Effects of Wet Air and Synthetic Combustion Gas Atmospheres on the Oxidation Behavior of Mo-Si-B Alloys

Matthew J. Kramer, Andrew J. Thom, Pranab Mandal, Vikas Behrani, and Mufit Akinc

Ames Laboratory and
Department of Materials Science and Engineering
Iowa State University, Ames, IA

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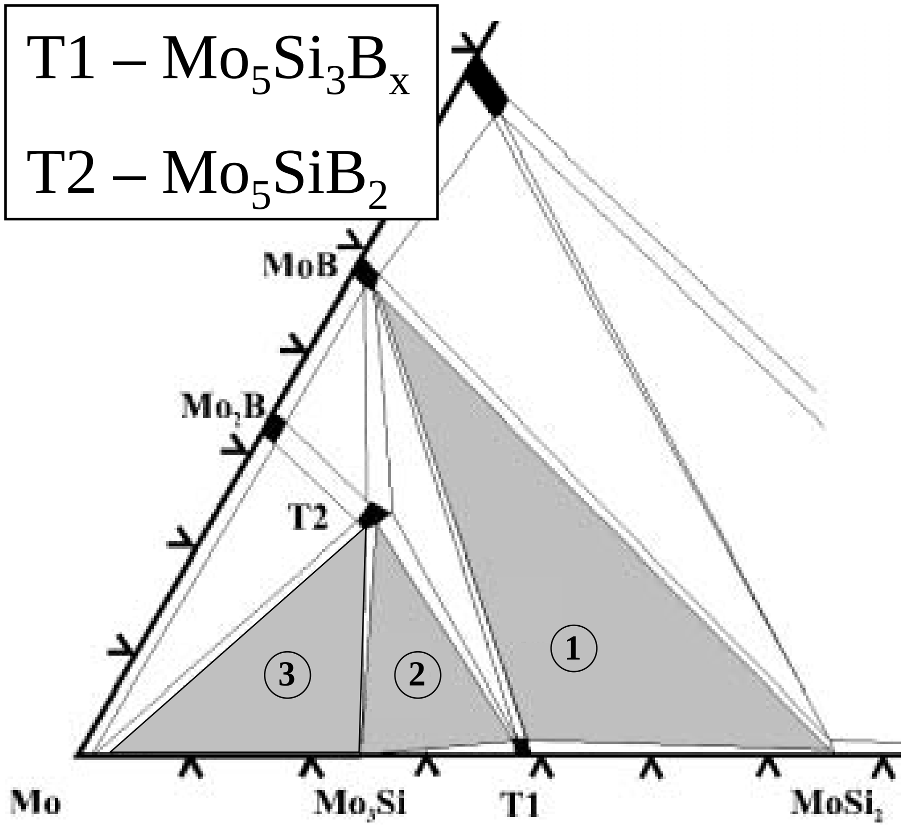
Mo-Si-B Intermetallic System



- **T1-containing assemblages ① & ②**
  - **Excellent oxidation resistance and creep strength**
  - **Low fracture toughness**
- **Mo-containing assemblage ③**
  - **Improved fracture toughness**
  - **Reduced oxidation resistance**
- **Processible by:**
  - **Casting, sintering, plasma spraying**
- **Electrically conductive**

Multiphase composites can meet several of the Vision 21 Goals, but additional research is needed to develop optimum alloy meeting all of the goals

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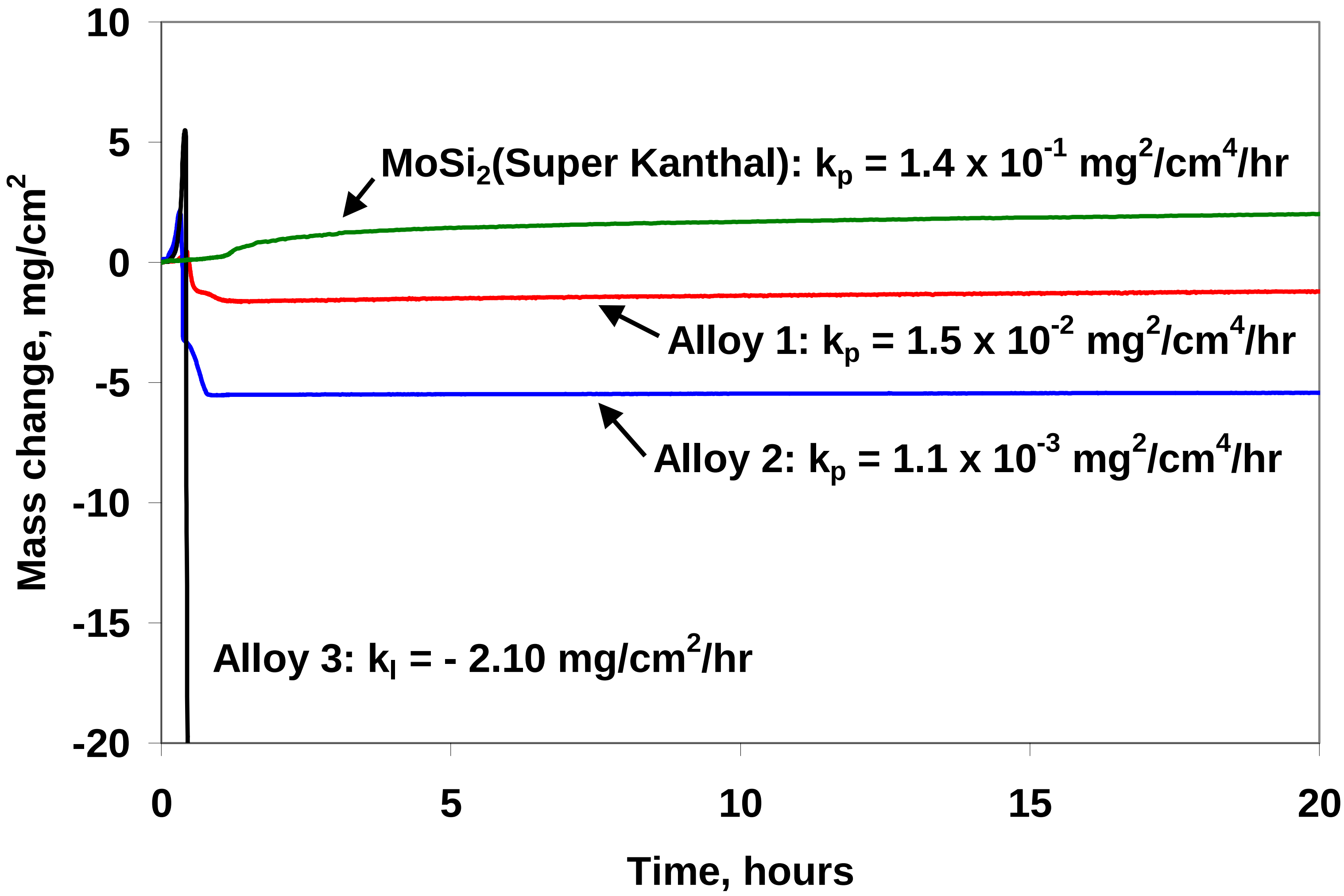
Isothermal Oxidation at 1600°C in Dry Air



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Looking to the Future: Vision 21 Goals to Develop New High Temperature Materials

- **Turbine Components**
  - **Target FY08**
    - ➢ **1000 hrs. 3000°F (1650°C)**
    - ➢ **Corrosive environment**
- **Heat Exchangers**
  - **Target FY04**
    - ➢ **Alloy-tube**

      1000 hrs. 2300°F (1260°C)
    - ➢ **Ceramic-tube**

      1000 hrs. 3000°F (1650°C)

- **Mo-Si-B Alloys**
  - ➢ **T1-based alloys stable for 240 hrs at 2900°F (1600°C) in dry air**
  - ➢ **Effect of combustion gases?**
  - ➢ **Enhance fracture toughness?**
  - ➢ **Fatigue tolerant?**

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Project Objectives

- **Near Term**
  - ➢ **Mo-Si-B**
  - ➢ **T1-based alloys now meet temperature criteria for heat exchangers**

    Issues to be addressed:
    - **Fabrication**
    - **Corrosion**
    - **Improvements with minor alloy additions**

- **Future**
  - ➢ **Derivative Mo-Si-B alloys**
  - ➢ **T1-based alloys now meet creep resistance and temperature criteria for turbine applications**

    Issues to be addressed:
    - **Near-net shape processing**
    - **Low fracture toughness**
    - **Long term oxidation resistance**
    - **Cyclic oxidation resistance**

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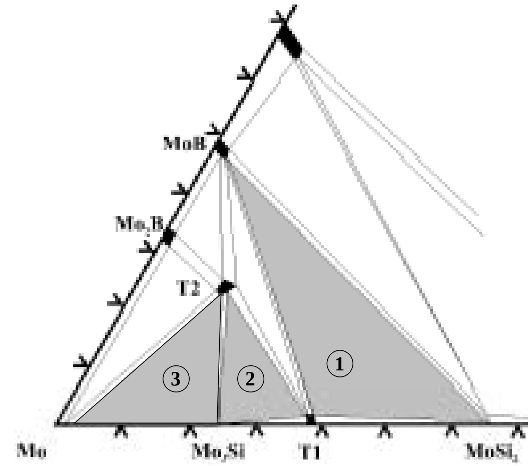
Alloy Compositions Tested

- Commercially procured, pre-alloyed powders
- Sintered at 1800°-1900°C in Ar atmosphere to > 95% density



	Wt %			Phase Fraction (Vol %)					
Alloy	Mo	Si	B	T1	MoB	$MoSi_2$	T2	Mo_3Si	Mo
1	84.0	13.4	2.6	66	22	12			
2	88.6	9.9	1.5	45			31	24	
3	94.6	4.3	1.1				30	27	43

