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

Ridwan Sakidja, Otto J. Lu-Steffes, and John H. Perepezko
Dept. Materials Science & Engineering, University of Wisconsin-Madison
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The need for ultra-high temperature materials

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


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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.
Mo-Si-B Phase Equilibrium at High Temperature

Oxidation Mechanism of Mo-Si-B Alloys

\[ \text{Mo}_3\text{Si} \rightarrow \text{T}_2 \]

As-Produced

MoO_3 (g)

MoO_3 (g)

\[ \text{O}_2 \rightarrow \text{SiO}_2 \rightarrow \text{MoO}_3 \rightarrow \text{SiO}_2 + \text{B}_2\text{O}_3 \]

High T

Time

\[ \rightarrow \text{Mo}_3\text{Si} \rightarrow \text{T}_2 \]

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

\[ y\text{NaF} + x\text{Si(s)} + \text{Al}_2\text{O}_3(s) \rightarrow \text{Si}_x\text{F}_y(g) + y\text{Na(g)} + \text{Al}_2\text{O}_3(s) \]

\[ v\text{NaF} + u\text{B(s)} + \text{Al}_2\text{O}_3(s) \rightarrow \text{B}_u\text{F}_v(g) + v\text{Na(g)} + \text{Al}_2\text{O}_3(s) \]

Initial period
Rate Controlling Step: Solid State Diffusion
After Initial period
Rate Controlling Step: Gas Diffusion

• Reaction Products: Mainly \( \text{MoSi}_2 \rightarrow \) Gas diffusion governs during the process
Multi-scale Designs & Synthesis Approach for Mo-Si-B Based Smart Coatings

Mo$_5$SiB$_2$ ($T_2$)  
$T_M \sim 2100^\circ$C

Mo$_5$Si$_3$ ($T_2$)  
$T_M=2180^\circ$C
Multi-scale Designs & Synthesis Approach for Mo-Si-B Based Smart Coatings
Multi-scale Designs & Synthesis Approach for Mo-Si-B Based Smart Coatings

CONTINUUM MODELING

ELECTRONIC STRUCTURE

ATOMISTIC MODELING

MICROSTRUCTURE SCALE
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

Microstructure-based FEM

Computational Thermodynamics

Thermal Stress Analysis

Electronic Structure

Mo-TM-Si-B COATING

Refactory Metal Substrate

HT EXPOSURE TO AIR

In-Situ TBC

Oxidation Barrier Layer

Oxidation Resistance Layer

Metalloid Diffusion Barrier

Refactory Metal Substrate

High-Temperature Phase Equilibria

BCC + T₁ + A₁₅
(Mo-Si-B + Cr/V)

BCC + T₁ + T₁
(Mo-6Si-B + W/ Nb/Ta)

BCC + T₁ + D₈₉
(Mo-Si-B + Hf/Ti/Zr)

Kinetic Biasing

(a) γ B

γ α β B
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 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

Diagram with ternary phase diagram showing compositions of MoB, Mo2B, Mo-14.2Si-9.6B, Mo-3Si-1B (wt. %), and MoSi2.
Consider Si+B-pack Cementation:
Source: NaF(l) + Si(s)+B(s)

1. \[3\text{NaF}(l) + \text{Si}(s) \Leftrightarrow \text{SiF}_4(g) + 3\text{Na}(g)\]
2. \[\text{Si}(s) + 3\text{SiF}_4(g) \Leftrightarrow 4\text{SiF}_3(g)\]
3. \[\text{Si}(s) + 2\text{SiF}_3(g) \Leftrightarrow 3\text{SiF}_2(g)\]
4. \[\text{Si}(s) + \text{SiF}_2(g) \Leftrightarrow 2\text{SiF}(g)\]
5. \[3\text{NaF}(l) + \text{B}(s) \Leftrightarrow \text{BF}_3(g) + 3\text{Na}(g)\]
6. \[\text{B}(s) + 2\text{BF}_3(g) \Leftrightarrow 3\text{BF}_2(g)\]
7. \[\text{B}(s) + 2\text{BF}_2(g) \Leftrightarrow 3\text{BF}(g)\]
8. \[\text{Na}(g) + \frac{1}{2} \text{F}_2(g) \Leftrightarrow \text{NaF}(l)\]

