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

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The need for ultra-high temperature materials

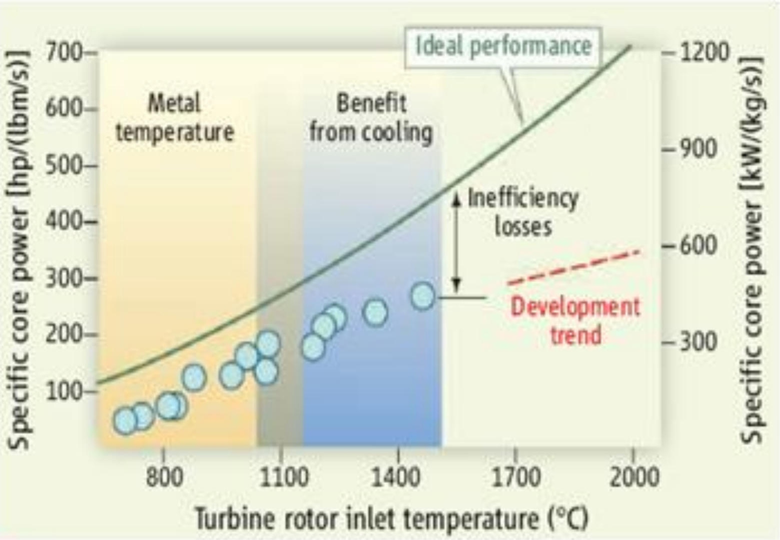
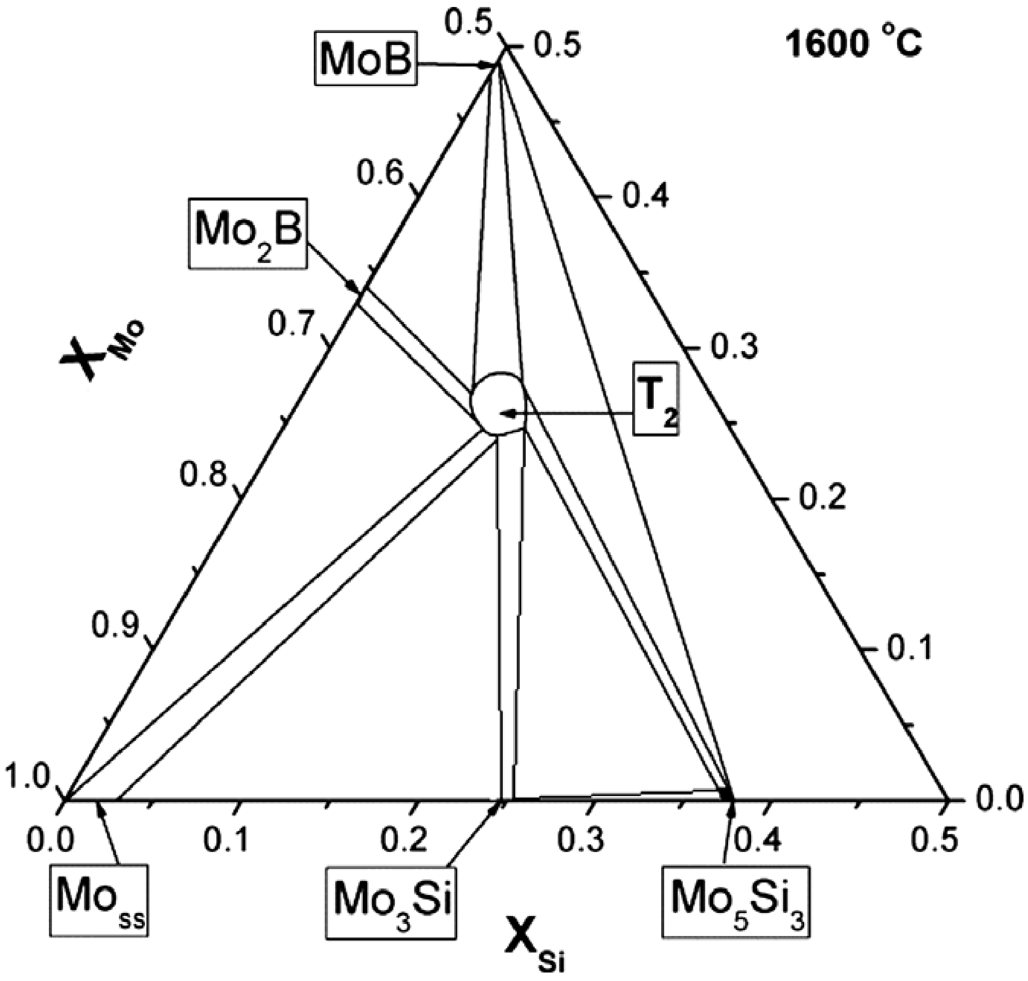


Figure 1 Core horsepower versus turbine inlet temperature for selected gas turbine engines. Data for specific engines spans about 70 years and is compared with the ideal or theoretical limit.

J. H. Perepezko, *The Hotter the Engine, the Better*, Science , 20 November 2009: 326 [5956] pp. 1068-1069

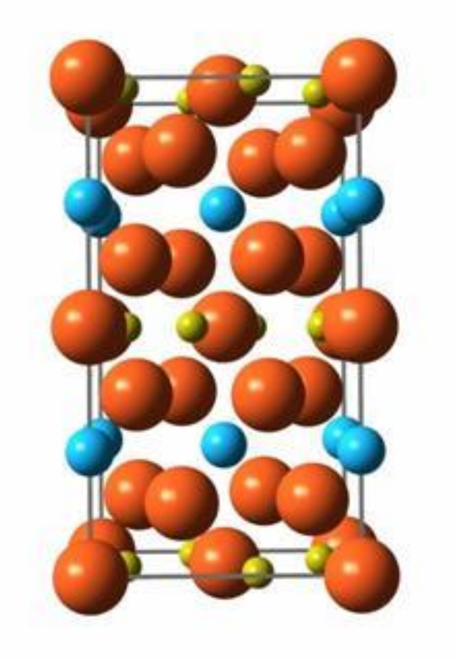
Refractory metals/alloys offer great opportunities to replace Ni-based Superalloys
However , their oxidation resistance is a significant problem => Need for Coating Strategies

Mo-Si-B Phase Equilibium at High Temperature



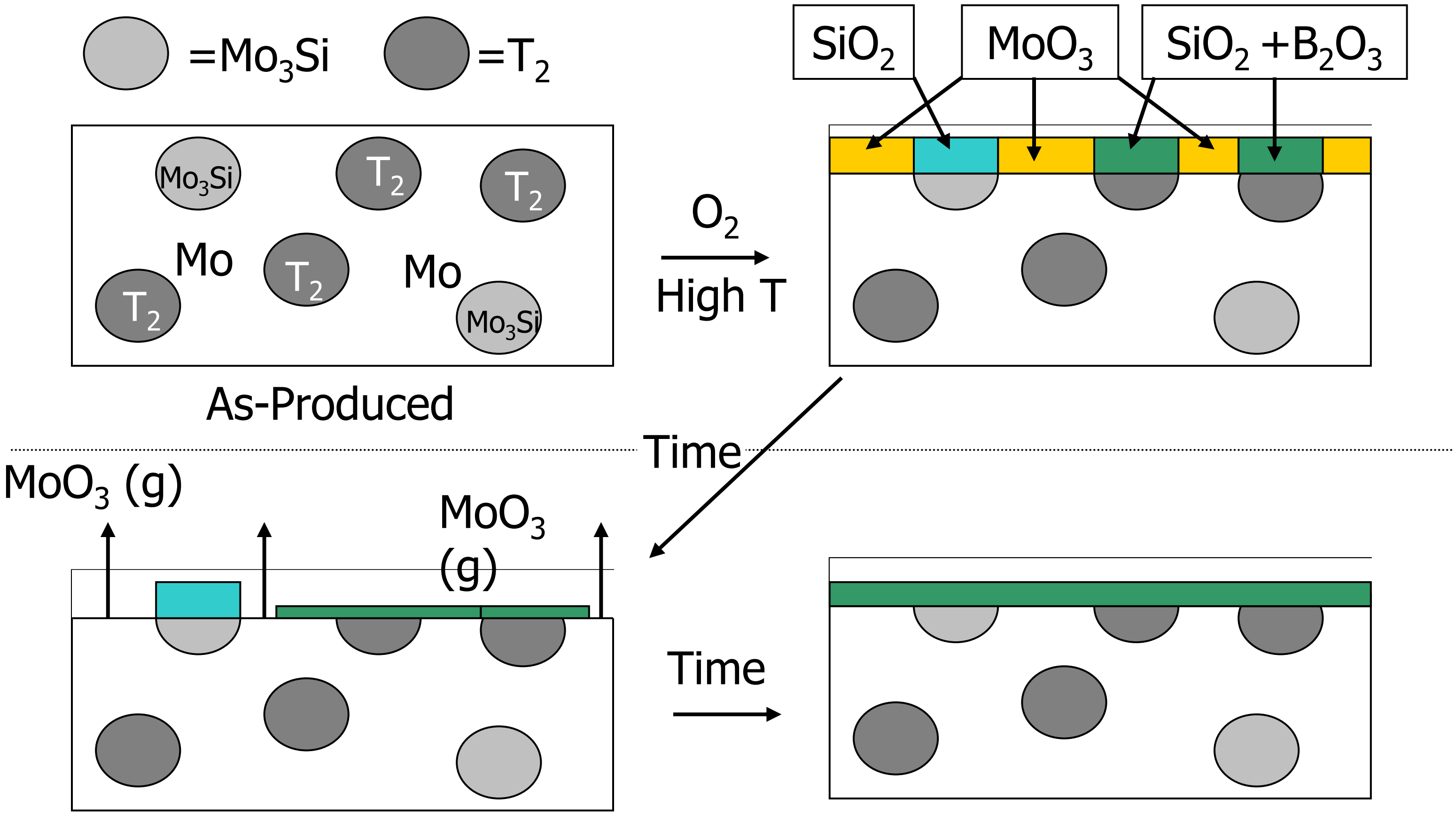
T$_2$≅Mo-12.5Si-25B

Mo$_5$SiB$_2$



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

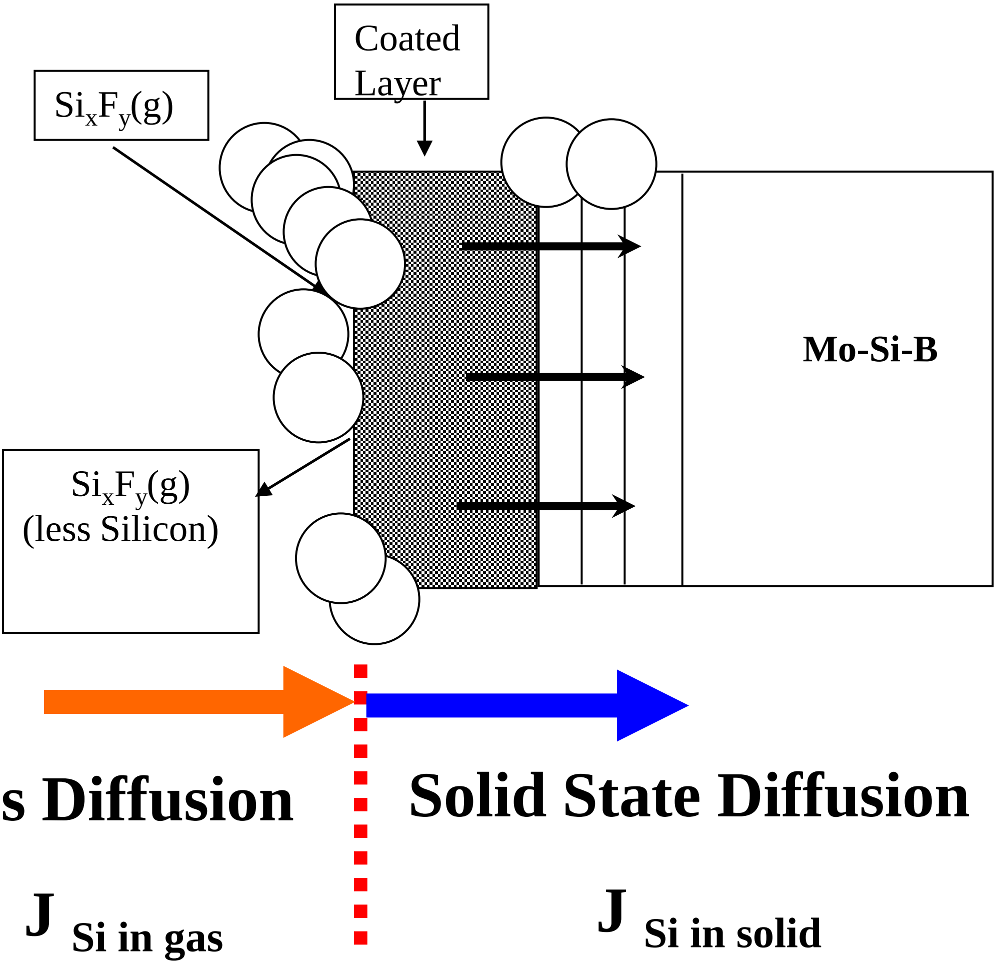
Oxidation Mechanism of Mo-Si-B Alloys



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

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

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



$Si_xF_y(g)$

Coated Layer

Mo-Si-B

$Si_xF_y(g)$ (less Silicon)

Gas Diffusion

Solid State Diffusion

$J_{\text{Si in gas}}$

$J_{\text{Si in solid}}$

Initial period

Rate Controlling Step : Solid State Diffusion

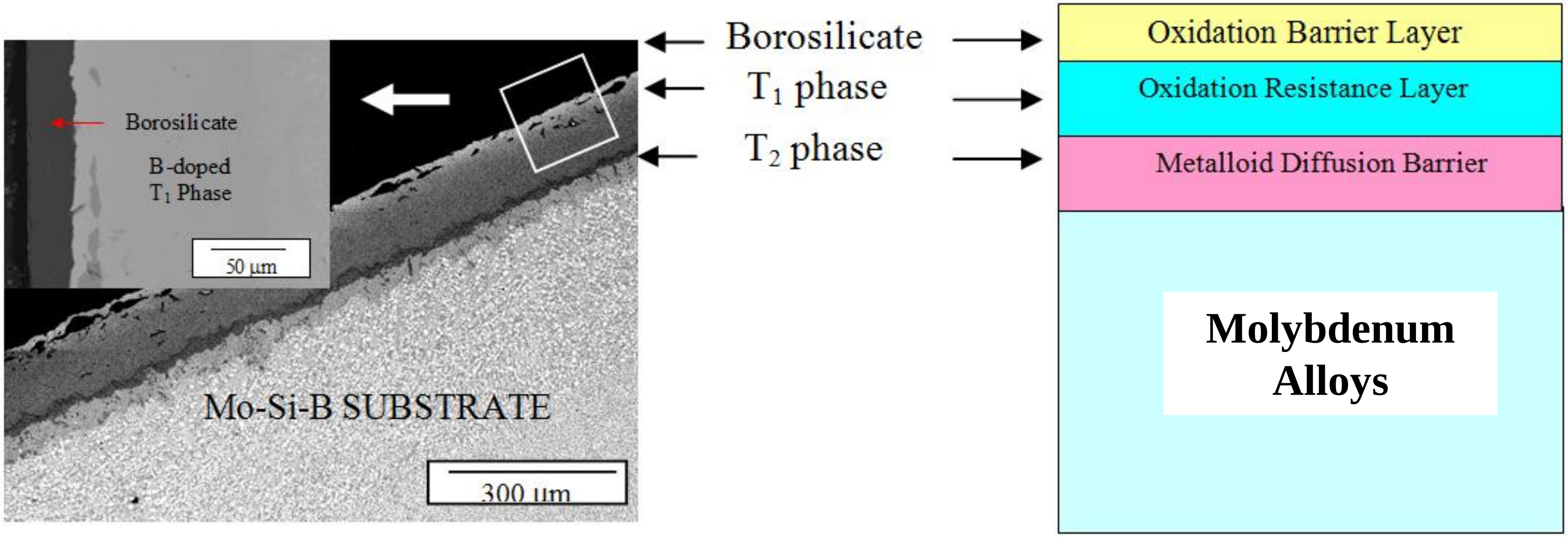
After Initial period

Rate Controlling Step : Gas Diffusion

- Reaction Products: Mainly

$MoSi_2$ → Gas diffusion governs during the process

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



Borosilicate

T_1 phase

T_2 phase

Oxidation Barrier Layer

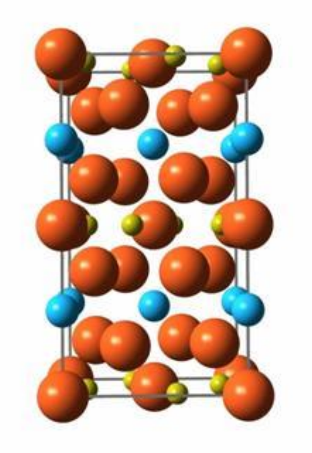
Oxidation Resistance Layer

Metalloid Diffusion Barrier

Molybdenum Alloys

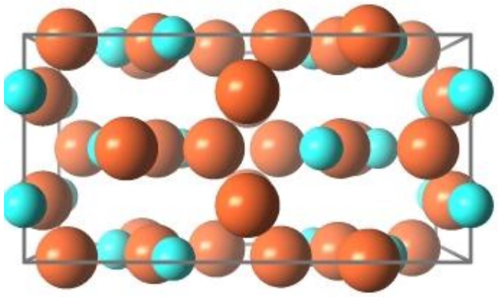
Mo_5SiB_2 (T_2)

