Creating Materials and Energy Solutions

Science of Multicomponent Alloys – a Roadmap for Theoretical and Experimental Research

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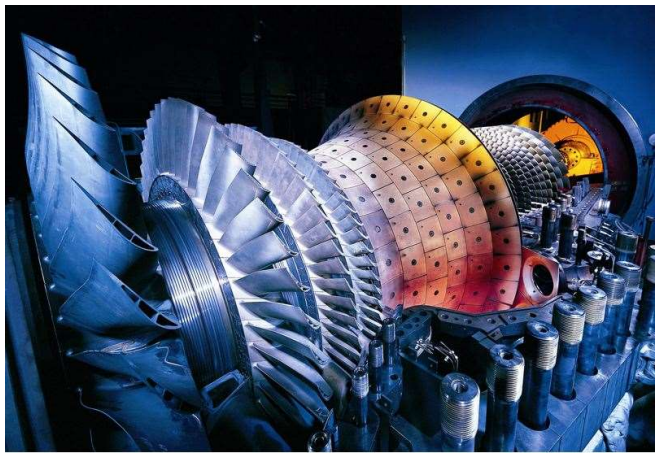
Alloy Design for Extreme Environments

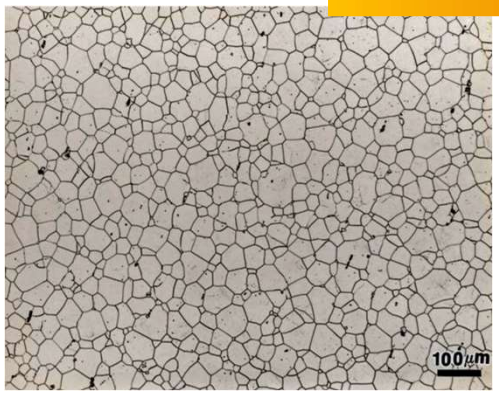
Higher temperature → Higher energy efficiency

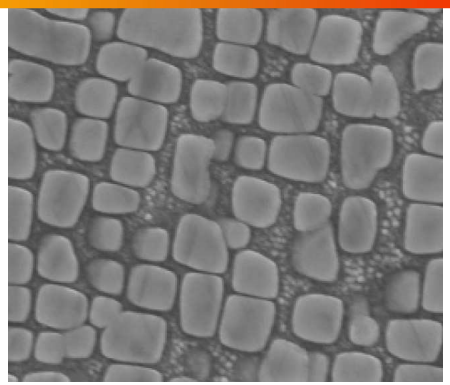


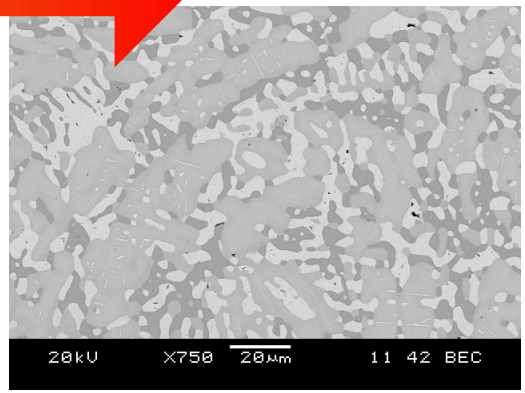
Challenges –

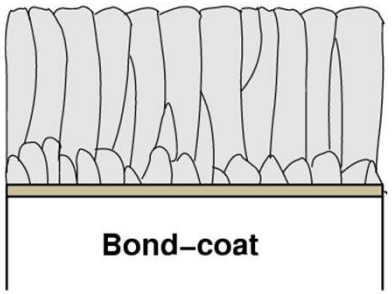
- **High T oxidation**
- **Moisture**
- **Creep and high T deformation**
- **Toughness & manufacturability**

Steels → Ni- superalloys → RM-silicides

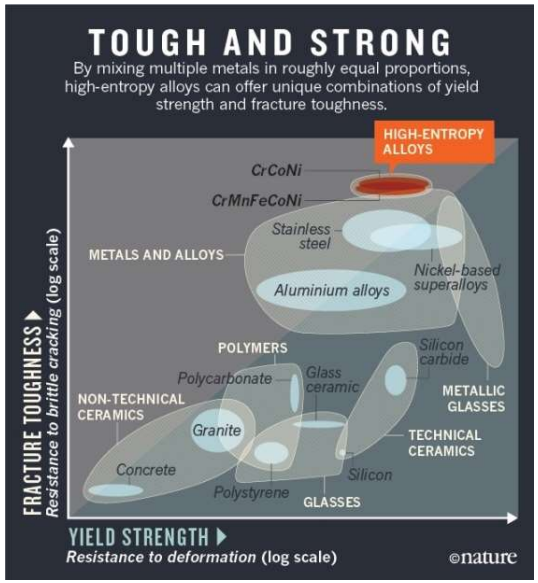


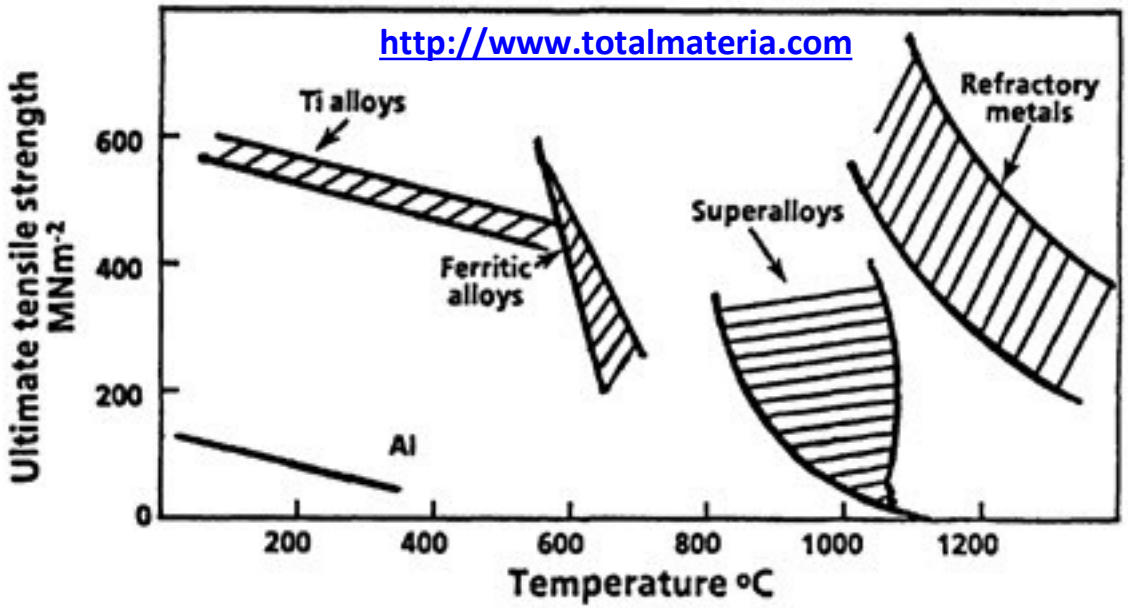






Exploratory Development of Multi-Principal Element Alloys (MPEA)





- **Need:** Alloys that raise high-T strength limit above Ni-base alloys & provide oxidation and corrosion resistance.
- **Design:** MPEAs have more space to tune properties.
- **Musts**: include all relevant mechanisms (not just chemical)
- **Predict:** Need Global and Local Stability, and their origins

Semi-empirical approaches to MPEA design

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

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

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

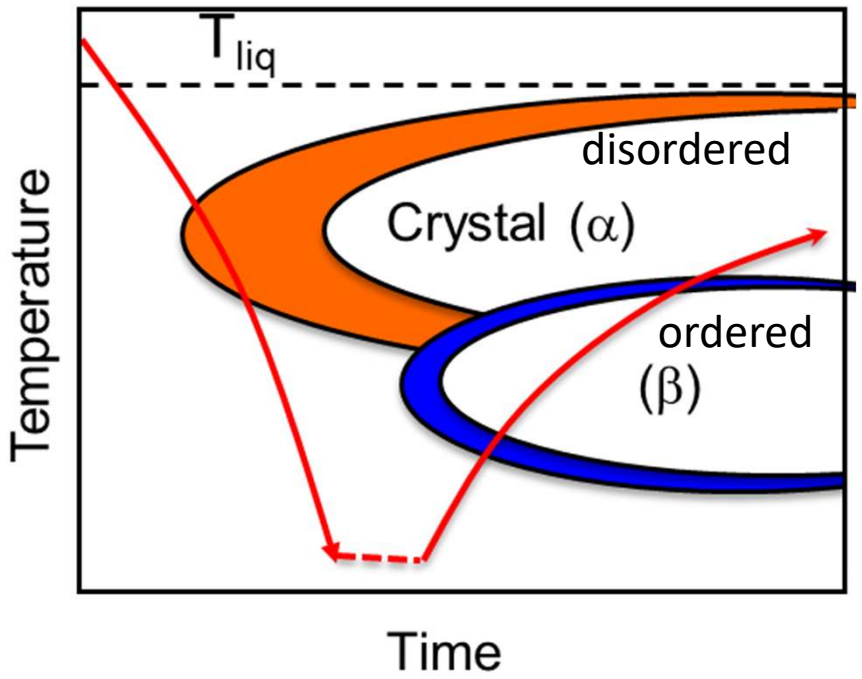
Y. Zhang, X. Yang and P.K. Liaw, JOM 64 (2012) 830

