Multi-Scale Computational Design and Synthesis of Protective Smart Coatings for Refractory Metal Alloys

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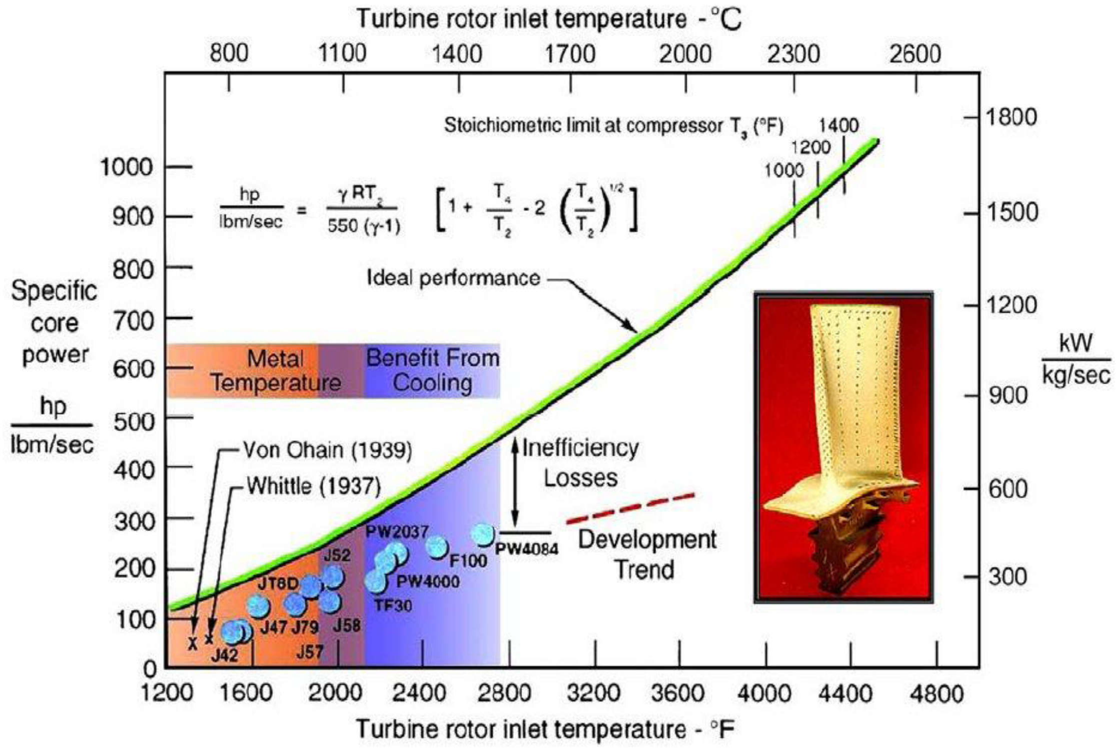
OUTLINE:

- Background on coating design and synthesis
- Gaseous Computational Thermodynamic Designs for Coating Deposition Process
- Phase Stability Analysis on the Coating Phase Constituents; emphasis on extended alloying capability
- Microstructure-based FEA designs in Mo-RM-Si-B Coating Structures
- Synthesis of Mo-Ti/Zr-Si-B Coatings
- Oxidation tests at ultra-high temperatures

Introduction

- Ni-based superalloys provide the necessary structural strength while at the same time remaining oxidation resistant in combustion systems
- Higher operational temperatures are needed in order to increase efficiency and power output
- Ni-based superalloys are reaching their limit in operational temperature

  Refractory metal alloys offer higher temperature capability to replace Ni-based Superalloys
- However , their oxidation resistance is a significant problem => Need for Coating Strategies

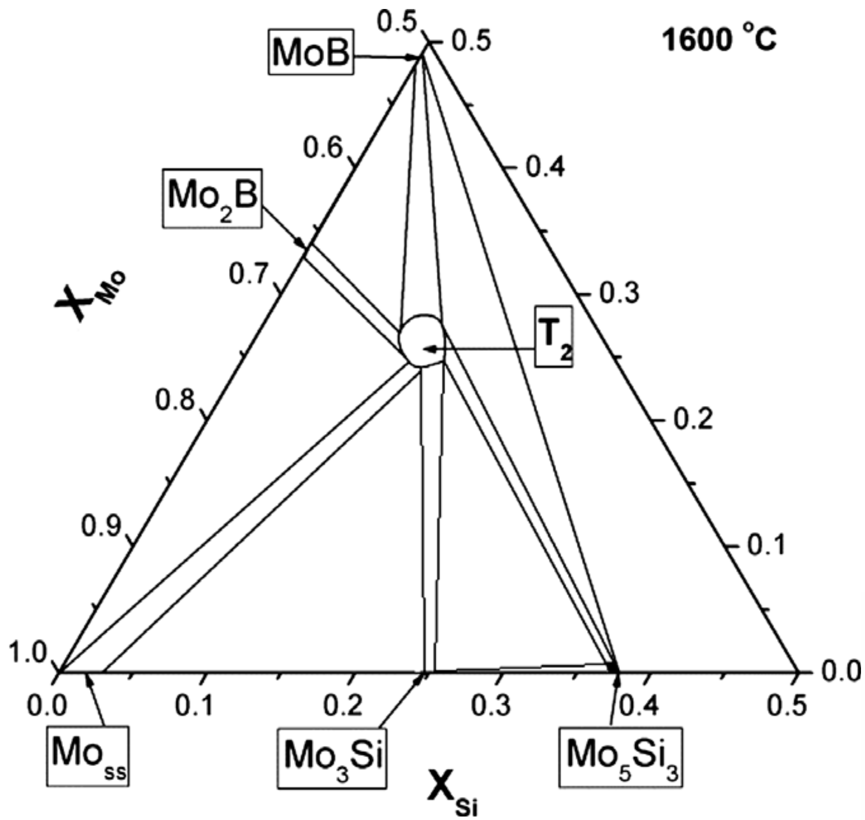


Core horsepower versus turbine inlet temperature for selected gas turbine engines [1]

[1] Dimiduk, D.M. and J.H. Perepezko, *Mo-Si-B Alloys: Developing a Revolutionary Turbine-Engine Materials. MRS Bulletin, 2003.* ***28: p. 639***

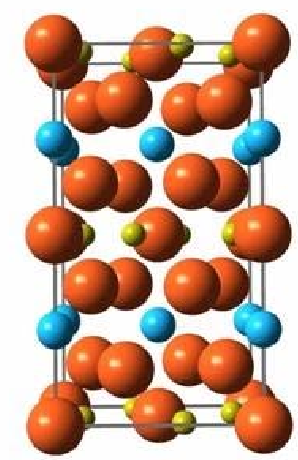
Mo-Si-B Phase Equilibium at High Temperature

- Alloys within the Mo-T_2-Mo_3Si three phase field
- $Mo_{(ss)}$ phase improves toughness and ductility, but degrades oxidation resistance
- T_2 and Mo_3Si provide silicon and boron for oxidation resistance [2]



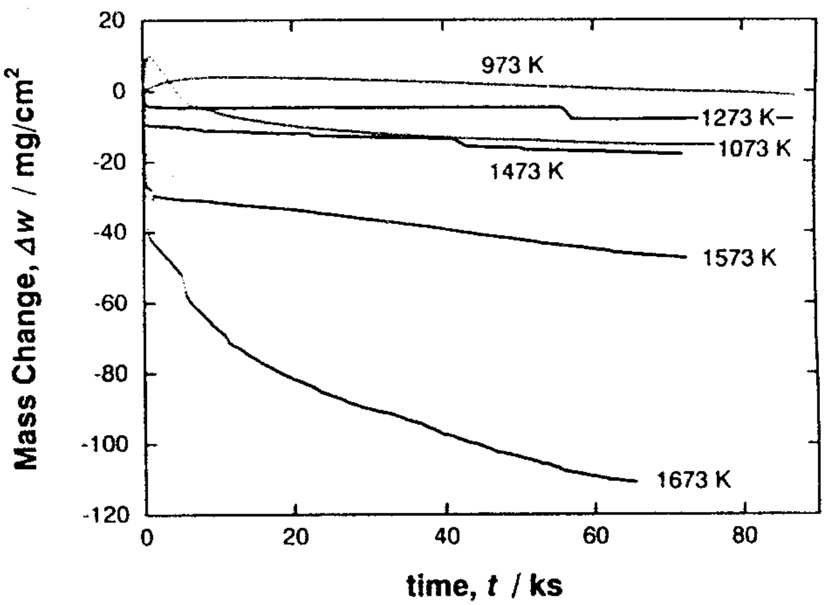
$T_2 \cong$ Mo-12.5Si-25B

Mo_5SiB_2

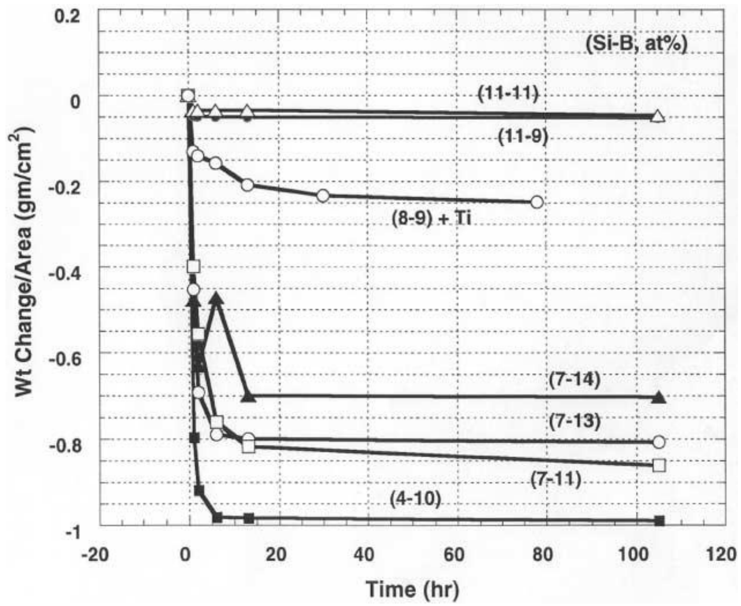


[2] R. Sakidja, J.H. Perepezko, S. Kim, N. Sekido, *Phase stability and structural defects in high-temperature Mo–Si–B alloys*, Acta Materialia 56 (2008) 5223–5244

Previous work on oxidation behavior of Mo-Si-B Alloys



TGA results between 700°C and 1400 °C*

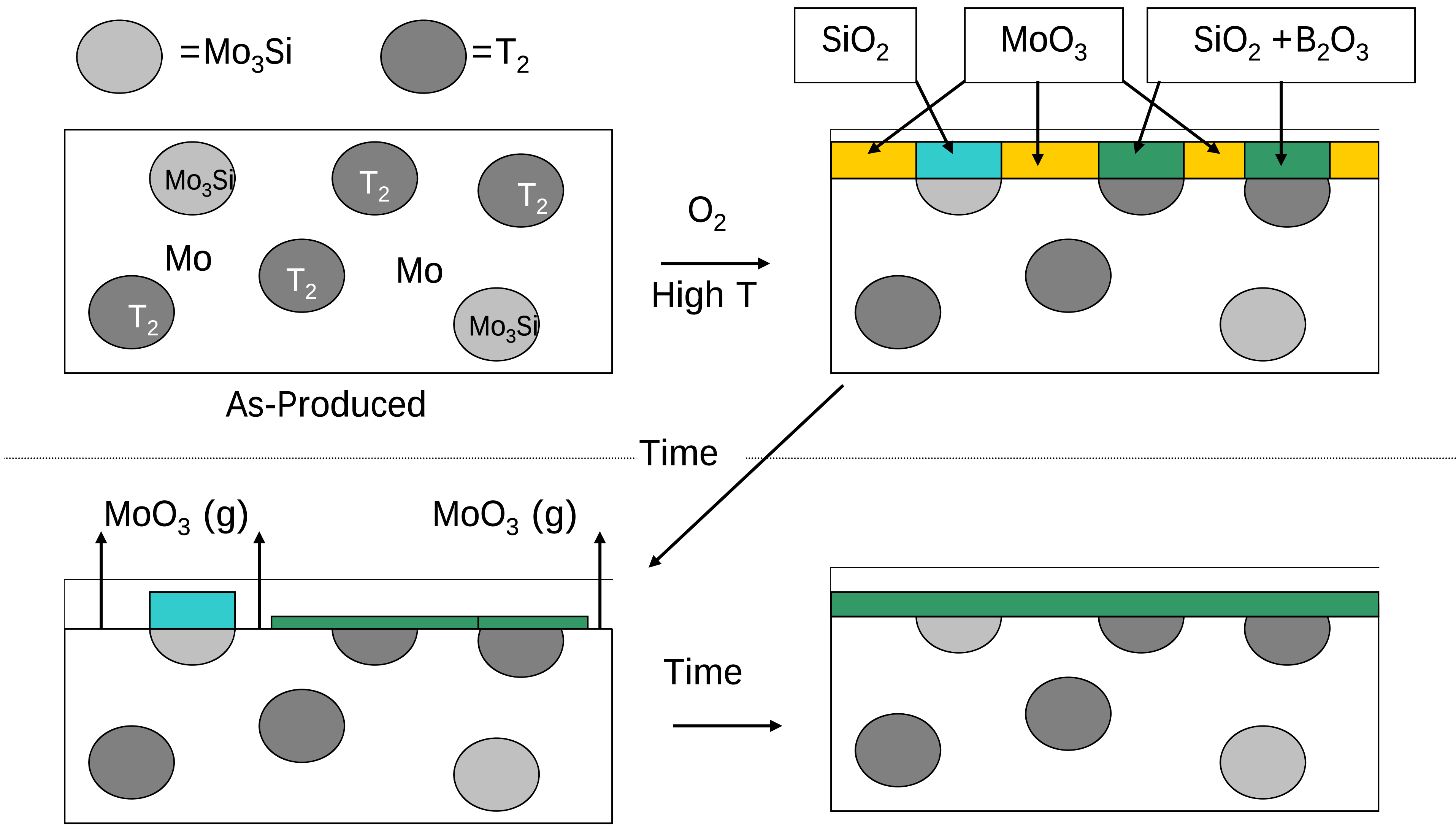


TGA results from cyclic oxidation tests at 1200°C**

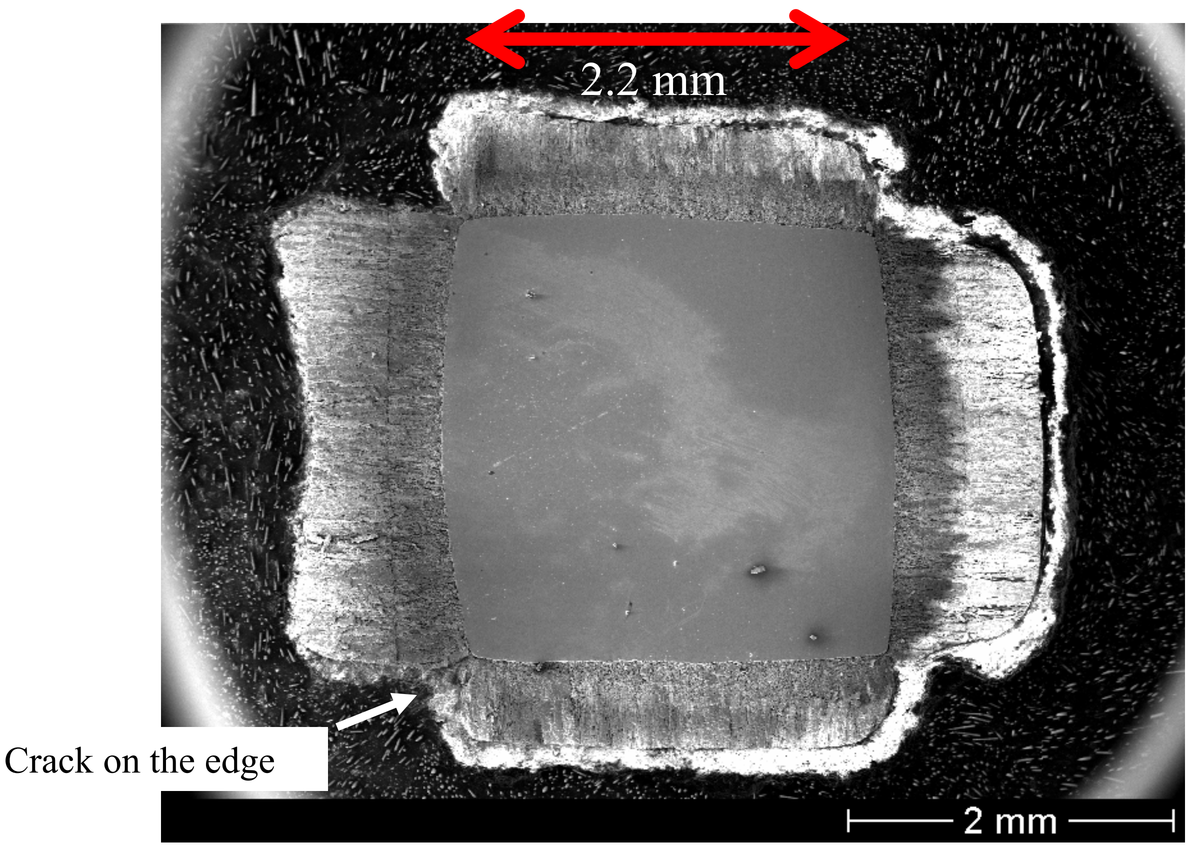
The B/Si ratio is critical to control the transient stage of oxidation kinetics

* Yoshimi et al, Intermetallics, 2002
** Mendiratta, Intermetallics, 2002

Mo-Rich Mo-Si-B Alloy Oxidation



Uncoated Mo-3Si-1B (700^{o}C/30 hrs)



