An Integrated Study on the Novel Thermal Barrier Coating for Nb-based High Temperature Alloy

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Outline

- Introduction
- Simulation and Experiment Results
- Future work
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Introduction

• Project Period: 10/1/2011 ~ 9/30/2013

• Project Manager: Richard Dunst

• Project Objectives:

(1) Perform interface energy and HPC simulation on the bond coat/Nb-based alloy and top coat/bond coat models to screen out the potential bond coat candidates.

(2) Study the high temperature properties and the oxidation resistance capabilities through molecular dynamics simulation.

(3) Perform experiments on the oxidation resistance of the most promising systems from the simulation. The isothermal oxidation and corrosiveness kinetics of TBCs for Nb-based alloy samples will be studied at high temperature in air environment by thermal-gravity analysis (TGA) and differential scanning calorimeter (DSC).
Introduction

• Nb-based alloys have advantages:

  high melting point (2469 °C), mediate density, and high thermal conductivity.

Disadvantages: high T oxidation (>600 °C).

• Optimize bond coat/Nb alloy (Nb$_2$AlC/Nb alloy) and top coat/bond coat (Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC) models by calculating interface energy, performing *ab initio* molecular dynamics (MD) and kinetic Monte Carlo (KMC) simulation.

• Experimental validation on the simulation results.
Why Nb$_2$AlC and Gd$_2$Zr$_2$O$_7$?

- Nb$_2$AlC/Nb$_4$AlC$_3$ is MAX phase ceramic that has good oxidation resistance capability. [J. Wang and Y. Zhou, Annu. Rev. Mater. Res. 39, 415 (2009); T. H. Scabarozi, et al., Thin Solid Film 517, 2920 (2009).] It is relatively easy to match the Nb-based substrate alloy.

- Gd$_2$Zr$_2$O$_7$ has very good phase stability at high temperature (>1650°C) and is very good candidate for top coat.

- Our first stag experiment shows that YSZ+Gd$_2$Zr$_2$O$_7$ has better corrosion resistance than YSZ.
### Methods: Interface Energy and MD/MC Simulation

- \[ \delta G = \delta \int \gamma \, dA_{SS} \]

  where \( G \) is the total interface energy of the system, \( \gamma \) is the solid–solid interface energies, and \( A_{SS} \) is the solid–solid interface area.

- \( \delta G \) can be calculated from the difference of the total energy of system and energies summation of each individual parts under the same boundary conditions.

- Increase the cell size, till the calculation converged.

- Molecular dynamics and long time kinetic Monte-Carlo simulation.
Current Status


• Postdoc Oleg N. Starovoytov was working on the project April 2012 ~ Dec. 2012.

• Doped Nb$_2$AlC MD simulation, Nb$_2$AlC/Nb interface and Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC interface MD simulation had been finished.

• Gd$_2$Zr$_2$O$_7$ corrosive resistance had been tested at LSU TIER.
1. In this work, we studied the properties of bulk Nb$_2$AlC with Y and Y-Mo co-doping at high temperatures using *ab initio* molecule dynamic DFT method.

Temperatures: 1200K~2100K

2. Supercell: 4×4×2 (128 Nb atoms, 64 Al atoms, 64 C atoms) unit cell. For Y and Mo doping, the 10 Nb atoms are randomly replaced by Y and Mo atoms.
Our simulation data shows:
1. The Nb$_2$AlC lattice is stable up to ~ 2100K.
2. When Y atoms are doped into Nb layer, the nearby C and Al atoms in the C and Al layers are fluctuated and jump out the layers forming local defects.
3. The MD trajectory shows that the Mo atoms doping enhanced the layered structure. Y and Mo doping improves the stability of high temperature mechanical property and blocks the O diffusion path.
Y and Mo Doped Nb$_2$AlC MD Simulation Results

(1). With oxygen atoms layer adding on Nb$_2$AlC alloy surface, the layered structure is broken at the studied 1700K. O atoms rarely bond with C atoms while bond strongly with Al and Y atoms.

(2). Y and Mo doping enhanced the oxidation resistance capability of the Nb$_2$AlC by forming strong Al-O and Y-O bonds;

(3). The doping also enhances the inter-layer bonding and thus improves the high temperature mechanical property.
$\text{Nb}_2\text{AlC}(001)/\text{Nb}(111)$ Interface
## The Interface Energy of Nb₂AlC/Nb

<table>
<thead>
<tr>
<th>Interface</th>
<th>Nb₂AlC(001)/Nb(001)</th>
<th>Nb₂AlC(001)/Nb(110)</th>
<th>Nb₂AlC(001)/Nb(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface Energy (eV/Å²)</td>
<td>-0.47</td>
<td>-0.51</td>
<td>-1.24</td>
</tr>
</tbody>
</table>
(110) plane difference charge density contours of Nb$_2$AlC(001)/Nb(111) interfaces showing partial covalence Al-Nb bondings and metallic Nb-Nb bondings in the two interfaces. The orange lines and red areas stand for charge accumulation while the blue lines and areas stand for charge depletion.
Charge Density Difference of Nb$_2$AlC(001)/Nb(111) Interfaces

3D difference charge density contours of Nb$_2$AlC(001)/Nb(111) interfaces. The brown balls stand for C, the light blue balls for Al, and the light green balls for Nb atoms. The charge accumulation areas are marked in yellow while the charge depletion areas are in blue.
3D difference charge density contours ofNb$_2$AlC(001)/Nb(001) interfaces.
3D difference charge density contours of Nb$_2$AlC(001)/Nb(110) interfaces.
Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC Interface


Supercell size: $a = 10.6$ Å, $b = 16.3$ Å, $c = 21.8$ Å.
Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC Interface Results

1. Ti doping: 10%, 20% and 40% of Nb and Zr.

2. O atoms form Al-O bond with Al atom at Nb$_2$AlC/Gd$_2$Zr$_2$O$_7$ interface.

3. Nb-C forms strong bonding so that the O-Nb bonding is very weak.

4. Ti doping can potentially enhance the interface stability by reducing the lattice mismatch and local stress.
Gd$_2$Zr$_2$O$_7$ and YSZ Thermal Cycling Test

1. The premature failure of the pure Gd$_2$Zr$_2$O$_7$ coatings can be mainly related to its low toughness.

2. At moderate surface temperature the functionally graded double layer 50% Gd$_2$Zr$_2$O$_7$/YSZ TBC system show best performance from the thermal cycling test.
1. Journal article:

- “First principles calculation of Nb₂AlC/Nb interfaces”, Liuxi Tan and Shizhong Yang, JOM 65, 326 (2013).


“Titanium dopant effects on the Nb$_2$AlC/Gd$_2$Zr$_2$O$_7$ interface from molecular dynamics simulation”, Liuxi Tan and Shizhong Yang, MS&T’12, PIttersburgh, PA, October 2012.

“Cr-based alloy Cr-Y-Mo-W oxidation study from first principles molecular dynamics simulation”, Lei Zhao, Shizhong Yang, Ebrahim Khosravi, and Shengmin Guo, APS March Meeting, Boston, Massachusetts, March 2012.

“Study on high temperature oxidation of Y doped Nb$_2$AlC (MAX phase) from ab initio molecular dynamics simulation”, Shizhong Yang, Lei Zhao, Ebrahim Khosravi, Kaiyang Wang, and Shengmin Guo, MS&T’11, Columbus, Ohio, October 19, 2011.
Future Work

1. HPC MD simulation on doped Nb$_2$AlC/Nb and doped Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC to finalize the stable structures.

2. TGA and DSC experimental verification on the screened candidates.

3. Students/postdoc training.
Acknowledgement

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