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

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

Tuneable effects in MPEAs



Schematic TTT diagram for a hypothetical alloy

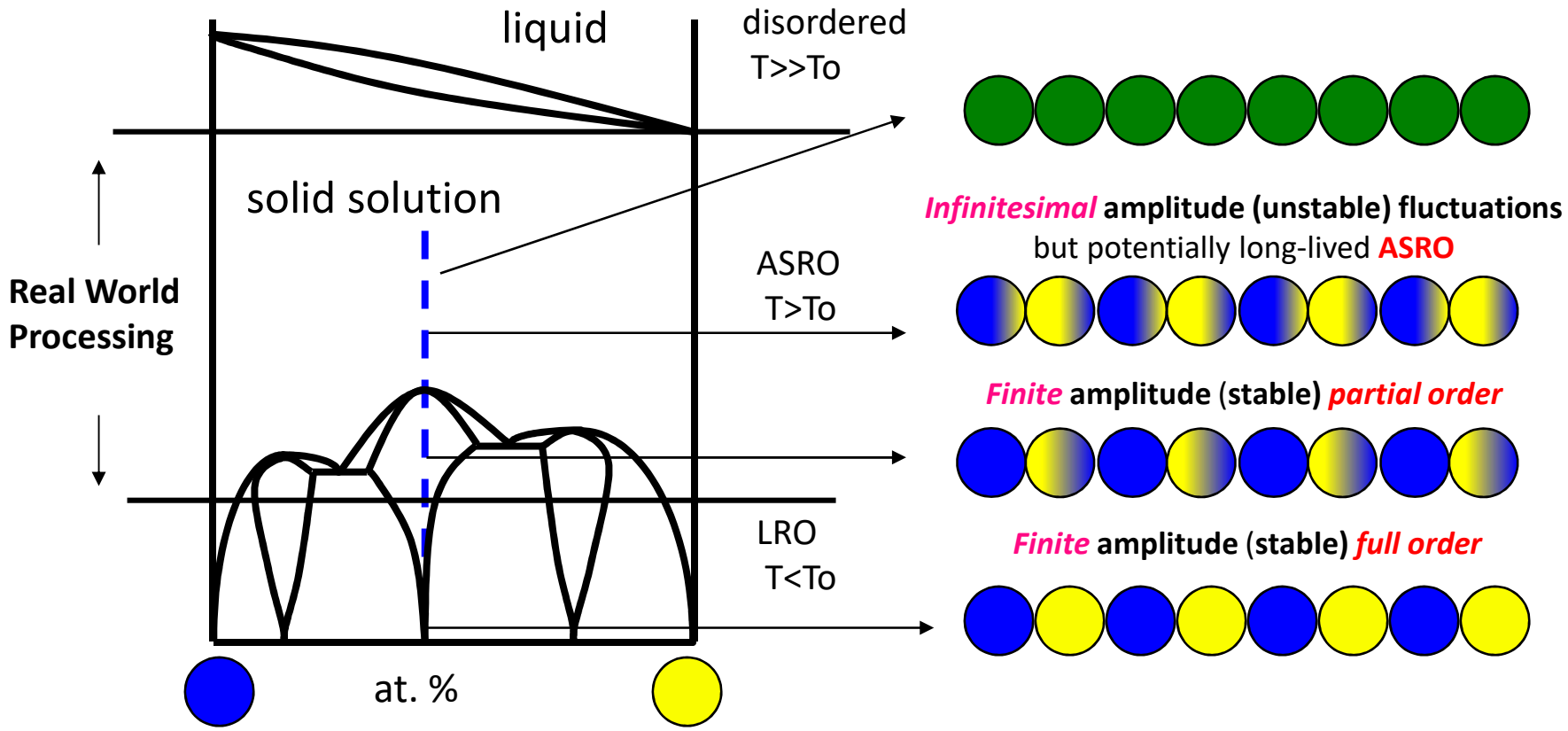
Synthesis and Processing

- Easily trapped in metastable energy basins due to sluggish kinetics
- Single-phase vs multi-phase MPEAs – are there potential benefits of operating at the edge of stability, by tuning phase selection?

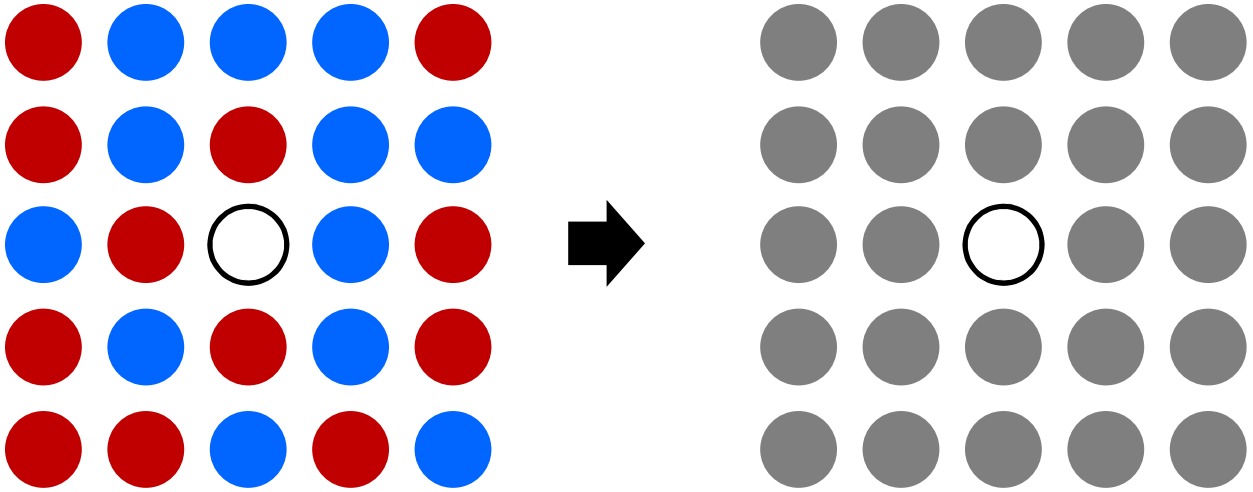
Key control parameters for processing – Competing effects on heat treatment – overcomes activation barrier, reaches equilibrium

Challenges in Disordered Systems

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



Modeling Disordered Solids: Thermodynamics



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

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

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

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

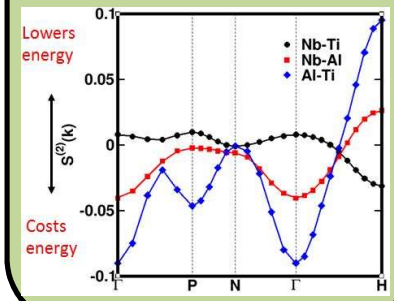
Thermodynamic Linear-Response calculations

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

Problem Definition and Approach

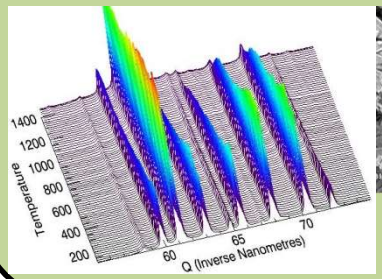
Grand Challenge: to accelerate the discovery and optimization of these chemically complex alloys and leverage our theoretical and experimental capabilities for assessing their long-term stability

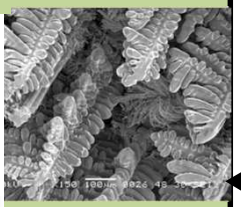
Theoretical tools (KKR-CPA)



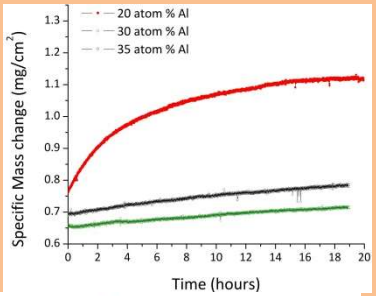
validation

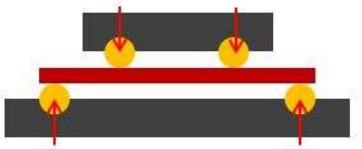
Structural studies





Stability in harsh environments





Theory will inform experiments on new chemistries while experiments will be used to validate models and access kinetics.

