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**
- **Acknowledgement**

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_2AlC/Nb alloy) and top coat/bond coat ($Gd_2Zr_2O_7$/Nb_2AlC) 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_2AlC and $Gd_2Zr_2O_7$?

- **Nb_2AlC/Nb_4AlC_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.**

- **$Gd_2Zr_2O_7$ 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+$Gd_2Zr_2O_7$ 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, γ is the solid−solid interface energies, and A_{SS} is the solid−solid interface area.

- **δG 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. 2013.
- Postdoc Oleg N. Starovoytov was working on the project April 2012 ~ Dec. 2012.
- Doped Nb_2AlC MD simulation, Nb_2AlC/Nb interface and Gd_2Zr_2O7/Nb_2AlC interface MD simulation had been finished.
- $Gd_2Zr_2O_7$ corrosive resistance had been tested at LSU TIER.

Y-Mo-Nb_2AlC MD Simulation

1. In this work, we studied the properties of bulk Nb_2AlC 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_2AlC MD Simulation Results

Our simulation data shows:

1. The Nb_2AlC 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.

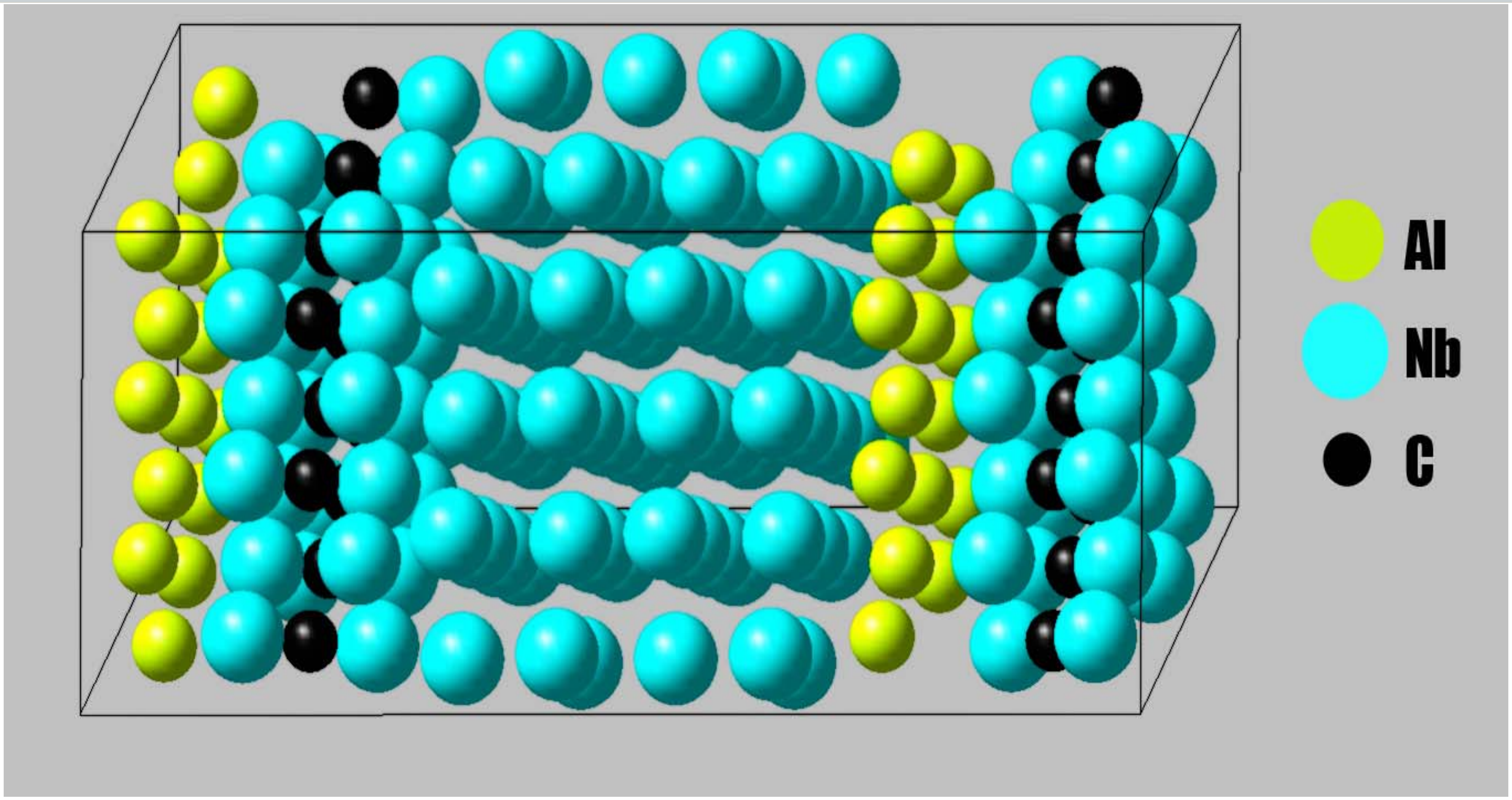
Y and Mo Doped Nb_2AlC MD Simulation Results