Severe oxidation at 700^{o}C due the absence of protective borosilica glass

The oxide scale is made of non-protective/evaporating MoO_3 consuming the sample

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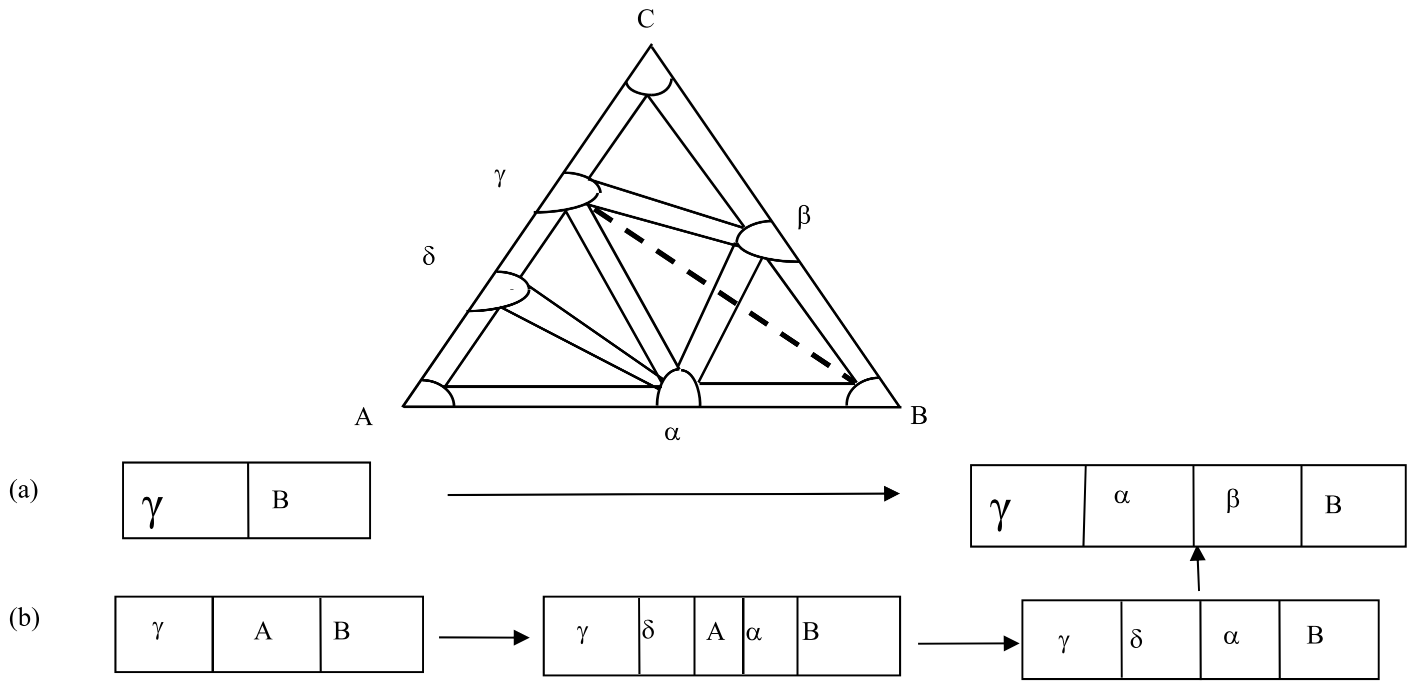
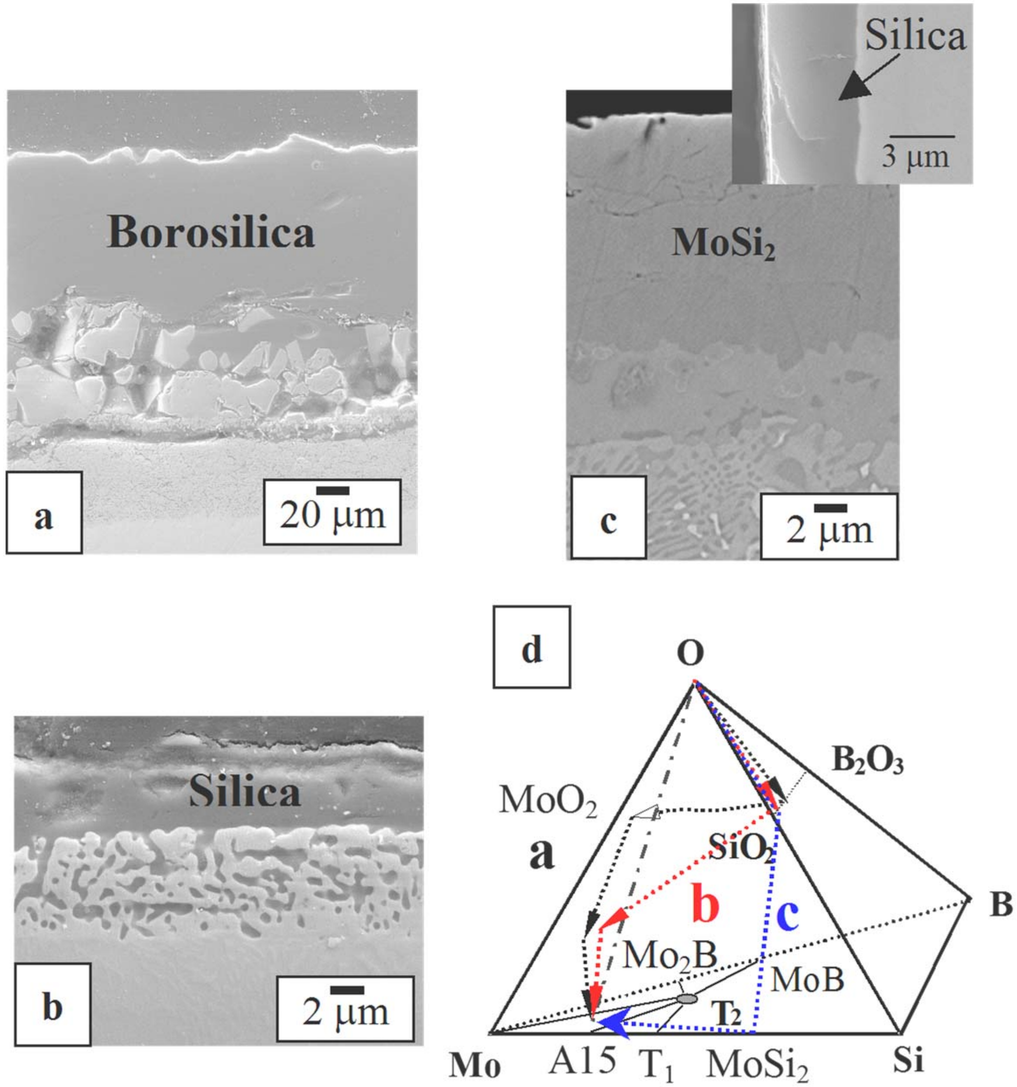


Potential reaction layer formation in a γ / B and γ / A/ B diffusion couple involving a stable pairing of phases.

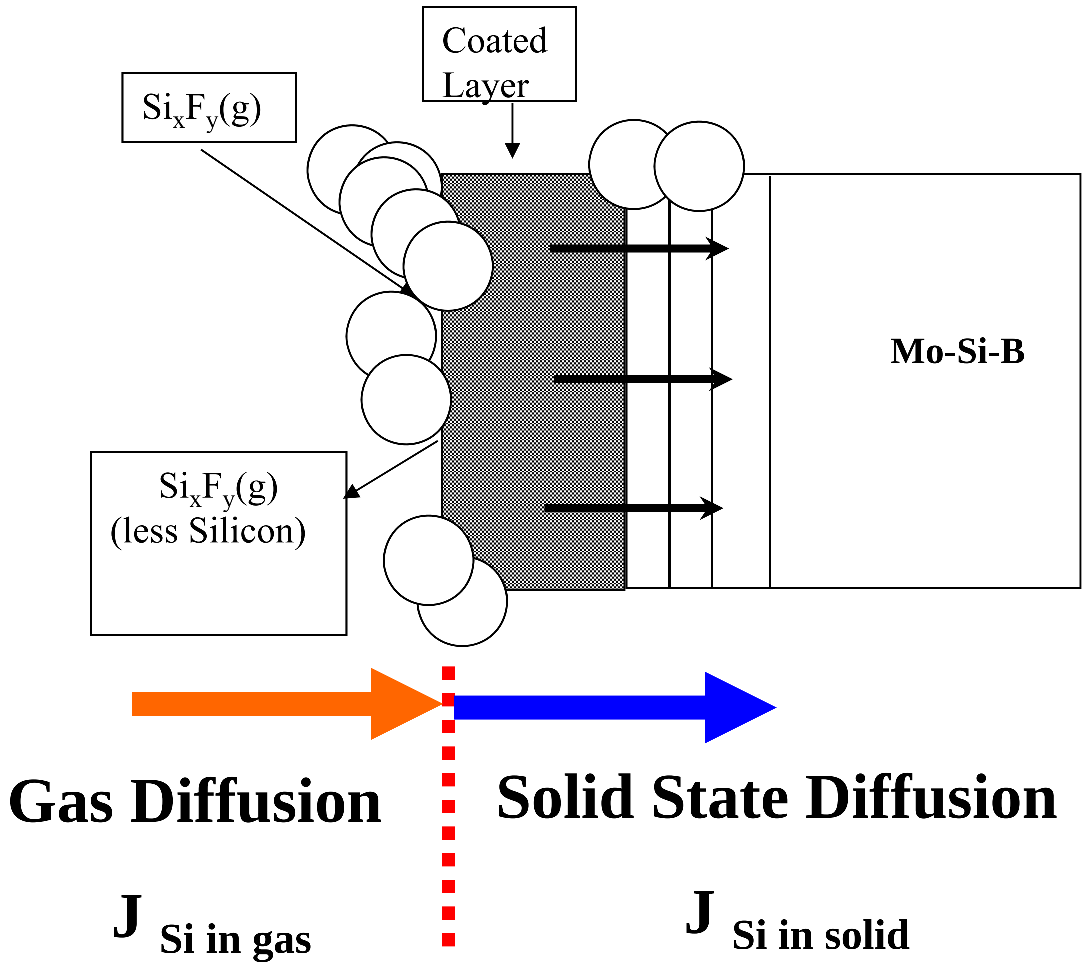


The protective borosilicate layer on Mo-Si-B alloys after oxidation at 1200°C for 100 hours (a). The oxidation resistance is enhanced by applying the silica (b) or silicide biasing (c). With the silicide coating (inset), less than 5 µm thick surface oxide (silica) develops on the surface. Three distinct diffusion pathways for a-c are depicted in (d).

Si + B Pack Cementation on Mo-Si-B alloy

$$yNaF + xSi(s) + Al_2O_3(s) \rightarrow Si_xF_y\,(g) + yNa(g) + Al_2O_3(s)$$

$$vNaF + uB(s) + Al_2O_3(s) \rightarrow B_uF_v\,(g) + vNa(g) + Al_2O_3(s)$$



Initial period

Rate Controlling Step : Solid State Diffusion

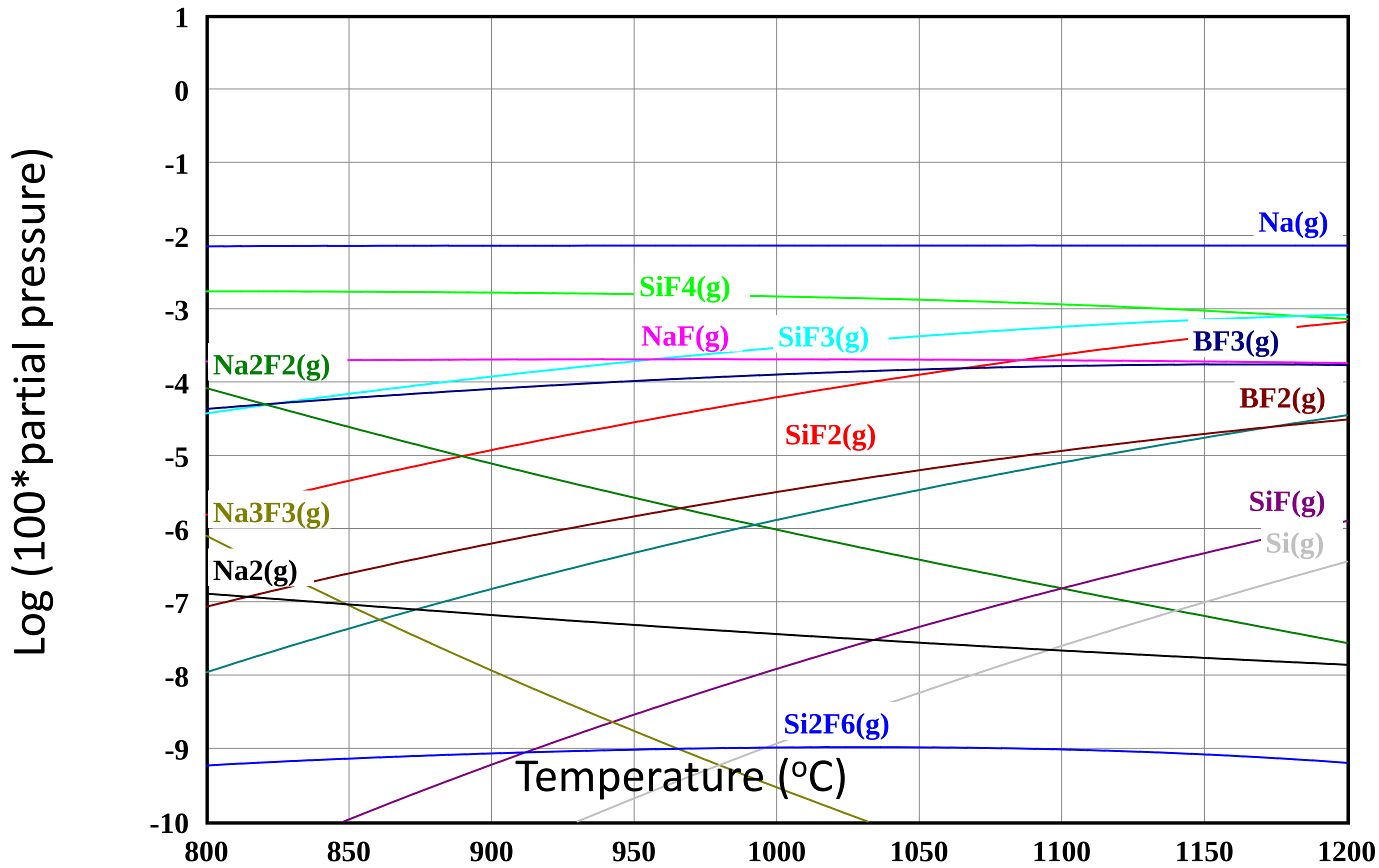
After Initial period

Rate Controlling Step : Gas Diffusion

- Reaction Products: Mainly

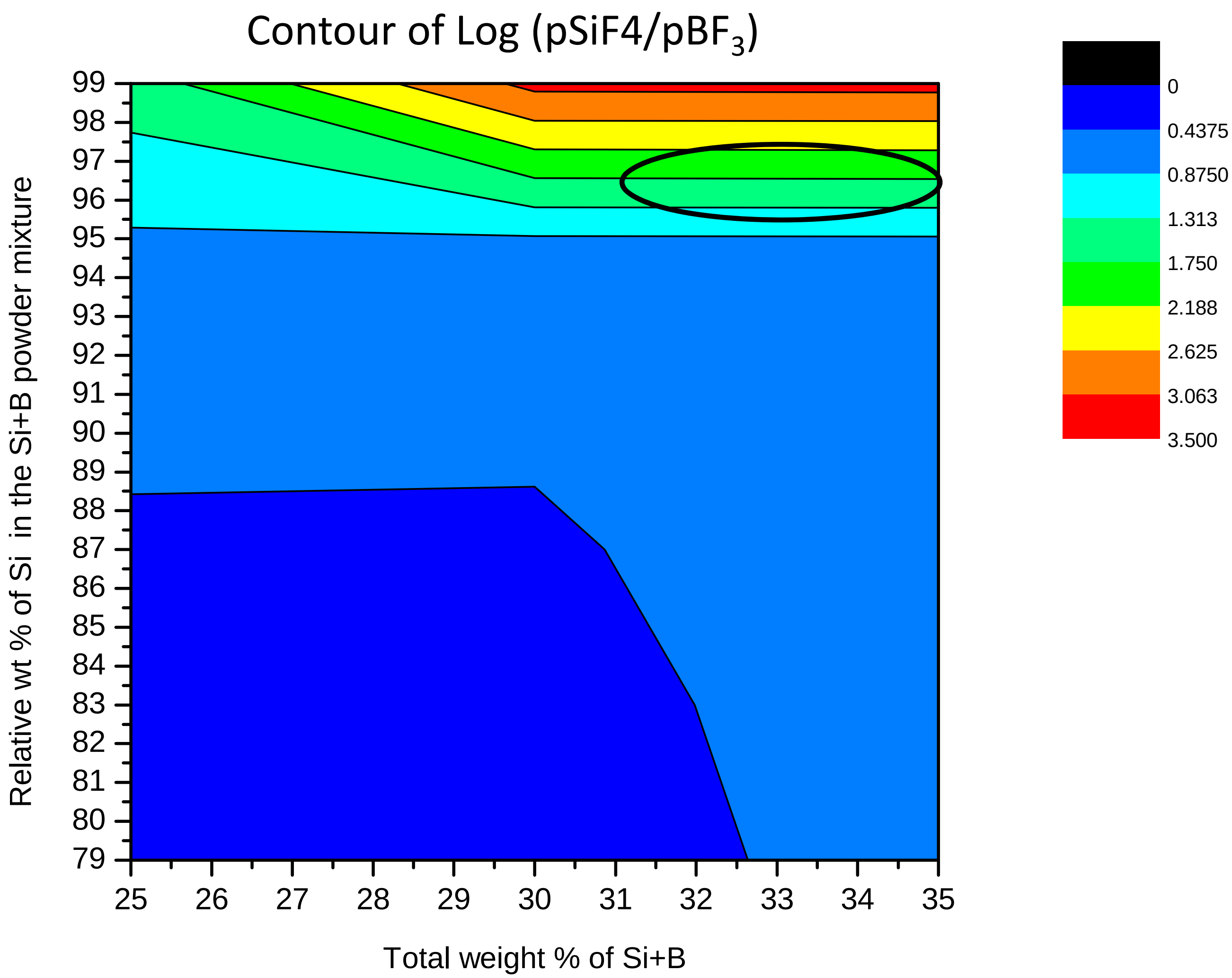
$MoSi_2 \rightarrow$ Gas diffusion governs during the process

