# Concepts for Smart Protective High-Temperature Coatings

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# Purpose of This Research

Explore feasibility of smart protective coatings in fossil systems based on state-of-the-art alloying and microstructural approaches to high-temperature corrosion resistance

# Why?

- Adequate resistance to environmental degradation is a critical material barrier to the operation of fossil energy systems meeting Vision 21 efficiency and emission goals
  - Reactive species ($O_2$, $H_2S$, $H_2O$, $H_2$, CO, HCl, etc.)
  - Slags, salts
  - High temperatures
  - Varying conditions
    - operation
    - fuels of opportunity

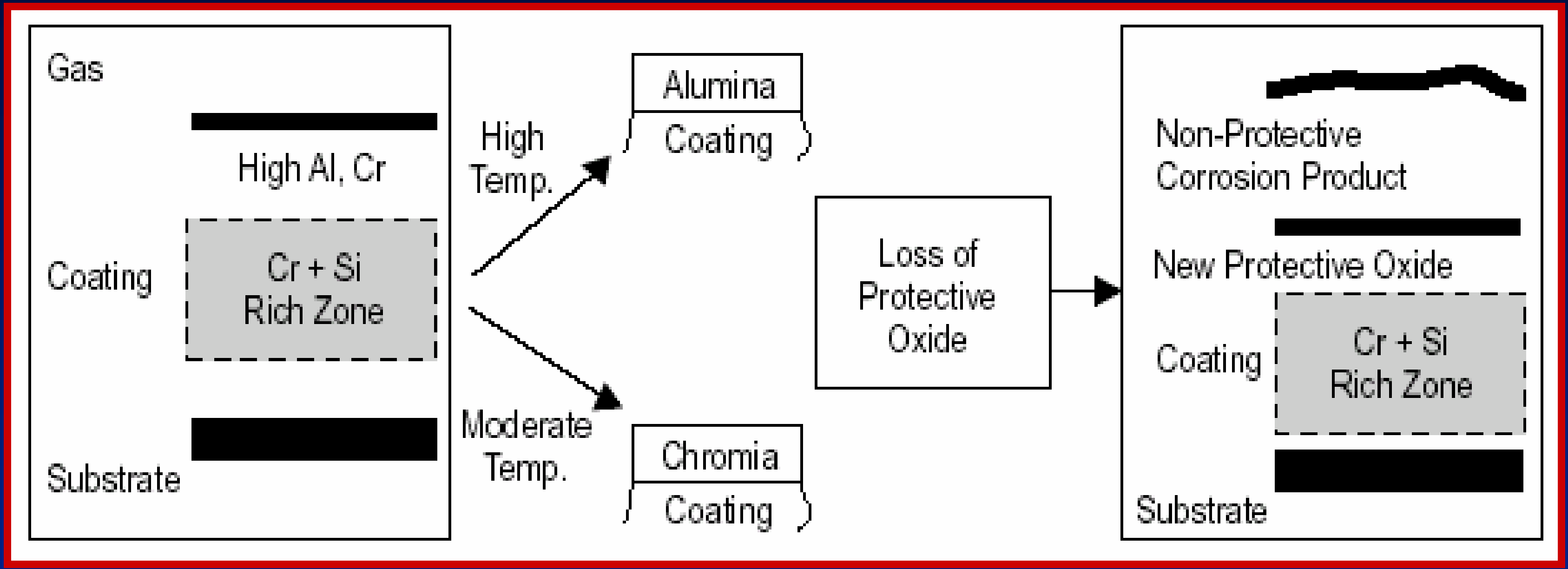
# Why?

- Adequate resistance to environmental degradation is a critical material barrier to the operation of fossil energy systems meeting Vision 21 efficiency and emission goals
- Need breakthrough advances in materials and materials protection that require new research, development, synthesis and/or performance approaches
- Smart coatings offer possibilities for corrosion protection under aggressive (and changing) environmental conditions

# Smart Protective Coatings For High-Temperature Corrosion Protection

- Smart = correctly sense and respond appropriately
- In present context, materials that sense particular environmental conditions and form protective barrier layers to provide high-temperature corrosion protection
- Many oxidation-resistant alloys and coatings are somewhat smart
- Want coatings that are multitasking!

# There Has Been Some Progress In Developing More Complex Smart Coatings




J.R. Nicholls, "Smart Coatings—A Bright Future", *Materials World*, vol. 4, 1996

# Project Approach

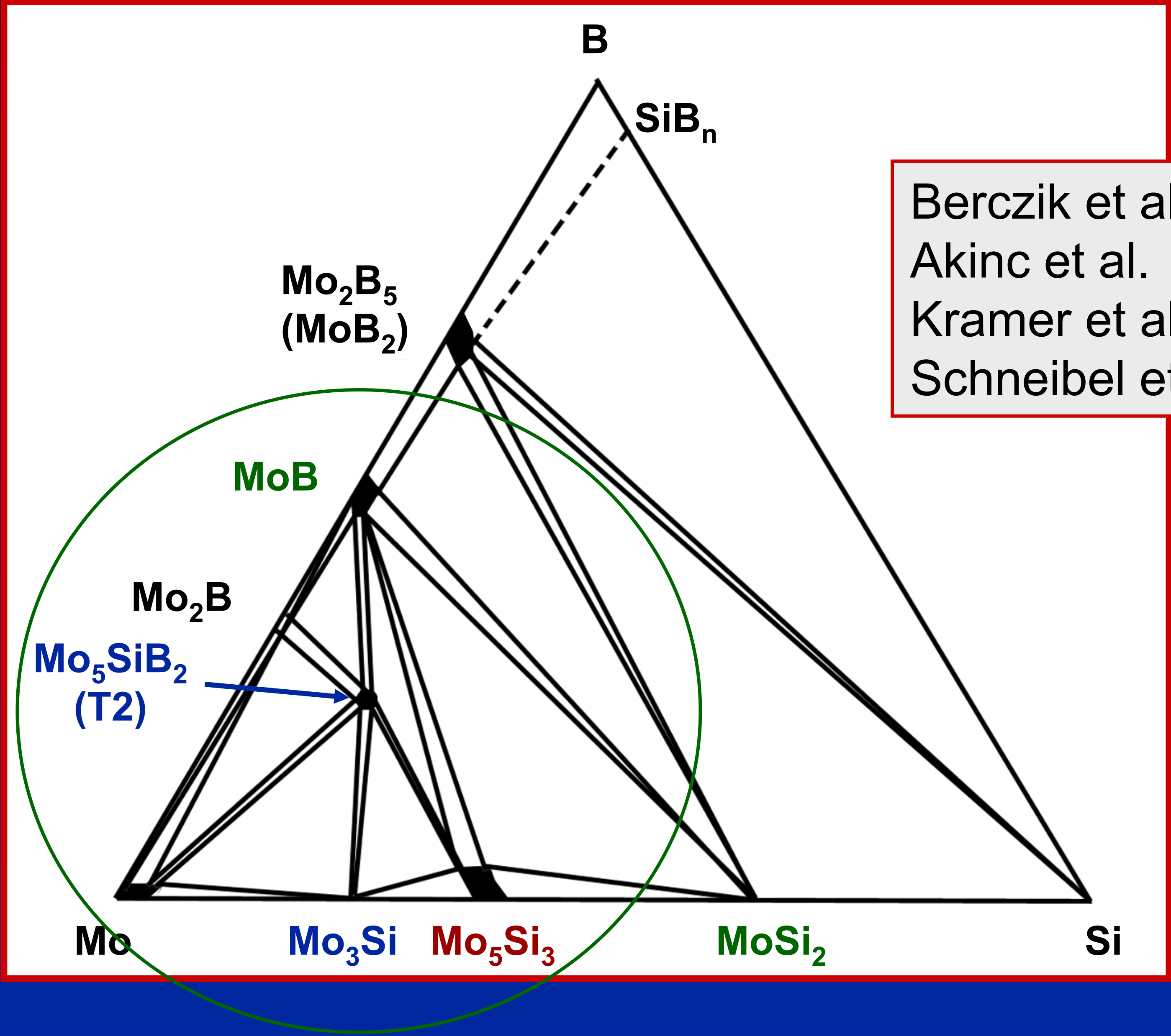
- Focus on concepts, not synthesis or detailed corrosion studies
- Explore compositional and microstructural manipulations and cooperative phenomena that have not been examined in any detail to date (cf. Brady, Gleeson, & Wright, *JOM* , 2000; Nicholls, *ibid*)
- Pursue structures that can react with the environment in various ways such that different protective barrier layers can form depending on the exposure conditions

