SMARTER: Science of Multicomponent Alloys – a Theoretical and Experimental Roadmap

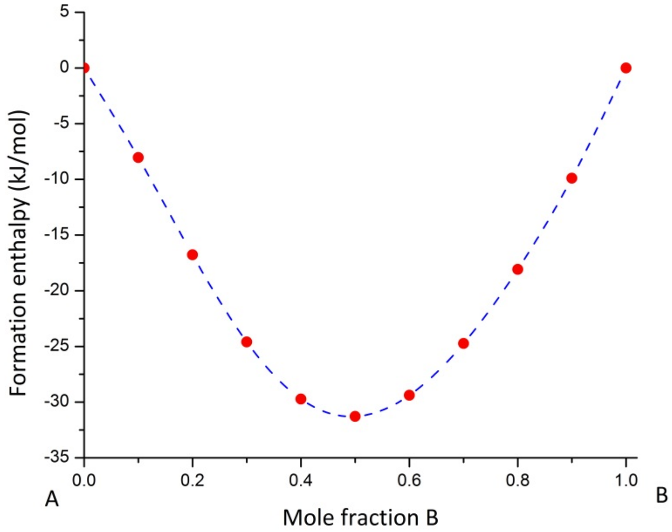
Matthew J. Kramer, Tyler R. Bell, Pratik K. Ray, Prashant Singh, Linlin Wang and Duane D. Johnson

*This work is supported by **Office of Fossil Energy (Cross-cutting Research Program), US-DOE** under the contract number DE-AC02-07CH11358*

U.S. DEPARTMENT OF ENERGY

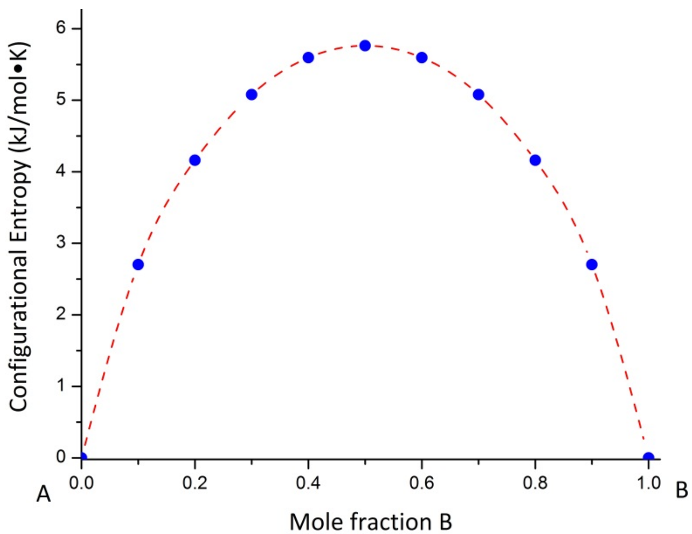
THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

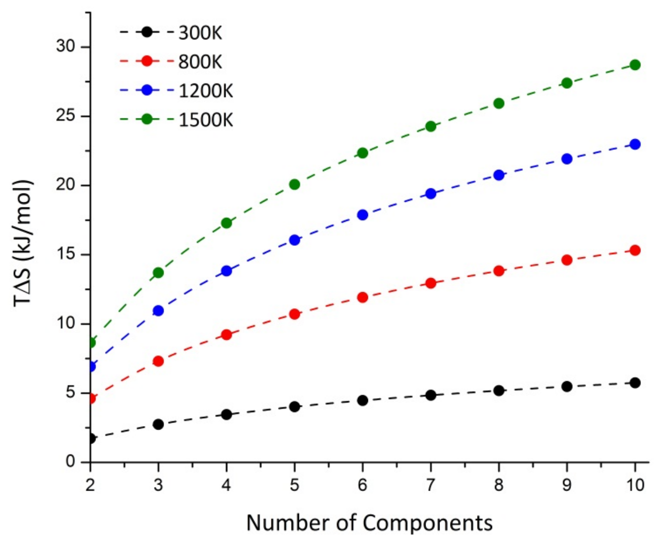
High Entropy Alloys: overview



Miscible systems show negative formation enthalpies, and a tendency to form intermetallics

Stabilizing disordered phase requires high entropy. This is favored by equiatomic compositions in multicomponent systems





Stability criteria

$$\Omega = \frac{T_M \Delta S_{mix}}{|\Delta H_{mix}|} > 1.1$$

$$T_M = \sum_{i=1}^{n} c_i (T_M)_i$$

Entropy (disordered phases) dominates enthalpy (ordered phases)

Multiple stability criterion – potential for *in-situ* functionalization?

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - r_i / \bar{r}\right)^2} < 6.6\%$$

Similar to Hume-Rothery rule, i.e. minimize size differences in order to form the solid solutions

Y. Zhang, X. Yang and P.K. Liaw, JOM 64 (2012) 830

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i$$

VEC < 6.87 *bcc* phases; VEC ≥ 8 *fcc* phases

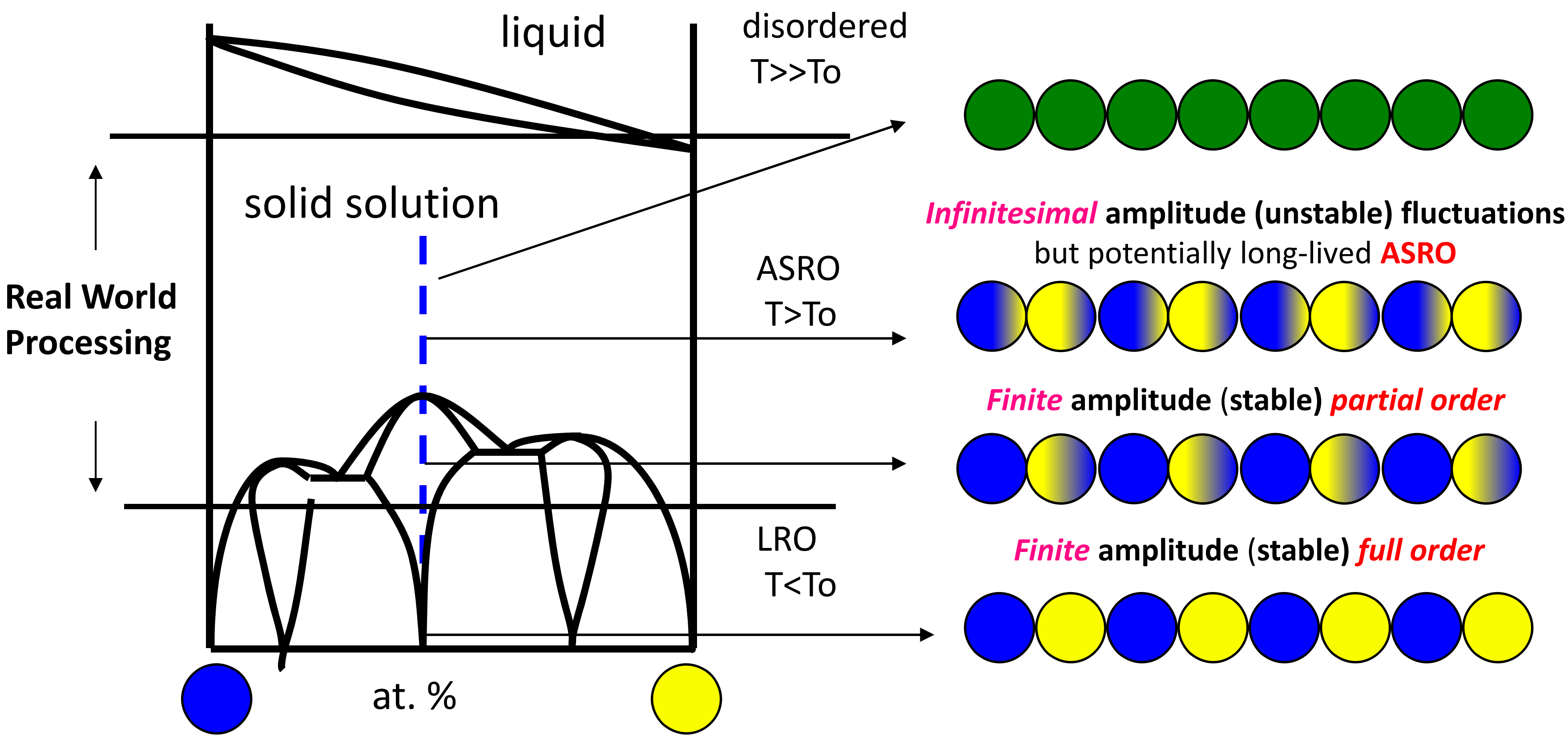
S. Guo, C. Ng, J. Lu and C.T. Liu, J Appl. Phys. 109(2011) 103505