T_M ~ 2100°C

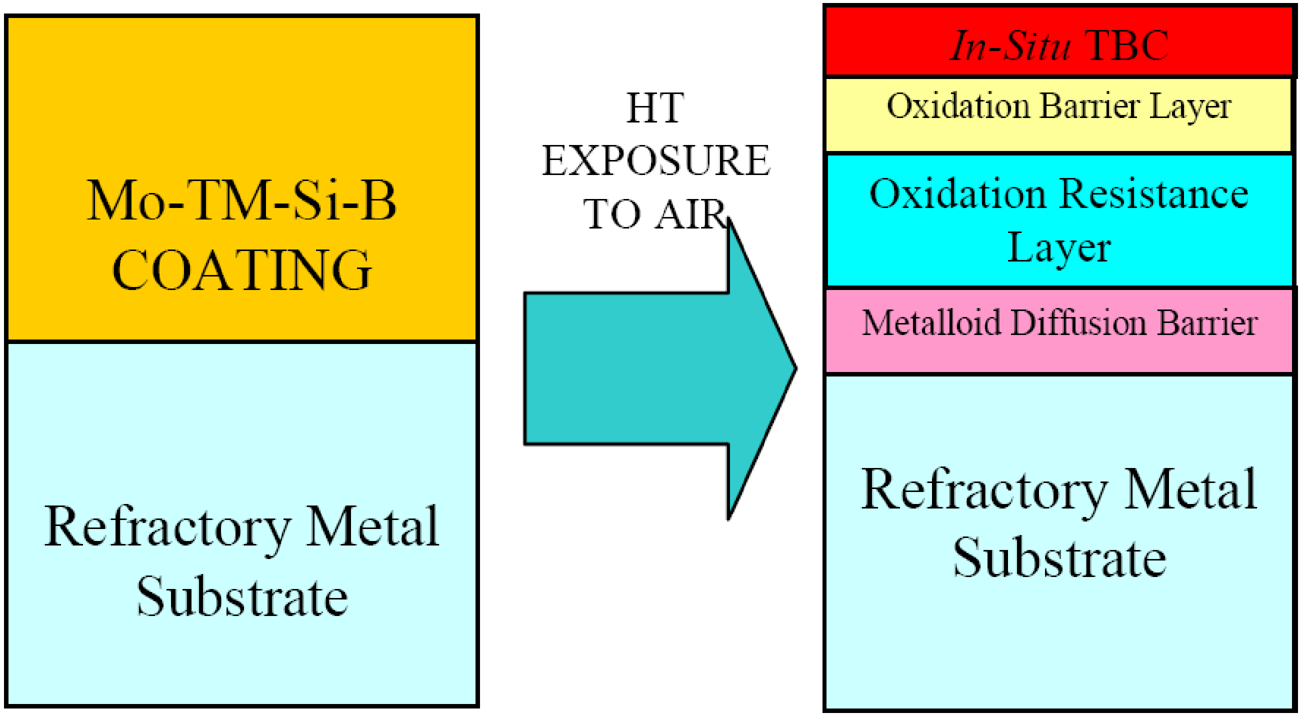


Mo_5Si_3 (T_2)

T_M=2180°C



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



Mo-TM-Si-B COATING

Refractory Metal Substrate

HT EXPOSURE TO AIR

In-Situ TBC

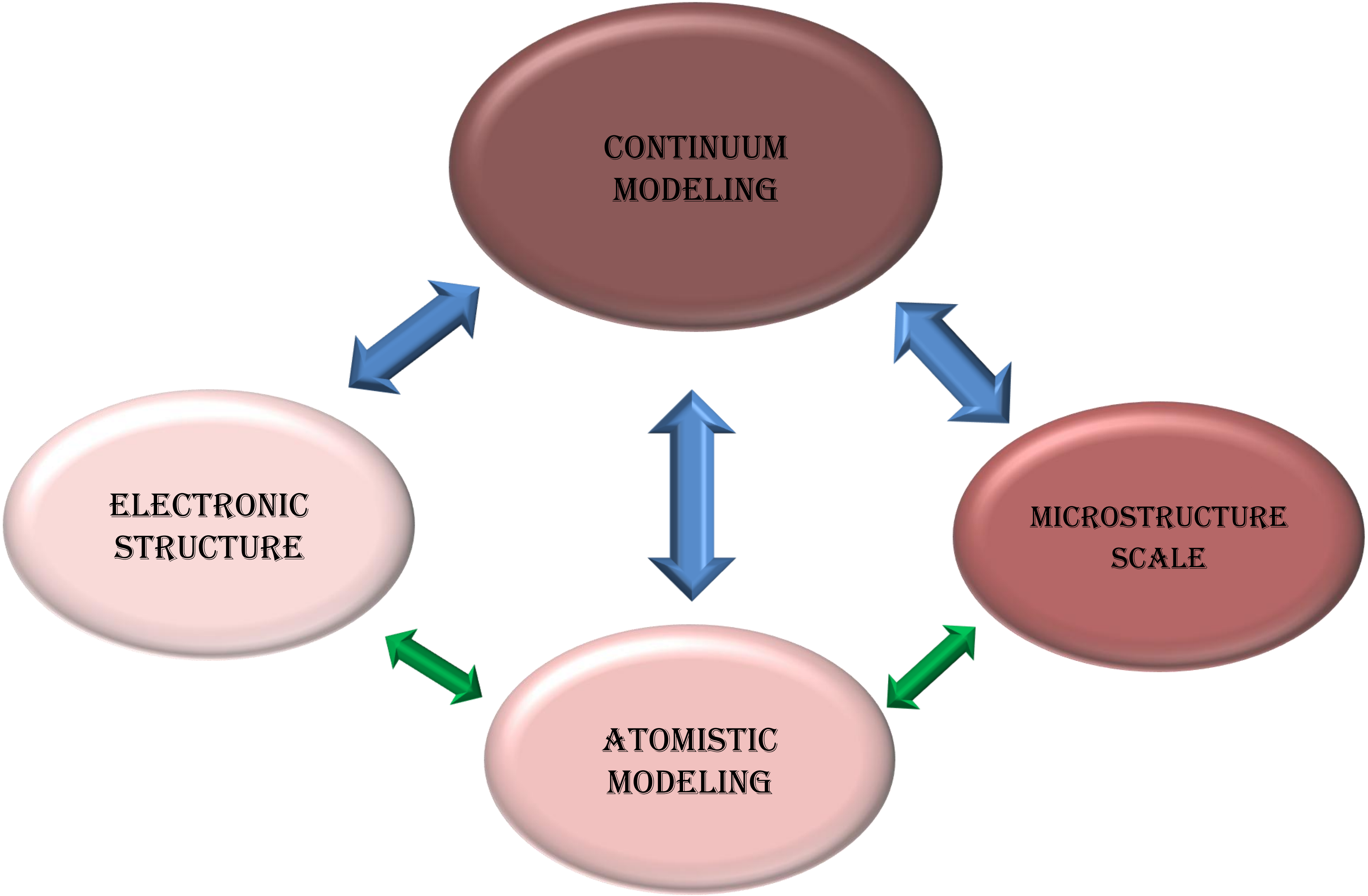
Oxidation Barrier Layer

Oxidation Resistance Layer

Metalloid Diffusion Barrier

Refractory Metal Substrate

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



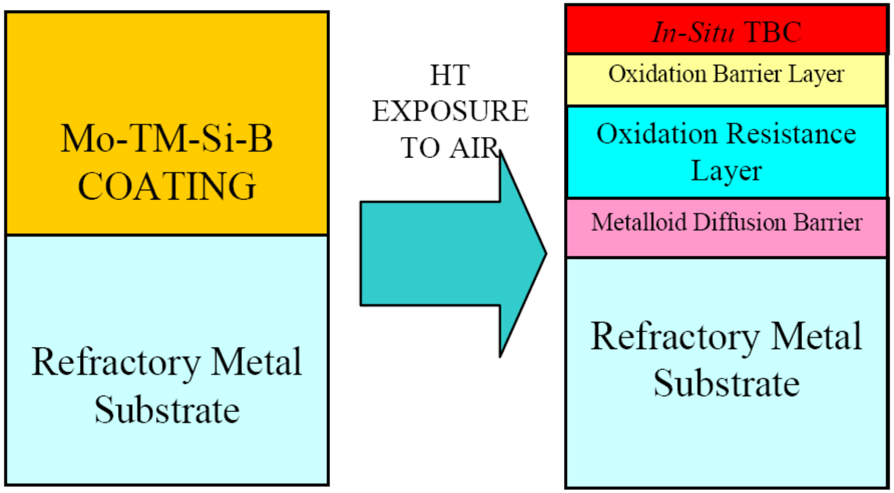
CONTINUUM MODELING

ELECTRONIC STRUCTURE

MICROSTRUCTURE SCALE

ATOMISTIC MODELING

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



Mo-TM-Si-B COATING

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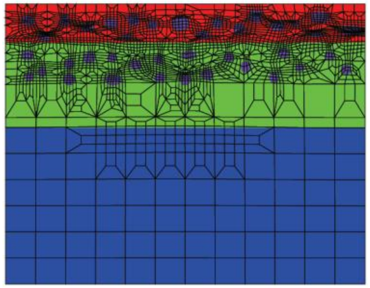
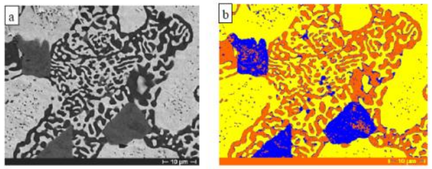
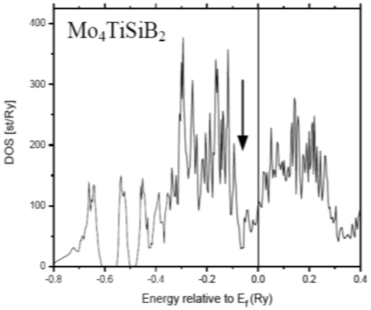
Multi-scale Designs & Synthesis Approach for Mo-Si-B Based Smart Coatings

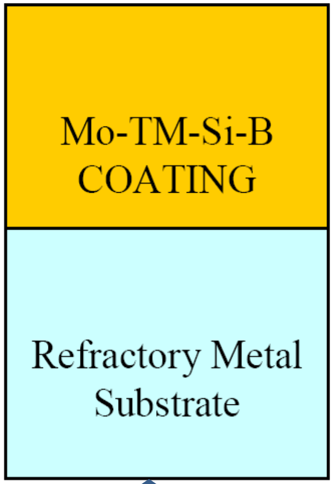
Microstructure-based FEM





Electronic Structure



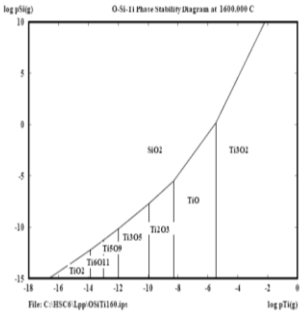


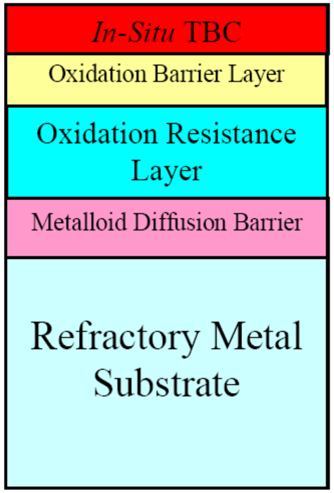
Mo-TM-Si-B COATING

Refractory Metal Substrate

HT EXPOSURE TO AIR

Computational Thermodynamics





In-Situ TBC

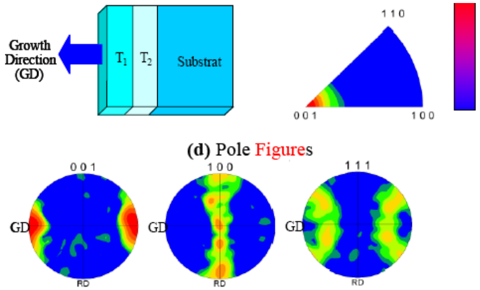
Oxidation Barrier Layer

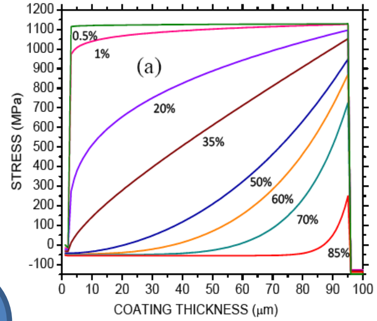
Oxidation Resistance Layer

Metalloid Diffusion Barrier

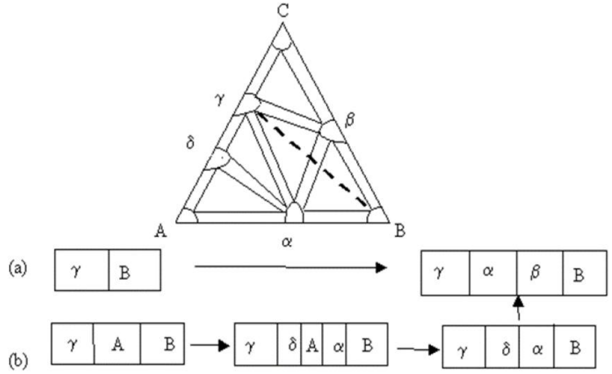
Refractory Metal Substrate

Thermal Stress Analysis





Kinetic Biasing



High-Temperature

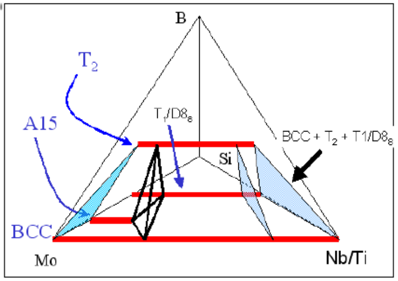
Phase Equilibria

Mo -Si- B

BCC + T_2+ A15 **A15+ T_2+ T_1**

BCC Stabilizer : Ti, Zr, Hf, V, Nb, Ta, Cr,W
T_2 Stabilizer : Ti, Zr, Hf, V, Nb, Ta, Cr,W
T_1 Stabilizer : W, Nb, Ta
A15 Stabizer : Cr, V
$D8_8$ Stabilizer : Ti, Zr, Hf