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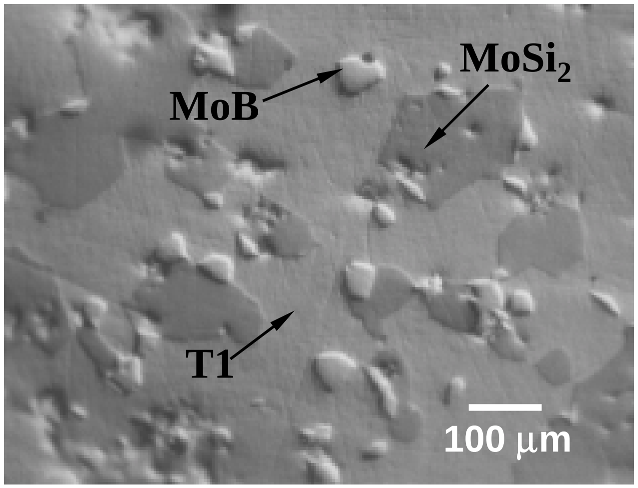
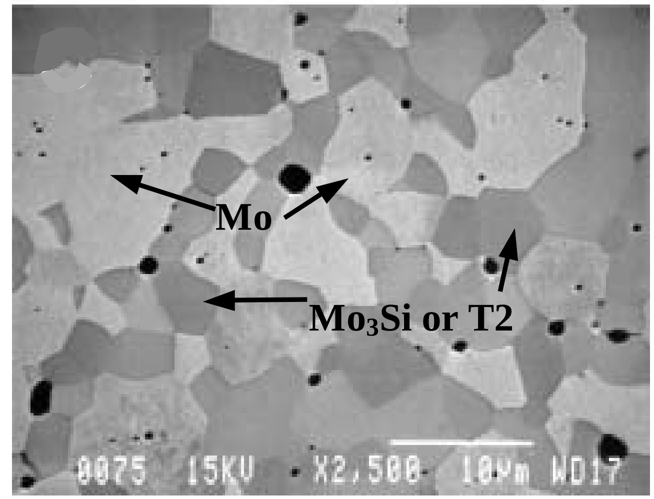
Typical Microstructures

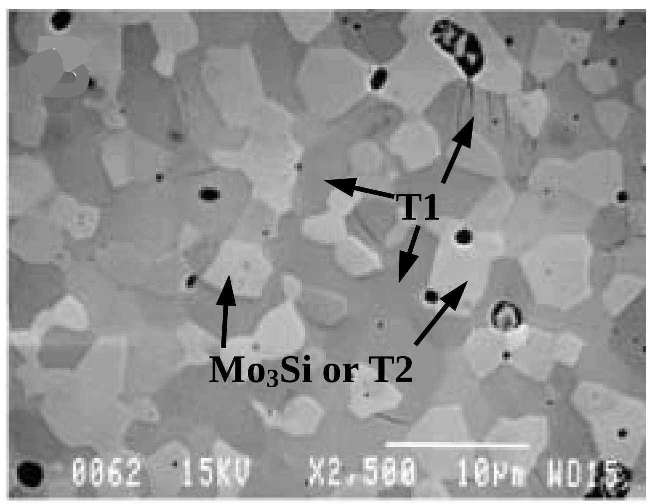


Alloy 1

Alloy 2



Alloy 3



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Results and Discussion
Outline

- **Review of alloy oxidation in dry and wet air (150 Torr H_2O)**
- **Isothermal oxidation in dry air to 1600°C and wet air to 1000°C**
- **Effect of pre-oxidation on scale formation of Alloy 3**
- **Effect of synthetic oxidizing combustion gas mixture N_2 - 13 CO_2 - 10H_2O - 4O_2 at 1000° and 1100°C**

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Isothermal Measurements in Wet/Corrosive Gases

- Requires use of purge and reactive gases to achieve gas separation and protect balance mechanism
- Condensation of MoO_3 onto hangdown can occur in Alloy 3
- Used pre-oxidation in tube furnace to induce initial mass loss

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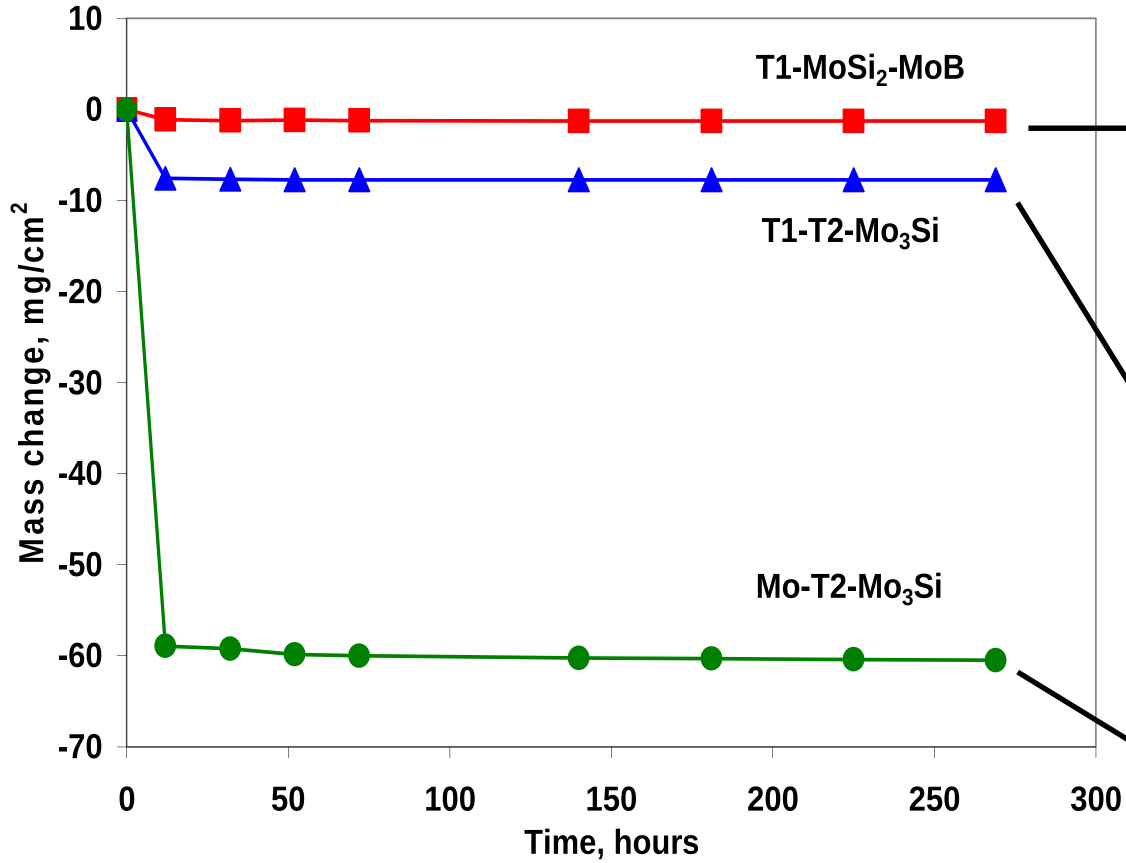
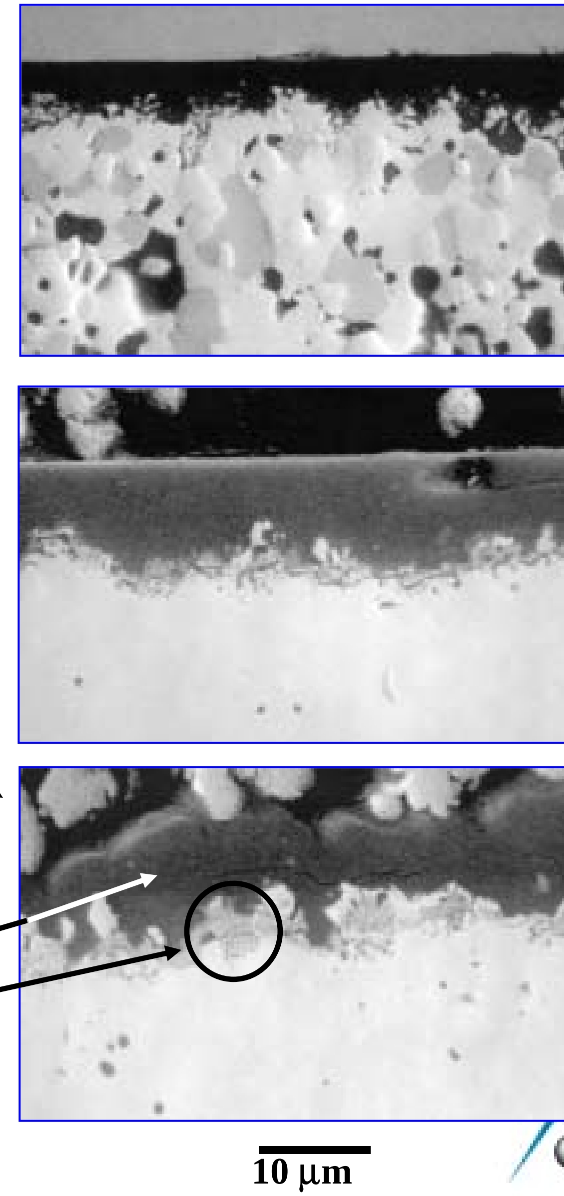
Oxidation in Dry Air at 1100°C





- **External borosilicate glassy scale with subscale Mo and MoO_2**

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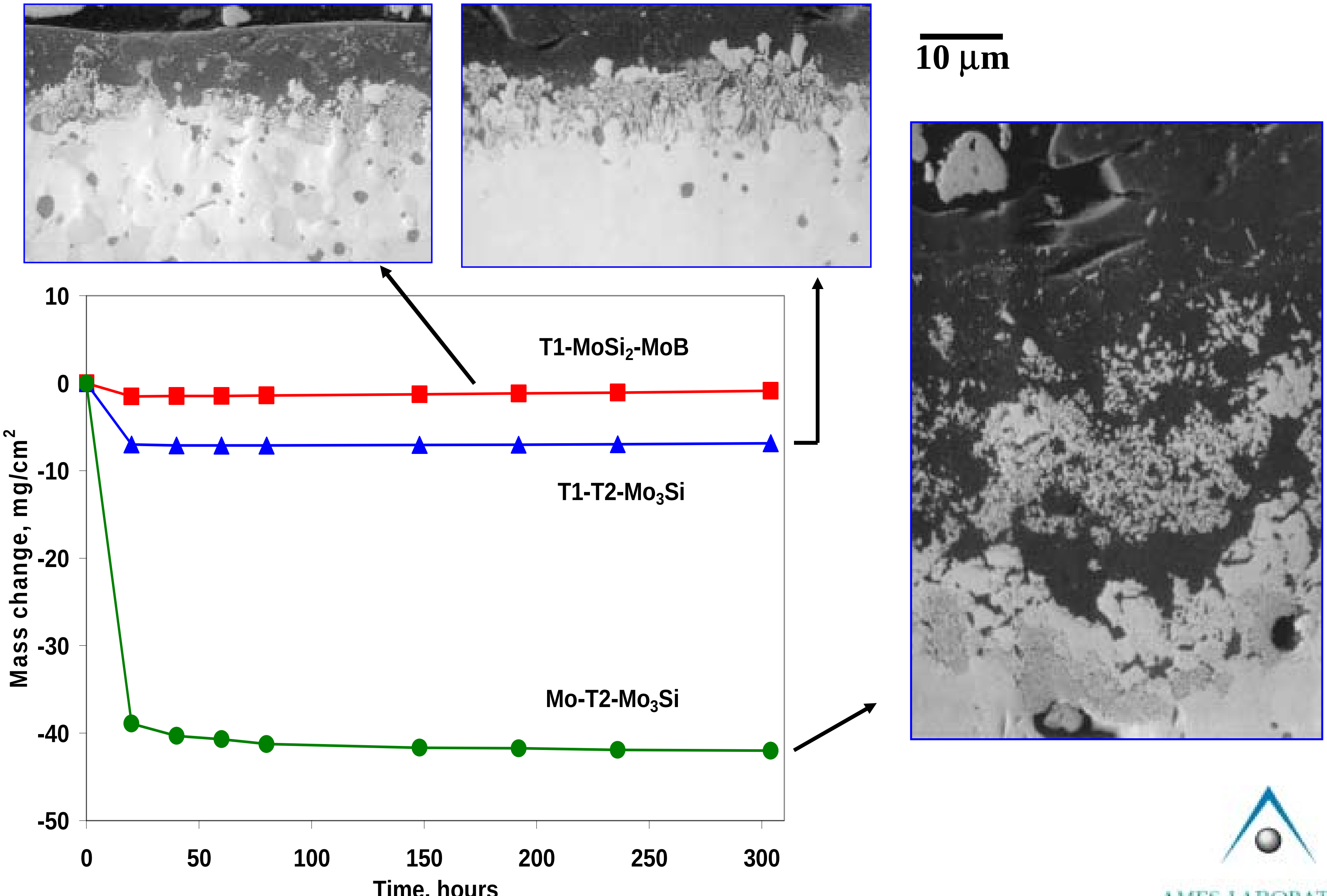
Oxidation in Wet Air at 1100°C



