alloys are called "high-entropy" alloys because the total entropy of these systems is increased due to a larger number of elements in the mix in near equal proportions[1]. Recently, there has been increased interest in HEAs due to their improved properties, e.g. enhanced strength and fracture toughness at low temperatures, and better corrosion and oxidation resistance[2].

1. Y.F. Ye *et al.* (2016), *Materials Today*. 19 (6): 349–362. 2. M.H. Tsai *et al.* (2014), *Materials Research Letters*. 2 (3): 107–123

Current HEA Processes Two common types of HEA fabrication processes are arc-melting and mechanical alloying. Although these methods are reliable, the equipment required to reach high melting temperatures and the operation of a high energy mill can be expensive and time consuming. Difficulties that result from these methods include dendritic structures with elemental segregation in arc-melted samples and nanocrystalline structure with an incorporation of milling media material in mechanical alloyed samples.

Oxide Reduction Method

Mix of Oxide Powders → Anneal in Reducing Environment → Form Metallic Alloy

Advantages

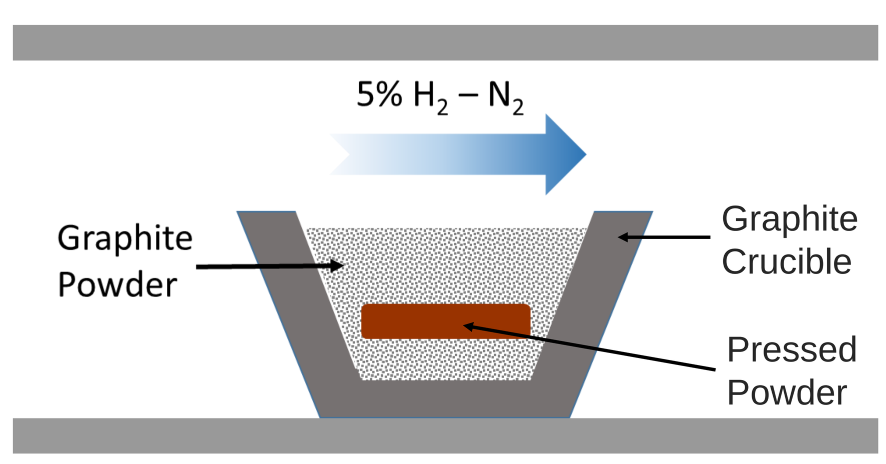
- Solid State Process
- Use of mixed oxides can achieve atomic scale mixing of metal cations
- Novel phase morphologies

Challenges

- Wide range of components with different melting temperatures
- Potential reaction with atmosphere

Procedure

High purity starting powders → Ball-milled in ethanol (8h) → Pressed into pellets (uniaxial) → Heat-treated at 1000 ºC in flowing 5% H_2/N_2 → Heating/Cooling rates 10 ºC/min



Fe_2O_3 (99.998%), Co_3O_4 (99.7%), NiO (99.998%), CuO (99.998%)

