CANFSA

Center for Advanced Non-Ferrous Structural Alloys
An Industry/University Cooperative Research Center

Project 55: Fe-Containing Multi-Principal Element Alloys for Protective Structures

Semi-annual Fall Meeting
October 2021

- Student: James Frishkoff (Mines)
- Faculty: Dr. Amy Clarke & Dr. Kester Clarke (Mines)
- Industrial Mentors: Bruce Antolovich (ATI), Hayley Brown (SFSA), *Steve Jansto (CBMM), Tanya Ros (Arcelor Mittal)*

COLORADO SCHOOL OF MINES NSF IOWA STATE UNIVERSITY

Project 55: Fe-Containing Multi-Principal Element Alloys for Protective Structures

CANFSA CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Student: James Frishkoff (Mines)
- Advisors: Amy Clarke, Kester Clarke (Mines)

Project Duration

MS: January 2021 to December 2022

- Problem: TRIP/TWIP MPEAs currently rely on costly high alloy content, and composition dependence not yet well understood.
- Objective: Achieve TRIP/TWIP & strength-ductility combinations in Co-lean MPEAs via experimental methods and high-throughput thermodynamic modeling.
- Benefit: Increasingly high strength-ductility combinations desired in many sectors, including vehicle protective structures.

Recent Progress

- Multi-factor computer-aided alloy design initiated and seven promising alloy candidates identified
- Microstructural evaluation of existing CoCrNi TRIP-MPEA family initiated
- Three baseline alloys sourced from ATI for comparison
- New arc melting furnace being installed – rapid small batch melting

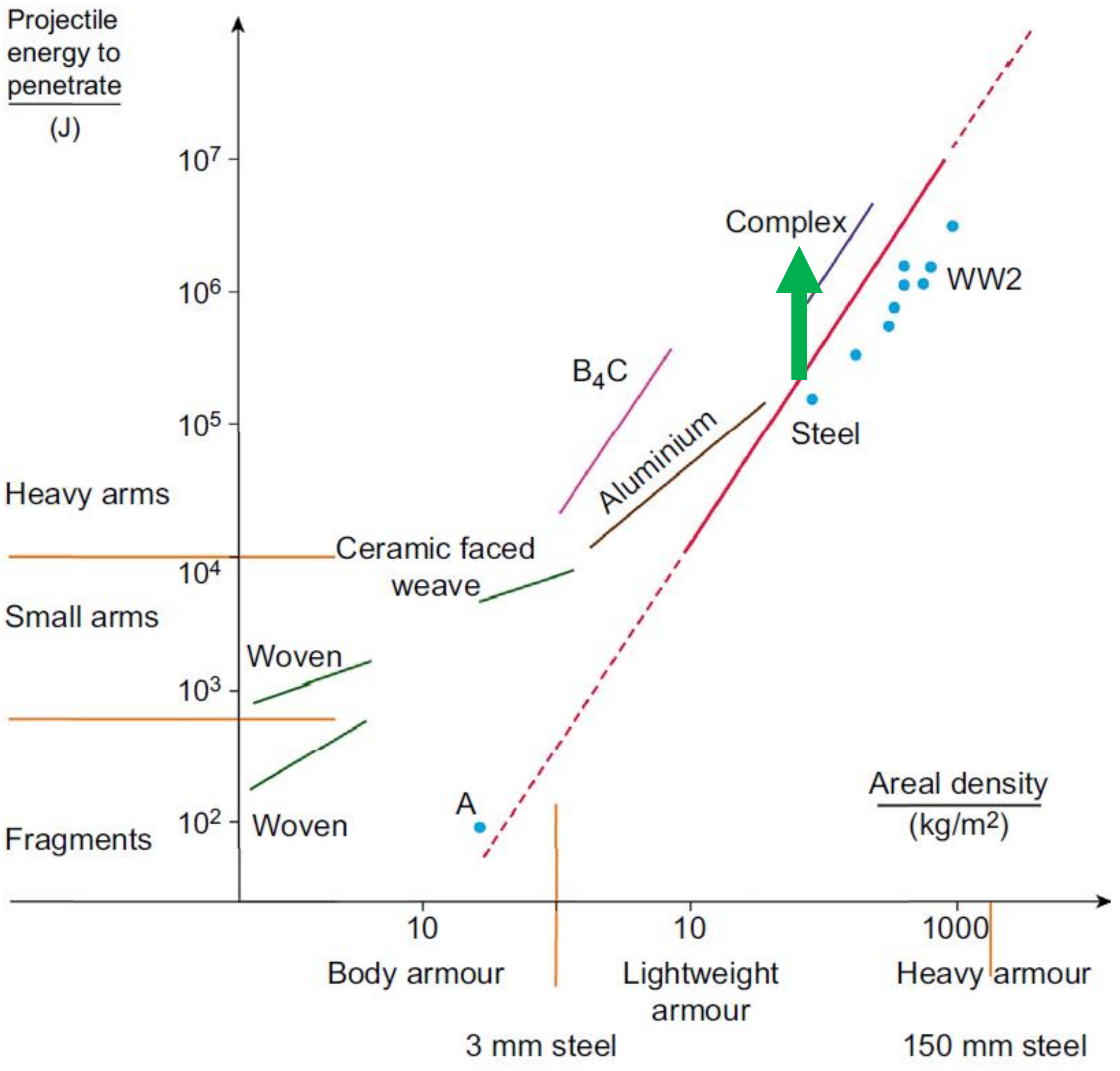
Metrics

Description	% Complete	Status
1. Literature review	40%	●
2. ThermoCalc, PanDat & LAMMPS modeling	60%	●
3. Obtain industrial baseline material	100%	●
4. Alloy downselect	15%	●
5. Gleeble experiments on downselected alloys and industrial reference material	5%	●

The Problem Space

Problem	Threat	Protection	Solution
Military ground/air platforms need armor/protective structures Platforms are weight-constrained	Increasing lethality of threats requires improved protective capabilities	Protection scales with weight "Weight is the penalty we pay for having nice things"	Higher performance armor materials Better performance at the same weight, or the same performance at a lower weight

The Problem Space – Protective Structure Performance Metrics

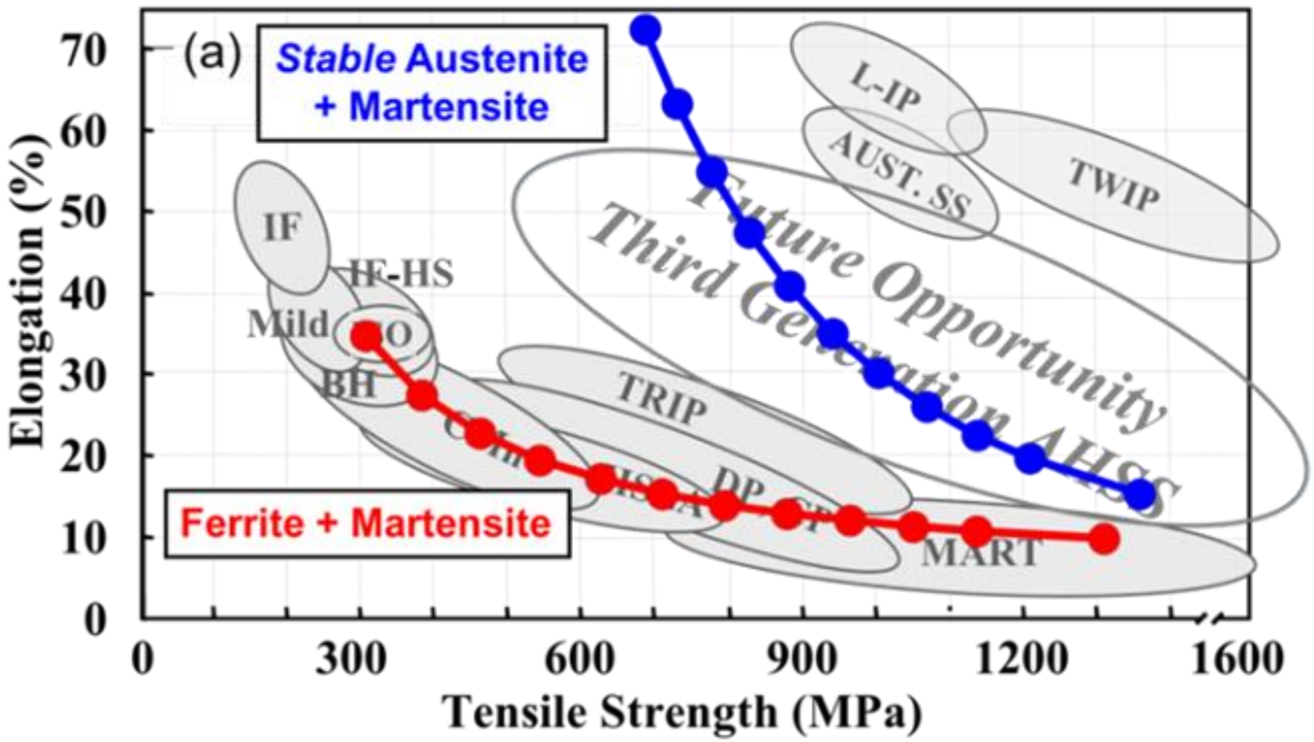


Wants and needs:

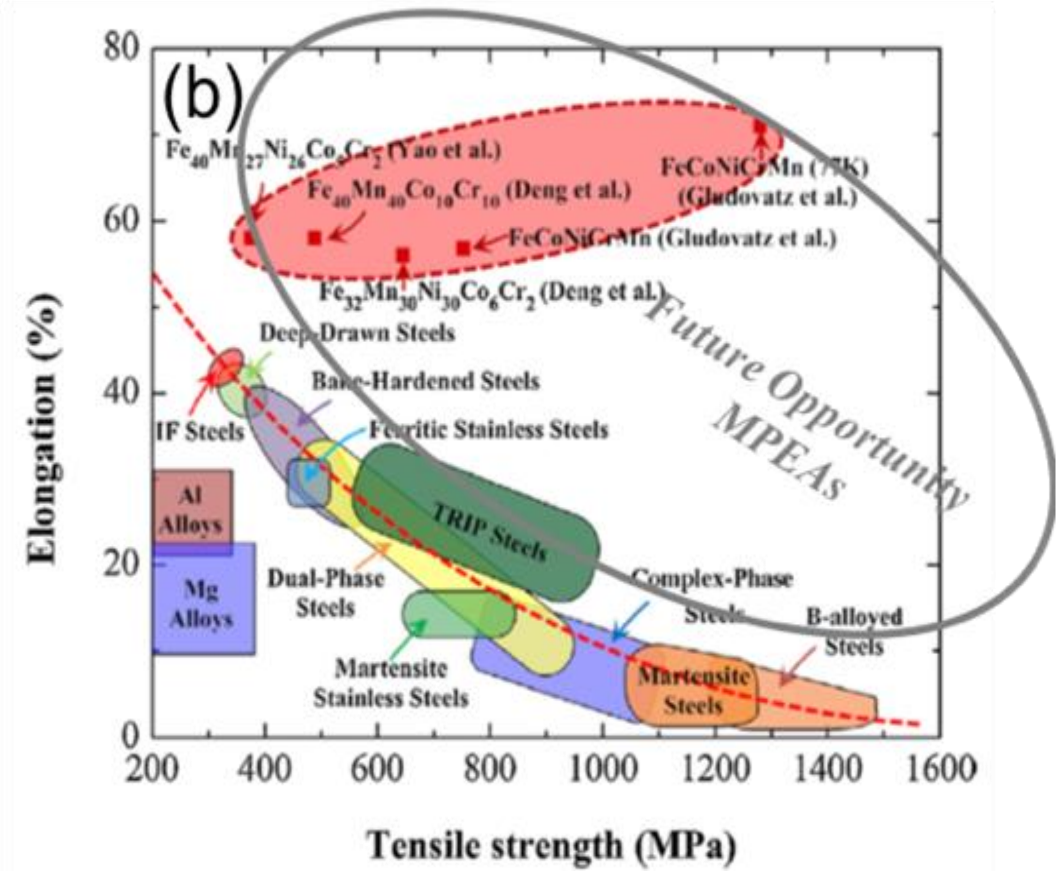
- Yield & Dynamic Flow Stress (quasistatic up to 10^4 s^{-1})
- Ultimate Tensile Strength
- Strain to Fracture
- Work Hardening Rate
- Shear Strain Localization Resistance
- Surface Hardness
- Weldability

I. Crouch, *The Science of Armour Materials*, Elsevier (2017). Reproduced from A. Doig, *Military Metallurgy*, Maney Publishing: London (1998)

Steel Example: Austenite/Martensite Mixtures Create Desirable Property Combinations



D.K. Matlock and J.G. Speer, "Design considerations for the next generation of advanced high strength steels", In Proceedings of The 3rd International Conference on Advanced Structural Steels, Gyeongju, Korea, 2006, pp. 774-781



Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang. "High-entropy alloy: challenges and prospects", Materials Today, 2011, 19(6):349-362