Opportunities and Challenges

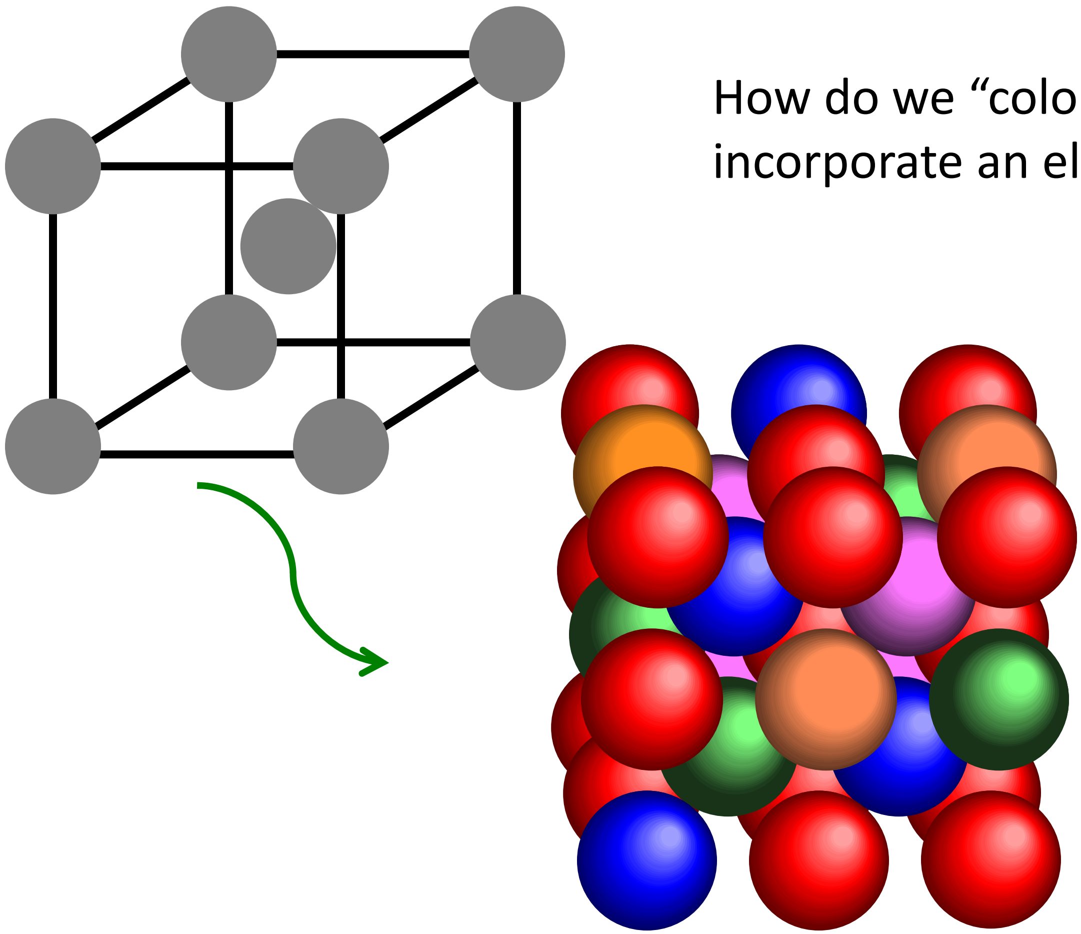
- Can we manipulate the short to medium range order?
  - Promote clustering to enhance strength or toughness?
  - Enhance diffusion of oxidatively stable phases?
- Requires highly accurate models
  - Atomistic simulations of highly complex chemistries are computationally intensive
  - Simulations must be accurate for long spatial and temporal scales

Challenges with disorder

- Experimental Measurement: quenched or annealed samples.
- Band calculations: not always related to experimentally assessed (thermal and off-stoichiometric effects).



A Coloring Problem



How do we "color" the unit cell, in order to incorporate an element of disorder?

Need extremely large cells, with randomly decorated sites

Need multiple decorations for accurate calculations

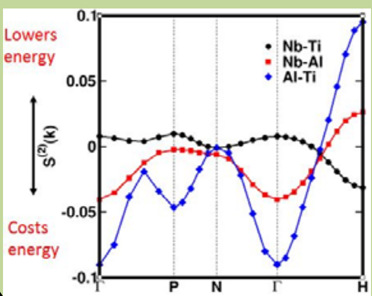
Prohibitively high computational cost

There are $n(n + 1)/2$ partial pairs for an n component system

Problem Definition and Approach

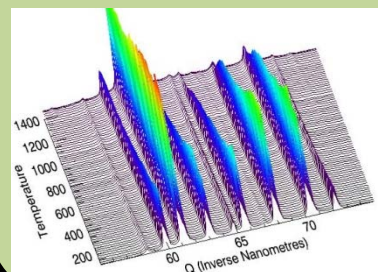
Grand Challenge: to speed the discovery and optimization of these chemically complex alloys and leverage our theoretical and experimental capabilities for assessing their long-term stability

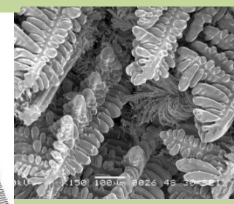
Theoretical tools (KKR-CPA)



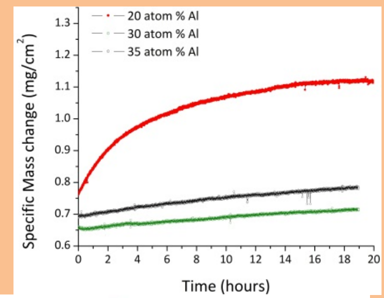
validation

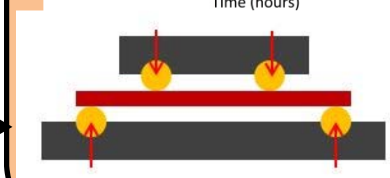
Structural studies

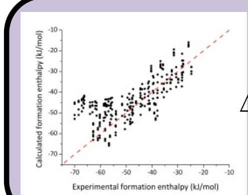




Stability in harsh environments

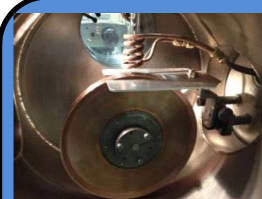






$$\Delta H = \phi_1 \Delta H_{AB}(\alpha) + \phi_2 \Delta H_{BC}(\beta) + \phi_3 \Delta H_{CA}(\gamma)$$

Rapid Assessments

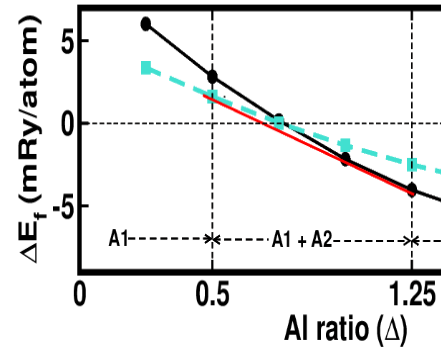


Processing

Year – I: Milestones and Approach

Validation of the KKR-CPA approach for multi-component systems

- Application to well-explored systems
- Applications to new systems and compositions



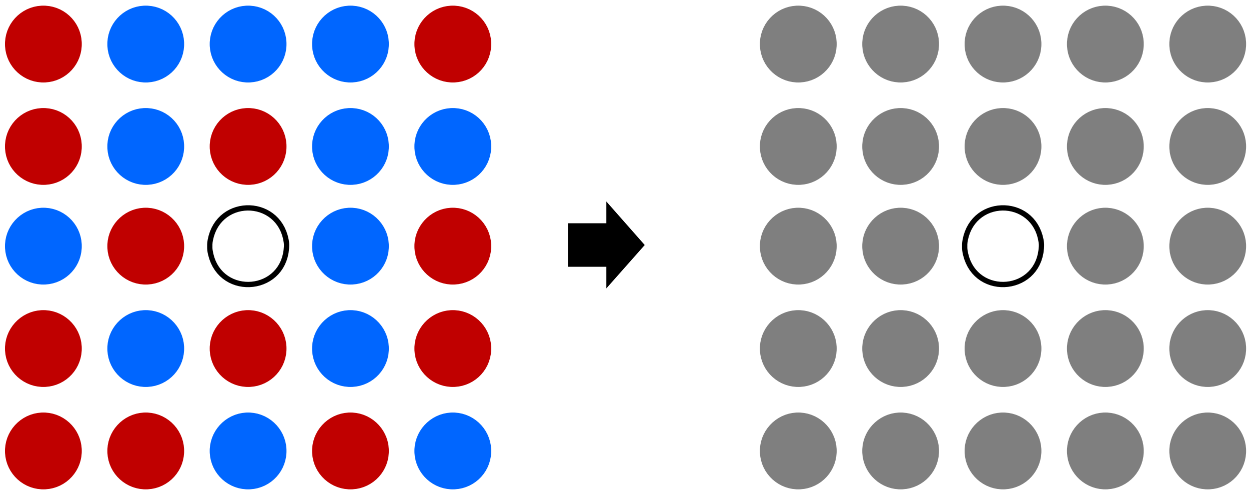
predict and interpret atomic short-ranged order in *n* -component substitutional disordered alloys, and provide its electronic-structure origins, e.g., low- temperature LRO behavior.