BCC + T_2 + A15
(Mo -Si- B + Cr/V)
BCC + T_2 + T_1
(Mo -Si-B + W/ Nb /Ta)
BCC + T_2 + $D8_8$
(Mo -Si-B + Hf/Ti/Zr)



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

OUTLINES:

- Gaseous Computational Thermodynamic Designs for Coating Deposition Process
- Phase Stability Analysis on the Coating Phase Constituents; emphasis on extended alloying capability (DFT Study)
- 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

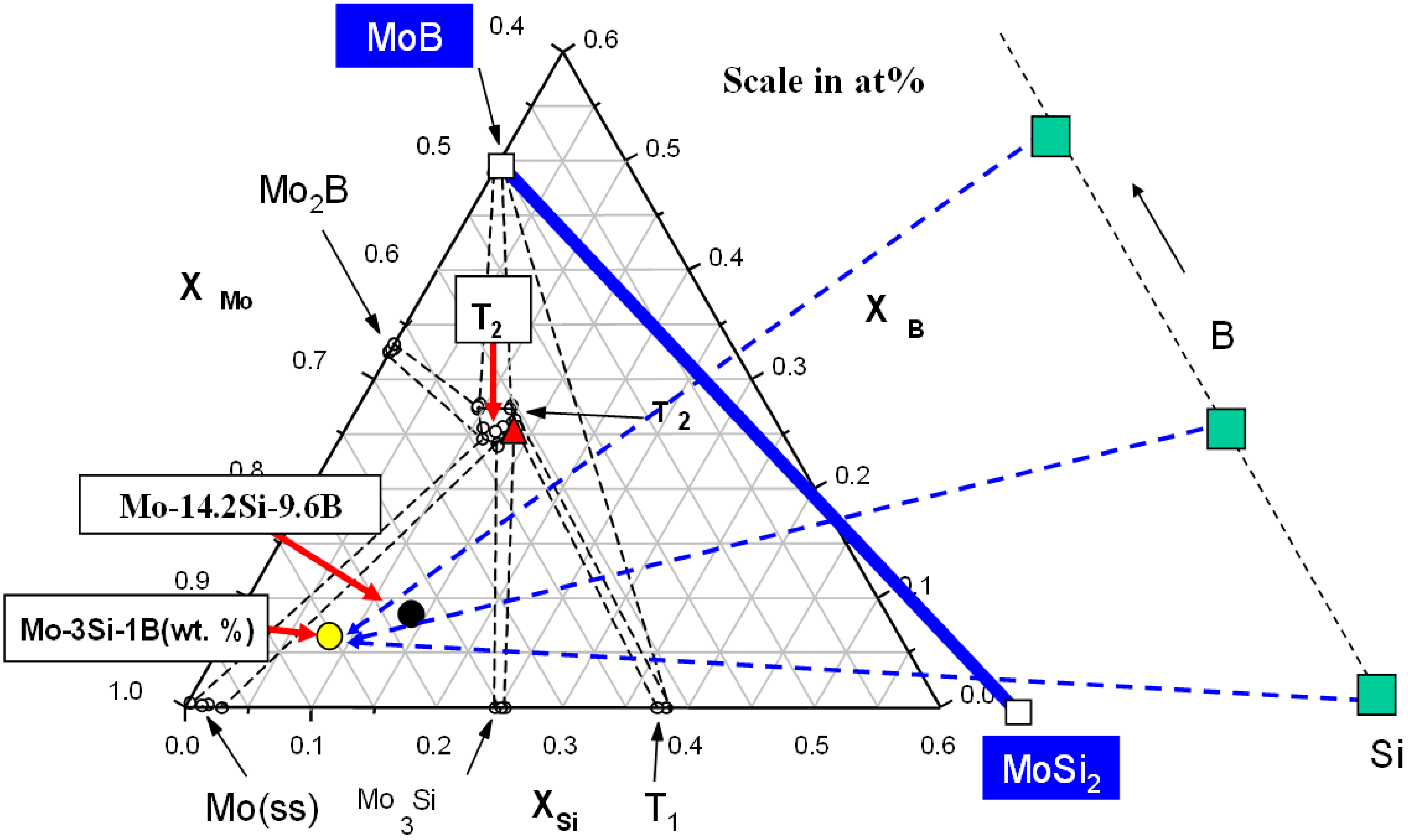
CONTINUUM
MODELING

Continuum Design: Gaseous Thermodynamics

Refinement of Gaseous Thermodynamic Parameters for the Si+B Co-Deposition Coating Processes

Coating Deposition: Pack–Cementation Process

CO-DEPOSITION with Silicon +Boron powder Source

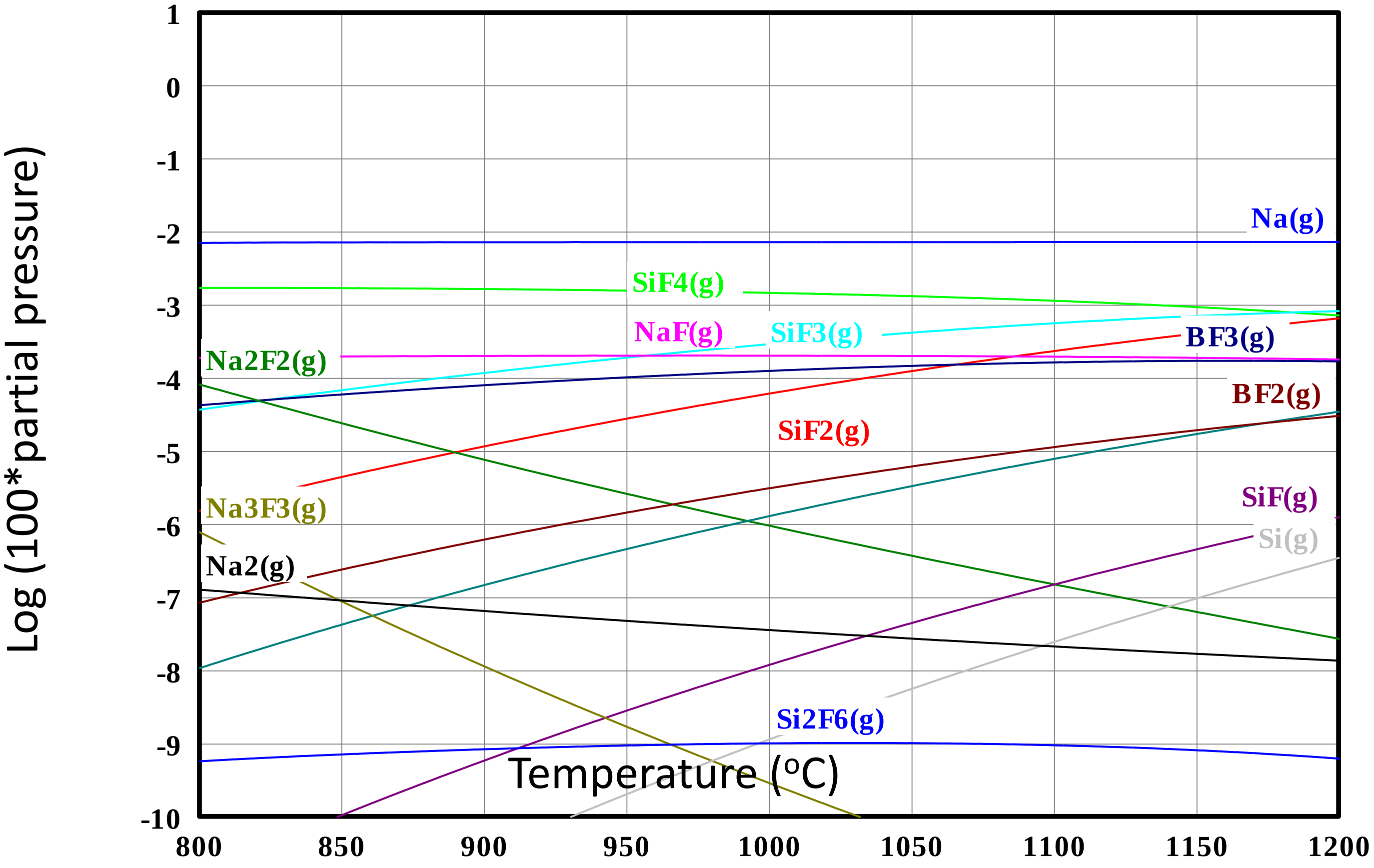


Consider Si+B-pack Cementation :
Source : NaF(l) + Si(s)+B(s)

1. $3NaF(l) + Si(s) \Leftrightarrow SiF_4(g) + 3Na(g)$
2. $Si(s) + 3SiF_4(g) \Leftrightarrow 4SiF_3(g)$
3. $Si(s) + 2SiF_3(g) \Leftrightarrow 3SiF_2(g)$
4. $Si(s) + SiF_2(g) \Leftrightarrow 2SiF(g)$
5. $3NaF(l) + B(s) \Leftrightarrow BF_3(g) + 3Na(g)$
6. $B(s) + 2BF_3(g) \Leftrightarrow 3BF_2(g)$
7. $B(s) + 2BF_2(g) \Leftrightarrow 3BF(g)$
8. $Na(g) + \frac{1}{2} F_2(g) \Leftrightarrow NaF(l)$
9. $$2p_{F_2(g)} + p_{NaF(g)} + 4p_{SiF_4(g)} + 3p_{SiF_3(g)} + 2p_{SiF_2(g)} + p_{SiF(g)} + 3p_{BF_3(g)} + 2p_{BF_2(g)} + p_{BF(g)} = p_{Na(g)}$$

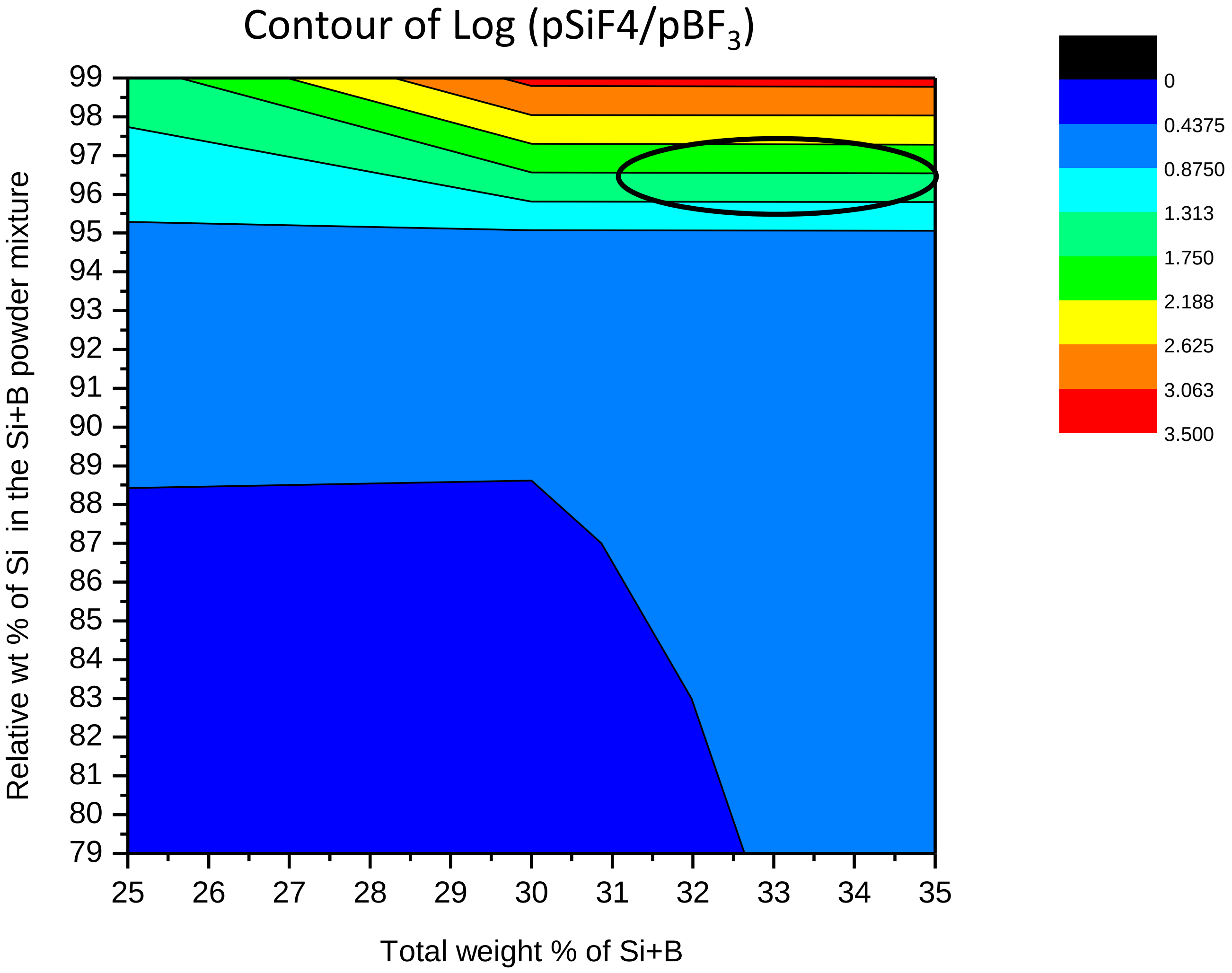
$SiF_4(g), SiF_3(g), SiF_2(g), SiF(g),\ BF_3(g), BF_2(g), BF(g), F_2(g), Na(g)$

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

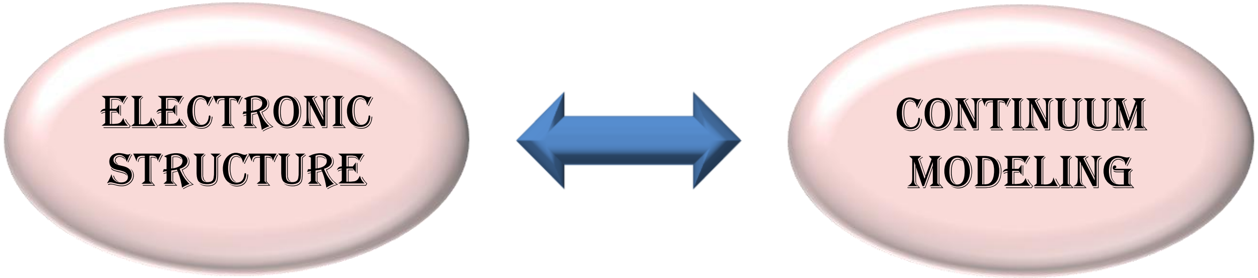


35-1 weight ratio Si:B

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.