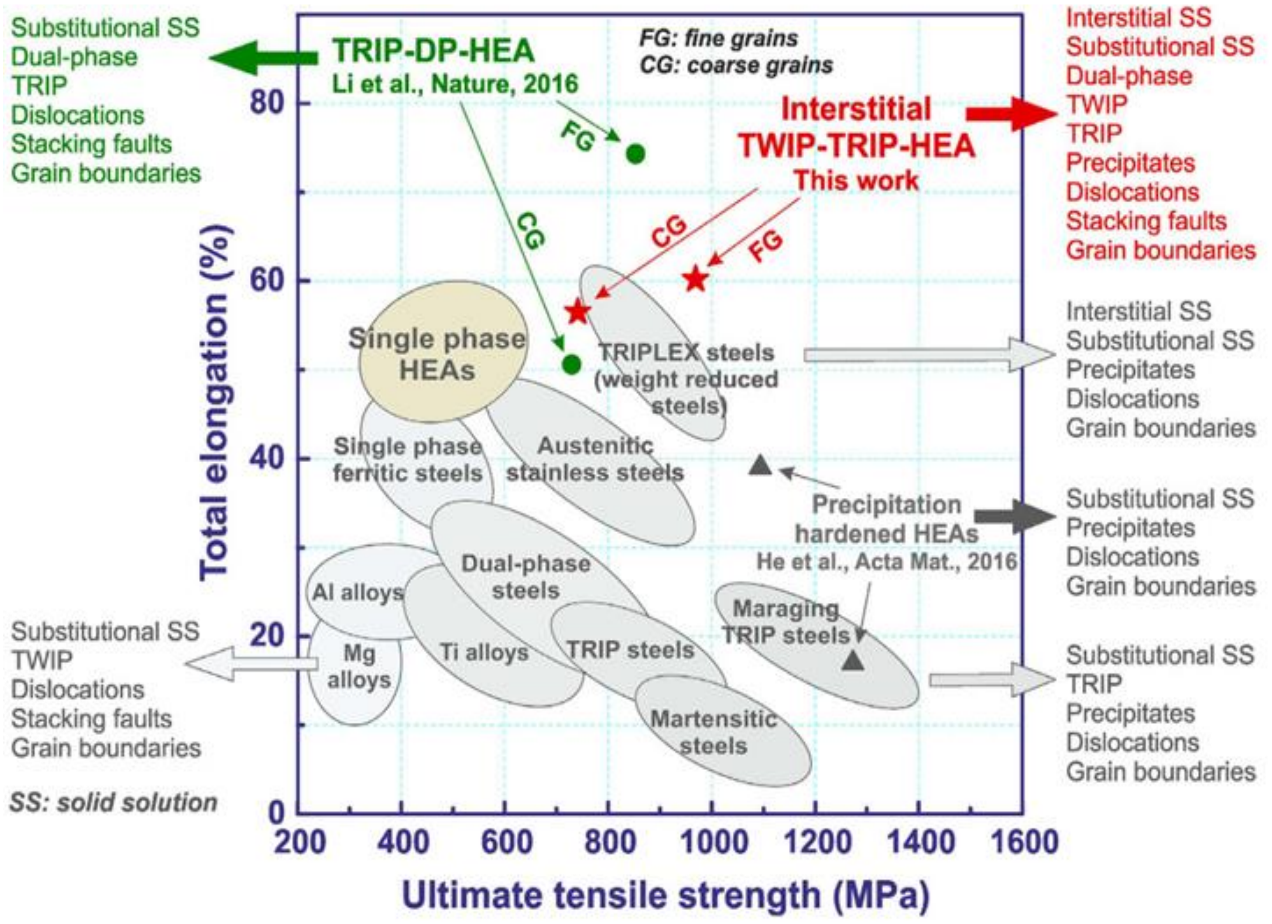
Alloy Design Concepts

Basic factors:

- Metastability (TRIP)
- Deformation twinning (TWIP)
- Solid solution strengthening
- Precipitation hardening
- Grain size

Microstructural features:

- Limit brittle IMs e.g sigma phase
- *γ'* precipitate strengthening
- Other precipitates (carbides, Fe_2SiTi)
- GB pinning – precipitates, Nb
- Overaged precipitates (reduce ASB)



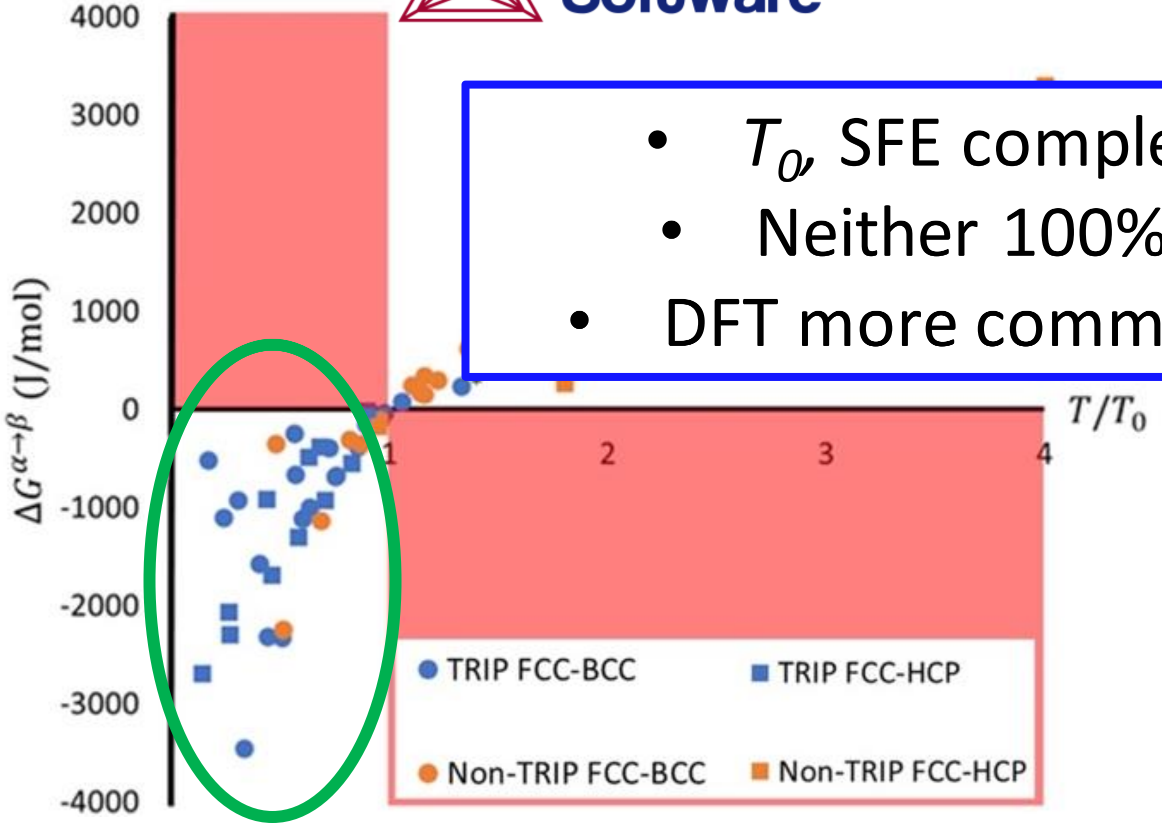
Z. Li et al, "Interstitial atoms enable joint twinning and transformation induced plasticity in strong and ductile high-entropy alloys", *Sci Rep*, 2017, 7:40704

Computer-Aided Alloy Design – Metastability

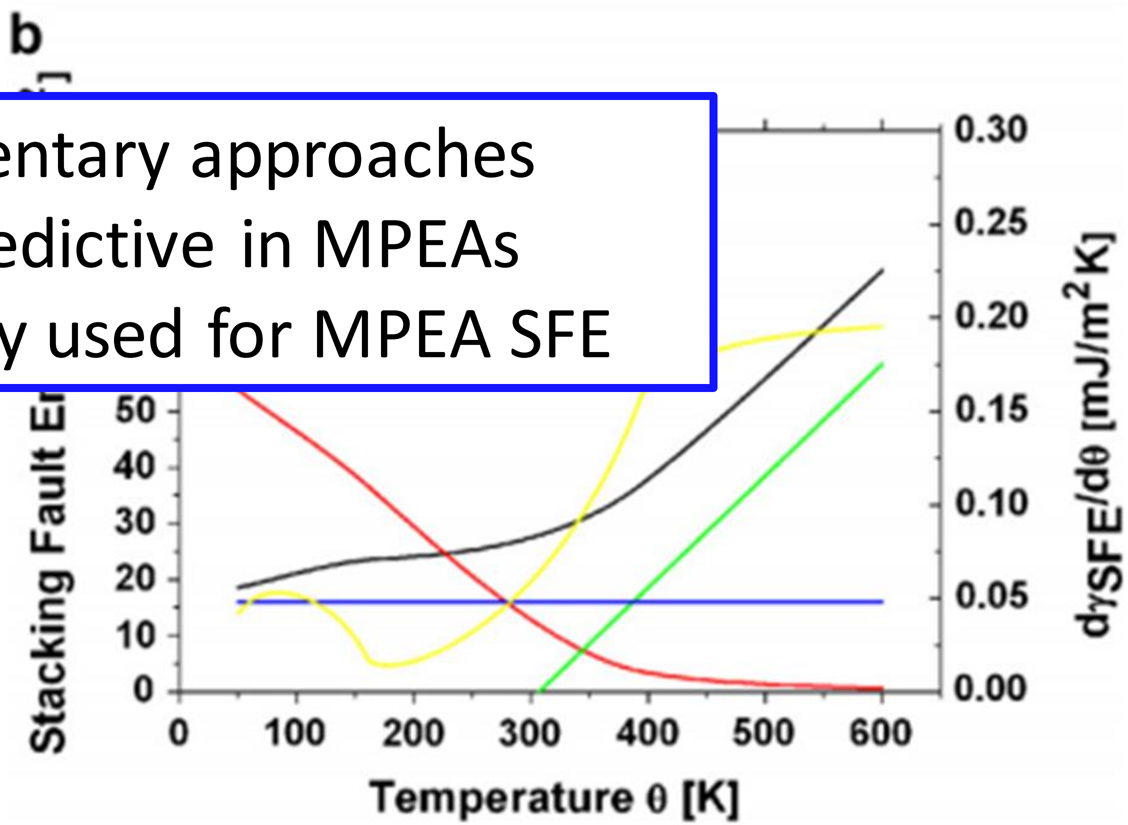
CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

Thermo-Calc Software

- T_0, SFE complementary approaches
- Neither 100% predictive in MPEAs
- DFT more commonly used for MPEA SFE



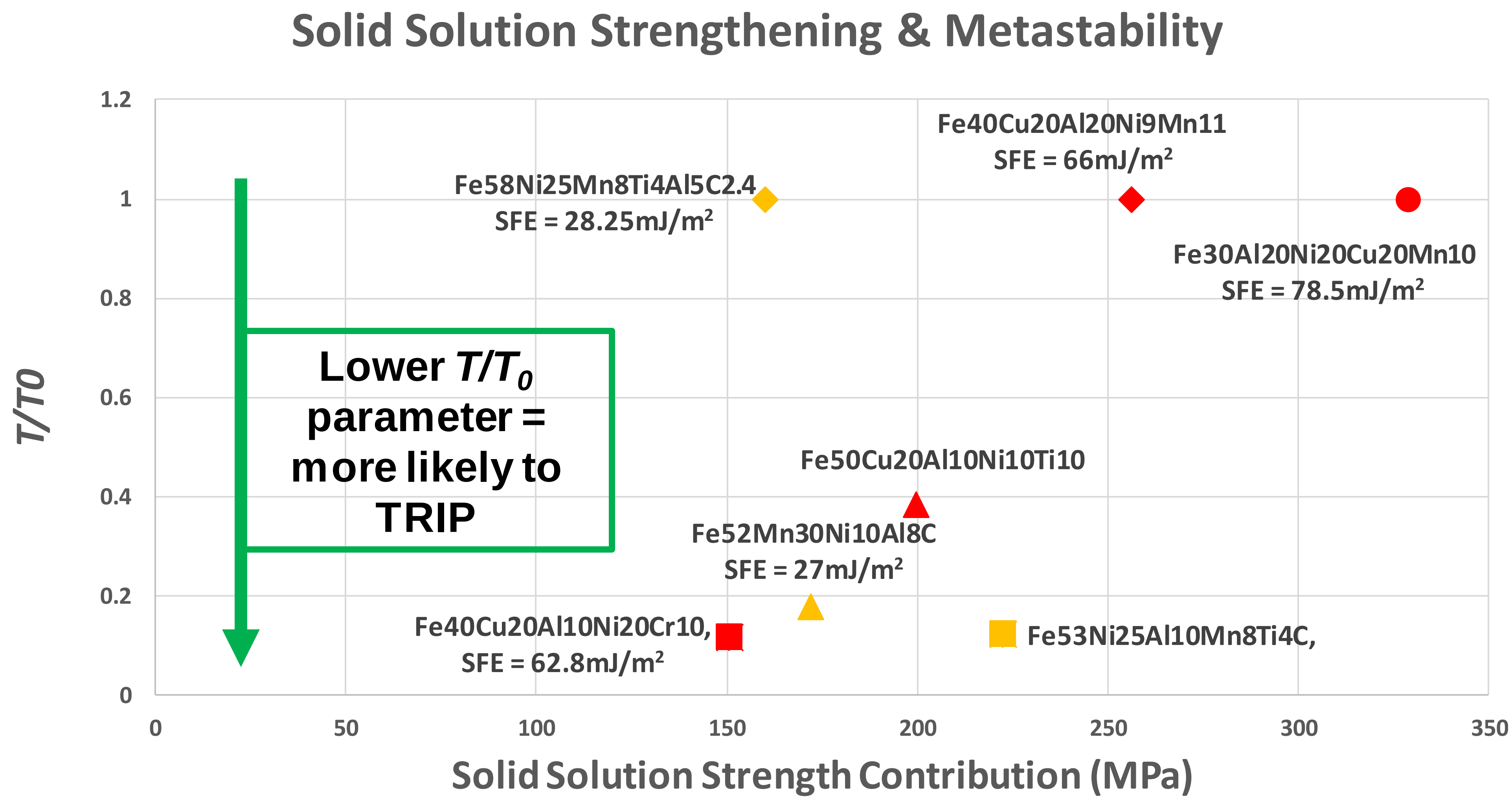
J.A. Copley, Prediction and Observation of Transformation-Induced Plasticity Behavior in CoCrNi Multi-Principal Element Alloys with In-Situ Synchrotron X-Ray Diffraction, MS Thesis, Colorado School of Mines, 2020



Curtze, S., and V. T. Kuokkala. "Dependence of Tensile Deformation Behavior of TWIP Steels on Stacking Fault Energy, Temperature and Strain Rate." *Acta Materialia* 58, no. 15 (September 1, 2010): 5129–41. https://doi.org/10.1016/J.ACTAMAT.2010.05.049.