(1). With oxygen atoms layer adding on Nb_2AlC 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_2AlC 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.

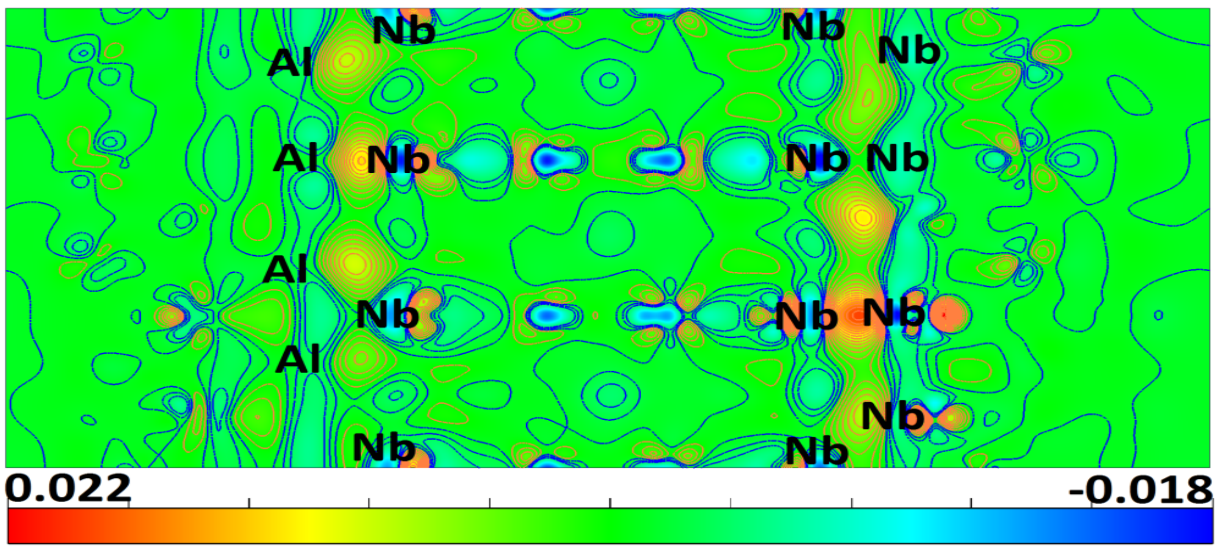
$Nb_2AlC(001)/Nb(111)$ Interface



The Interface Energy of Nb_2AlC/Nb

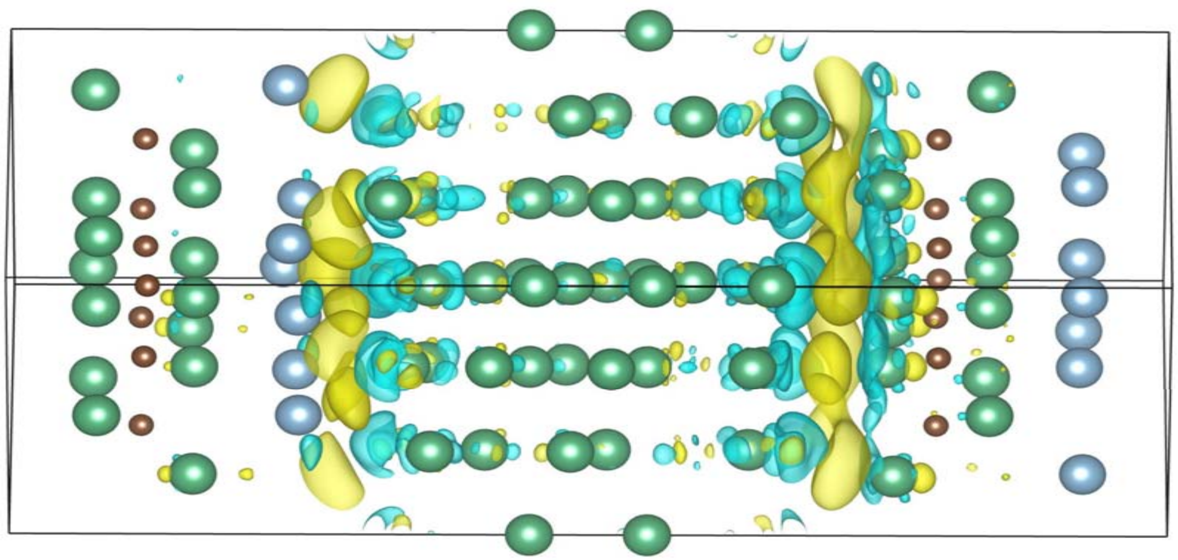
Interface	$Nb_2AlC(001)/Nb(001)$	$Nb_2AlC(001)/Nb(110)$	$Nb_2AlC(001)/Nb(111)$
Interface Energy (eV/Å^2)	-0.47	-0.51	-1.24

Charge Density of $Nb_2AlC(001)/Nb(111)$ Interfaces



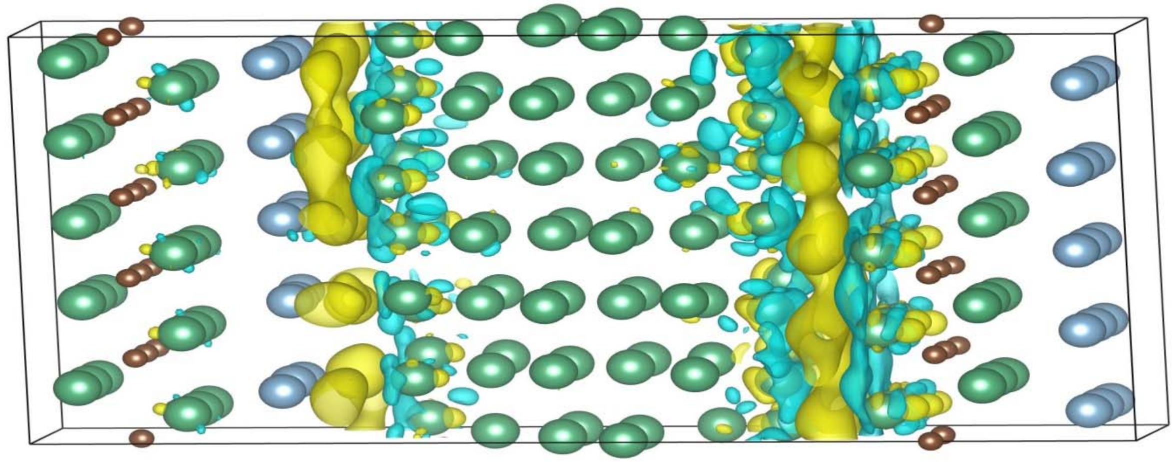
(110) plane difference charge density contours of $Nb_2AlC(001)/Nb(111)$ interfaces showing partial covalence Al-Nb bondings and metallic Nb-Nb bondings in the two interfaces. The orange lines and red areas stand for charge accumulation while the blue lines and areas stand for charge depletion.

Charge Density Difference of Nb2AlC(001)/Nb(111) Interfaces



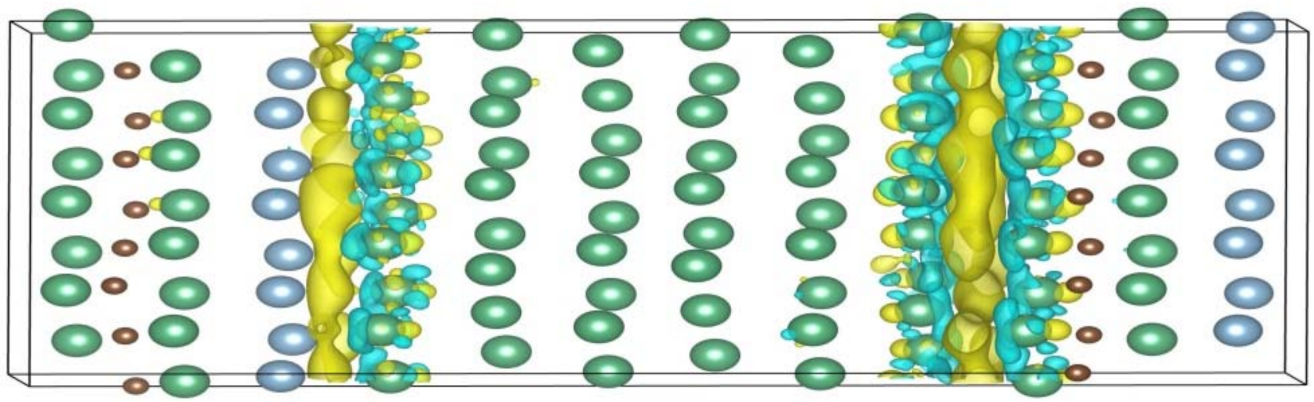
3D difference charge density contours of $Nb_2AlC(001)/Nb(111)$ interfaces. The brown balls stand for C, the light blue balls for Al, and the light green balls for Nb atoms. The charge accumulation areas are marked in yellow while the charge depletion areas in blue.

$Nb_2AlC(001)/Nb(001)$ Interface



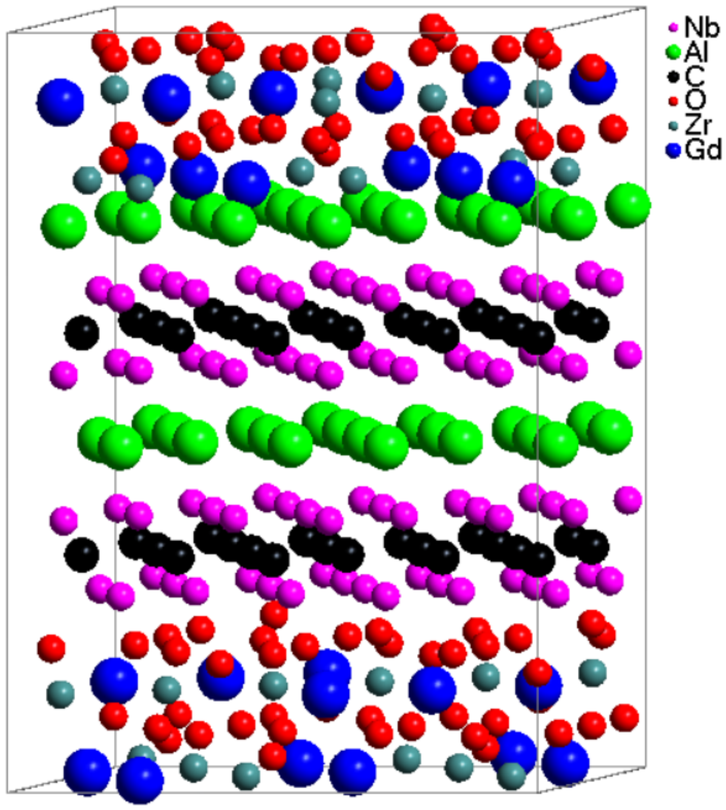
3D difference charge density contours of $Nb_2AlC(001)/Nb(001)$ interfaces.

$Nb_2AlC(001)/Nb(110)$ Interface



3D difference charge density contours of $Nb_2AlC(001)/Nb(110)$ interfaces.

$Gd_2Zr_2O_7/Nb_2AlC$ Interface



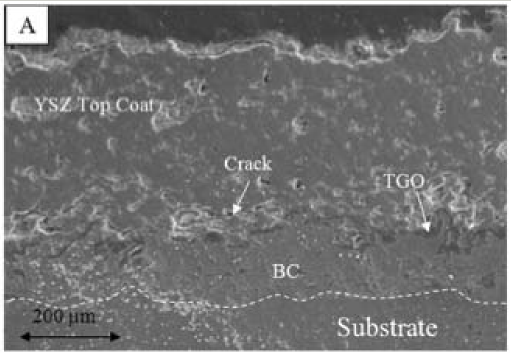
292 atoms in total and Nb–80, Al–40, C–40, Gd–24, Zr–24 and O-84.

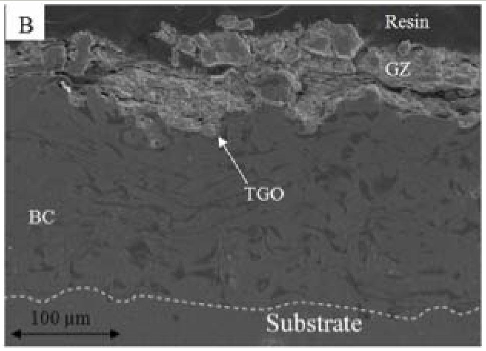
Supercell size: *a* = 10.6 Å, *b* = 16.3 Å, *c* = 21.8 Å.

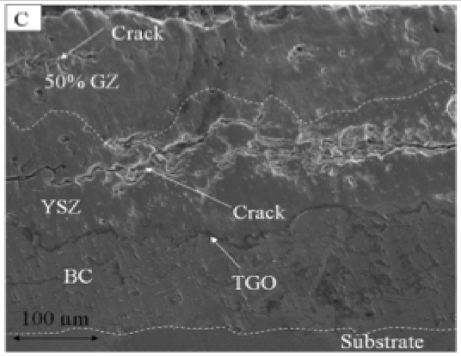
$Gd_2Zr_2O_7/Nb_2AlC$ Interface Results

1. Ti doping: 10%, 20% and 40% of Nb and Zr.
2. O atoms form Al-O bond with Al atom at $Nb_2AlC/Gd_2Zr_2O_7$ 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.

$Gd_2Zr_2O_7$ and YSZ Thermal Cycling Test







YSZ **$Gd_2Zr_2O_7$** **50%$Gd_2Zr_2O_7$/YSZ**

SEM Micrographs of Cross-Section of Coatings after Thermal Cycling at 1100^{o}C

1. The premature failure of the pure $Gd_2Zr_2O_7$ coatings can be mainly related to its low toughness.

2. At moderate surface temperature the functionally graded double layer 50% $Gd_2Zr_2O_7$/YSZ TBC system show best performance from the thermal cycling test.

Publications

1. Journal article:

- "First principles calculation of Nb_2AlC/Nb interfaces", Liuxi Tan and Shizhong Yang, JOM **65**, 326 (2013).

- "Nitrogen-doped fullerene as a potential catalyst for hydrogen fuel cells", F. Gao, G. L. Zhao, S. Yang, and J. L. Spivey, Journal of the American Chemical Society **135**, 3315 (2013).

- "Texture of nanocrystalline nickel: probing the lower size limit of dislocation activity", B. Chen, S. V. Raju, J. Yuan, W. Kanitpanyacharon, J. Lei, S. Yang, H. R. Wenk, H. K. Mao, and Q. C. Williams, Science **338**, 1448 (2012).

- "Deposition of silicide based protective coatings on C-103 niobium alloy with different surface microstructures", Kaiyang Wang, Jiandong Liang, Li Wang, Shengmin Guo, and Shizhong Yang, Materials Science & Technology 2011 Conference and Exhibition (MS&T Partner Societies), pp1078-1085, October 2011.

Presentations

"Properties of zirconia gadolinia ytterbia yttria thermal barrier coating studied by first principles simulation", Liuxi Tan, Lei Zhao, Shengmin Guo, Ebrahim Khosravi, and Shizhong Yang, TMS 2013, San Antonio, Texas, March 2013.

"Titanium dopant effects on the $Nb_2AlC/Gd_2Zr_2O_7$ 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_2AlC (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_2AlC/Nb and doped $Gd_2Zr_2O_7$/Nb_2AlC to finalize the stable structures.
2. TGA and DSC experimental verification on the screened candidates.
3. Students/postdoc training.

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