Baseline oxidation metrics

- Oxidation resistance in High Entropy Alloys as a function of temperature
- Comparison with Ni alloys
- Potential for improvements

Two example systems
Zr-Hf-Nb
Al-Ni-Fe-Cr-Co

Modeling disorder



Idea of CPA
(**C**oherent **P**otential **A**pproximation)

Velicky et. al., Phys Rev 165 (1968) 747

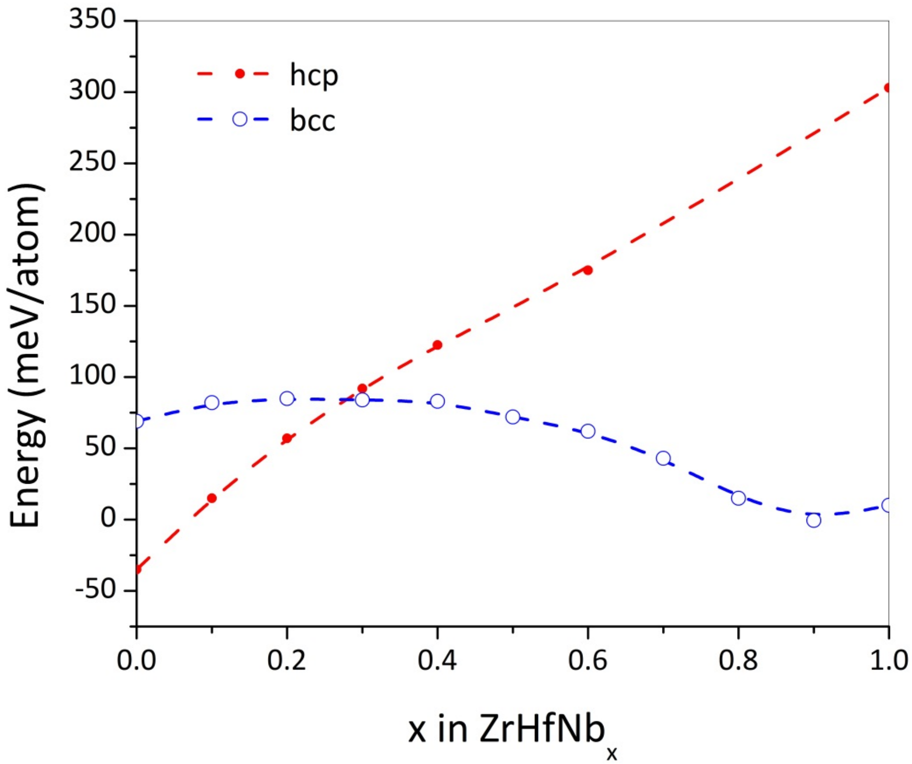
Thermodynamic Linear-Response calculations

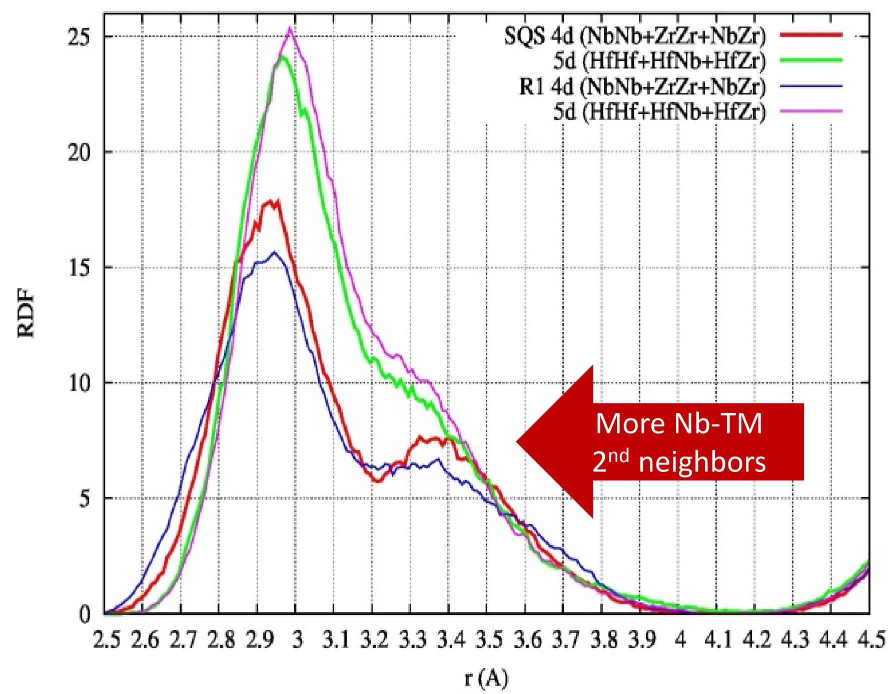
- KKR-CPA based chemical or magnetic susceptibilities
- Directly calculate the energy associated with ASRO

Direct calculation of energetics for Disordered/Partially-Ordered/ Ordered States

- DFT-based multi-sublattice KKR-CPA (configurational averaging)