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Scale Formation Reactions

- **T1 phase (Alloy 1 and Alloy 2):**

$$Mo_5Si_3B + (x+\tfrac{15}{4})\,O_2 \rightarrow (5\text{-}x)\,Mo + x\,MoO_2 + 3\,SiO_2 + \tfrac{1}{2}B_2O_3$$

$$Mo_5Si_3B + 2(x+\tfrac{15}{4})\,H_2O \rightarrow (5\text{-}x)\,Mo + x\,MoO_2 + 3\,SiO_2 + \tfrac{1}{2}\,B_2O_3 + 2(x+\tfrac{15}{4})\,H_2$$

$$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$$

borosilicate glass ~ 14 at% B_2O_3

- **T2 phase (Alloy 2 and Alloy 3):**

$$Mo_5SiB_2 + (x+\tfrac{5}{2})\,O_2 \rightarrow (5\text{-}x)\,Mo + x\,MoO_2 + SiO_2 + B_2O_3$$

$$Mo_5SiB_2 + 2(x+\tfrac{5}{2})\,H_2O \rightarrow (5\text{-}x)\,Mo + x\,MoO_2 + SiO_2 + B_2O_3 + 2(x+\tfrac{5}{2})\,H_2$$

borosilicate glass ~ 50 at% B_2O_3 $\eta(T2) << \eta(T1)$

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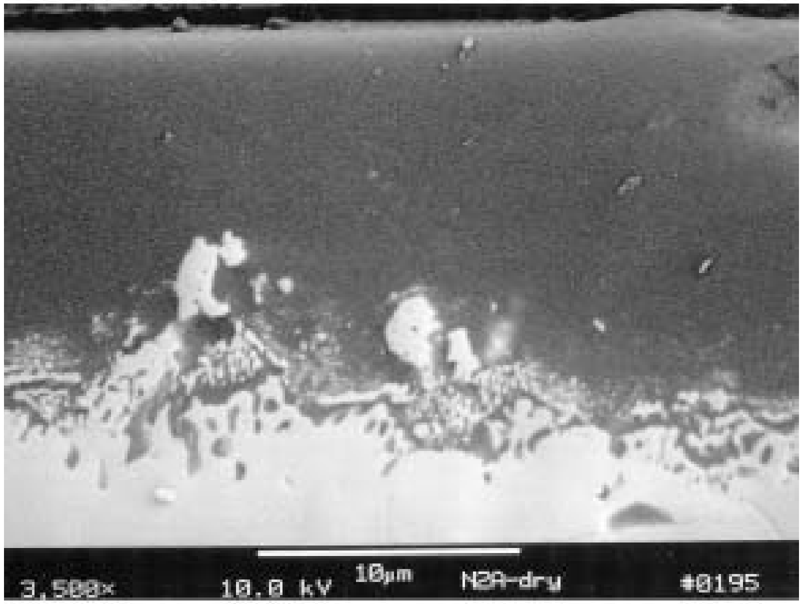
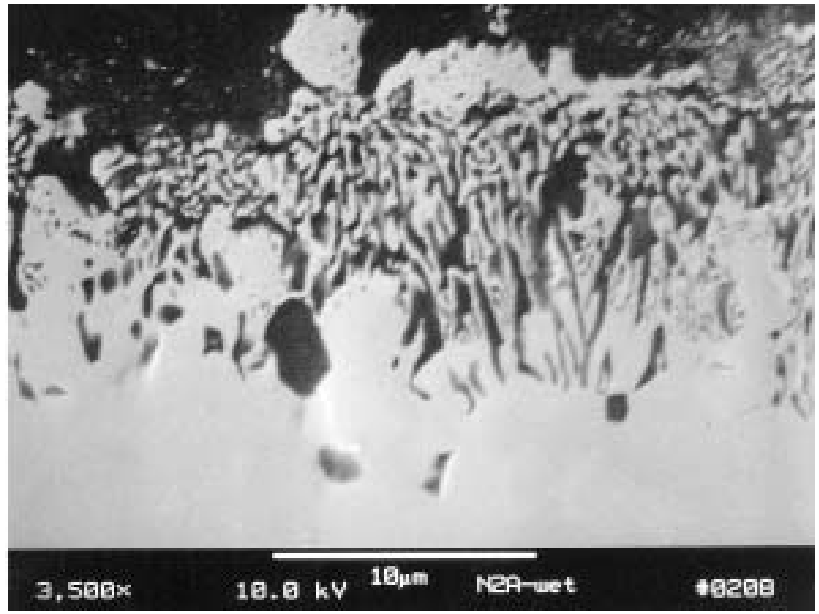
Enhanced Interlayer Growth (Alloy 2 as example)

Dry Air



Wet Air



- **Interlayer appears as fine, eutectic-like Mo-rich phase dispersed in a thin, continuous matrix of darker silica; larger grains of MoO_2 are detectable**
- **Insufficient spatial resolution for EDS to determine if eutectic-like areas correspond to Mo or MoO_2**

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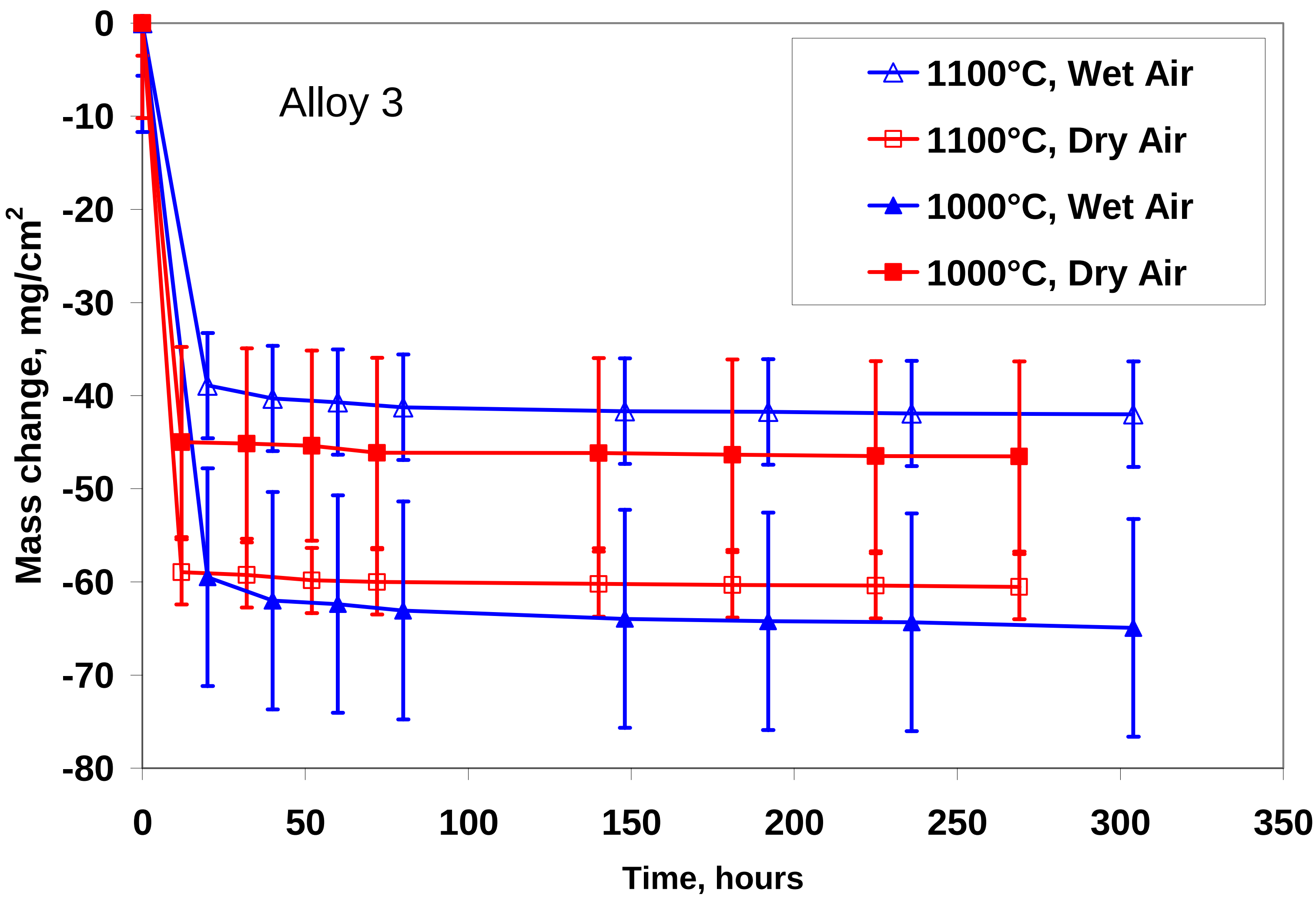
Why Isothermal Oxidation Measurements?



