Project 26: Deformation Mechanisms in Refractory-Based Complex, Concentrated Alloys

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Student: Francisco Gil Coury (CSM)
Faculty: Drs. Michael Kaufman and Amy Clarke (CSM)
Industrial Mentor: Drs. Kevin Chaput and Todd Butler (AFRL)
Other Participants : John Foltz (ATI), Paul Mason (Thermo-Calc)

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Center for ADVANCED NONFERROUS STRUCTURAL ALLOYS

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Project 26: Deformation Mechanisms in Refractory-Based Complex, Concentrated Alloys

- Student: Francisco Coury (Mines)
- Advisor(s): Michael Kaufman, Amy Clarke (Mines)

Project Duration

PhD: August 2015 to July 2018

Problem: Main factors that control strength and ductility of refractory complex, concentrated alloys (RCCAs) are not fully understood

Objective: Describe the mechanical behavior of RCCAs by means of conventional strengthening theories

Benefit: Improved understanding of strength and ductility will lead to more efficient alloy design.

Recent Progress

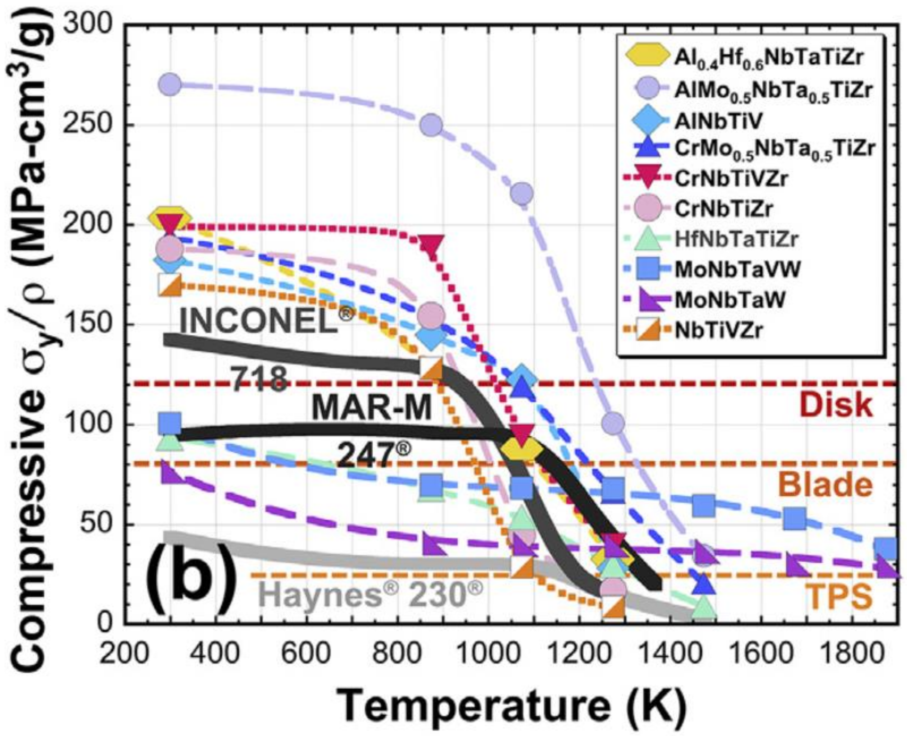
- Finished alloy characterization on as-cast and heat-treated conditions
- Started compression tests at different temperatures in different single phase alloys
- Developed modelling framework to interpret thermally activated deformation
- Modified athermal solid solution strengthening model for body centered cubic alloys

Metrics

Description	% Complete	Status
1. Literature review	100%	●
2. Production and characterization of as-cast alloys	100%	●
3. Heat-treating, processing and characterization of the heat-treated/processed material	100%	●
4. Mechanical testing the different alloys at different temperatures	90%	●
5. Develop methodology for interpreting strength of the RCCAs	50%	●

Industrial Relevance

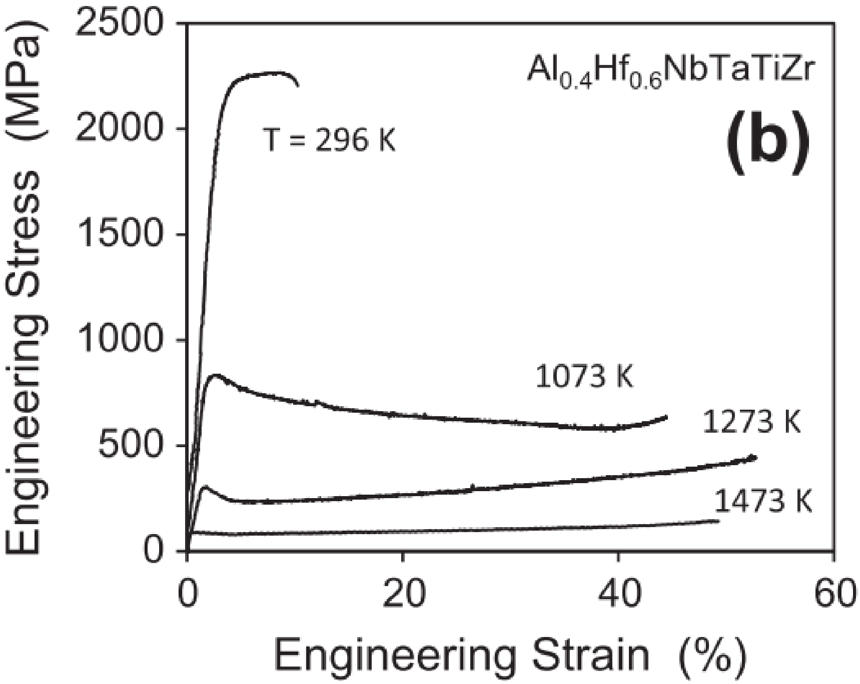
- New class of materials – early work by Senkov et al. (2011)
- Goal of expanding the applicability of refractory metals
    - High temperature strength
    - Low density
    - Easy to process
    - Better oxidation resistance



D.B. Miracle and O.N. Senkov, Acta Mater. **122**, 448 (2017).

Challenges in RCCA Development

- Typical drawbacks with refractory alloys
  - Poor room temperature ductility and toughness
  - Poor corrosion and oxidation resistance
- Specific challenges with RCCA approach
  - Broad composition space
    - Several possible compositions
    - Experimentally challenging



Senkov, O. N., Senkova, S. V. & Woodward, *Acta Mater.* **68,** 214–228 (2014).

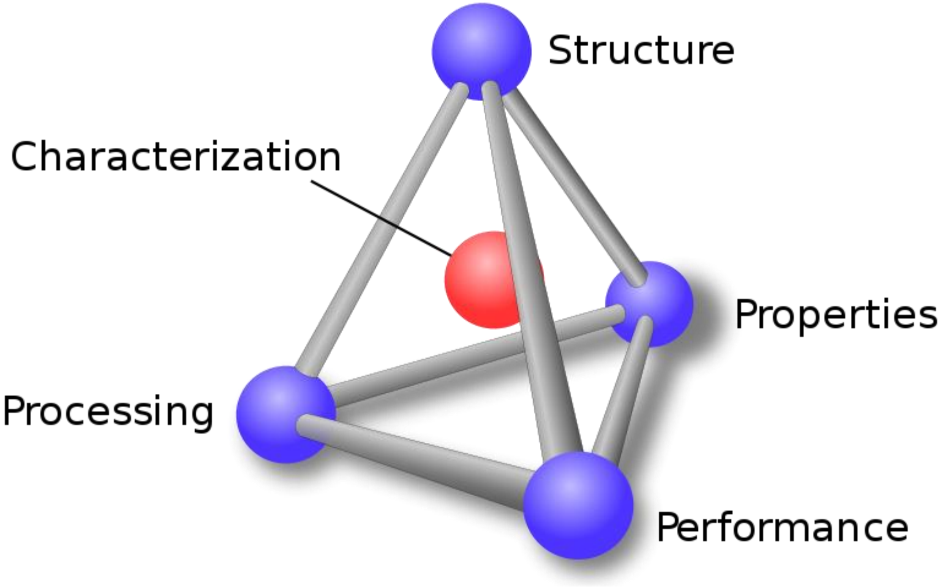
Butler, T. M., Chaput, K. J., Dietrich, J. R. & Senkov, O. N.. *J. Alloys Compd.* **729,** 1004–1019 (2017).

Where Do We Start?