Processing

Objectives

- Validation of the KKR-CPA code for MPEAs
- Modeling and experimental assessments of MPEAs with KKR-CPA and *in-situ* experiments for understanding the role of SRO, defects, vec and size effects
- Assessment of oxidation behavior of a model Al + Cr MPEA

Choice of alloy systems and techniques driven by these objectives

Alloy Systems and Significance

ZrHfNb	Model equiatomic alloy – Does Nb additions result in ordering? Does it transform hcp → bcc?	Objective 1: Model validation
TiZrHfAl	Electron counting suggests possibility of brass-like structures	Objective 2: Exploring effects of SRO, vec and size mismatch through theory and experiments
AlCuNiTiZr	Resolvable in to two quarternaries – AlCuNi(Ti,Zr) and Al(Cu,Ni)TiZr	
AlFeCoCrNi	Likely to have high oxidation resistance, due to presence of Al and Cr. What is the effect of Al:Cr ratio? How do we control the microstructure of the alloy?	Objective 3: Assessment of High Temperature Oxidation resistance

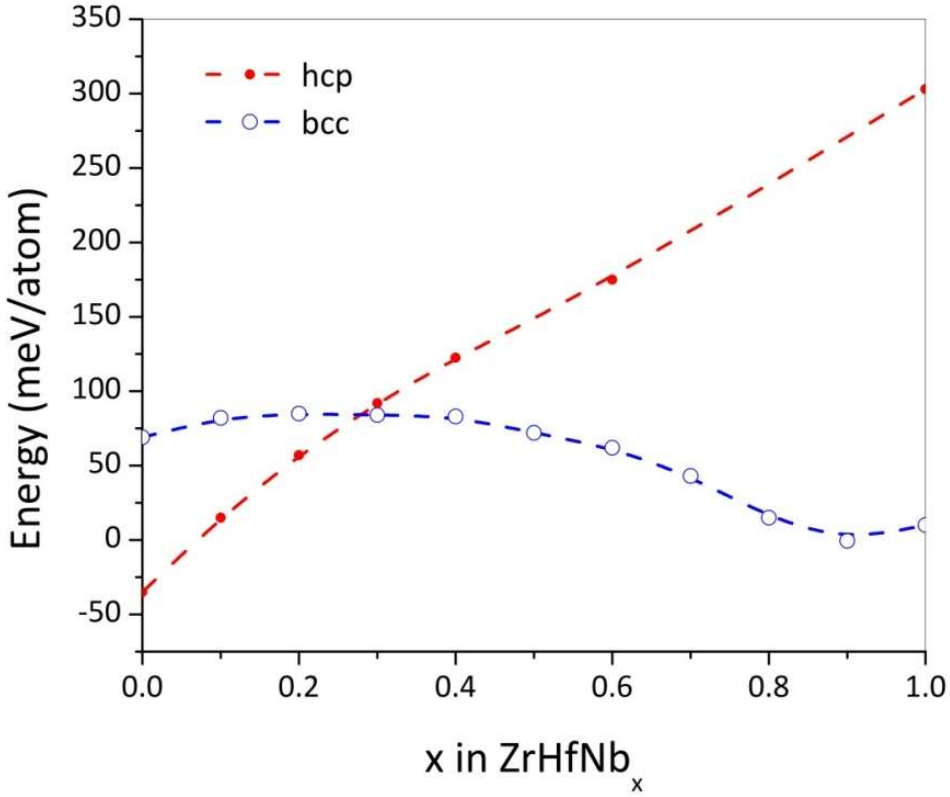
Objective 1: Model validation – ZrHfNb alloys

ZrHfNb

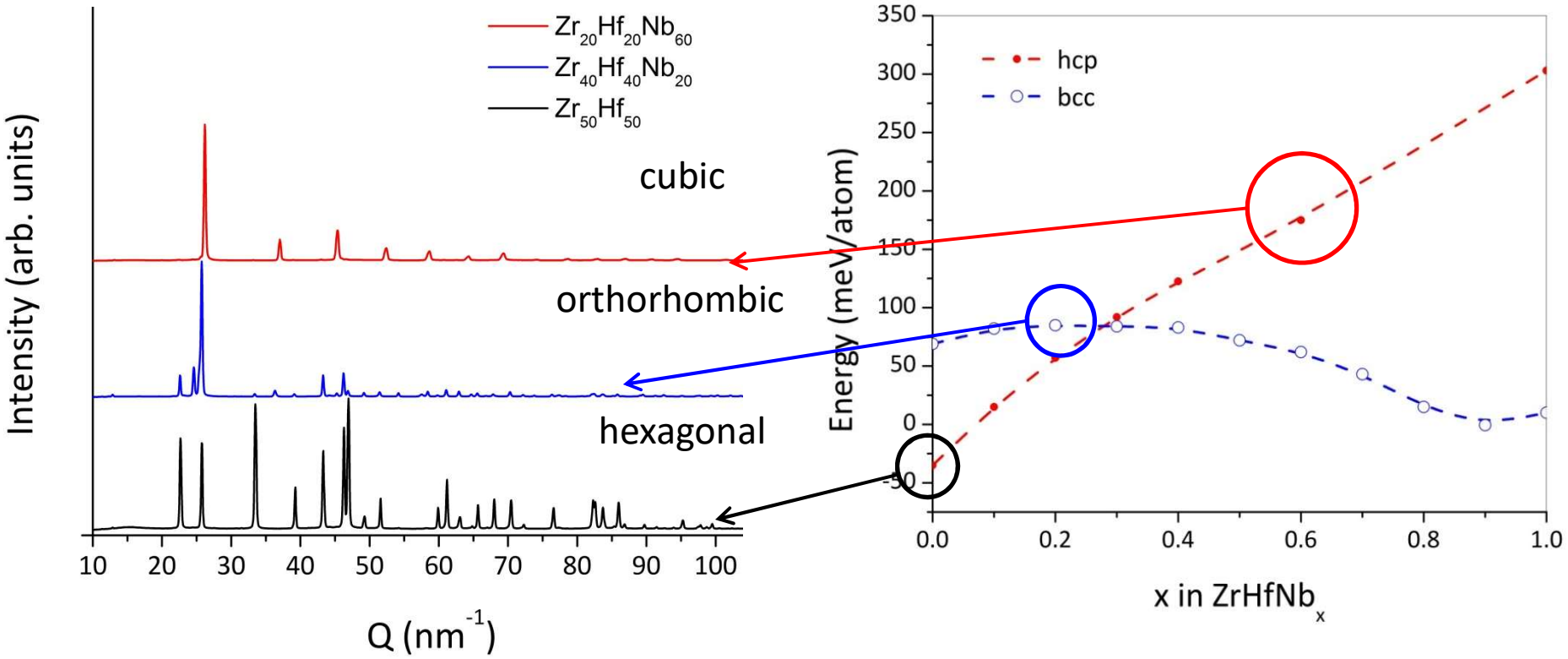
Sc	Ti	V	Cr
Y	**Zr**	**Nb**	Mo
La-Lu	**Hf**	Ta	W

2.06Å (hcp) 1.98Å (bcc)