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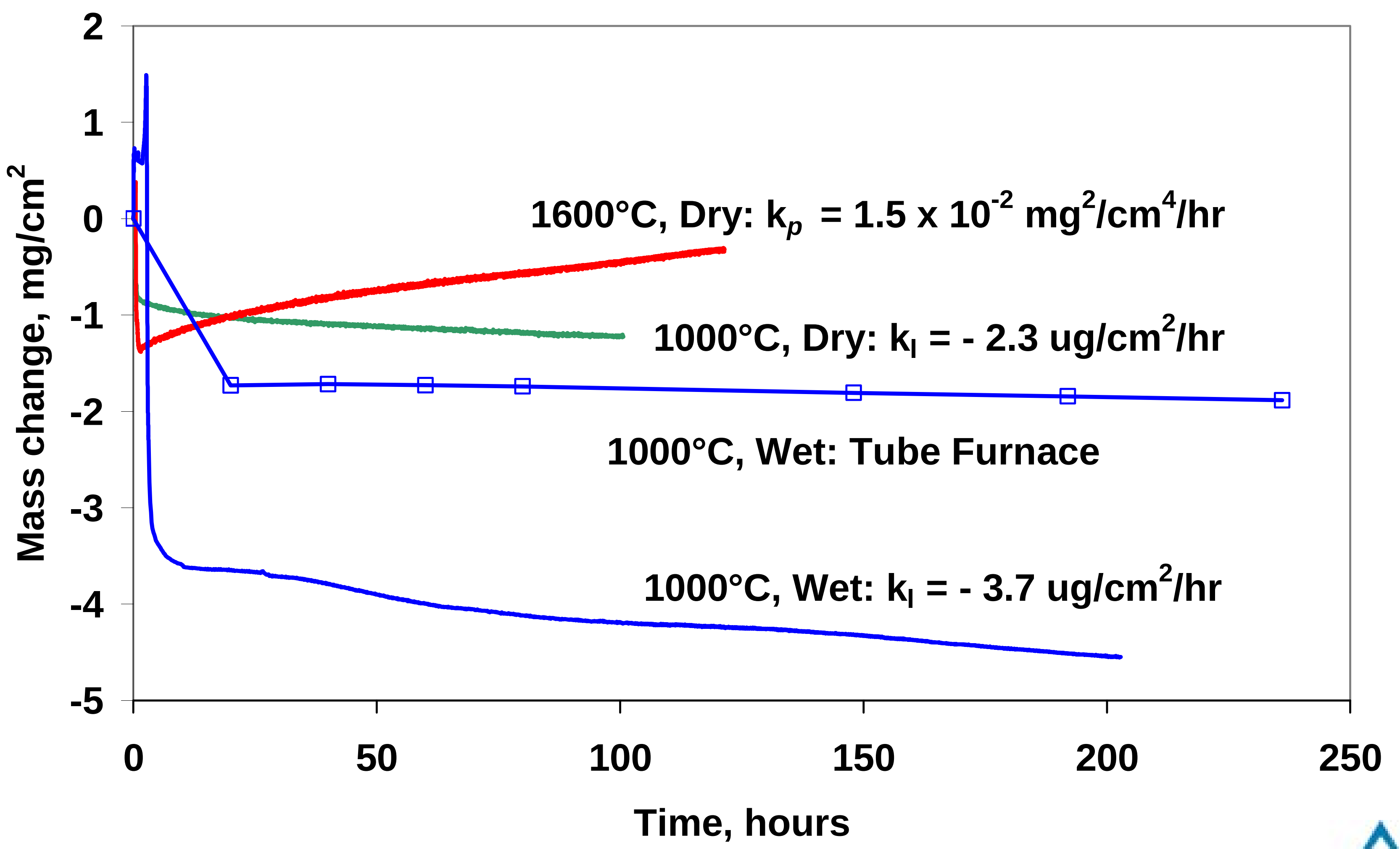
Isothermal Oxidation of Alloy 1



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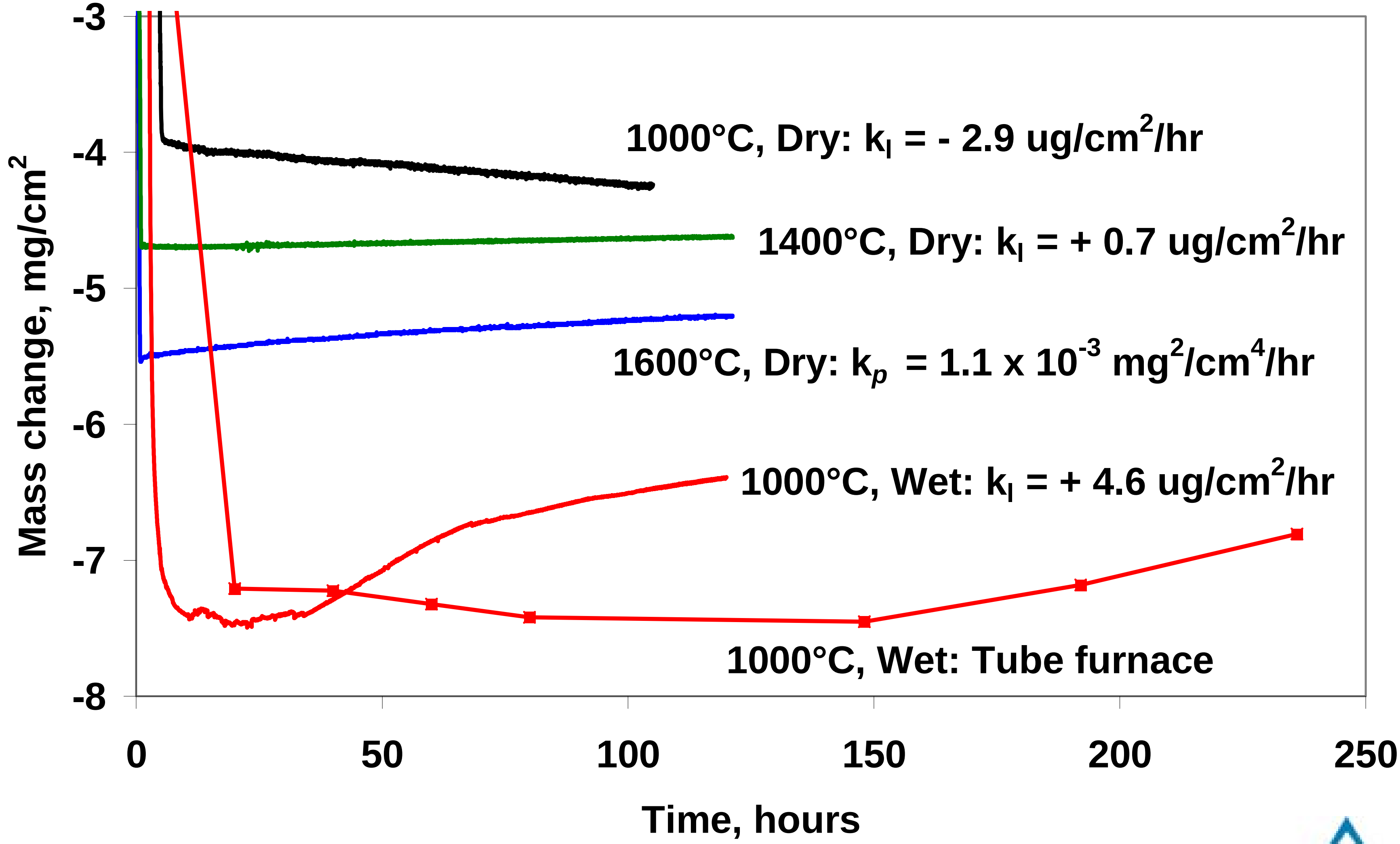
Isothermal Oxidation of Alloy 2



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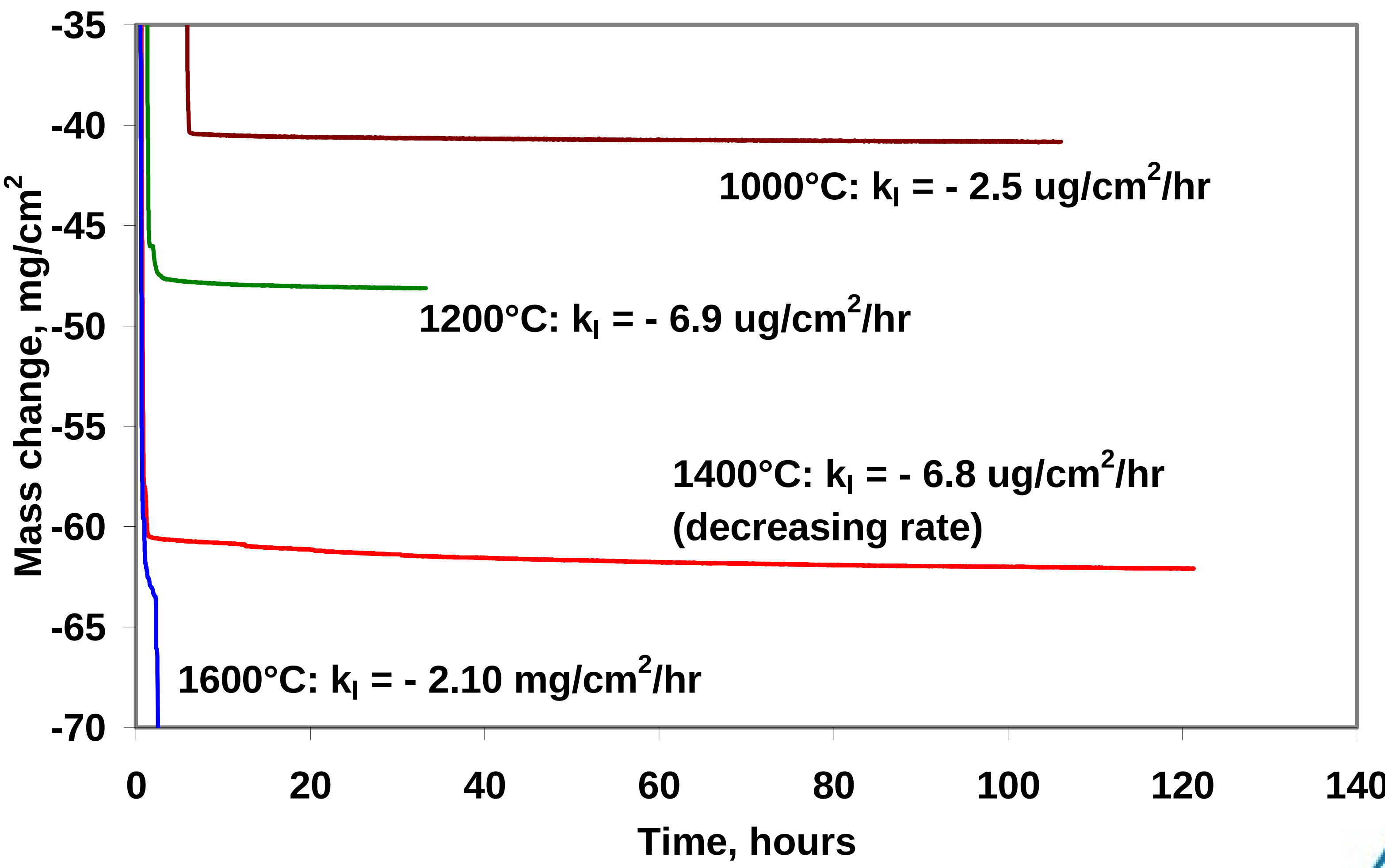
Isothermal Oxidation of Alloy 3 in Dry Air