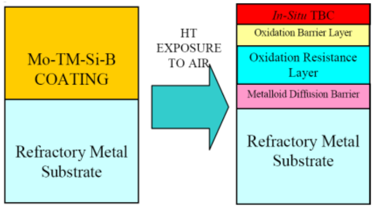
ELECTRONIC STRUCTURE

CONTINUUM MODELING

Phase Stability Analysis

Stability of Compositionally Graded Borosilicide
T_2 Phase as a Buffer Layer

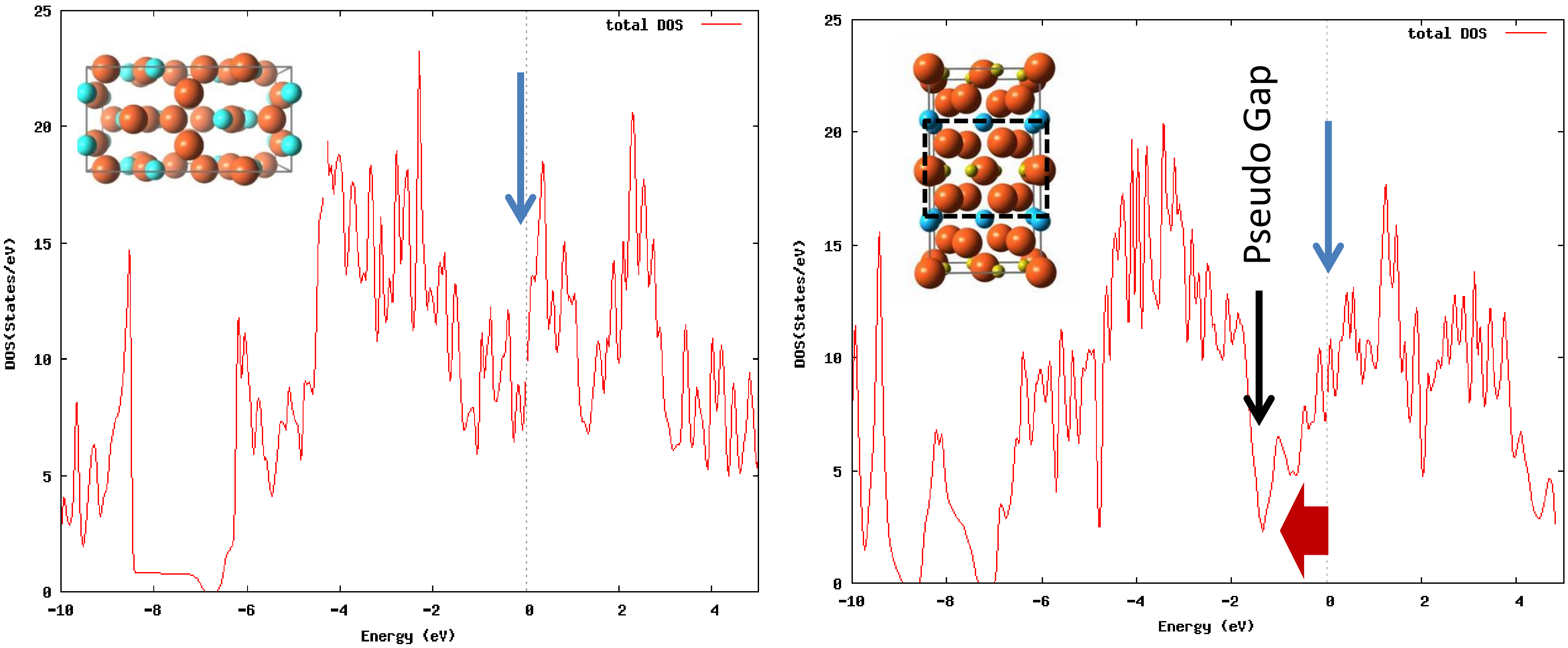
Mo-rich $T_2 \rightarrow$ RM-rich T_2



Phase Stability Analysis on Silicides (T_1) & Borosilicides (T_2) based on Electronic Structure (DFT Calculations)

T_2 PHASE AS BOTH DIFFUSION & BUFFER LAYERS

Total Density of States (TDOS)

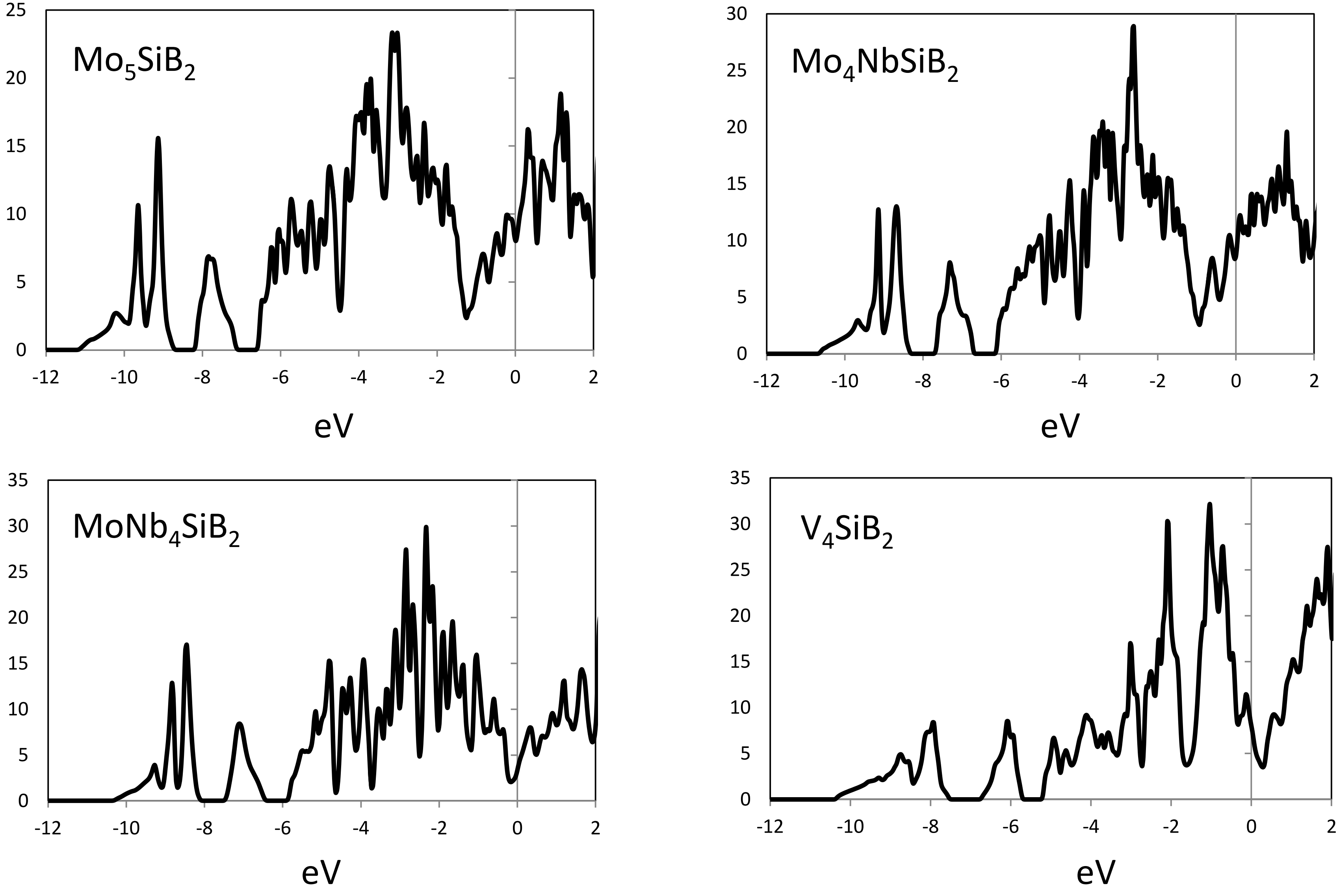


THE ENERGY FERMI LEVEL OF THE T_2 PHASE'S DOS RESIDES NEAR THE PSEUDO GAP

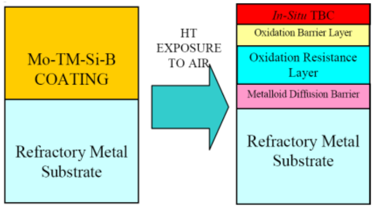
SUBSTITUTION OF Mo WITH REFRACTORY METALS WITH VALENCE ELECTRON ≤ 6 IS ENERGETICALLY FAVORABLE (E.G. Nb, W, Ti)

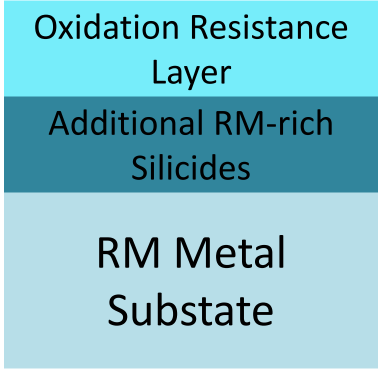
Stability of RM-rich T_2 Phase

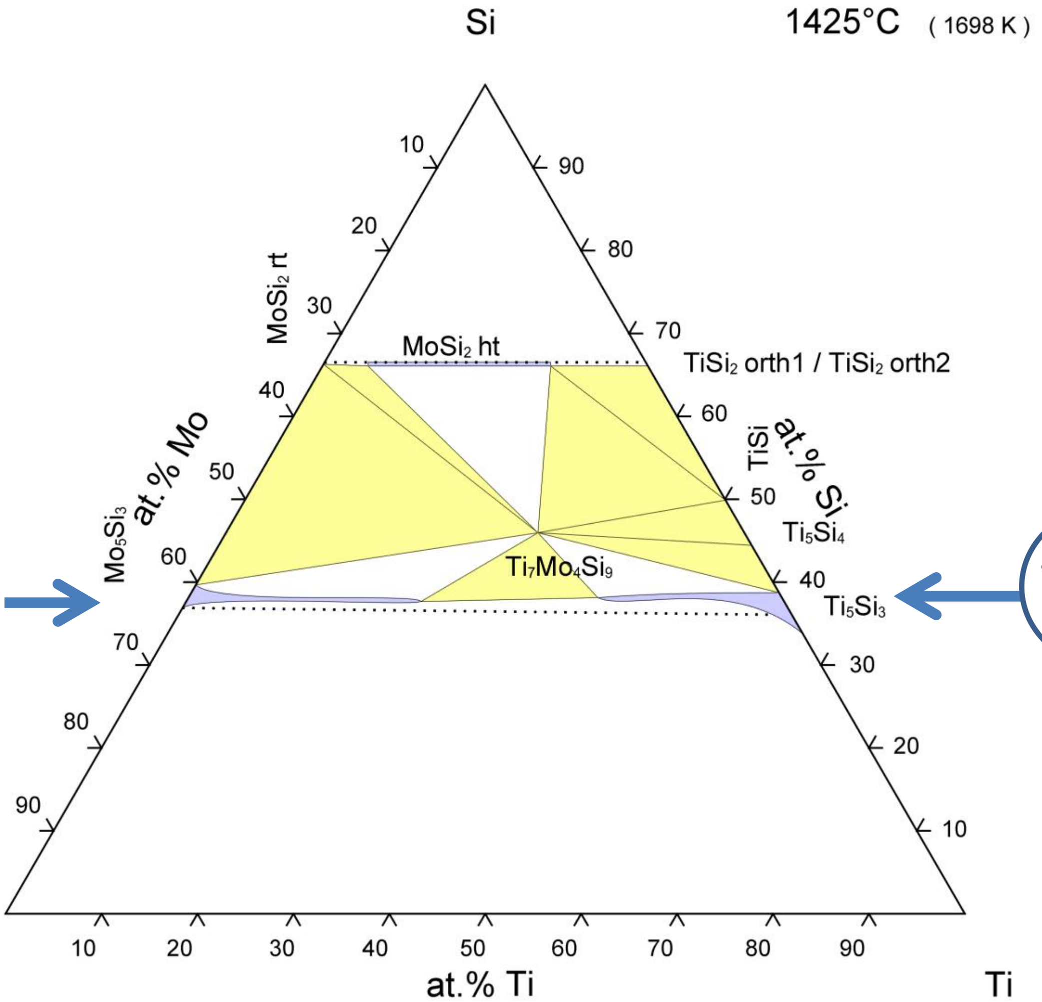
Total Density of States (TDOS)



T_2 PHASE AS BOTH METALLOID DIFFUSION & BUFFER LAYERS





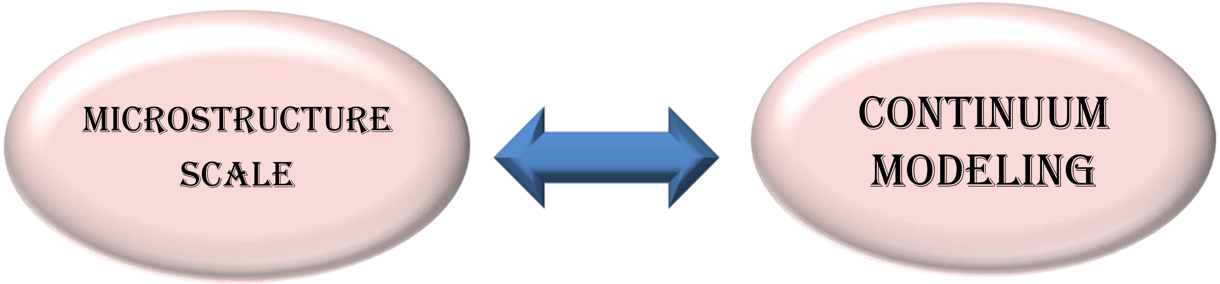


Mo_5Si_3

Ti_5Si_3

Unlike Borosilicide T2 phase, the Mo-rich silicide T1 phase has a more limited extended solid solution with refractory metals

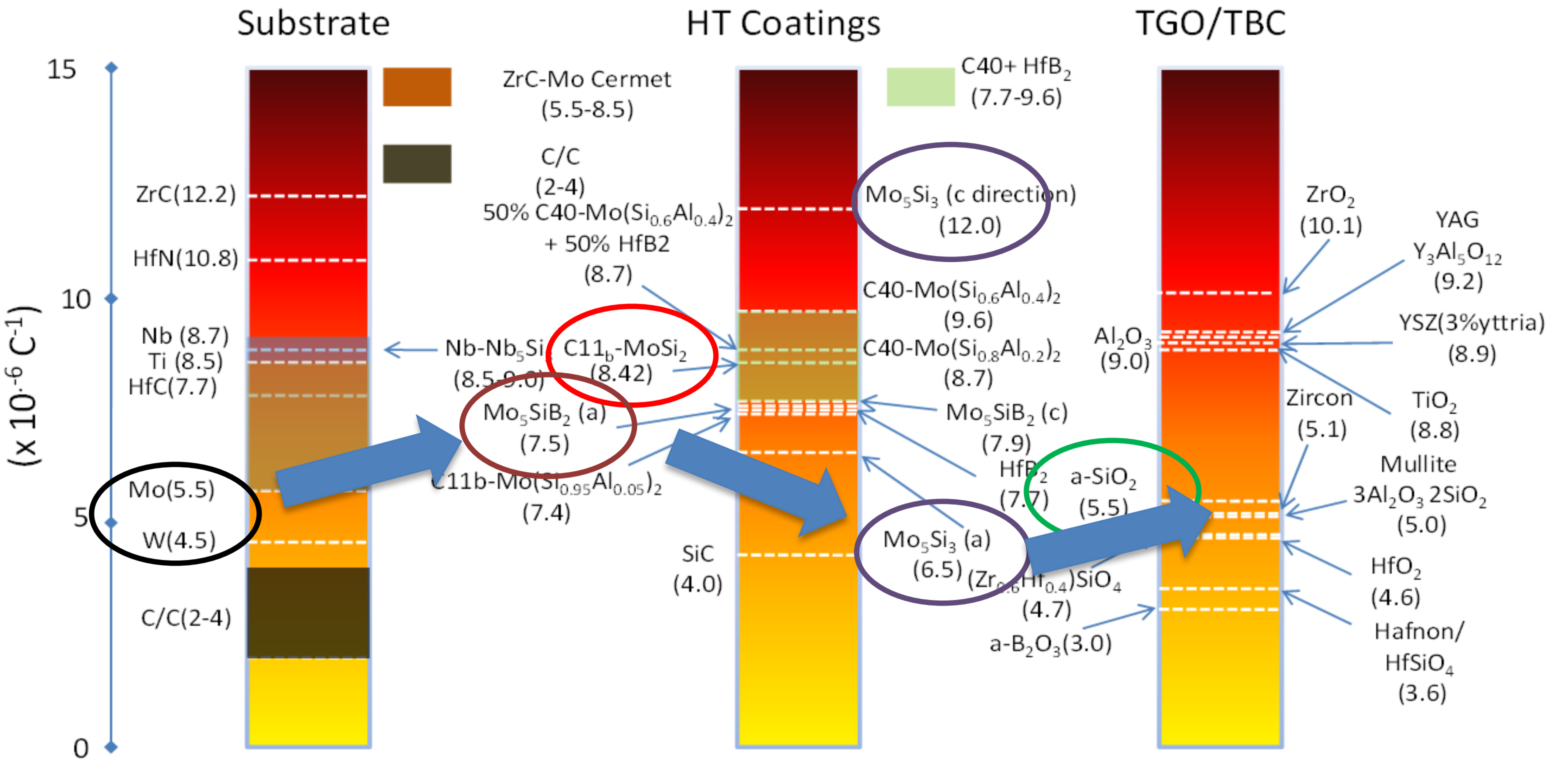
SILICIDES => Mo-rich SILICIDES + RM(e.g. Ti) DILICIDES