Computer-Aided Alloy Design – Metastability

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS



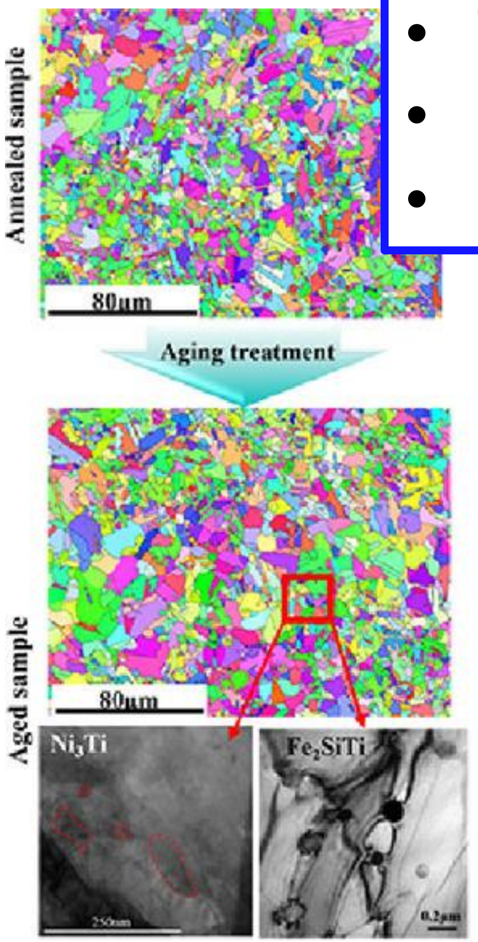
Solid solution strengthening calculated via TC-EARS method, Coury et al, *Sci Reps* June 2018 (https://doi.org/10.1038/s41598-018-26830-6)

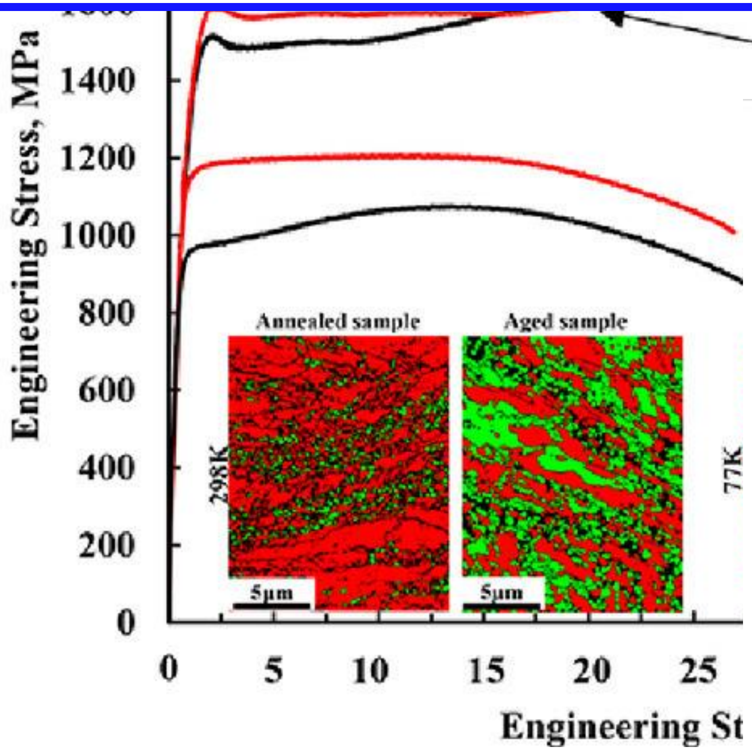
All SFE values calculated via modified Olson-Cohen method of Curtze et al., *Acta* Feb. 2011 (doi.org/10.1016/j.actamat.2010.10.037)

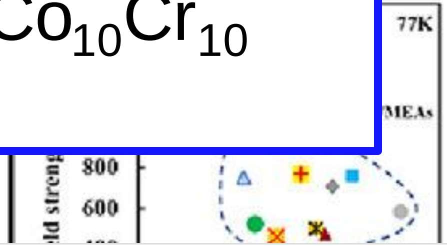
New Developments in Literature

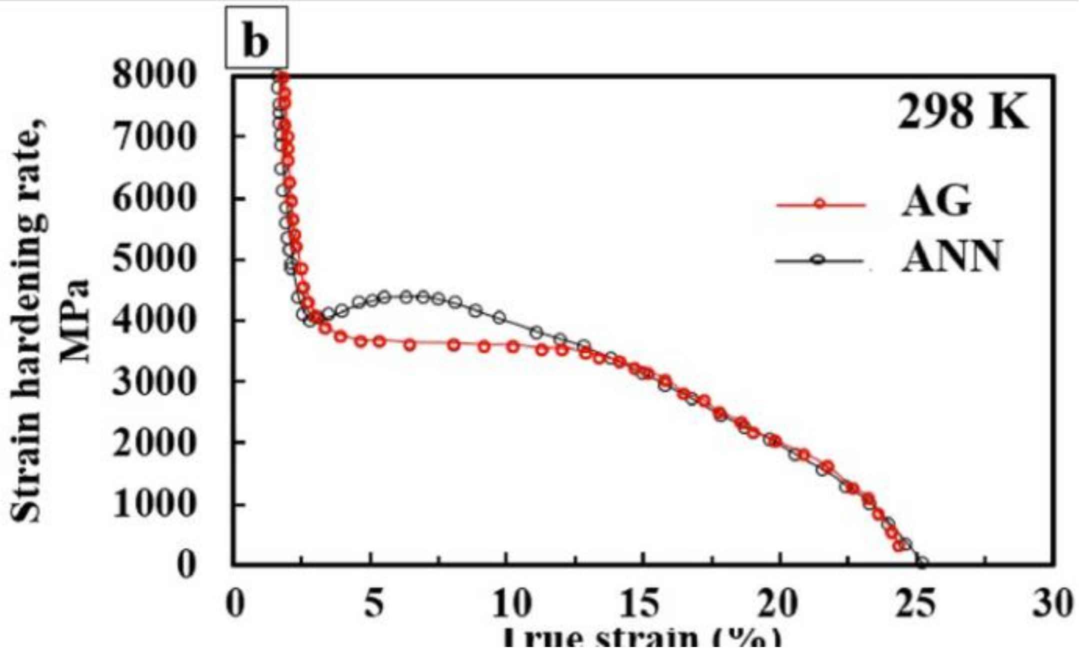
$Fe_{65}Ni_{15}Co_8Mn_8Ti_3Si$– Nene et al. 2021

- TRIP/TWIP active with fine precipitates
- >1GPa YS, higher WHR than $Fe_{50}Mn_{30}Co_{10}Cr_{10}$
- Can we remove Co?