Gaseous Thermodynamics Equilibria in the Si+B Co-pack Cementation Process



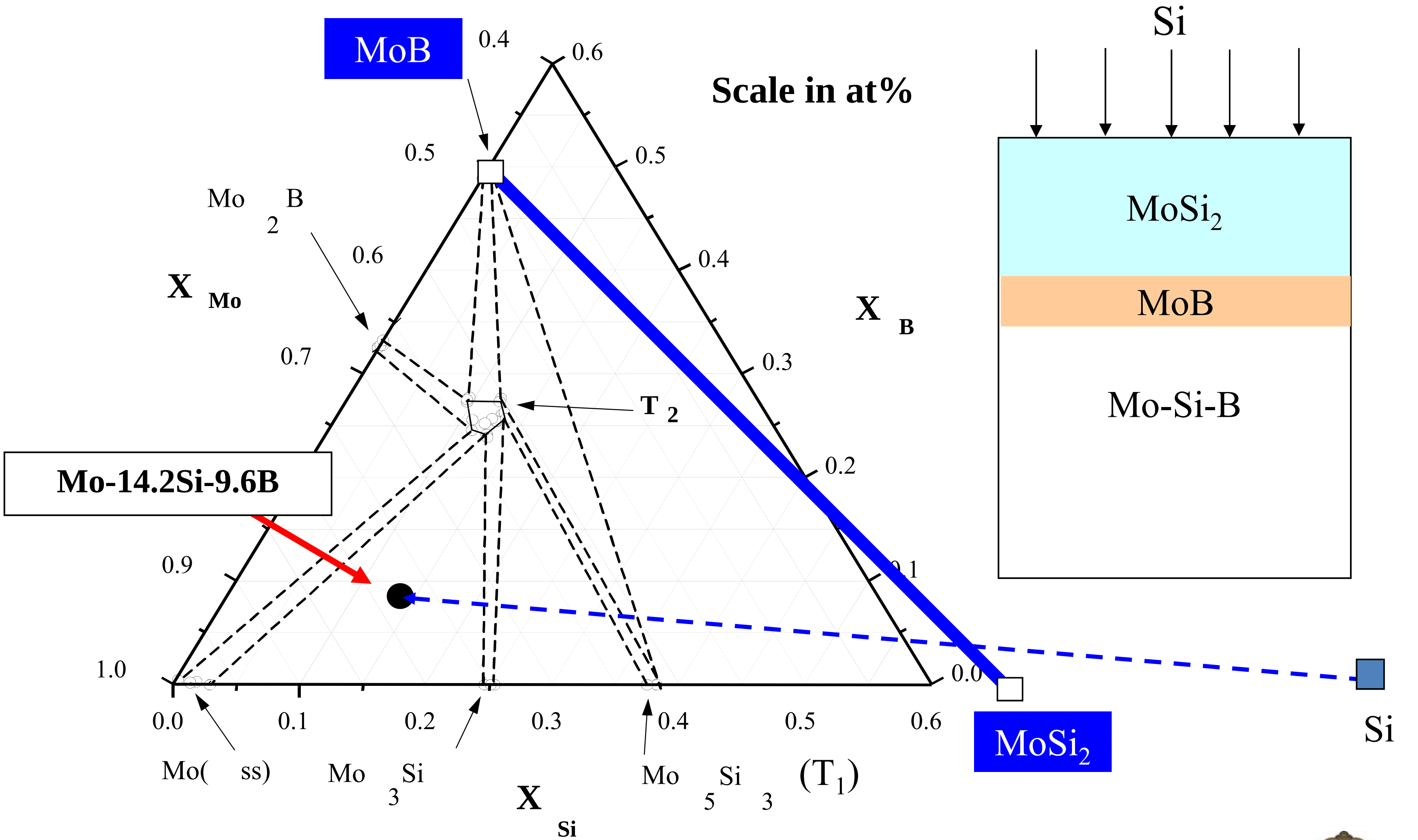
35-1 weight ratio Si:B

Refinement in Processing Map for Si+B Co Deposition

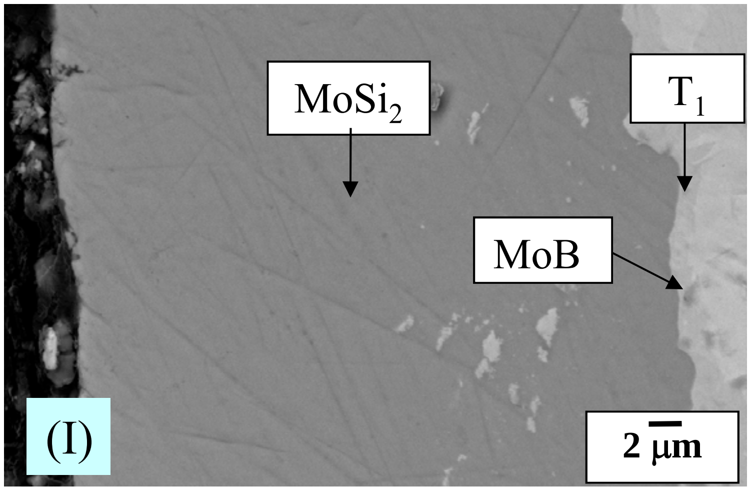


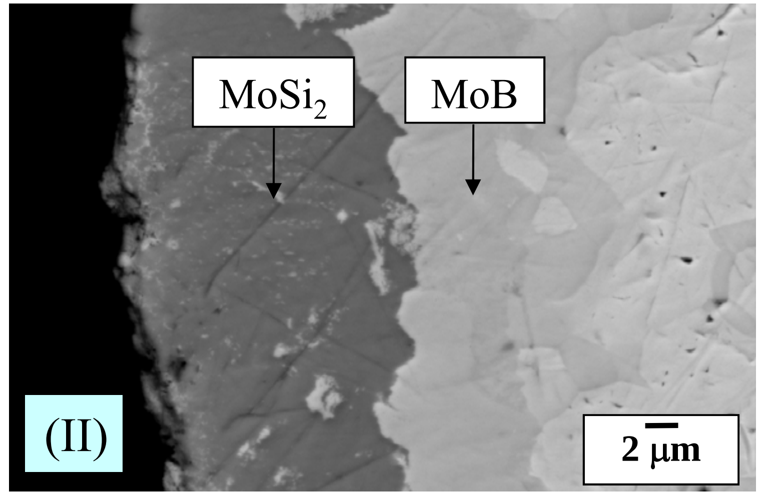
To stabilize a co-deposition of B and Si , the vapor pressure of Si-containing halides/ B-containing halides must be comparable.

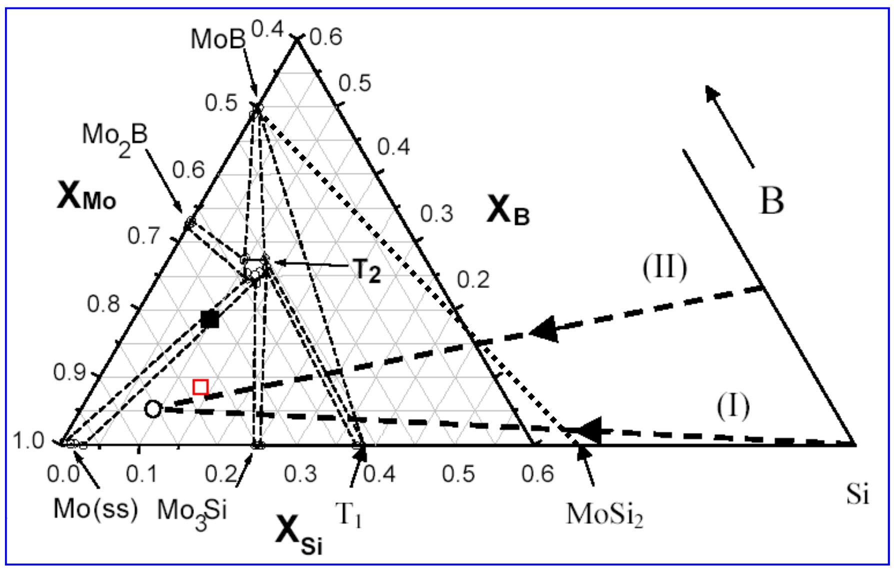
Schematics of Si-Pack Cementation onto Mo-Si-B Alloys



20:1 Si/B Pack Cementation of Mo-3Si-1B wt %

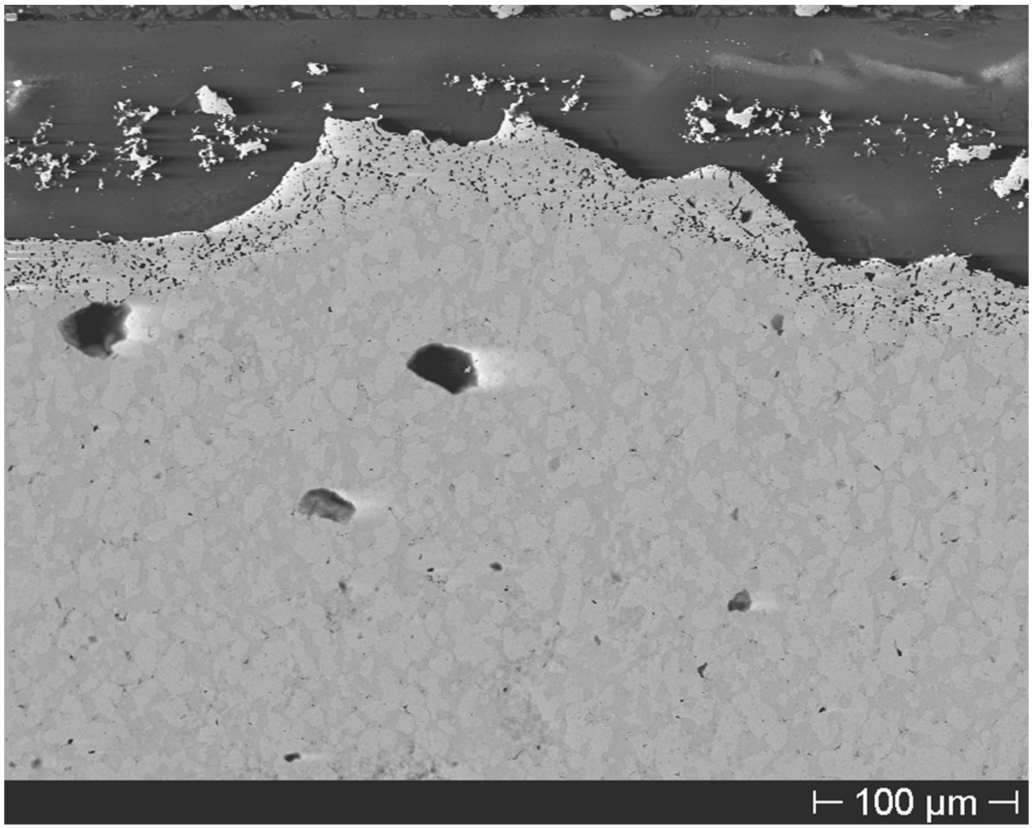






Pack-cementated Mo-3Si-1B (wt %) (I) without and (II) with a partial substitution of Si with B (1:20 B to Si weight ratio) A full development of the boride phase underneath the silicide phase is observed with the partial substitution.

Uncoated , Oxidized in Air at 1400^oC for 30 hours



Thick Borosilicate Glass

Intermediate Region
(Glass + Substrate, depleted of Silicon and Boron)

SUBSTRATE

Region Evaporated/Loss ~ 400 µm
Remaining Oxidized Region ~ 150 µm

Affected Ox. Region ~ 550 µm

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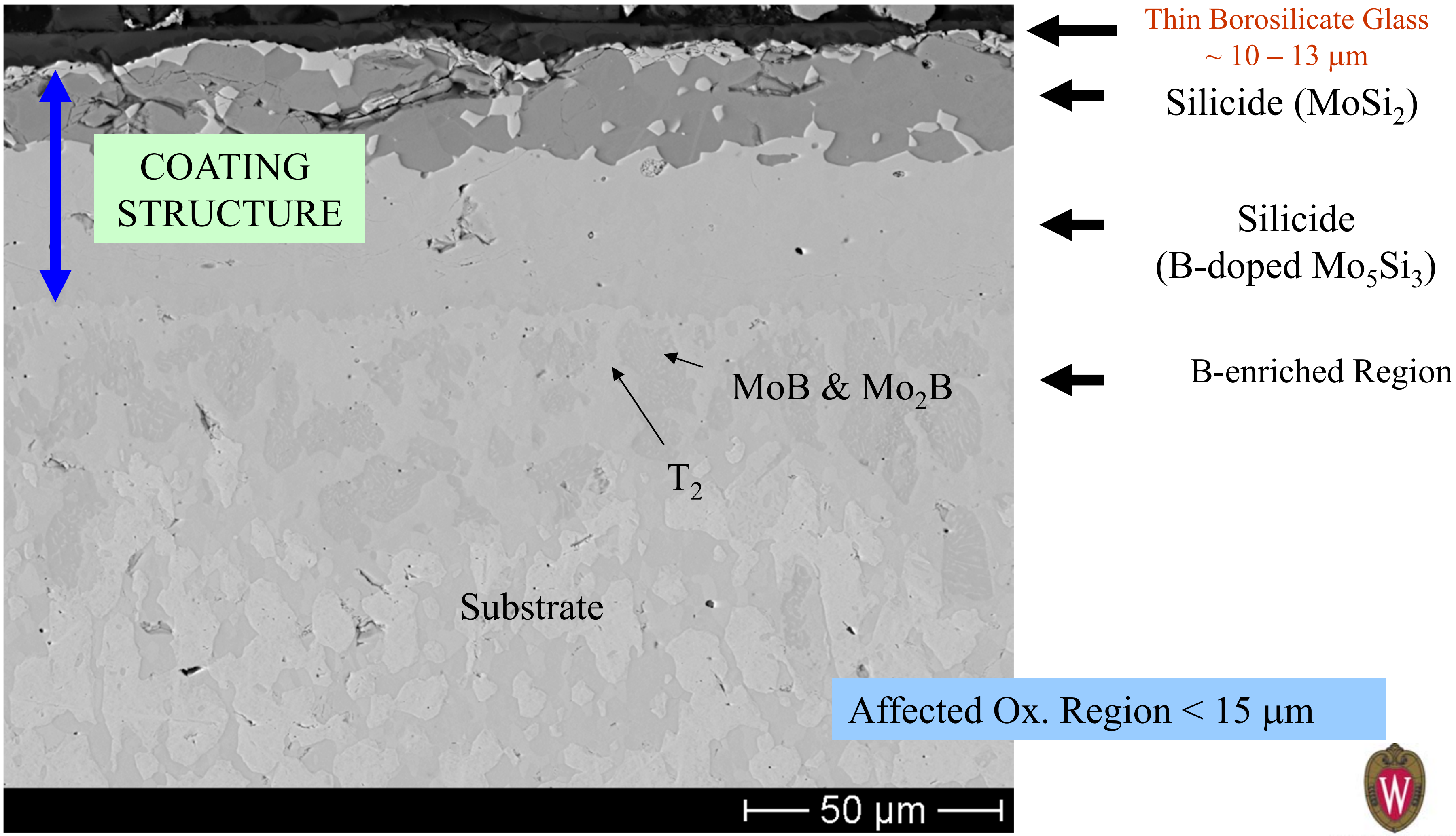
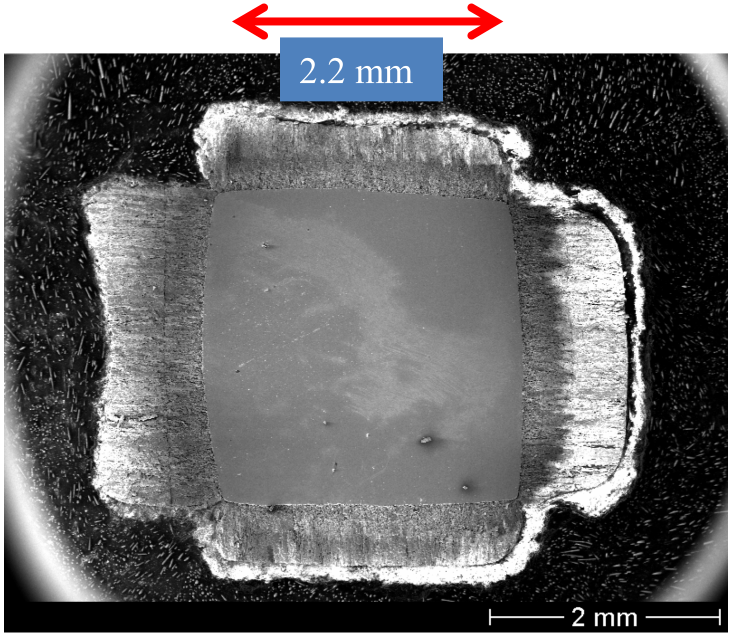
25:1 Si/B Pack Cementation + 1400°C Oxidation (30 hrs)

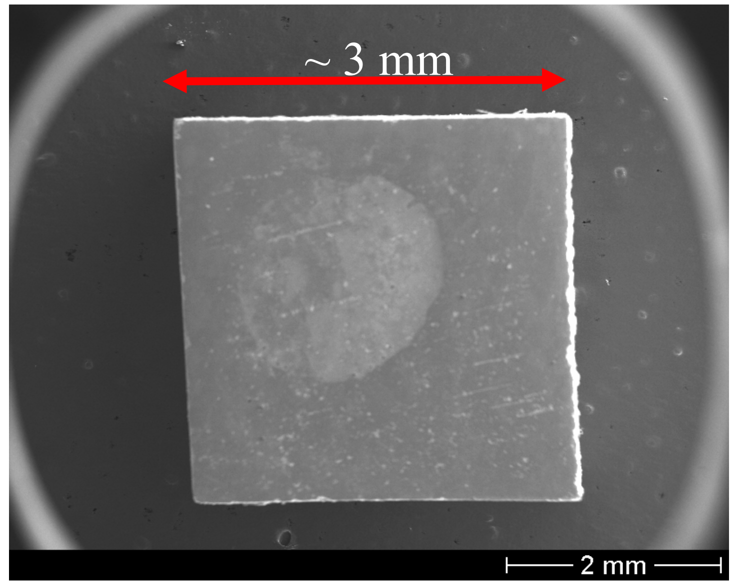


Oxidation Test at 700°C for 30 hrs (Mo-3Si-1B wt %)

UNCOATED

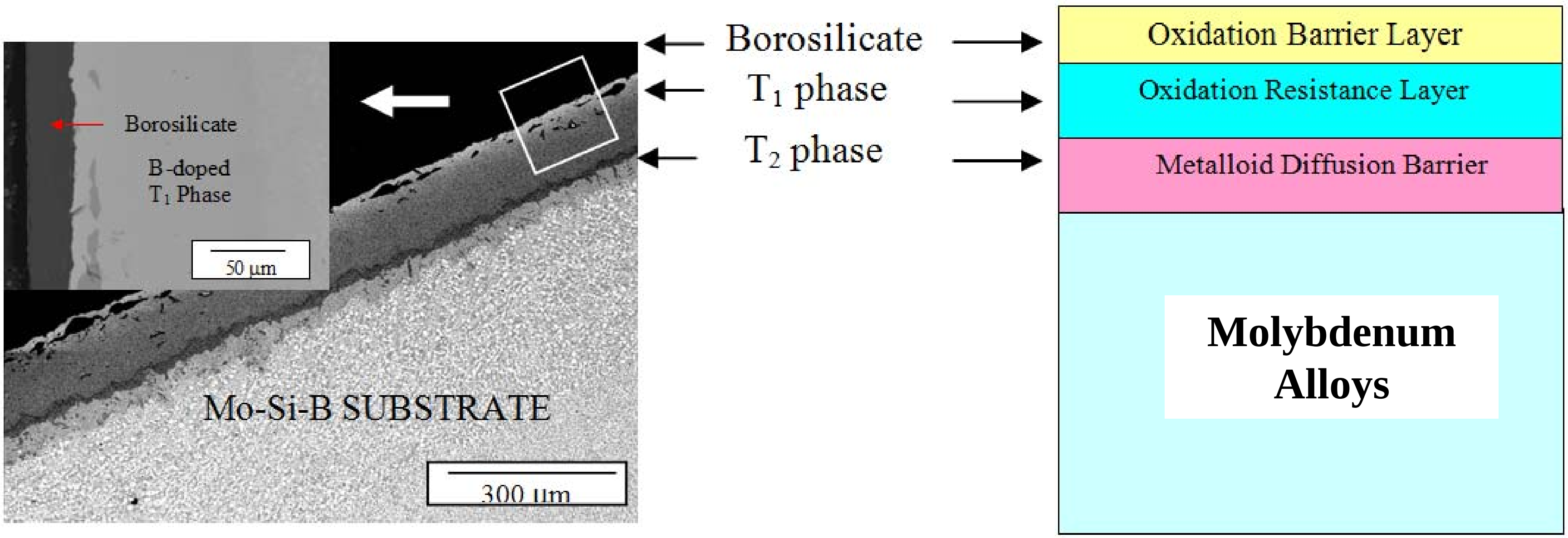


COATED



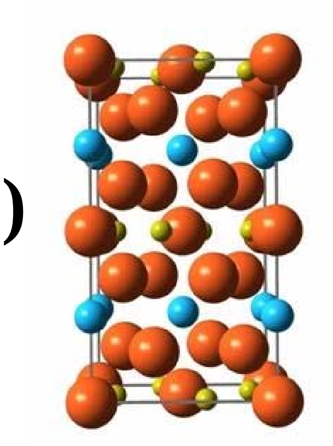
The coated sample remains intact – virtually no consumption of thickness

Mo-Si-B Coating



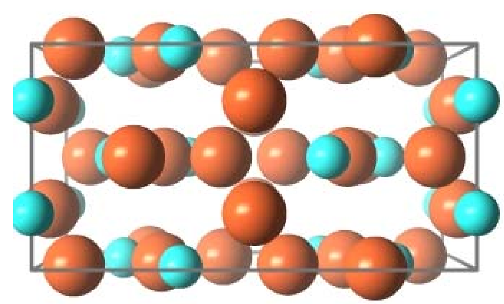
Mo_5SiB_2 (T_2)