# Approach (Cont'd.)

- Specifically examine the response of multiphase alloys and composite structures to various reactive gases and salts for alumina, chromia, and silica-formers

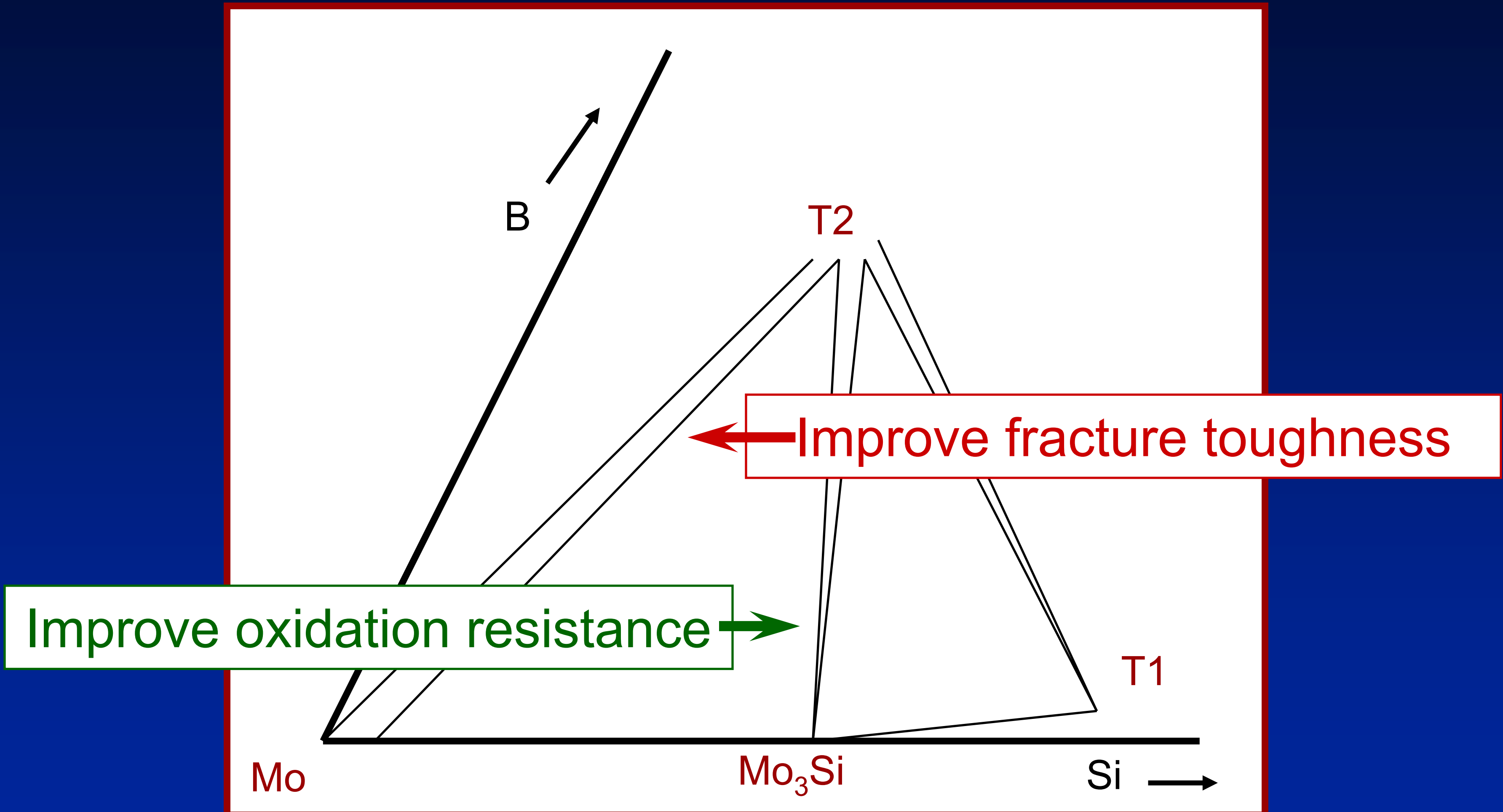
- We've started with silicides
  - Potentially good oxidation and/or sulfidation resistance
  - Coatings possible
  - Recent progress in developing multiphase Mo-Si-B alloys that have high-temperature oxidation resistance and some fracture toughness

# First System Being Explored Is Mo-Si-B




Berczik et al.
Akinc et al.
Kramer et al
Schneibel et al.