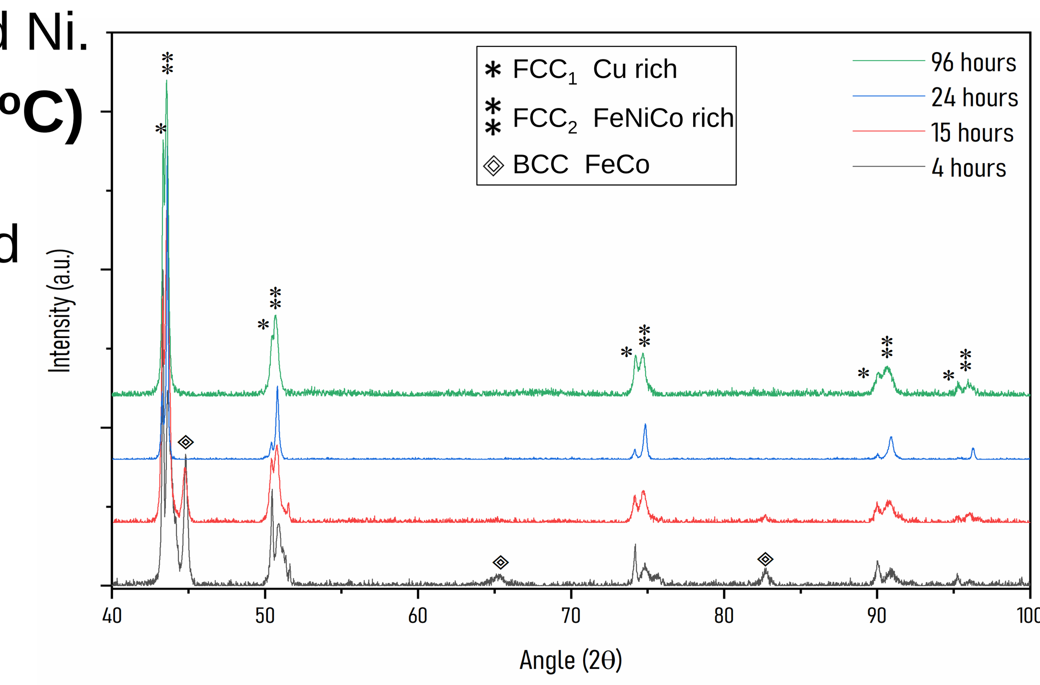
Background on FeCoCuNi

These 4 components are a base to a large family of HEAs and their corresponding oxides are readily reducing using forming gas. Possible property improvements of this composition are improved mechanical behavior with Fe and Co and corrosion resistance with Cu and Ni.

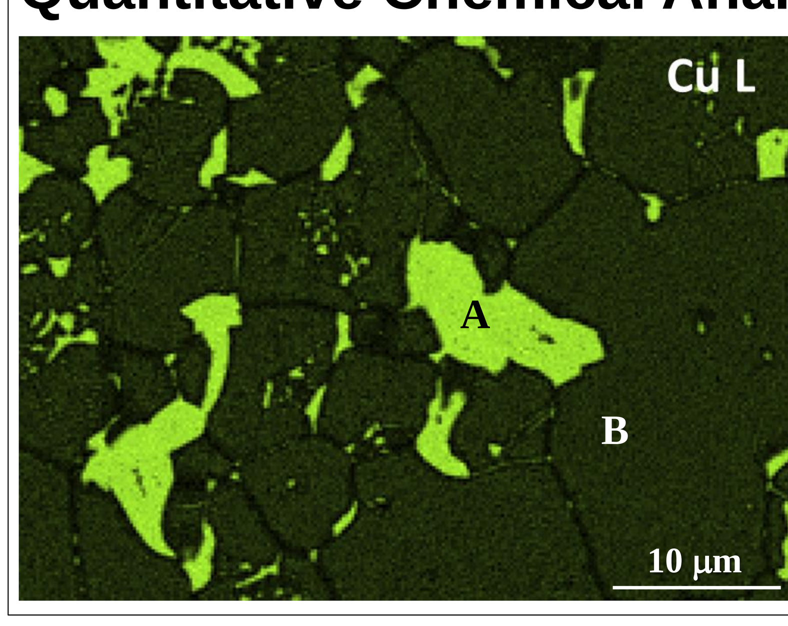
XRD Temporal Phase Evolution (1000ºC)

After 4 hours, the composition is completely reduced to metal. Three phases are achieved in the shorter times and two phases are achieved in the longer times. The longer the sample anneals the difference in the relative amount of each FCC phase decreases.

Annealing Time (hr)	15	24	96
*FCC_1 (%)	21	23	40
**FCC_2 (%)	79	77	60



Quantitative Chemical Analysis of Phases - (Reduced 24h at 1000ºC)