Assessment on Mechanical Integrity at Microstructural Scales

Evaluation on mechanical integrity of the coating structures under thermal stresses

CTE Compatibility in Ultra-high Temperature System

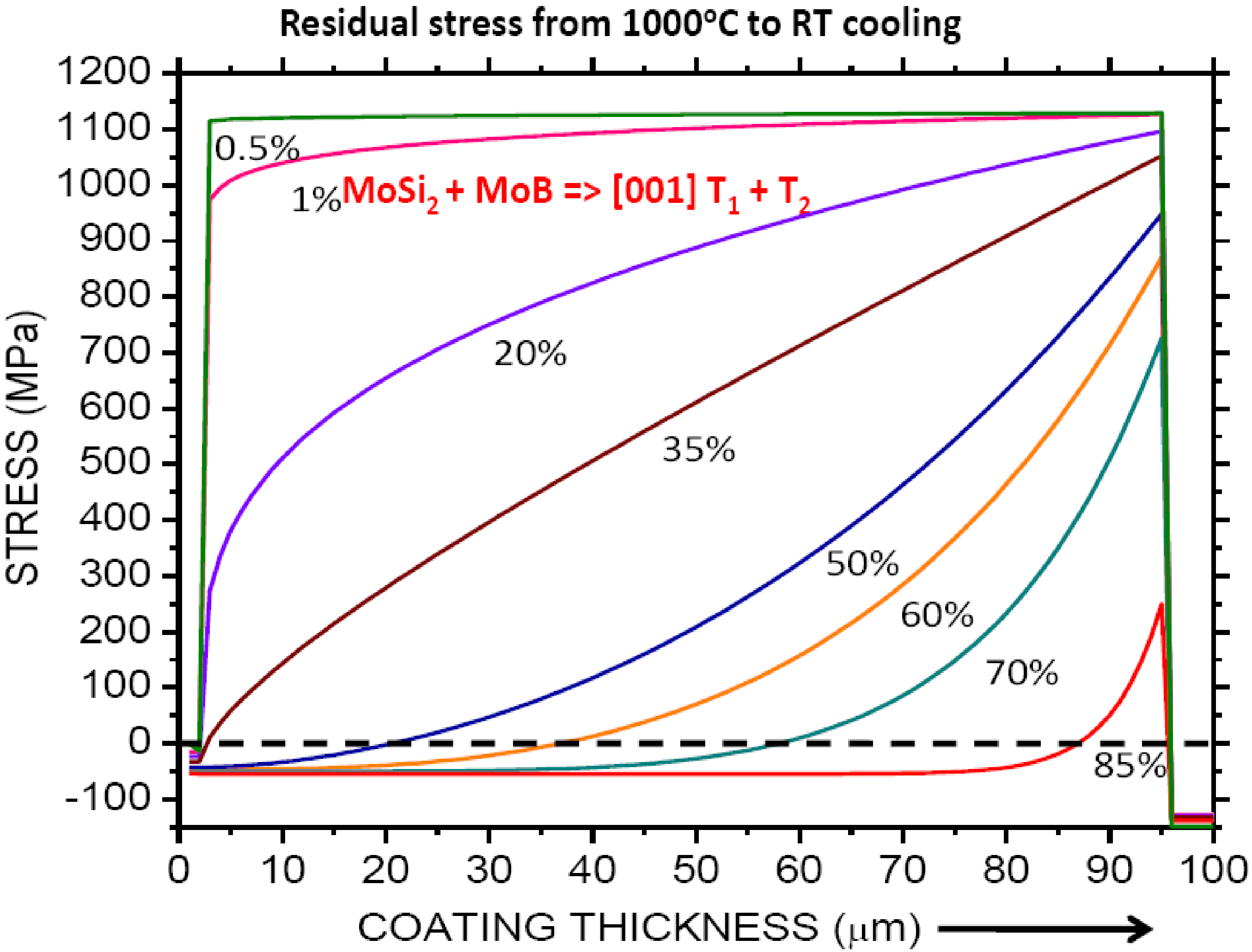


COMPOSITE AND GRADED APPROACHES TO HT COATING DESIGN

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)

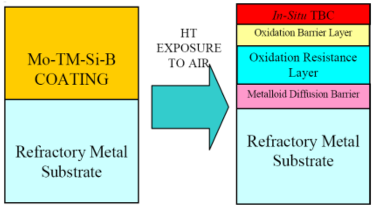
KEY : MAINTAIN THE T_1 PHASE TEXTURED ALONG C AXIS TO MINIMIZE RESIDUAL STRESS

Effect of Conditioning on the Thermal Residual Stress


Residual stress from 1000°C to RT cooling

Analysis on the residual stress within the coatings shows with an increasing degree of the conversion, the maximum stress within the coatings can be significantly reduced.

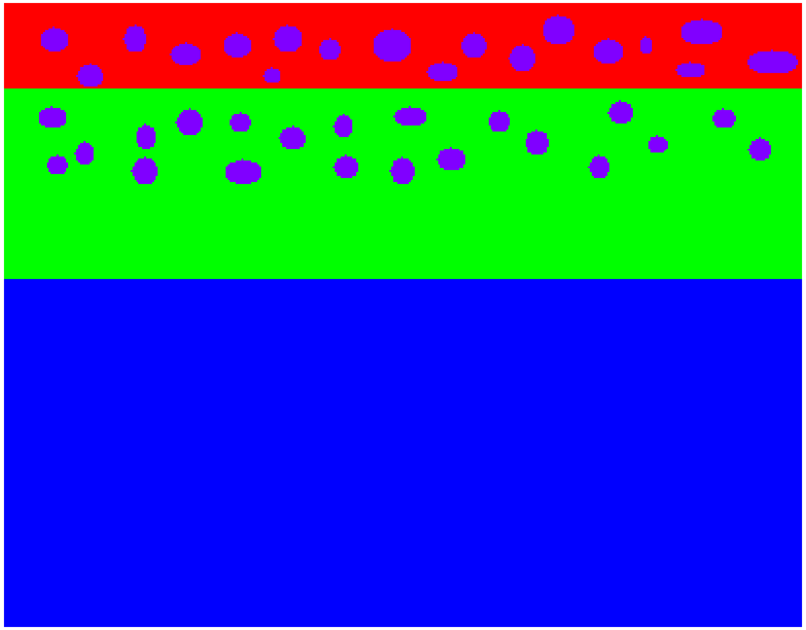
(analysis adapted from Zhang. et.al, Thin Solid Films 497 [2006] 223 – 231)



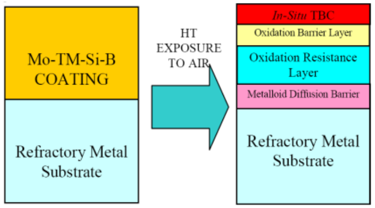
FEM Study on the effects of microstructure and additional material

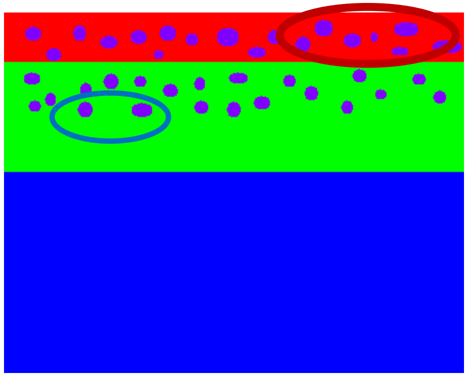
- Add another material to the system: ZrO_2
- Consider particles of ZrO_2 dispersed throughout the silica and disilicide layer
- OOF2 is public domain finite element analysis (FEA) software created by NIST to investigate the properties of microstructures

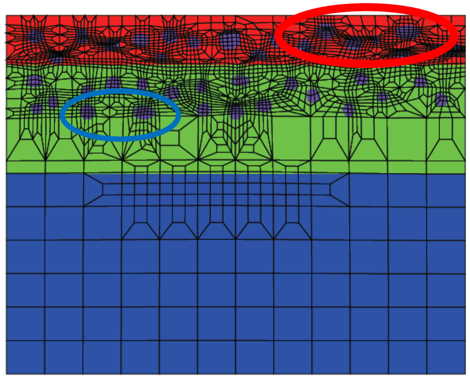
Material	Young’s Modulus (GPa)	Poisson's Ratio	Thermal Conductivity (W/mK)	Thermal Expansion (um/m ºC)
Mo	330	0.29	138.00	6.5
MoSi2	432	0.15	28.60	10.4
T2 (Mo_5SiB_2)	383	0.27	28.00	7.7
SiO2	64	0.19	1.10	4.0
ZrO2	239	0.30	1.68	7.0

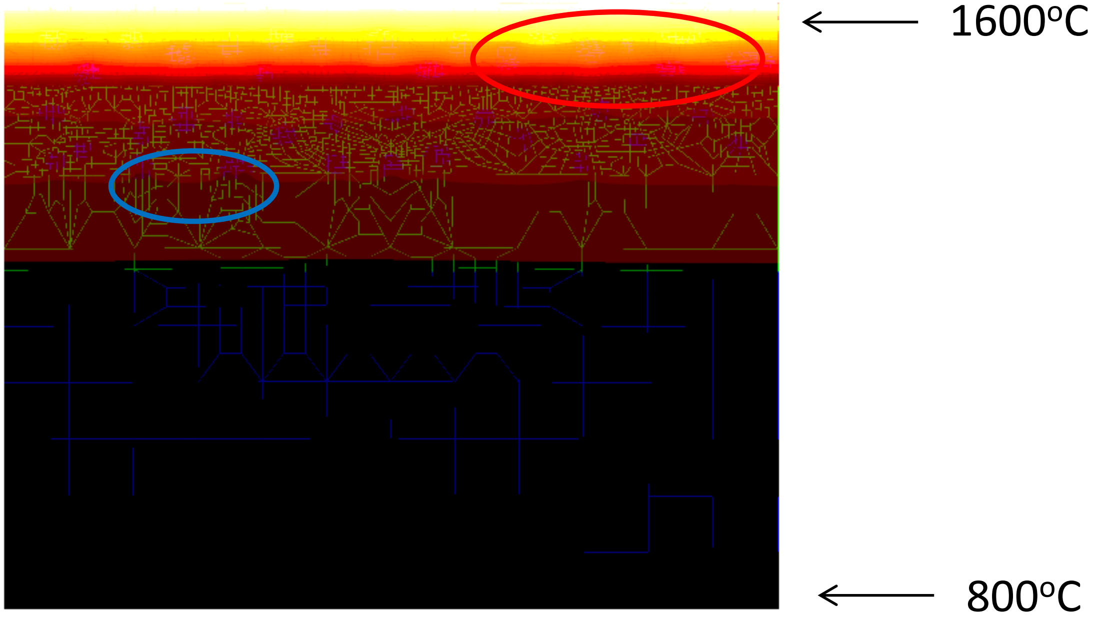


FEM Study on the effects of microstructure and additional material



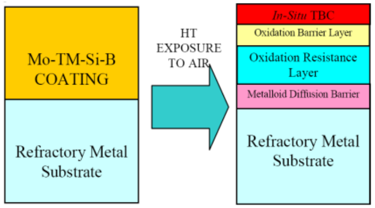




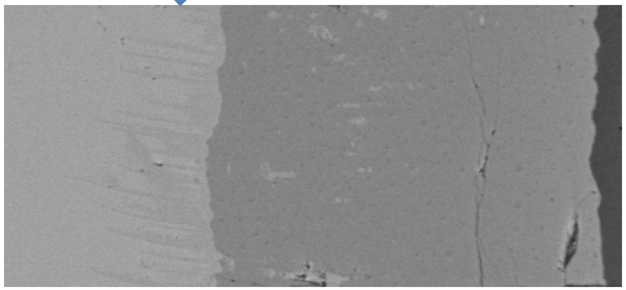


Addition of ZrO_2 particles creates a heat sink in the silica glass & a heat barrier in silicide coatings

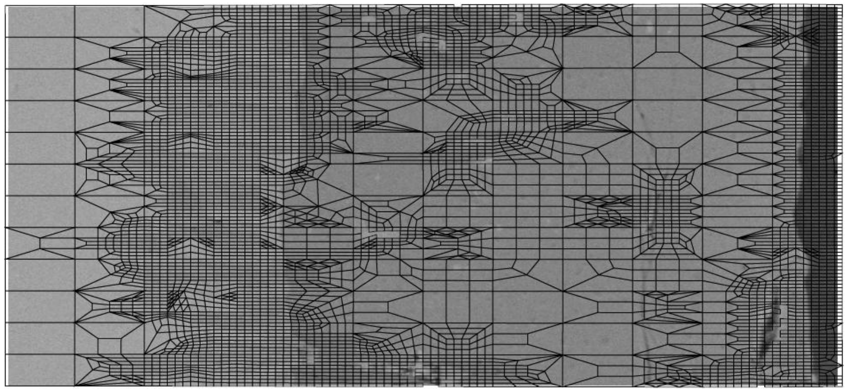
OOF2 application to real Mo-RM-Si-B coating microstructures



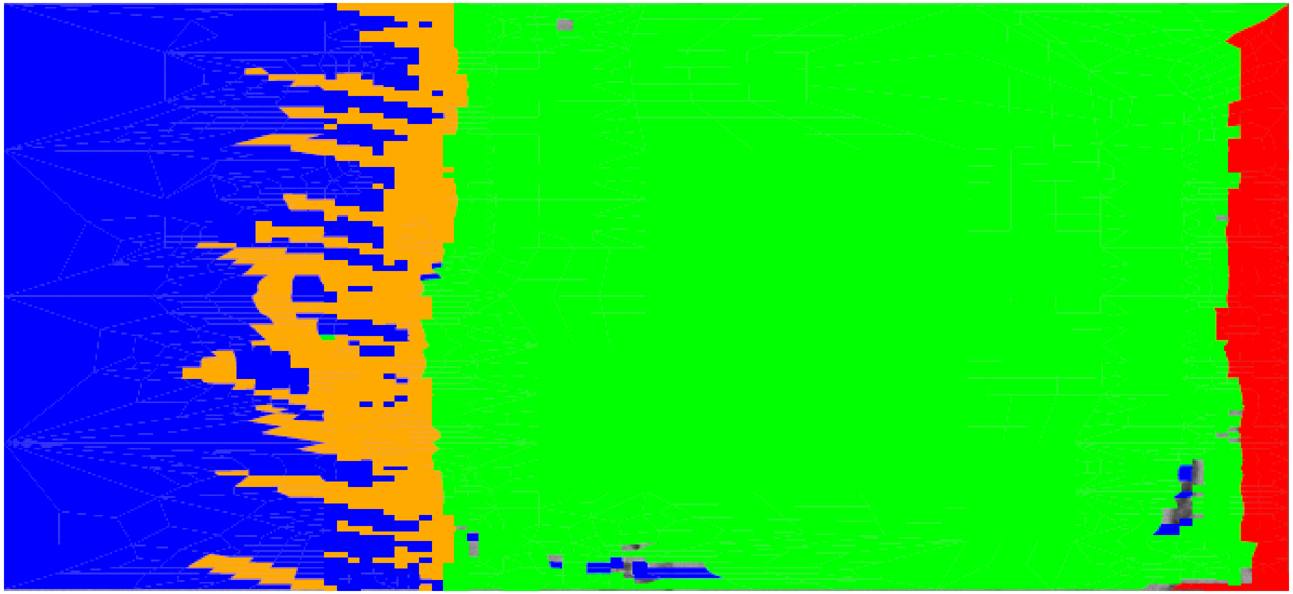
Borides+Borosilicides



Mo + Ti Silicide Phases



Pixilated microstructure



Blue: Mo
Orange: T2
Green: Mo(Ti) Si2
Red: SiO2

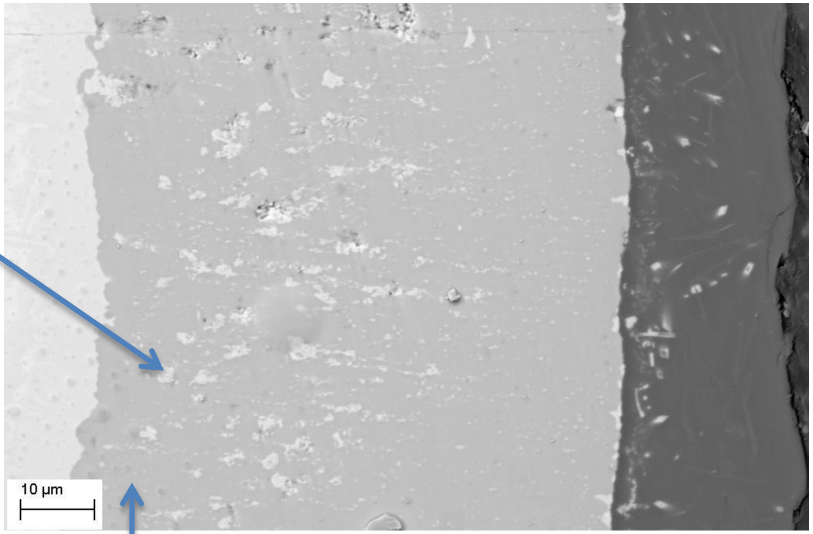
Synthesis of Mo-RM-Si-B Coatings on Mo-RM Substrate