T_M ~ 2100°C

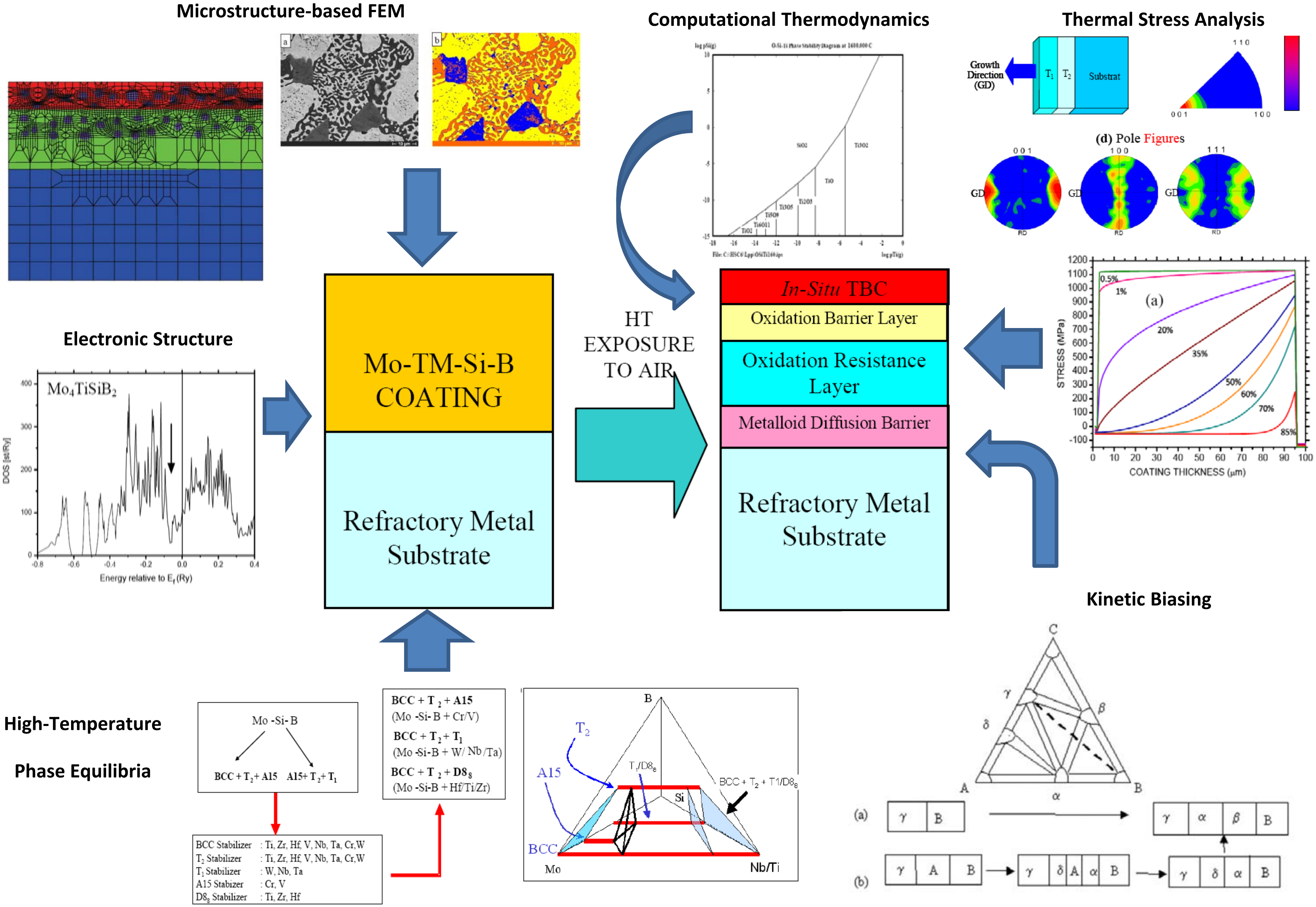


Mo_5Si_3 (T_1)

T_M=2180°C



Multi-scale Designs & Synthesis Approach for Mo-Si-B Based Smart Coatings

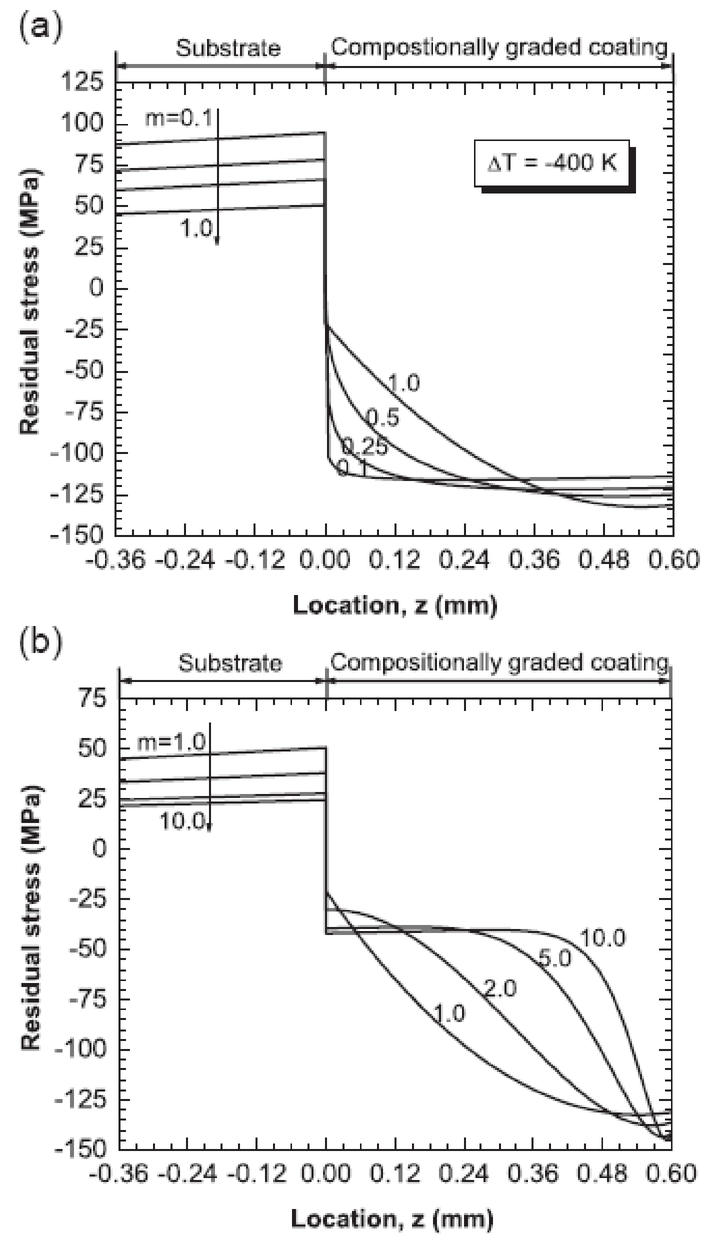


Mo-Si-B Alloys	1. Mo-3Si-1B wt. 2. Mo-14.2Si-9.8B (at.%)
Nb-Based Alloys	1. Nb- 24Ti -16Si- 6Cr -6Al-2Hf (at %) 2. Nb-26.6Ti-4.2Hf-2.5Cr-1.0Si-3.0Ge (at.%)

	Linear CTE ($x10^{-6}$)	Elastic Modulus (GPa)	Thermal Conductivity (W/m*K)	Oxygen Diffusivity at 1000°C (m^2/s)	Tm (°C)	Specific Heat ($Jmol^{-1}K^{-1}$)
Yttria stabilized zirconia	11.5	40	2.1 (1000°C)	10^{-11}	2715	206
Al_20_3	9.6	30	5.8 (1127°C)	10^{-21}	2050	90
$Hf0_2$	5.8	280	1.5 (1000°C)	$>10^{-15}$ (900°C)	2758	-
$Ti0_2$	9.4	181	3.3 (1127°C)	10^{-17}	1843	55
Mullite ($3Al_2O_3$: $2Si0_2$)	5.3	30	3.3 (1127°C)	10^{-18}	1850	-
Molybdenum	5.4	276	143.6	-	2896	28
Niobium	7.3	105	53.7	-	2741	24.6

Graded coating Structure

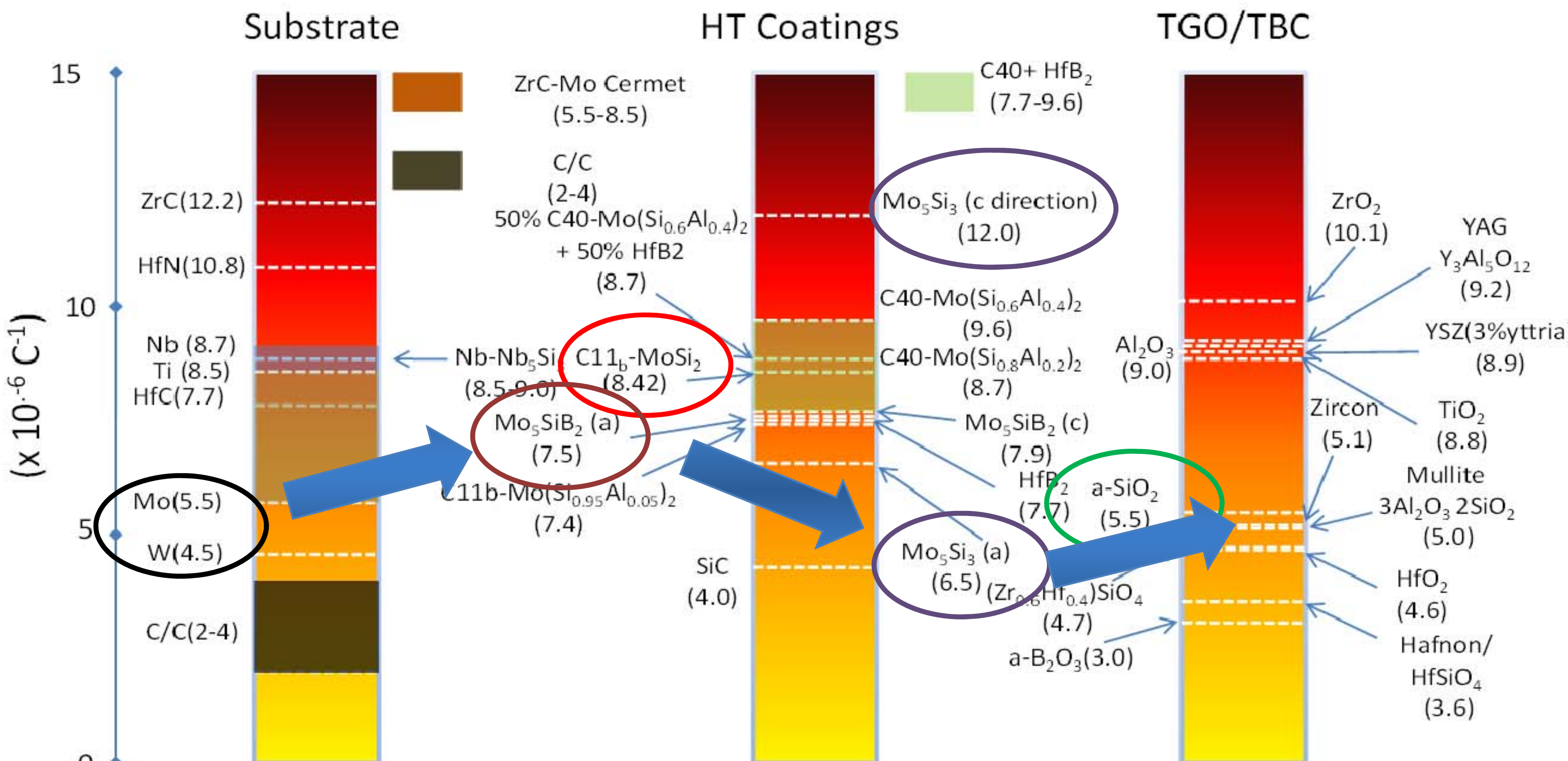
- Coatings with a compositional gradient decrease residual stresses
  - Sharp changes in stresses may result in delamination of the coating
- Increasing CTE of substrate also increases residual stresses in coating



Effect of gradient expononet on the magnitude and distribution of thermal stresses within a ZrO2Y 2O3/NiCrAlY TBC [3].

[3] X.C. Zhang, B.S. X u, H.D. Wang, Y. Jiang, Y.X. Wu, Thin Solid Films, 497 (2006) 223-231

CTE Compatibility in Ultra-high Temperature System



COMPOSITE AND GRADED APPROACHES TO HT COATING DESIGN

In thermodynamically compatible systems, the thermal expansion of the phase mixture as a first estimate is monotonic: $CTE(A_xB_{1-x}) = xCTE(A) + (1-x)CTE(B)$

KEY : MAINTAIN THE T_1 PHASE TEXTURED ALONG C AXIS TO MINIMIZE RESIDUAL STRESS

Mo-Si-B Coatings for Nb

- Niobium alloys are a potential candidate to replace nickel-base superalloys
- Kurokawa et.al. conducted a study demonstrating the oxidation resistance of several types of silicides [4]
- Different study from Kurokawa et. al. showed that increasing boron content in sintered $NbSi_2$ samples improved oxidation resistance [5]
  - Increasing boron additions in Si-B coatings could have the same effect
- Mo-Si-B coatings shown to be effective for Mo, W, cermets, and SiC

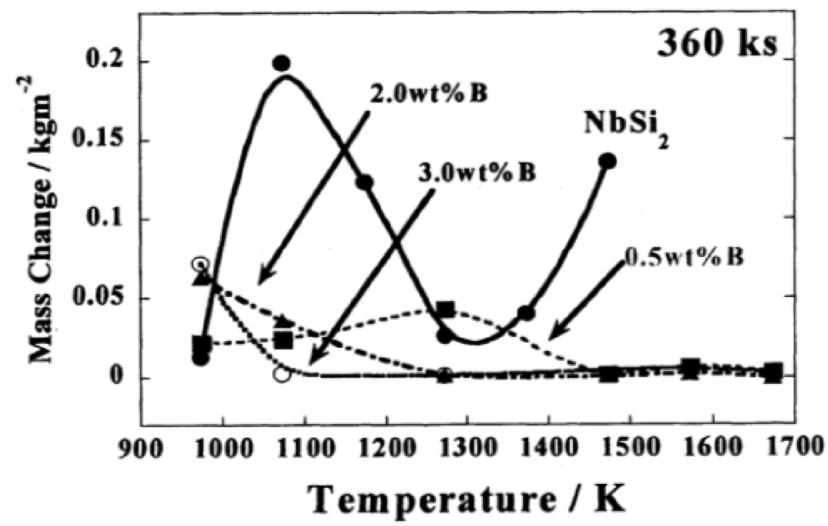
[4] Kurokawa, K. and A. Yamauchi, *Classification of Oxidation Behavior of Disilicides.* Solid State Phenomena, 2007. **127**: p. 227-232.

[5] Kurokawa, K., A. Yamauchi, and S. Matsushita. *Improvement of Oxidation Resistance of NbSi2 by Addition of Boron*. in *Materials Science Forum*. 2005. Trans Tech Publications Inc.

Table 1 Structure of oxide scale on disilicide and oxidation resistance.

Oxide scale structure	Silicide	Oxid. resistance	Temp. region
SiO_2 scale	$FeSi_2$	◎	<1273K
	$CoSi_2$	◎	<1273K
	$MoSi_2$	◎	>1073K
	WSi_2	◎	>1573K
	VSi_2	○	>1173K
	$ReSi_{1.75}$	△	>1273K
	$ReSi_{1.75}$	×	<1273K
Double layer scale	$CrSi_2$	◎	<1373K
		×	>1473K
Mixed oxide scale	$NbSi_2$	×	<1773K
	$TaSi_2$	×	<1773K
	$MoSi_2$	×	773−1073K
	WSi_2	×	1073−1573K
	VSi_2	○	<1173K
	$TiSi_2$	×	>773K
	Ti_5Si_3	×	>773K

◎ Excellent ○ Good △ poor × very poor



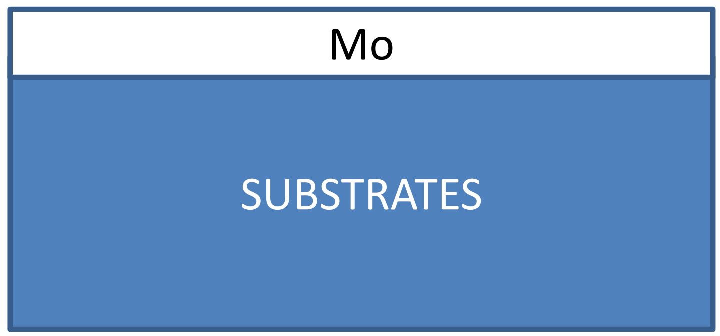
Mass gain after 360 ks-oxidation of B-$NbSi_2$ in air [5]

Synthesis of Mo-Si-B Coatings on RM Substrates

- 2 step processes:

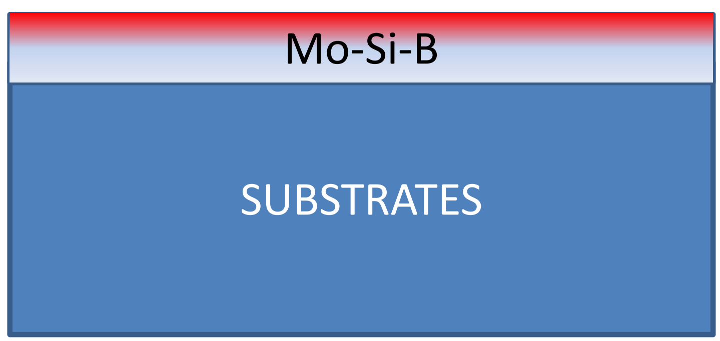
1. **Mo deposition onto UHTC for < 5 minutes at 250°C using $Mo(CO)_6$ decomposition process or plasma spray**

$Mo(CO)_6 \Rightarrow Mo(s)\downarrow + 6CO(g)$



2. Co-deposition of Si+B into Mo deposit and substrate ~ 50 hours at 1000°C.

$3NaF + 2Si(s) \leftrightarrow 2SiF(g) + 3Na(g) + ½F_2(g)$
$3NaF + 2B(s) \leftrightarrow 2BF(g) + 3Na(g) + ½F_2(g)$
$3SiF(g) \leftrightarrow SiF_2(g) + Si(s)\downarrow$
$3SiF_2(g) \leftrightarrow 2SiF_3(g) + Si(s)\downarrow$
$4SiF_3(g) \leftrightarrow 3SiF_4(g) + Si(s)\downarrow$
$3BF(g) \leftrightarrow BF_2(g) + B(s)\downarrow$
$3BF_2(g) \leftrightarrow 2BF_3(g) + B(s)\downarrow$



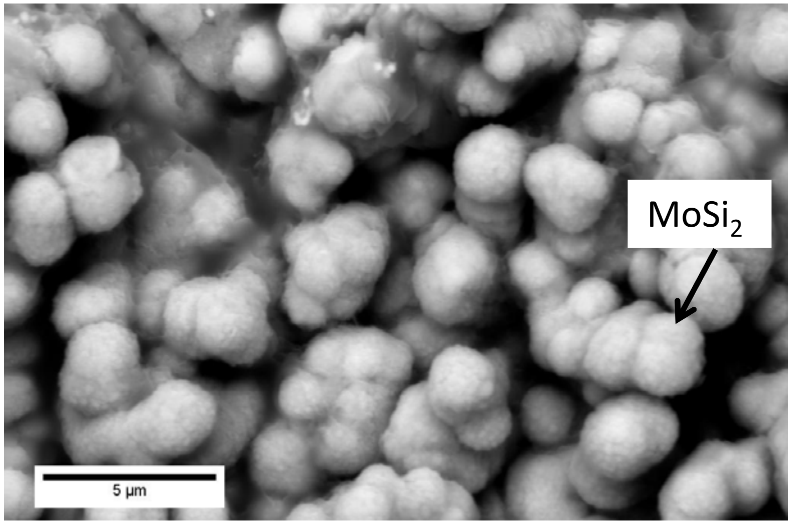
Mo-Si-B coatings for Nb: Experimental Procedure

- Mo-Si-B coating have been deposited onto Nb samples
  - Etch samples prior to Mo deposition
    - Etchant: 20mL HNO_3, 10mL HF, 10mL H_2O (etched for 5 minutes)
  - Decomposition of molybdenum hexacarbonyl followed by Si-B pack cementation
  - Si-B (35:1) pack cementation applied to Mo coated samples (50 hours 1000°C)
- Nb samples coated with Si-B with Si:B ratios of 35:1, 25:1, 10:1 (50 hours 1000°C)
- Oxidation tests carried out at 1000°C for 5,10, and 24 hr exposures