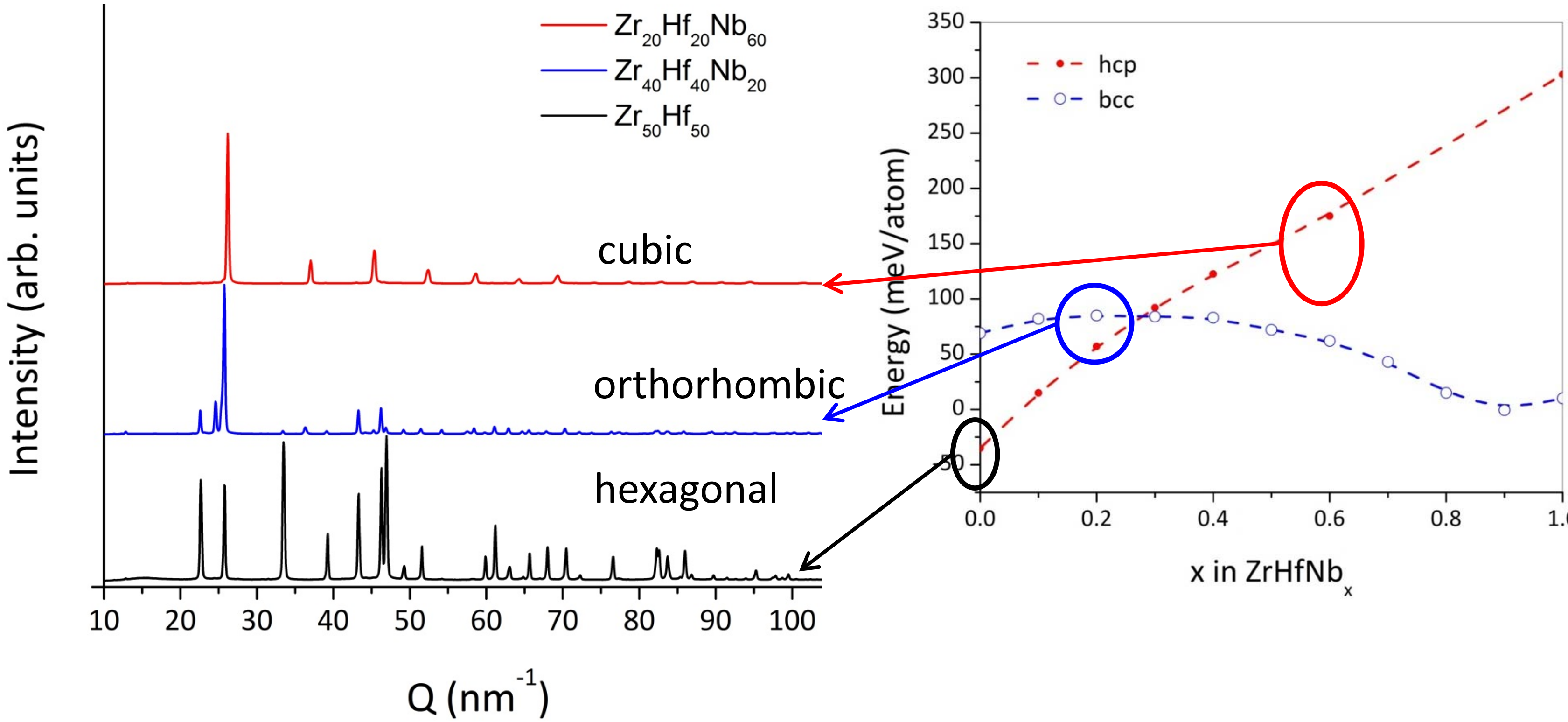
The Zr-Nb-Hf system





Theoretical prediction: Nb additions promote B2 ordering, resulting in a hcp → bcc transition with increasing Nb content

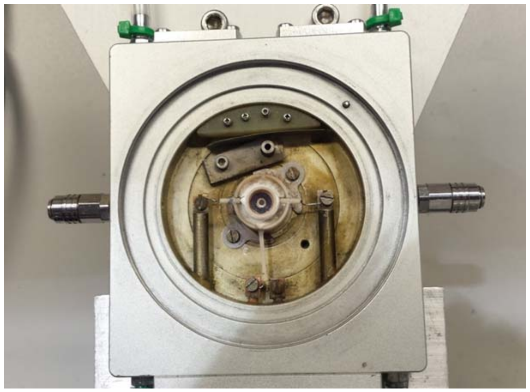
In-situ diffraction: Zr-Nb-Hf alloys

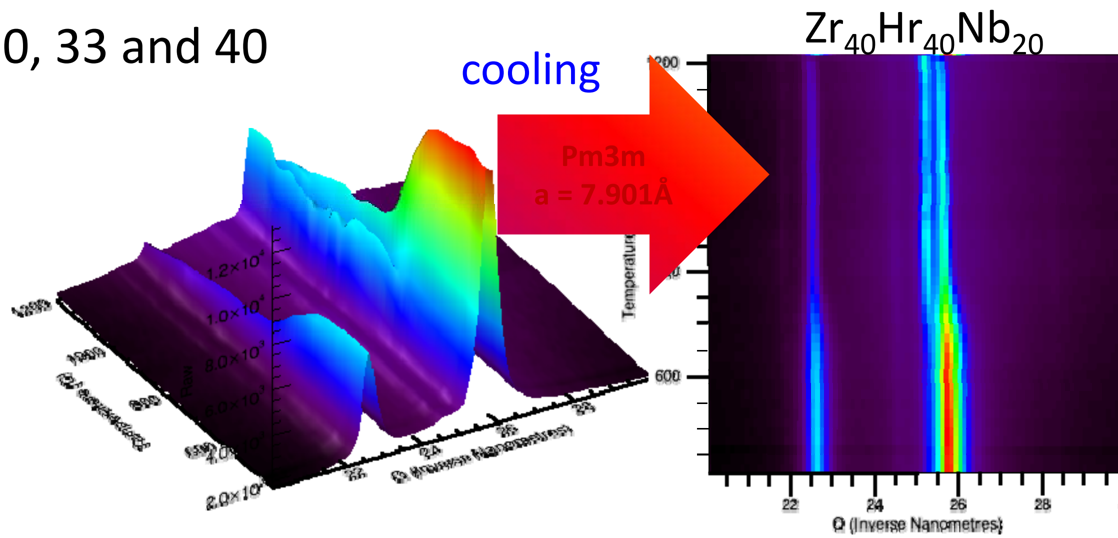


Key Issues – validate CPA code with predictions of the T dependent stability

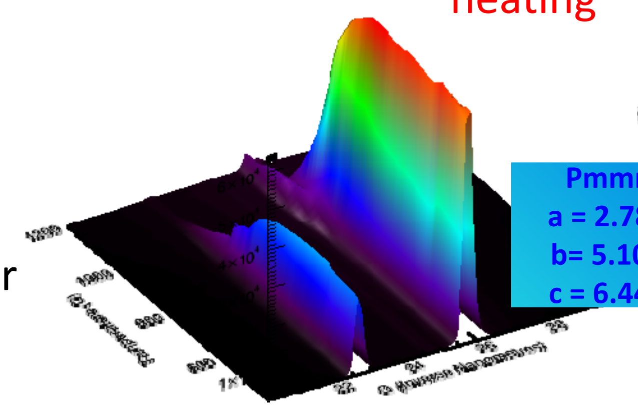
In-situ diffraction: Zr-Nb-Hf alloys

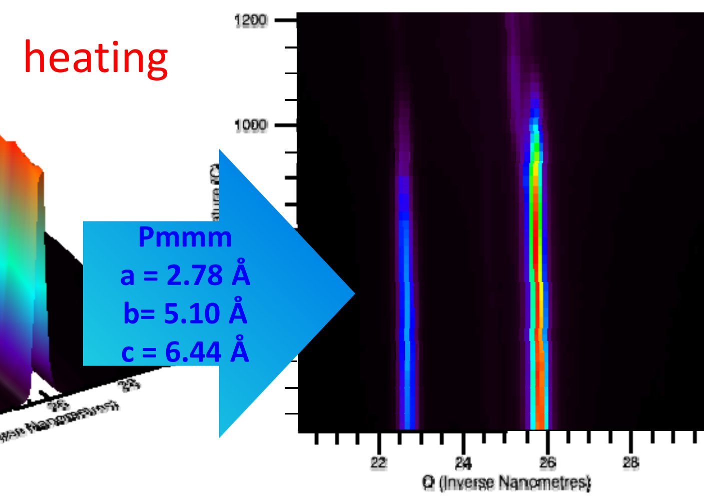
$(Zr,Hr)_{1-x}Nb_x$ for x = 0, 10, 20, 33 and 40



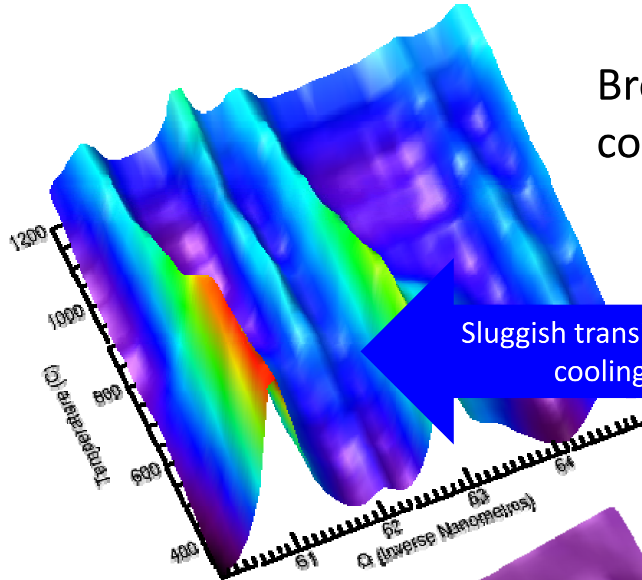


High energy XRD at 11-ID-B at Advanced Photon Source, ANL
(PDF and Rietveld analysis)
heating and cooling rates
~ 50°C/min, hold 2 min every 50°C
exposure time = 0.25 s in flowing Ar