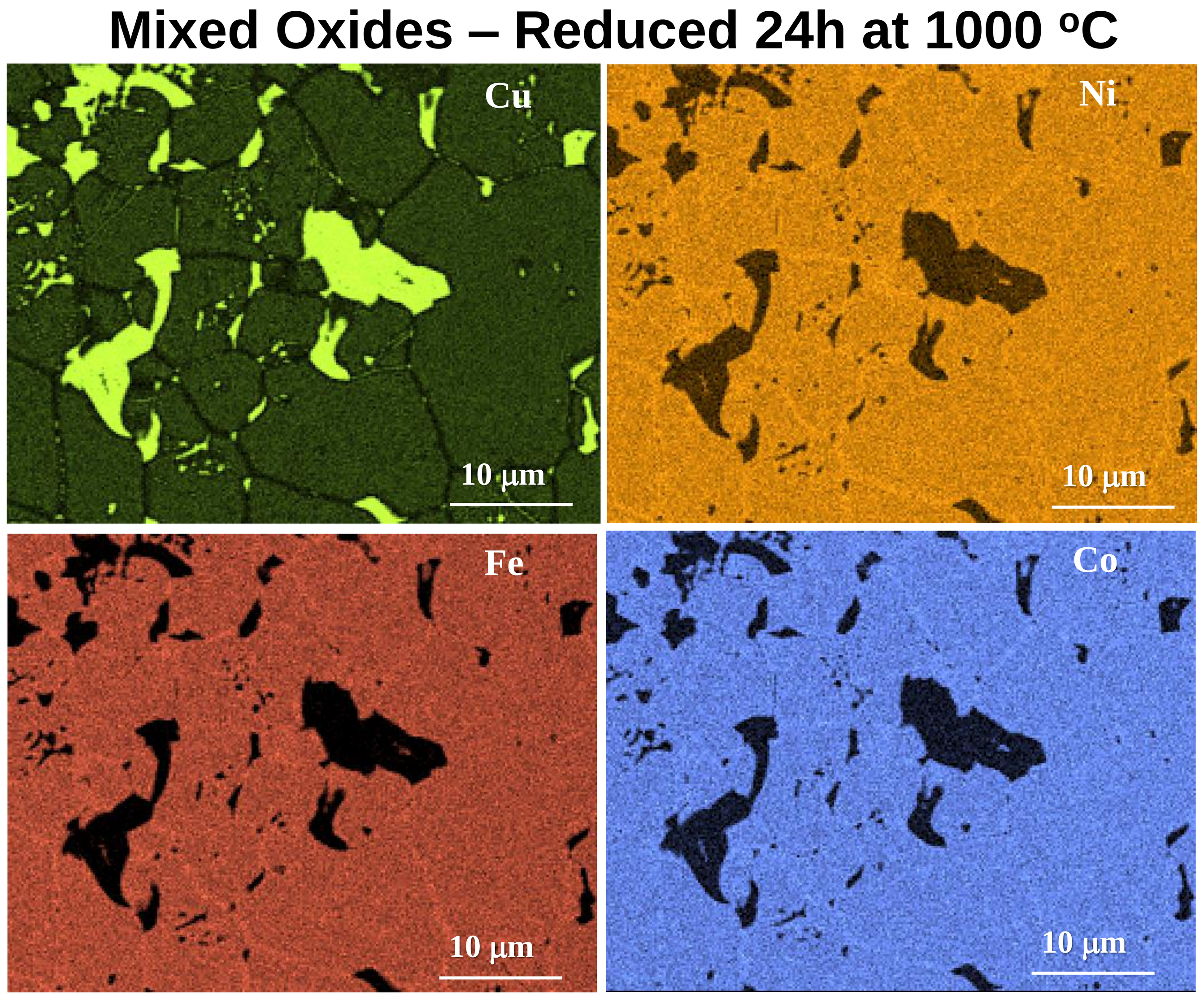
A: Copper rich phase		
Element	Wt.%	At.%
Co	5.1	5.2
Cu	80.6	76.8
Fe	5.0	5.4
Ni	12.2	12.6

Region A: Cu makes up almost 80% of this phase. This region may be gaining Cu from the grain boundaries as well as from the matrix phase.

Region B: The 4 elements are closer to equimolar but there is a slight deficiency in Cu.

B: Matrix phase		
Element	Wt.%	At.%
Co	28.2	28.2
Cu	19.6	18.1
Fe	25.3	26.6
Ni	27.1	27.1