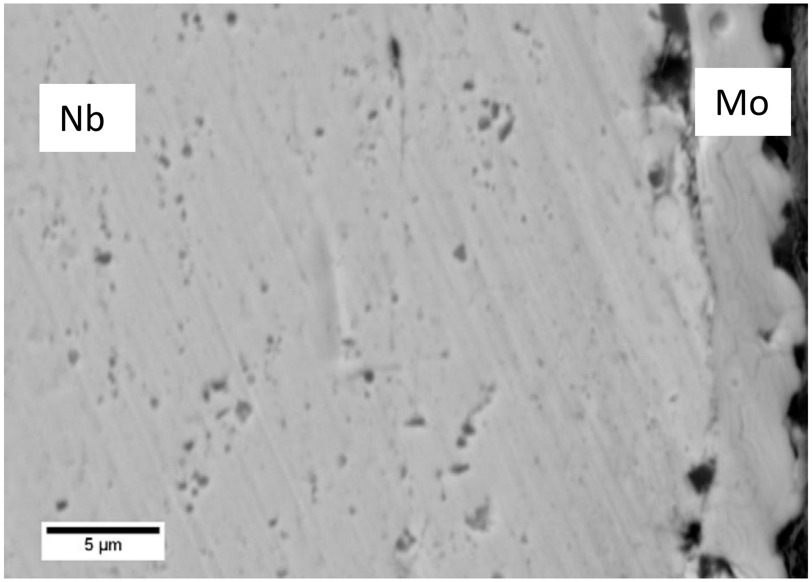
Powder wt%	35:1	25:1	10:1
NaF activator (g)	2.5	2.5	2.5
Al_2O_3 (g)	62.5	62.5	62.5
B (g)	0.97	1.346	3.182
Si (g)	34.03	33.654	31.818

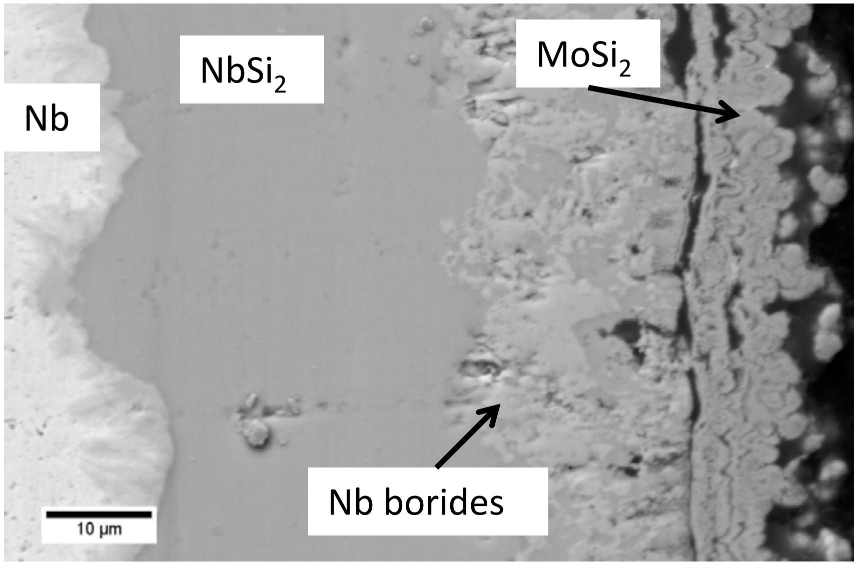
Mo-Si-B Coatings on Nb (as-packed)

- Mo deposition produced a 4µm layer
- Si-B (35:1) pack cementation applied to Mo coated samples
- Mo-Si-B coated sample consists of $MoSi_2$, $NbSi_2$, and Nb boride
- Aluminosilica top layer a by product of the pack cementation treatment

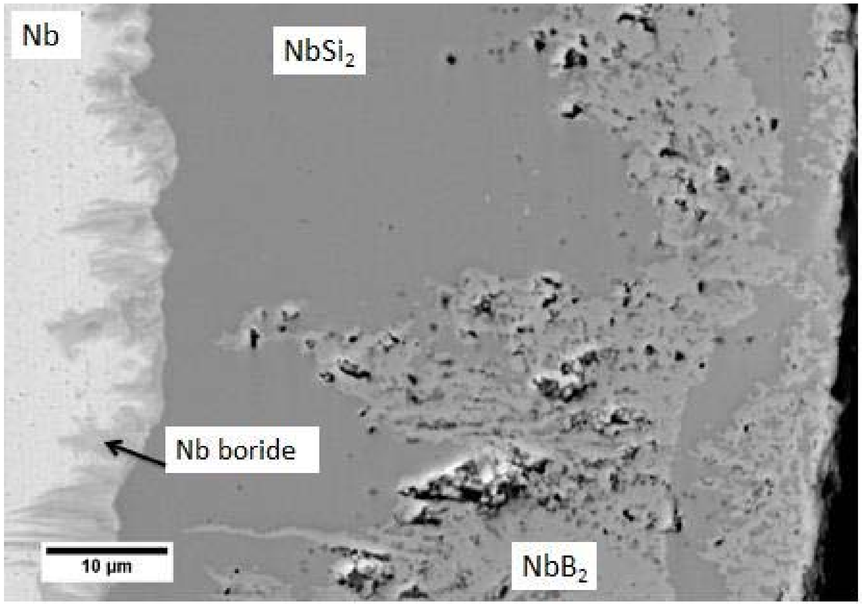


Plan view of Mo-Si-B coating on Nb

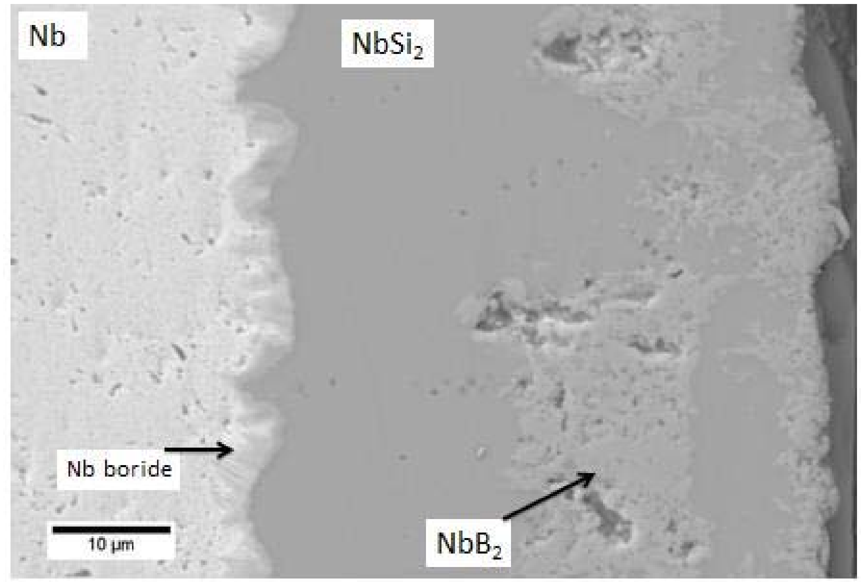




As-Packed Results: 35:1, 25:1



Si-B on Nb (35:1)

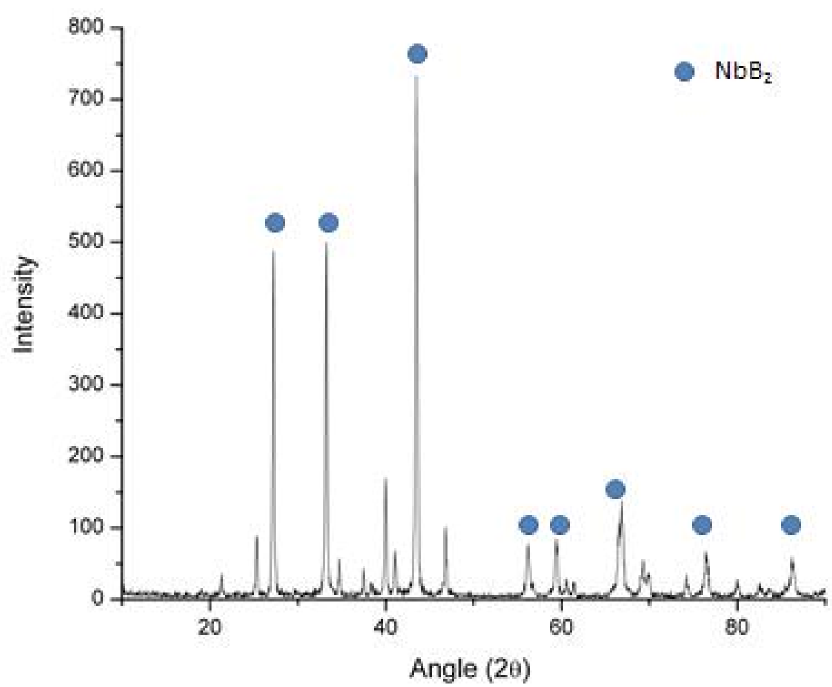


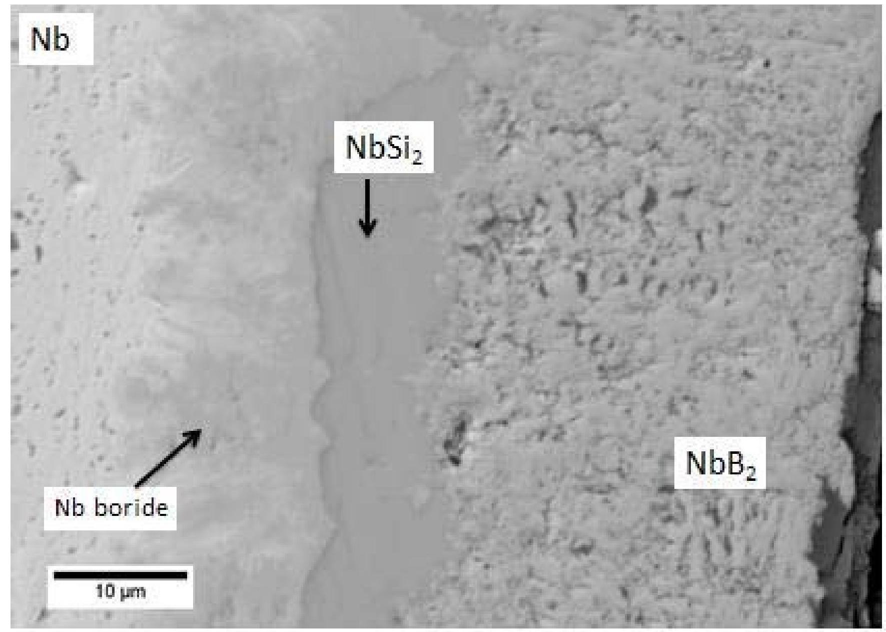
Si-B on Nb (25:1)

- Large amounts of borides are present in the Si-B coatings
  - Borides formed at the substrate/silicide interface as well as within silicide
- Total coating thickness about 50µm

As-Packed Results: 10:1

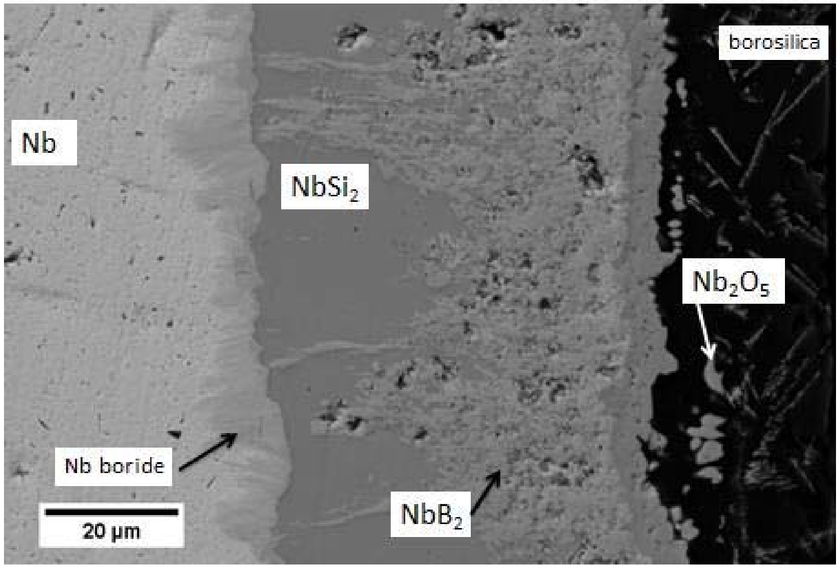
- Significant boride layer formed on the surface
- XRD shows peaks corresponding to NbB_2



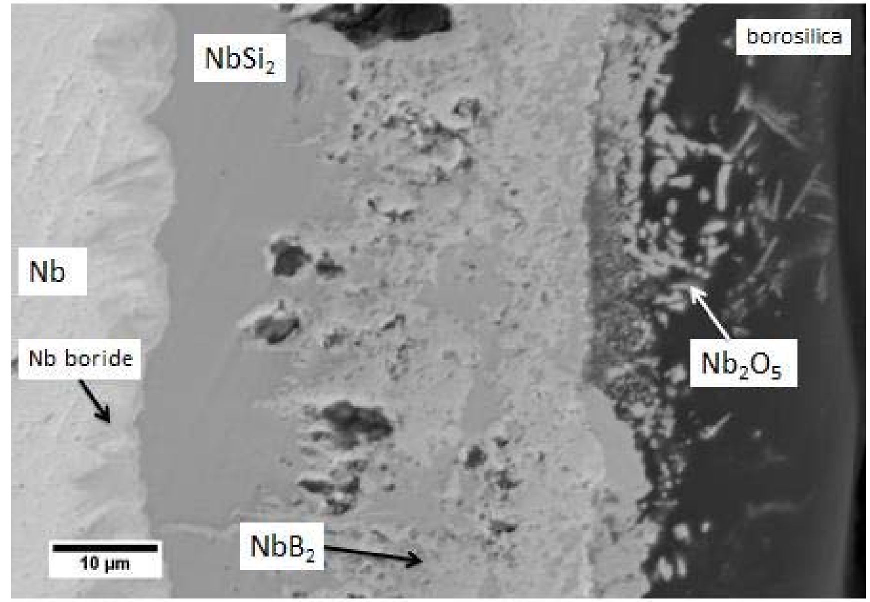


Si-B on Nb (10:1)

Oxidation Tests: 5 hours at 1000°C



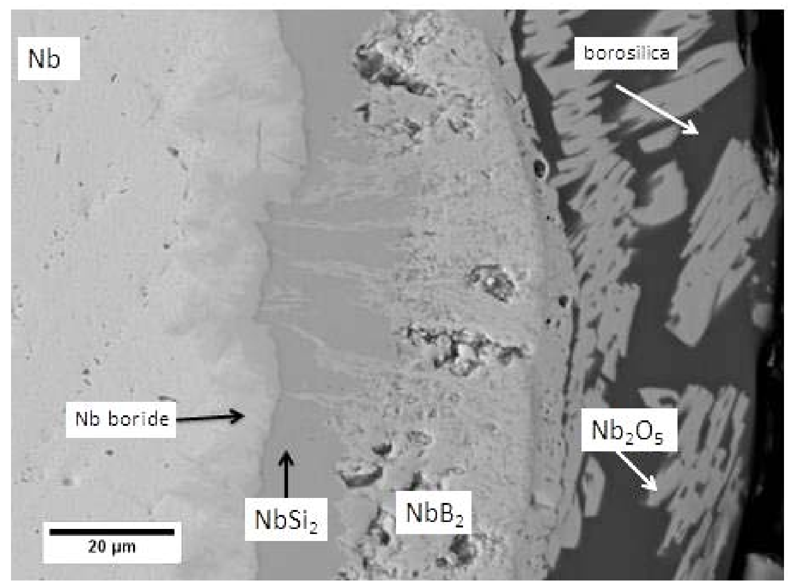
Si-B on Nb (35:1)



Si-B on Nb (25:1)

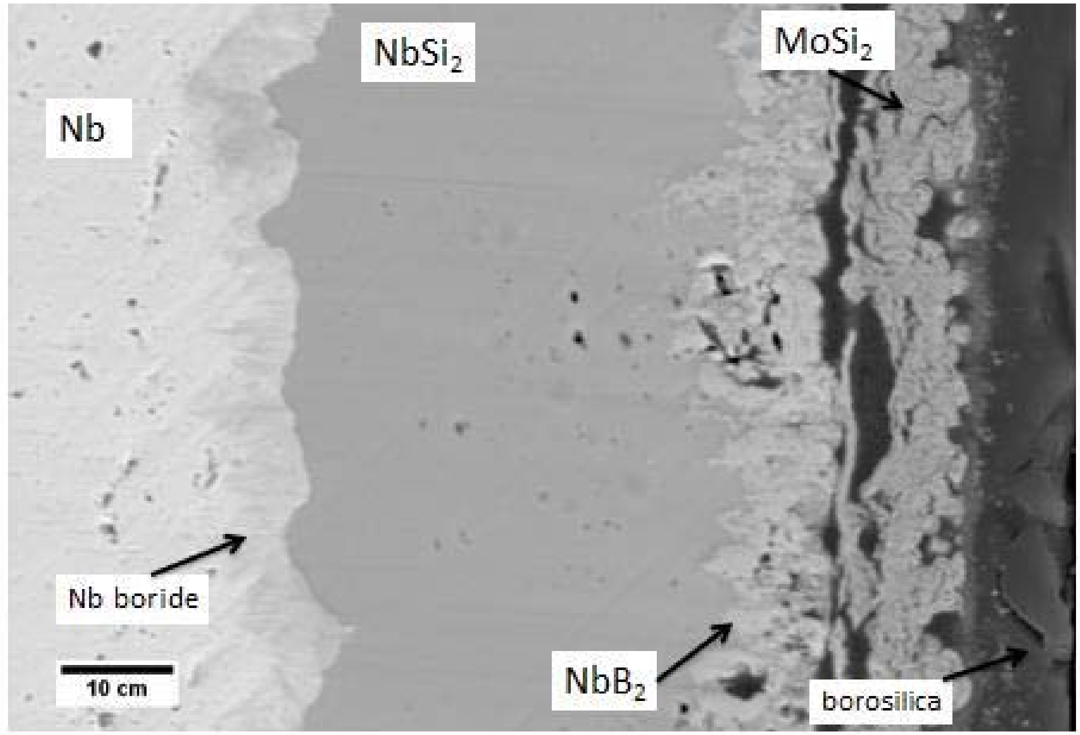
- Si-B coatings have large mixed oxide regions
- Nb_2O_5 does not evaporate off the surface of the sample

Si-B on Nb (10:1)