# There Is A Trade-Off Between Toughness And Oxidation Behavior




(cf. Schneibel et al., MRS Proc., 2002)

# Mo-Si-B

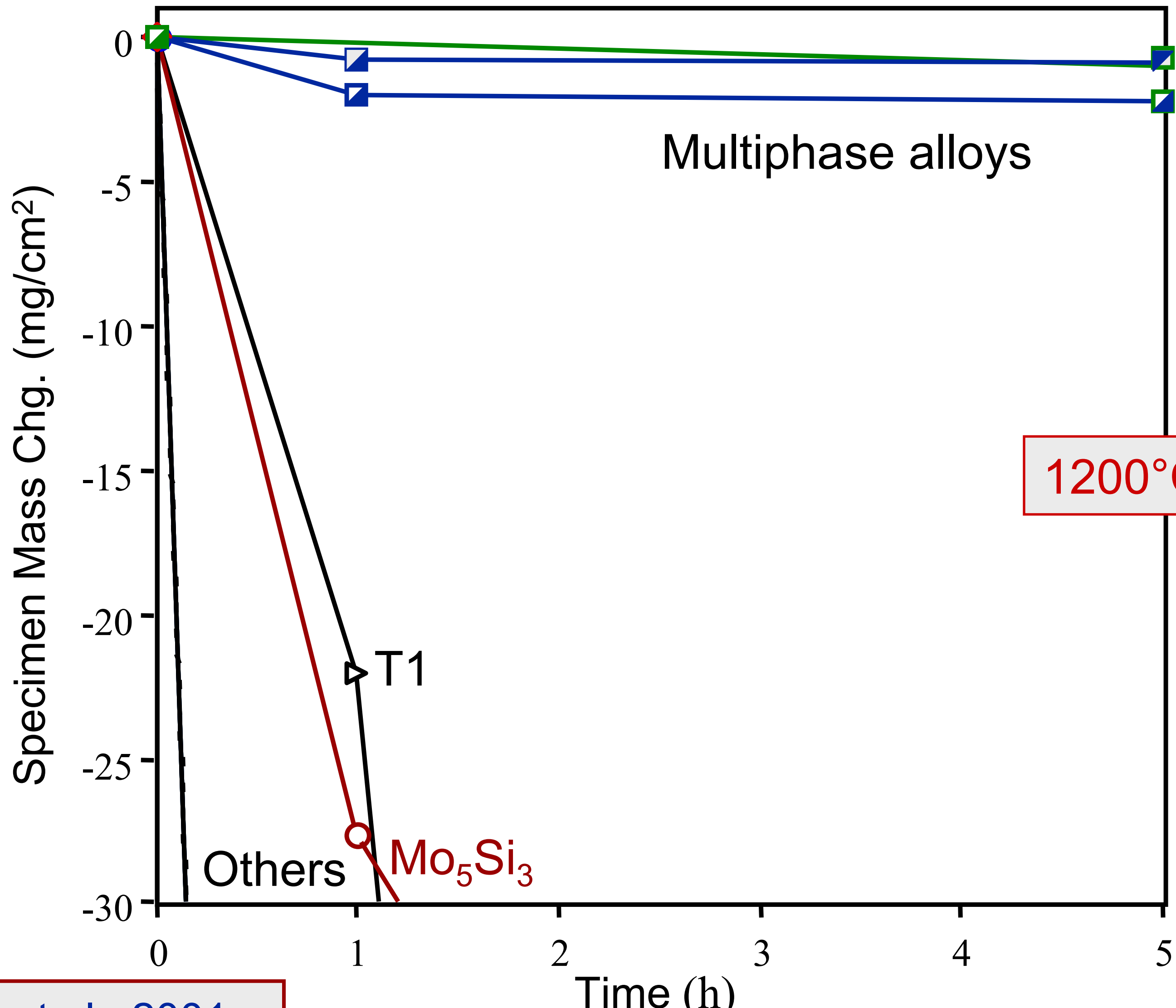
- Si can provide means to establish protective silica or borosilicate layers (Meyer et al., Thom et al., Mendiratta et al., Natesan, Tortorelli et al., Schneibel et al., Petit & Meier, etc.)
- Mo sulfidizes slowly (cf. Mrowec, Douglass et al.)
- $MoS_2$ more stable than Si sulfides
- Can we manipulate the phase assemblage of Mo-Si-B so that effective barrier layers can form in different environments?
  - started with oxidation experiments
  - explore compositional/microstructural routes to protective oxide formation
  - follow with exposures in oxidizing/sulfidizing atmospheres

# Cyclic Oxidation Exposure Conditions

$$\Delta W_{spec} = \Delta W_{o} - \Delta W_{spall} - \Delta W_{volatile}$$

- Dry air
- 1 h at 1200°C,
  10 min out of furnace
- Specimens weighed at 1, 5, 20, 40, 60, 80, 100, 200, 300, 400, 500 h
- Thermal cycling can exacerbate oxidation susceptibility

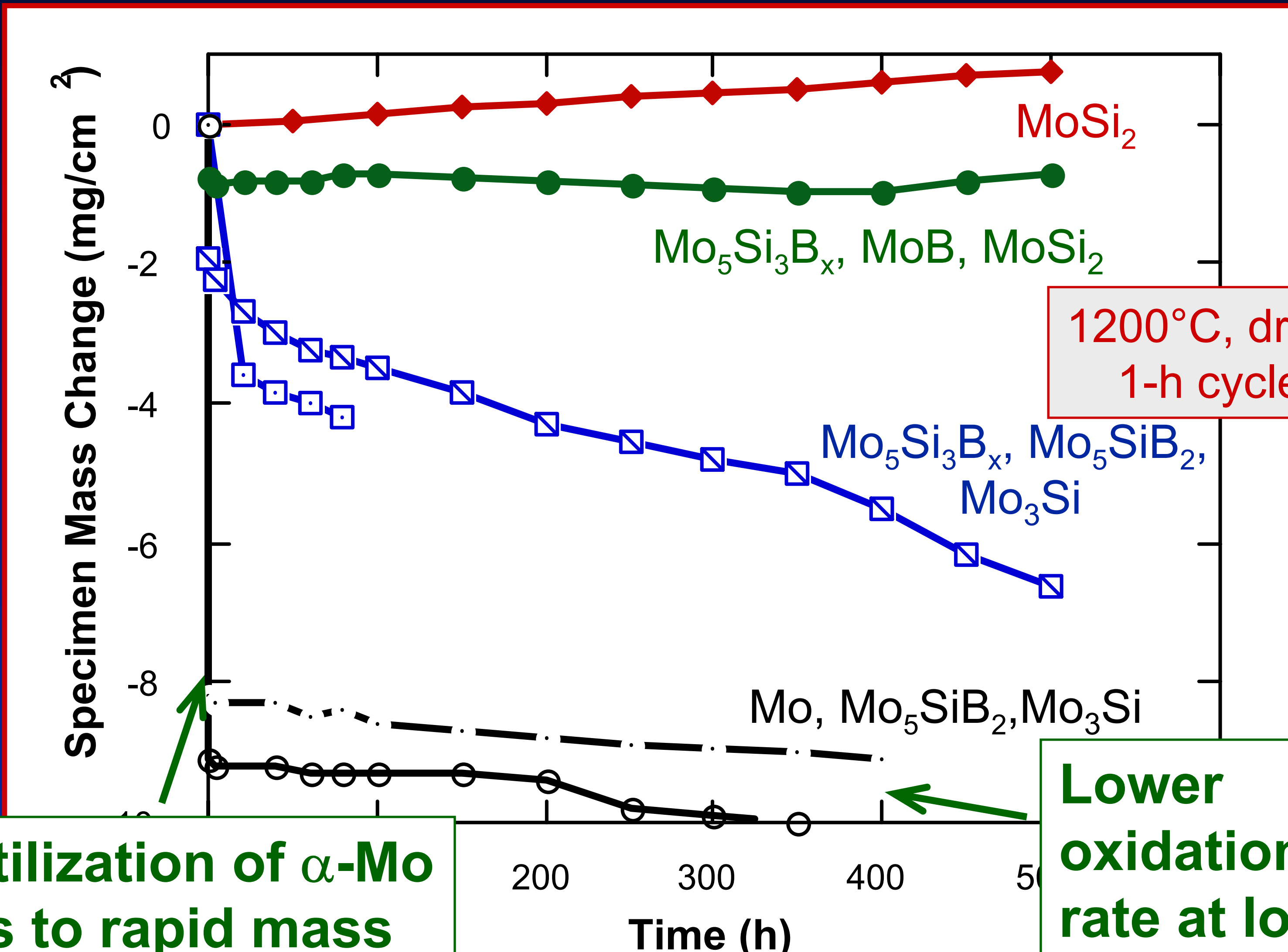
# The Multiphase Alloys Were Clearly Better With Respect To Cyclic Oxidation Behavior