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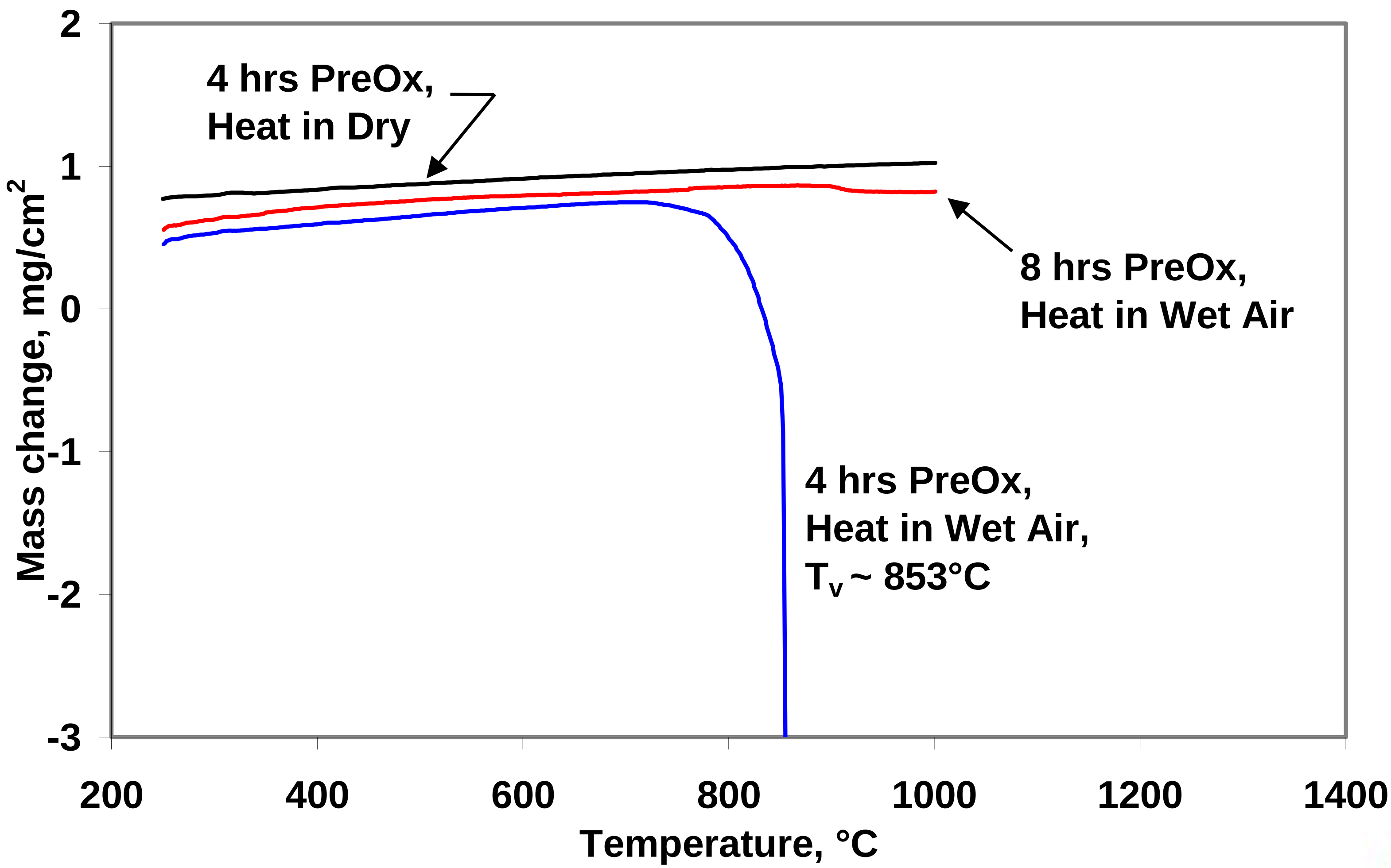
Pre-Oxidation Effect on Alloy 3 Scale Formation



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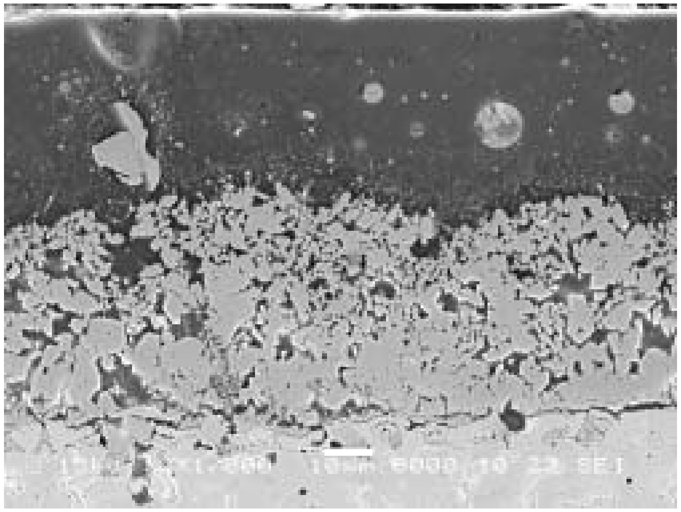
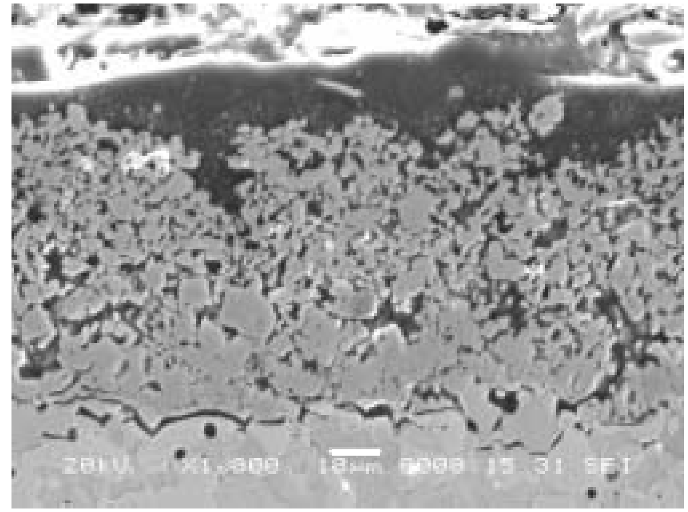
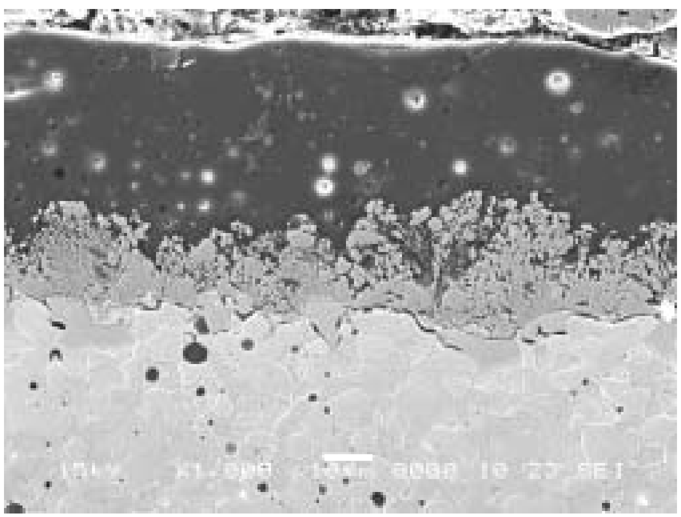
Alloy 3 Pre-Oxidation and Scale Formation