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



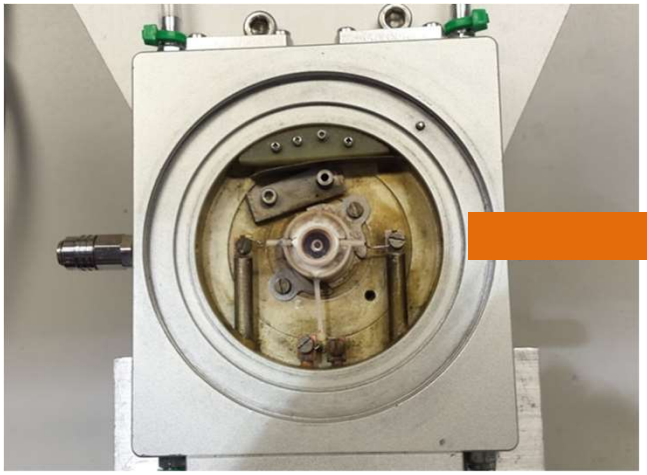
Objective 1: Model predictions

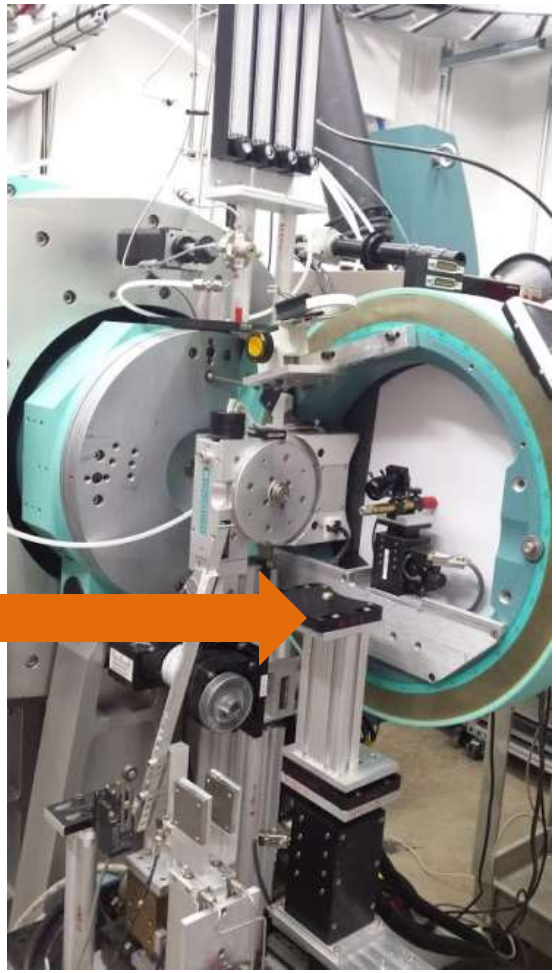


Key Issues – validate CPA code with predictions of the T dependent stability

Objective 1: Experimental conditions

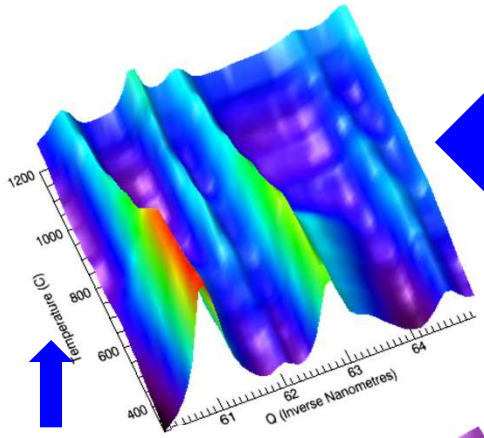
$(Zr,Hr)_{1-x}Nb_x$ for x = 0, 10, 20, 33 and 40





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

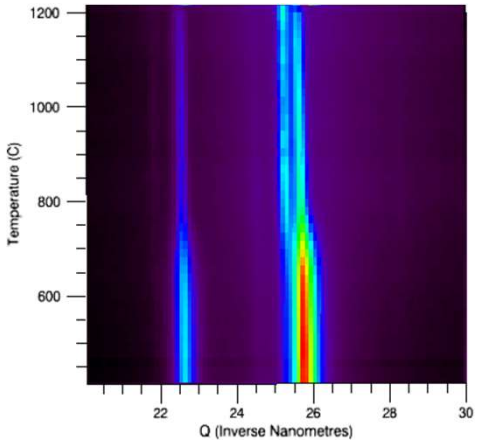
Objective 1: Experimental Assessments



Transition suppressed ~ 200C Sluggish on cooling

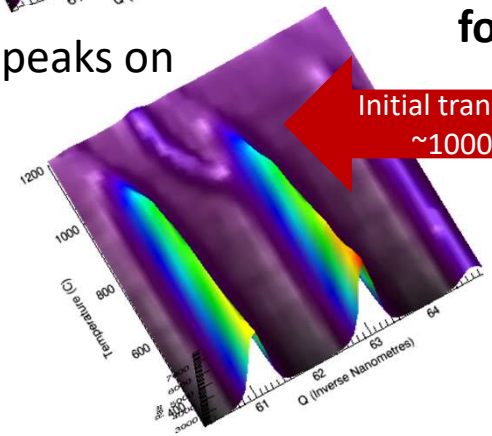
Transition to a cubic phase is observed

Pm3m
a = 7.901Å



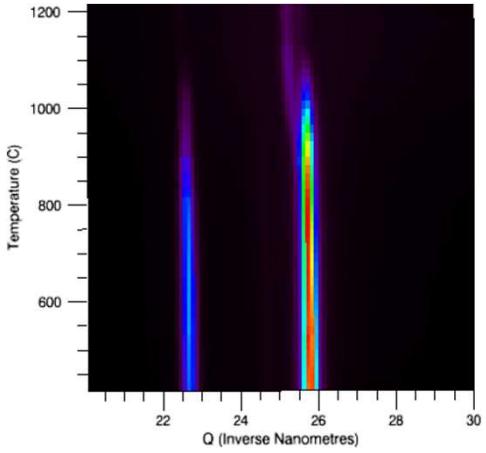
***In-situ* experiments in line with CPA showing Nb promotes B2 formation**

Broader peaks on cooling



Initial transition ~1000C

Pmmm
a = 2.78 Å
b= 5.10 Å
c = 6.44 Å



Objective 2a: Effect of SRO and Defects – TiZrHfAl

Phase selection sequence in ZrHfNb alloys (function of T and Nb):
hcp → orthorhombic → disordered cubic → B2

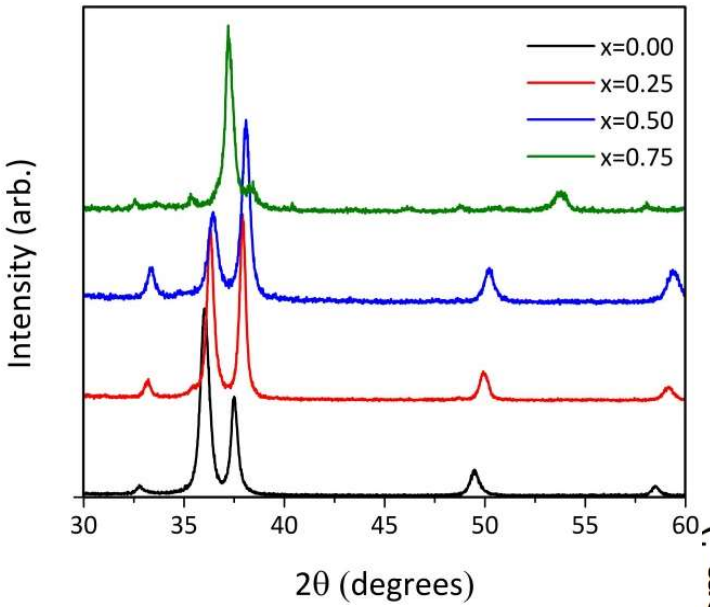
TiZrHf ternary alloys

- Low T $P6_3/mmc$ phase (hcp)
- High T Im-3m phase (B2, predicted)

Structurally, TiZrHf is similar to low Nb content alloys in ZrHfNb system. By adding Al,

1. electron counting suggests existence of brass like structure (implying ordered vacancies)
2. In other cubic systems like AlFeCoCrNi, Al addition promotes B2 ordering and phase separation

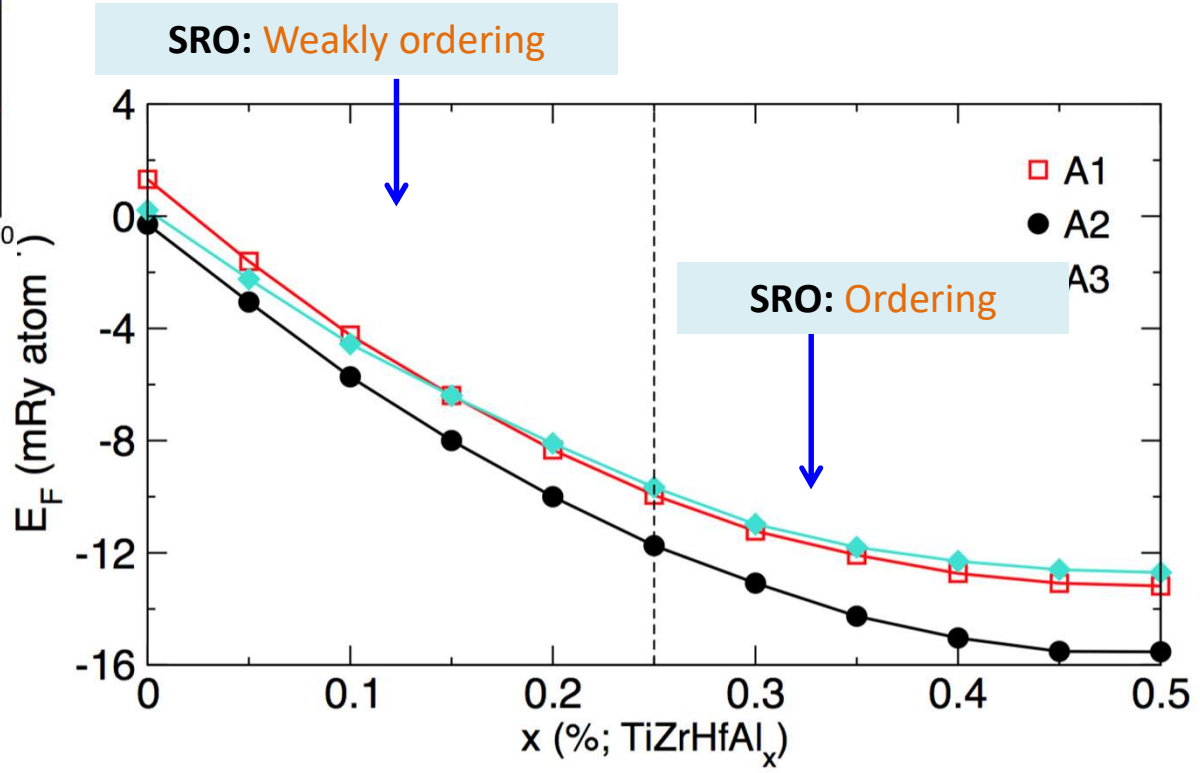
Objective 2a: Model predictions – thermodynamics