1200°C, dry air

Tortorelli et al., 2001

# Of The Multiphase Compositions, T1-MoB-$MoSi_2$ Performed Significantly Better




**Volatilization of α-Mo leads to rapid mass loss**

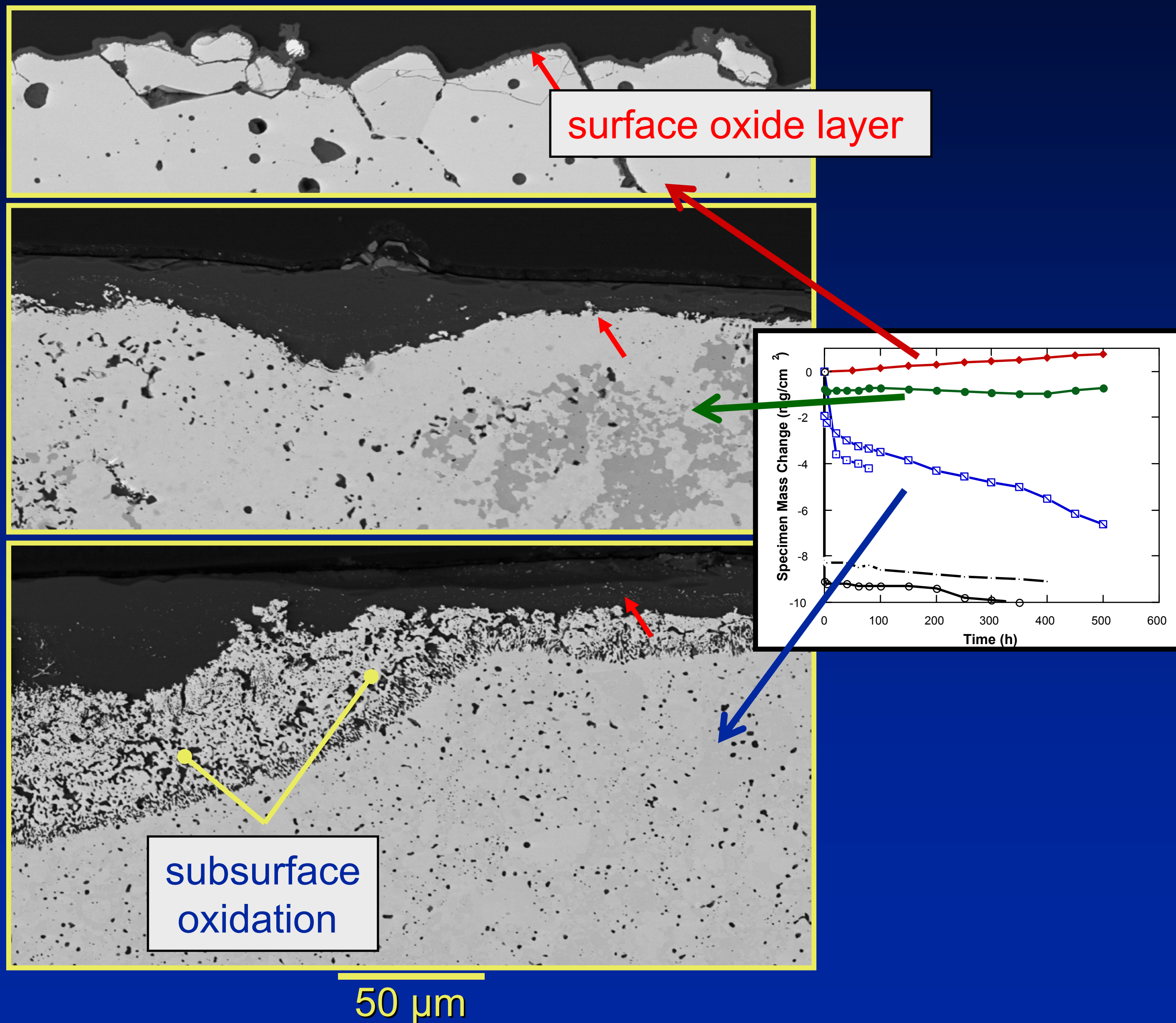
**Lower oxidation rate at longer times**