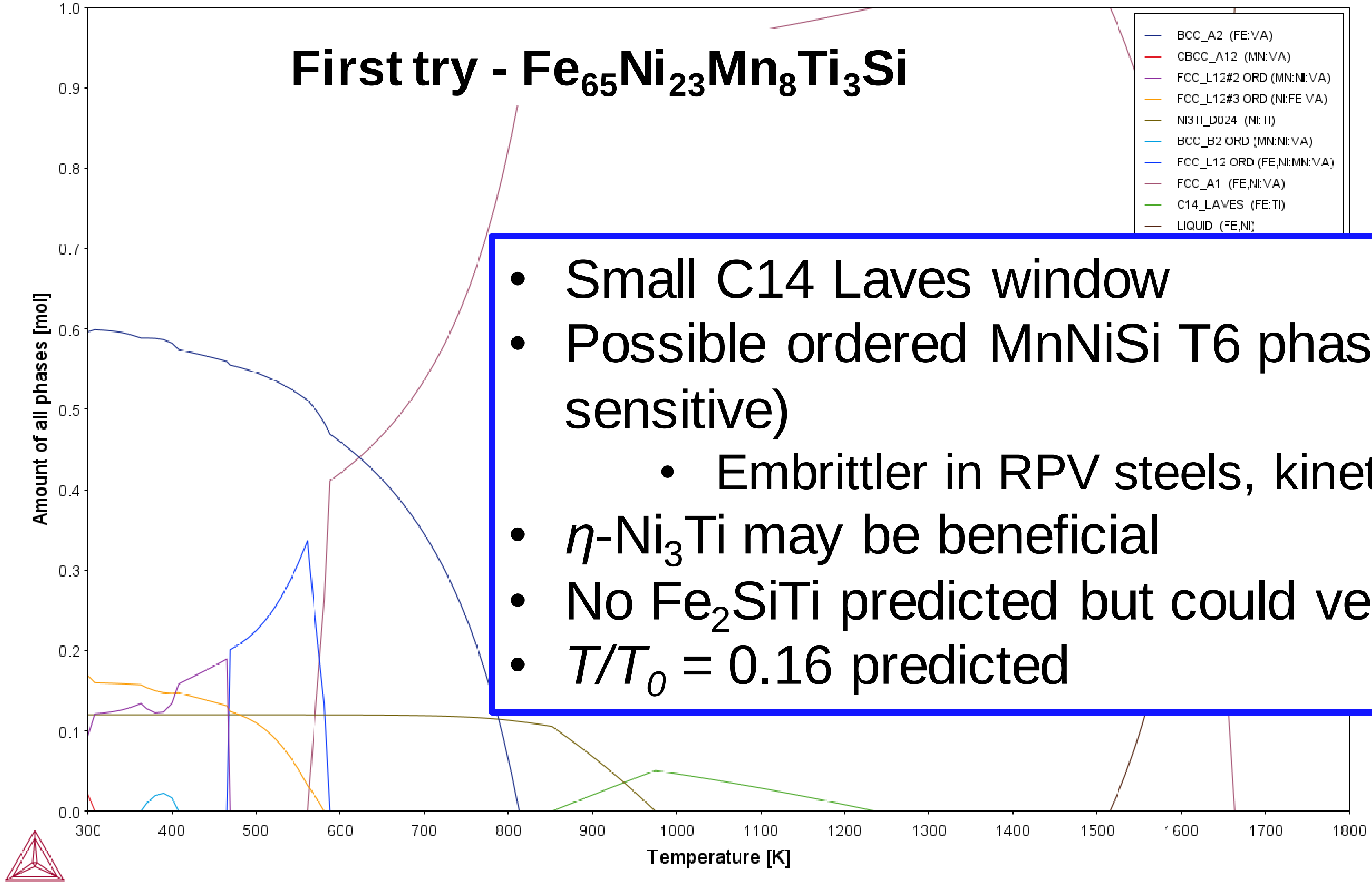






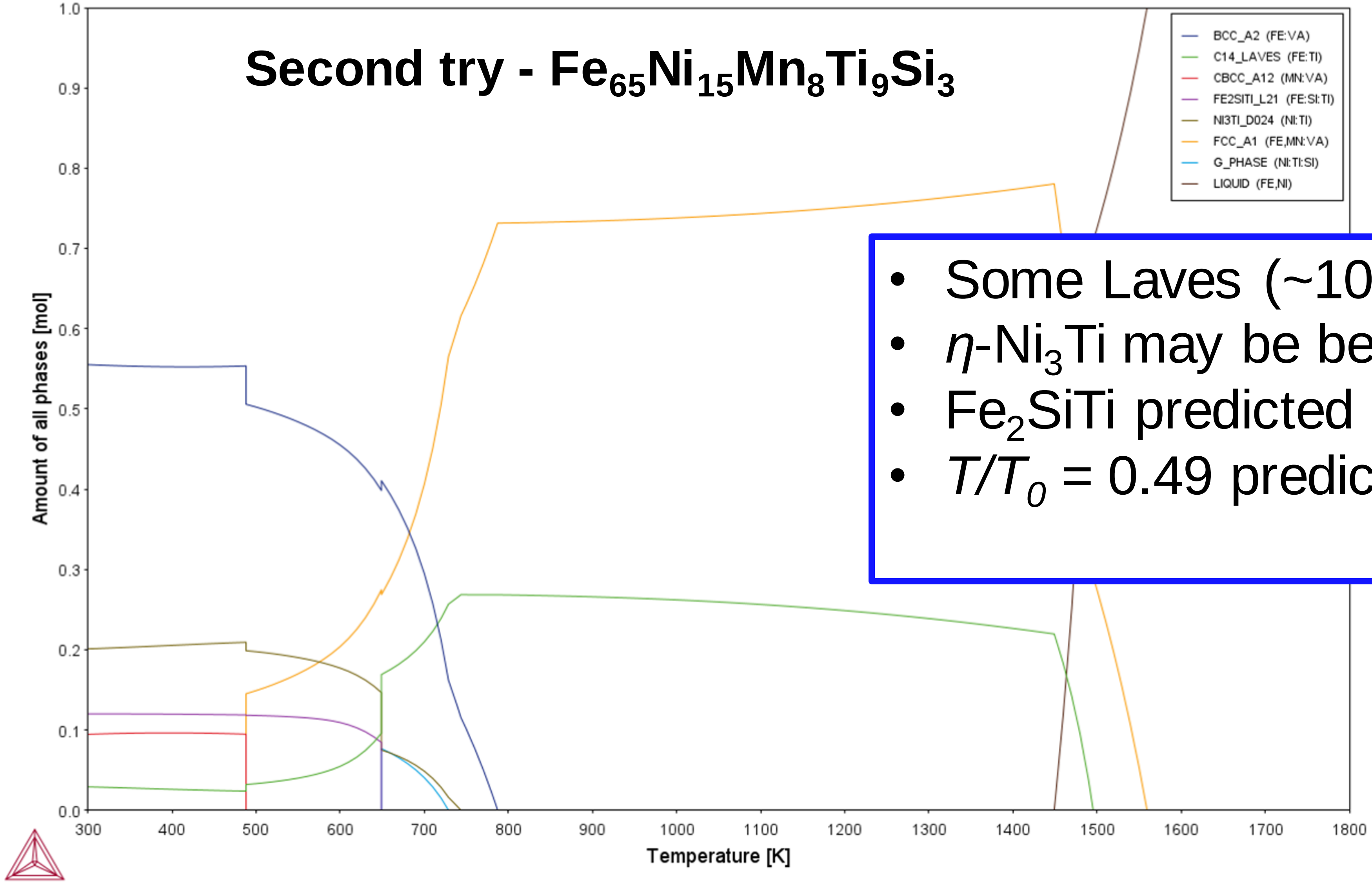
New Developments in Literature

First try - $Fe_{65}Ni_{23}Mn_8Ti_3Si$



- Small C14 Laves window
- Possible ordered MnNiSi T6 phase (database sensitive)
  - Embrittler in RPV steels, kinetics unknown
- η-Ni_3Ti may be beneficial
- No Fe_2SiTi predicted but could verify experimentally
- T/T_0 = 0.16 predicted

New Developments in Literature

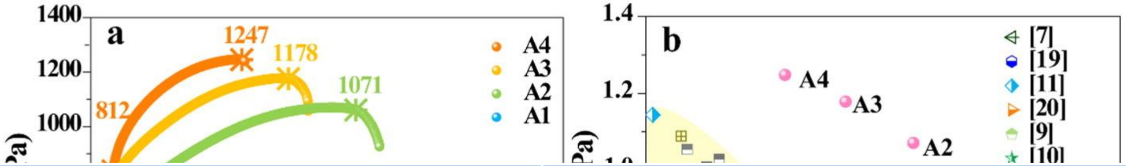


- Some Laves (~10% <350°C)
- η-Ni_3Ti may be beneficial
- Fe_2SiTi predicted (12%)
- T/T_0 = 0.49 predicted

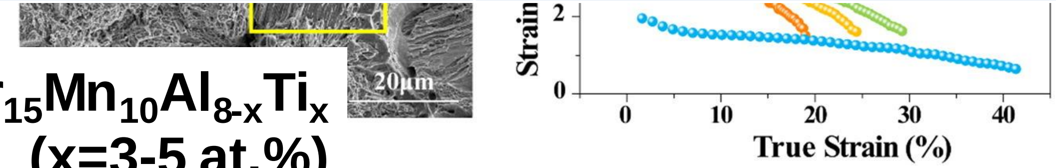
Computer-Aided Alloy Design – *γ/γ’* Strengthening

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- *γ’* strengthened TRIP-assisted armor steel (Wengrenovich 2016)



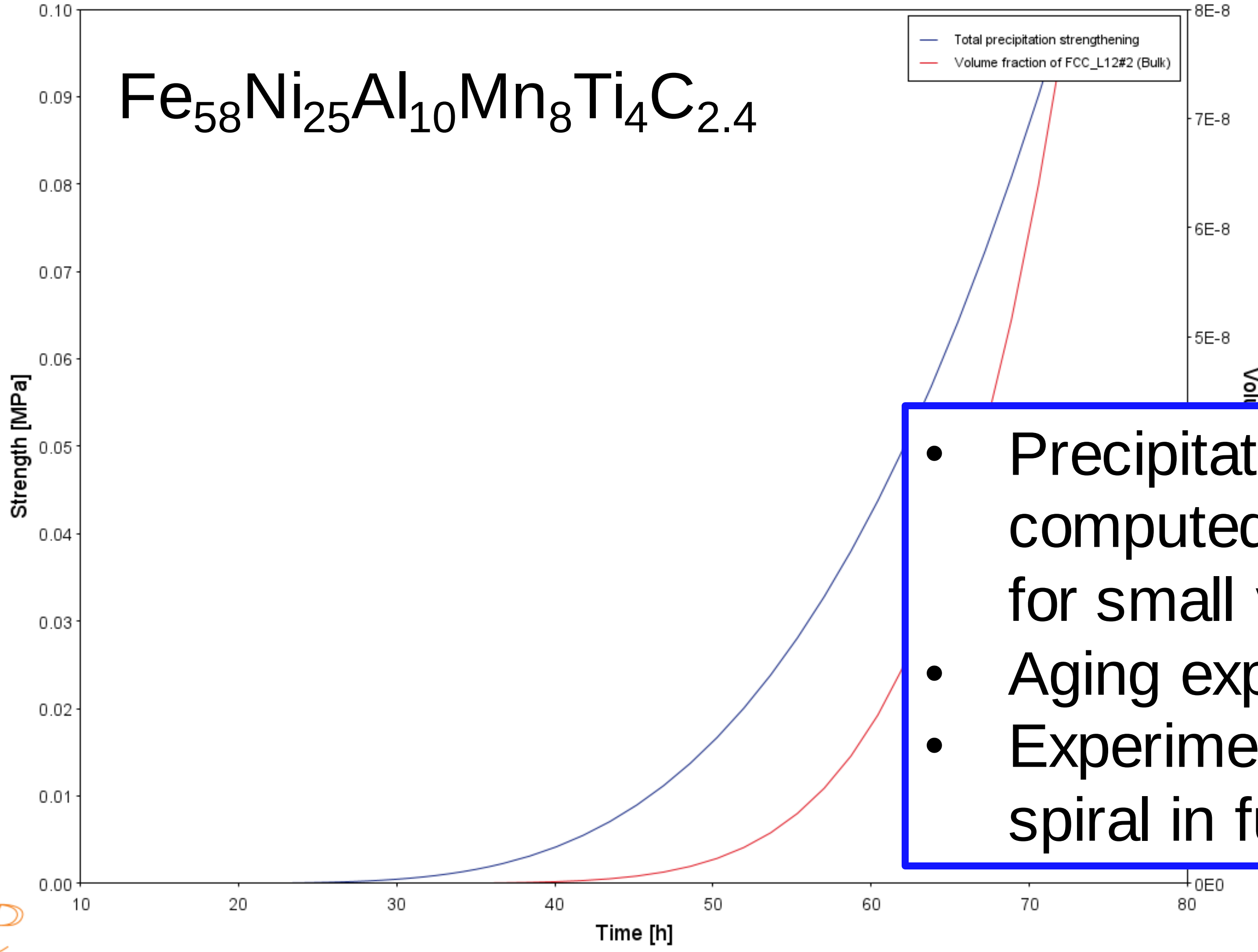
Composition	Max *γ’* %	Sigma phase	Other Precipitates
$Fe_{58}Ni_{25}Al_{10}Mn_{8}Ti_{4}C_{2.4}$	15% - 330°C	None	*η*-Ni_3Ti (5%)
$Fe_{45}Ni_{28}Cr_{8}Mn_{8}Al_{5}Ti_{6}Nb_{.25}$	28% - 225°C	Present @ all *γ’* T, ~20%	*η*-Ni_3Ti (26% @ 500°C)
$(FeNi)_{67}Cr_{15}Mn_{10}Al_{3}Ti_{5}Nb_{.25}$	32% - 350°C	Present @ all *γ’* T, ~35%	*η*-Ni_3Ti (26% @ 550°C)



$(FeNi)_{67}Cr_{15}Mn_{10}Al_{8-x}Ti_{x}$ (x=3-5 at.%)

Zhao, Y. L. et al. Development of high-strength Co-free high-entropy alloys hardened by nanosized precipitates. *Scr. Mater.* 148, 51–55 (2018).

Computer-Aided Alloy Design – *γ/γ'* Strengthening



- Precipitate/age hardening MPEAS: computed kinetics slow (100s of hours for small vol.%)
- Aging experiments needed
- Experimental data → positive feedback spiral in future modeling efforts

Constitutive Modeling

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

Johnson-Cook

- Empirical
- Many modifications, but all have *T*, strain rate params
- Common in high rate & ballistics studies

$$\sigma_{\mathrm{eq}} = [A + Bp^n]\,[1 + \dot{p}^*]^C\,[1 - T^{*m}]$$

Borvik, T., O. S. Hopperstad, T. Berstad, and M. Langseth. "A Computational Model of Viscoplasticity and Ductile Damage for Impact and Penetration." *European Journal of Mechanics - A/Solids* 20, no. 5 (September 1, 2001): 685–712. https://doi.org/10.1016/S0997-7538(01)01157-3.

Zerilli-Armstrong

- Dislocation theory based
- Variants for crystal structure
- Also frequently modified, common in ballistics

$$\sigma_{\mathrm{eq}} = \sigma_{\mathrm{a}} + B\exp(-\beta T) + A\varepsilon_{\mathrm{eq}}^n$$

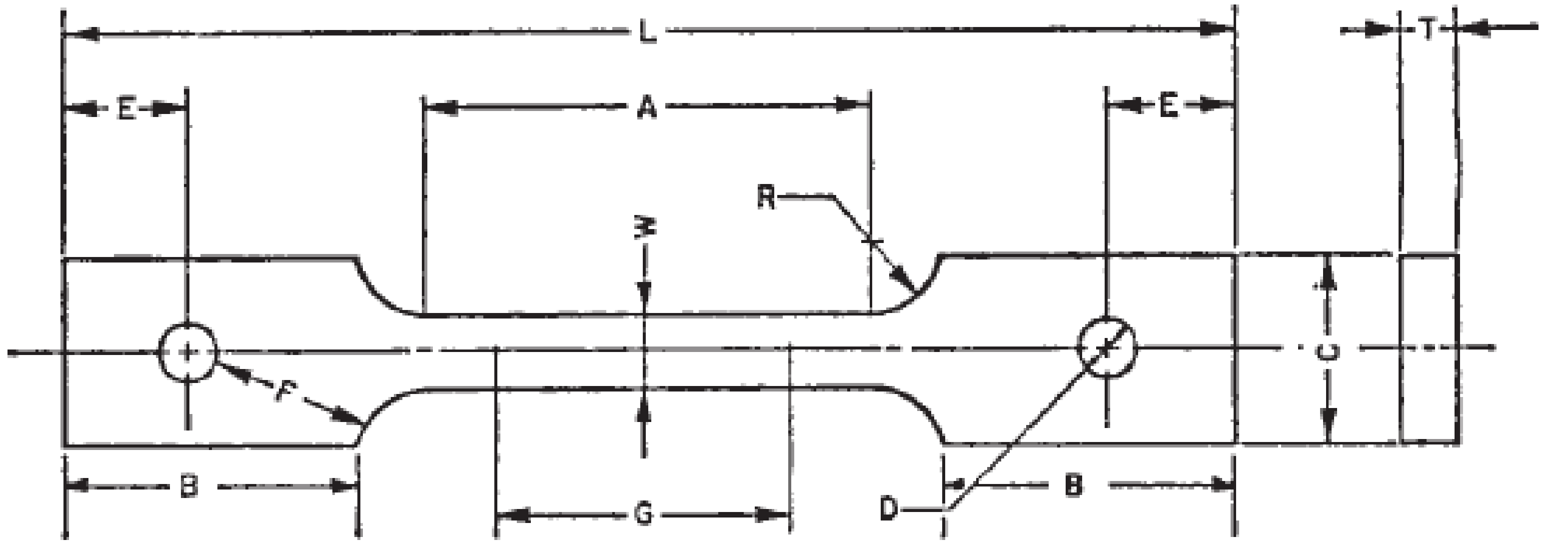
↑ **BCC** ↓ **FCC**

$$\sigma_{\mathrm{eq}} = \sigma_{\mathrm{a}} + A\varepsilon_{\mathrm{eq}}^n \exp(-\alpha T)$$

Dey, S., T. Børvik, O. S. Hopperstad, and M. Langseth. "On the Influence of Constitutive Relation in Projectile Impact of Steel Plates." *International Journal of Impact Engineering* 34, no. 3 (March 1, 2007): 464–86. https://doi.org/10.1016/J.IJIMPENG.2005.10.003.