Oxidation Tests: 5 hours at 1000°C

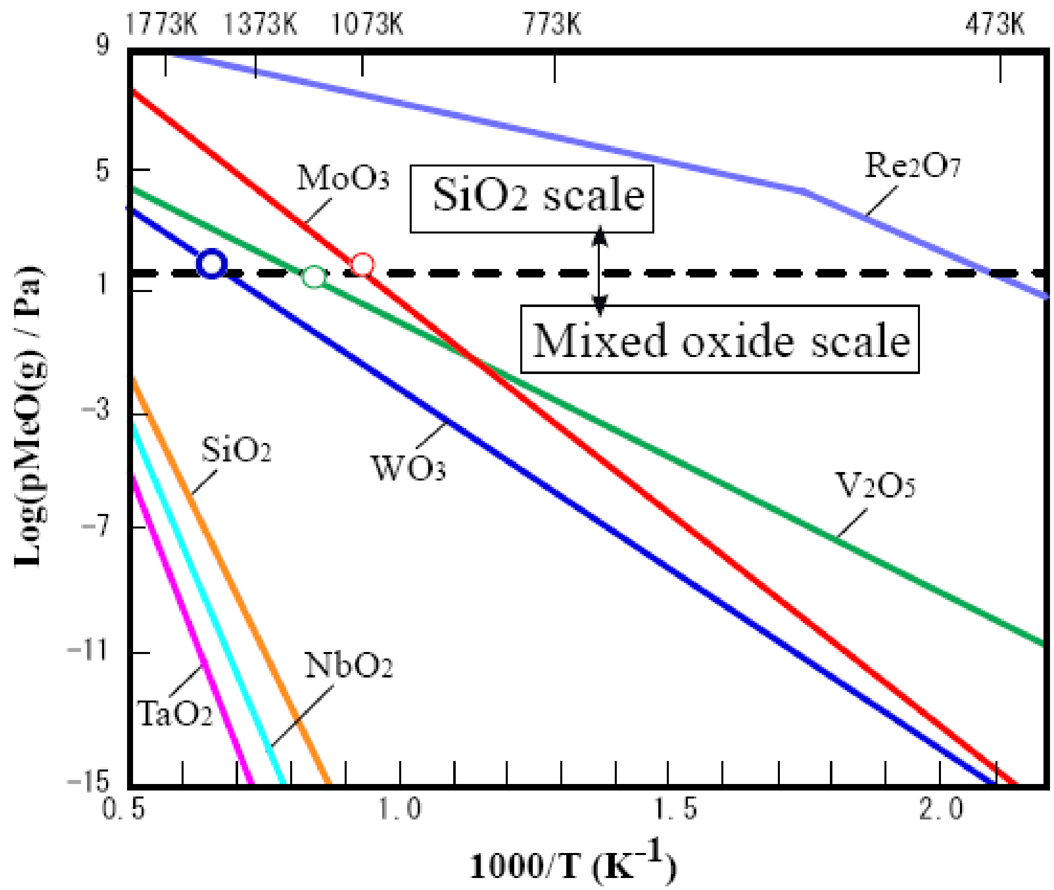
- Mo-Si-B coating produced a protective borosilica scale
  - Borosilica layer reduced by half compared to Si-B coated samples
- MoO_3 evaporates off the surface, allowing for uniform borosilica scale to form



Mo-Si-B on Nb (35:1)

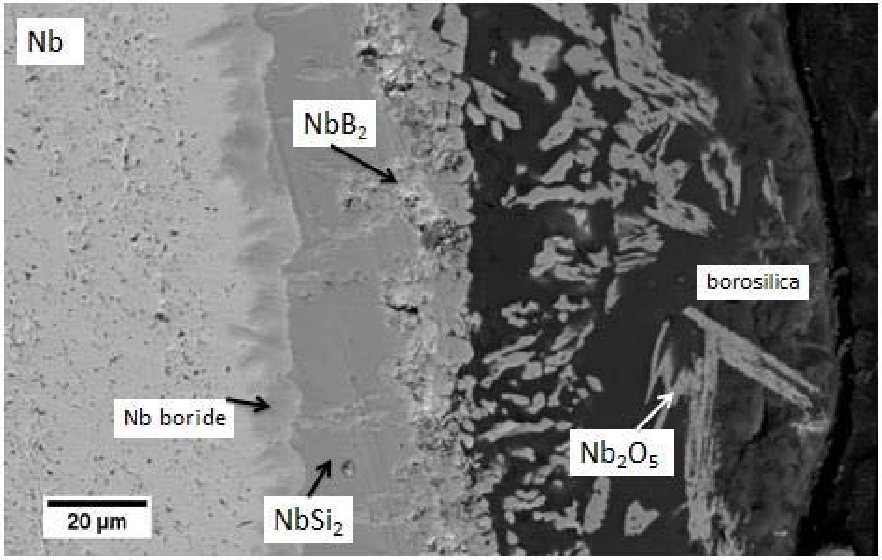
Volatility

- Evaporation of the metal oxide is a crucial component to forming the protective silica layer

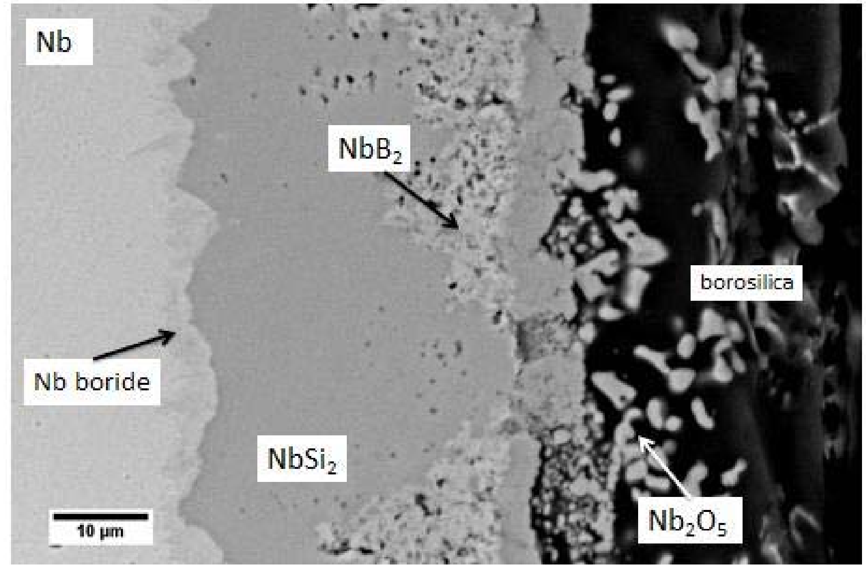


Calculated vapor pressures for various metal oxides [4]

Oxidation Tests: 10 hours Si-B coating



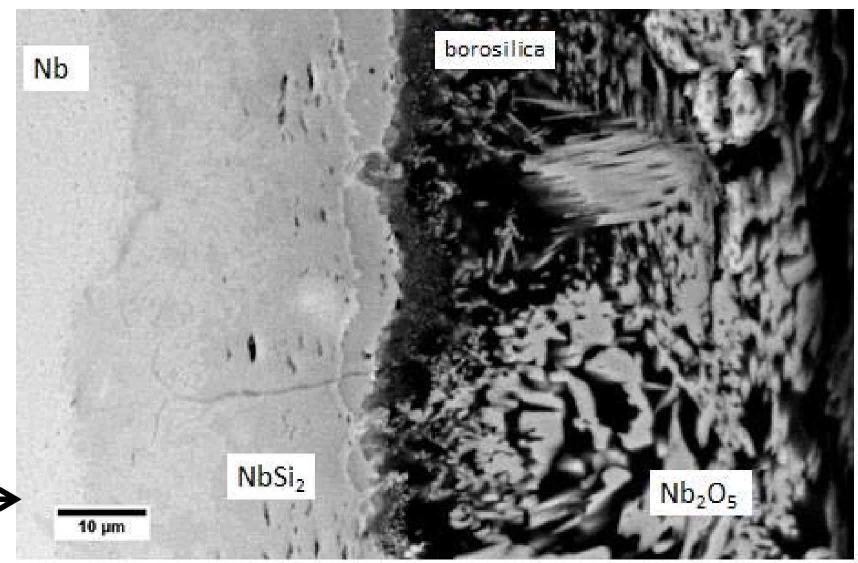
Si-B on Nb (35:1)



Si-B on Nb (25:1)

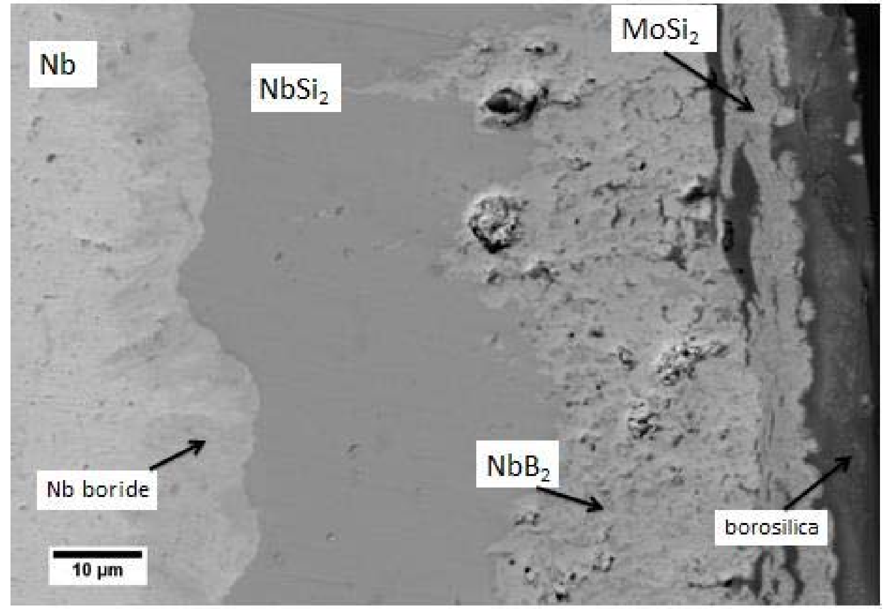
- Mixed oxides continue to increase for 35:1 and 10:1
  - 25:1 had the same thickness
- 10:1 scale almost composed entirely of Nb_2O_5

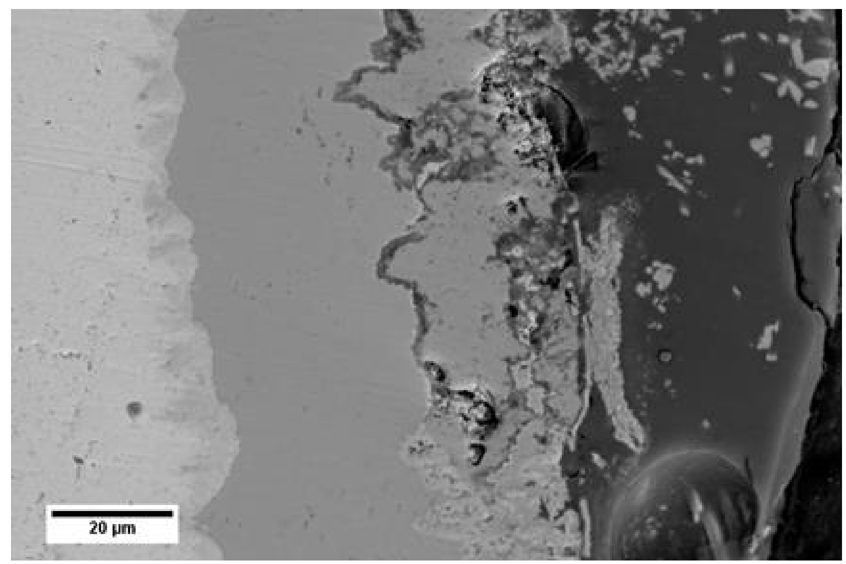
Si-B on Nb (10:1) →



Oxidation Tests: 10 hours Mo-Si-B Coating

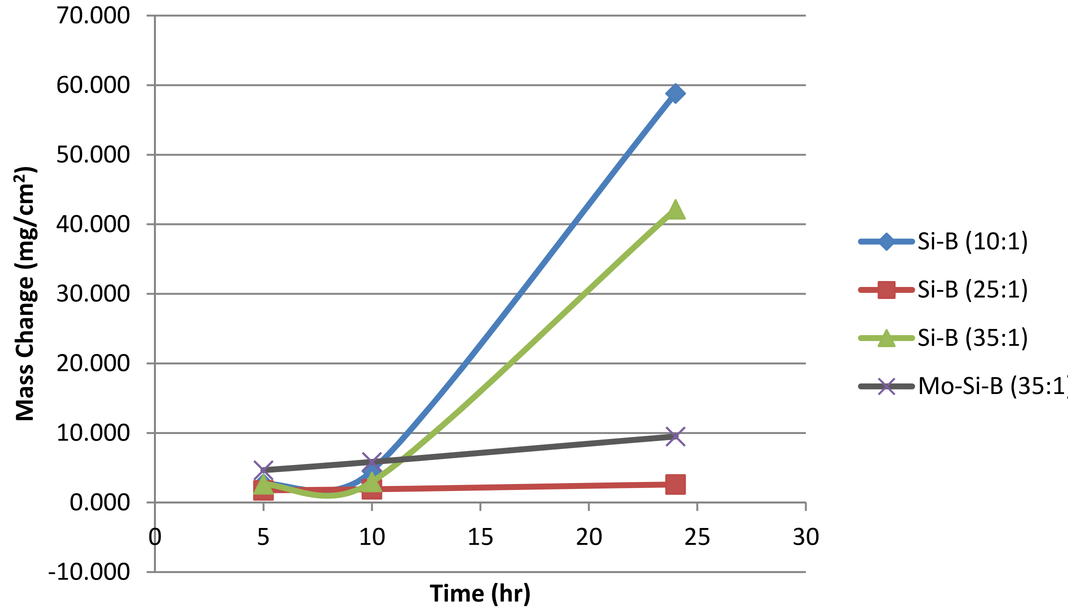
- Oxide scale approximately 8 microns thick
- Some areas showed a coating breach
  - Lack of Mo-Si-B coating results in oxidation similar to samples coated only with Si-B
  - Demonstrates effectiveness of the Mo-Si-B coating as well as the necessity for complete coverage

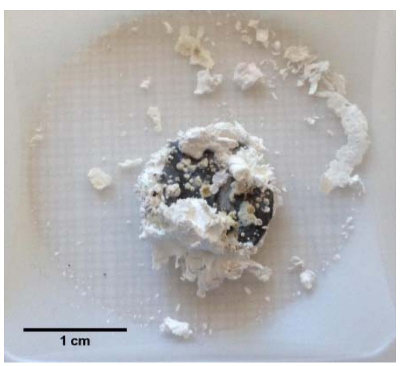


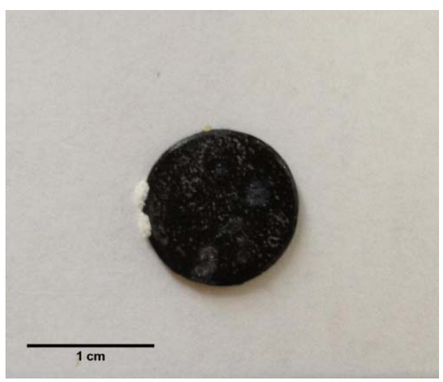


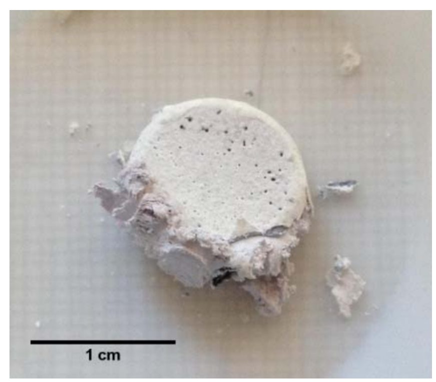
Oxidation Tests: 24 hours

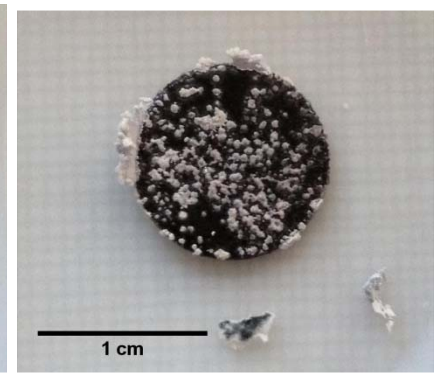
- Increasing Boron additions to 25:1 show increased oxidation protection
  - Lowers viscosity of silica, allowing for faster coverage
- Mo-Si-B coating shows better performance for longer oxidation times
  - Significantly better performance compared to 35:1 Si-B coating











Nb-Si-B (10:1) Nb-Si-B (25:1) Nb-Si-B (35:1) Nb-Mo-Si-B (35:1)

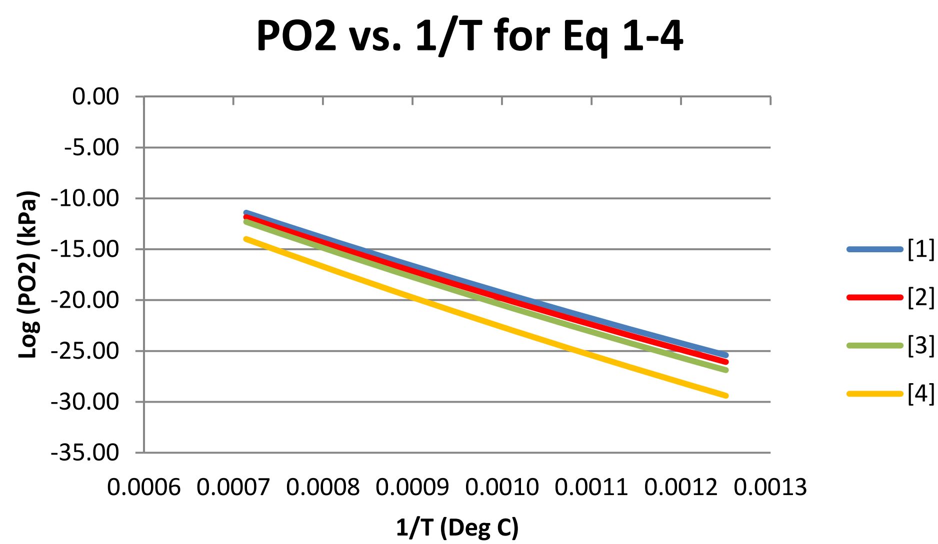
Formation of Nb oxides

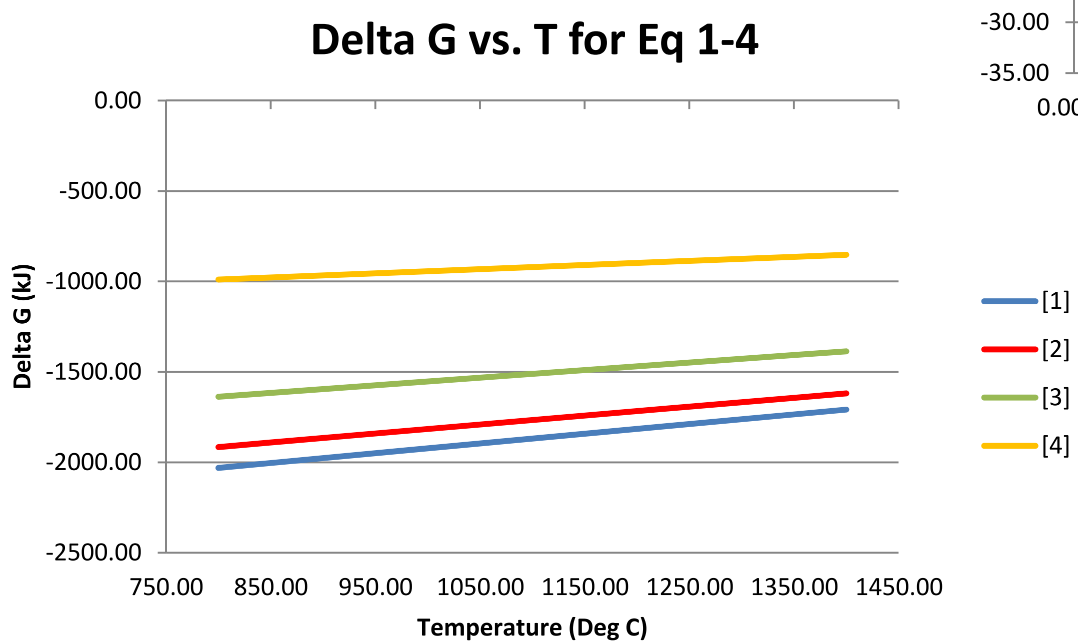
$$NbSi_2 + 3.25O_{2(g)} \rightarrow 0.5Nb_2O_5 + 2SiO_{2(l)} \quad (1)$$