# Significant Differences In Surface Reaction Product Morphologies Were Noted

$MoSi_2$

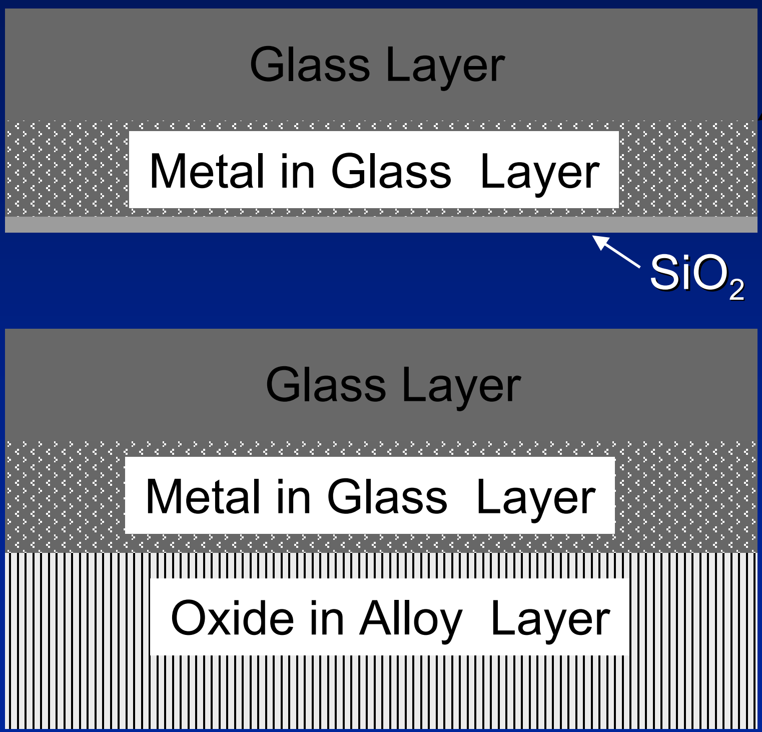
$Mo_5Si_3B_x$, $MoB$, $MoSi_2$

$Mo_5Si_3B_x$, $Mo_5SiB_2$, $Mo_3Si$

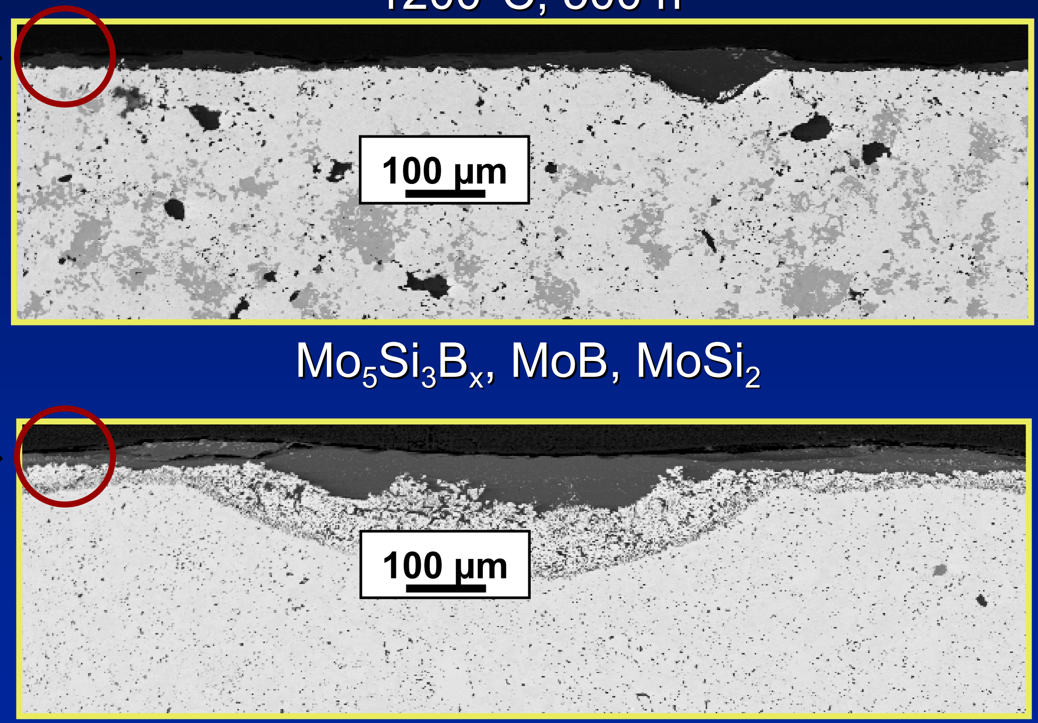


# "Higher" Alloy Si Content Can Prevent Subsurface Oxidation

- Sufficient Si to form glass layer
- Si-enriched phases can act as Si reservoir/source




1200°C, 500 h




$Mo_5Si_3B_x$, MoB, $MoSi_2$

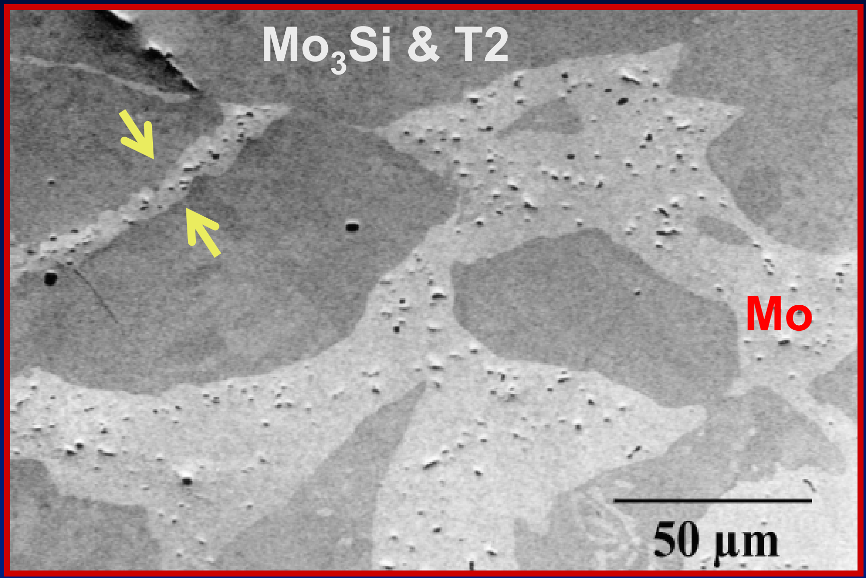
T1, T2, $Mo_3Si$

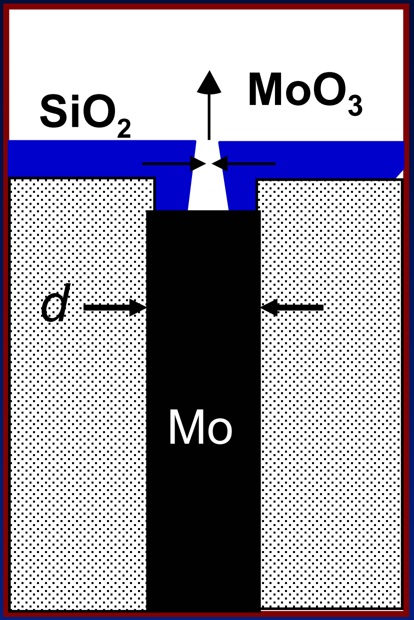
# Multiphase Nature of These Systems Present Opportunities To Improve Corrosion Resistance

- Manipulate microstructural geometric/size effects
- Alter subsurface depletion paths (e.g., noble alloying additions)

( cf. Brady, Gleeson, & Wright, *JOM*, 2000)