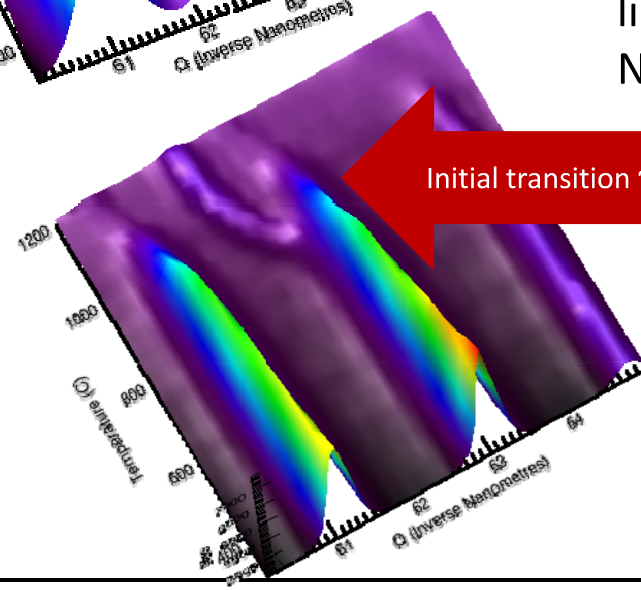


In-situ diffraction: Zr-Nb-Hf alloys



Broader peaks on cooling

Sluggish transition on cooling

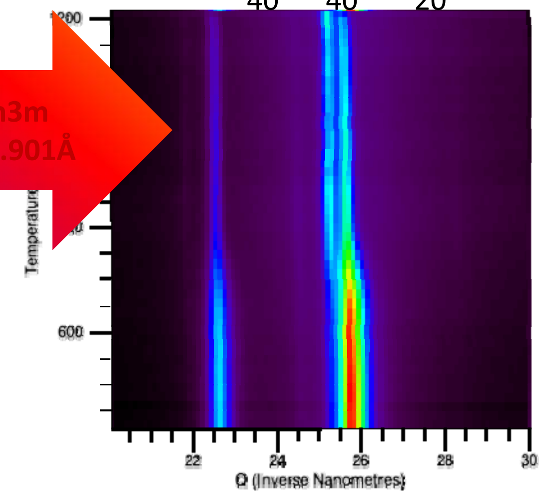


Initial transition ~1000C

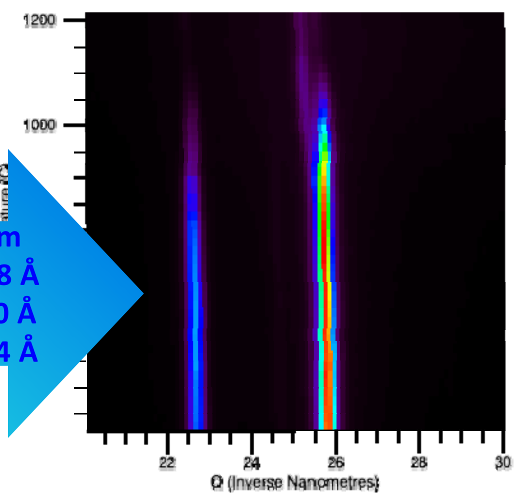
In situ experiments in line with CPA showing Nb promotes disorder

$Zr_{40}Hr_{40}Nb_{20}$

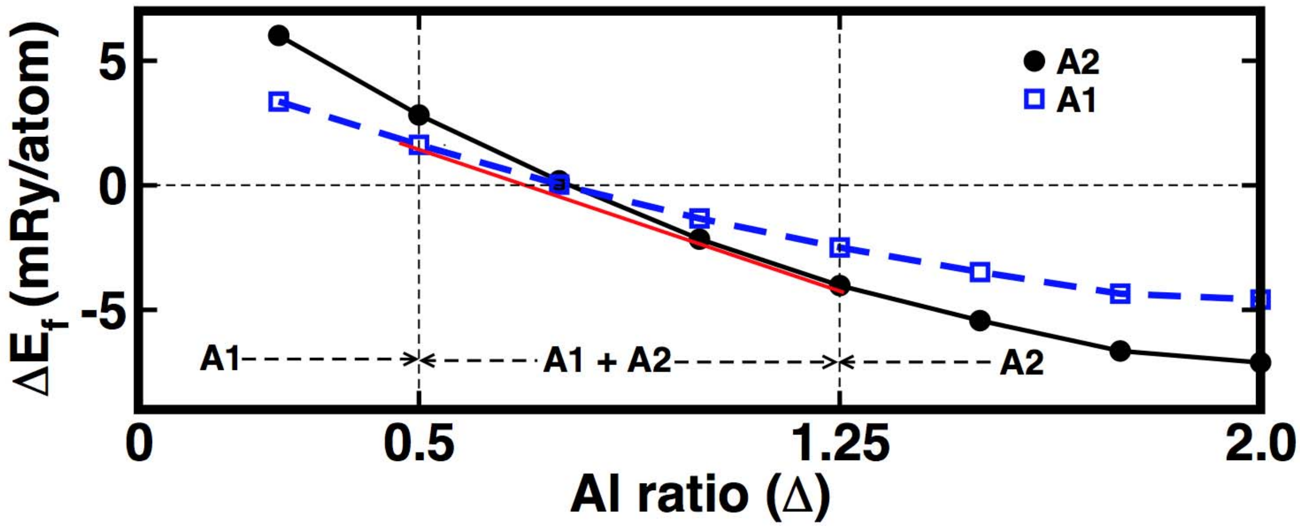
Pm3m
a = 7.901Å



Pmmm
a = 2.78 Å
b= 5.10 Å
c = 6.44 Å



The Al-Ni-Fe-Cr-Co system



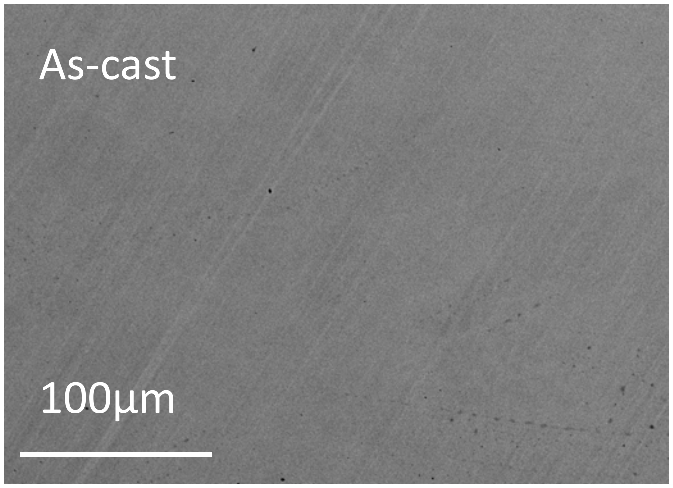
Adding Al-stablizes BCC-phase in $Al_xCoCrFeNi$

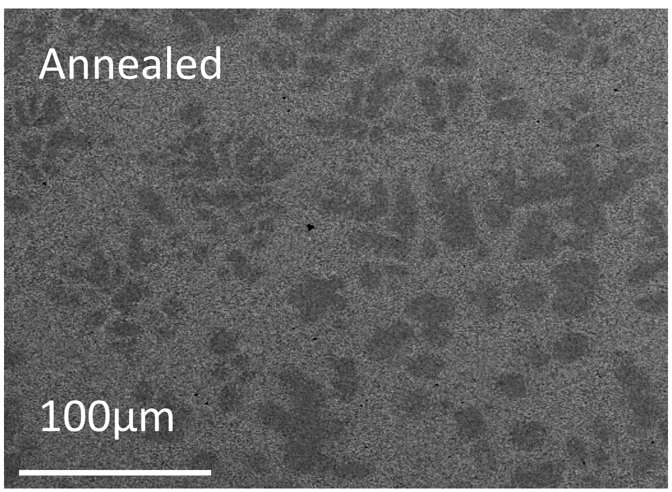
In agreement with Experiments.

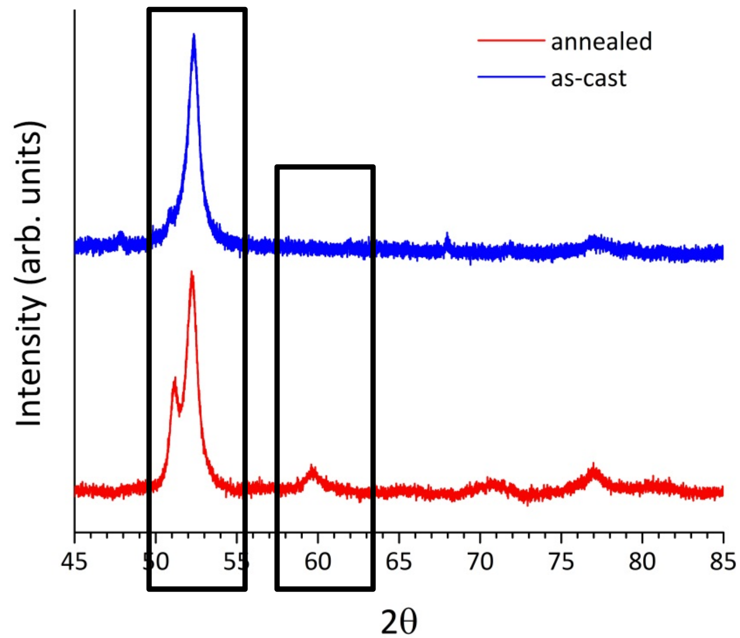
KKR-CPA calculations predict the existence of two phases at the equiatomic concentration – possibility of developing functionality in service, if we can synthesize the alloy as a single phase.