9. \[2p_{\text{F}_2(g)} + p_{\text{NaF}(g)} + 4p_{\text{SiF}_4(g)} + 3p_{\text{SiF}_3(g)} + 2p_{\text{SiF}_2(g)} + p_{\text{SiF}(g)} + 3p_{\text{BF}_3(g)}
+ 2p_{\text{BF}_2(g)} + p_{\text{BF}(g)} = p_{\text{Na}(g)}\]

\(\text{SiF}_4(g), \text{SiF}_3(g), \text{SiF}_2(g), \text{SiF}(g), \text{BF}_3(g), \text{BF}_2(g), \text{BF}(g), F_2(g), \text{Na}(g)\)
Gaseous Thermodynamics Equilibria in the Si+B Co-pack Cementation Process

Log (100*partial pressure) vs Temperature (°C) for a 35-1 weight ratio Si:B.
To stabilize a co-deposition of B and Si, the vapor pressure of Si-containing halides/ B-containing halides must be comparable.
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 $\leq 6$ IS ENERGETICALLY FAVORABLE (E.G. Nb, W, Ti)
Stability of RM-rich $T_2$ Phase

Total Density of States (TDOS)

Mo$_5$SiB$_2$

Mo$_4$NbSiB$_2$

MoNb$_4$SiB$_2$

V$_4$SiB$_2$
Unlike Borosilicide T2 phase, the Mo-rich silicide T1 phase has a more limited extended solid solution with refractory metals.

\[ \text{SILICIDES} \Rightarrow \text{Mo-rich SILICIDES} + \text{RM(e.g. Ti) DILICIDES} \]
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

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

KEY: MAINTAIN THE T_1 PHASE TEXTURED ALONG C AXIS TO MINIMIZE RESIDUAL STRESS
Effect of Conditioning on the Thermal Residual Stress

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.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's Modulus (GPa)</th>
<th>Poisson's Ratio</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Thermal Expansion (µm/m °C)</th>
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<td>Mo</td>
<td>330</td>
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<td>T2 (Mo(_5)SiB(_2))</td>
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<td>0.30</td>
<td>1.68</td>
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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°C for 24 hr (Ti/Zr doped)
### Experimental Results:

1 wt% Ti–doped MoSiB + Ox at 1200°C

#### 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

   $\text{Mo(CO)}_6 \rightarrow \text{Mo(s)} + 6\text{CO(g)}$

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

   
   $3\text{NaF} + 2\text{Si(s)} \leftrightarrow 2\text{SiF(g)} + 3\text{Na(g)} + \frac{1}{2}\text{F}_2(g)$
   $3\text{NaF} + 2\text{B(s)} \leftrightarrow 2\text{BF(g)} + 3\text{Na(g)} + \frac{1}{2}\text{F}_2(g)$
   $3\text{SiF(g)} \leftrightarrow \text{SiF}_2(g) + \text{Si(s)}$
   $3\text{SiF}_2(g) \leftrightarrow 2\text{SiF}_3(g) + \text{Si(s)}$
   $4\text{SiF}_3(g) \leftrightarrow 3\text{SiF}_4(g) + \text{Si(s)}$
   $3\text{BF(g)} \leftrightarrow \text{BF}_2(g) + \text{B(s)}$
   $3\text{BF}_2(g) \leftrightarrow 2\text{BF}_3(g) + \text{B(s)}$
Results:
Oxyacetylene Torch Test on MoSiB-coated Tungsten Rod

MoSiB Coating

Tungsten Rod
Results: Torch Test

- Mo-Si-B coating on W rod showed no degradation during torch testing
- Uniform borosilica layer formed after testing
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 MoL$_\alpha$/Si K$_\alpha$ 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...**