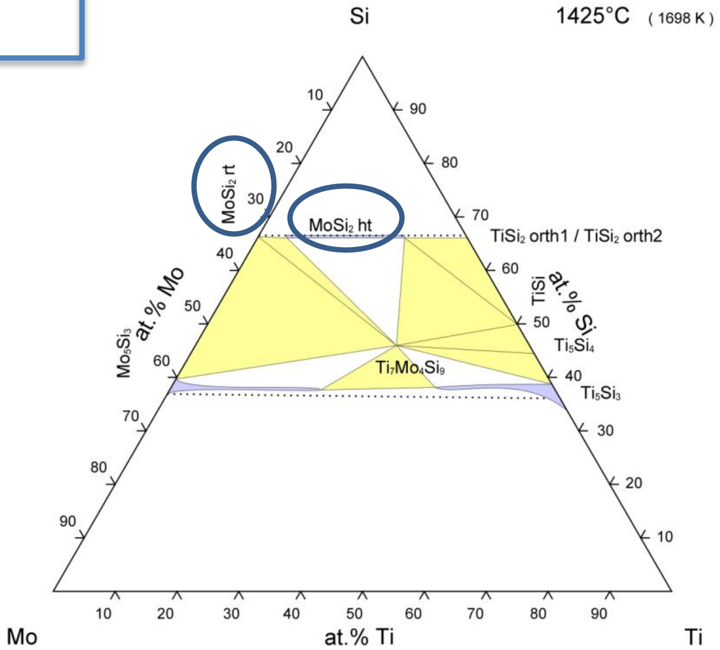
- Samples consisted of arc melted Mo doped with either Zr or Ti
  - 1 wt% and 5 wt%
- Si-B pack was applied (35:1)
- Oxidation tests performed on samples at 1200^{o}C for 24 hr (Ti/Zr doped)

Experimental Results:
1 wt% Ti –doped MoSiB +Ox at 1200°C

Element Line	*Net Counts*	*Atom %*	*Atom % Error*
Si K	92624	23.4	+/- 0.2
Si L	0	---	---
Ti K	21113	6.6	+/- 0.2
Ti L	0	---	---
Mo L	642034	70.0	+/- 0.3
Mo M	0	---	---
Total		100.0	

Element Line	*Net Counts*	*Atom %*	*Atom % Error*
Si K	384559	74.8	+/- 0.3
Si L	0	---	---
Ti K	7082	1.9	+/- 0.1
Ti L	0	---	---
Mo L	184522	23.3	+/- 0.2
Mo M	0	---	---
Total		100.0	



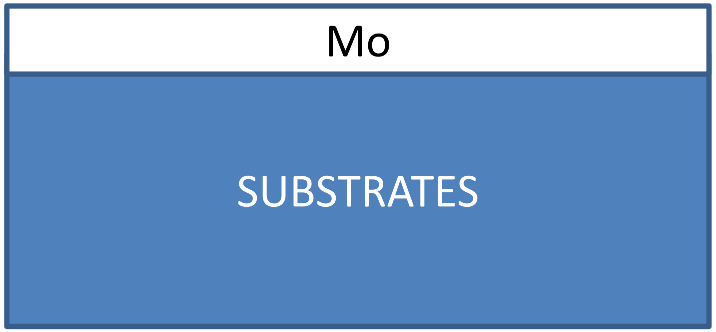


Dual structures of silicides produced to yield mixed oxides

Synthesis of Mo-Si-B Coatings on RM Substrates

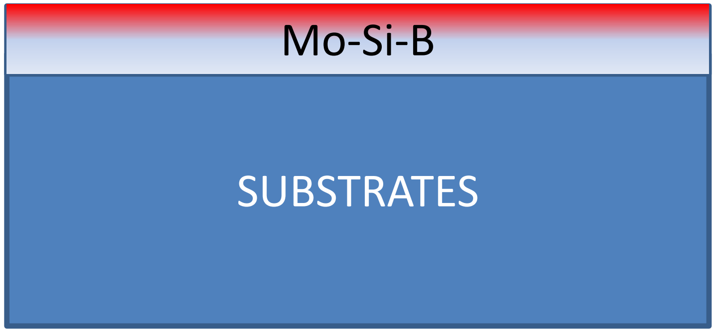
- 2 step processes:
  1. **Mo deposition onto UHTC for < 5 minutes at 250°C using $Mo(CO)_6$ decomposition process or plasma spray**

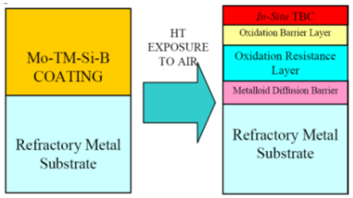
$Mo(CO)_6 \Rightarrow Mo(s)\downarrow + 6CO(g)$



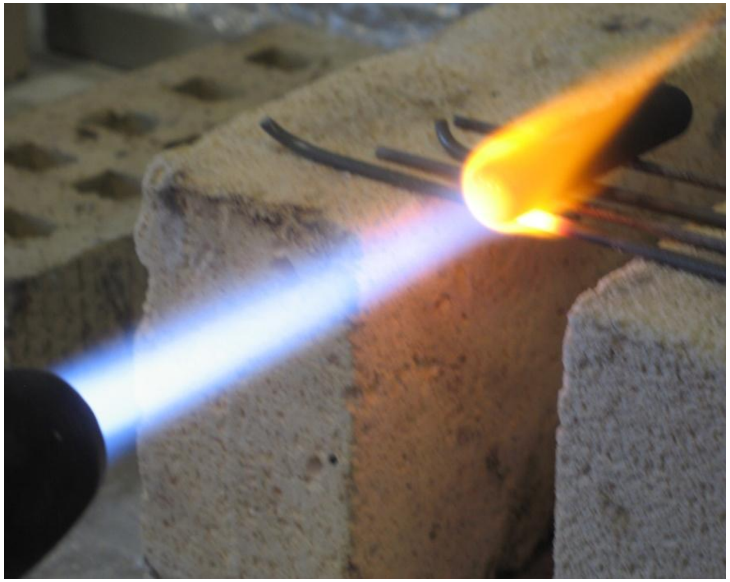
  2. Co-deposition of Si+B into Mo deposit for ≈20 minutes at 1000°C.

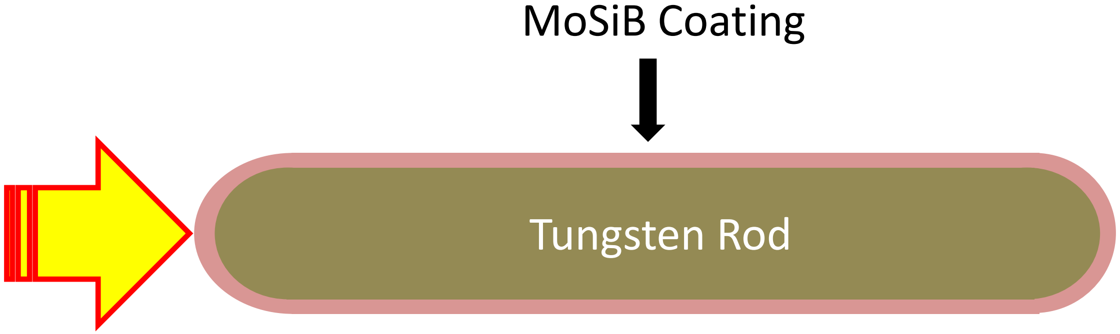
$3NaF + 2Si(s) \leftrightarrow 2SiF(g) + 3Na(g) + \frac{1}{2}F_2(g)$
$3NaF + 2B(s) \leftrightarrow 2BF(g) + 3Na(g) + \frac{1}{2}F_2(g)$
$3SiF(g) \leftrightarrow SiF_2(g) + Si(s)\downarrow$
$3SiF_2(g) \leftrightarrow 2SiF_3(g) + Si(s)\downarrow$
$4SiF_3(g) \leftrightarrow 3SiF_4(g) + Si(s)\downarrow$
$3BF(g) \leftrightarrow BF_2(g) + B(s)\downarrow$
$3BF_2(g) \leftrightarrow 2BF_3(g) + B(s)\downarrow$

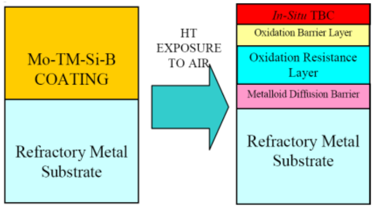




Results:
Oxyacetylene Torch Test on MoSiB-coated Tungsten Rod

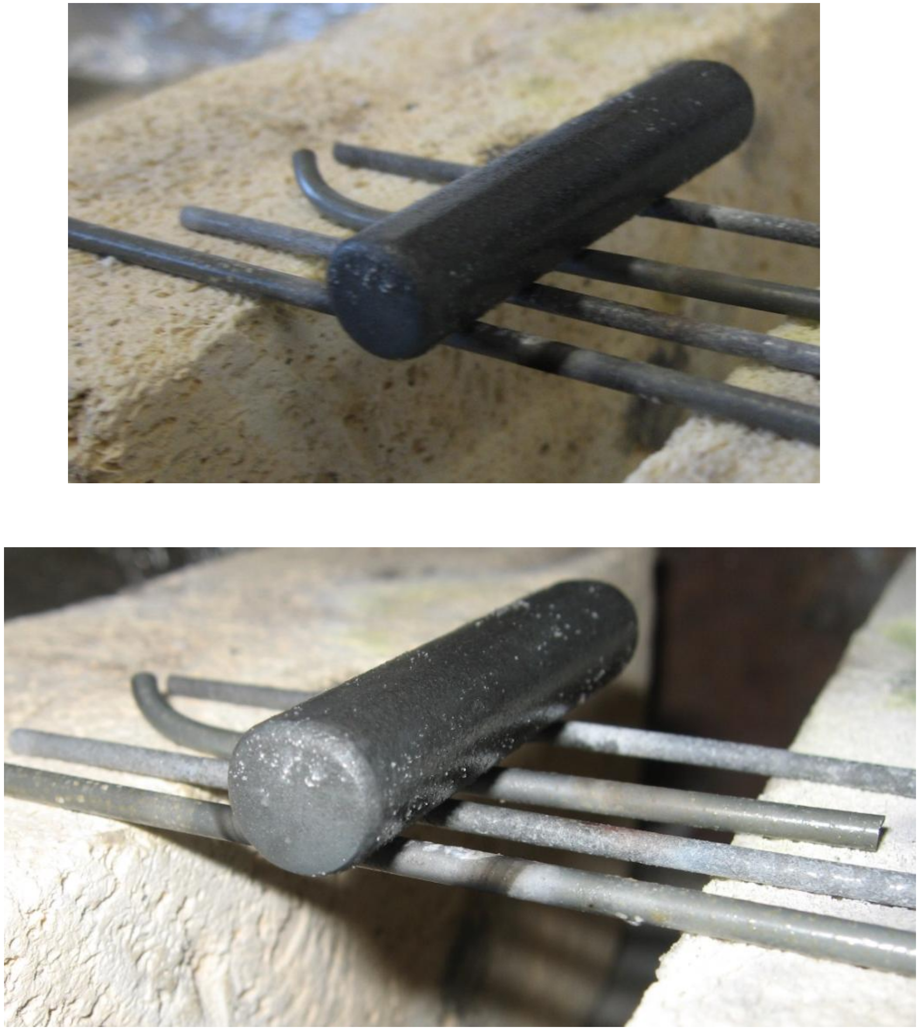




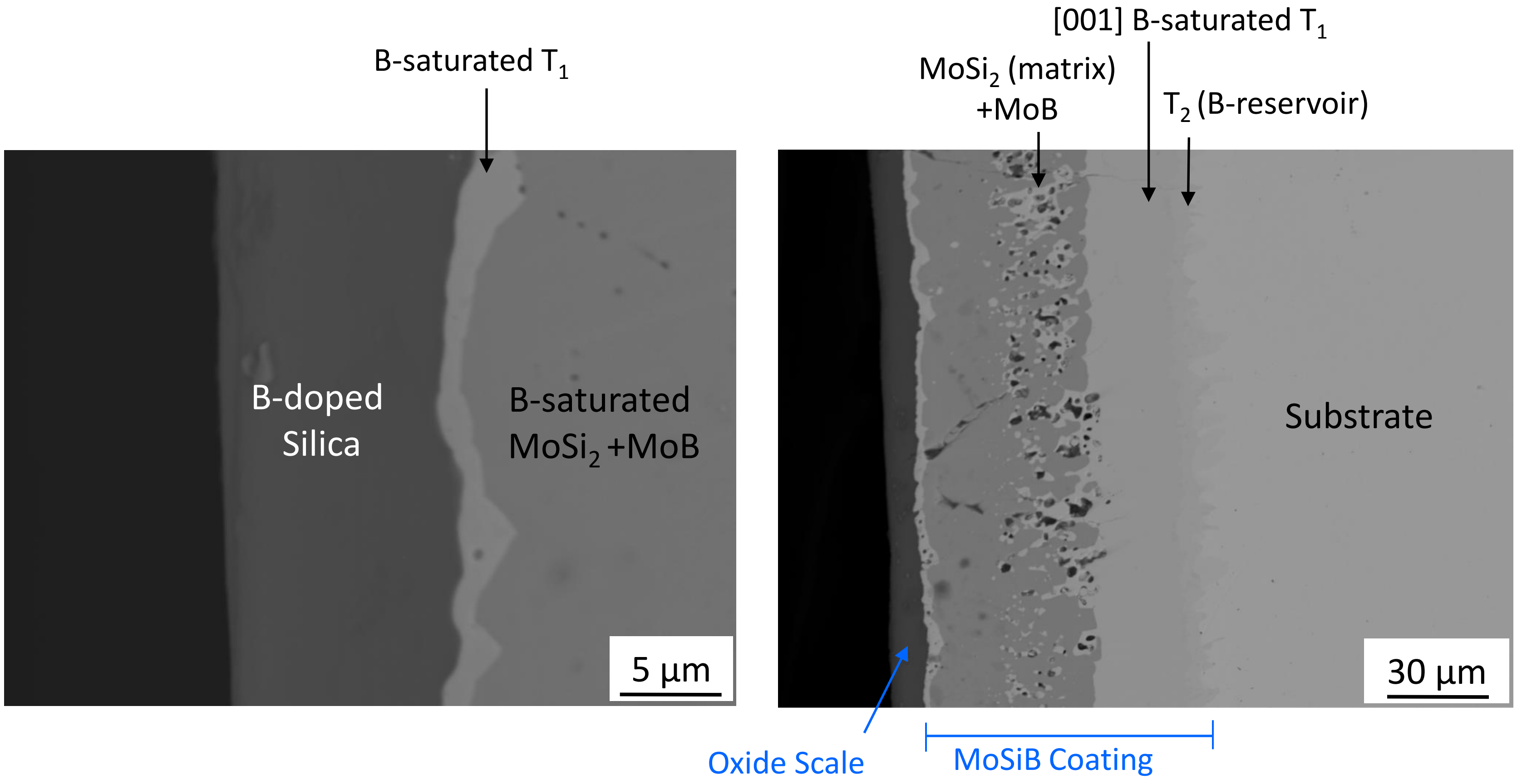


Results: Torch Test

- Mo-Si-B coating on W rod showed no degradation during torch testing
- Uniform borosilica layer formed after testing



Mo-Si-B Coated Mo Coupon (5min torch test ~2000°C)



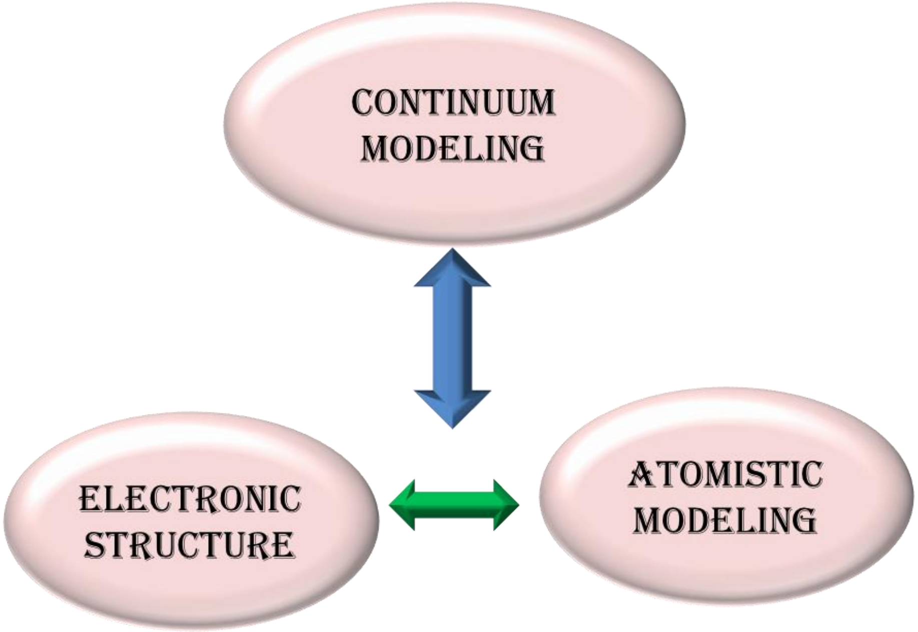
B-saturated T_1 phase provides high temperature oxidation resistance.
Boron reservoir is supplied by the underlying $MoSi_2$+MoB and T_2 layers

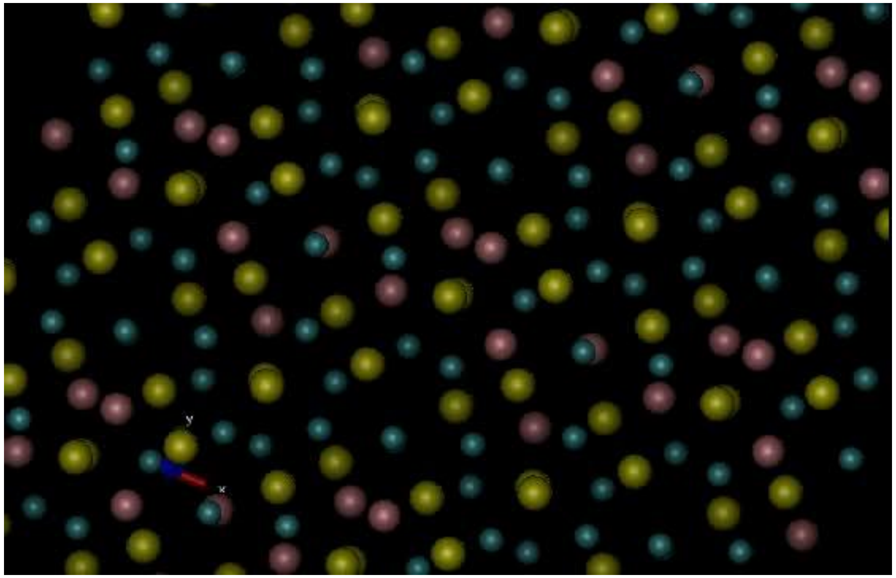
Note: There is a low Z contrast difference between MoB and B-saturated T_1 phase.
EDS spectra have been used to identify/differentiate the phases based on MoLα/Si Kα energy lines.
Some porosity was observed in MoB phase shown with the dark contrast.

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

Year 1 to finish…



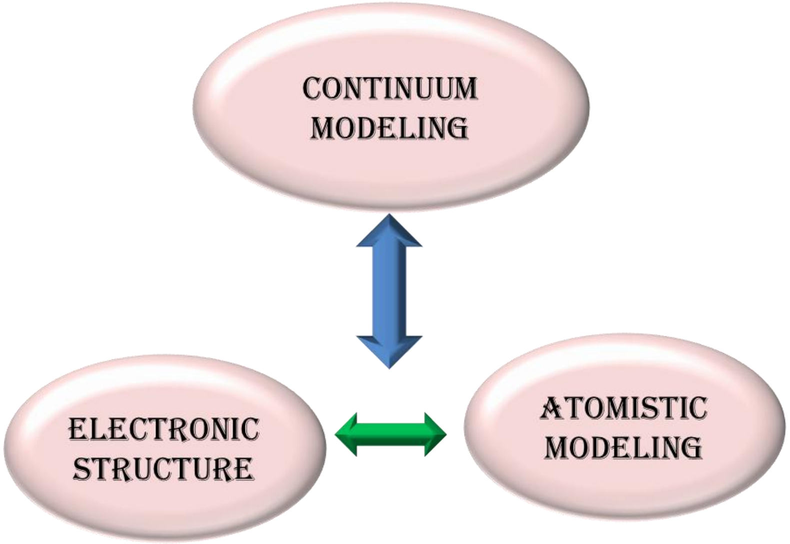


$Mo_2Ti_3Si_3$ (T1) Phase at 1500K

Ab-initio Molecular Dynamics (AIMD)+ FEM Analysis:

- High-temperature Simulations in both NVT and Isothermal–isobaric (*NPT*) Ensemble.
- Extract Coefficient Thermal Expansion (CTE) Anisotropy in Alloyed Silicides & Borosilicides
- Extract elastic properties in Alloyed Silicides & Borosilicides

Year 2: Dynamics Modeling + Coating Performance

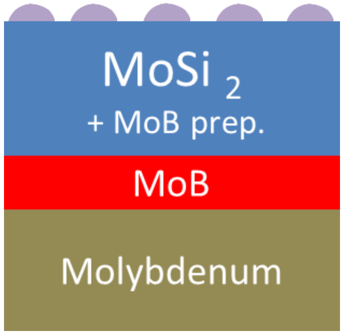


AIMD or Ab-initio-optimized Classical MD + Kinetic Analysis:

- High-temperature Simulations in both NVT and Isothermal–isobaric (*NPT*) Ensemble.
- Self-diffusion mechanism of B & Si in Alloyed Silicides & Borosilicides.
- Oxygen Diffusivities & Viscosity of Borosilicate glass and the effect of Na, Al (from CVD process) and RM dopants

Additional Slides

Coating Structures

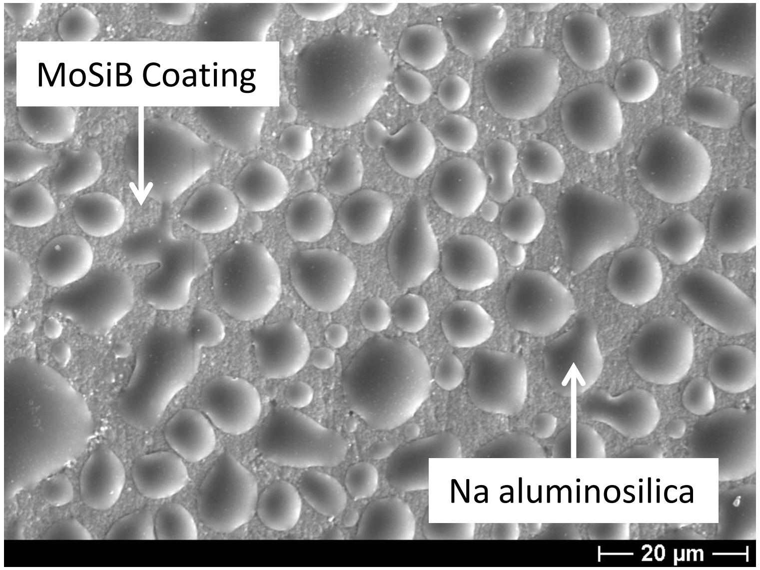


$MoSi_2$
+ MoB prep.

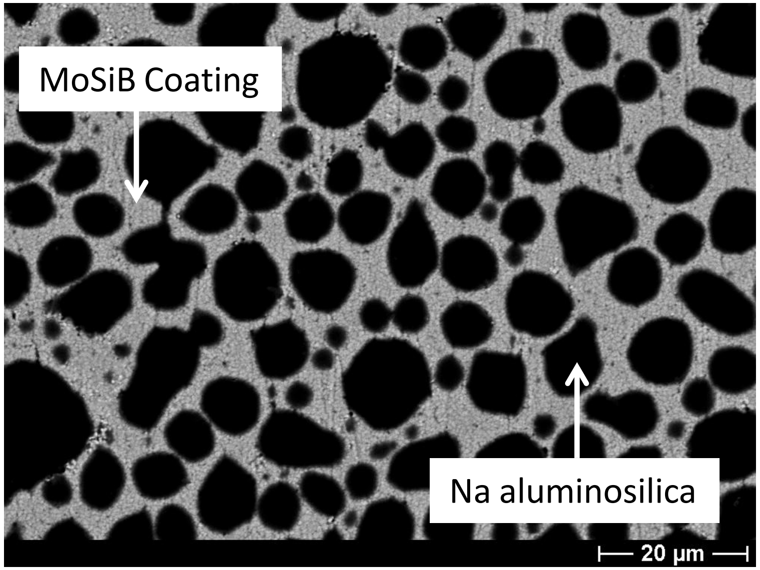
MoB

Molybdenum

- MoSiB Coating: Na aluminosilica formation

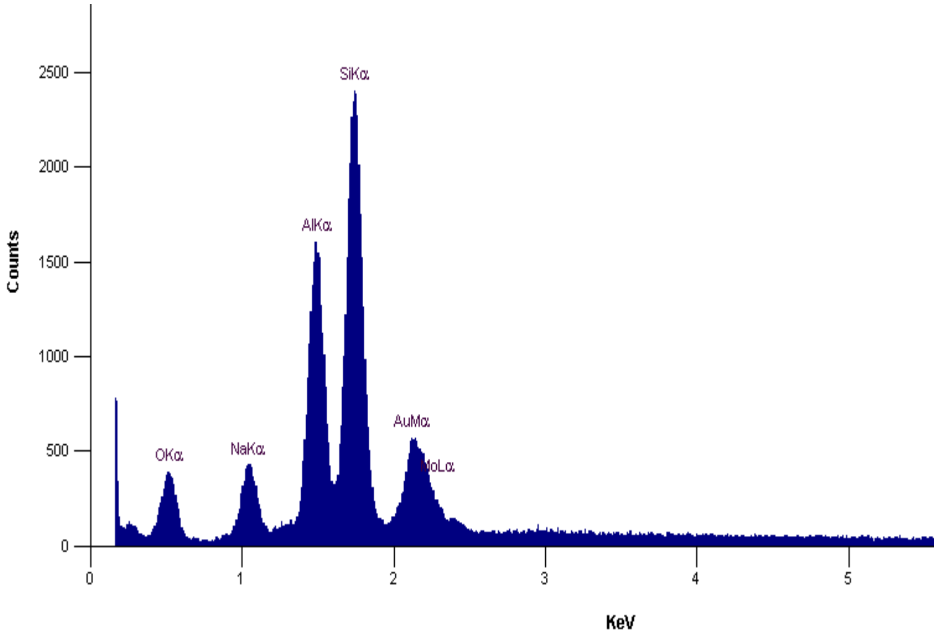


Secondary Electron - SEM Plan View



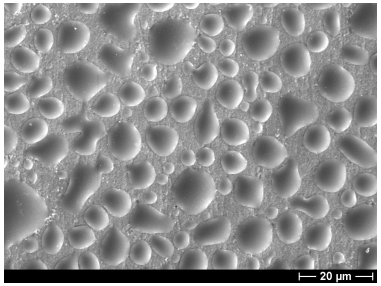
Back-scattered Electron - SEM Plan View

Coating Structures



Element	Atoms%	Compound	Weight%	Error(±)	Norm%
Si	25.75	Si	33.88	0.34	33.88
Na	6.77	Na	7.29	0.15	7.29
O	51.46	O	38.57	0.71	38.57
Al	16.02	Al	20.25	0.25	20.25
<Total>	100		100		100