Mixed Oxides – Reduced 24h at 1000 ºC



Elemental Mapping (EDS) of Phases

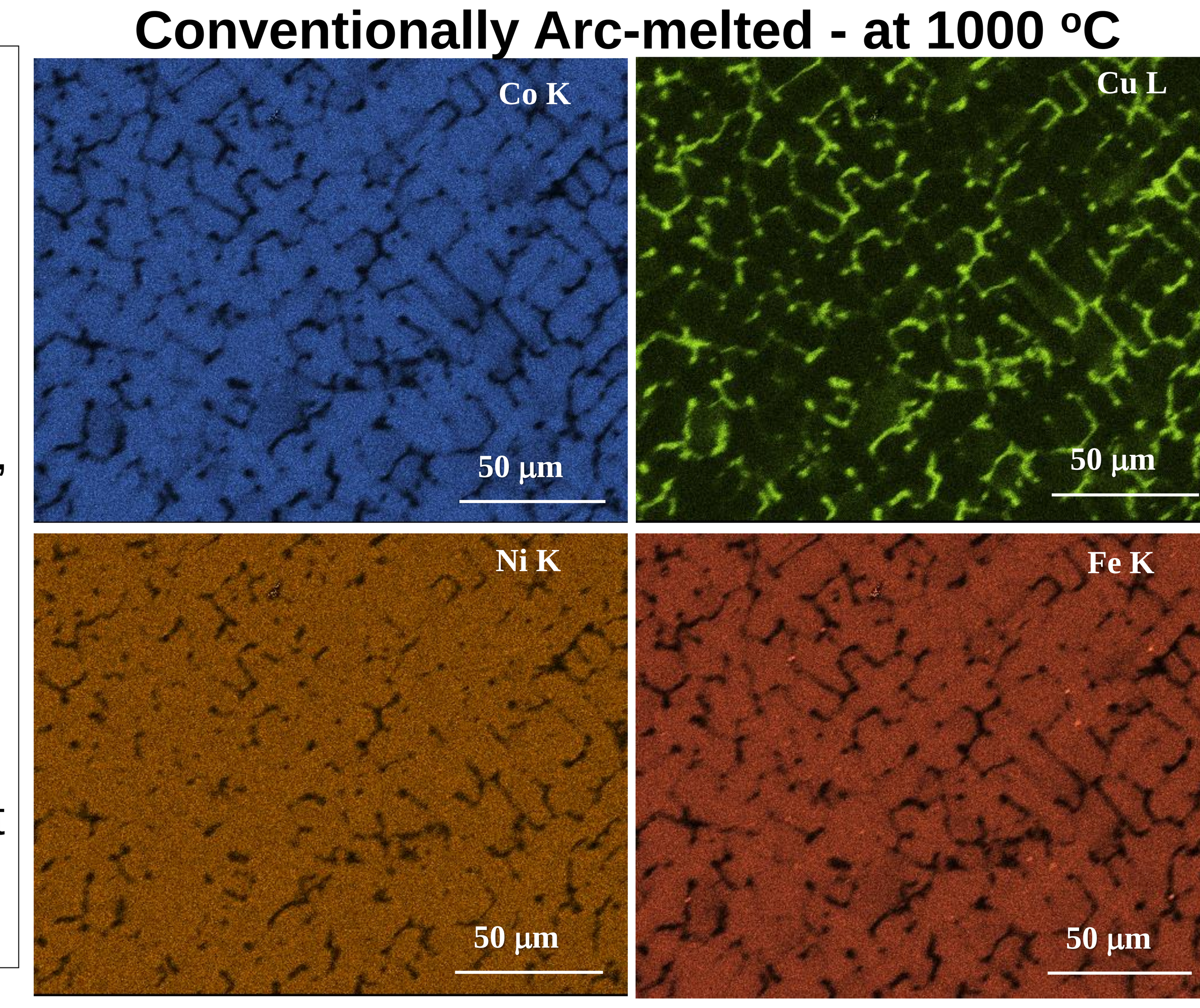
Oxide Reduction Method *(left)*

- Cu-rich phase in which the regions highlighted in the Cu map are inverse of those highlighted in the Ni, Fe, and Co maps
- There is a uniform dispersion of Cu, Co, Fe, Ni within matrix grains
- Cu depletion along grain boundaries

Arc-Melted Method *(right)*

- The same if not similar phases are achieved in both fabrication methods
- The arc-melted sample produces a different microstructure compared to the oxide reduced sample.

Conventionally Arc-melted - at 1000 ºC



Summary

- Multi-oxide reduction is viable method for fabricating FeCoCuNi HEA
- Microstructure consists of two FCC phases (copper rich, & Fe-Co-Ni rich)
- Equiatomic composition is not a single solid solution HEA
- Phases equivalent to those obtained by arc melting

Future Work

- Explore other MPEA compositions (CoCrMnFeNi & $Al_{0.5}CrFeCuNi_2$)
- Combine mixed oxide and metal starting powders
- Perform mechanical testing (FeCoCuNi)
- Create FeCoCuNi samples with the atomic percentage of the matrix phase

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