**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

Mo$_2$Ti$_3$Si$_3$ (T1) Phase at 1500K
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 Silicidies & Borosilicides.
- Oxygen Diffusivities & Viscosity of Borosilicate glass and the effect of Na, Al (from CVD process) and RM dopants.
Additional Slides
Coating Structures

- MoSiB Coating: Na aluminosilica formation
Coating Structures

EDS Measurements

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<tr>
<th>Element</th>
<th>Atoms%</th>
<th>Compound</th>
<th>Weight%</th>
<th>Error(±)</th>
<th>Norm%</th>
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<td>&lt;Total&gt;</td>
<td>100</td>
<td></td>
<td>100</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
Oxidation Results

- MoSiB Coating+Na-aluminosilica: Long-Term Test: 500°C/ 61 hrs
Oxidation Test at 700°C for 30 hrs
(Mo-3Si-1B wt %)

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$_2$O$_3$ to aluminosilicate.

Calculation on the residual stresses of compositionally graded coating

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:

\[(V_B)_i = \left(\frac{i - 1}{n - 1}\right)^m\]

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 :

\[E_i = E_B(V_B)_i + E_A(1 - (V_B)_i)\]

\[\alpha_i = \alpha_B(V_B)_i + \alpha_A(1 - (V_B)_i)\]

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

\[\Delta \varepsilon = (\alpha_s - \alpha_i)\Delta T = \Delta \alpha \Delta T\]

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:

\[\sigma_c = E_c [\varepsilon_c^0 + K(z + \delta)] \quad (0 \leq z \leq t_c)\]

\(\varepsilon_c^0\) is the stress strain of the coating defined as:

\[\varepsilon_c^0 = \frac{F_c}{\int_0^{t_c} E_c dz} = \bar{\varepsilon} - \alpha_c \Delta T\]

\[\bar{\varepsilon} = \frac{(m + 1)(E_B - E_A)(\alpha_B - \alpha_A)t_c + (2m + 1)(E_A \alpha_B + E_B \alpha_A - 2E_A \alpha_A)t_c \Delta T}{(2m + 1)(m + 1)E_s t_s + (2m + 1)(E_B + mE_A)t_c}\]

\[+ \frac{(2m + 1)(m + 1)(E_s t_s \alpha_s + E_A \alpha_A t_c)}{(2m + 1)(m + 1)E_s t_s + (2m + 1)(E_B + mE_A)t_c} \Delta T\]
Calculation on the residual stresses of compositionally graded coating

Curvature parameter can be defined as:

\[ K = \frac{P_1}{P_2} \]

where the parameters \( P_1, P_2 \) are:

\[
P_1 = (E_B - E_A)(x_B - x_A)\Delta T t_c \left( \frac{t_c}{2m + 2} + \frac{\delta}{2m + 1} \right)
+ E_A x_A \Delta T t_c \left( \frac{1}{2} t_c + \delta \right)
+ (E_A x_B - E_B x_A - 2E_A x_A) \Delta T t_c \left( \frac{t_c}{m + 2} + \frac{\delta}{m + 1} \right)
+ E_s x_s \Delta T t_s \left( \frac{1}{2} t_s - \delta \right)
\]

\[
P_2 = E_s t_s \left( \frac{t_c^2}{3} - t_s \delta + \delta^2 \right) + (E_B - E_A) \frac{t_c \delta^2}{m + 1}
+ t_c \left\{ (E_B - E_A) \frac{t_c^2}{m + 3} + 2(E_B - E_A) \frac{t_c \delta}{m + 2}
+ E_A \left( \frac{t_c^2}{3} + t_c \delta + \delta^2 \right) \right\}
\]

The distance \( \delta \) is defined as:

\[
\delta = \frac{1}{2} \left( \frac{(m + 1)(m + 2)(E_s t_s^2 - E_A t_c^2) + (m + 1)(E_A - E_B)t_c^2}{(m + 1)(m + 2)(E_s t_s + E_A t_c) + (m + 2)(E_B - E_A)t_c} \right)
\]

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 \( \mu \text{m} \) 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.