Mechanical Test Plan

T (°C)	Room T		rature
Strain rate (s^-1)			
Quasistatic (10^-3)	Tensi		e
High (~100) -- Mid -- Low (10^-2)			
	Tensi		e
	Tensile		Gleeble Tensile



ASTM E8 tensile

- 3 samples/condition
- More conditions = better constitutive model fitting
- Example T, $\dot{\varepsilon}$ from literature: 400 – 1000°C, 10^{-2} – 10^{2}/s (Saxena et al., *J Mater Eng Perf*, Sept 2019)

Mechanical Test Plan

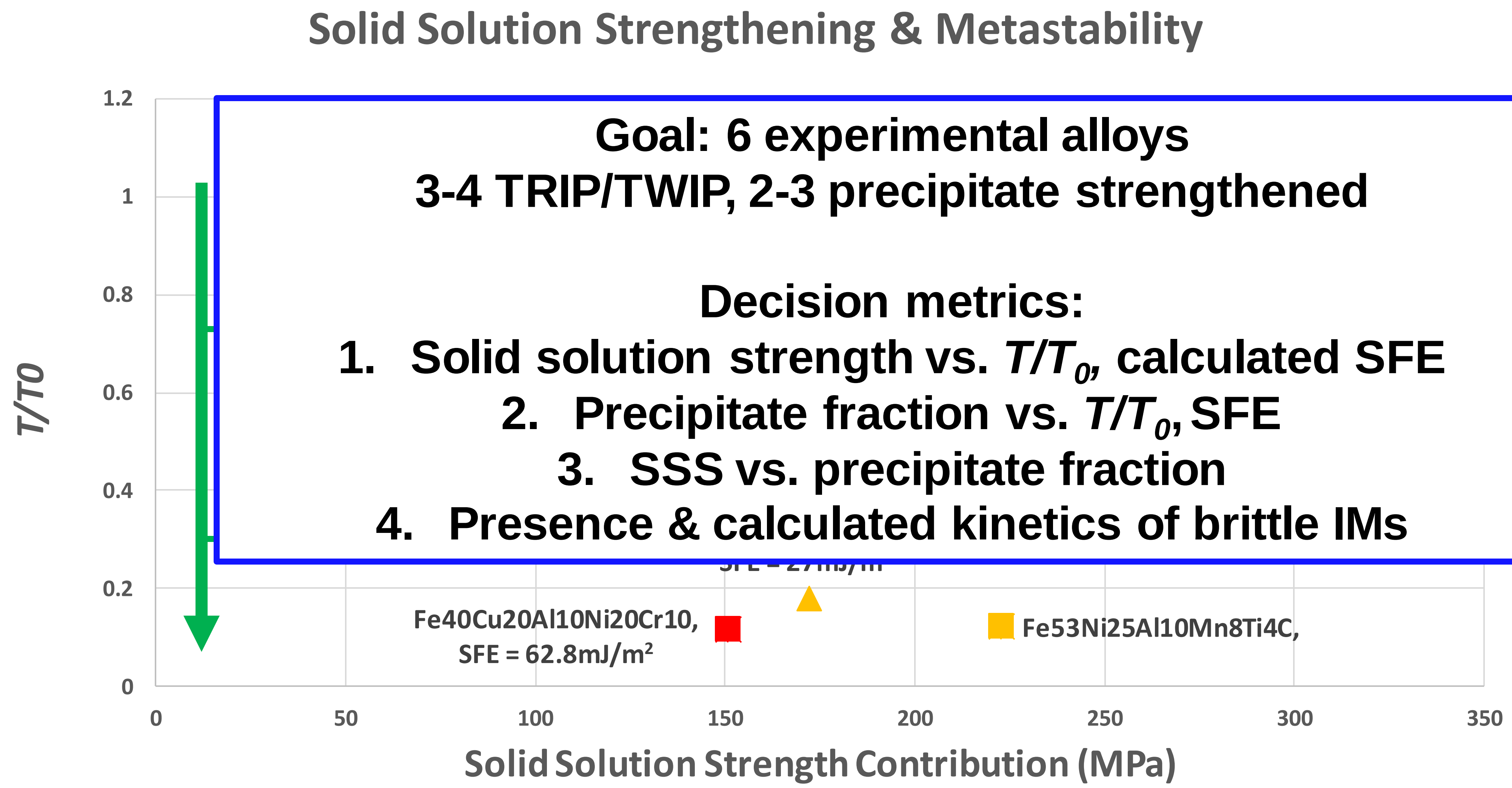
CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

T (°C)	Room Temp	Warm Work Temperature	Hot Work/Supersolvus
Strain rate (s^-1)			
Quasistatic (10^-3)	Gleeble Compression	Gleeble Compression	Gleeble Compression
High (~100) -- Mid -- Low (10^-2)			
	Gleeble Compression	Gleeble Compression	Gleeble Compression
		Gleeble Compression	Gleeble Compression

- 3 samples/condition
- Baseline processing data vs. conventional alloys
- Support future microstructural optimization work

Downselect Progress

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS



Goal: 6 experimental alloys
3-4 TRIP/TWIP, 2-3 precipitate strengthened

Decision metrics:

1. **Solid solution strength vs. T/T_0, calculated SFE**
2. **Precipitate fraction vs. T/T_0, SFE**
3. **SSS vs. precipitate fraction**
4. **Presence & calculated kinetics of brittle IMs**

Industry Partner – ATI Specialty Materials

Added Capability

- 25 & 50 lb. vacuum melted ingots
- VAR/ESR for cleanliness
- Industrial thermomechanical processing & heat treatment

Baseline Alloys

- ATI 188 – Co-base high-temp austenitic alloy; high work-hardening; TRIP?
- A286 – Legacy NiCr high-temp austenitic steel; TRIP?
- Datalloy HP – Highly alloyed steel; quasi-MPEA

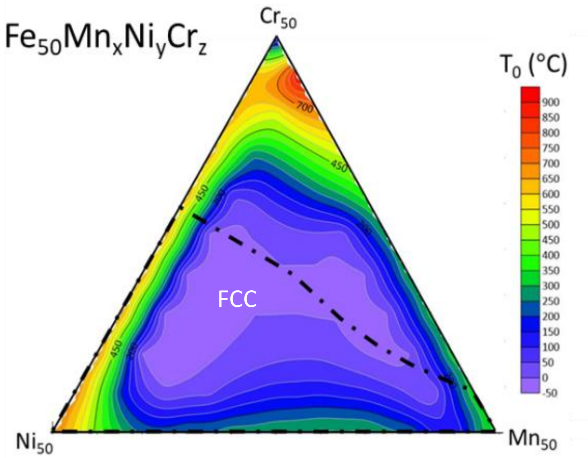
Composition Range (UNS N08830)			
Element	Wt. %	Element	Wt. %
Carbon	0.015	Manganese	3.0 – 6.0
Phosphorous	0.035	Sulfur	0.010
Silicon	1.00	Nickel	29.0 – 34.0
Chromium	20.0 – 24.0	Molybdenum	4.5 – 6.5
Copper	0.50 – 2.00	Cobalt	0.50 – 3.50
Tungsten	0.20 – 1.80	Nitrogen	0.20 – 0.55
Iron	balance		
Maximum % unless a range is indicated.			

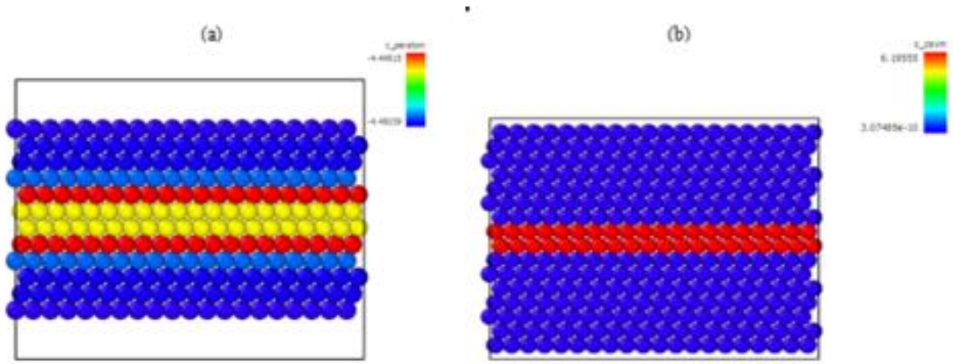
Datalloy HP

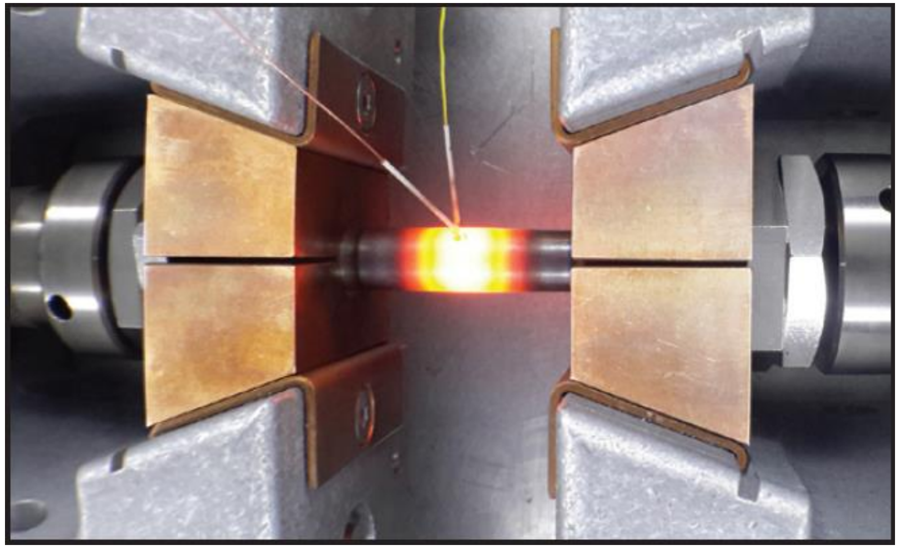
T/T_0 = 0.13 (FCC→BCC)

Year 1 Roadmap

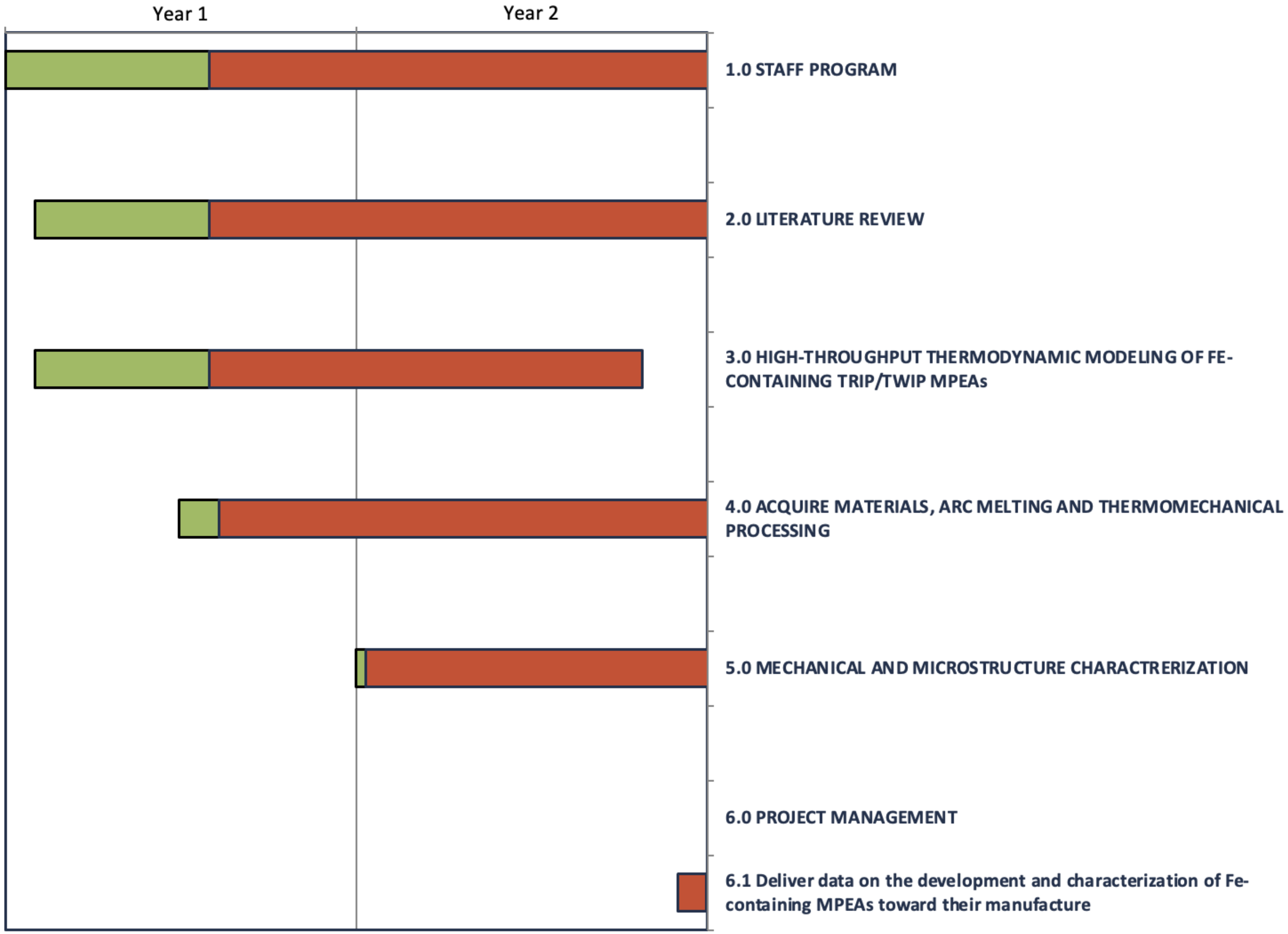
- High-throughput thermodynamic modeling
  - ThermoCalc & PanDat – T_0, precipitation, phase diagrams
  - LAMMPS – SFE, SRO
  - TC-EARS models – solid solution strengthening
- Gleeble thermomechanical processing of baseline commercial products (ATI) – **Materials are on campus**
- Rapid small-scale arc melting of promising Fe-MPEAs – **Equipment ready for commissioning**