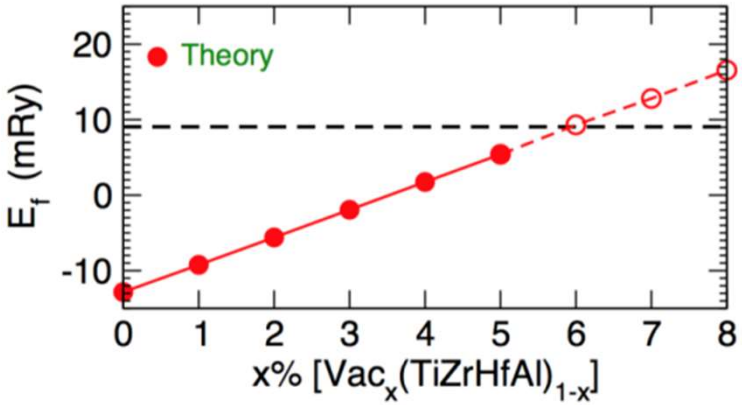
- ✓ Adding Aluminum **promotes** the A2 phase
- ✓ *A2 and A3 compete at low %Al, but A2 is lowest*

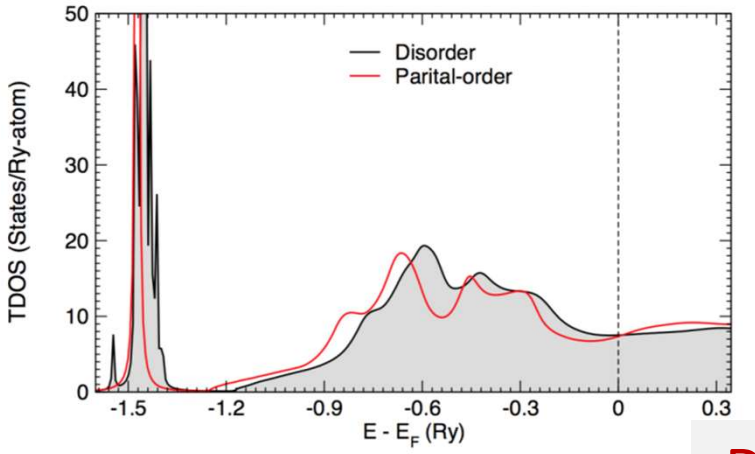
(A1: fcc; A2: bcc; A3: hcp)

Structural transition occurs as a function of composition

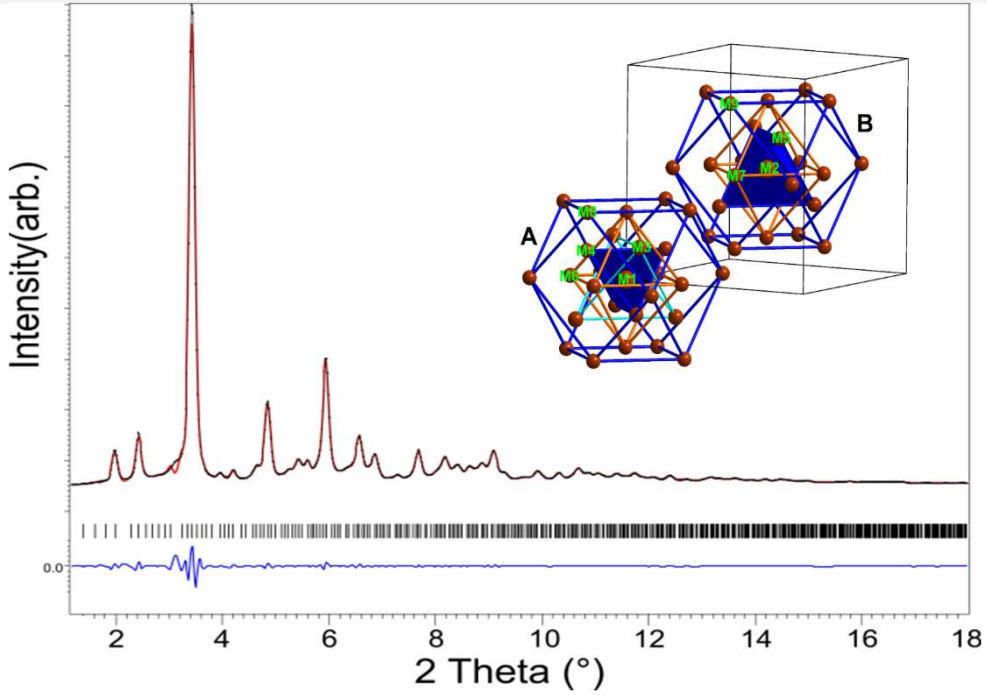


Objective 2a: Model predictions – effect of defects





Model hints a possible defect mediated phase selection mechanism



Discovery of a γ-brass like structure in MPEA

Structure solved by a combination of synchrotron and single-crystal diffraction

Objective 2b: Relative role of vec and size

AlCuNiTiZr

Resolvable in to two quarternaries – AlCuNi(Ti,Zr) and Al(Cu,Ni)TiZr

Size effects

vec effects

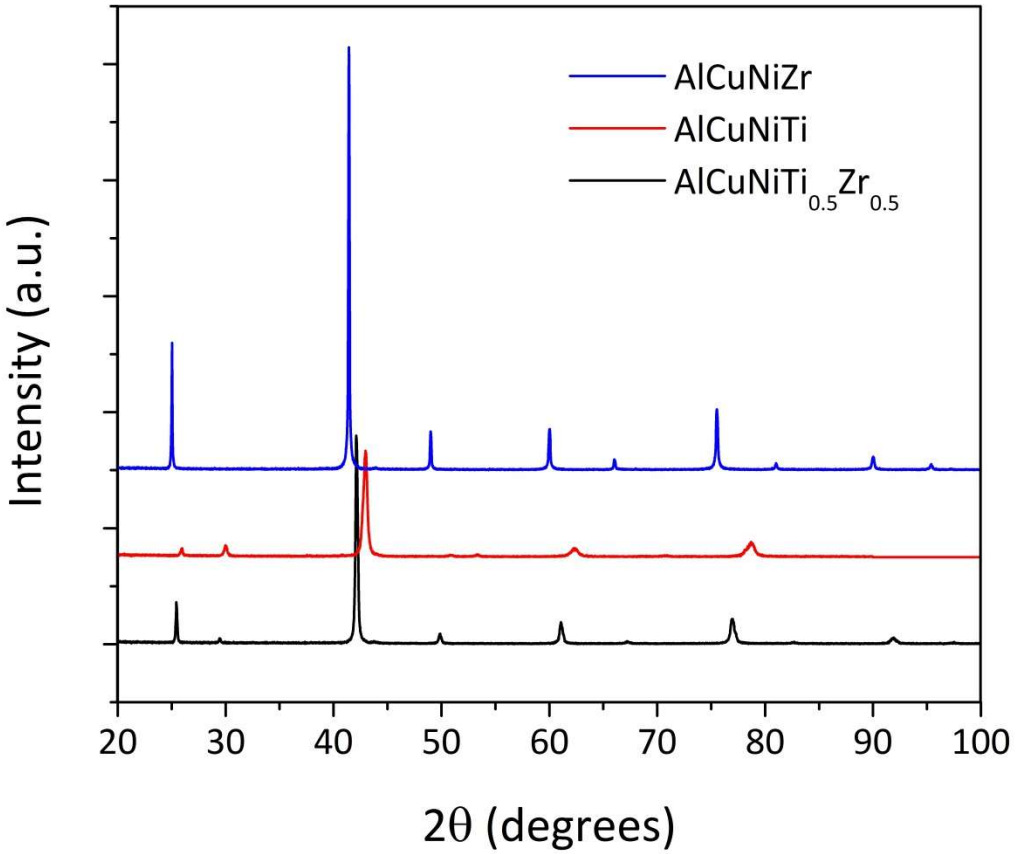
Model predicts bcc motif, but with significant ordering