# We Are Examining Optimization Of Oxidation Resistance Based On Phase Size Effects

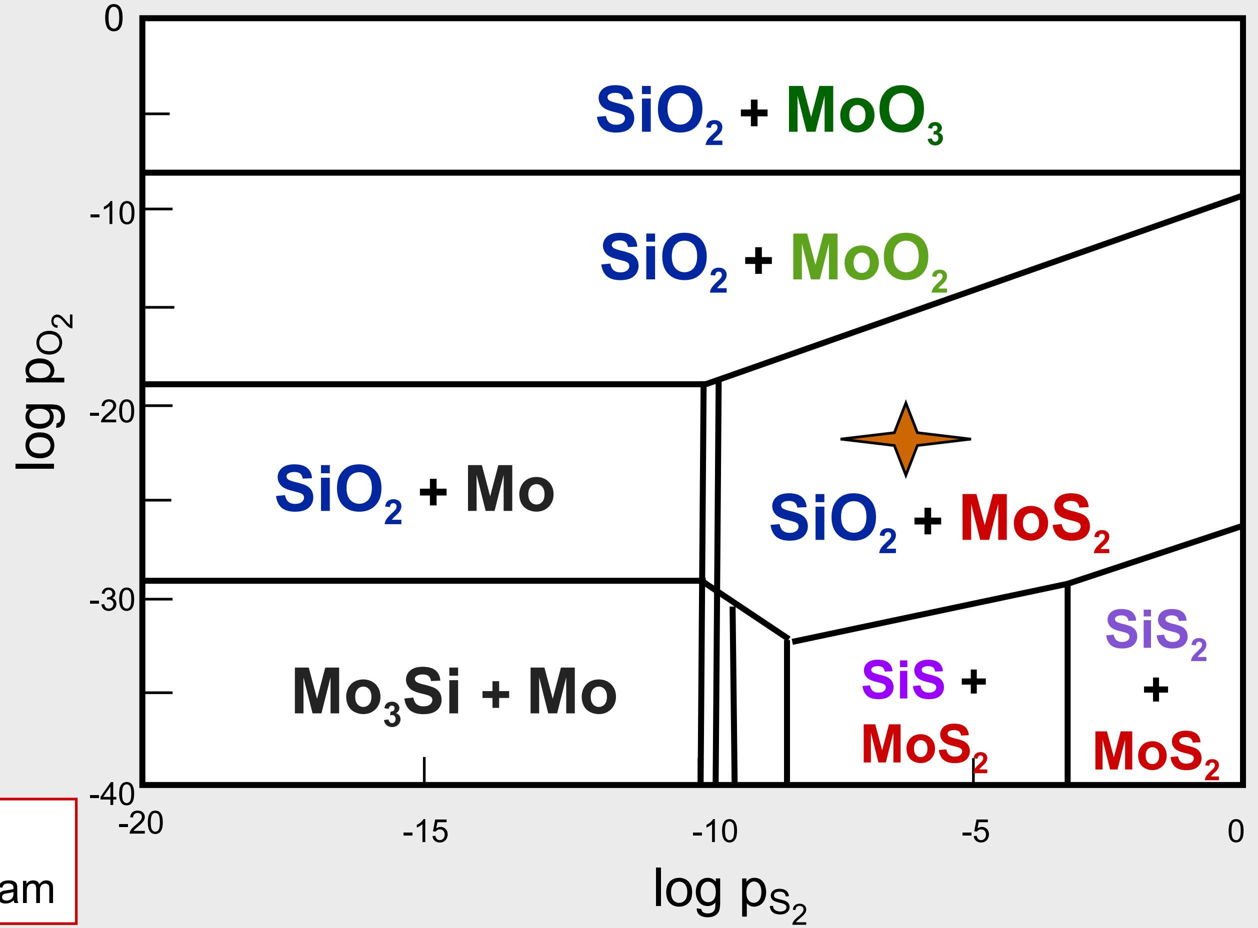



- Mo preferentially oxidizes and volatilizes as $MoO_3$, enriching $Mo_3Si$ & T2 in Si
- Eventually, protective $SiO_2$/borosilicate may seal reactive Mo phase; whether and how fast this occurs depends on
  - thickness of continuous Mo phase - minimize *d*
  - size and distribution of Si-, B-enriched phases
  - temperature

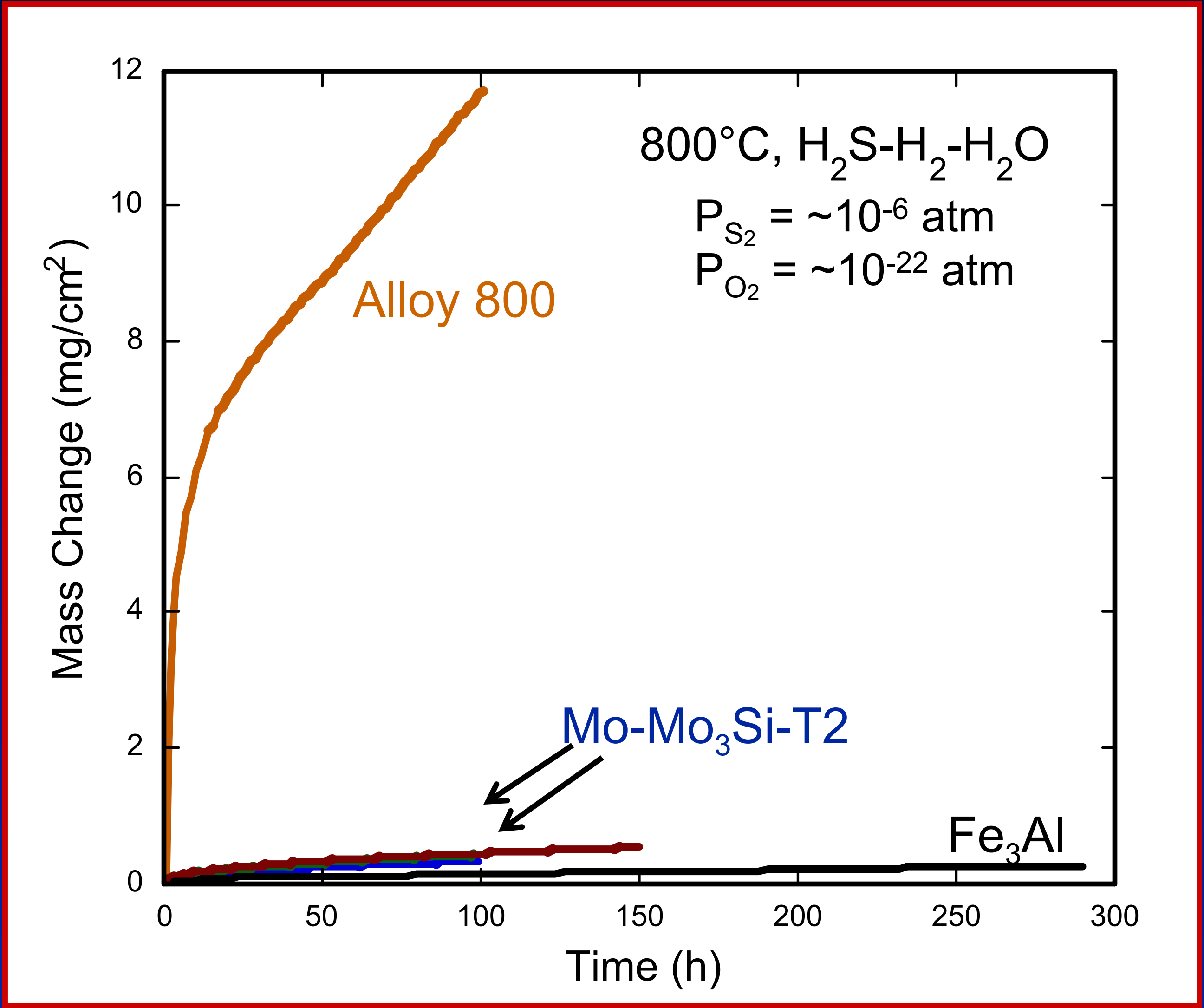
# Preliminary Exposures Under Sulfidizing Type Of Conditions Conducted On Mo-$Mo_3Si$-$Mo_5SiB_2$

- $H_2S$-$H_2$-$H_2O$, 800°C, mass continually measured
- $p_{S_2}$ = ~$10^{-6}$ atm, $p_{O_2}$ = ~$10^{-22}$ atm
  (severe coal gasification conditions)

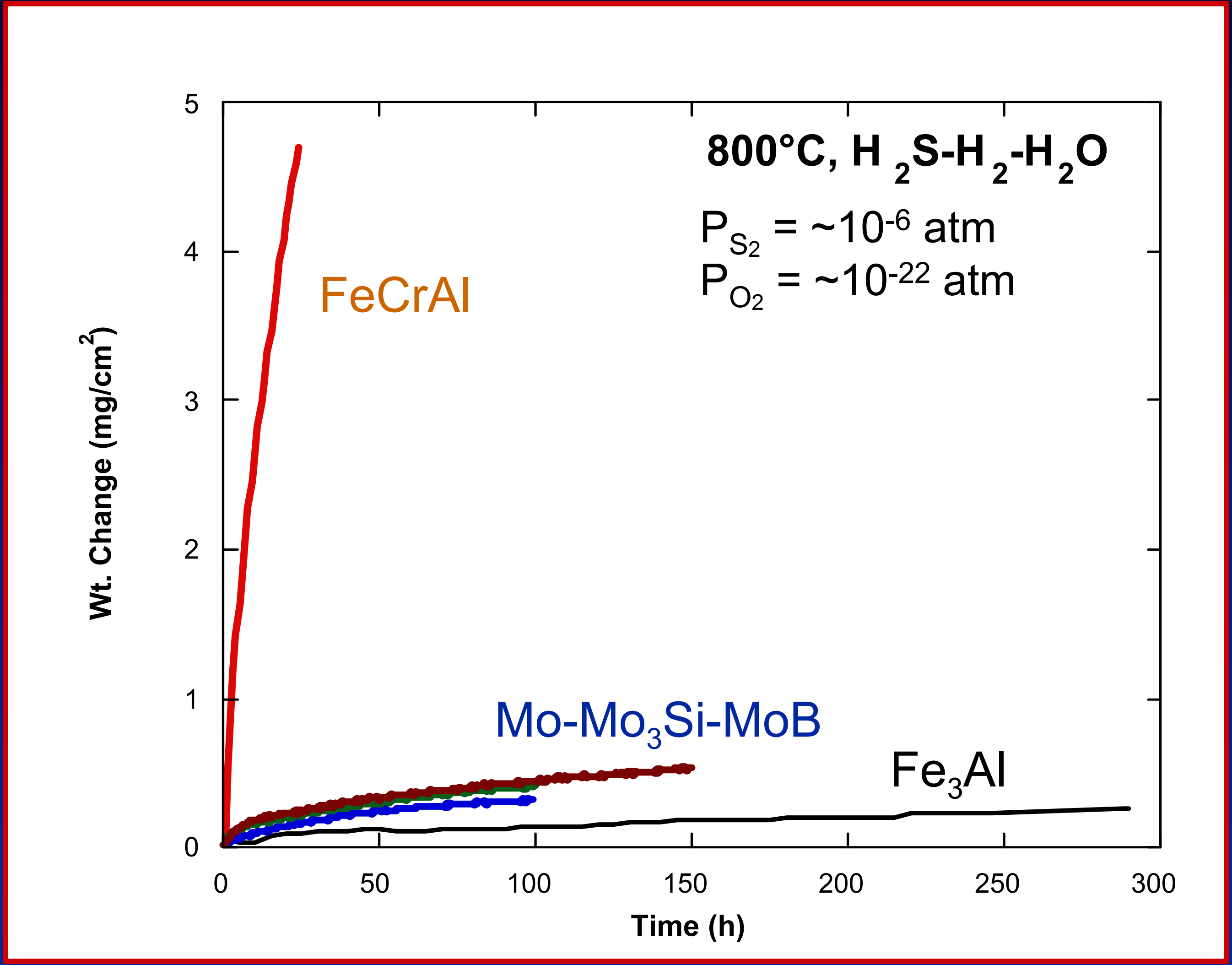



calculated stability diagram

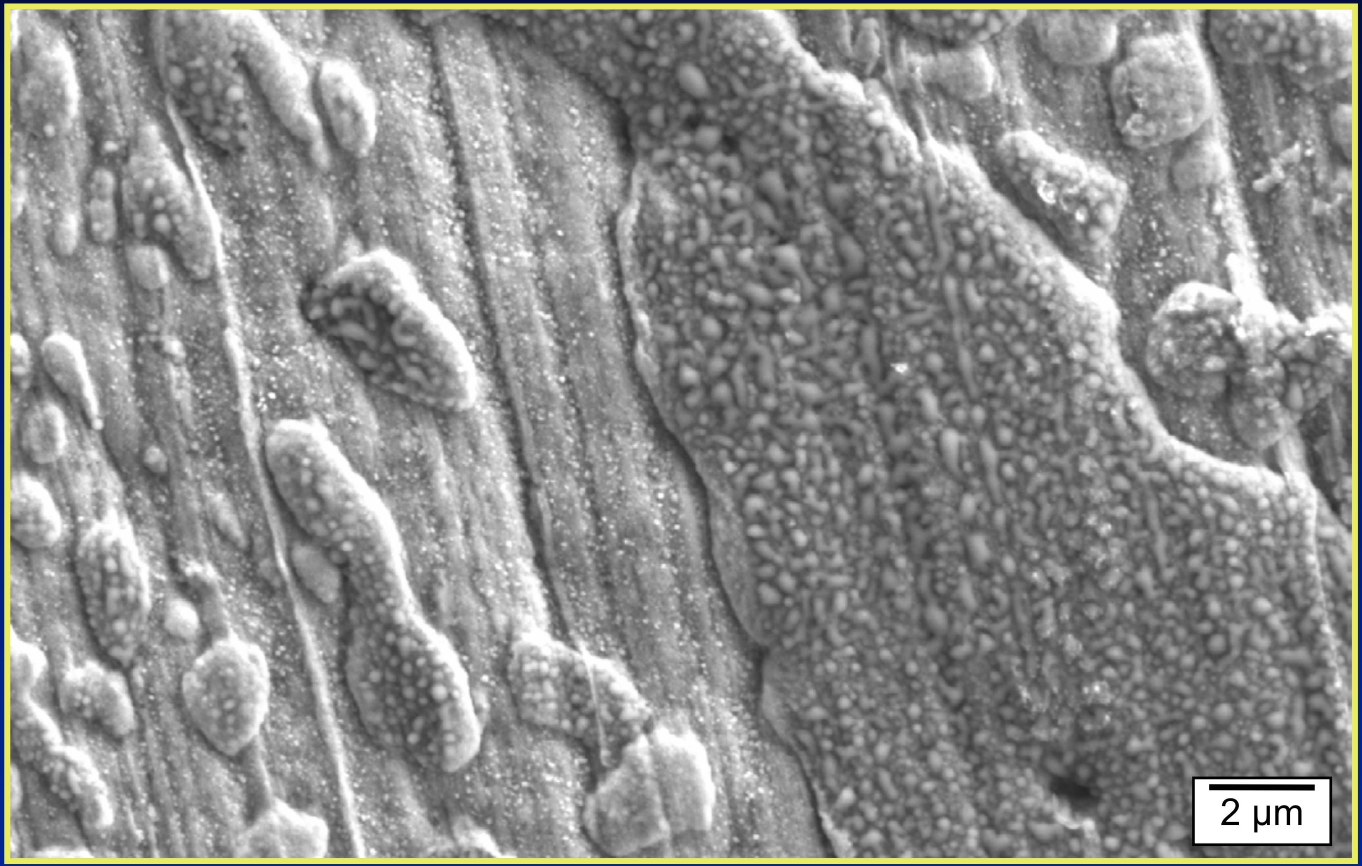
# $Mo\text{-}Mo_3Si\text{-}Mo_5SiB_2$ Showed Very Good Sulfidation Resistance



# $Mo-Mo_3Si-Mo_5SiB_2$ Showed Very Good Sulfidation Resistance

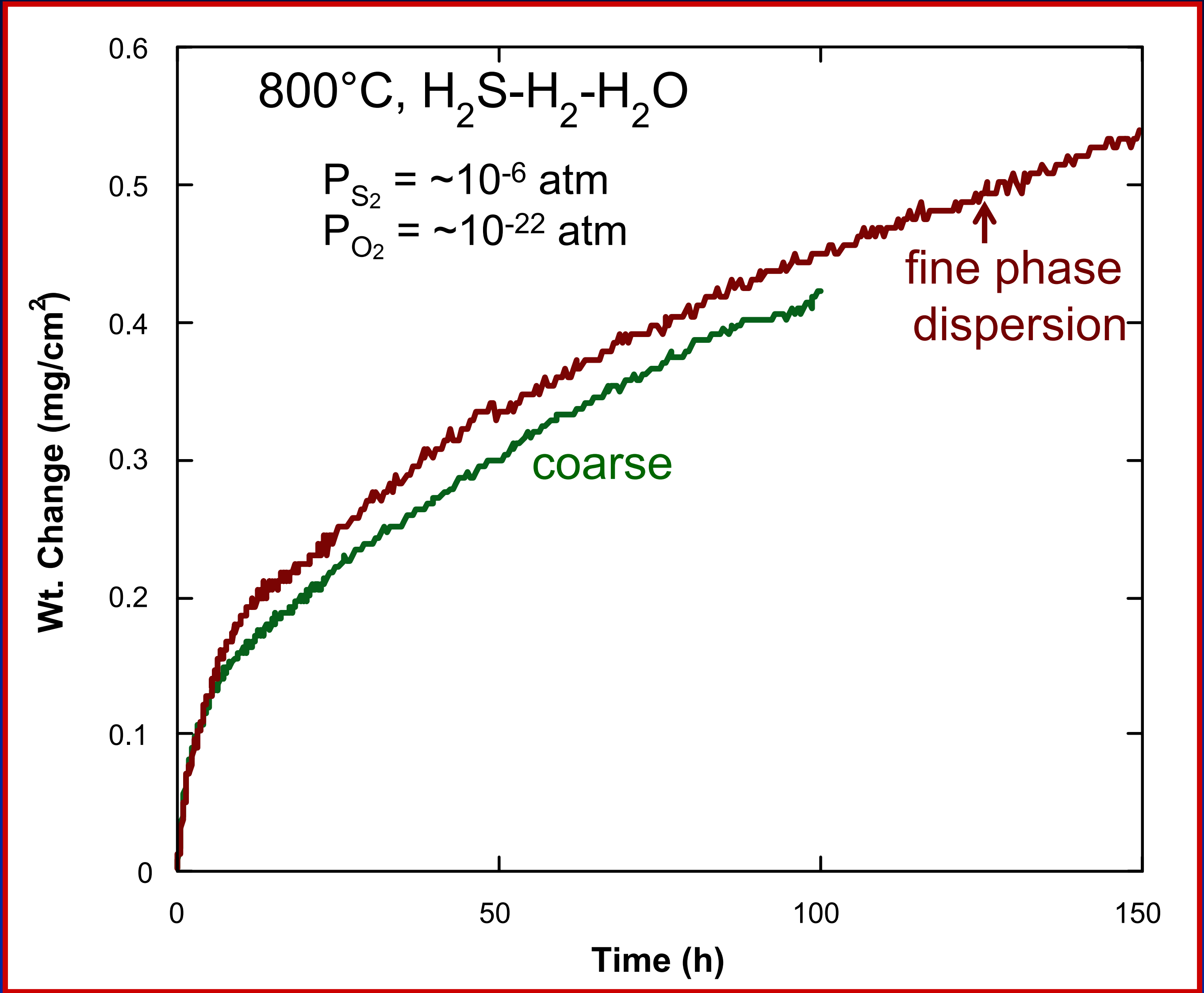


# Thin Corrosion Products Were Observed; Replicated Underlying Alloy Microstructure




$H_2S$-$H_2$-$H_2O$, 800°C, 150 h

# Phase Sizes Appeared To Have Little Effect On Sulfidation Behavior



# Summary

- Smart protective coatings may provide one of the breakthrough areas to overcome material barriers imposed by the requirements of advanced fossil energy systems
- Multiphase Mo-silicides are being examined as the first attempt in evaluating smart coating concepts for high-temperature corrosion resistance in fossil environments
- Mo-rich, B-containing silicides can have adequate oxidation resistance at high-temperature
- Preliminary results show Mo-rich silicides have excellent sulfidation resistance