Gantt Chart



Year 1
Year 2
1.0 STAFF PROGRAM
2.0 LITERATURE REVIEW
3.0 HIGH-THROUGHPUT THERMODYNAMIC MODELING OF FE-CONTAINING TRIP/TWIP MPEAs
4.0 ACQUIRE MATERIALS, ARC MELTING AND THERMOMECHANICAL PROCESSING
5.0 MECHANICAL AND MICROSTRUCTURE CHARACTRERIZATION
6.0 PROJECT MANAGEMENT
6.1 Deliver data on the development and characterization of Fe-containing MPEAs toward their manufacture

Acknowledgements

- This program is sponsored by the Defense Logistics Agency – Troop Support, Philadelphia PA and the Defense Logistics Agency Information Operations, J68, Research & Development, Ft. Belvoir, VA.
- Special thanks is also given to ATI Specialty Materials for providing test materials.

Thank you for your time!
Questions?

Supplementary Slides

Modified Olson-Cohen SFE Algorithm

$$\gamma_{SFE} = 2\rho\ \Delta G^{\gamma\to\varepsilon} + 2\sigma$$

$$\rho = \frac{4}{\sqrt{3}}\frac{1}{a^2 N}$$

$$\Delta G^{\gamma\to\varepsilon}_{N(bulk)} = E^{\varepsilon}_{N} - E^{\gamma}_{N} \text{ (see Eq. 12)}$$

interstitial nitrogen

$$\Delta G^{\gamma\to\varepsilon} = \sum_i \chi_i \Delta G_i^{\gamma\to\varepsilon} + \sum_{ij} \chi_i \chi_j \Omega_{ij}^{\gamma\to\varepsilon} + \Delta G_{mg}^{\gamma\to\varepsilon} + \Delta G_{seg\,(int)}^{\gamma\to\varepsilon}$$

substitutionals

$$\Delta G_{\varphi}^{\gamma\to\varepsilon} = (G_{\varphi}^{\varepsilon} - G_{\varphi}^{\gamma})$$

$$G_{\varphi}^{\Phi} = a + bT + cT\ln(T) + \sum dT^n$$

$$\Omega_{\varphi\phi}^{\gamma\to\varepsilon} = ({}^0L^{\varepsilon} - {}^0L^{\gamma}) + ({}^1L^{\varepsilon} - {}^1L^{\gamma})(\chi_{\varphi} - \chi_{\phi})$$

$$\Delta G_{mg}^{\gamma\to\varepsilon} = G_{mg}^{\varepsilon} - G_{mg}^{\gamma}$$

$$D = \frac{518}{1125} + \frac{11692}{15975}\left(\frac{1}{p} - 1\right)$$

$$G_{mg}^{\Phi} = RT\ln(\beta^{\Phi}+1) f^{\Phi}(\tau^{\Phi})$$

$\tau^{\Phi} \le 1$

$\tau^{\Phi} > 1$

$$\tau^{\Phi} = T / T^{\Phi}_{N\acute{e}el}$$

$$f^{\Phi}(\tau^{\Phi}) = -\left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right] / D$$

$$f^{\Phi}(\tau^{\Phi}) = 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{497}\left(\frac{1}{p} - 1\right)\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right] / D$$

$$\Delta G_{chem\,(int)}^{\gamma\to\varepsilon} = RT\left[\chi_{N(bulk)} \ln\frac{\chi_{N(seg)}}{\chi_{N(bulk)}} + (1 - \chi_{N(bulk)})\ln\frac{1-\chi_{N(seg)}}{1-\chi_{N(bulk)}}\right]$$

$$\Delta G_{seg\,(int)}^{\gamma\to\varepsilon} = \Delta G_{chem(int)}^{\gamma\to\varepsilon} + \Delta G_{surf\,(int)}^{\gamma\to\varepsilon} + \Delta G_{el\,(int)}^{\gamma\to\varepsilon}$$

$$\Delta G_{surf\,(int)}^{\gamma\to\varepsilon} = \frac{1}{4}\Lambda(\chi_{N(seg)} - \chi_{n(bulk)})^2$$

$$\Delta G_{el(int)}^{\gamma\to\varepsilon} = \frac{2}{9}\mu\frac{1+\upsilon}{1-\upsilon}\left(\frac{dV}{dX}\right)\frac{1}{V}(\chi_{N(seg)} - \chi_{N(bulk)})^2$$

a: lattice parameter
a, b, c, d: coefficients
G_{φ}^{Φ} : Gibbs energy of pure elements
G_{mg}^{Φ} : magnetic contribution to Gibbs energy
${}^0L^{\rho}$: linear function of T
${}^1L^{\varphi}$:constant
n: set of integers
N: Avogadro's constant
p: fraction of magnetic enthalpy absorbed above $T_{N\acute{e}el}$
R: gas constant
$T_{N\acute{e}el}$, T: (Néel) temperature

V: molar volume
β^{Φ} : magnetic moment
$\Delta G^{\gamma\to\varepsilon}, \Delta G_{\varphi}^{\gamma\to\varepsilon}, \Delta G_{mg}^{\gamma\to\varepsilon}$
$\Delta G_{seg\,(int)}^{\gamma\to\varepsilon}$ ($\Delta G_{chem(int)}^{\gamma\to\varepsilon}$, $\Delta G_{surf\,(int)}^{\gamma\to\varepsilon}$
$\Delta G_{el(int)}^{\gamma\to\varepsilon}$): change in Gibbs energy upon $\gamma - \varepsilon$ phase transformation, chemical, magnetic, and nitrogen segregation contributions (chemical, surface, elastic)

γ_{SFE}: stacking fault energy
μ: shear modulus
$\Omega_{\varphi\phi}^{\gamma\to\varepsilon}$: excess free energies
Λ : nitrogen atom-dislocation interaction energy
ρ: {111}molar surface density
σ: γ/ε-interface energy
ν: Poisson's ration
χ: molar fractions

Curtze, S., V. T. Kuokkala, A. Oikari, J. Talonen, and H. Hänninen. "Thermodynamic Modeling of the Stacking Fault Energy of Austenitic Steels." *Acta Materialia* 59, no. 3 (February 1, 2011): 1068–76. https://doi.org/10.1016/J.ACTAMAT.2010.10.037.

Industry Partner – ATI Specialty Materials

Added Capability

- 25 & 50 lb. vacuum melted ingots
- VAR/ESR for cleanliness
- Industrial thermomechanical processing & heat treatment

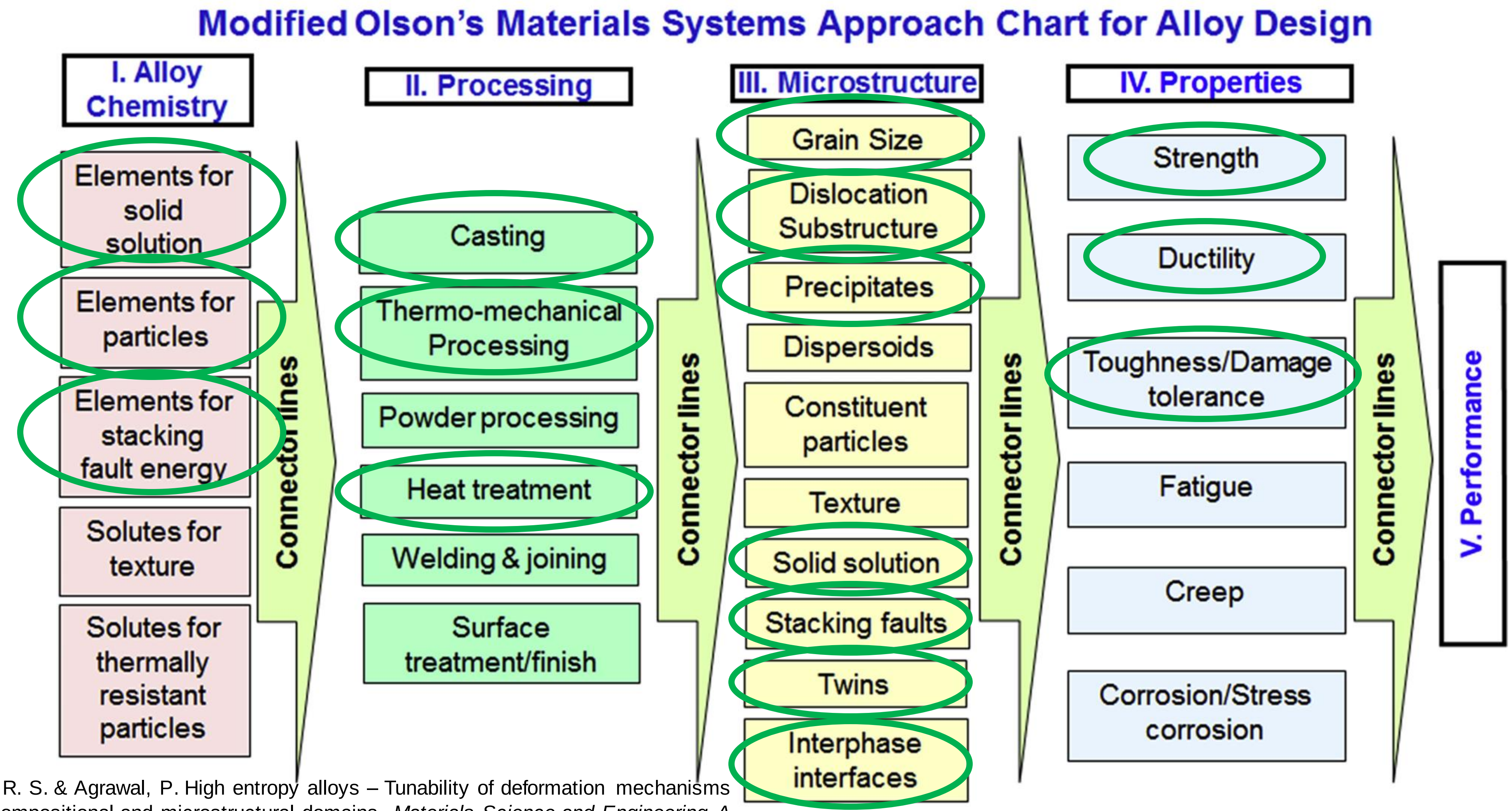
Baseline Alloys

- ATI 188 – Co-base high-temp austenitic alloy; high work-hardening; TRIP?
- A286 – Legacy NiCr high-temp austenitic steel; TRIP?
- Datalloy HP – Highly alloyed steel; quasi-MPEA

Composition Range (UNS N08830)			
Element	Wt. %	Element	Wt. %
Carbon	0.015	Manganese	3.0 – 6.0
Phosphorous	0.035	Sulfur	0.010
Silicon	1.00	Nickel	29.0 – 34.0
Chromium	20.0 – 24.0	Molybdenum	4.5 – 6.5
Copper	0.50 – 2.00	Cobalt	0.50 – 3.50
Tungsten	0.20 – 1.80	Nitrogen	0.20 – 0.55
Iron	balance		
Maximum % unless a range is indicated.			