Singh, Smirnov, and Johnson, Phys. Rev.B **91**, 224204 (2015)

The Al-Ni-Fe-Cr-Co system







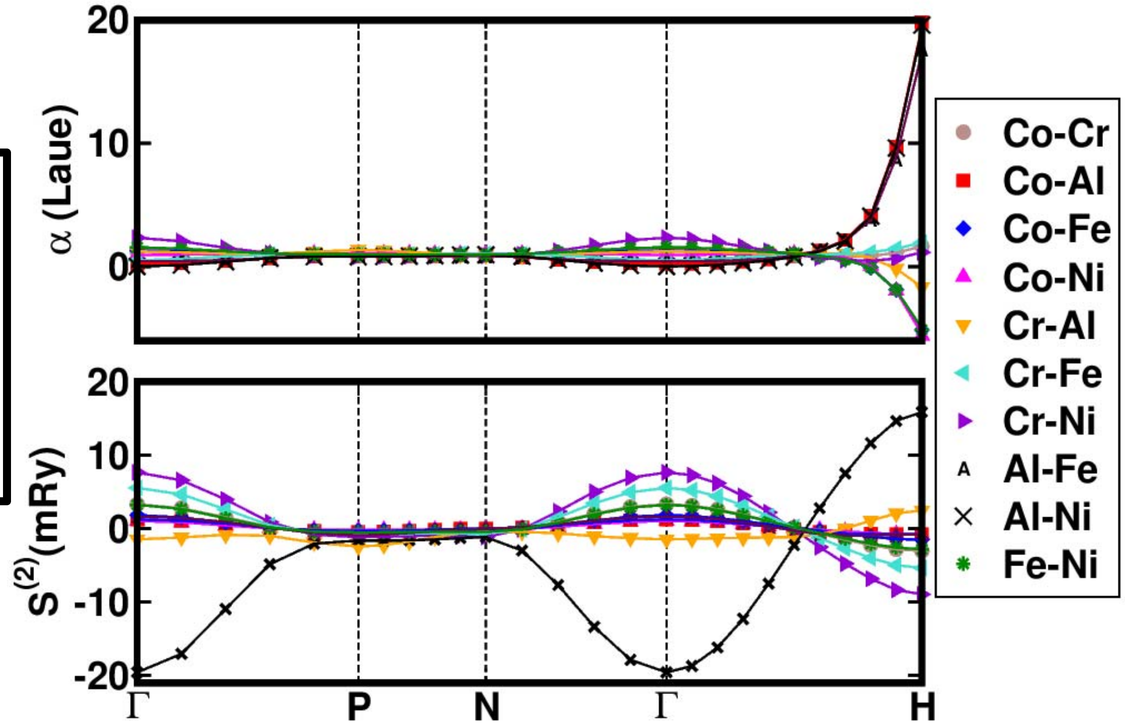
Phase separation:

- Al-Ni rich [$Ni_{30}Al_{30}Co_{20}Fe_{10}Cr_5$]
- Fe-Cr rich [$Fe_{30}Cr_{35}Co_{20}Ni_{10}Al_{10}$]
- FCC + BCC type phases

Model Output and Interpretation

KKR-CPA Linear Response
Short-Range Order

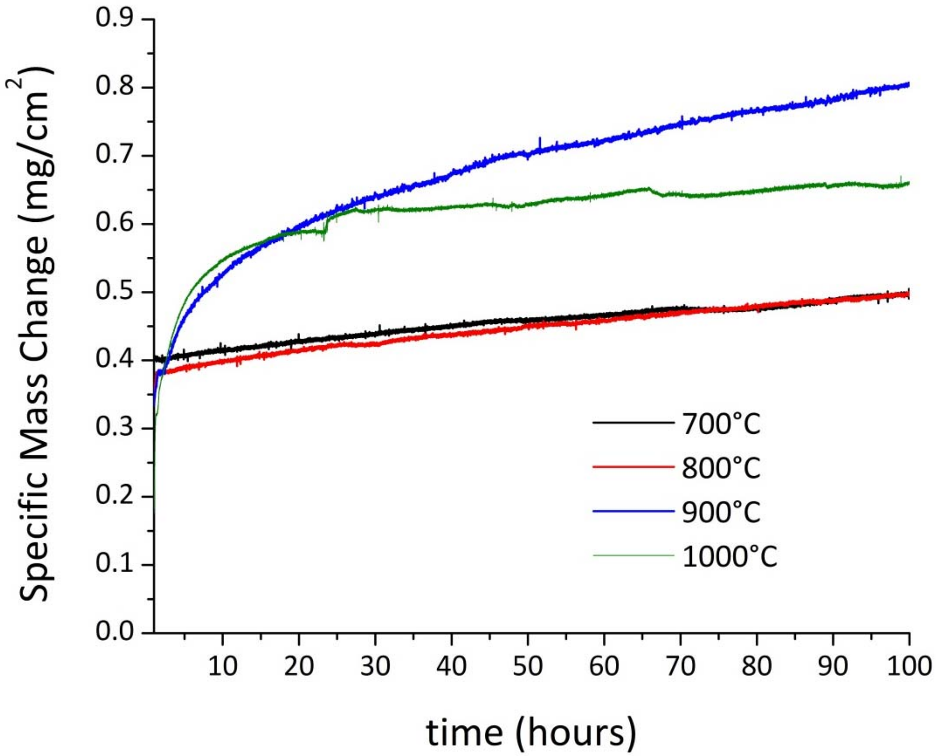
SRO: k_0 = [111] Long ranged B2-ordering
SRO: Unstable Modes (Al-Ni and Co-Al)
$S^{(2)}$: Ni-Al destablizes SRO
T_{sp} = 1217 K (estimated)



Singh, Smirnov, and Johnson,
Phys. Rev.B **91**, 224204 (2015)

- Stable B2 phase found in Experiments and CALPHAD (Al>0.25%).
- KKR-CPA also shows stability of B2 phases.
- Good agreement b/w ***predictions***, CALPHAD, and expt.

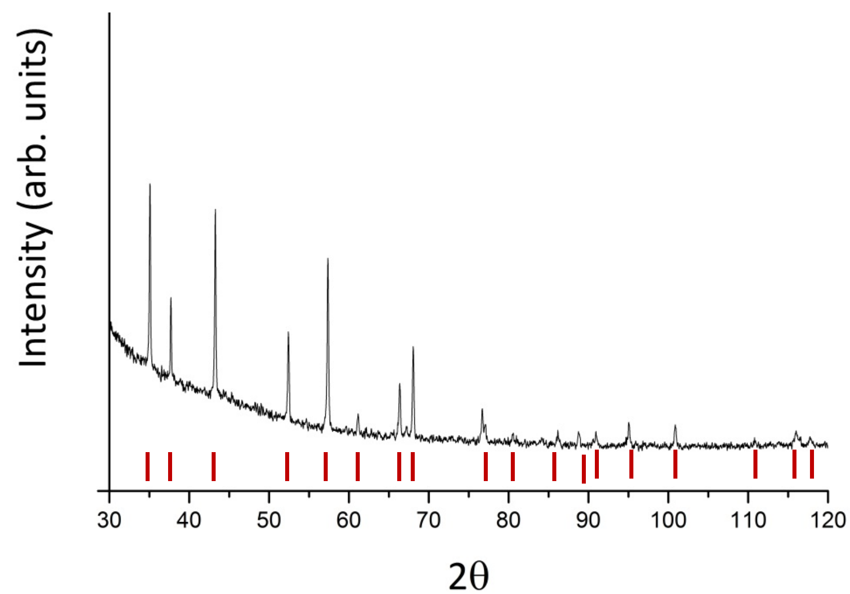
Oxidation kinetics: Al-Ni-Fe-Cr-Co



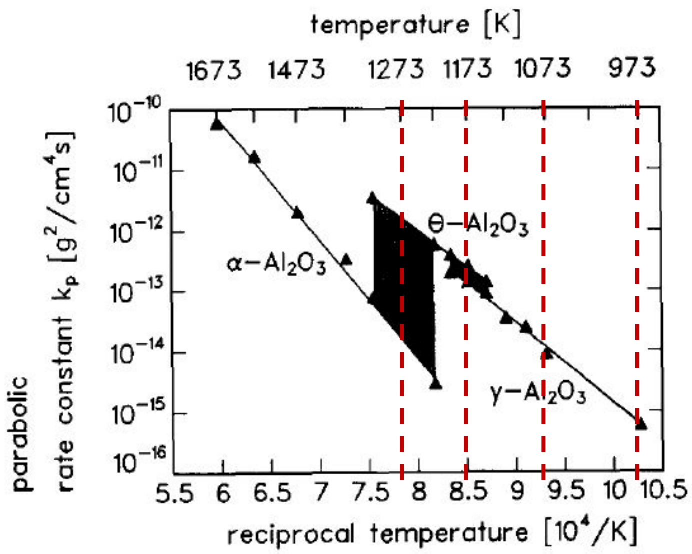
Key questions –

- How does the microstructure change during oxidation – can we develop a "skin" *in-situ*
- Temperature limits imposed by oxidation on the current alloy.

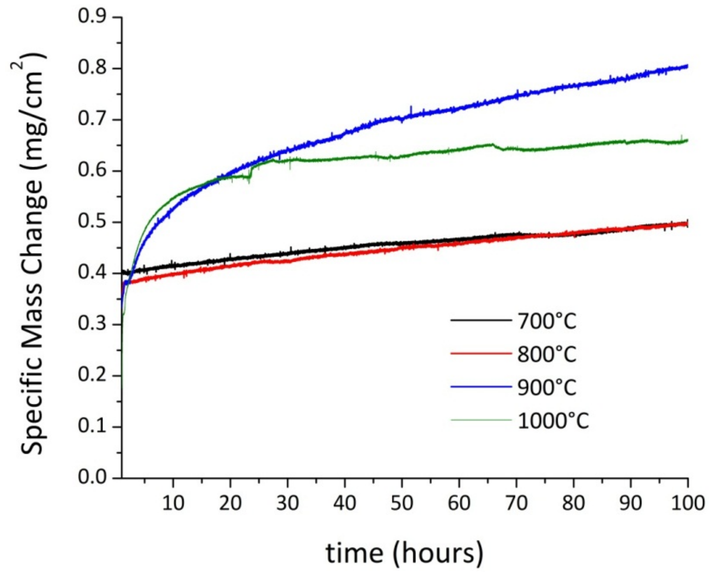
XRD pattern from the oxide scale corresponds to single-phase α-Al_2O_3



Oxidation kinetics: Al-Ni-Fe-Cr-Co



Brumm and Grabke, Corrosion Science 33 (1992) 1167

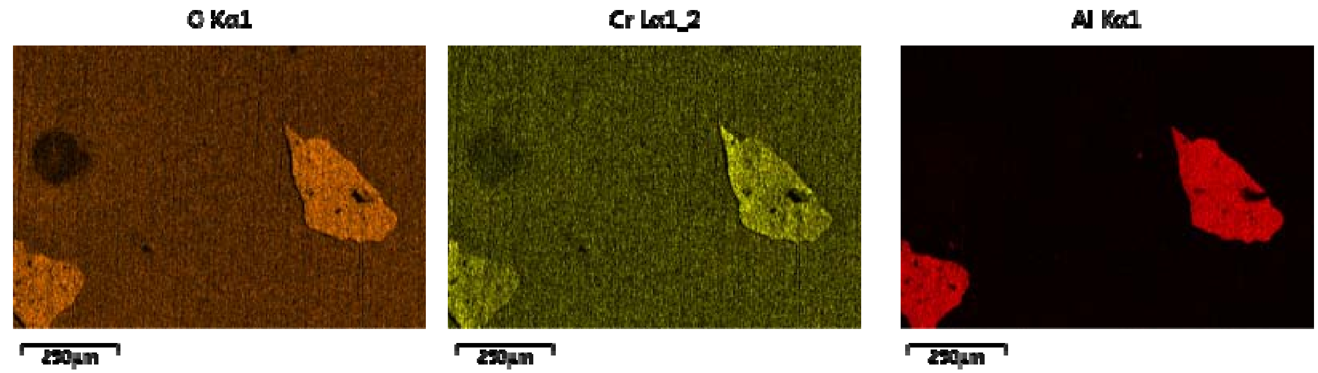


k_p^{1273K}
HEA: 1.6×10^{-12} g^2/cm^4s^{-1}

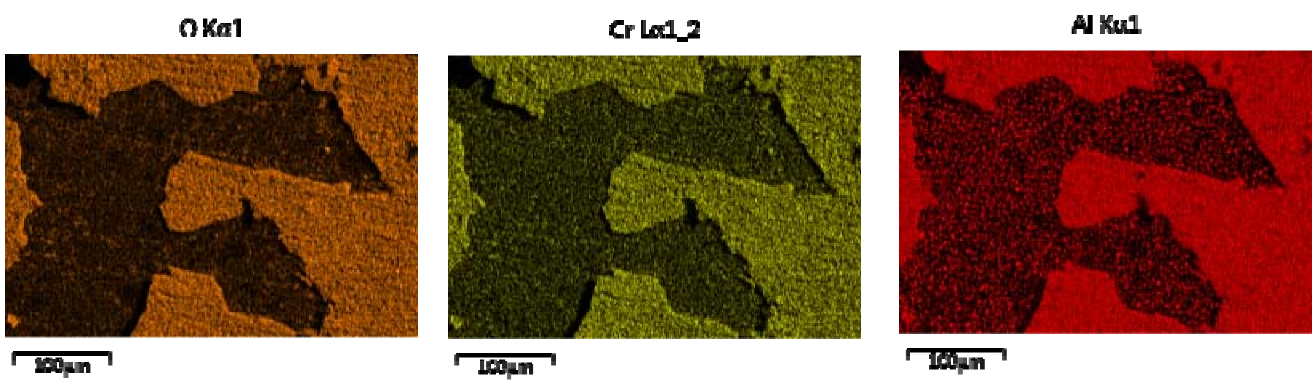
Phase	k_p ($g^2/cm^4.s^{-1}$)	E_A (kJ/mol)
α-Al_2O_3	3.5×10^{-13}	231
θ-Al_2O_3	6.3×10^{-13}	382

θ-Al_2O_3 forms at lower temperatures, whereas, the external scale consists of α-Al_2O_3 at higher temperatures (>1000°C)

Evolution of oxidized surface

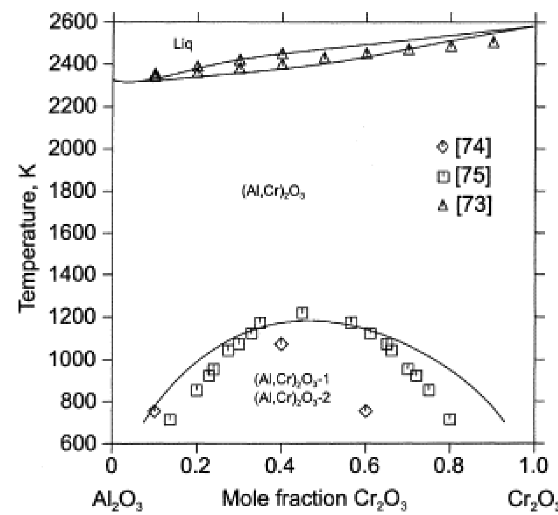


1 hour @ 1000°C

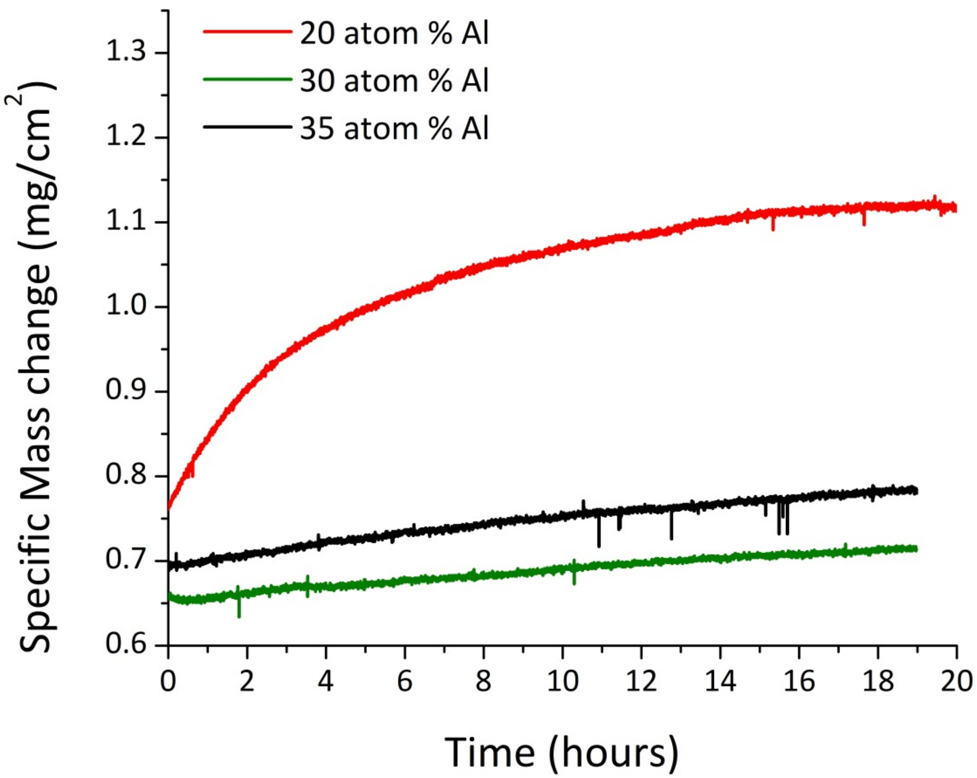


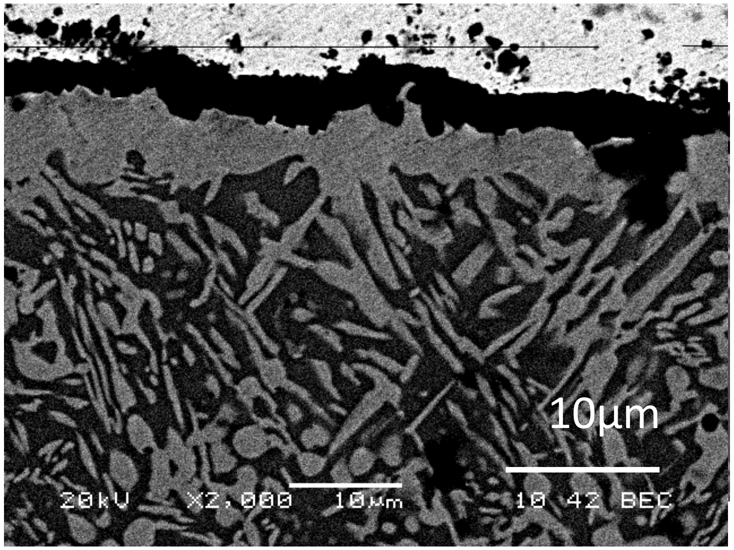
100 hours @ 1000°C

The initial oxide is rich in Cr content, and becomes Al rich with time.



Effect of Al:Cr ratios on oxidation

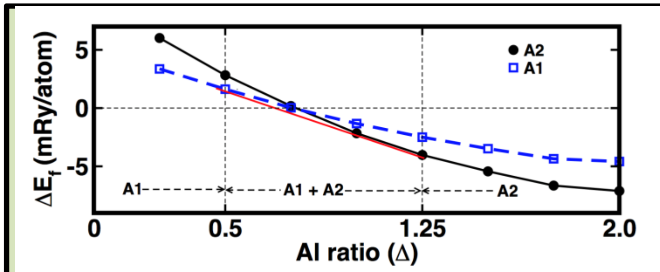


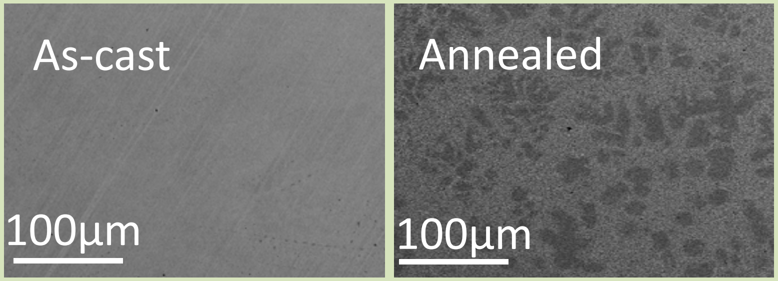


- Given the relatively low stability of chromia, increased Al content helps with oxidation.

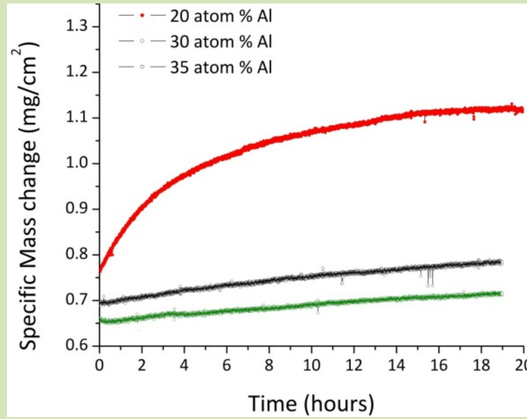
- But the initial formation of Cr_2O_3 promotes the growth of Al_2O_3, hence extremely low Cr content may not be desirable either

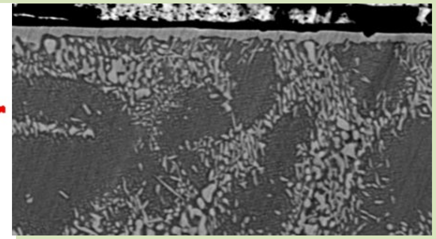
General Summary





- Model validation for High Entropy Alloys





- Baseline oxidation behavior of AlNiFeCrCo High Entropy Alloys
- Preliminary work on composition optimization

- Model extension for hexagonal system
- Microstructure / composition optimization

Proposed Work

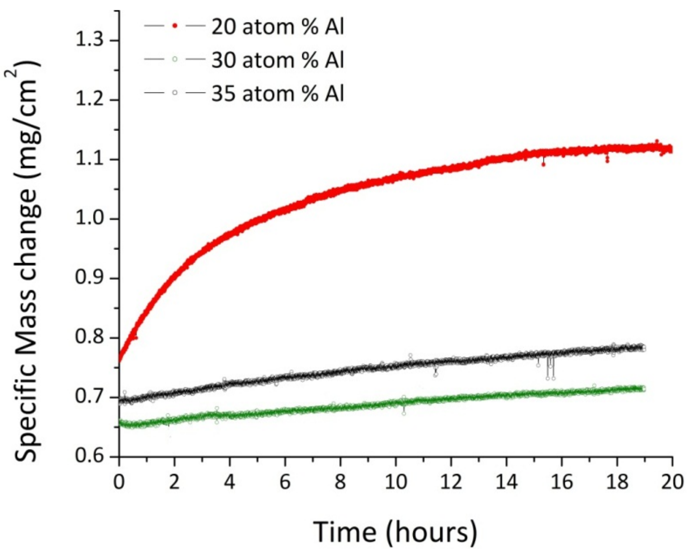
Improvements in KKR-CPA approach

- Extension of the KKR-CPA approach to general lattices, i.e. N components, N sub-lattices. Eg: hcp structures
- Combined KKR-CPA, ASRO and planar defect energies (with Suzuki effect) will guide the design of improved alloys, e.g., High-Entropy Alloys.

Alloy selection and microstructural design

- Adoption of a hierarchical screening approach, with a combination of multicomponent Miedema, KKR-CPA and Nudged Elastic Band methods (diffusion through oxide scales)

Proposed Work



- Composition optimization for improved oxidation resistance in AlNiFeCrCo alloys
- Oxidation studies on alloys down-selected via Miedema + KKR-CPA and NEB approaches
- *In-situ* synchrotron diffraction studies on the evolution of the oxide scale at elevated temperatures
- Diffusion multiple analyses for optimizing microstructures, phase assemblages and processing conditions

Acknowledgements

This work is supported by the **DOE-FE (Cross-cutting Research program)** through Ames Laboratory contract no. DE-AC02-07CH11358

We would like to acknowledge –

- Srini Thimmaiah, single crystal diffraction
- Kurt Koch, EDS maps on oxidized surfaces
- Jim Anderegg, X-ray Photoelectron Spectroscopy
- Bryce Thoeny, Sample Preparation and castings