Experimental Assessments:
$AlCuNiTi_{1-x}Zr_x$
X = 0, 0.25, 0.5, 0.75, 1.0

Work in progress:

- Model calculations (lots of competing structures)
- Will be followed by suitable experiments

Objective 2b: Effect of size mismatch

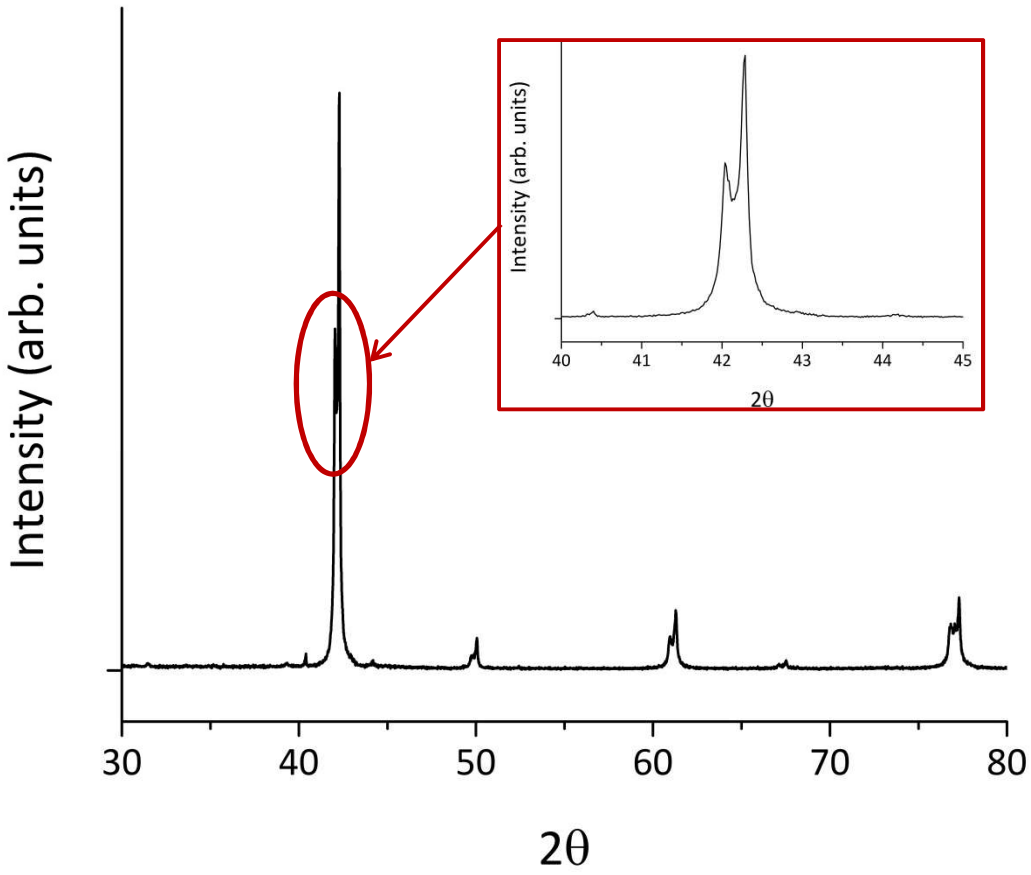


Phase analysis of cast alloys

- Cast samples found to have $AlCu_2Ti$ 'Heusler' type structure.
  - $Al(Cu,Ni)_2(Ti,Zr)$, Fm-3m.
  - Lattice parameter:
    - AlCuNiTi - 5.95 Å
    - $AlCuNiTi_{0.5}Zr_{0.5}$ - 6.06 Å
    - AlCuNiZr - 6.16 Å

Are these structures thermodynamically stable?

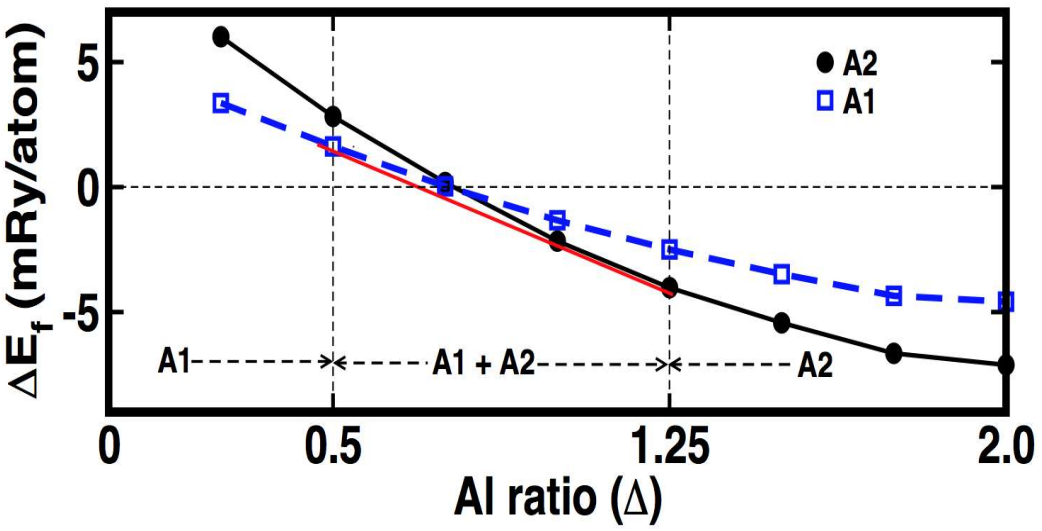
Objective 2b: Effect of size mismatch

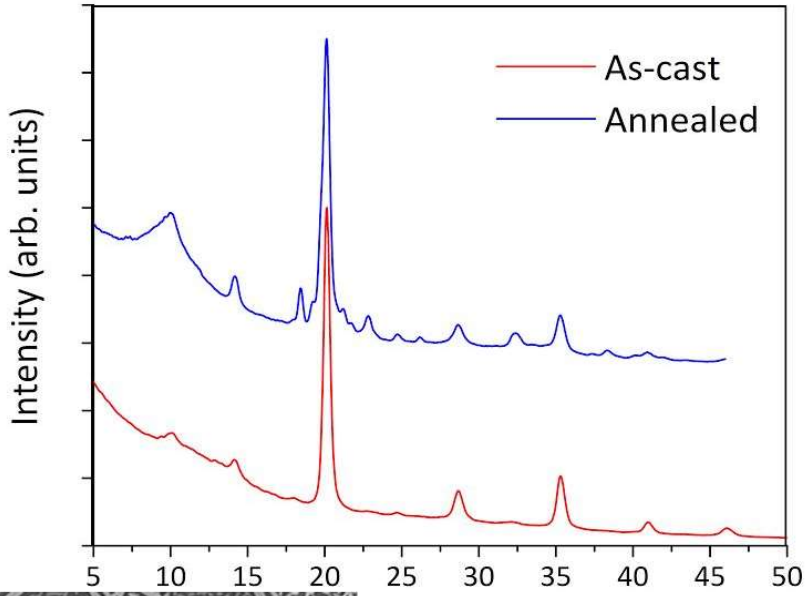


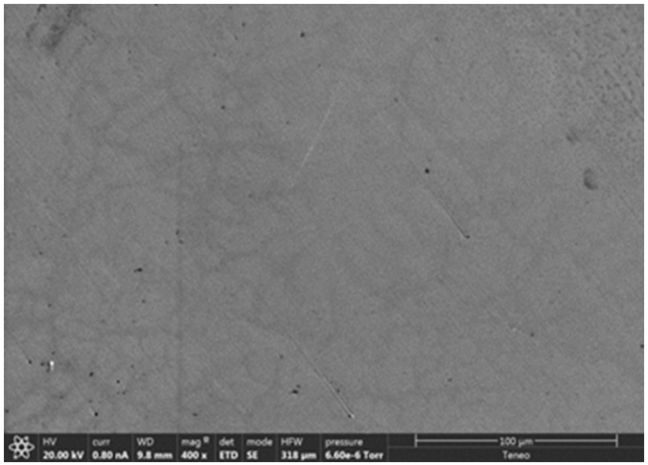
- Single-crystal diffraction indicated the formation of twinned structure
- Annealing results in clear peak splitting – does this result in a $Ni_2MAl + Cu_2MAl$ Heusler phases?

