An Integrated Study of a Novel Thermal Barrier Coating for Nb-based High Temperature Alloy

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Outline

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- TBC for Nb-based Alloy Simulation and Experiment
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Introduction

- **Project Period:** 10/1/2011 ~ 9/30/2014
- **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 a very good candidate for top coat.

- Our first stage experiment shows that Gd$_2$Zr$_2$O$_7$ has better hot 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

• The project period: Oct. 2011 ~ Sept. 2014.

• Postdoc Liuxi Tan has been working on the project Jan. 2013 ~ present (Dr. Starovoytov).

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

• Gd$_2$Zr$_2$O$_7$ corrosive resistance had been tested at LSU TIER. Gd$_2$Zr$_2$O$_7$/YSZ compress/decompress radial synchrotron XRD experiment was done at Lawrence Berkeley National Lab (LBNL) beamline 12-2-2.
Y-Mo-Nb$_2$AlC MD Simulation

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.
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.
Nb$_2$AlC(001)/Nb(111) Interface
Charge Density of Nb$_2$AlC(001)/Nb(111) Interfaces

(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.
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 in blue.
3D difference charge density contours of 
\( \text{Nb}_2\text{AlC}(001)/\text{Nb}(001) \) interfaces.
3D difference charge density contours of \( \text{Nb}_2\text{AlC}(001)/\text{Nb}(110) \) 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.
Ti doped Gd$_2$Zr$_2$O$_7$/Nb$_2$AlC Interface Model

292 atoms in total and (Nb+Ti)--80, Al--40, C--40, Gd--24, (Zr+Ti)--24 and O-84.

Supercell size: $a = 10.6$ Å, $b = 16.3$ Å, $c = 21.8$ Å.
Ti Doped 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 strain/stress.
The premature failure of the pure \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) coatings can be mainly related to its low toughness.

At moderate surface temperature the functionally graded double layer 50% \( \text{Gd}_2\text{Zr}_2\text{O}_7/\text{YSZ} \) TBC system meets the expectations, as the thermal cycling performance is similar to those of YSZ TBCs.
Gd$_2$Zr$_2$O$_7$/YSZ Compress/Decompress at LBNL BL-12-2-2 (a summary)

1. To understand the phase stability of Gd$_2$Zr$_2$O$_7$/YSZ at different pressures (up to 30 Gpa), we performed radial synchrotron XRD experiment at Lawrence Berkeley National Lab (LBNL) beamline 12-2-2 using platinum powder as a comparison media from April 18 to April 30, 2014.

2. Both Rietveld refinement and computer simulation are ongoing to pin down exact crystal structure and properties finalizing.

3. We plan to perform further radial XRD experiment in Fall 2014 based on our current experiment and simulation results using the LBNL DD beamtime.
Publications

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


• “Detecting grain rotation at the nanoscale”, B. Chen, K. Lutker, J. Lei, J. Yan, S. Yang, and H.K. Mao, PNAS 111, 3350 (2014).

• “Phase stability and hot corrosion behavior of ZrO₂-Ta₂O₅ compound in Na₂SO₄-V₂O₅ mixtures at elevated temperatures”, M. H. Habibi, S. Yang, and S. Guo, Ceramic International 40, 4077 (2014).
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. Data processing. Phase stability study at LBNL BL-12-2-2. TGA and DSC experimental verification on the screened candidates.

3. Students/postdoc training.
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