$$NbSi_2 + 3O_{2(g)} \rightarrow NbO_2 + 2SiO_{2(l)} \quad (2)$$

$$NbSi_2 + 2.5O_{2(g)} \rightarrow NbO + 2SiO_{2(l)} \quad (3)$$

$$NbSi_2 + 1.4O_{2(g)} \rightarrow 0.2Nb_5Si_3 + 1.4SiO_{2(l)} \quad (4)$$

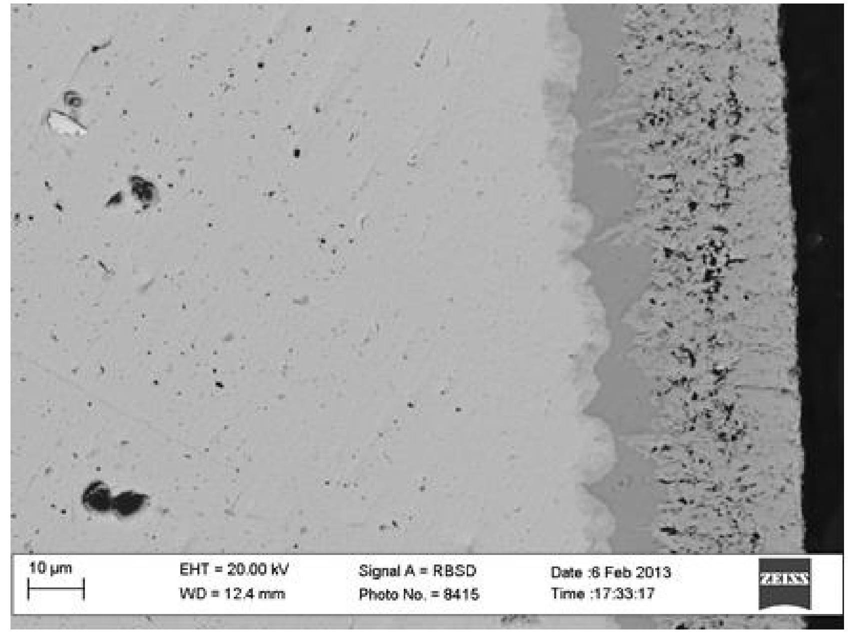




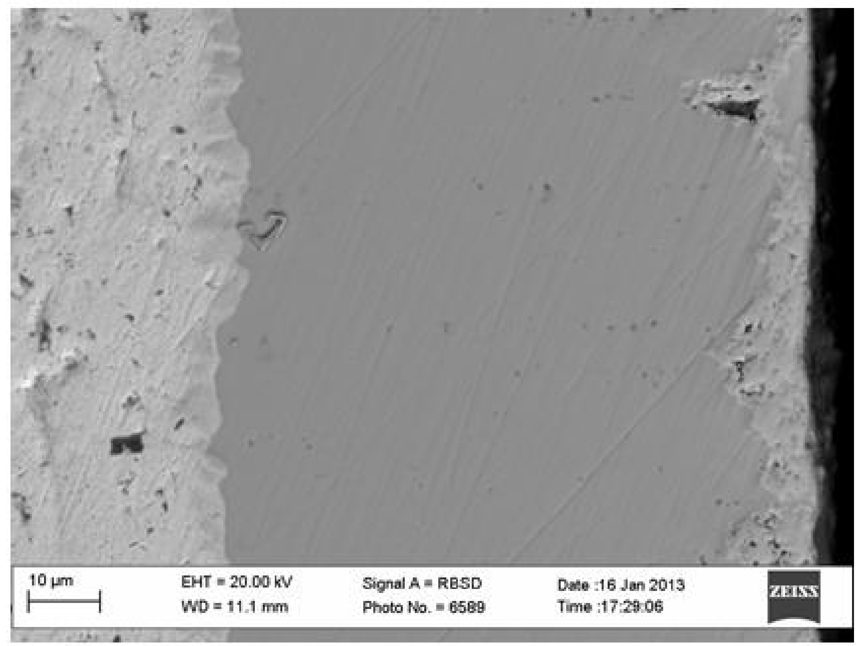
- Equations 1 and 2 have largest free energies and highest PO_2
- Eq. 4 (protective reaction) least likely to form

Pack Optimization

- 35:1 Si-B for 10 hours
  - Total coating thickness reduced to approximately half
  - Majority of the coating composed of NbB_2
- Si-B coating ratio of 50:1 was also produced in order to further reduce the borides in the coating
  - Coating structure shows reduced borides near the surface while still retaining boride layer at substrate/silicide interface
- Suggests that in the Nb case, there is a large preference to form NbB_2



Si-B (35:1) on Nb for 10 hr pack



Si-B (50:1) on Nb

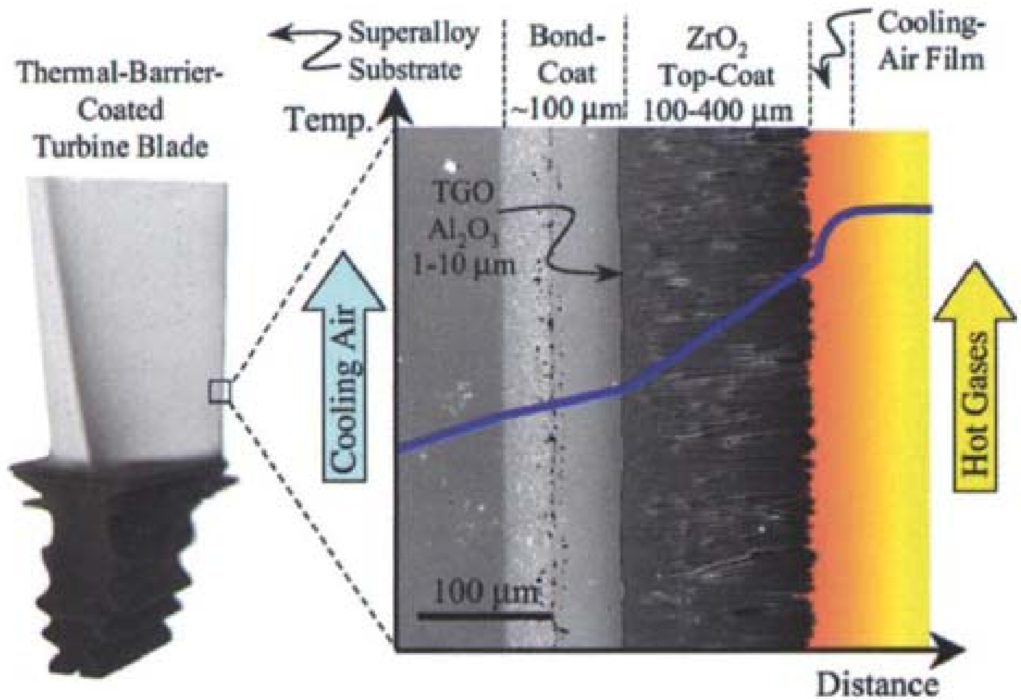
Oxidation of 50:1 Samples (1000°C 24 hours)

- While the mass change is small between the two samples, optically, significant improvement for 50:1 Mo-Si-B coating
  - 50:1 Si-B mass change reduced compared to 35:1 samples (5.20 mg/cm^2 vs. 9.50 mg/cm^2)

Sample	Mass Change (mg/cm^2)
Nb-MoSiB (50:1)	5.186
Nb-Si-B (50:1)	6.249

Smart Coating: Benefits of TBC

- Thermal barrier coatings (TBC) are used to limit thermal exposure
  - reduce the substrate temperature of a superalloy by as much as 300^{o}C [6]
- CTE mismatch between the TBC and underlying layers can result in failure of the coating [7]



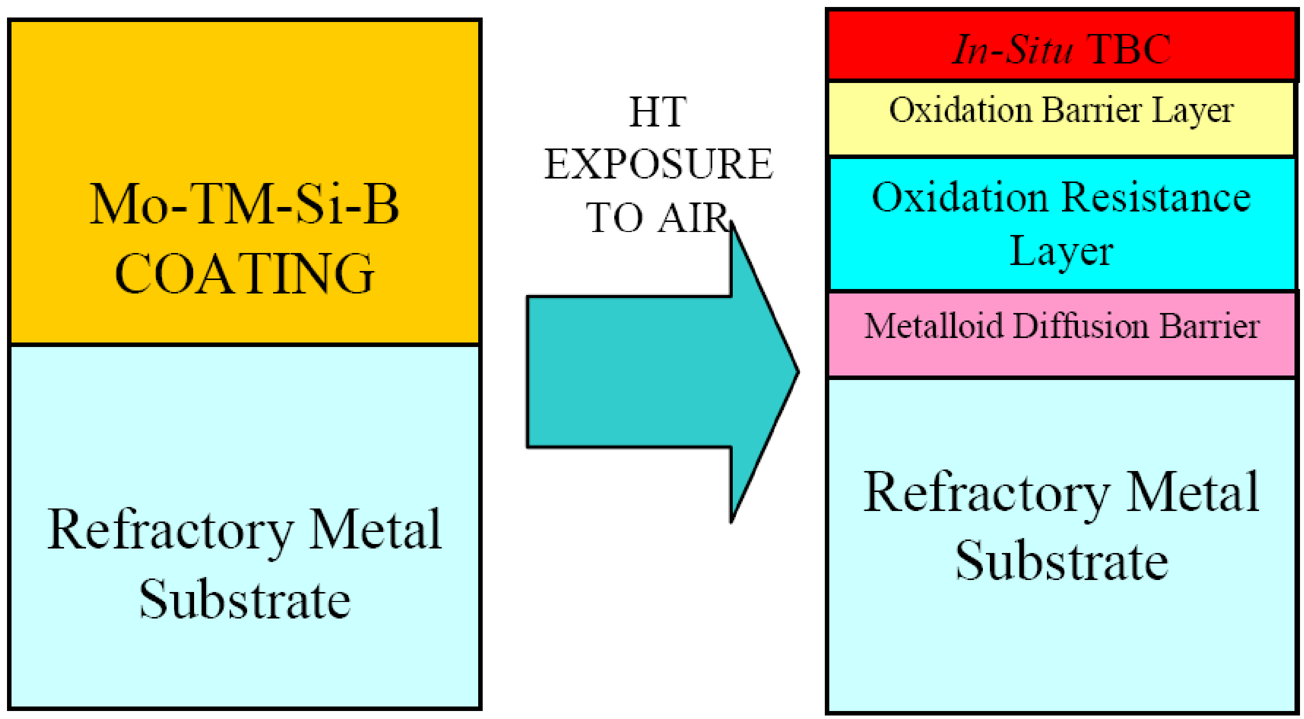
Schematic temperature profile of a turbine blade coated with a TBC [6]

$$Q = -k\frac{dT}{dx}$$

[6] N.P. Padture, M. Gell, E.H. Jordan, Science, 296 (2002) 280-284
[7] W. Beele, G. Marijnissen, A. van Lieshout, Surf Coat Tech, 120 (1999) 61-67.

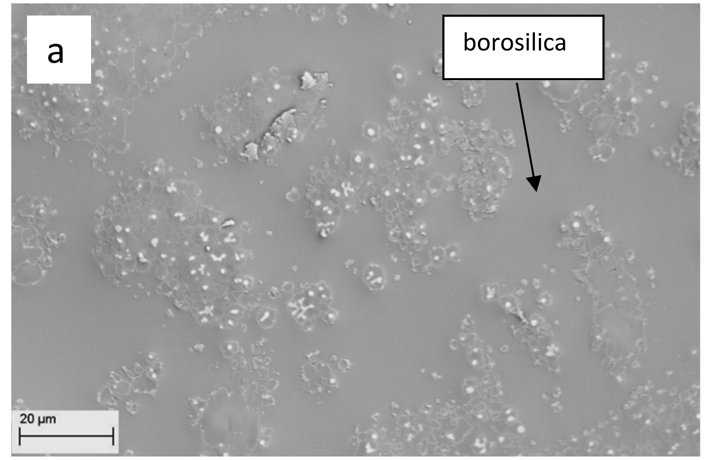
Smart Coating: Mo-TM-Si-B

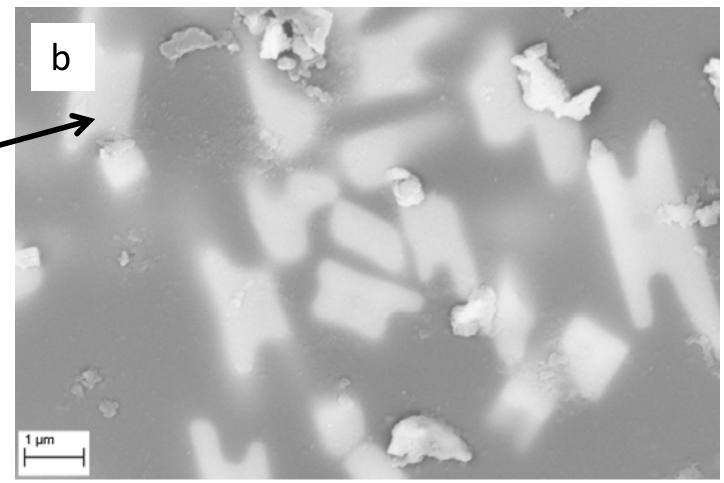
Research is focused on trying to create a graded coating that contains advantageous properties of both TBC and Mo-Si-B and coatings



Mo-Zr alloys oxidation Results: 1500°C, 5 hrs

- Surface is covered by protective borosilica
- Increased mass change with increasing Zr additions
- EDS identifies Si,Zr, and O in lighter regions
  - Formation of ZrO_2
- Shows that Zr can be incorporated into the Mo-Si-B coating





Plan view of oxidized coated samples at 1500°C for 5 hrs for a) Mo-1at%Zr b)Mo-5wt%Zr

Sample	Testing conditions	Mass Change (mg/cm2)
Mo-1at%Zr Si-B	1500°C 5 hr	0.27
Mo-5wt% Zr-Si-B	1200°C 24 hr	0.04
Mo-5wt% Zr-Si-B	1500°C 5 hr	0.38

Element Line	*Atom %*
O K	62.9
Na K	1.5
Al K	2.7
Si K	12.2
Zr L	20.8
Total	100.0

Conclusions

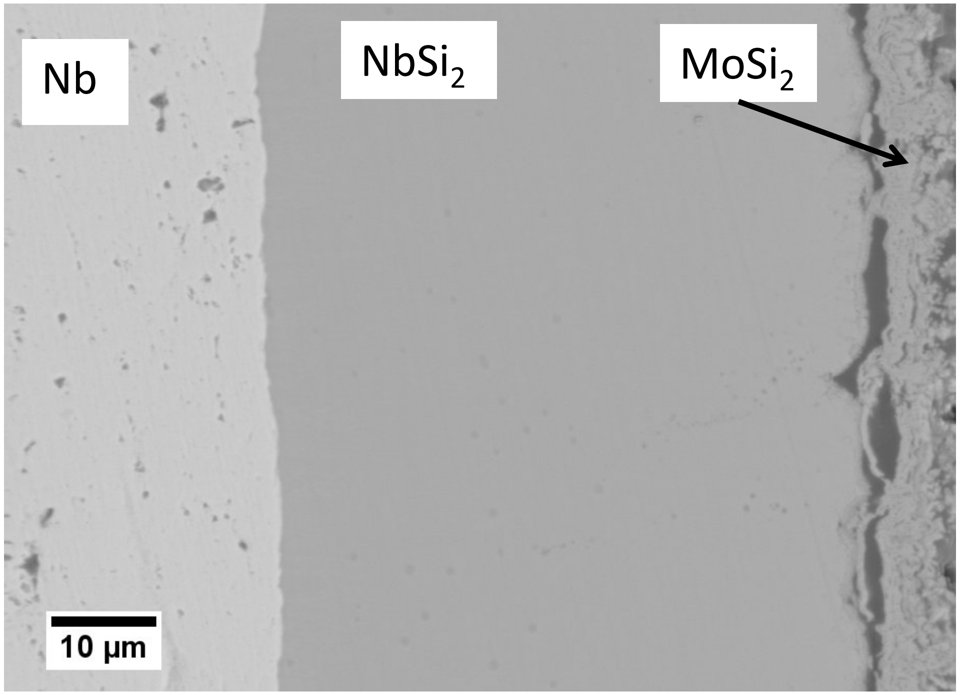
- Gaseous thermodynamics calculations provide processing parameters for the CVD processing.
- Diffusion barrier T_2 Phase (Borosilicides) can provide the necessary graded structures with a wide range of refractory metal substrates due to its extended solid solution.
- OOF2 allows one to analyze a microstructure subjected to thermal and mechanical stress
- Results indicate a need for a graded structure to reduce strain on the coating
- ZrO2 additions effect the heat flow through the coating based on placement and microstructure

Conclusions

- Mo-Si-B coatings have been produced on Nb substrates using decomposition of $Mo(CO)_6$ followed by co-pack cementation
- Oxidation tests show that for a given Si:B ratio, Mo-Si-B coatings offer better protection compared to Si-B coatings
- Early experimental results show that Zr can be incorporated into the Mo-Si-B coating without degrading oxidation resistance
  - Allow for a graded structure for TBC
  - Oxidation tests will be carried out for a range of temperatures and times

Future Work: Optimize Mo-Si-B coating for Nb

- TiB2 addition to suppress boride formation
  - There appears to be a very high activity for boron during the pack cementation process
  - Study by Cockeram et al. used TiB_2 as boron source to lower the partial pressure of the boron flourides in the pack process [8]
- Substitution of TiB_2 in place of B in pack cementation treatment supresses boride formation
  - more desirable coating structure

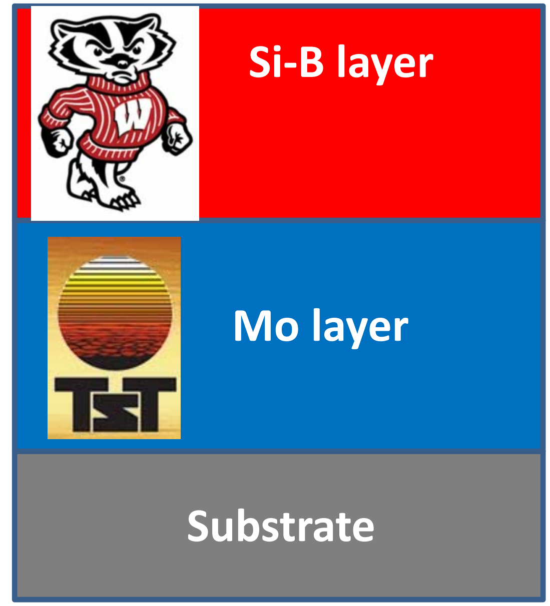


Mo-Si-B coating on Nb using Si:TiB_2 of 35:1

[8] Brian V. Cockeram, "Growth and oxidation resistance of boron-modified and germanium-doped silicide diffusion coatings formed by the halide-activated pack cementation method", *Surface and Coatings Technology*, Volumes 76–77, Part 1, November 1995, Pages 20-27

Future Work: Utilize plasma spray deposition

- Thermal spray process combined with Si-B pack cementation technique is an effective process to produce Mo-Si-B coatings on larger samples [9]
  - Plasma spray deposition of Mo allows for samples to be scaled up in size and complexity



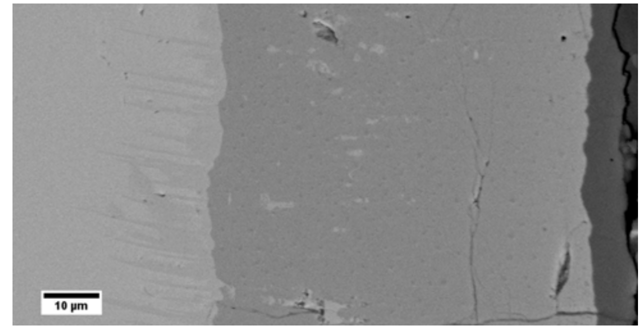
[9] Patrick Ritt, Otto Lu-Steffes, Ridwan Sakidja, John H. Perepezko, William Lenling, Daryl Crawmer, Jesse Beske. "Application of Plasma Spraying as a Precursor in the Synthesis of Oxidation Resistant Coatings." *Journal of Thermal Spray Technology*