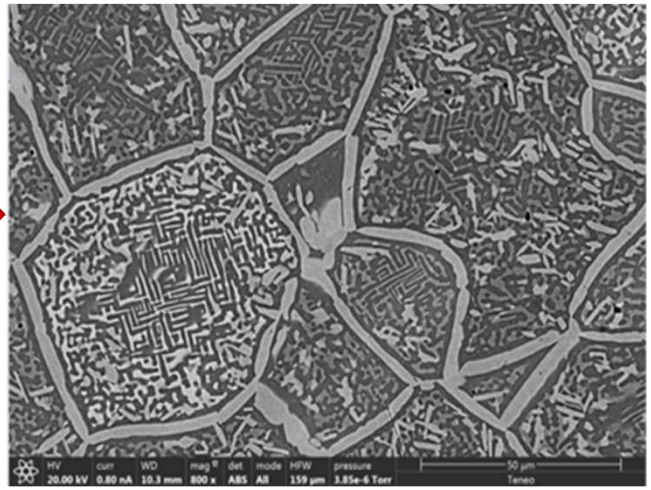
Is this transition driven by size or chemistry (electron effects!) Going forward, these are the critical questions to be answered

Objective 3: Assessment of Oxidation behavior



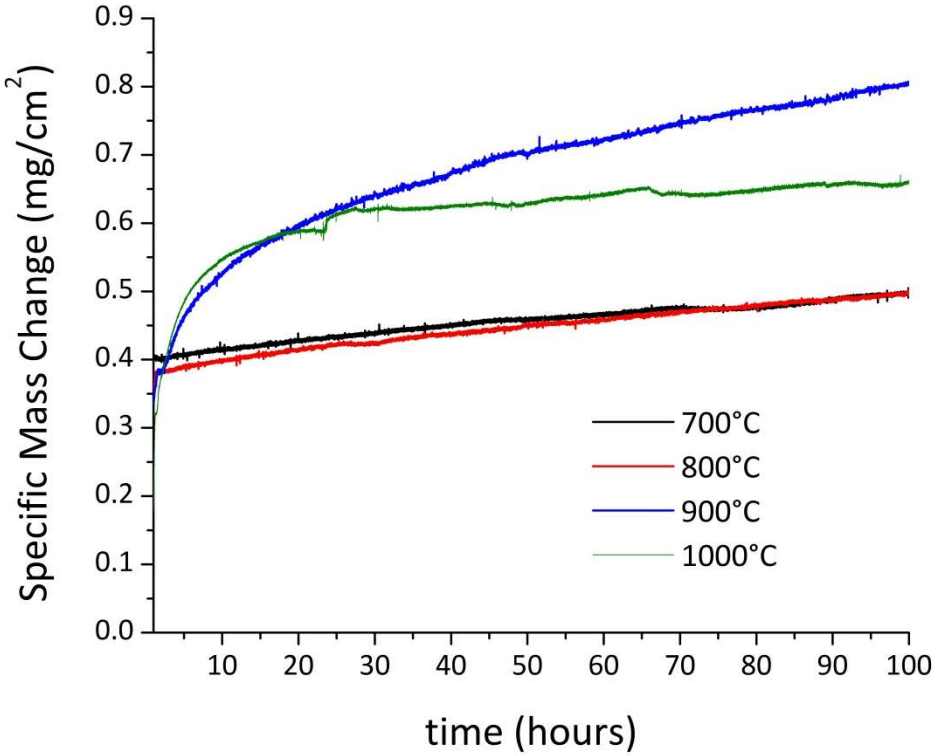






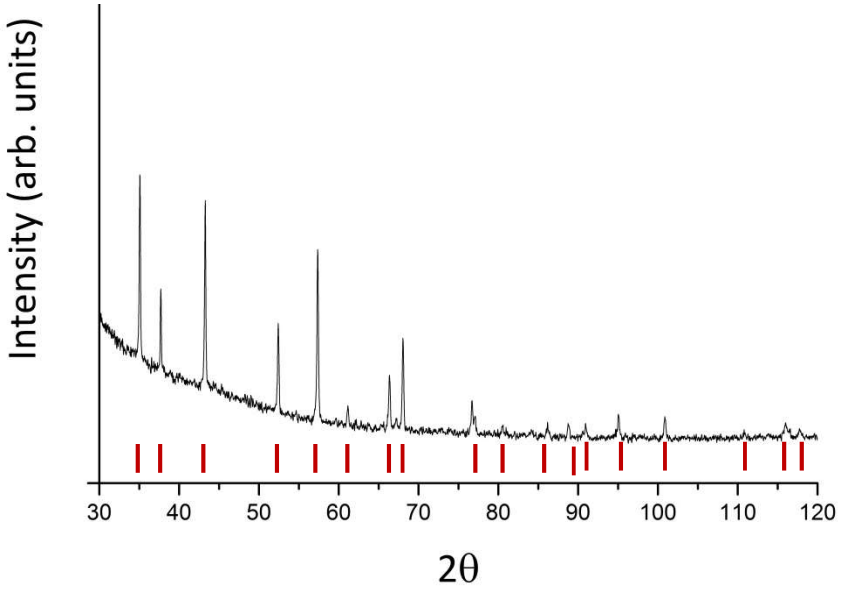
Rapid cooling traps single phase, annealing results in two-phase structure

Objective 3: Assessment of Oxidation behavior



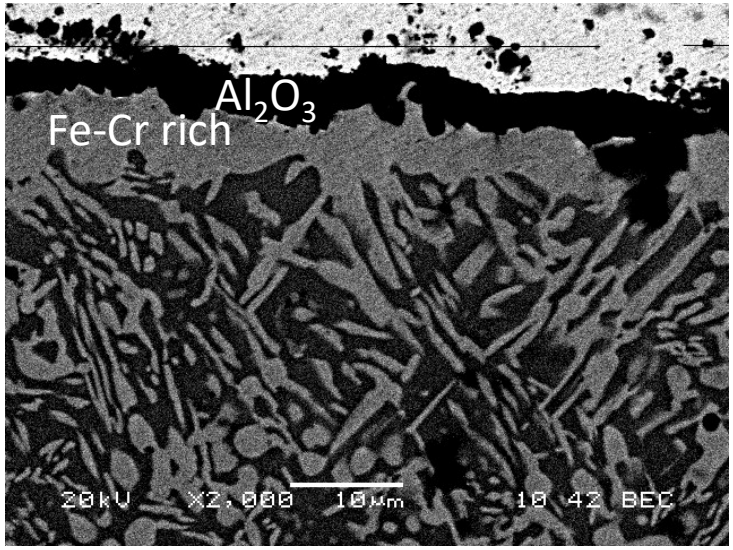
Key questions –

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

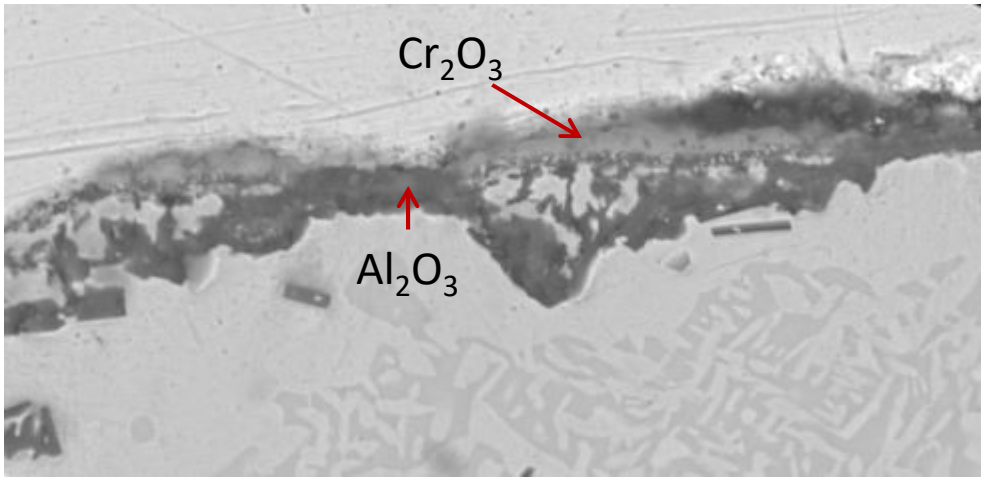


XRD pattern from the oxide scale corresponds to single-phase α-Al_2O_3

Objective 3: Assessment of Oxidation behavior

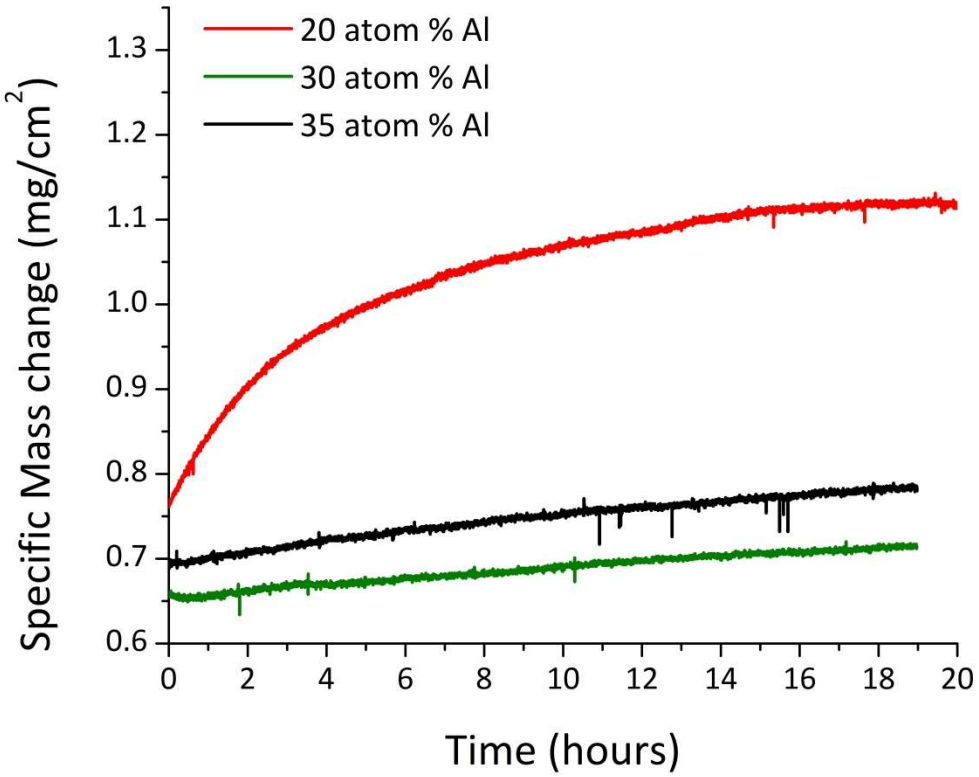


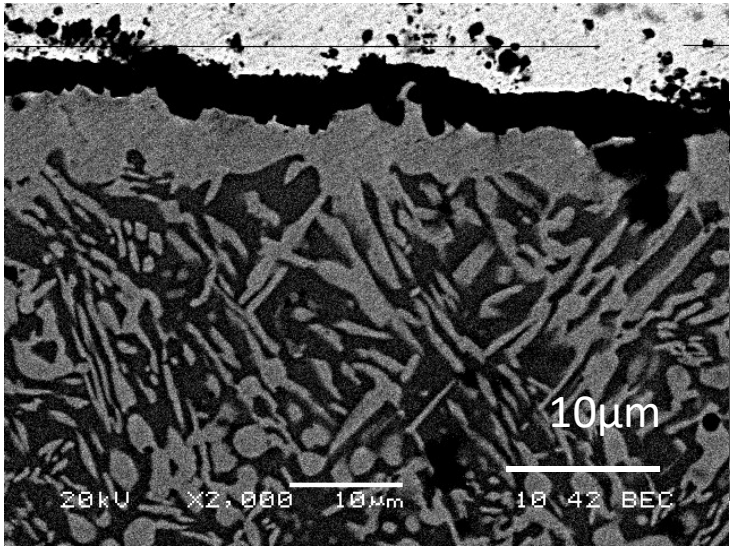
Oxide scale, after 100 hours of oxidation at 900°C shows the formation of exclusive Al_2O_3 layer



Oxide scale after 5 hours of oxidation indicates the formation of both Al_2O_3 and Cr_2O_3, with the latter forming in the external region and the former forming in the internal oxide/alloy interface

Objective 3: Effect of Al:Cr ratio





- 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

Milestone Report and Future Work

Milestone 1: Model validation – completed

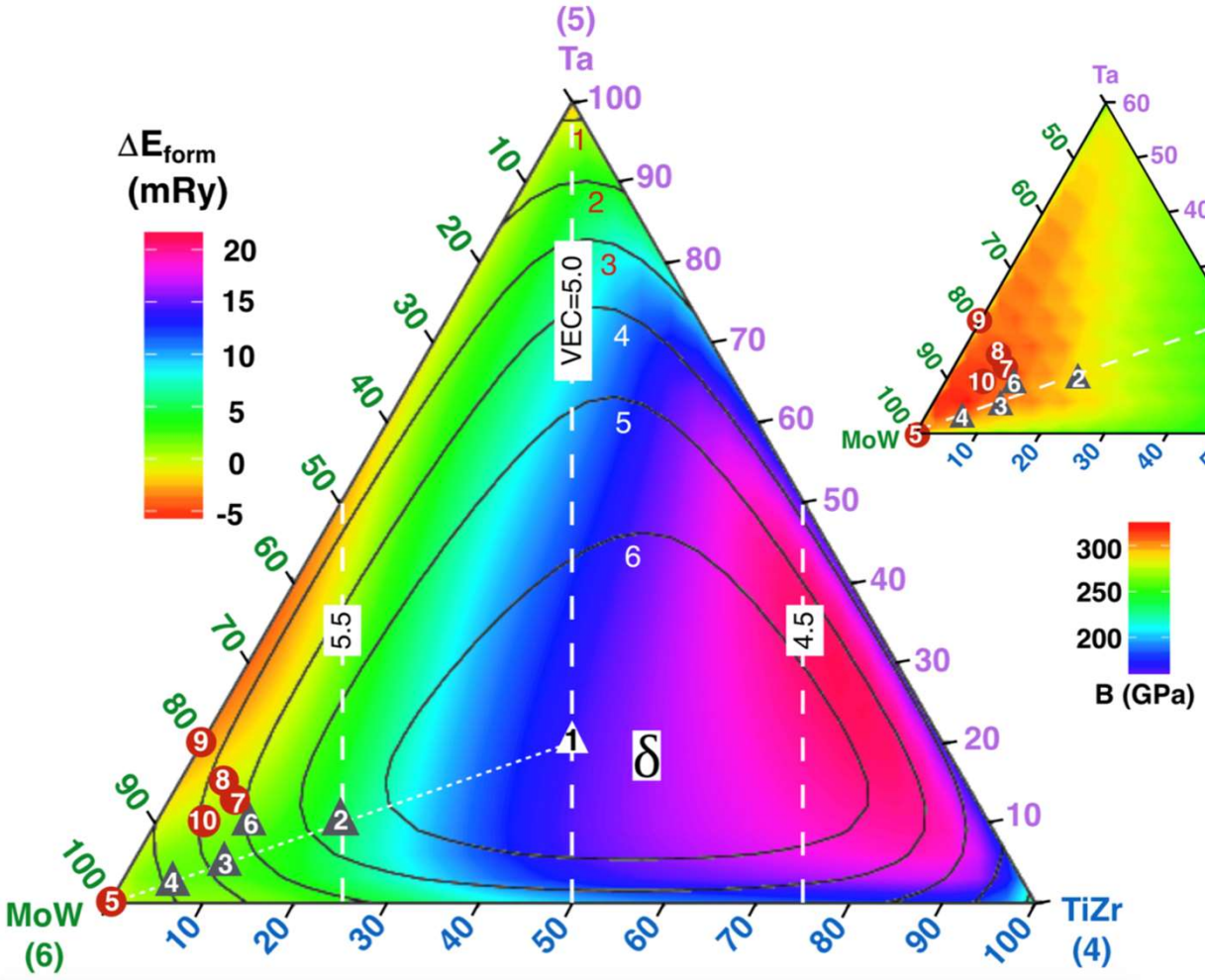
Milestone 2a: Defect mediated phase selection – completed
Milestone 2b: Effect of varying Cu:Ni ratio in Al(CuNi)TiZr alloys, synhcrotron studies on Al(TiZr)CuNi alloys for ascertaining definitively the role of size and vec on phase selection

Milestone 3: Assessment of Oxidation behavior and estimation of Al:Cr ratios – completed

Implications for Alloy Design:

- Designing strong and tough alloys through defect mediated mechanisms in conjunction with vec/size constraints and oxidation resistance
- **Significance of processing:** Accessing metastable structures with long residence times, kinetically – need for better understanding of soldification processing

Outcome – Novel Design concepts for MPEAs



Bulk Moduli

Singh, et al., *nature computational materials* (In press)

Designing high strength refractory alloys through control on size and vec – Collaboration with Prof. Ganesh Balasubramanian, Lehigh University

Acknowledgements

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Program Manager: Charles Miller

- Srinivasa Thimmaiah, Bryce Thoeny and Pierre Alameda
- Aayush Sharma and Ganesh Balasubramanian

Milestone Report

Milestone 1: Validation of the KKR-CPA approach for MPEAs

Milestone 2: Demonstrate possibilities of defect mediated phase selection and vacancy ordering

Milestone 3: Assessment of oxidation resistance, and determination of Al:Cr range for enhanced oxidation resistance

<u>Upcoming Deliverable</u>

Determine the relative role of size effects and vec on phase selection