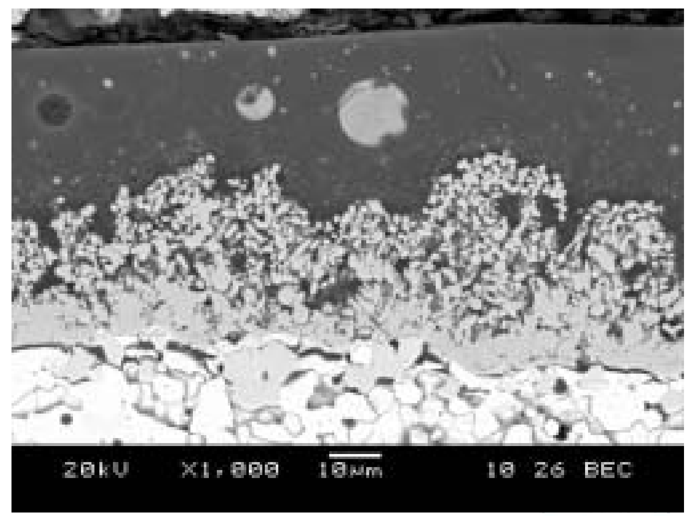
4 hrs Pre-Ox in Dry Air

8 hrs Pre-Ox in Dry Air





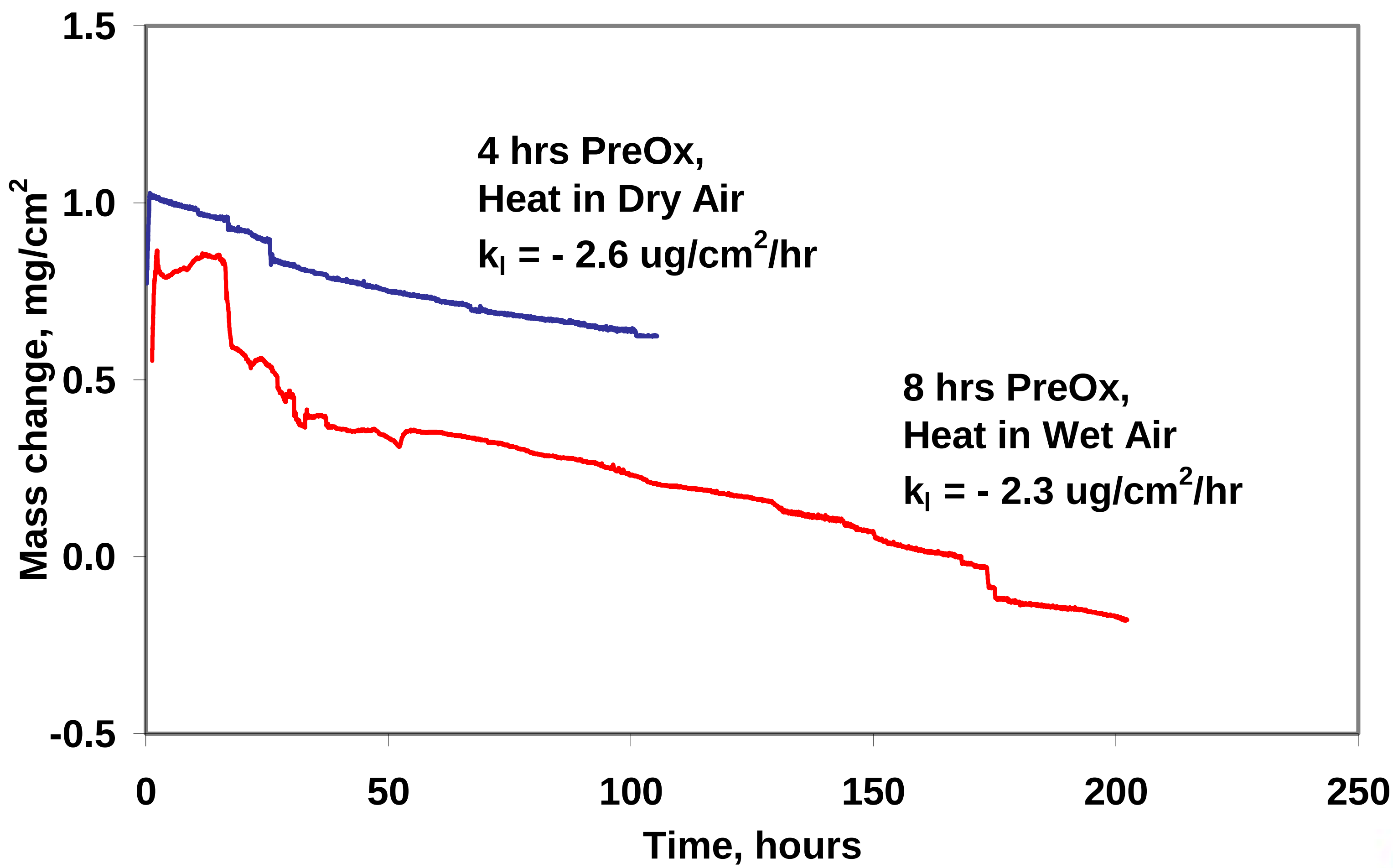




3 hr exposure to Wet Air

10µm

Oxidation of Alloy 3 in Wet Air at 1000°C



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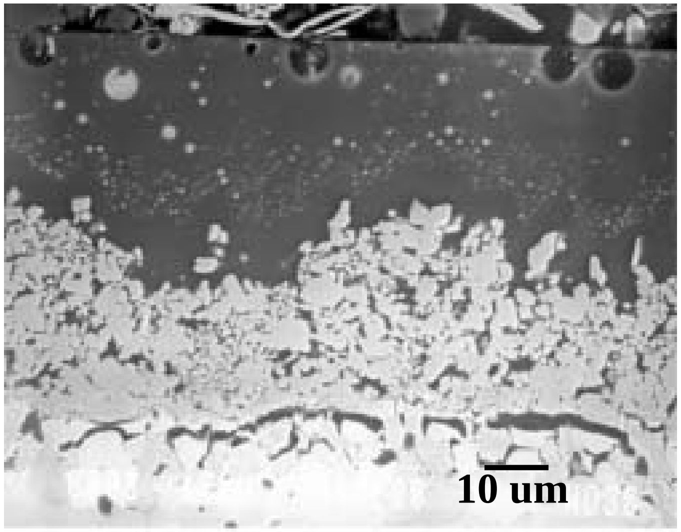
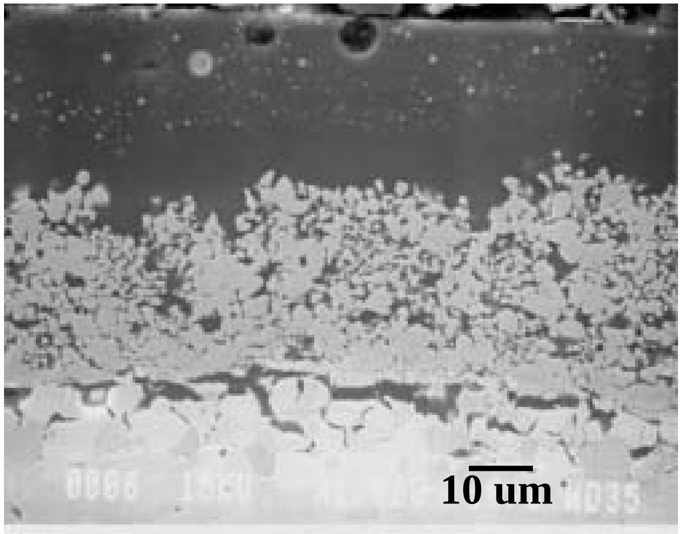
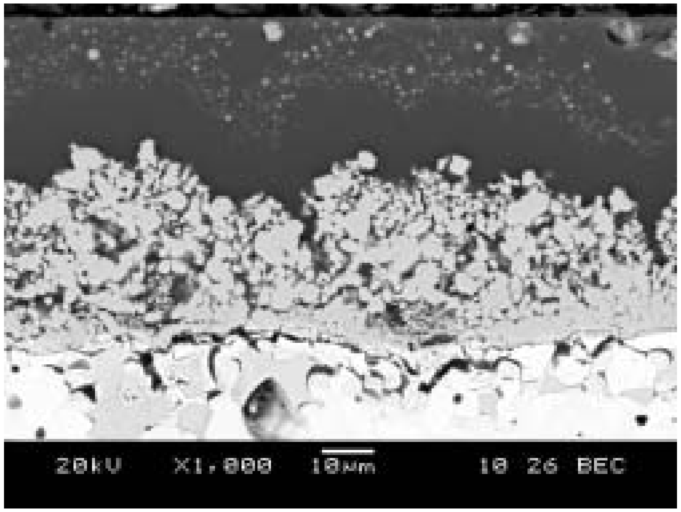
Scale Evolution During Alloy 3 Oxidation



8 hrs Dry Air,
100 hrs Wet Air



8 hrs Dry Air,
200 hrs Wet Air



200 hrs Dry Air

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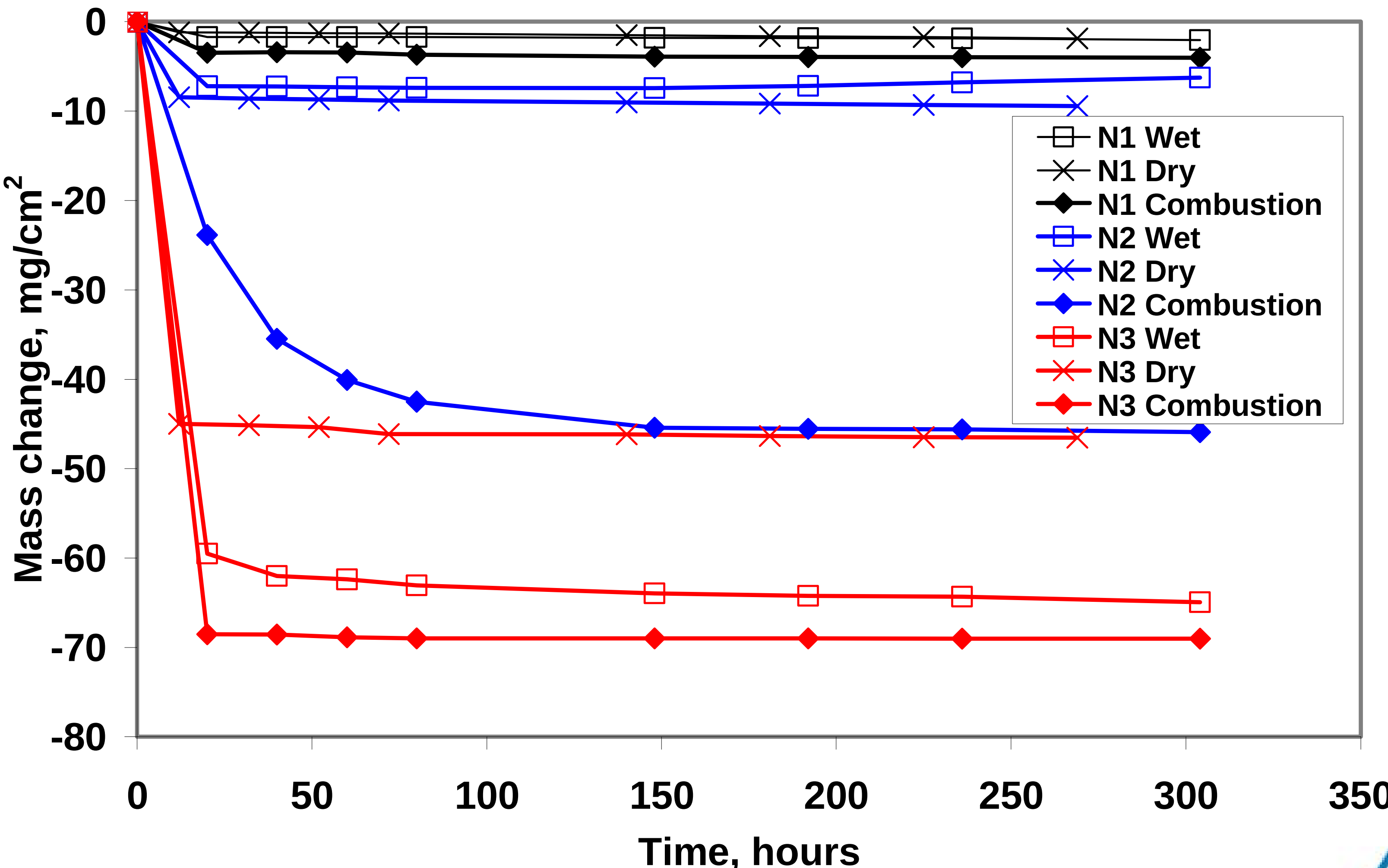
Synthetic Combustion Gas Exposure at 1000°C



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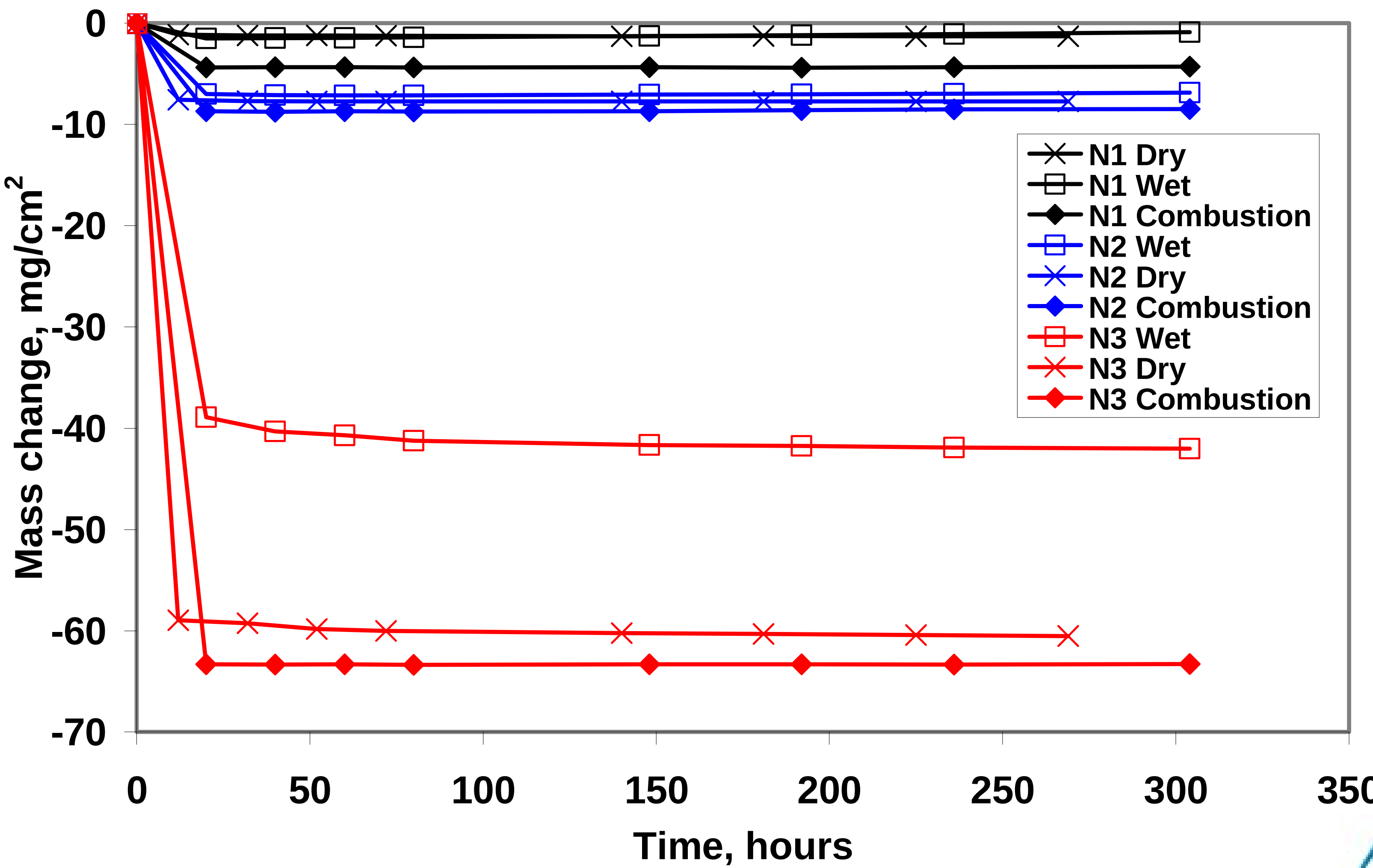
Synthetic Combustion Gas Exposure at 1100°C



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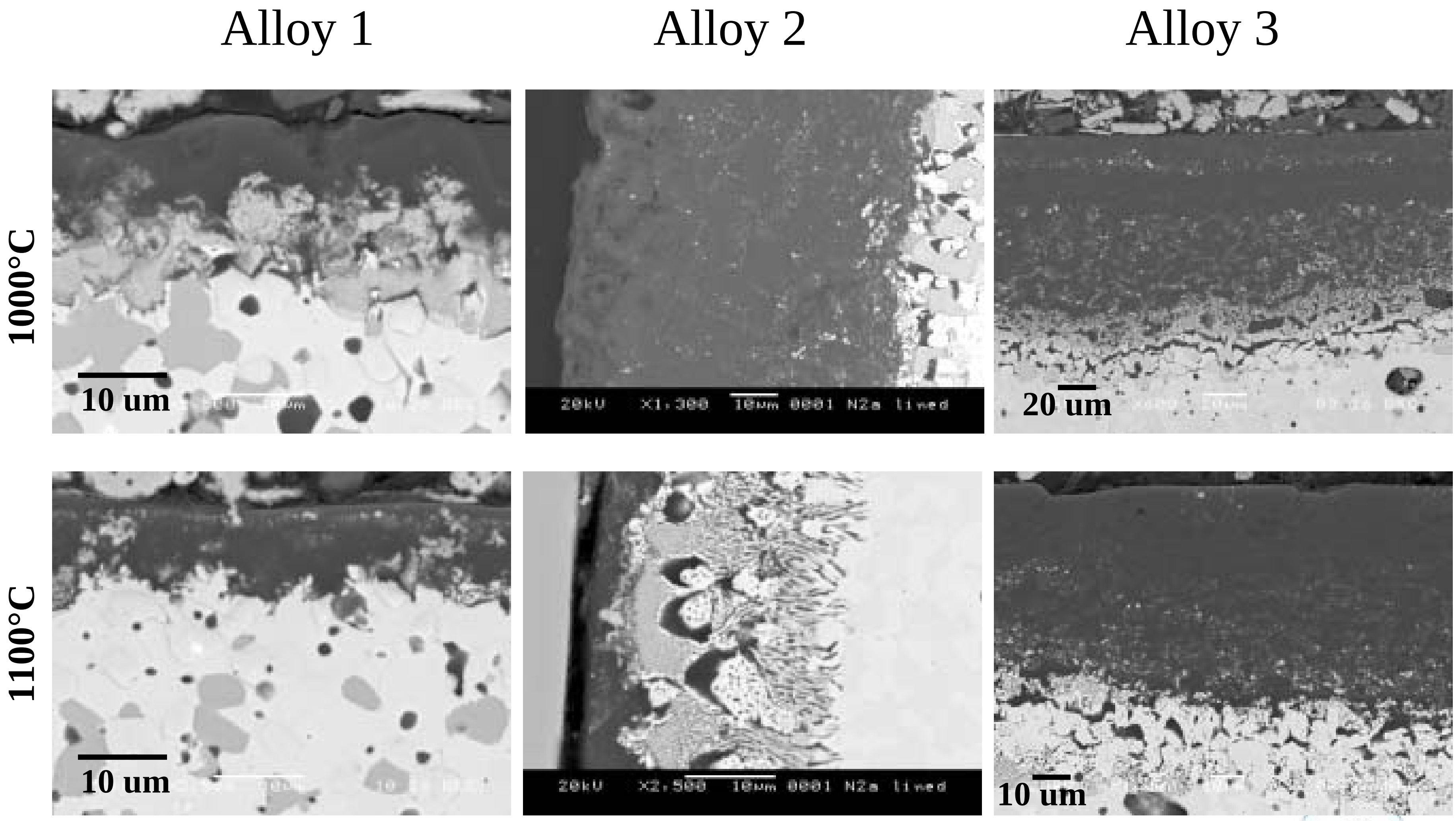
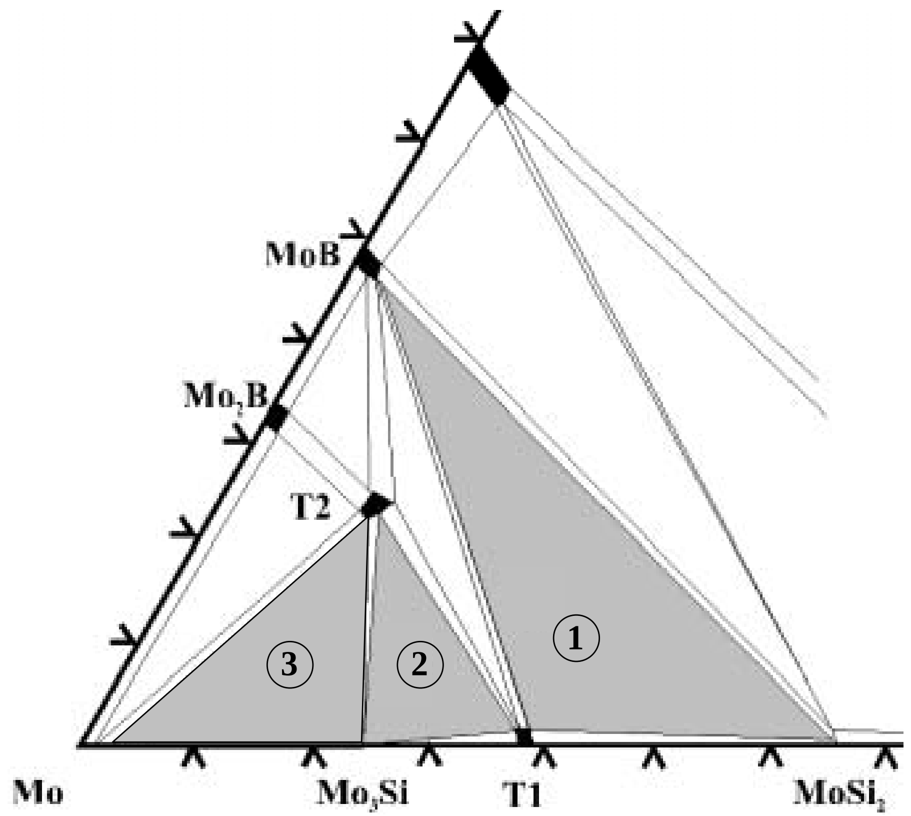
Effect of Combustion Gas Exposure



Summary

- **Dry Air**
  - **All alloys show protective silica scale**
    - **T up to 1600 C**
- **Wet Air**
  - **Alloys 1 & 2 protective silica scale**
    - **Thicker than dry air**
  - **Alloy 3, highly variable**
    - **Due to overall low Si content**
    - **Size and distribution of metal phase**
- **Combustion Gas**
  - **Alloys 1 & 2 mixed results**
    - **Better with higher T**
      - **Viscosity?**
  - **Alloy 3**
    - **Pretreatment or protective coatings may be necessary**
- **Stability of the Scale**
  - **Source and amount of Si**
  - **Rate of MoO_2 formation**
  - **Rate of MoO_3 transportation**