Datalloy HP
T/T_0 = 0.13 (FCC→BCC)

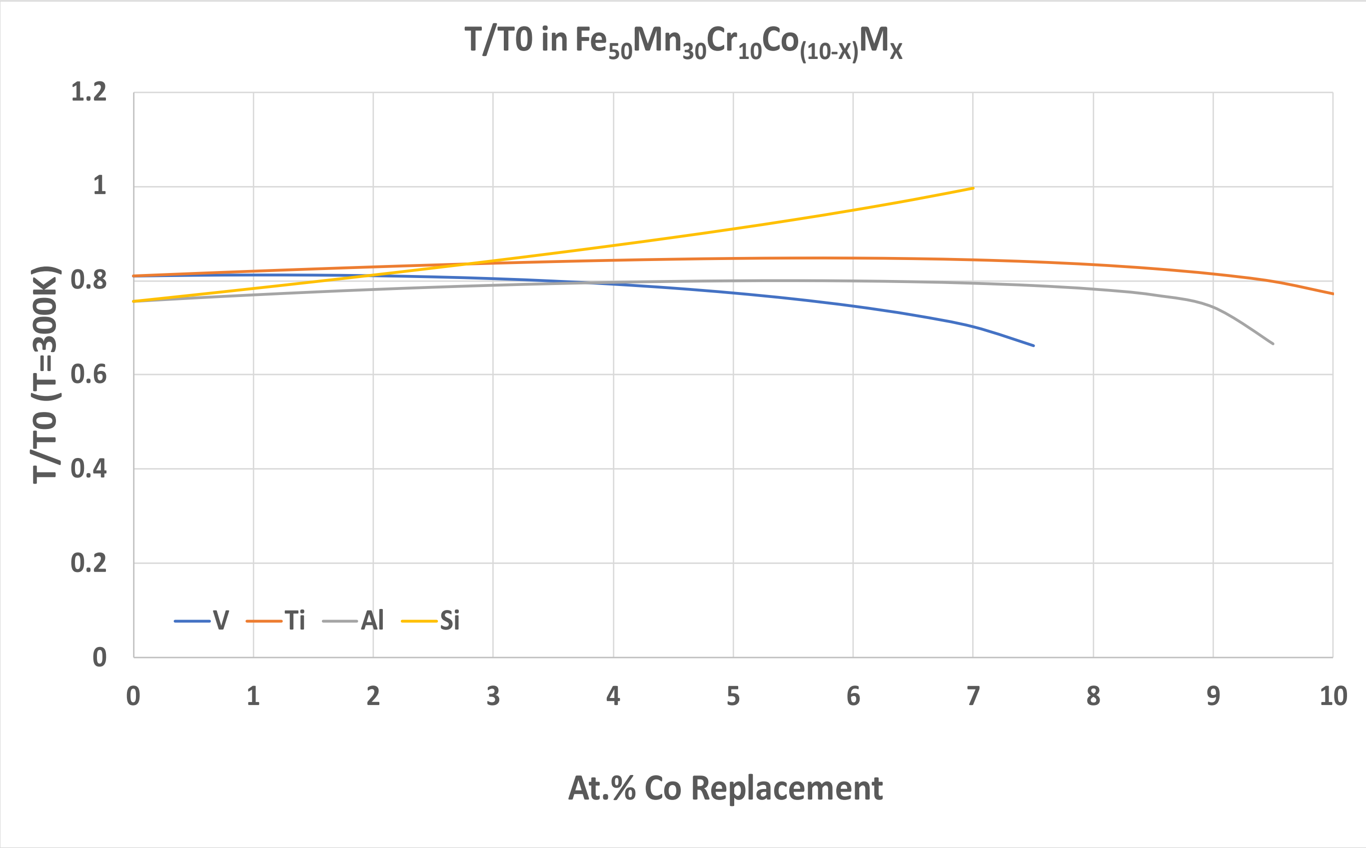
Performance-Driven Systems Approach to Alloy Design



Mishra, R. S., Haridas, R. S. & Agrawal, P. High entropy alloys – Tunability of deformation mechanisms through integration of compositional and microstructural domains. *Materials Science and Engineering A* vol. 812 141085 (2021).

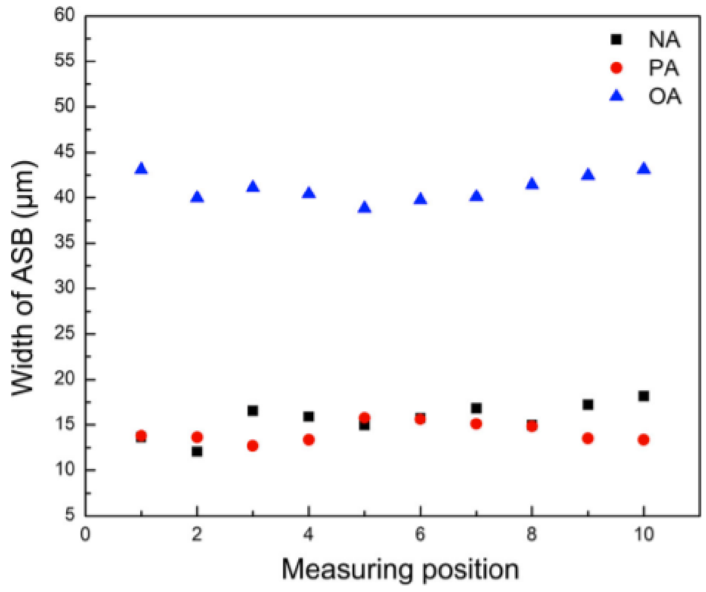
T_0 Screening - $Fe_{50}Mn_{30}Cr_{10}Co_{(10\text{-}X)}M_X$ Family

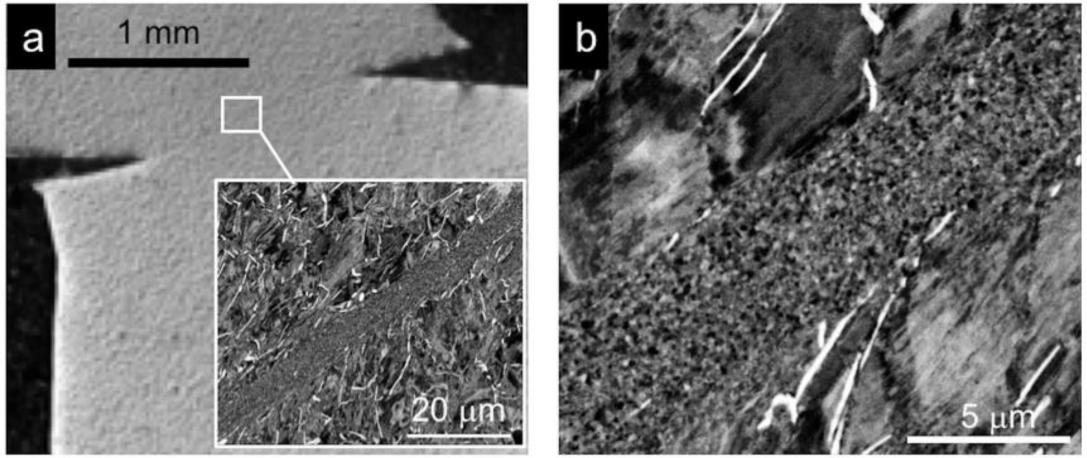
- Tried many $Fe_{50}Mn_{30}Cr_{10}Co_{(10\text{-}X)}M_X$ derivatives of landmark TRIP-MPEA
- V, Ti, Al all reduce T/T_0 (i.e promote TRIP)
- V is strongest T/T_0 reducer
- Problem – avoiding σ phase formation – need kinetics studies
- Are $M_{23}C_6$, M_7C_3 & η carbides preferable to σ in this setting?



Adiabatic Shear Banding & Microstructure

- Some evidence that aging affects ASB formation, morphology
- Zhang et al. (*J Mater Sci* June 2020) – ASBs in Al-Zn-Mg-Cu wider in overaged vs peak
- Wider ASB → higher critical strain/strain rate to form (Xue et al., *Acta* 44 1996)
- Peak age vs overage – different substructure in dynamic loading → diff shear localization behavior
- Torsion Kolsky best way to assess
- Also evidence of ASB dissolution of γ' (Colliander et al. *Phil Letters* Sept 2020)

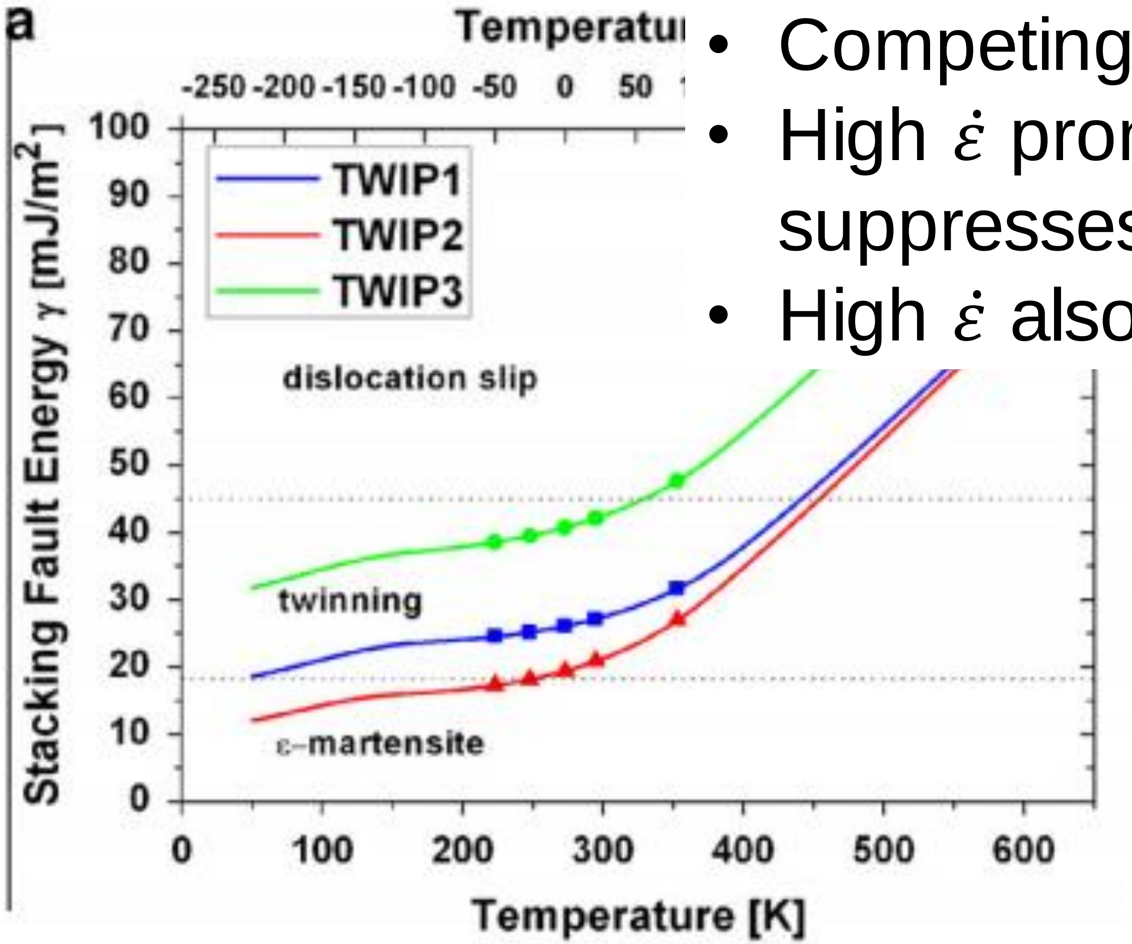


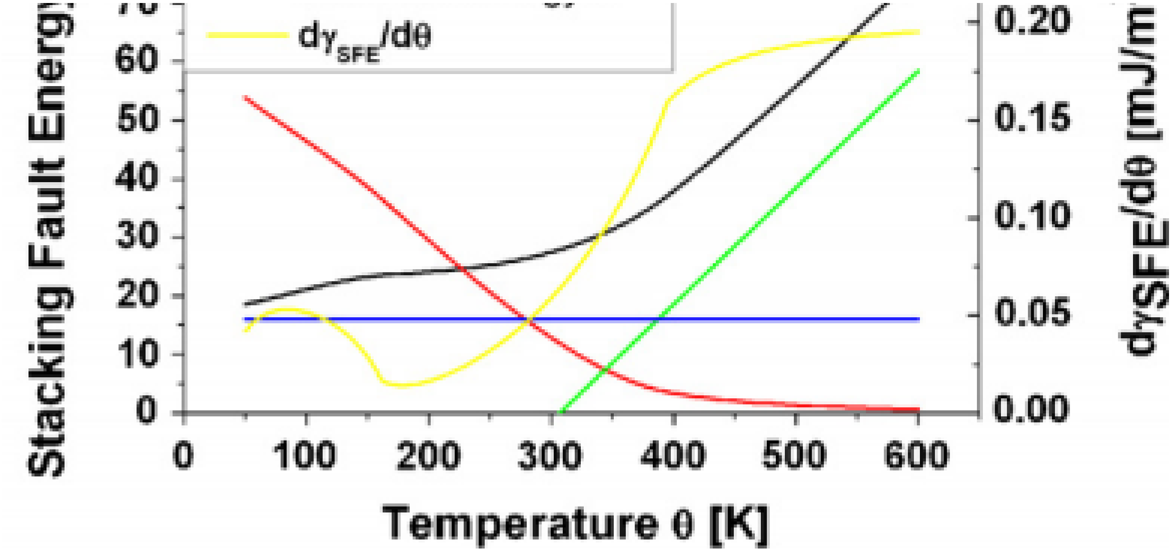


SFE, Temperature & Strain Rate Effects on Deformation Mechanism

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Competing $\dot{\varepsilon}$ effects
- High $\dot{\varepsilon}$ promotes twinning, but also raises T → suppresses twinning
- High $\dot{\varepsilon}$ also promotes HCP TRIP but not BCC