- Need composition dependent models to predict properties
- For RCCAs:
    - Phase equilibria
    - Strength
    - Ductility
    - Oxidation

Motivation and Methodology

- Can we understand the strength and ductility?
  - Industrially-relevant compositions
- Approach
  - Phase equilibria
  - Microstructure
  - Processing
  - Mechanical properties

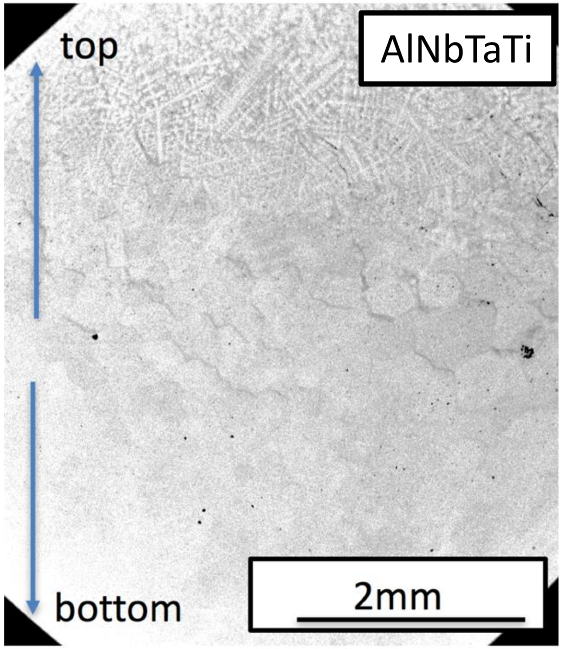


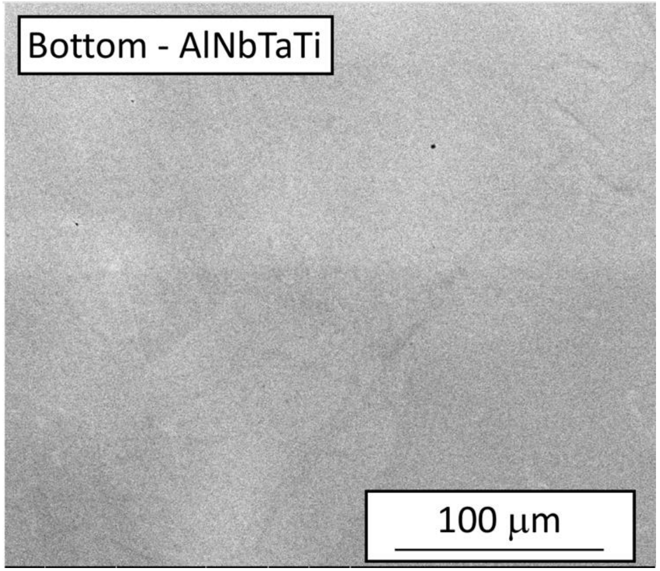
Alloy Selection

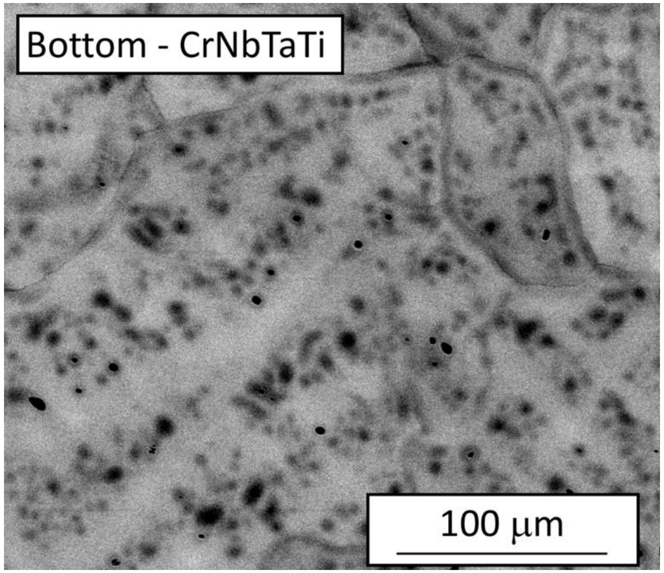
- 13 alloys using the following criteria:
  - BCC crystal structure
  - Density < 13 g/cm^3
  - Cost < $500/kg
  - No noble or rare elements
  - Fraction of binaries in thermodynamic database > 0.5
  - Small solidification range
  - No volatile elements
  - Low content of σ phase
- Cast and heat-treated at 1400 °C for 35 h

AlCrMoNb
AlHfTaTi
AlHfNbTi
AlMoNbTi
AlNbTaTi
WNbTaTi
HfNbTaTi
MoNbTaTi
CrNbTaTi
CrMoTaTi
CrMoNbTi
CrNbTiW
CrTaTiW

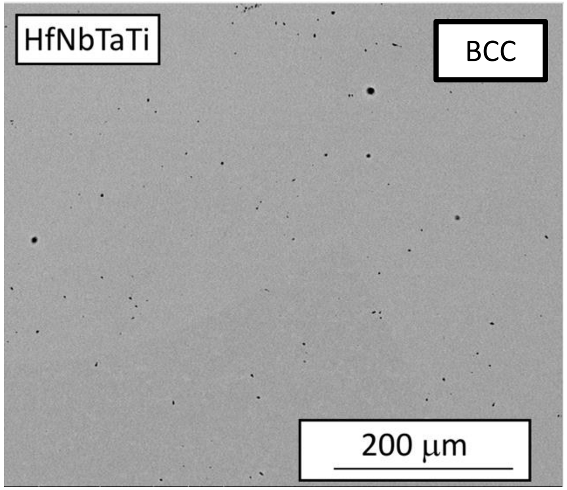
Microstructure of As-Cast Alloys

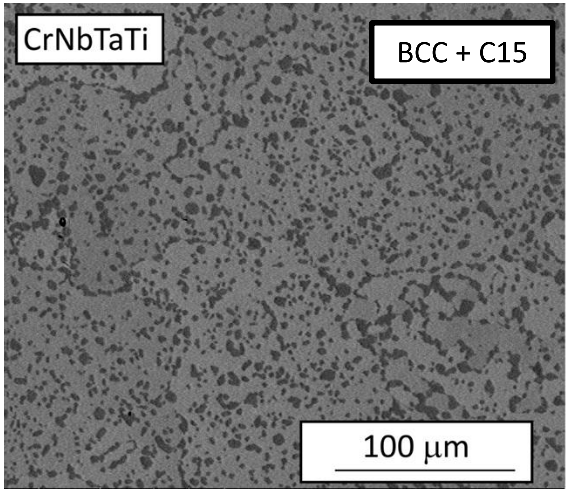


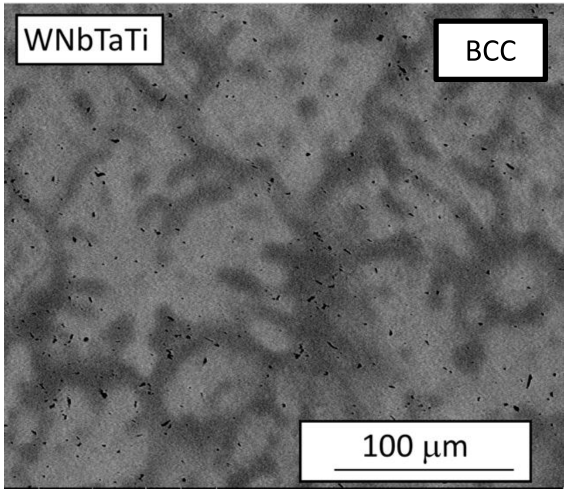


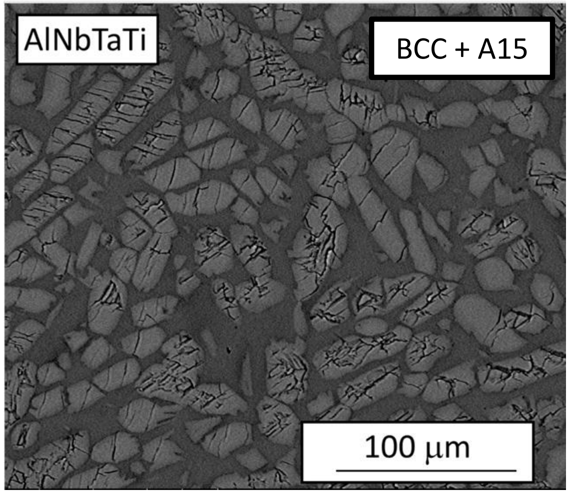


Microstructure of Heat-Treated Alloys

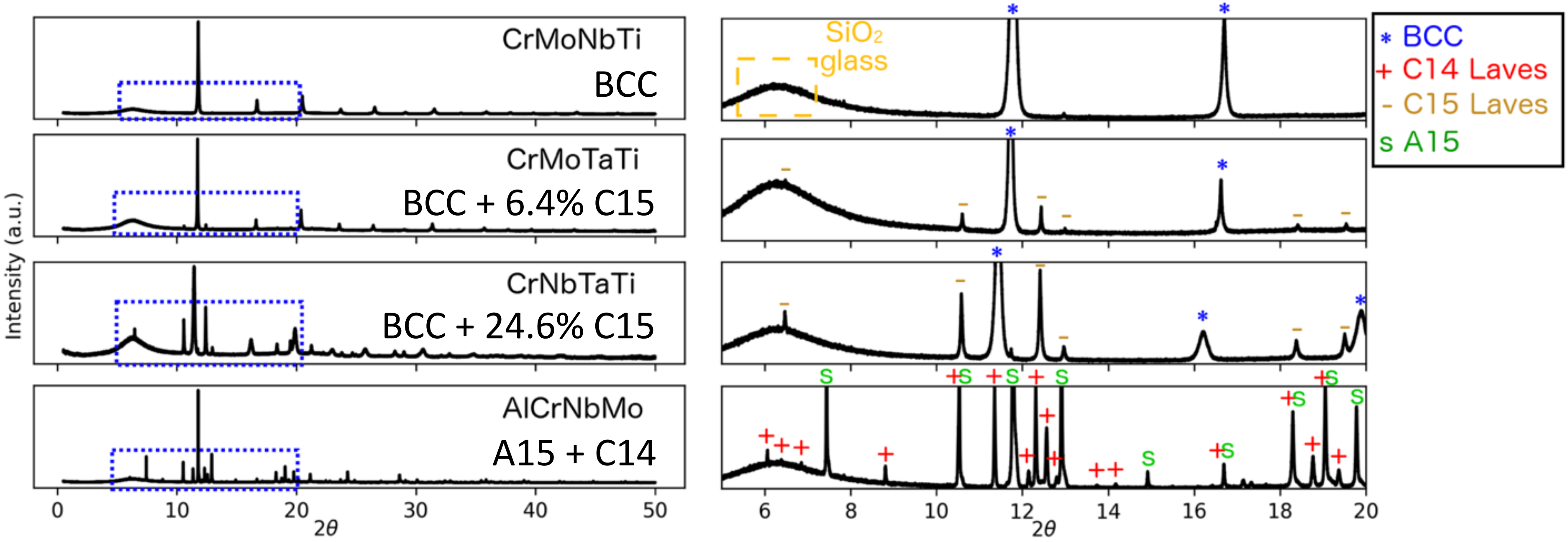








Synchrotron XRD Analysis of Cr-Containing Alloys



Models for Phase Prediction

- Empirical models based on Hume-Rothery rules
  - Delta (δ): atomic radii differences
  - Omega (Ω): differences in enthalpies, entropies of mixing and melting temperature
  - Delta chi ($\Delta\chi$): electronegativity

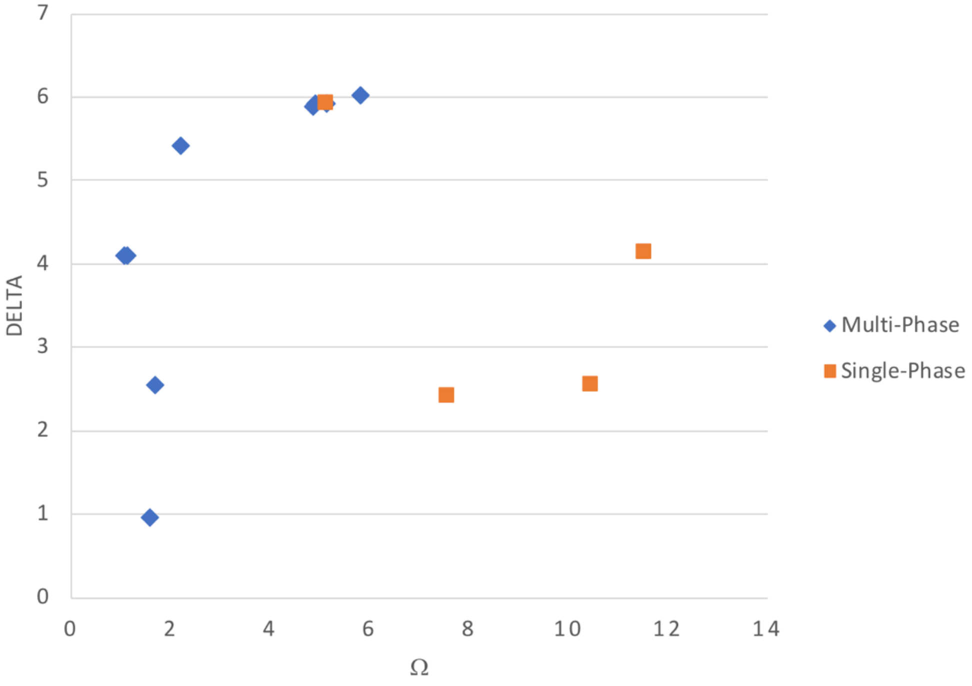
$$\delta = \sqrt{\sum_{i=1}^{N} x_i \left(1 - x_i / \sum_{j=1}^{N} x_j r_j\right)^2}$$

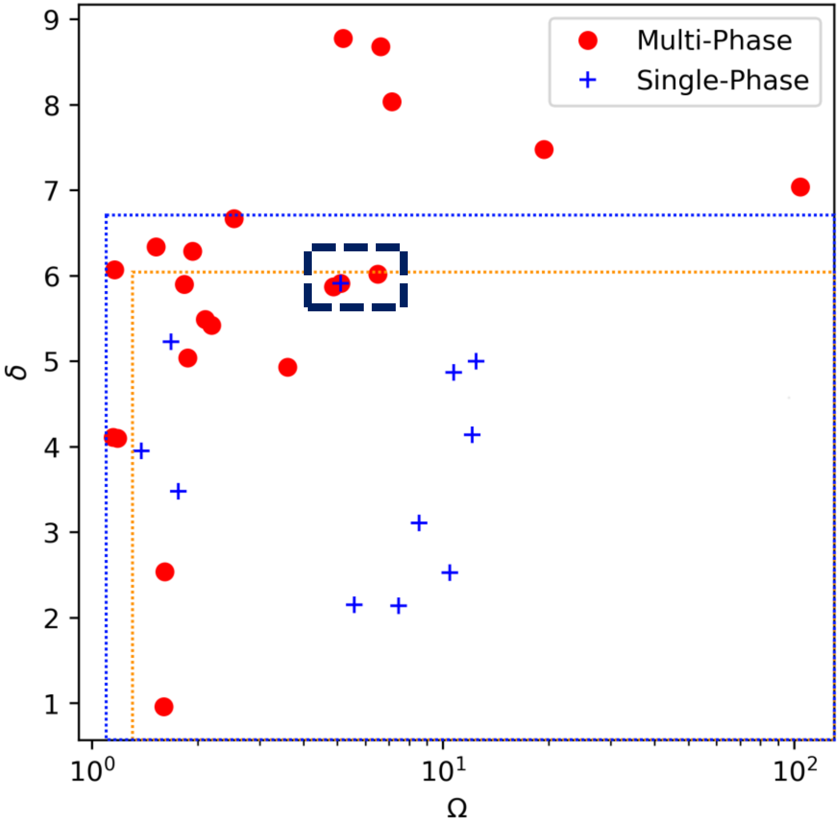
$$\Omega = \frac{T_\mathrm{m} \Delta S_\mathrm{mix}}{|\Delta H_\mathrm{mix}|}$$

$$\Delta\chi = \sqrt{\sum_{i=1}^{N} x_i \left(\chi_i - \sum_{j=1}^{N} x_j \chi_j\right)^2}$$

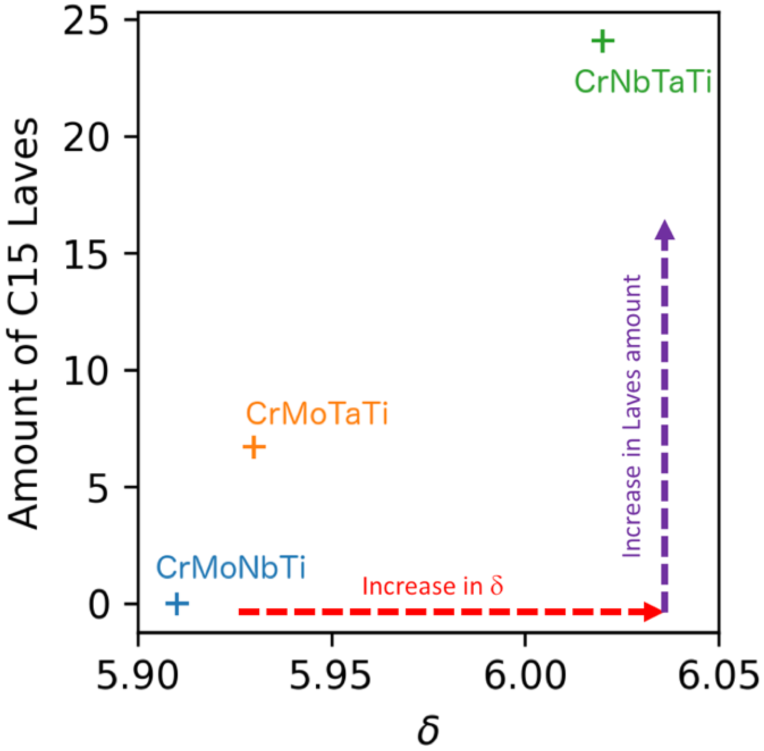
- CALPHAD: Thermo-Calc®, Pandat™
  - Minimize free energy in a given system

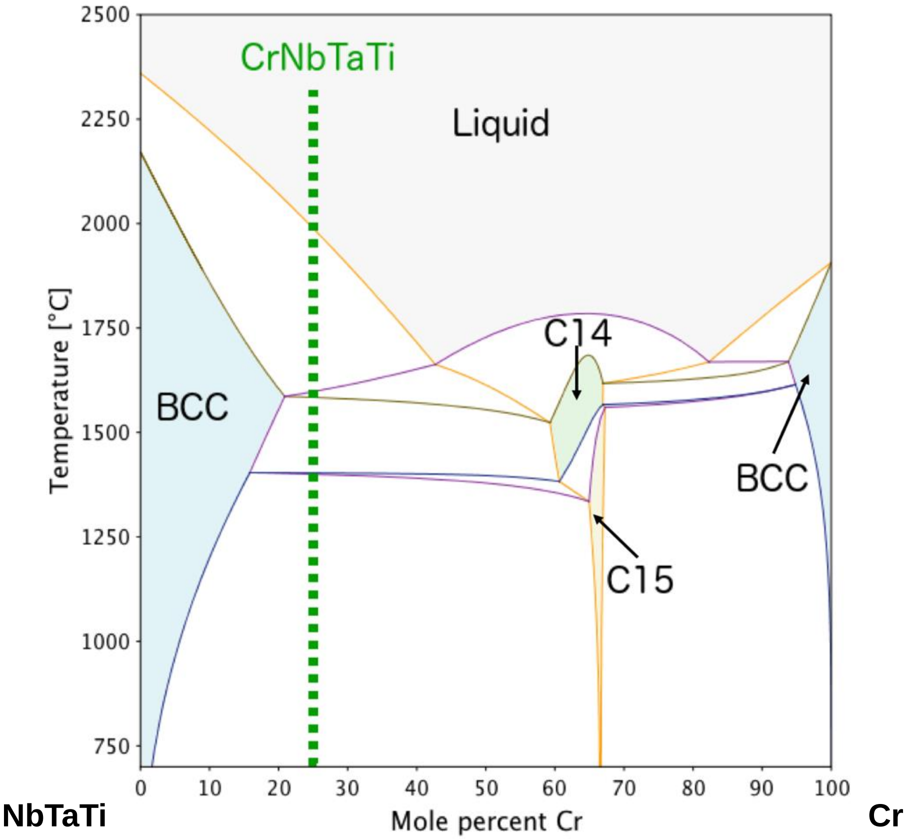
Empirical Phase Predictions





C15 Laves Phase Scales With δ





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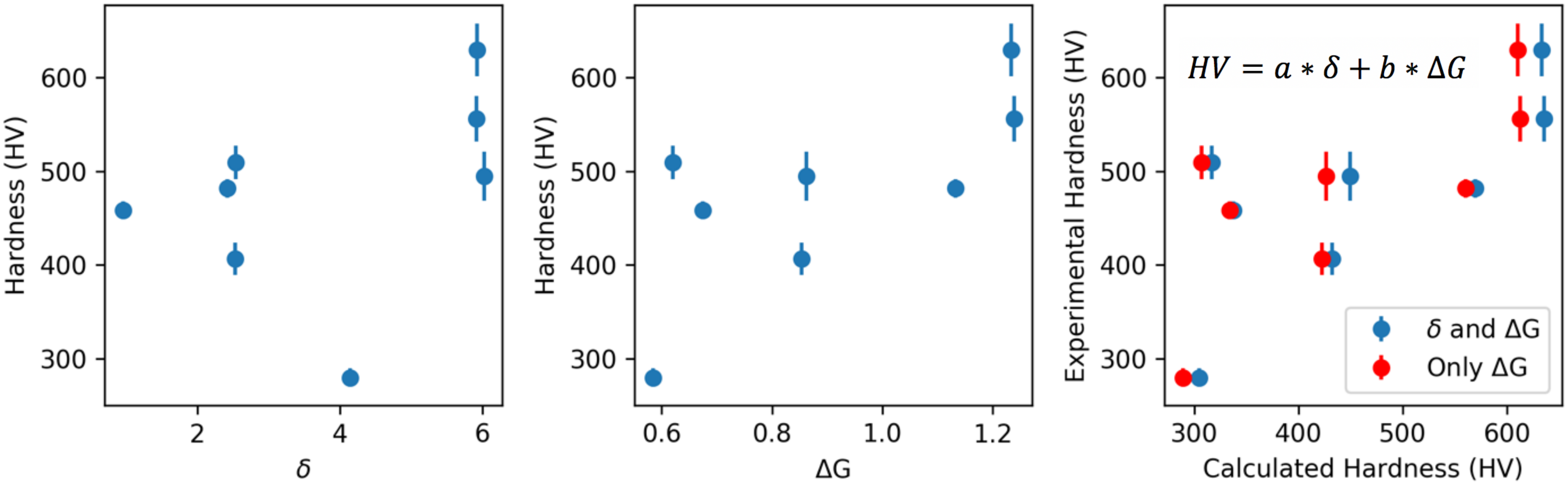
CALPHAD Predictions

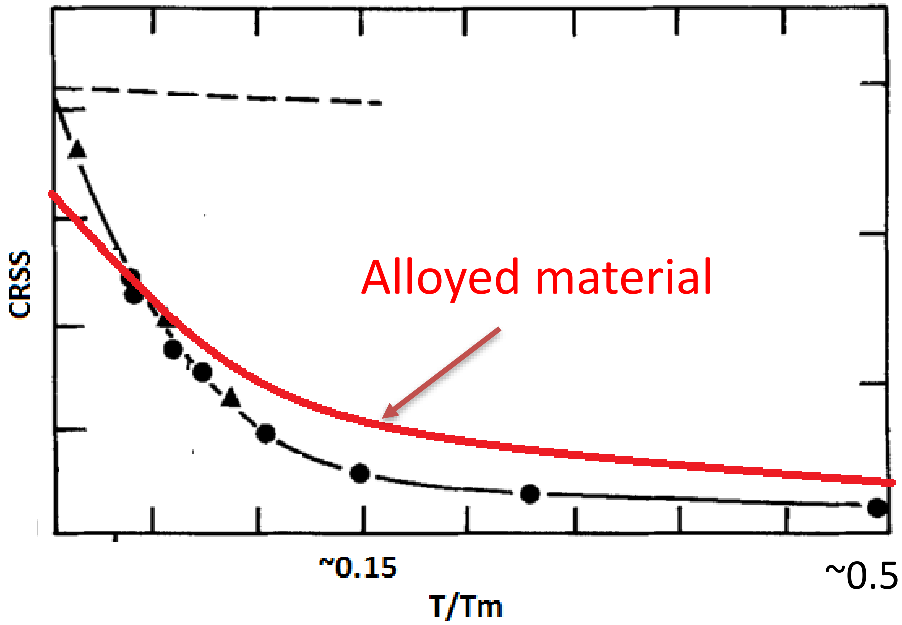
- TCHEA2 predicts correct phases in 9 of 12 alloys
  - Except B2 phase in AlHfNbTi and AlHfTaTi
  - AlMoNbTi is not single-phase
- Temperatures and volume fractions need further refinement
- Significant improvement over TCHEA1
  - C14, C15 and A15

Single-Phase RCCA Hardness

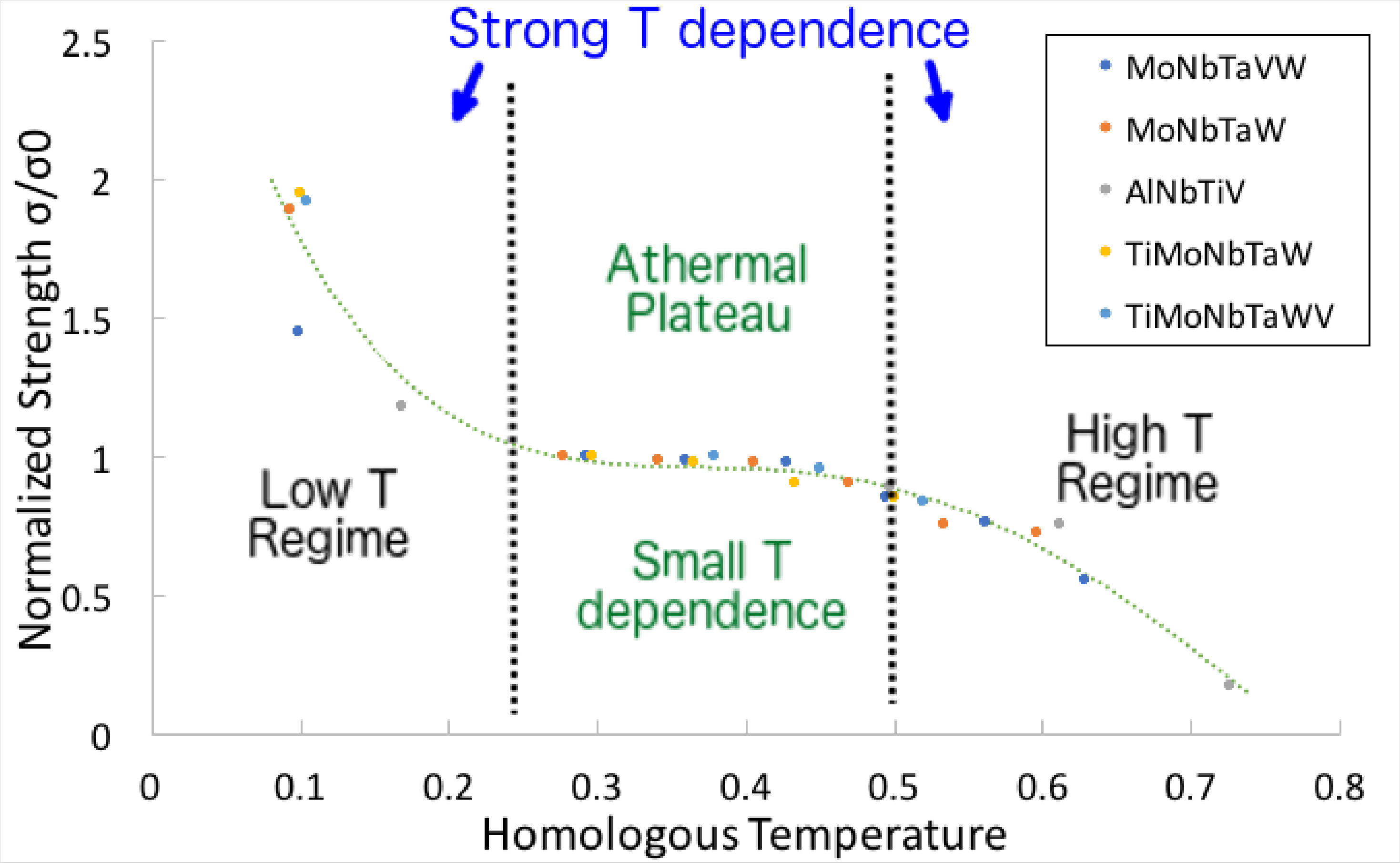


BCC Metals Deformation

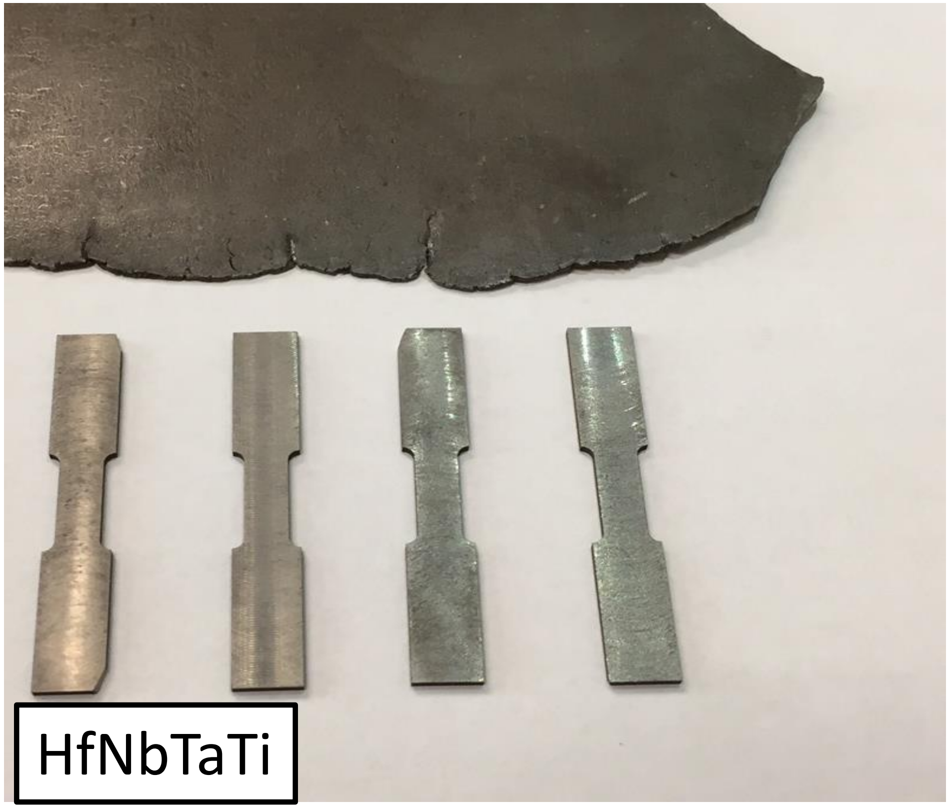
- Regimes II and III
  - High temperature dependence
  - Low mobility of screw dislocations
  - Brittle
- Regime I: athermal
  - Behavior closer to FCC metals
- Alloying changes the shape of the curve
  - Increases the plateau stress
  - Decreased temperature dependence in regime II
  - Softening in regime I

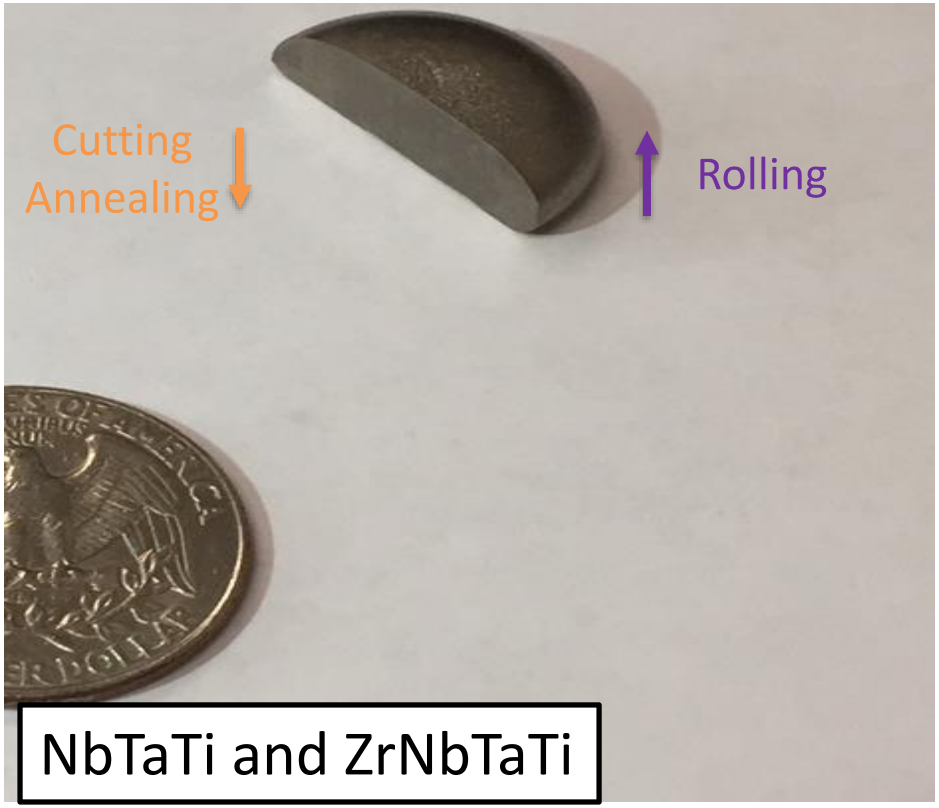


BCC RCCA Deformation



RCCA Cold Rolling


HfNbTaTi



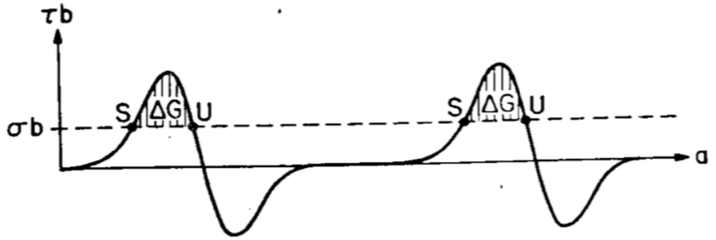
NbTaTi and ZrNbTaTi

Thermally Activated Deformation Modelling

Thermal and athermal contributions to strength:

$$\tau = \tau^* + \tau^a$$

Thermally activated barriers:



Activation barrier:

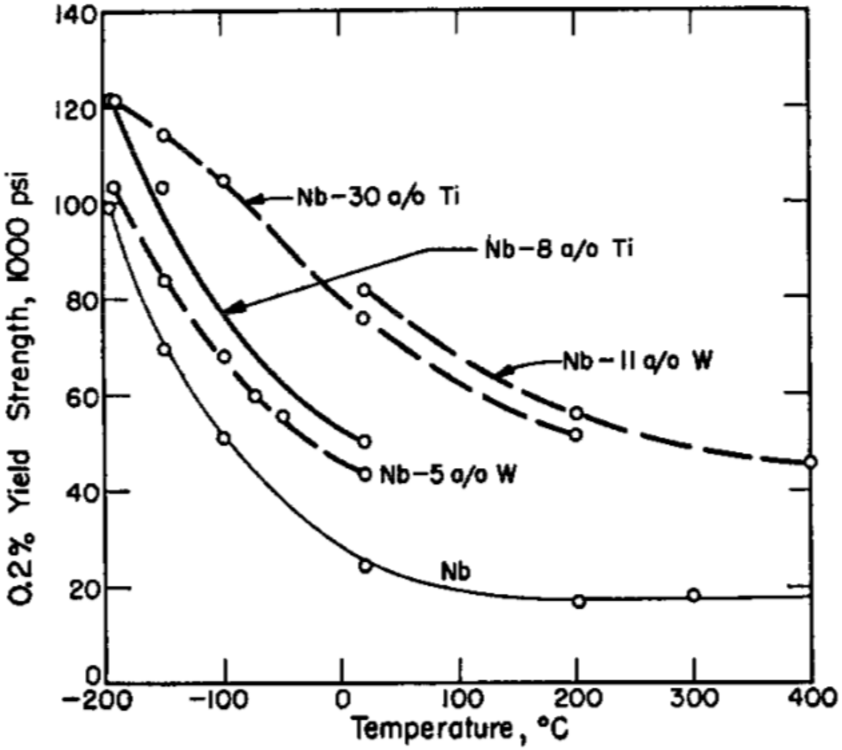
$$\Delta G = F_0 \left[1 - \left(\frac{\tau - \tau_i}{\tau_0 - \tau_i} \right)^p \right]^q = F_0 \left[1 - \left(\frac{\tau^*}{\tau_0^*} \right)^p \right]^q$$

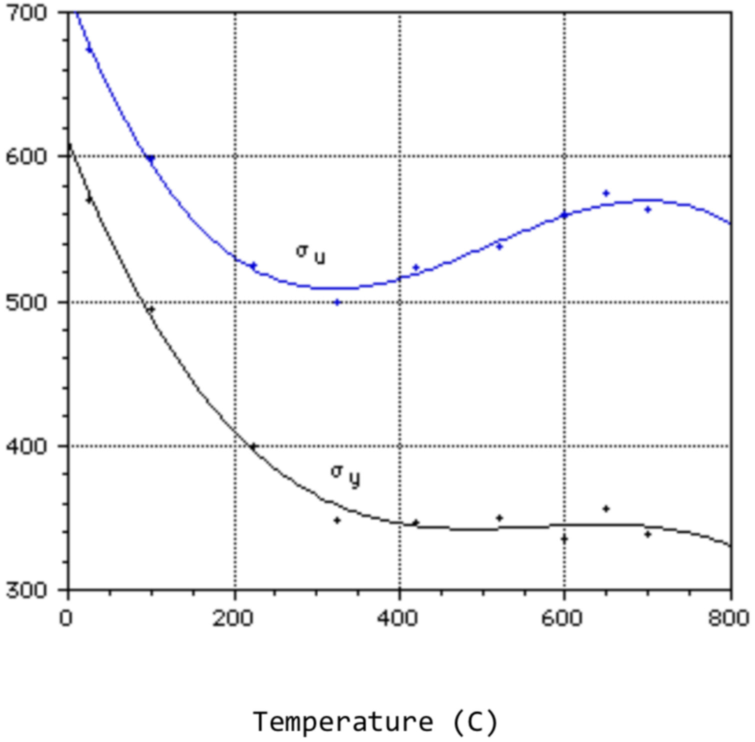
Elastic modulus softening correction:

$$\frac{\mu(T)}{\mu_0} = f(T)$$

The p and q values:
Shape of the barrier

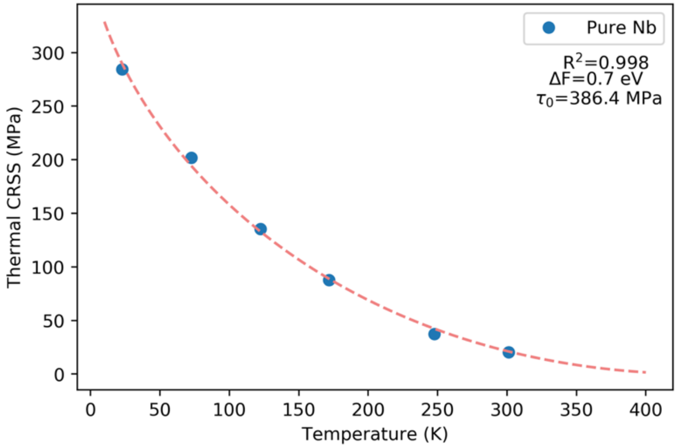
Application to Conventional Refractory Alloys

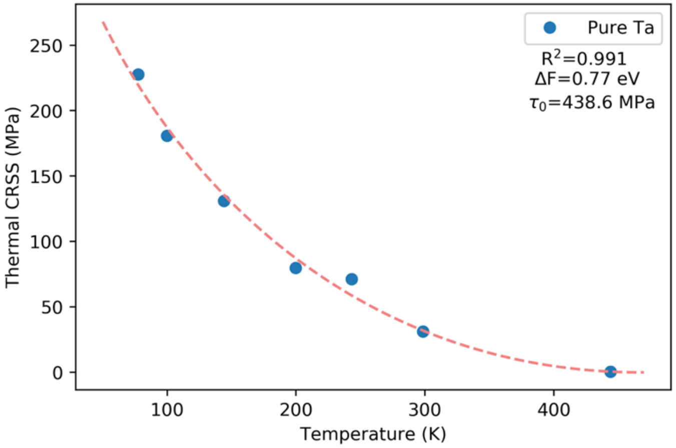


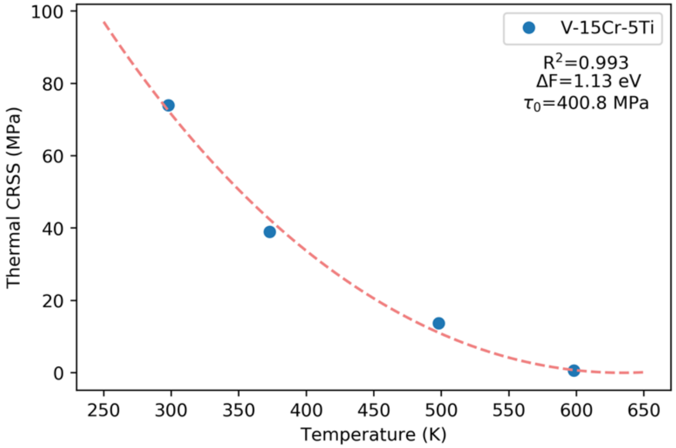


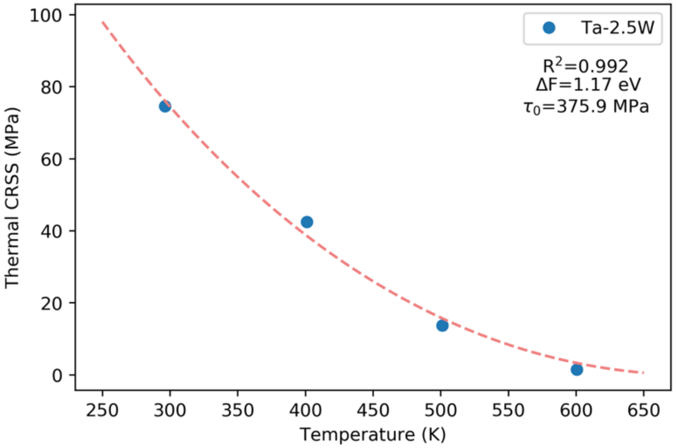
J.H. Bechtold, B. Road, J. Less-Common Met. 3 (1961) 1–12.
S. Stud, VANADIUM ALLOY (V-15Cr-5Ti), 2018.

Conventional Refractory Alloy Thermal Activation

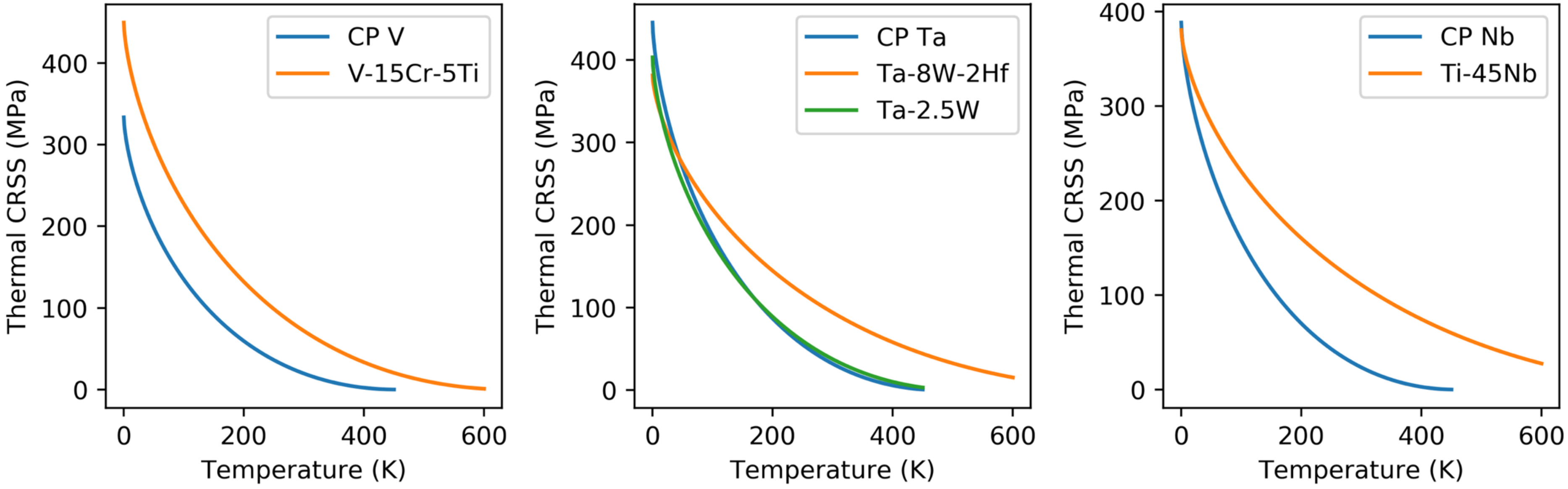






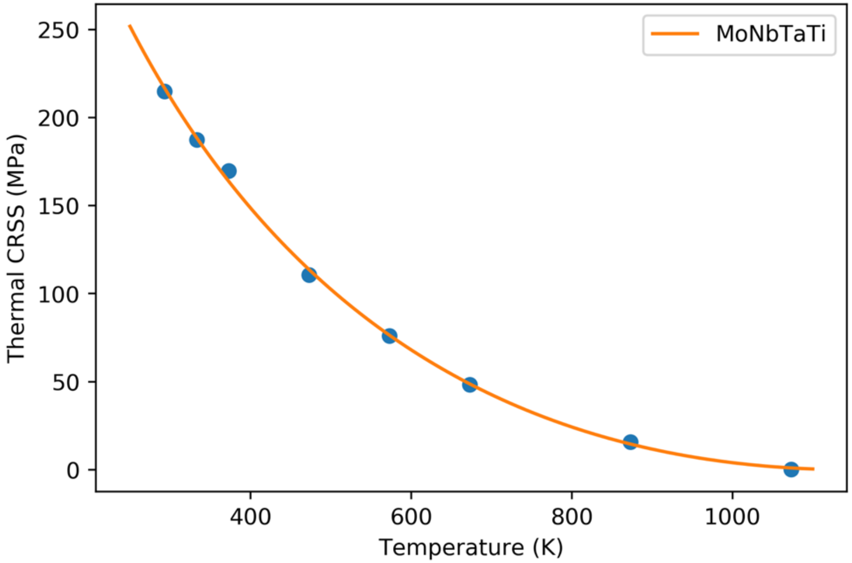


Conventional Refractory Alloy Comparison

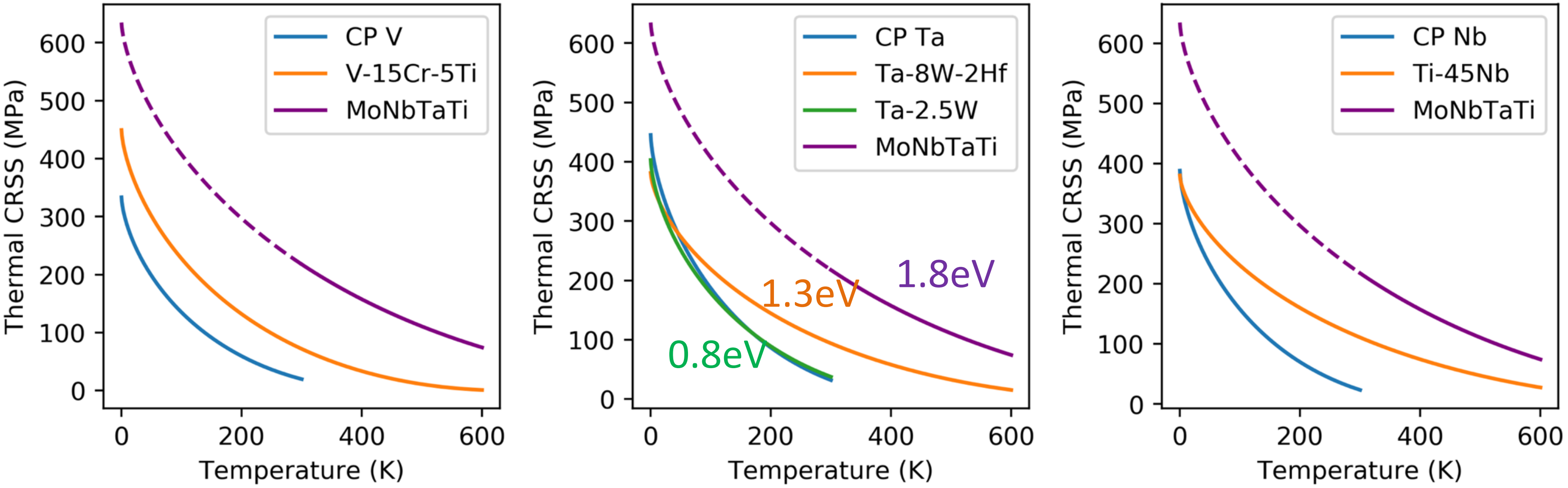


BCC Deformation at Low Temperatures

- Adapt σ-T models
  - Extract activation energies for double kink mechanism
  - Extrapolate the Peierls stress at 0K



Thermal Activation of RCCAs



Athermal Deformation Component

- Toda-Caraballo model (semi-empirical):

Original formulation:
Does not consider elastic modulus mismatch

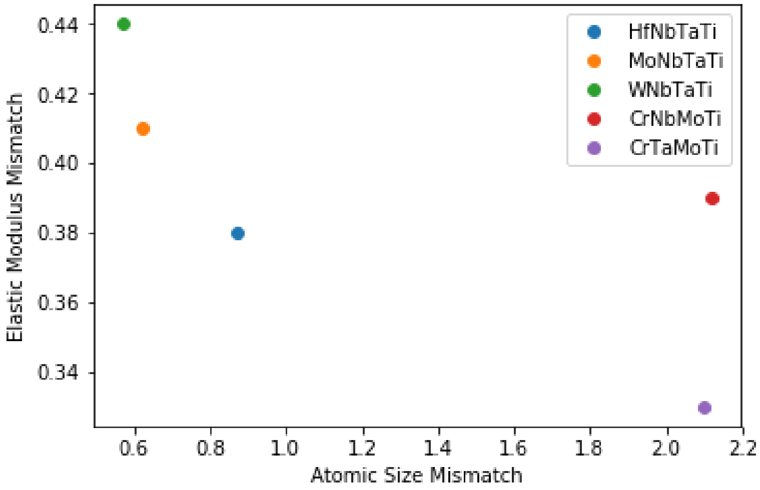
$$B = 3\mu Z\left[\xi\left(\boxed{\eta'^2} + \boxed{\alpha^2\delta^2}\right)^{1/2}\right]^{4/3}$$

Elastic Mismatch

Size Mismatch

$$\Delta\sigma_{ss}^{m} = 3Z\mu\left(\frac{\xi\alpha}{a}\right)^{4/3}(x_1,x_2,\ldots,x_n)\begin{pmatrix} 0 & \left|\frac{da}{x_1^2}\right|^{4/3} & \cdots & \left|\frac{da}{x_1^n}\right|^{4/3} \\ \left|\frac{da}{x_2^1}\right|^{4/3} & 0 & \cdots & \left|\frac{da}{x_2^n}\right|^{4/3} \\ \vdots & \cdots & \ddots & \vdots \\ \left|\frac{da}{x_n^1}\right|^{4/3} & \left|\frac{da}{x_n^2}\right|^{4/3} & \cdots & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}$$

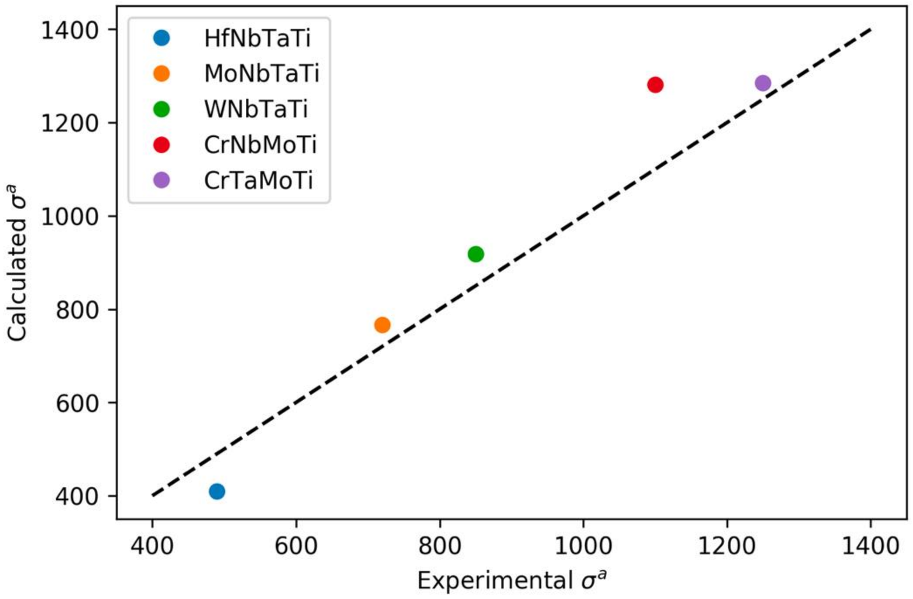
Alloy	Experimental σ^a (MPa)	Calculated σ^a (MPa)
HfNbTaTi	490	448
MoNbTaTi	720	580
WNbTaTi	850	608
CrMoNbTi	1000	2248
CrMoTaTi	1250	2475



Athermal Deformation Component

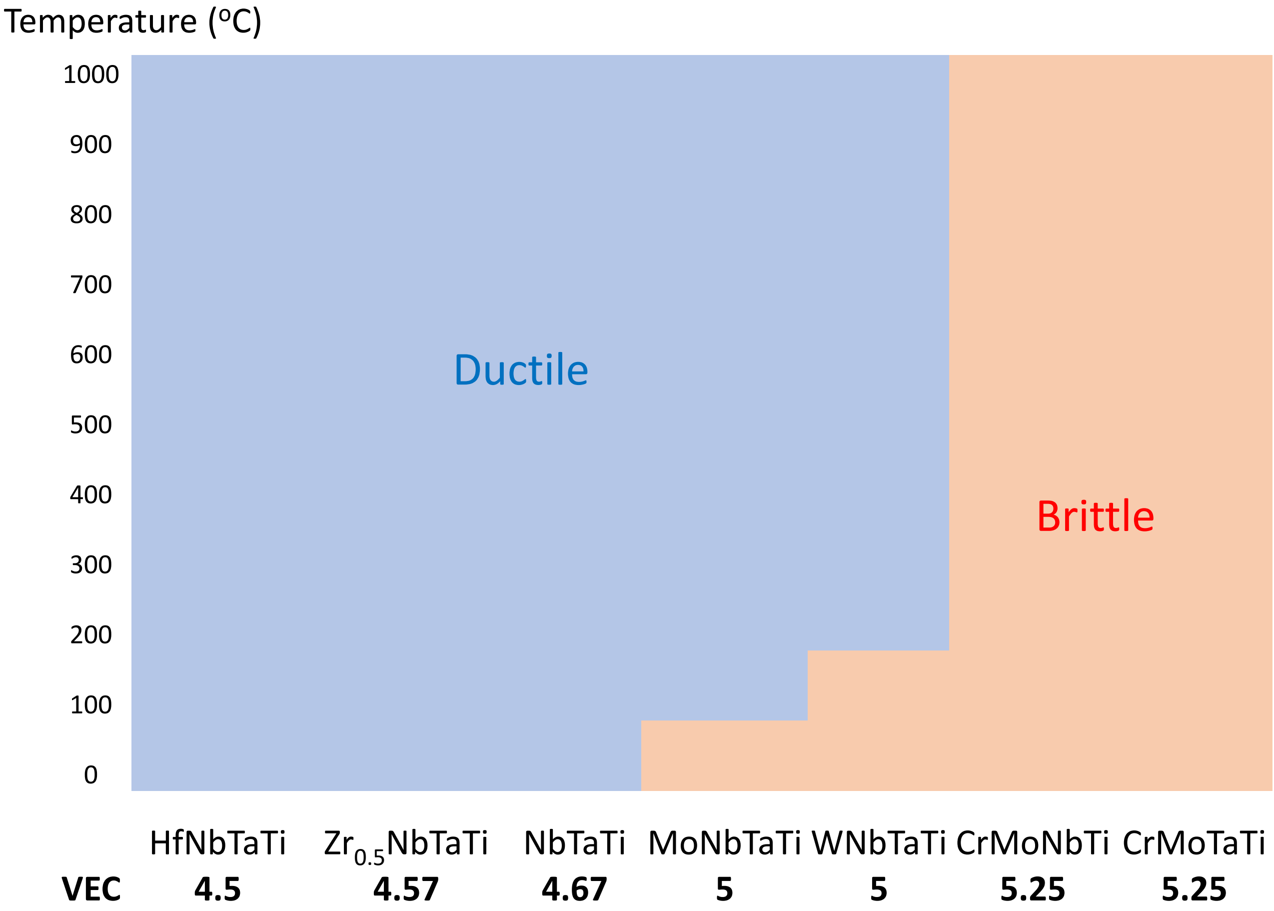
- Incorporate elastic mismatch
- Stronger alloys are outliers

Alloy	Experimental σ^a (MPa)	Calculated σ^a (MPa)
HfNbTaTi	490	410
MoNbTaTi	720	767
WNbTaTi	850	919
CrMoNbTi	1100	1282
CrMoTaTi	1290	1285



Ductility of RCCAs

- Ductility criteria
  - 30% compression without fracture
- Ductility increases with VEC



Summary

- TCHEA2 provides improved predictions
- Narrower δ and Ω window for RCCAs
- Athermal and thermal components needed for RCCAs
- The activation energy of RCCAs is larger than conventional refractory alloys
- Current models do not describe the athermal component
  - Incorporating elastic modulus mismatch improves predictions

Gantt Chart


Tasks
11 / 1 / 16
12 / 15 / 16
2 / 1 / 17
3 / 15 / 17
5 / 1 / 17
6 / 15 / 17
8 / 1 / 17
9 / 15 / 17
11 / 1 / 17
12 / 15 / 17
2 / 1 / 18
3 / 15 / 18
5 / 1 / 18
6 / 15 / 18
8 / 1 / 18
9 / 15 / 18
1 Literature Review
1.1 State of the Art of HEAs
1.2 Strength of Conventional Metals
2 Strength of A1 Alloys
2.1 Selection of Alloys
2.2 Casting and Rolling
2.3 Characterization
2.4 Mechanical Testing
2.5 Solid Solution Modeling
2.6 Nanoindentantion Modeling
3 Strength and Diuctility of A2 Alloys
3.1 Selection of Alloys
3.2 Castting
3.3 Characterization
3.4 Mechanical Testing
3.5 Solid Solution Modeling
3.6 Ductility Modeling
4 Writing Thesis

Thank you very much!

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