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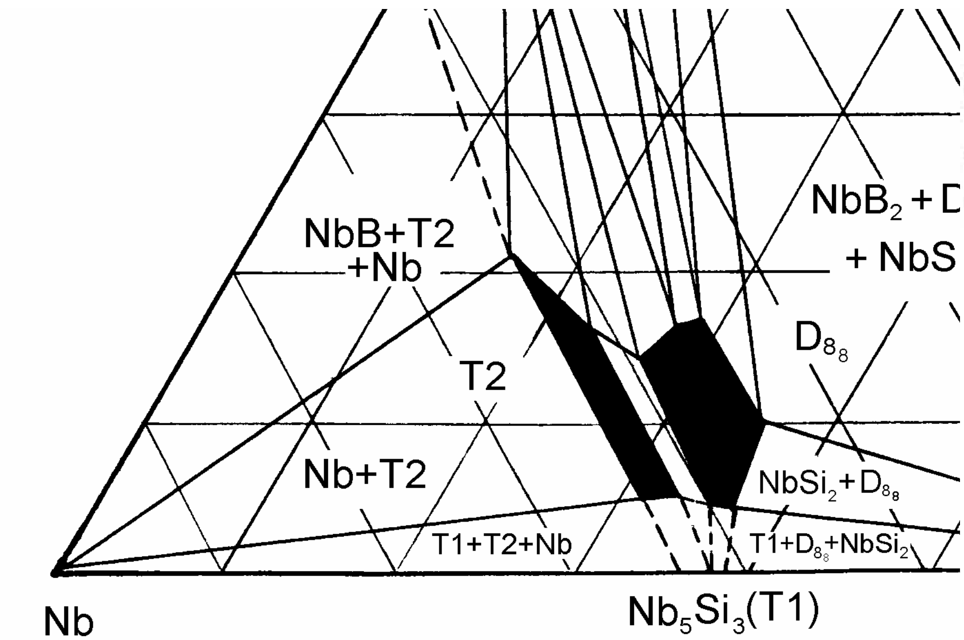
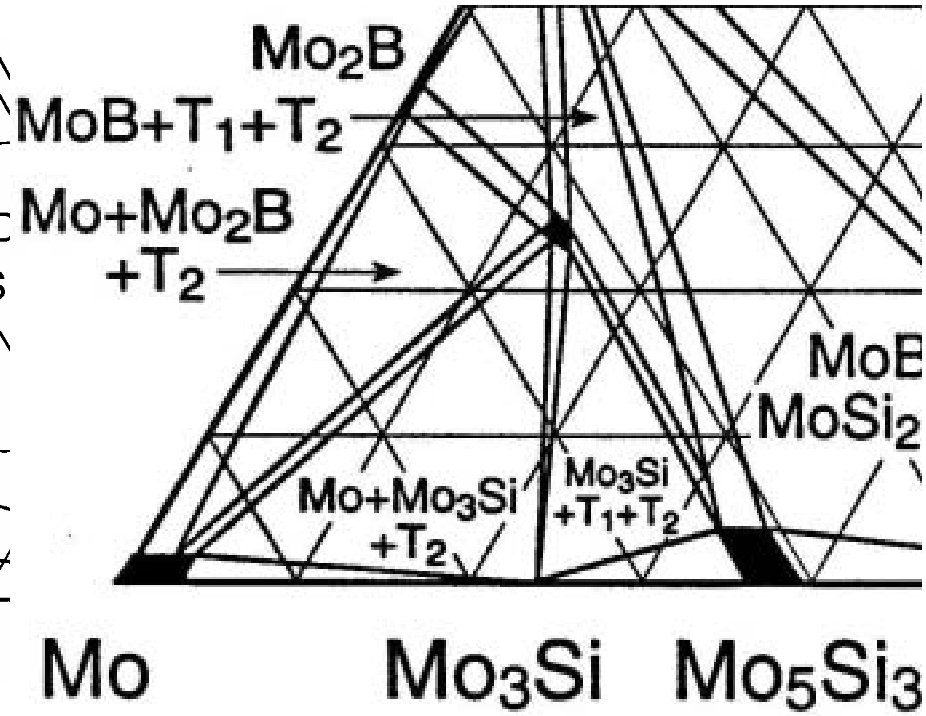
Comparison of Nb-Si-B and Mo-Si-B Phase Diagrams





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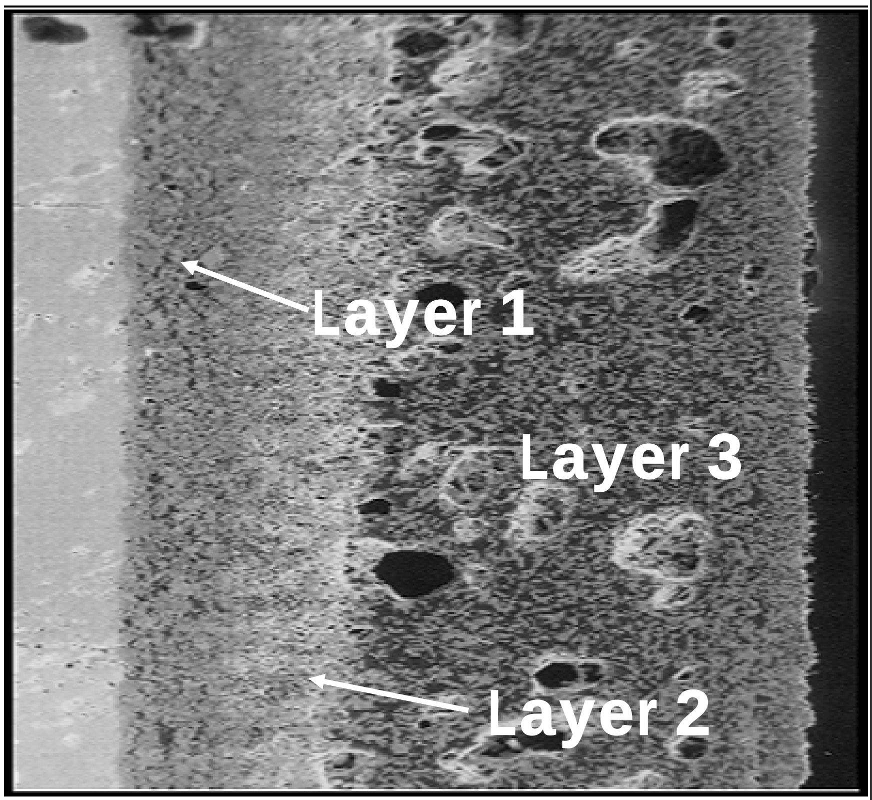
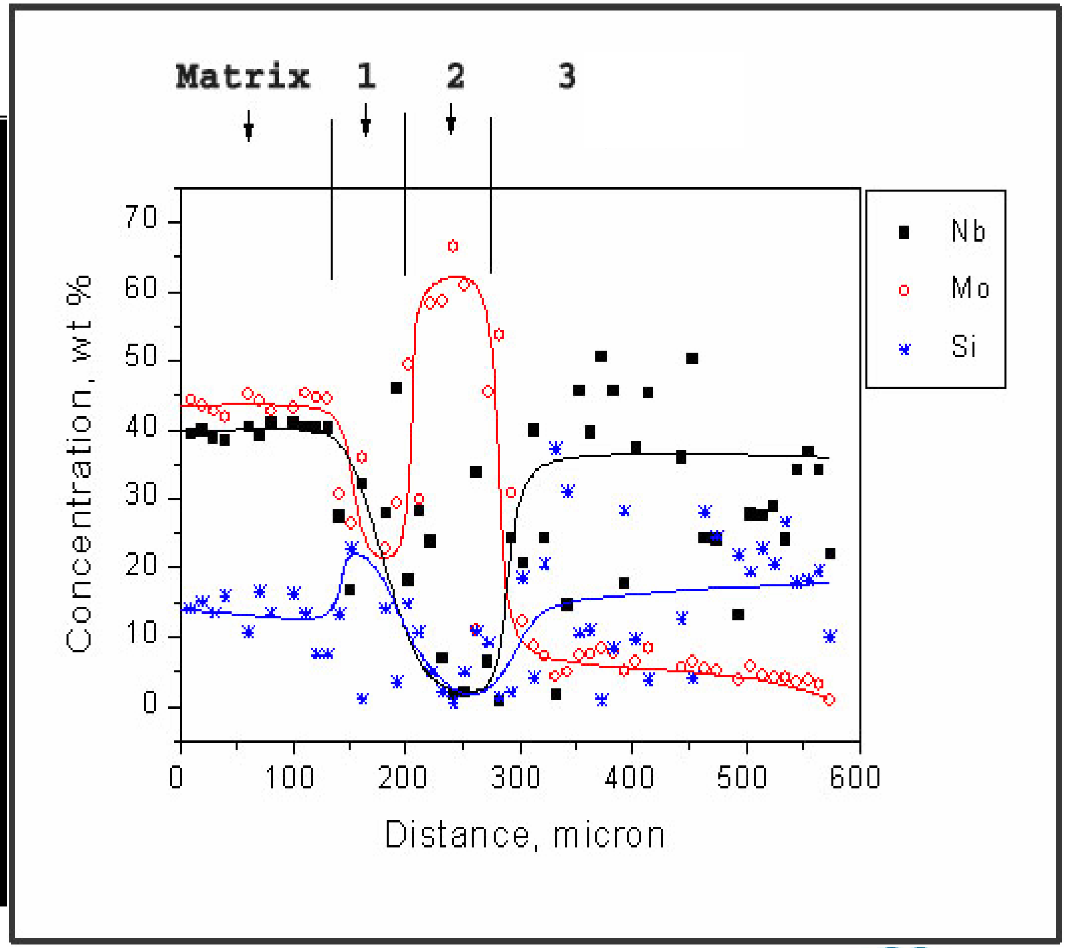
EPMA Analysis of Oxide Scale of Nb-Mo-Si-B Alloy





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Future Work

- Oxidation
  - Cyclic testing: scale adherence
  - Selected testing in synthetic oxidizing combustion atmosphere to 1500°C
  - Consider alloying strategies to improve Alloy 3 oxidation at higher temps
- Advanced processing techniques
  - Injection molding: test bars (3 x 4 x 25 mm), example components
  - Plasma spraying: Alloy 1/2 coating on Alloy 3 substrates for oxidation testing
- Develop Nb-Mo-Si-B compositions
  - Coexistence of (Nb,Mo) with oxidation resistant quaternary silicide
  - Processing strategies to selectively remove Nb from surface

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