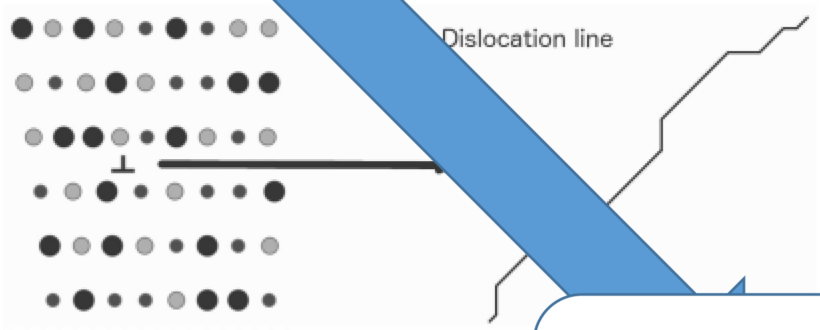


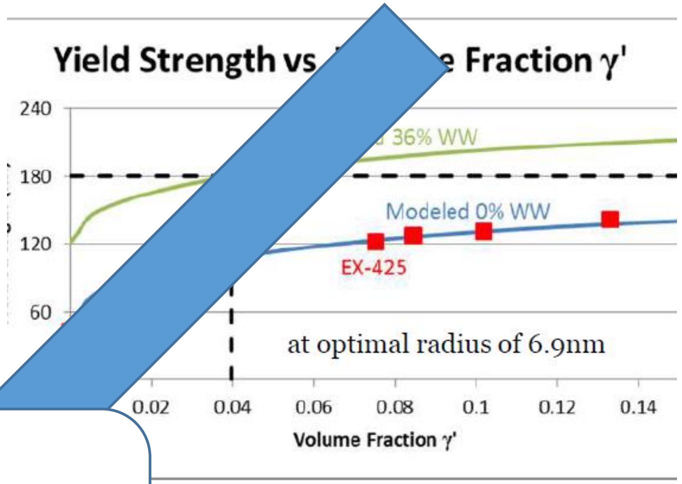
Curtze, S., and V. T. Kuokkala. "Dependence of Tensile Deformation Behavior of TWIP Steels on Stacking Fault Energy, Temperature and Strain Rate." *Acta Materialia* 58, no. 15 (September 1, 2010): 5129–41. https://doi.org/10.1016/J.ACTAMAT.2010.05.049.

Alloy Design Strategy – Yield Strength

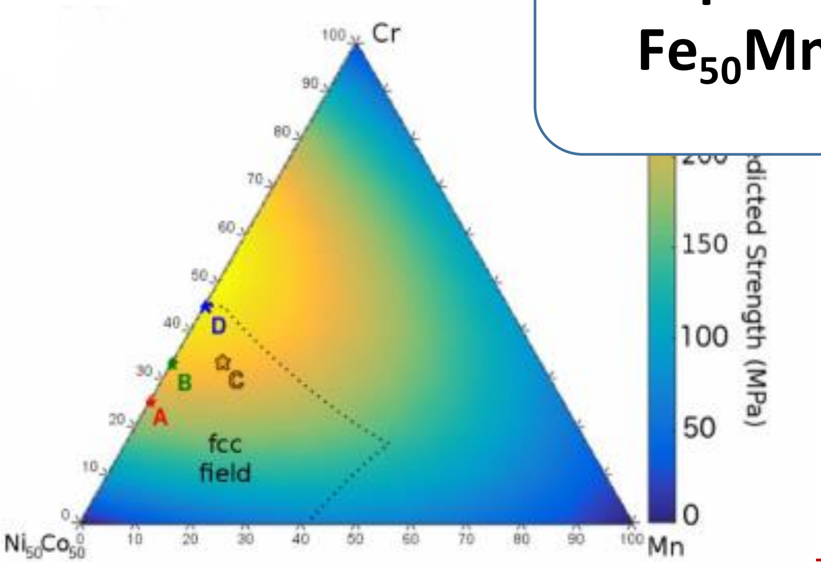
Solid Solution Strengthening

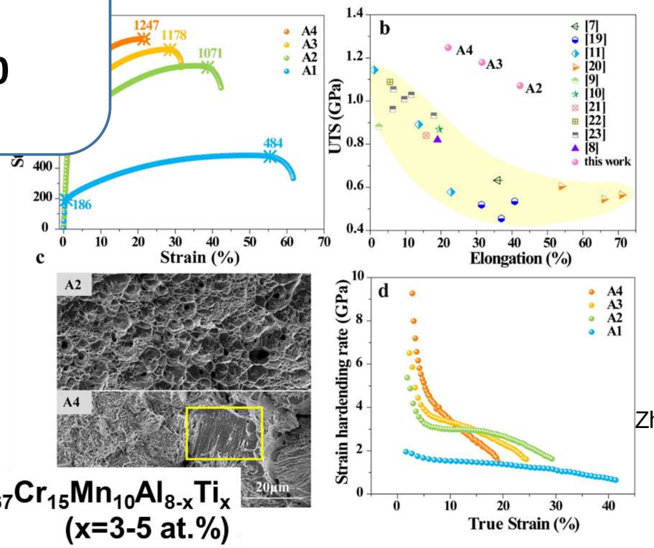
γ' Precipitate Strengthening





Improved YS over $Fe_{50}Mn_{30}Co_{10}Cr_{10}$



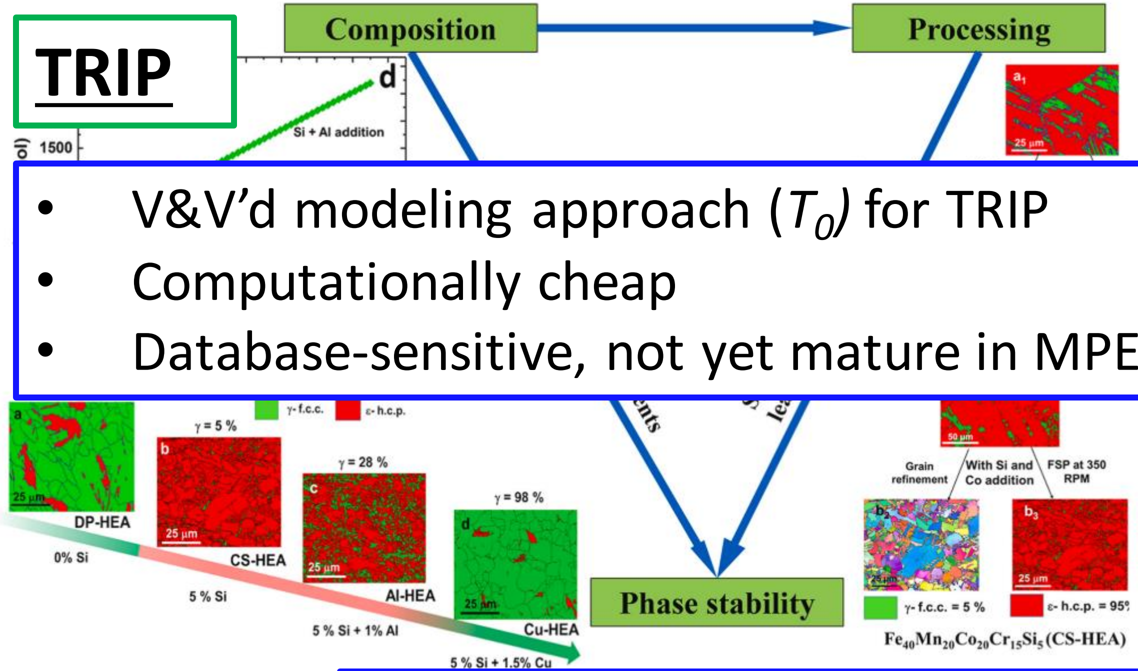


$(FeNi)_{67}Cr_{15}Mn_{10}Al_{8-x}Ti_x$ (x=3-5 at.%)

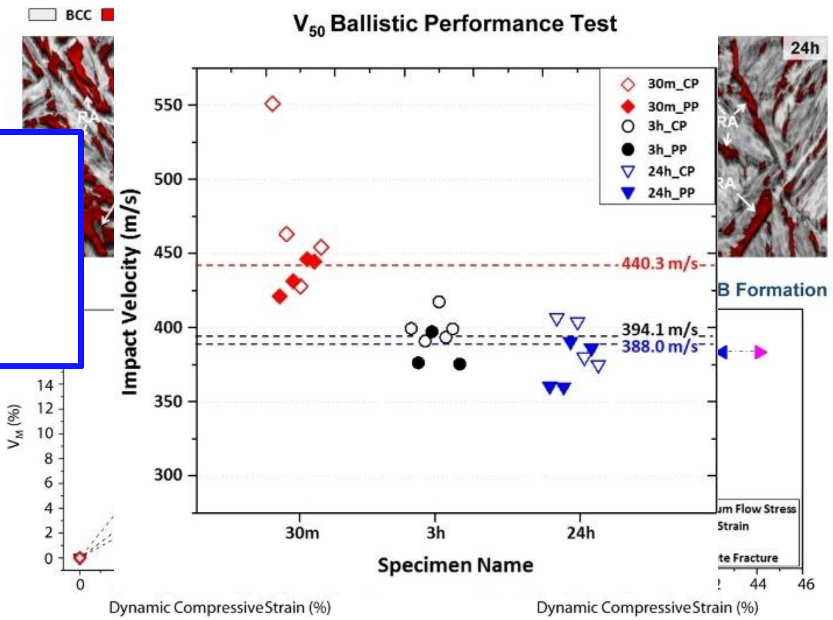
Zhao, Y. L. et al. Development of high-strength Co-free high-entropy alloys hardened by nanosized precipitates. *Scr. Mater.* 148, 51–55 (2018).

Alloy Design Strategy – Post-Yield Behavior

TRIP



- V&V'd modeling approach (T_0) for TRIP
- Computationally cheap
- Database-sensitive, not yet mature in MPEAs

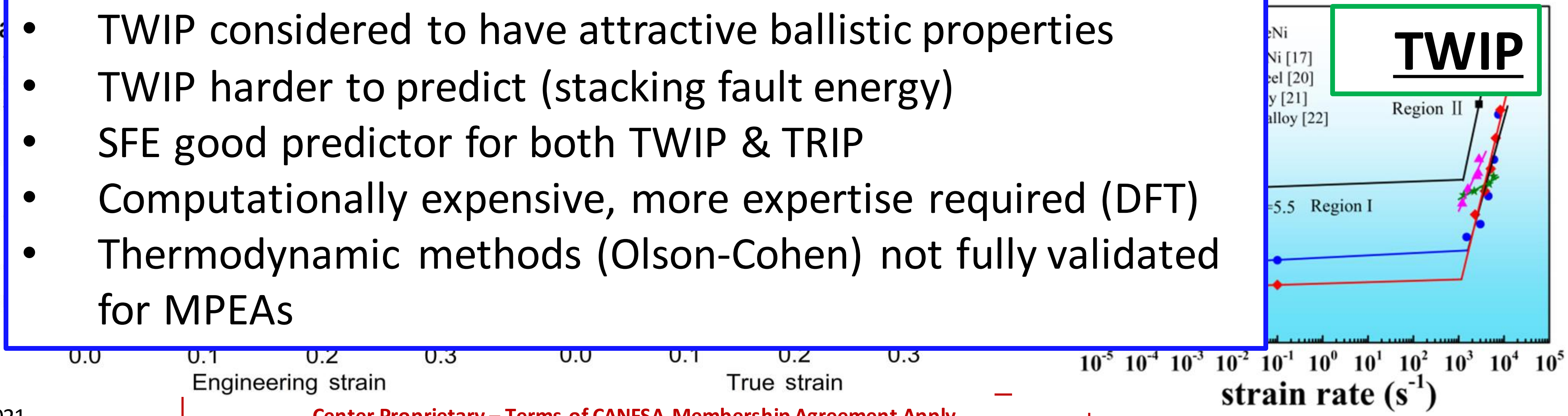


W. Jiang et al, Dynamic impact behavior and deformation mechanisms of Cr26Mn20Fe20Co20Ni14 high-entropy alloy, *Mater Sci Eng A* (824) September 2021

L. Wang et al, Mechanical response and deformation behavior of Al0.6CoCrFeNi high-entropy alloys upon dynamic loading, *Mater Sci Eng A* (727) June 2018

- TWIP considered to have attractive ballistic properties
- TWIP harder to predict (stacking fault energy)
- SFE good predictor for both TWIP & TRIP
- Computationally expensive, more expertise required (DFT)
- Thermodynamic methods (Olson-Cohen) not fully validated for MPEAs

TWIP



End User Context – Growth in Protective Structure Requirements

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS