

# **Oxidation, Environmental Coatings and Phase Stability in Mo-Si-B Alloys and Diboride Systems**

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# Mo-Si-B Alloys and Diboride Systems for High-Enthalpy Environments : Design and Evaluation

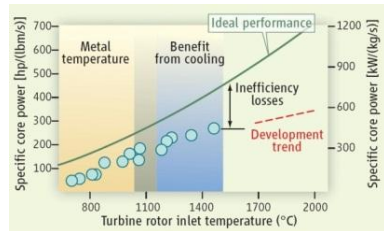
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## DESIGN STRATEGY

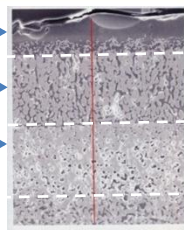
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SILICA

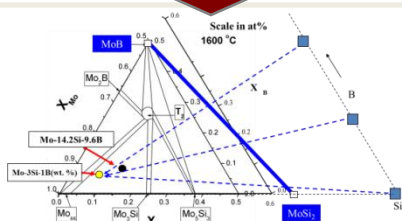
ZIRCONIA

ZrB<sub>2</sub>

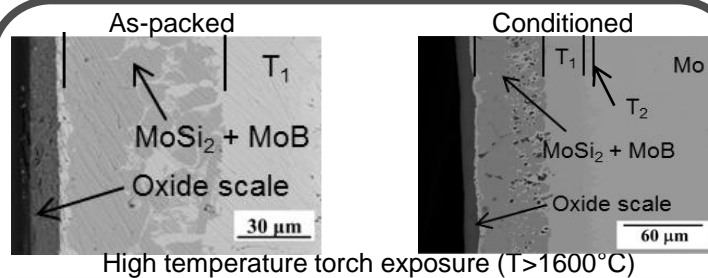


Oxidation test at 1627°C (air) for ten 10 min cycles

- Ni superalloys have reached a physical limit set by melting – coatings and new materials emerging
- Current coatings to increase operating temperature give marginal improvement and are susceptible to attack from salt and sand
- UHTCs show excessive recession during oxidation
- Novel high temperature coating needed



- Mo-Si-B alloys show phase stability at high temperature
- Mo-Si-B based coating can be deposited onto several different substrates independent of substrate types/compositions
- The resulting coating is adherent, provides protection from oxidation and is non-reactive with the underlying substrate (ZrB<sub>2</sub>/SiC/Al<sub>2</sub>O<sub>3</sub>)

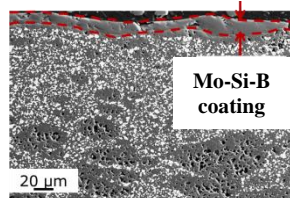
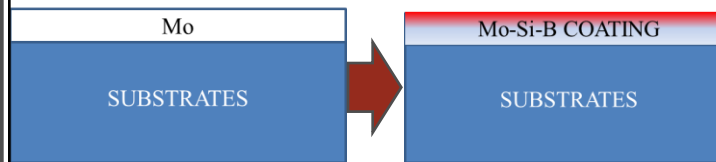


High temperature torch exposure ( $T > 1600^{\circ}\text{C}$ )

## EXTENDED COATING APPLICATION: 2-STEP PROCESS

Deposition of Mo via decomposition of  $\text{Mo}(\text{CO})_6$

Co-deposition of Si and B via pack cementation



Mo-Si-B coated 80SiC-20ZrB<sub>2</sub> after 12 hours at 1500°C in air

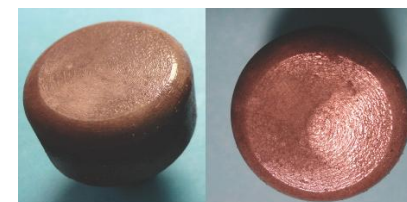
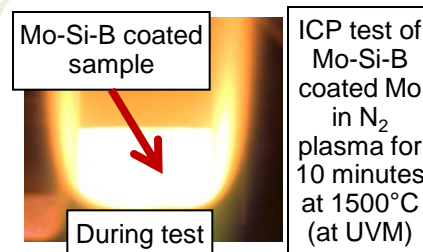
## HOW IT WORKS:

Conditioning treatment in air develops an outer layer of aluminoborosilica with good adherence and low permeability of oxygen

## ASSUMPTIONS AND LIMITATIONS:

- Mo is present within the glass
- Stability – retain B and Si in coating
- Long-term environmental resistance: high T plasma

QUANTITATIVE IMPACT



Pre-test Post-test

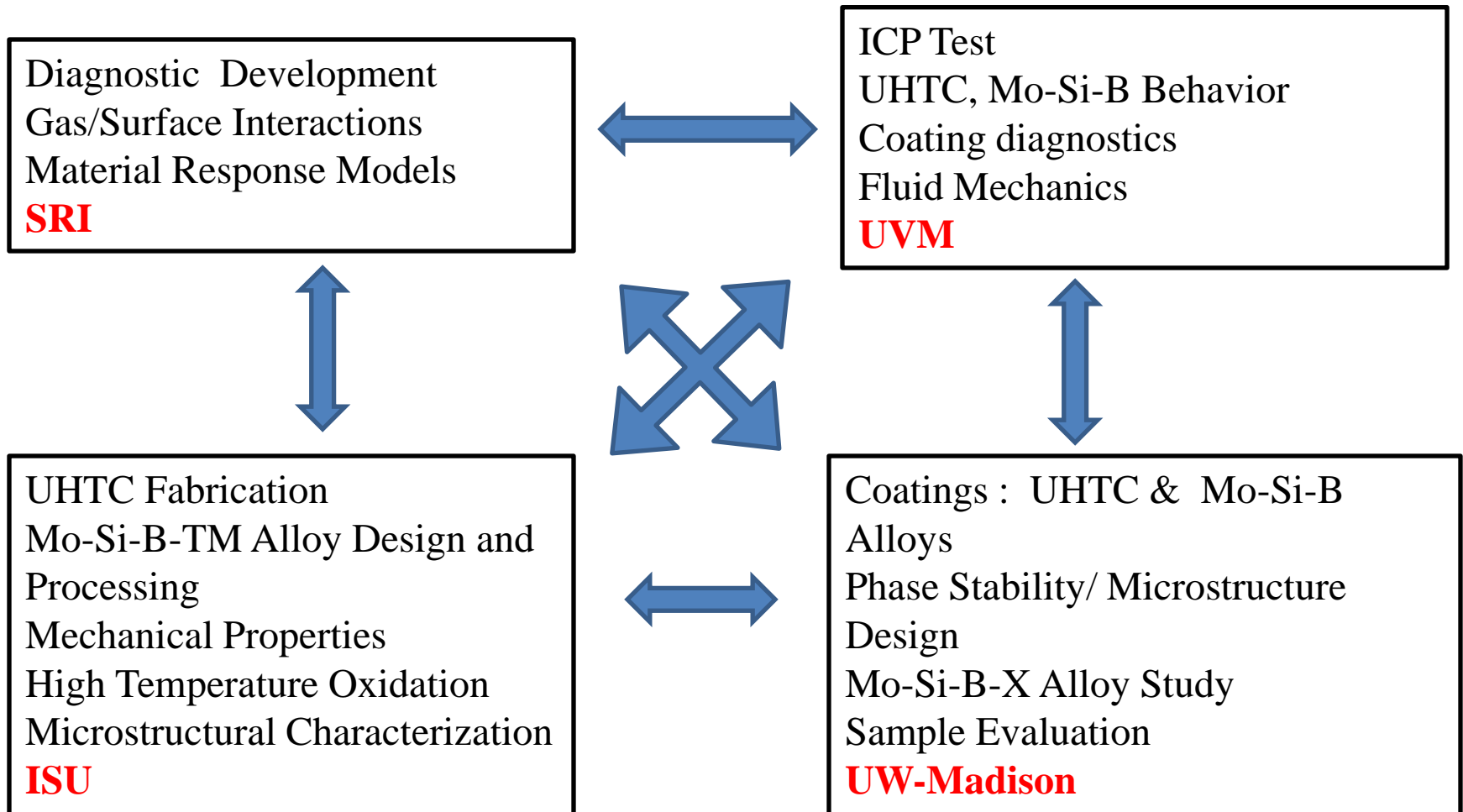
**Proof of concept demonstrated: Mo-Si-B coated samples showed robust performance and negligible weight loss in ICP test**

END-OF-PHASE GOAL

- Raise operating engine temperature to at least 1450°C yielding increased power ( $> 50\%$ ) with the use of Mo-Si-B coated refractory metals and even higher temperatures with coated diboride composites and CMCs
- Confirm performance during non-static testing and aggressive environments

Ultra-high temperature materials provide for enhanced performance and enable new engine designs.

# High-Temperature Aerospace Materials –Design and Evaluation



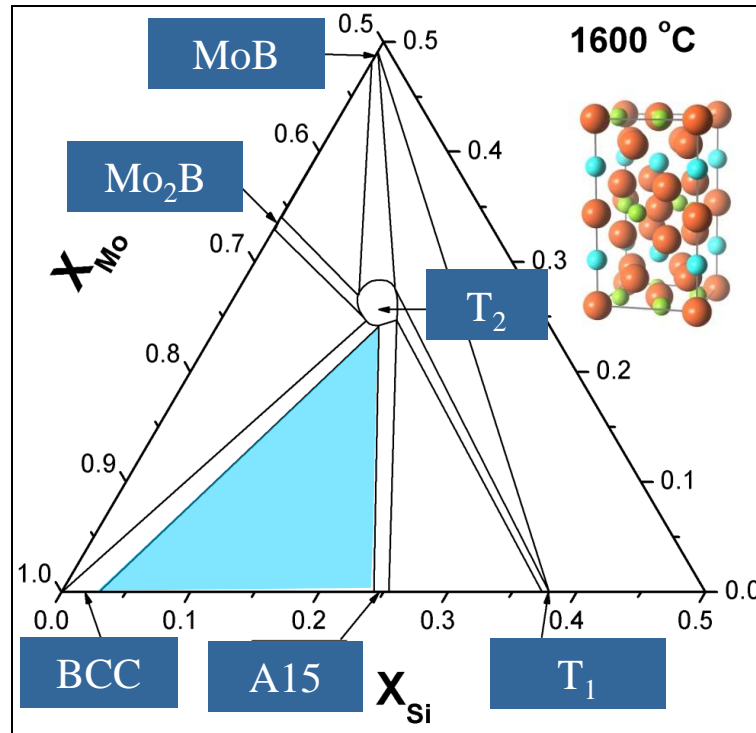
Collaboration Strategy: Regular Telecoms, joint analysis, sample exchange, student exchange, joint meetings (annual review)

## Research Focus (First Year)

- Coated Samples for High Enthalpy Environment
  - MoSiB Coated Mo for ICP facility--4 samples for UVM
  - MoSiB coated Mo coupons---10 samples for SRI
  - First test results for ICP samples---Proof of Concept
- Phase Stability in Mo-Si-B Alloys
  - Some refractory metal (RM) silicides ( $\text{RM}_5\text{Si}_3$ ) exhibit a  $T_2 \rightarrow T_1$  transition at elevated temperature
  - The phase instability can yield a structural instability
  - The  $T_2 \rightarrow T_1$  transition was examined in Mo-Nb-Si alloys
  - The transition can be suppressed with modest Mo addition levels
- Research Plans

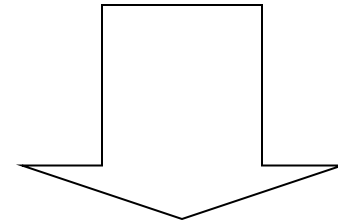
# Mo-rich, Mo-Si-B Alloys for High-Temperature Applications

## HIGH THERMAL STABILITY

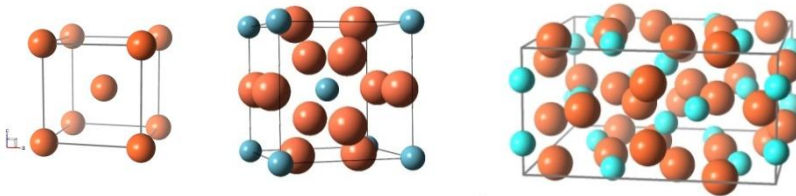


Phase Equilibria:

- BCC - Mo(ss) Phase
- A15 - Mo<sub>3</sub>Si Phase
- T<sub>2</sub> - Mo<sub>5</sub>SiB<sub>2</sub> Phase



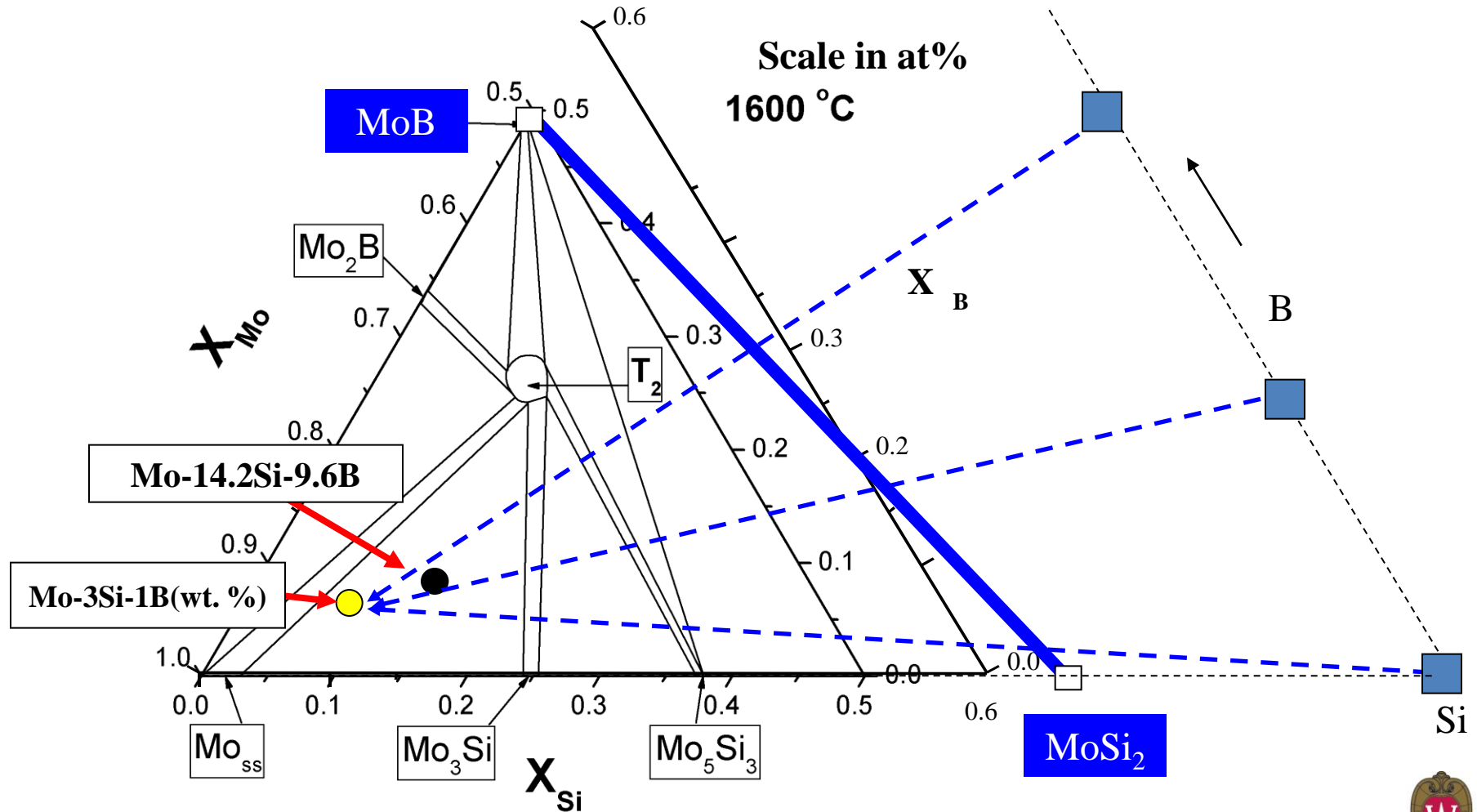
*Optimal Balance of :  
Low Temp. Toughness  
High Temp. Strength & Oxidation  
This is a difficult challenge!*



**CHALLENGE:** *Mo-Si-B composition for optimum mechanical properties is not optimum for oxidation resistance that is controlled by Si/B*

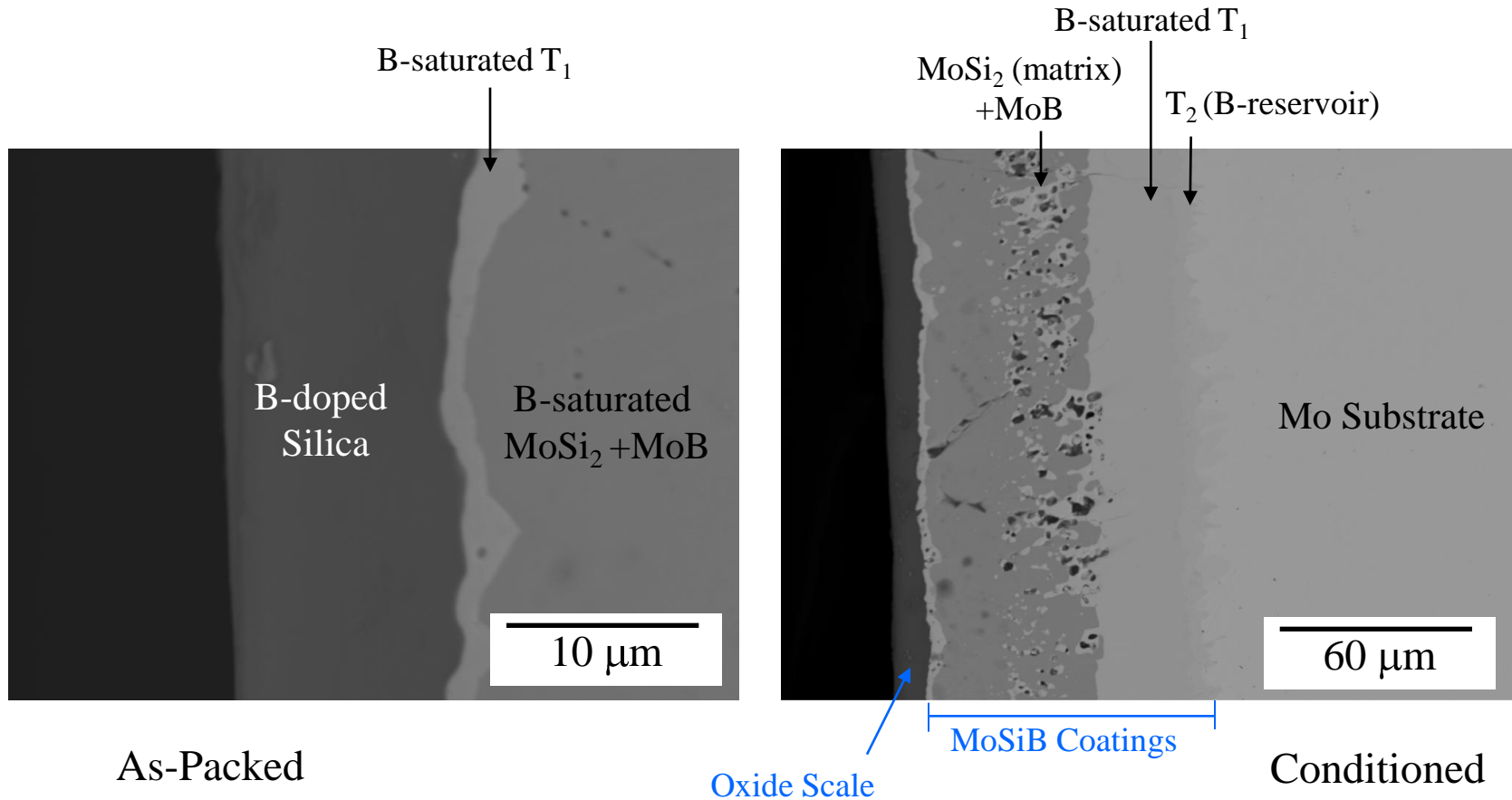
**SOLUTION:** *CO-DEPOSITION with Silicon + Boron powder Source (Kinetic Bias)*

**IMPACT:** *Excellent oxidation resistant coatings; independent of substrate composition*



# Ultra-High Temperature Exposure ( torch test Temp > 1900 C)

## POST EXPOSURE CROSS-SECTION SEM MICROGRAPHS



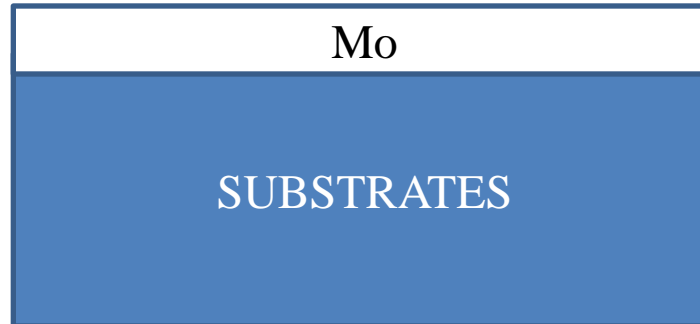
B-saturated  $T_1$  phase provides high temperature oxidation resistance.  
Boron reservoir is supplied by the underlying  $\text{MoSi}_2 + \text{MoB}$  and  $T_2$  layers

Note: There is a low Z contrast difference between MoB and B-saturated  $T_1$  phase.  
EDS spectra have been used to identify/differentiate the phases based on  $\text{MoL}\alpha/\text{Si K}\alpha$  energy lines.  
Some porosity was observed in MoB phase shown with the dark contrast.

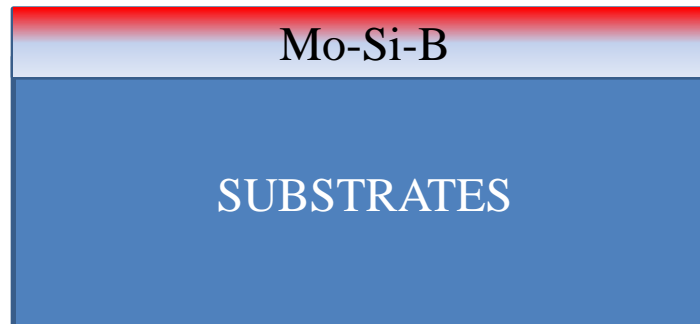
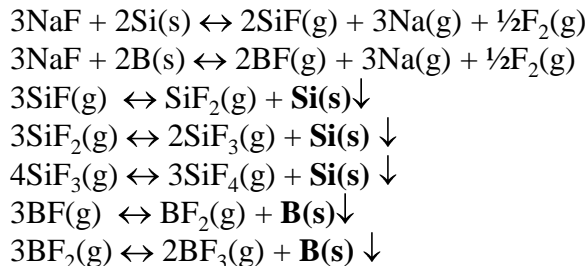
# Application of Mo-Si-B Coatings Beyond Mo Substrates

## ➤ 2 step process:

1. **Mo deposition onto UHTC for < 5 minutes at 250°C using Mo(CO)<sub>6</sub> decomposition process.**



2. **Co-deposition of Si+B into Mo deposit for ≈20 minutes at 1000 C.**

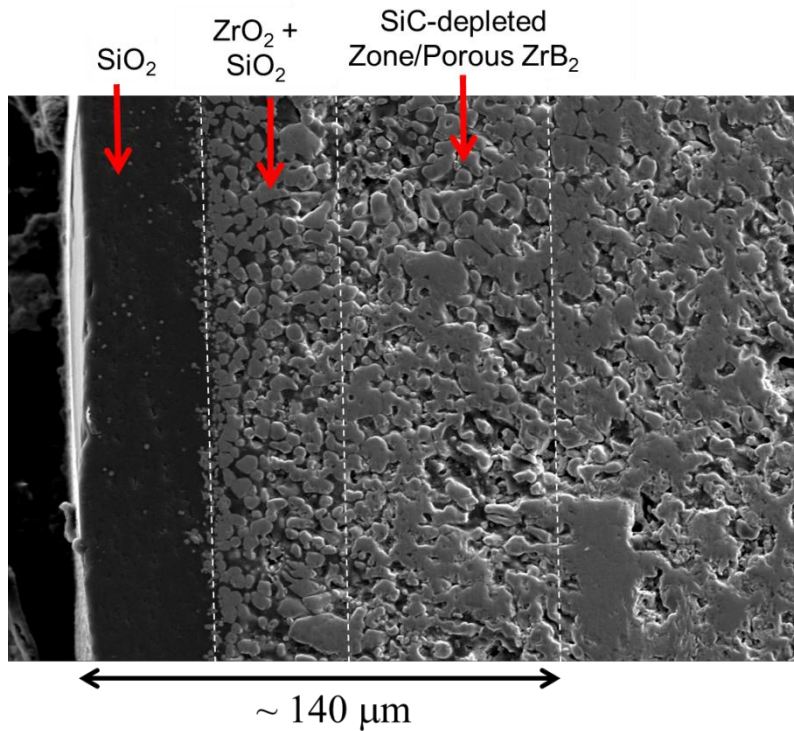




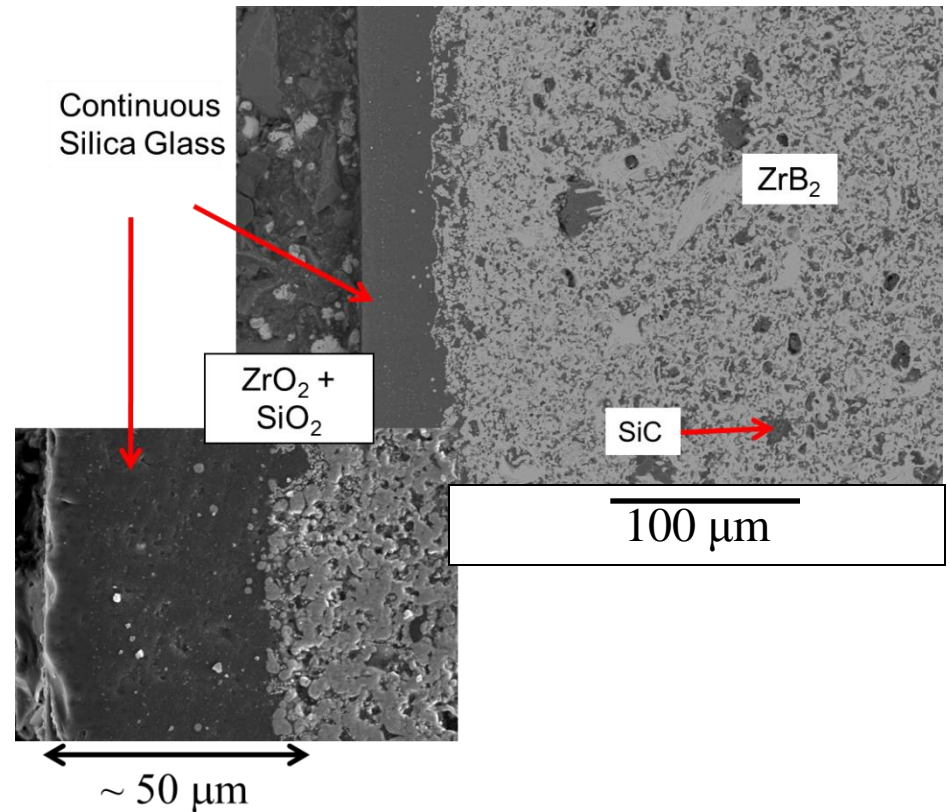
# UHTC: 20SiC + 80ZrB<sub>2</sub>

Oxidized at 1650°C for 5 hours

## UNCOATED

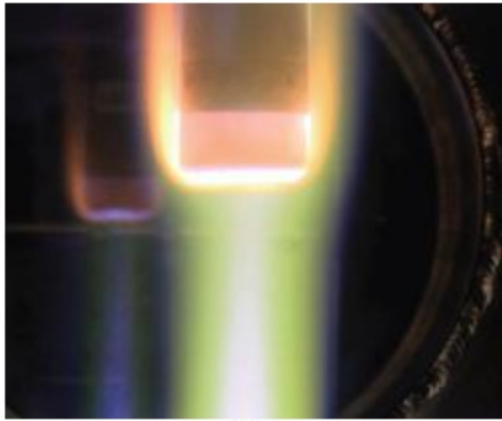


## MoSiB-COATED

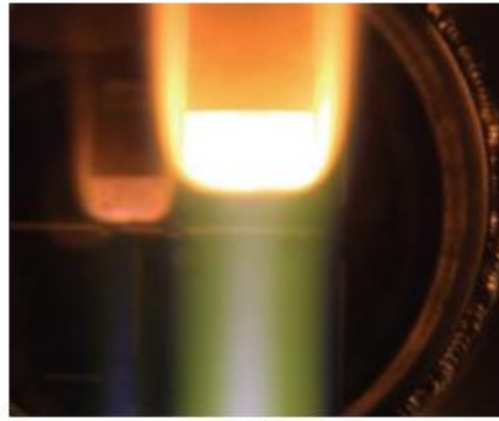


MoSiB coatings enhance the oxidation resistance of ZrB<sub>2</sub>-rich composite by limiting the growth of ZrO<sub>2</sub> particles due to reduced oxygen mobility through the silica scale. Note that Si/B Ratio in MoSiB Coatings = 35:1 (wt.%) ~ 13.5:1 (at.%)

## ICP Test on MoSiB Coated Mo Sample



50 s



370 s

ICP Test Conditions:  
Nitrogen, 40 LPM,  
160 Torr, 1500 K,  
60 W/cm<sup>2</sup>

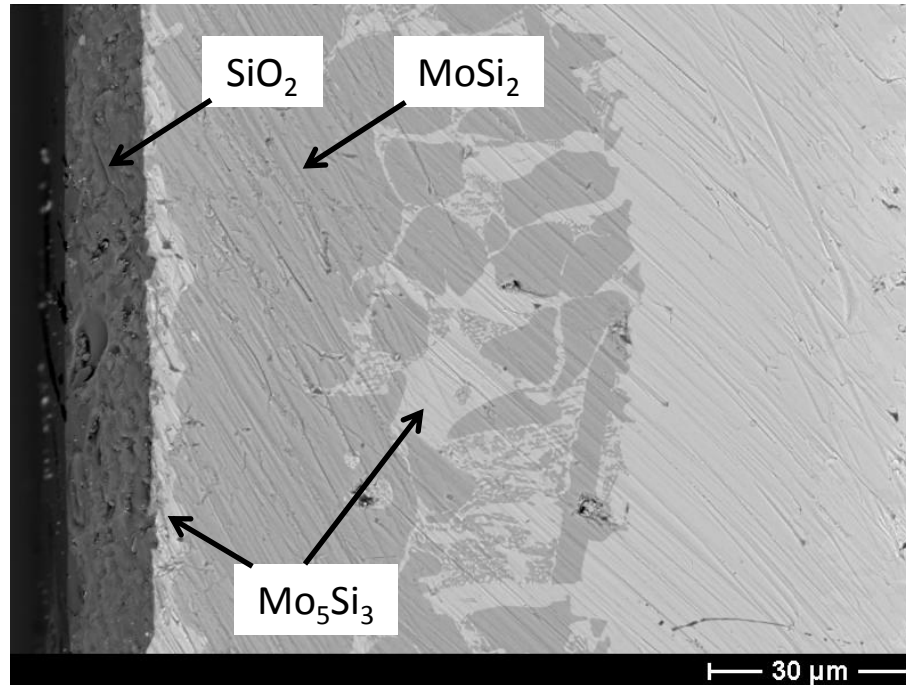


Pre-Test

Post-Test

Negligible sample  
weight change after  
test

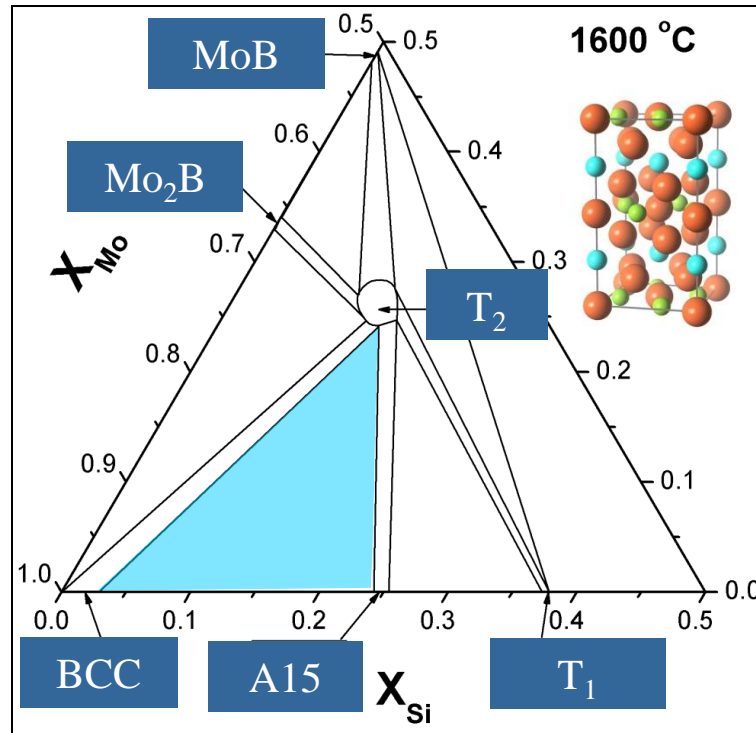
## BSE Cross-Sectional Image After Exposure



A cross-sectional image after the exposure shows the MoSiB coating structure. The  $\text{MoSi}_2$  layer provides the initial silicon for the  $\text{SiO}_2$  layer. Over time, silicon from the  $\text{MoSi}_2$  layer is consumed forming a metal-rich silicide ( $\text{Mo}_5\text{Si}_3$ ) at the  $\text{SiO}_2/\text{MoSi}_2$  interface

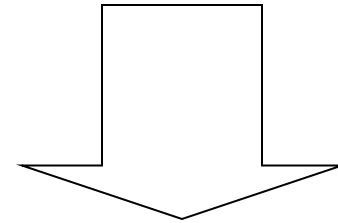
# Mo-rich, Mo-Si-B Alloys for High-Temperature Applications

## HIGH THERMAL STABILITY

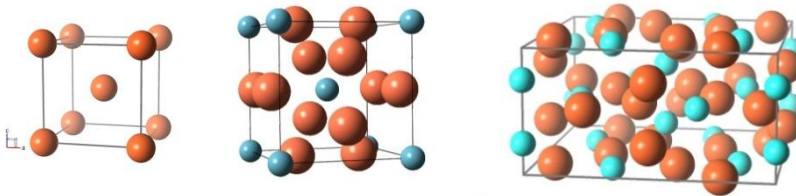


Phase Equilibria:

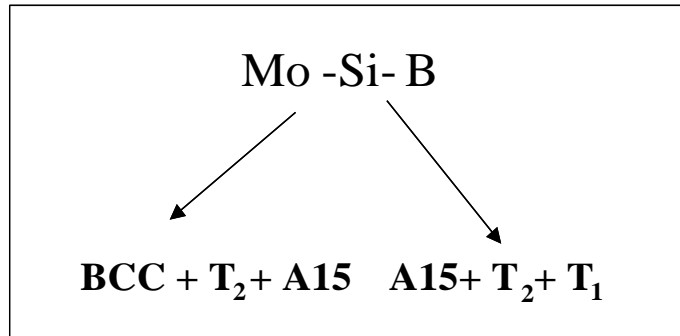
- BCC - Mo(ss) Phase
- A15 -  $\text{Mo}_3\text{Si}$  Phase
- $T_2$  -  $\text{Mo}_5\text{SiB}_2$  Phase



*Optimal Balance of :  
Low Temp. Toughness  
High Temp. Strength & Oxidation  
This is a difficult challenge!*



# ALLOYING STRATEGY IN Mo-Si-B SYSTEM\*



**BCC + T<sub>2</sub> + A15**  
 (Mo -Si- B + Cr/V)

**BCC + T<sub>2</sub> + T<sub>1</sub>**  
 (Mo -Si-B + W/Nb/Ta)

**BCC + T<sub>2</sub> + D8<sub>8</sub>**  
 (Mo -Si-B + Hf/Ti/Zr)

BCC Stabilizer : Ti, Zr, Hf, V, Nb, Ta, Cr, W  
 T<sub>2</sub> Stabilizer : Ti, Zr, Hf, V, Nb, Ta, Cr, W  
 T<sub>1</sub> Stabilizer : W, Nb, Ta  
 A15 Stabilizer : Cr, V  
 D8<sub>8</sub> Stabilizer : Ti, Zr, Hf

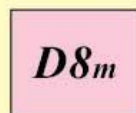
Ti substitution : BCC+A15+T<sub>2</sub> => BCC + D8<sub>8</sub> + T<sub>2</sub>

Nb substitution: BCC+A15+T<sub>2</sub> => BCC + T<sub>1</sub> + T<sub>2</sub>

\*D. Dimiduk and J. Perepezko, MRS Bulletin, 28, No. 9, 639 (2003).

# Structure Map for Binary $M_5Si_3$ -type Compounds

3	4	5	6	7	8	9	10
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Lu	Hf	Ta	W	Re	Os	Ir	Pt



*T1*



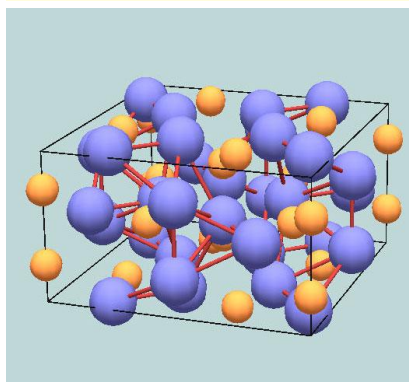
*T2*



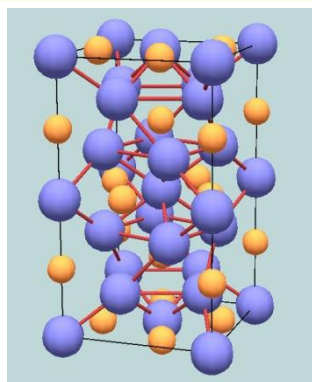
*No  $M_5Si_3$  type compounds*

**T1-T2 transformation appears in the Nb-Si and Ta-Si system.**

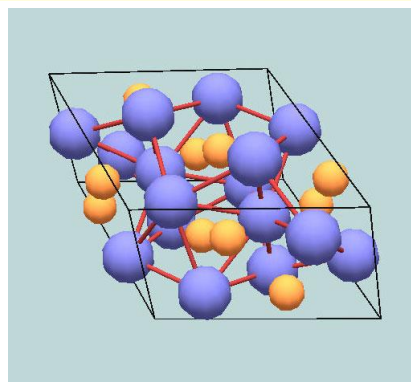
**Nb-Si is better established than Ta-Si**



**$D8_m$  (T1)**



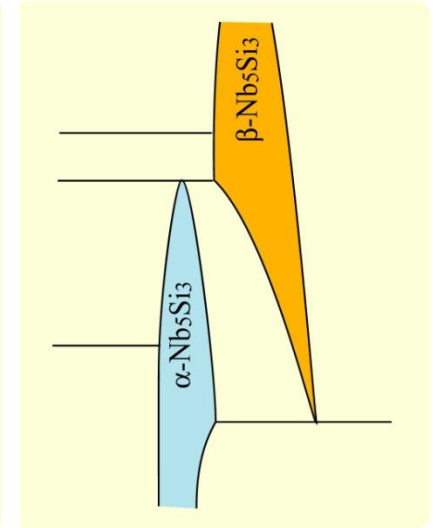
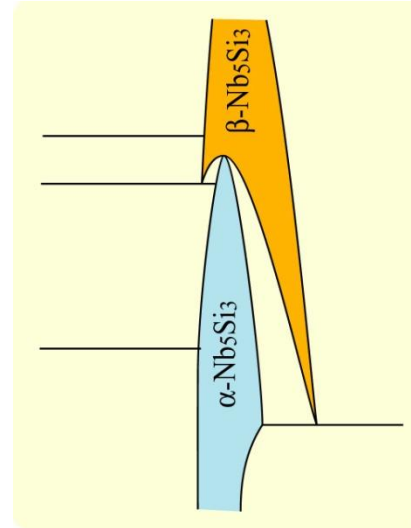
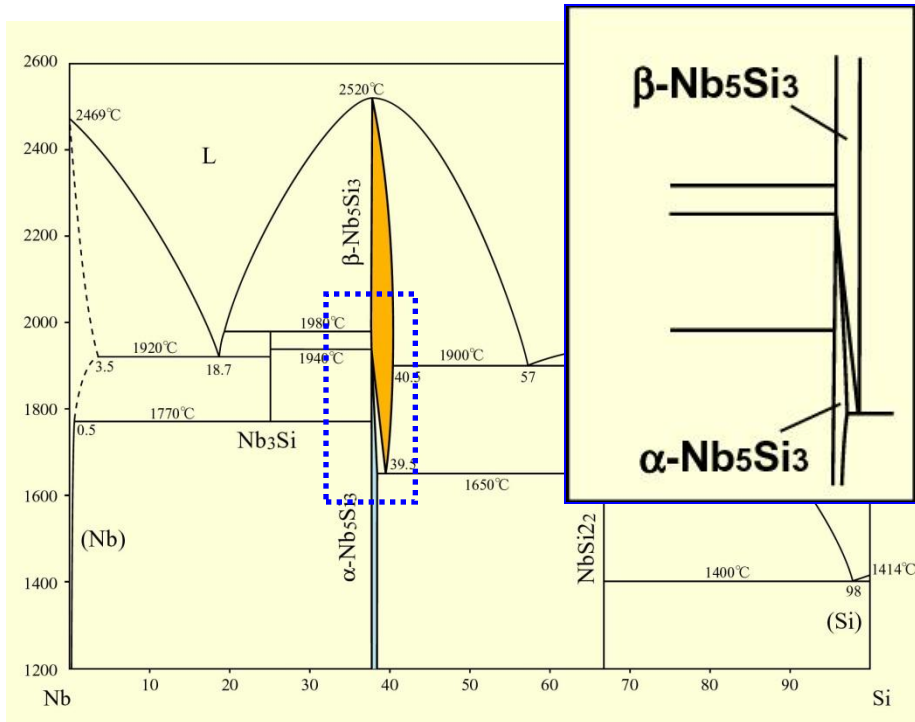
**$D8_l$  (T2)**



**$D8_g$**

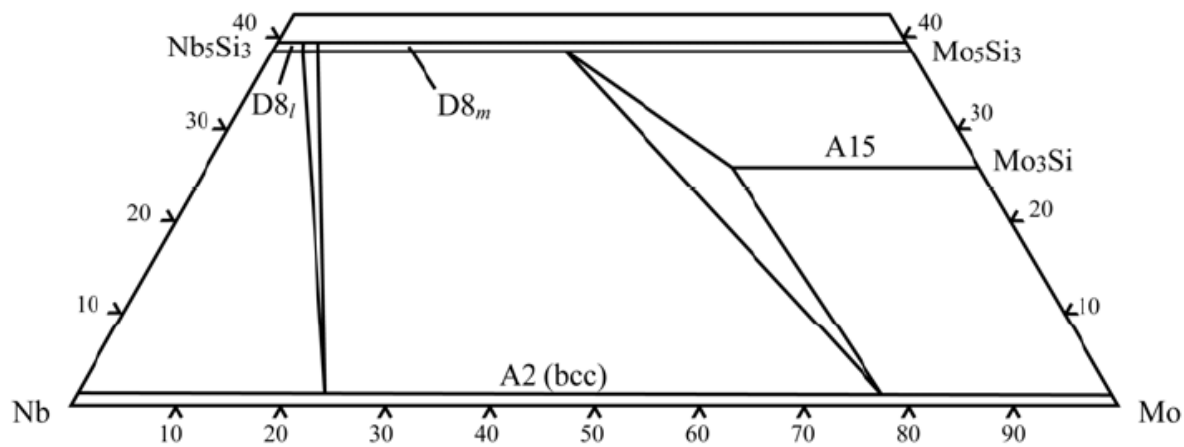
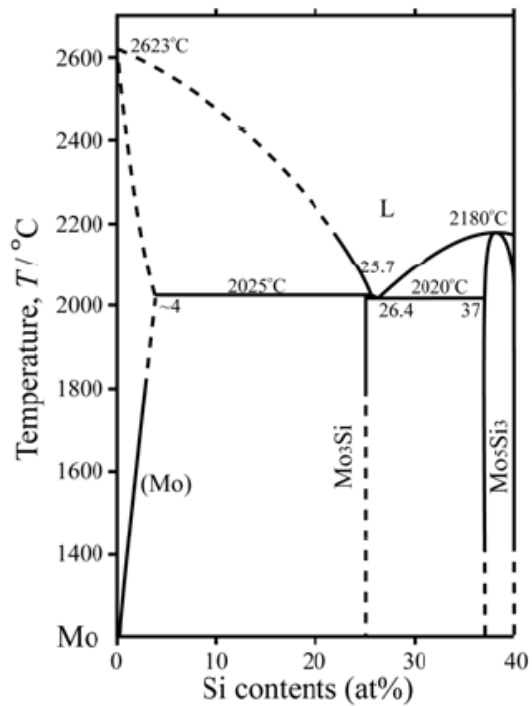
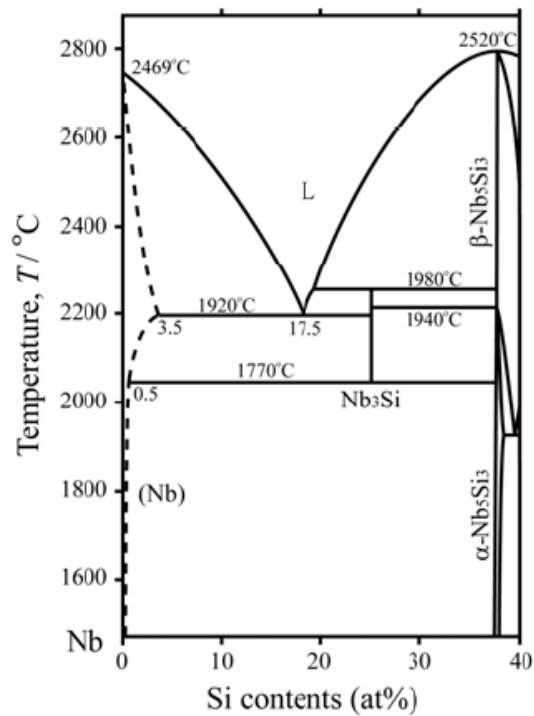


# Nb-Si Binary Phase Diagram



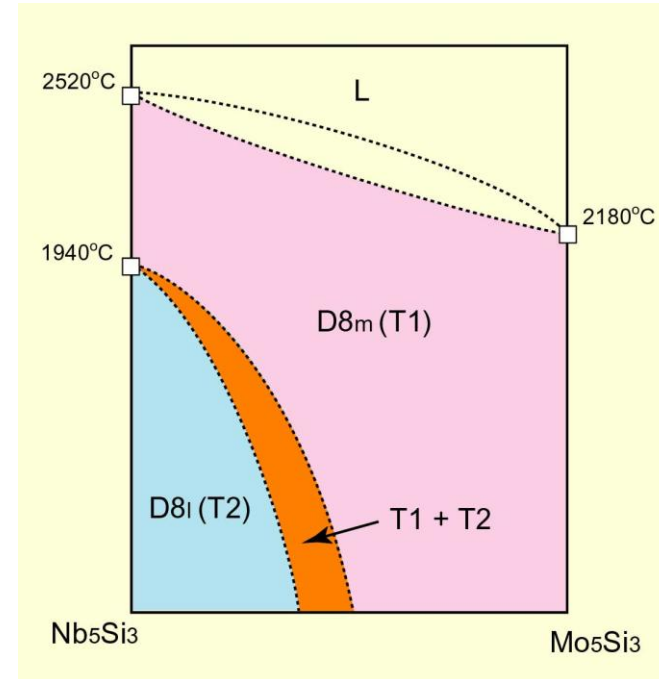
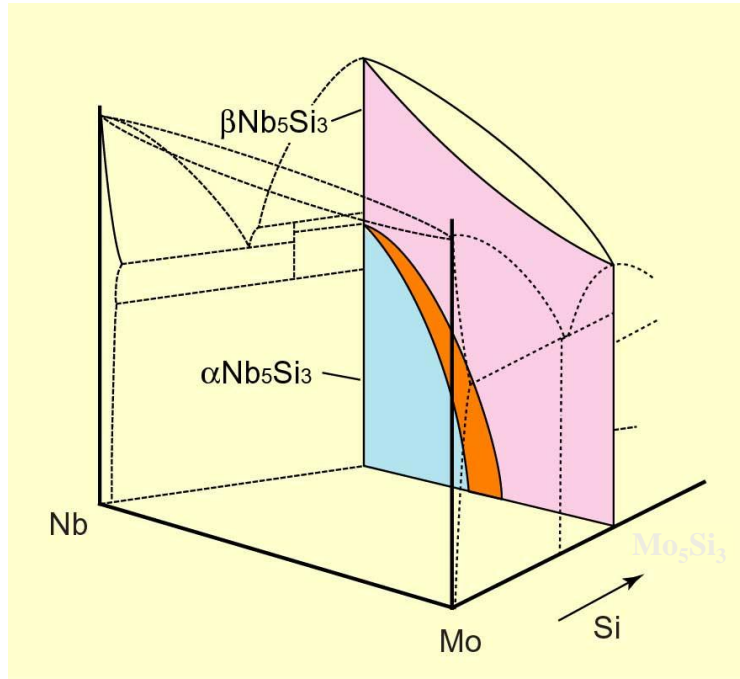
**T1/T2 Two phase field is small in the binary system**

➡ **Mo addition**





# T1/T2 Two Phase Field in the Nb-Mo-Si Ternary System

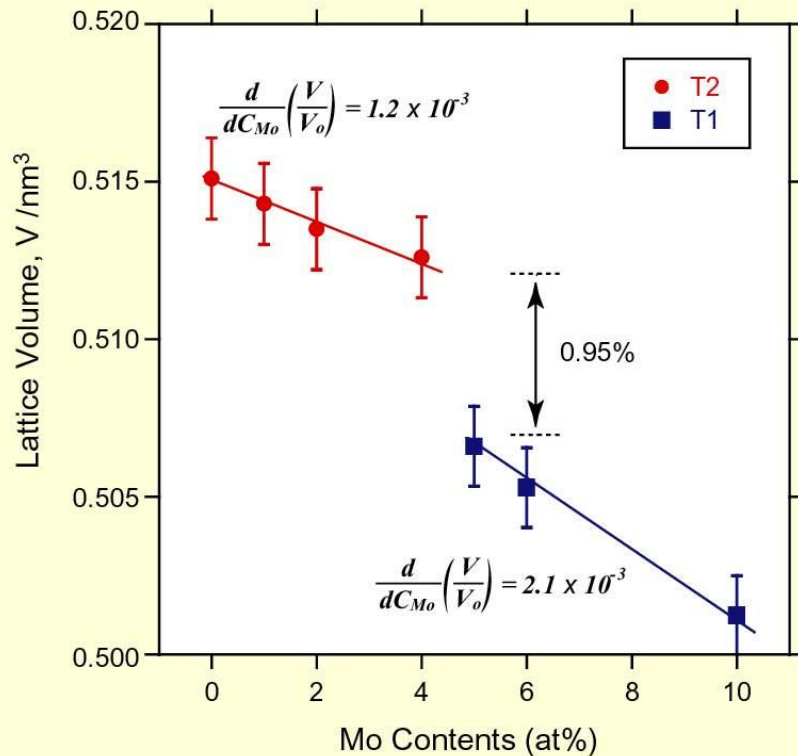


Schematic

**Widen T1/T2 Two Phase Field**

➡ **Easier to detect the T1-T2 transformation**

# Variation of Lattice Volume for Mo additions



*(Nb,Mo) solid solution*

$$\frac{d}{dC_{\text{Mo}}} \left( \frac{V}{V_o} \right) = 2.0 \times 10^{-3}$$

**No CTE data is available  
for  $\text{Nb}_5\text{Si}_3$**

**$\text{Mo}_5\text{Si}_3$  (T1) :**

$$\alpha_a = 8.0 \times 10^{-6}$$

$$\alpha_c = 1.6 \times 10^{-5}$$

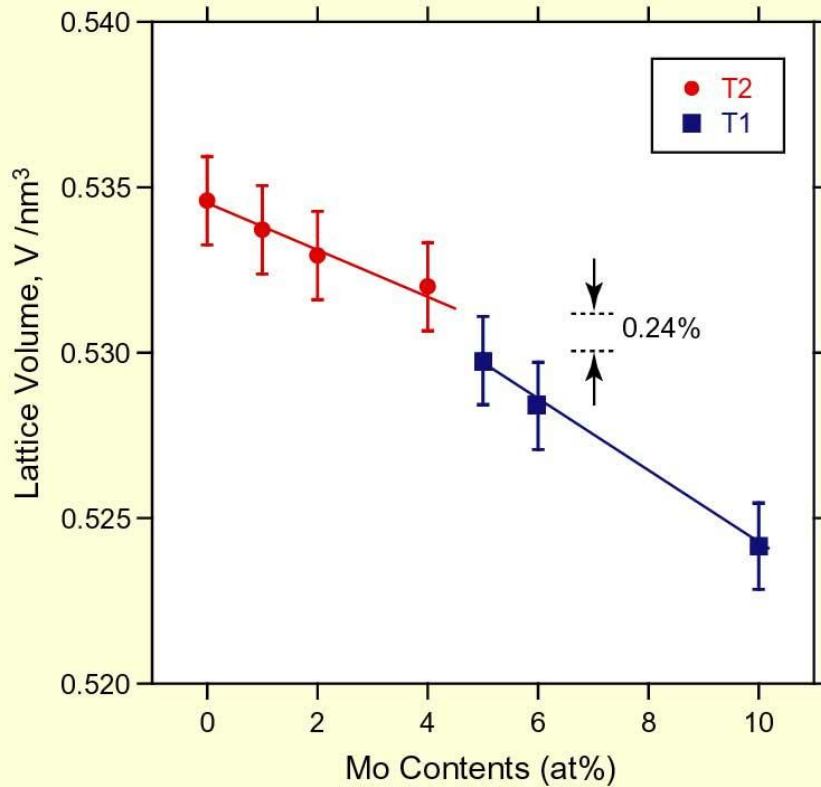
**$\text{Mo}_5\text{SiB}_2$  (T2) :**

$$\alpha_a = 9.2 \times 10^{-6}$$

$$\alpha_c = 8.1 \times 10^{-6}$$

*Fu et al. (2000)*

# Expected Volume change at 1400°C



## - Volume Changes by Phase Transformation -

**Fe ( $\alpha$ - $\gamma$ ) : 1~2%**

**ZrO<sub>2</sub> : 4%**

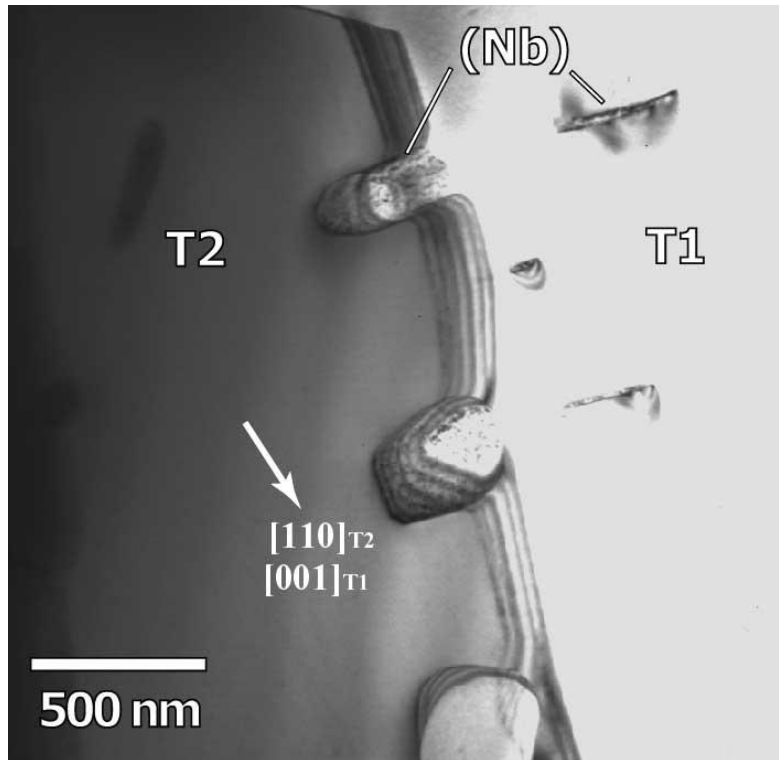
**Martensite**

**TiNi : 0.34%**

**CuAlNi: 0.3%**

**Volume change by T1-T2 transformation is small**

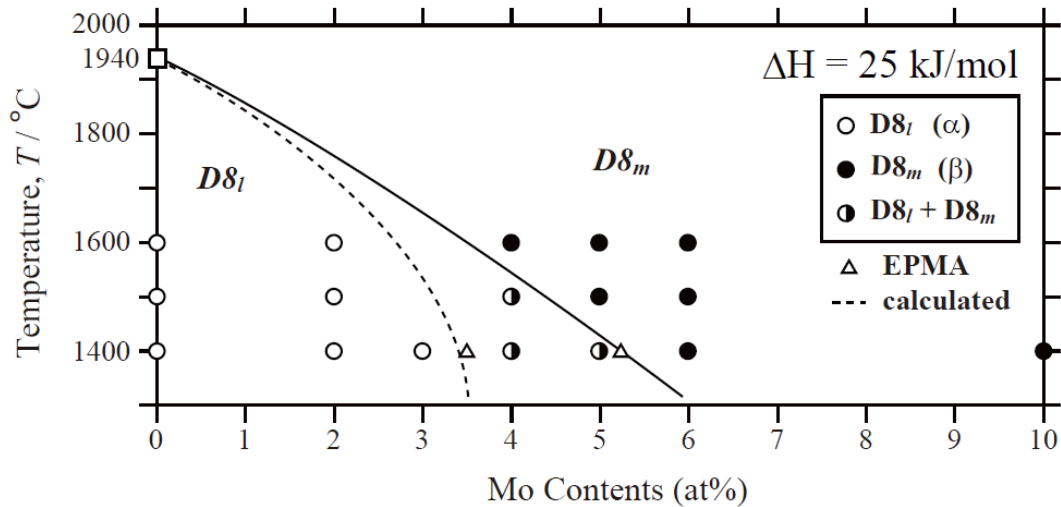
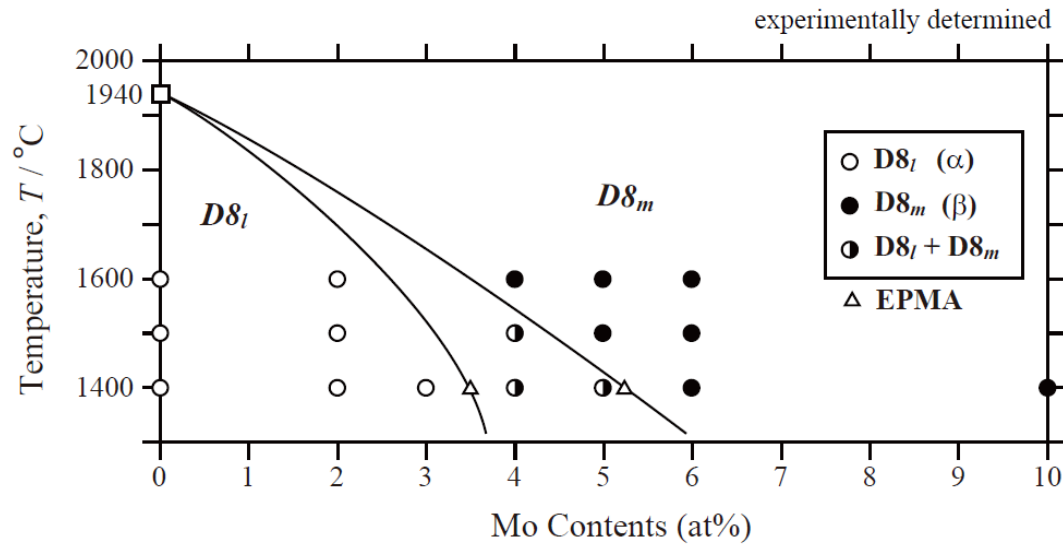
# Partial Transformation

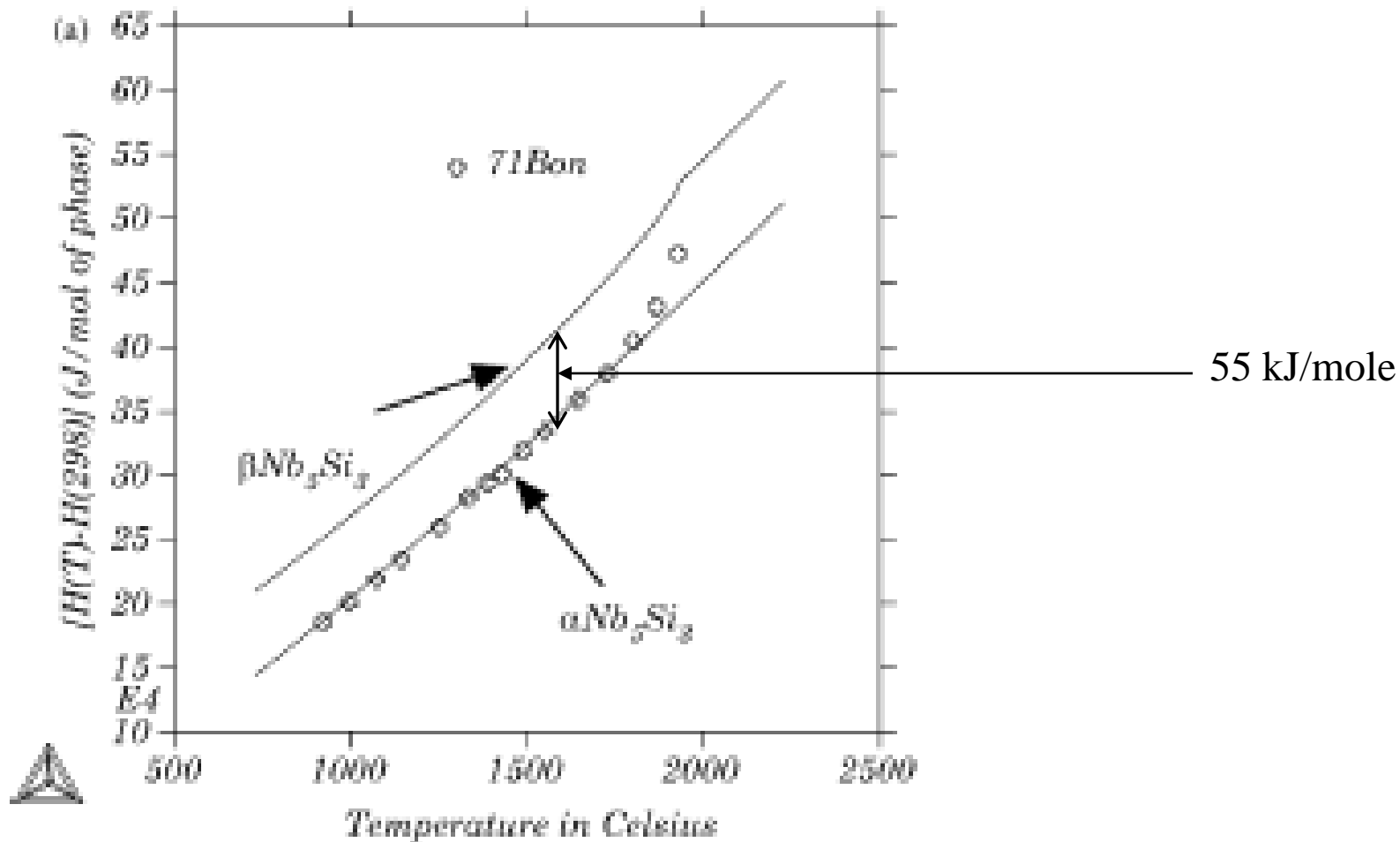


Anneal: 1400 °C for 100 hrs in Ar

T1- T2 Orientation Relationship  
 $(110)_{T2} // (001)_{T1}$   
(with about 8% misfit)

# Vertical section at 37.5 at% Si for (Mo,Nb)-Si





Previous estimate of the  $T_2/T_1$  transformation enthalpy based upon computational thermodynamics is more than twice the experimentally determined value.

## Summary Highlights

- Coated Samples for High Enthalpy Environment
  - MoSiB Coated Mo for ICP facility--4 samples for UVM
  - MoSiB coated Mo coupons---10 samples for SRI
  - First test results for ICP samples---Proof of Concept Demonstrated
- Phase Stability in Mo-Si-B Alloys
  - Some refractory metal (RM) silicides ( $\text{RM}_5\text{Si}_3$ ) exhibit a  $T_2 \rightarrow T_1$  transition at elevated temperature
  - The phase instability can yield a structural instability
  - The  $T_2 \rightarrow T_1$  transition was examined in Mo-Nb-Si alloys
  - The transition has sluggish kinetics and can be suppressed with modest Mo addition levels
  - The  $T_2 \rightarrow T_1$  transition enthalpy was determined as 25 kJ/mole

## Research Plan

### Year 2

- Process ZrB<sub>2</sub>/SiC and ZrB<sub>2</sub>/SiC/AlN composites and carry out detailed microstructural characterization.
- Implement the integration of Mo-Si-B coating technology at UWM onto both Mo-Si-B alloys and Diboride composites provided by ISU.
- Apply kinetic biasing and diffusion barriers to coatings to mitigate the development of any incompatible interphase reaction products at UWM.
- Examine new microstructure designs in Mo-Si-B-X (X=Ti, RE) and mechanical compatibility between the coating and substrate materials at UWM.
- UWM will provide coated samples for ICP facility testing and evaluate sample performance.