Future Work

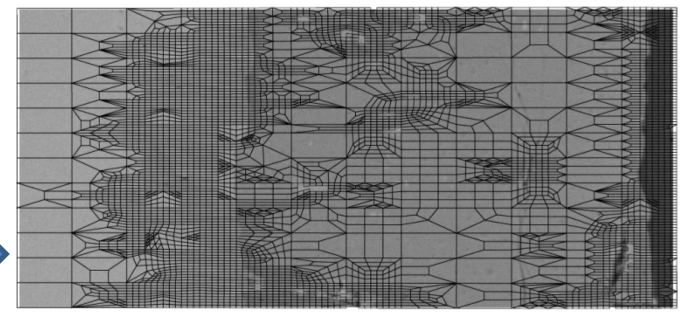
- Optimization of parameters for the CVD coating processes
- Establish the oxidation kinetics control parameters of the selected coating materials under both dry and wet conditions
- Establish lifetime criteria for the borosilicide coatings integrated into Mo-based substrates under aggressive/wet environment with both static and cyclic conditions
- Integration of the smart coating into an expanded range of other TM-based alloys with emphasis on Nb-based alloys under aggressive/wet oxidation and cyclic conditions.
- Establish lifetime criteria for the smart coatings with the expanded range of substrate materials under aggressive/wet environment with both static and cyclic conditions based upon kinetics measurements and coating structure analysis with the OOF-2 FEM heterogeneous structure simulation

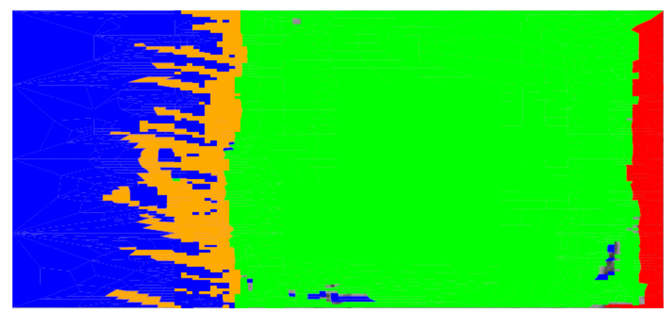
Proposed FEM Work

- Use FEM to analyze mechanical and thermal reliability of a coatings
  - ANSYS
  - Object Oriented FEM (OOF2) is public domain finite element analysis (FEA) software created by NIST to investigate the properties of microstructures
- Inputs: a microstructure(real micrograph or computer generated), material properties and boundary conditions
  - Isotropic and anisotropic values allowed
- FEM with the actual microstructures of the coatings as input for the OOF-2 software
- To simulate a gradient, apply a constant temperature on top (T_{hot}) and bottom (T_{cold})



Material	Young’s Modulus (GPA)	Poisson's Ratio	Thermal Conductivity (W/mK)	Thermal Expansion (um/m C)
Mo	330	0.29	138.00	6.5
MoSi2	432	0.15	28.60	10.4
T2	383	0.27	28.00	7.7
SiO2	64	0.19	1.10	4.0





Blue: Mo
Orange: T1
Green: MoSi2
Red: SiO2

- **LIST OF PAPERS PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATIONS, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH, STUDENTS SUPPORTED UNDER FE0007377**
- Publications:
  - Lu-Steffes, O. J., Sakidja, R., Bero, J. & Perepezko, J. H. Multicomponent coating for enhanced oxidation resistance of tungsten. *Surface and Coatings Technology* **207**, 614-619, doi:10.1016/j.surfcoat.2012.08.011 (2012)
- Publications under preparation:
  - Patrick Ritt, Otto Lu-Steffes, Ridwan Sakidja, John H. Perepezko, William Lenling, Daryl Crawmer, Jesse Beske. "Application of Plasma Spraying as a Precursor in the Synthesis of Oxidation Resistant Coatings." *Journal of Thermal Spray Technology* (accepted)
- Conferences
  - Research results were presented at the 2012 Materials Science and Technology conference(October 2012, Pittsburgh,PA) in the symposium "Beyond Nickel Based Superalloys-II." The title of the presentation was "Transition Metal Doped Mo-Si-B Coatings."
  - Research results were presented at the 2012 First ACEEES International Forum (Hawaii, December 2012) The title of the presentation was "Design and Synthesis of Zr Doped Mo-Si-B Coatings"
- Support
  - John Perepezko; PI
  - Otto John Lu-Steffes: Graduate student
  - Dana Jackson: Undergraduate laboratory assistant

Task 1.1. Formulate the computational stability analysis for the hierarchy of the smart coating structures
Task 1.2. Down-select the coating candidates based on the integrity of the coating structures and phase constituents as well as their performance under static dry and wet conditions at temperature up to 1600^{o}C.

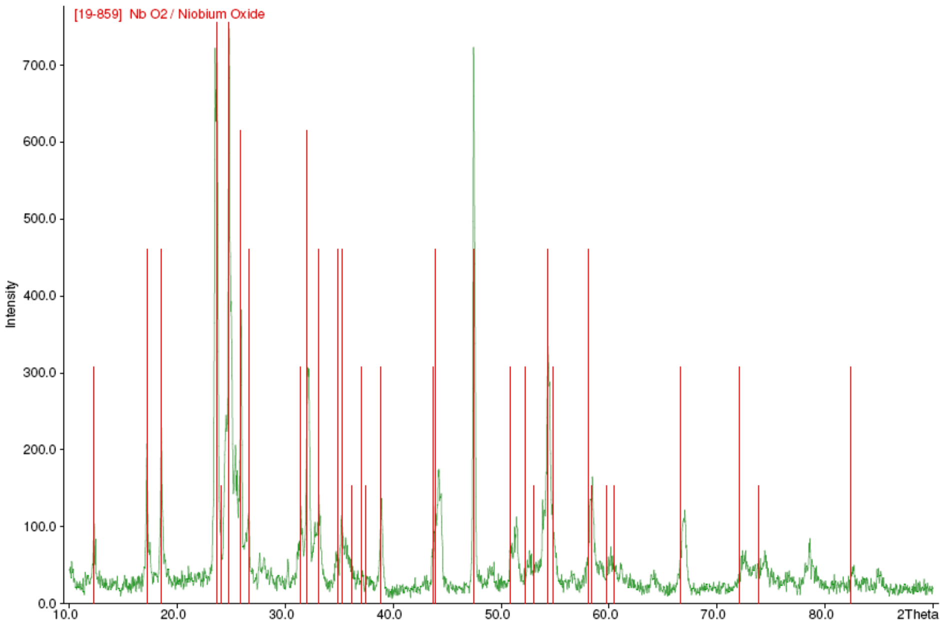
Task 2.1. Formulate the key chemical thermodynamic metrics for the synthesis process
Task 2.2. Establish the oxidation kinetics control parameters of the selected coating materials under both dry and wet conditions.
Task 2.3. Establish lifetime criteria for the borosilicide coatings integrated into Mo-based substrates under aggressive/wet environment with both static and cyclic conditions.

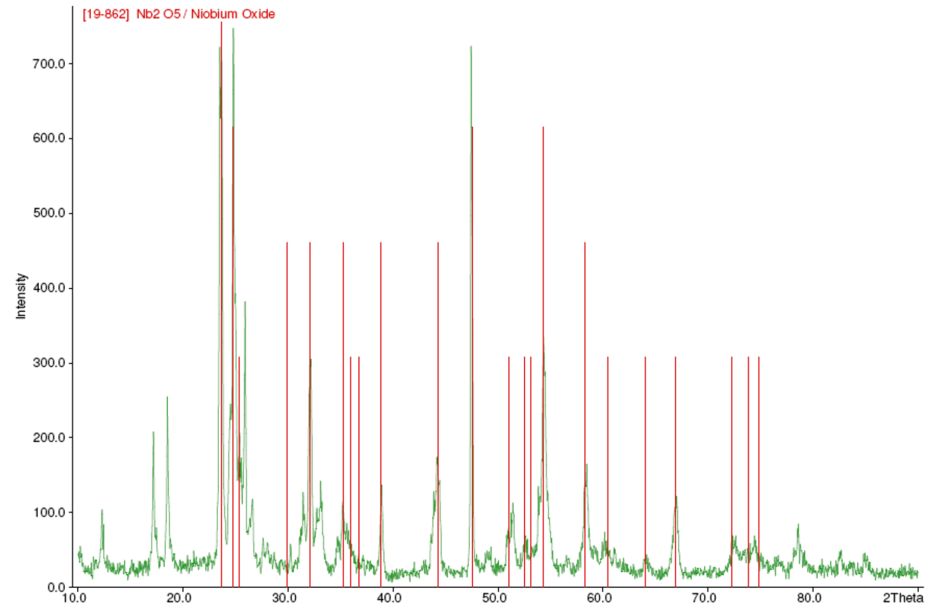
Task 3.1 Integration of the smart coating into an expanded range of other TM-based alloys with emphasis on Nb-based alloys
Task 3.2. Establish lifetime criteria for the smart coatings with the expanded range of substrate materials under aggressive/wet environment with both static and cyclic conditions based upon kinetics measurements and coating structure analysis with the OOF-2 FEM heterogeneous structure simulation tools
Task 3.3. Testing of the coated structures under simulated corrosive conditions

Thank You!

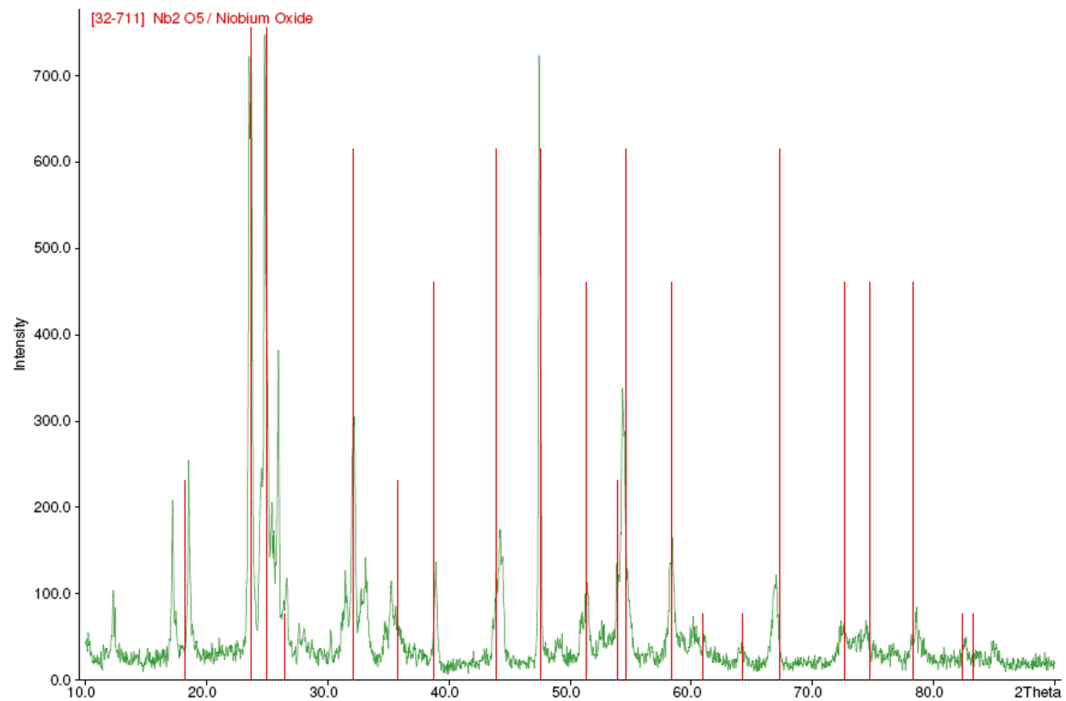
Experimental Procedure

- Mo-Zr alloys were coated with Si-B using pack cementation treatment
- CVD technique that uses halide vapor species to diffuse to the substrate and decompose, depositing the desired elements
- The powder mixture used for pack cementation consisted of 2 wt.% NaF, 34.028 wt.% Si, 0.972 wt.% B, and the remainder Al_2O_3 powder.
- The samples were packed in the powder mixture and placed in the furnace at 1000°C for 50 hours under a protective atmosphere of Ar
- Oxidation tests were carried out at 1200°C and 1500°C





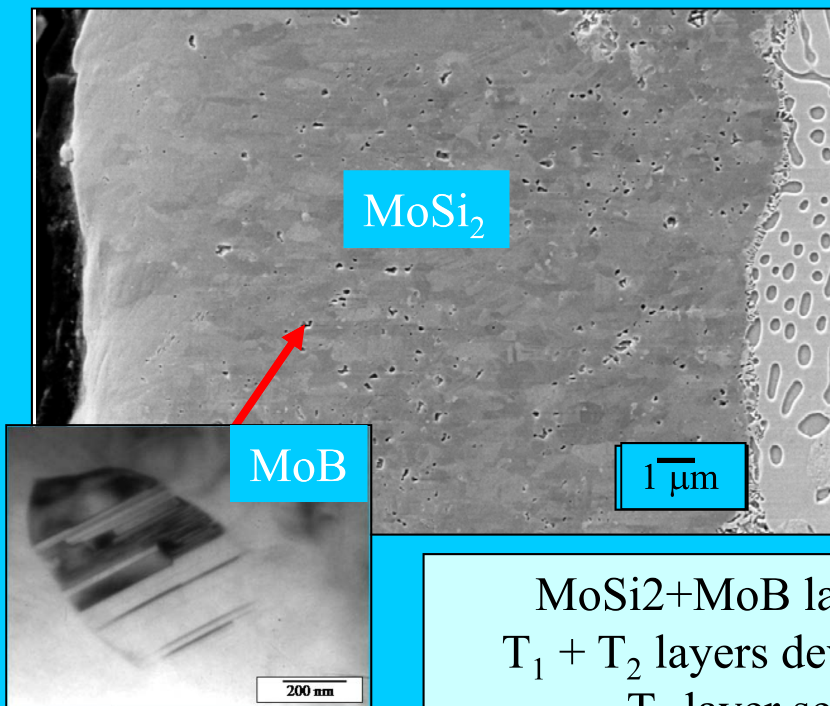
XRD of Si-B (35:1) coating on Nb oxidized for 24 hours at 1000°C



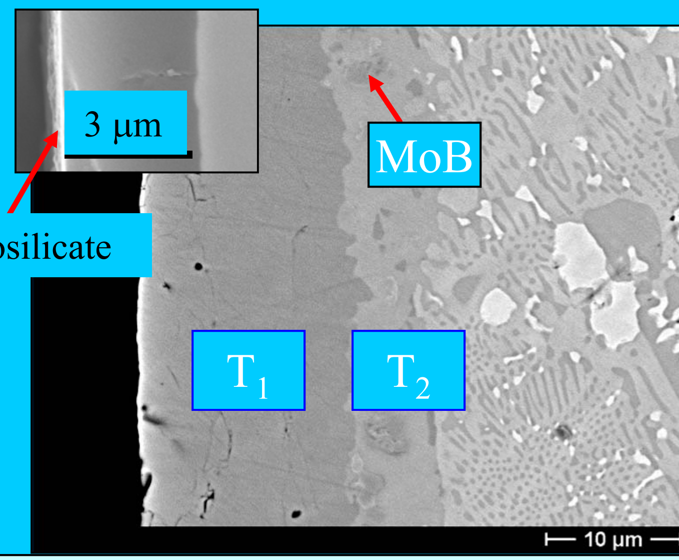
- XRD (green lines) on the surface of oxidized Si-B (35:1) coating sample shows peaks for Nb_2O_5 and NbO_2 (red lines)

Si Pack Cementation on Mo-14.2Si– 9.6B Alloys

As-Pack



Pack + 1300°C/ 25 hrs in air



MoSi2+MoB layer initially forms after Si-pack process

$T_1 + T_2$ layers develop after heat treatment at 1300°C in air

T_1 layer serves as the oxidation resistant layer

T_2 (MoB) layer functions as the diffusion barrier layer

R. Sakidja, J. S. Park, J. Hamann and J. H. Perepezko, "Synthesis of Oxidation Resistant Silicide Coatings on Mo-Si-B Alloys", Scripta Materialia 52[6] (2005) pp. 723-28 .

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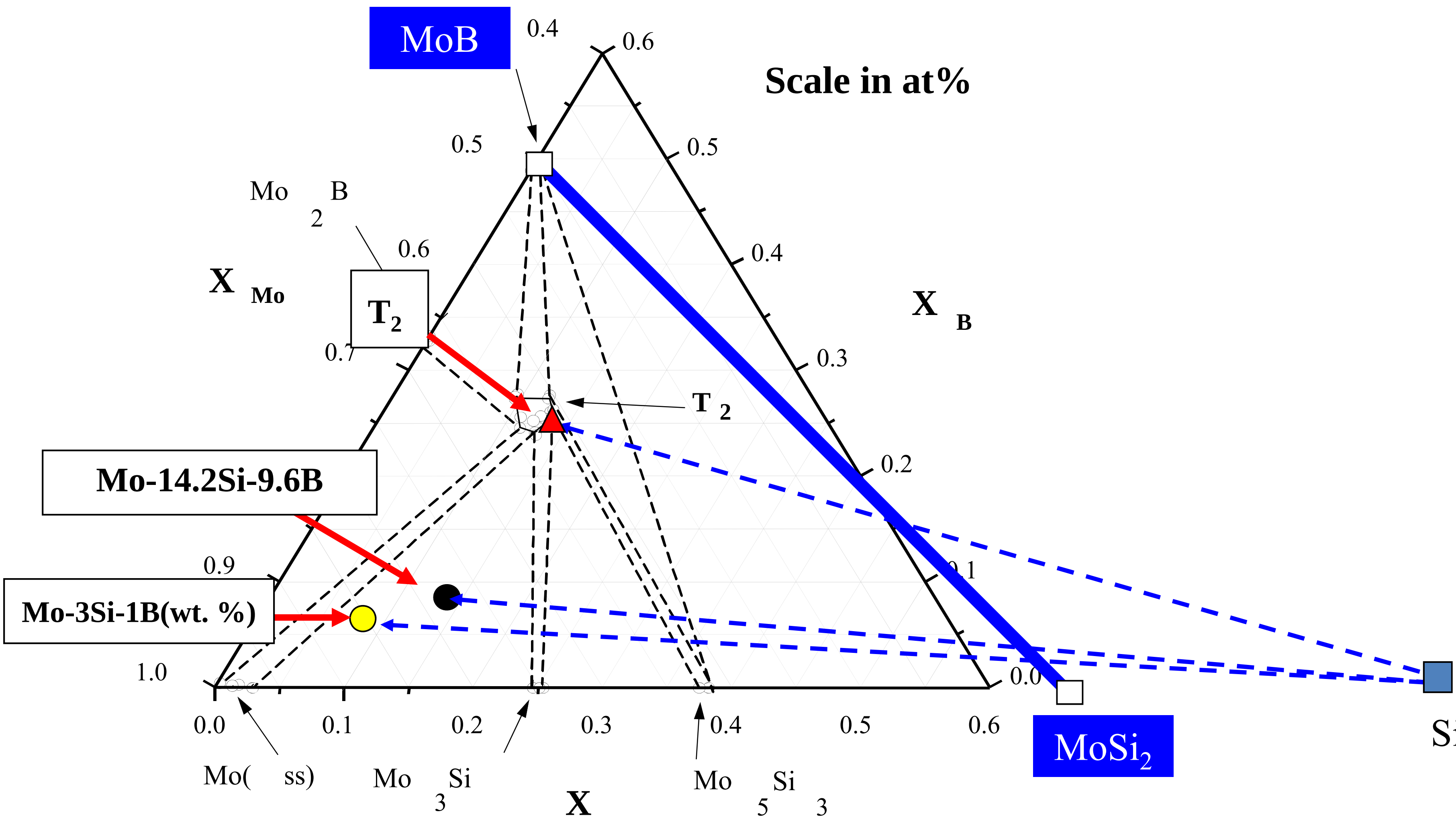
Practical Limitation of Si-Pack Cementation onto Mo-Si-B Alloys



To form a continuous boride layer, [B] must be sufficiently high within the Mo-Si-B substrate.

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