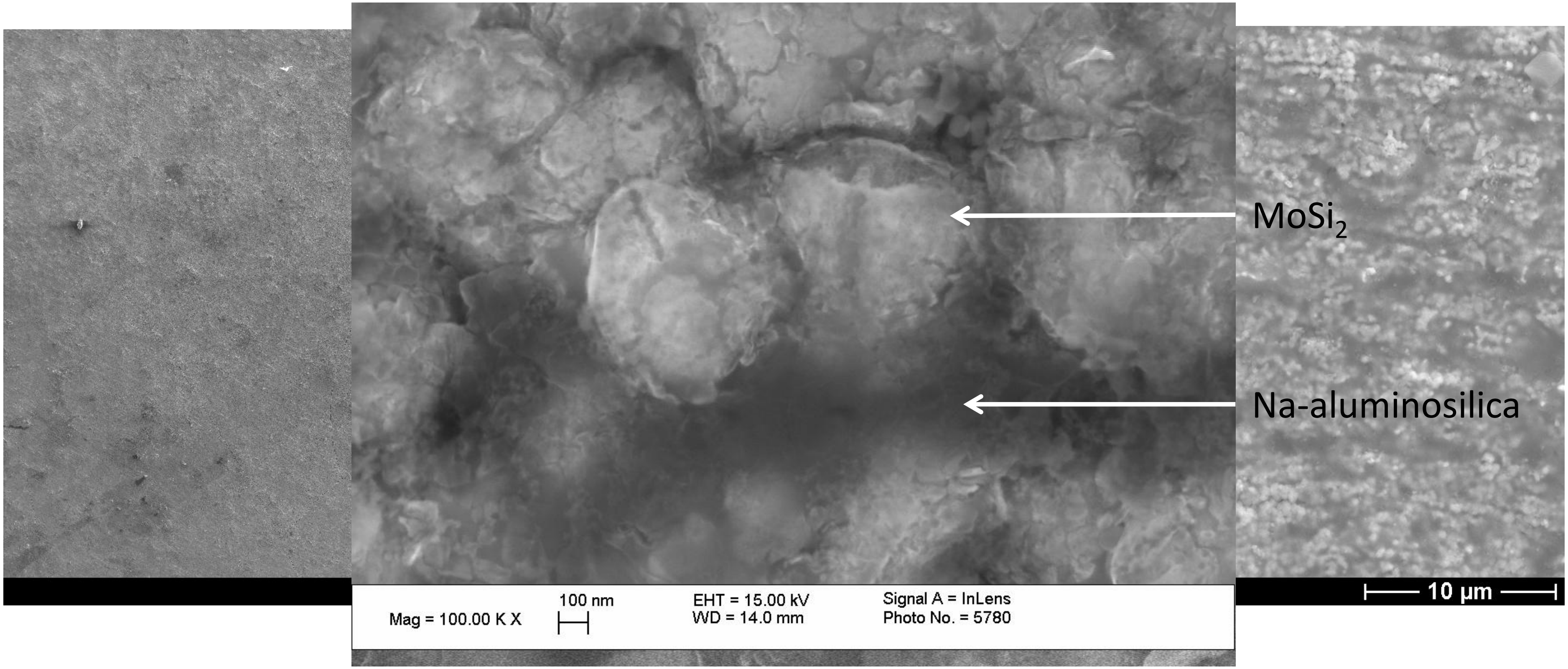
EDS Measurements



Oxidation Results

THE UNIVERSITY of WISCONSIN MADISON

- MoSiB Coating+Na-aluminosilica: Long-Term Test: 500°C/ 61 hrs

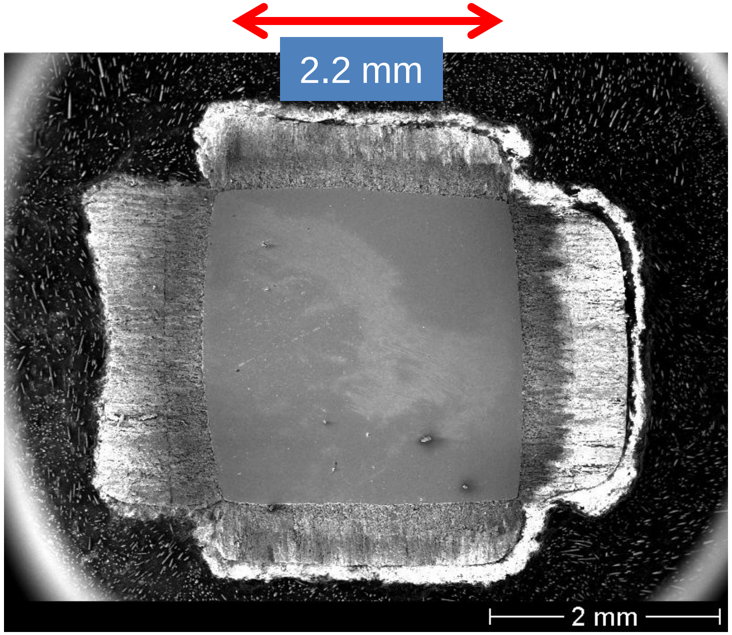


SEM Plan-View

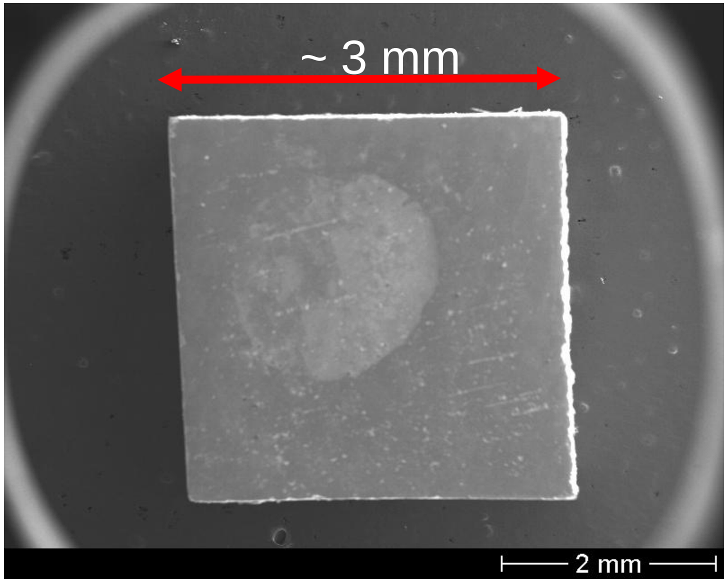
October 16-20, 2011 – Columbus, Ohio

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

UNCOATED

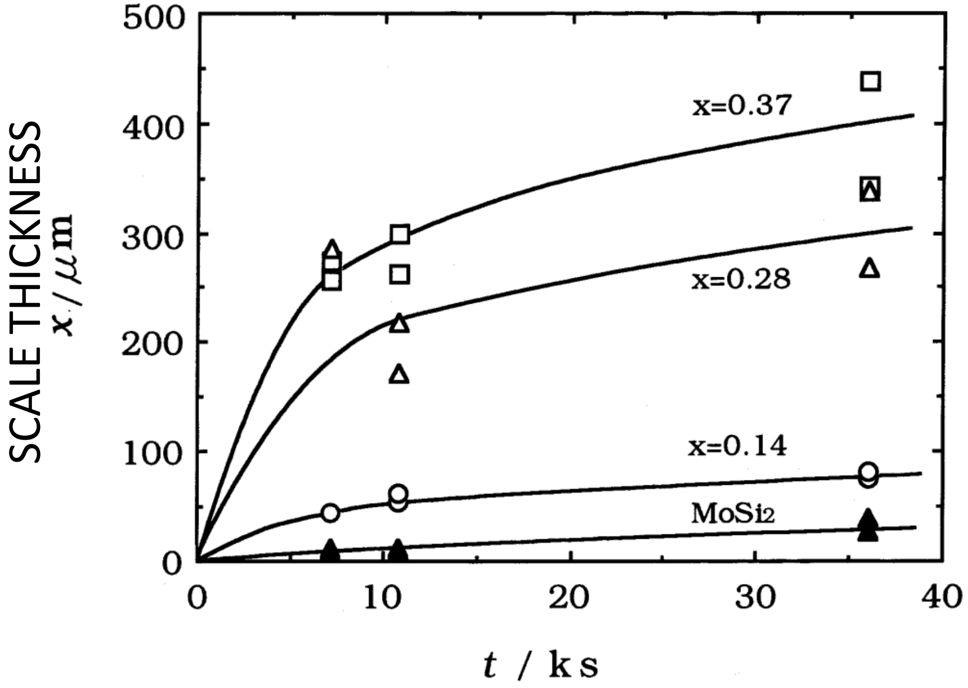


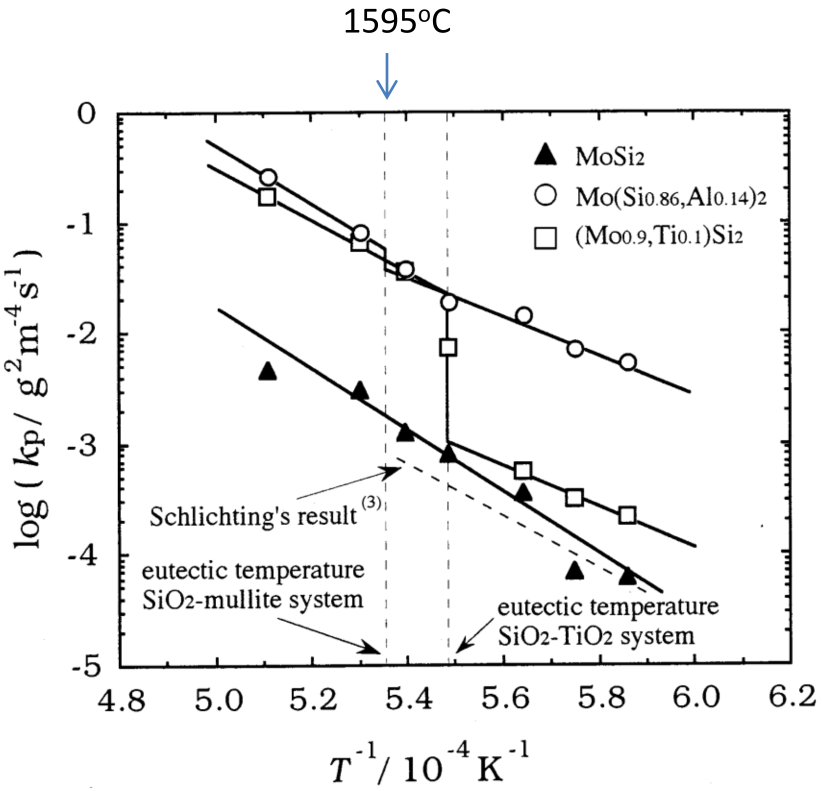
COATED



The coated sample remains intact – virtually no consumption of thickness

High Temperature Oxidation of $Mo(Si,Al)_2$ (C40 Phase)



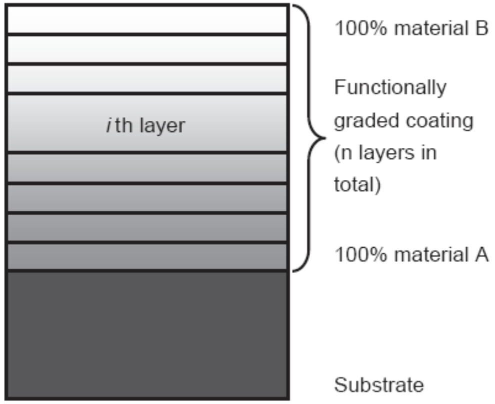


- **Aluminum dissolves into silica glass and forms protective aluminosilicate**
- **An increase in the Al content in the C40 phase yields a corresponding increase in the scale thickness.**
- **There is a switch in the oxidation mechanism from Al_2O_3 to aluminosilicate**

REF: T. Maruyama and K. Yanagihara, "High temperature oxidation and pesting of $Mo(Si,Al)_2$", Materials Science and Engineering A239–240 (1997) 828–841.

Calculation on the residual stresses of compositionally graded coating

(adapted from Zhang. et.al, Thin Solid Films 497 [2006] 223 – 231)



- For a given graded coating comprised of A & B phases, the volume fraction of material B in i th layer (n = total number of layers), $(V_B)_i$, can be approximated by:

$$(V_{\mathrm{B}})_i = \left(\frac{i-1}{n-1}\right)^m$$

where m is the gradient exponent that controls the shape of nonlinear or linear compositional gradient.

- Using the Vegard's rule of mixtures, the elastic property for the i th layer :

$$E_i = E_{\mathrm{B}}(V_{\mathrm{B}})_i + E_{\mathrm{A}}\left(1-(V_{\mathrm{B}})_i\right)$$

$$\alpha_i = \alpha_{\mathrm{B}}(V_{\mathrm{B}})_i + \alpha_{\mathrm{A}}\left(1-(V_{\mathrm{B}})_i\right)$$

- Considering the whole coating system cooled from a stress free state, a misfit strain, $\Delta\varepsilon$, due to the temperature difference, ΔT, is created and can be expressed as:

$$\Delta\varepsilon = (\alpha_{\mathrm{s}} - \alpha_i)\Delta T = \Delta\alpha\Delta T$$

where as is the CTE of the substrate, Da is the thermal expansion mismatch between the substrate and the ith coating layer.

- By a force balance argument in the length direction of the coating system, the residual stress within the coating is obtained by:

$$\sigma_{\mathrm{c}} = E_{\mathrm{c}}\left[\varepsilon_{\mathrm{c}}^0 + K(z+\delta)\right] \qquad (0 \le z \le t_{\mathrm{c}})$$

- ε_c^0 is the stress strain of the coating defined as:

$$\varepsilon_{\mathrm{c}}^0 = \frac{F_{\mathrm{c}}}{\int_0^{t_{\mathrm{c}}} E_{\mathrm{c}} dz} = \bar{\varepsilon} - \alpha_{\mathrm{c}}\Delta T$$

$$\bar{\varepsilon} = \frac{(m+1)(E_{\mathrm{B}}-E_{\mathrm{A}})(\alpha_{\mathrm{B}}-\alpha_{\mathrm{A}})t_{\mathrm{c}} + (2m+1)(E_{\mathrm{A}}\alpha_{\mathrm{B}} + E_{\mathrm{B}}\alpha_{\mathrm{A}} - 2E_{\mathrm{A}}\alpha_{\mathrm{A}})t_{\mathrm{c}}}{(2m+1)(m+1)E_{\mathrm{s}}t_{\mathrm{s}} + (2m+1)(E_{\mathrm{B}}+mE_{\mathrm{A}})t_{\mathrm{c}}}\Delta T + \frac{(2m+1)(m+1)(E_{\mathrm{s}}t_{\mathrm{s}}\alpha_{\mathrm{s}} + E_{\mathrm{A}}\alpha_{\mathrm{A}}t_{\mathrm{c}})}{(2m+1)(m+1)E_{\mathrm{s}}t_{\mathrm{s}} + (2m+1)(E_{\mathrm{B}}+mE_{\mathrm{A}})t_{\mathrm{c}}}\Delta T$$

Calculation on the residual stresses of compositionally graded coating

(adapted from Zhang. et.al, Thin Solid Films 497 [2006] 223 – 231)

- Curvature parameter can be defined as :

$$K = \frac{P_1}{P_2}$$

where the parameters P_1, P_2 are:

$$\begin{aligned} P_1 = {} & (E_\mathrm{B} - E_\mathrm{A})(\alpha_\mathrm{B} - \alpha_\mathrm{A})\Delta T t_\mathrm{c}\left(\frac{t_\mathrm{c}}{2m+2} + \frac{\delta}{2m+1}\right) \\ & + E_\mathrm{A}\alpha_\mathrm{A}\Delta T t_\mathrm{c}\left(\frac{1}{2}t_\mathrm{c} + \delta\right) \\ & + (E_\mathrm{A}\alpha_\mathrm{B} - E_\mathrm{B}\alpha_\mathrm{A} - 2E_\mathrm{A}\alpha_\mathrm{A})\Delta T t_\mathrm{c}\left(\frac{t_\mathrm{c}}{m+2} + \frac{\delta}{m+1}\right) \\ & + E_\mathrm{s}\alpha_\mathrm{s}\Delta T t_\mathrm{s}\left(\frac{1}{2}t_\mathrm{s} - \delta\right) \end{aligned}$$

$$\begin{aligned} P_2 = {} & E_\mathrm{s}t_\mathrm{s}\left(\frac{t_\mathrm{s}^2}{3} - t_\mathrm{s}\delta + \delta^2\right) + (E_\mathrm{B} - E_\mathrm{A})\frac{t_\mathrm{c}\delta^2}{m+1} \\ & + t_\mathrm{c}\left\{(E_\mathrm{B} - E_\mathrm{A})\frac{t_\mathrm{c}^2}{m+3} + 2(E_\mathrm{B} - E_\mathrm{A})\frac{t_\mathrm{c}\delta}{m+2} \right. \\ & \left. + E_\mathrm{A}\left(\frac{t_\mathrm{c}^2}{3} + t_\mathrm{c}\delta + \delta^2\right)\right\} \end{aligned}$$

- The distance δ is defined as:

$$\delta = \frac{\frac{1}{2}(m+1)(m+2)\left(E_\mathrm{s}t_\mathrm{s}^2 - E_\mathrm{A}t_\mathrm{c}^2\right) + (m+1)(E_\mathrm{A} - E_\mathrm{B})t_\mathrm{c}^2}{(m+1)(m+2)(E_\mathrm{s}t_\mathrm{s} + E_\mathrm{A}t_\mathrm{c}) + (m+2)(E_\mathrm{B} - E_A)t_\mathrm{c}}$$

- Application to the MoSiB Coatings:
  - Calculations were done following analysis on residual stress distribution of multi-layer graded coating structure with a total thickness of 100 μm and Mo substrate.
  - Vegard's rule of mixture is assumed to determine the E_i for each layer with respect to the effective Elastic Moduli and CTE.
  - Distribution of phases follow a function ((i-1)/(n-1))m with m as the distribution constant. For initial coating, m is set to 0.01 to reflect the abrupt MoB/$MoSi_2$ interface.