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

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Outline

- Introduction
- TBC for Nb-based Alloy Simulation and Experiment
- Results and work to be done
- Acknowledgement

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_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 a very good candidate for top coat.**
- **Our first stag experiment shows that $Gd_2Zr_2O_7$ has better hot corrosion resistance than YSZ.**

Methods: Interface Energy and MD/MC Simulation

- $$\delta G = \delta \int \gamma \, \mathrm{dAss}$$

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. 2014.
- Postdoc Liuxi Tan has been working on the project Jan. 2013 ~ present (Dr. Starovoytov).
- Doped Nb_2AlC MD simulation, Nb_2AlC/Nb and Gd_2Zr_2O7/Nb_2AlC interface simulation had been finished.
- $Gd_2Zr_2O_7$ corrosive resistance had been tested at LSU TIER. $Gd_2Zr_2O_7$/YSZ compress/decompress radial synchrotron XRD experiment was done at Lawrence Berkeley National Lab (LBNL) beamline 12-2-2.

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.

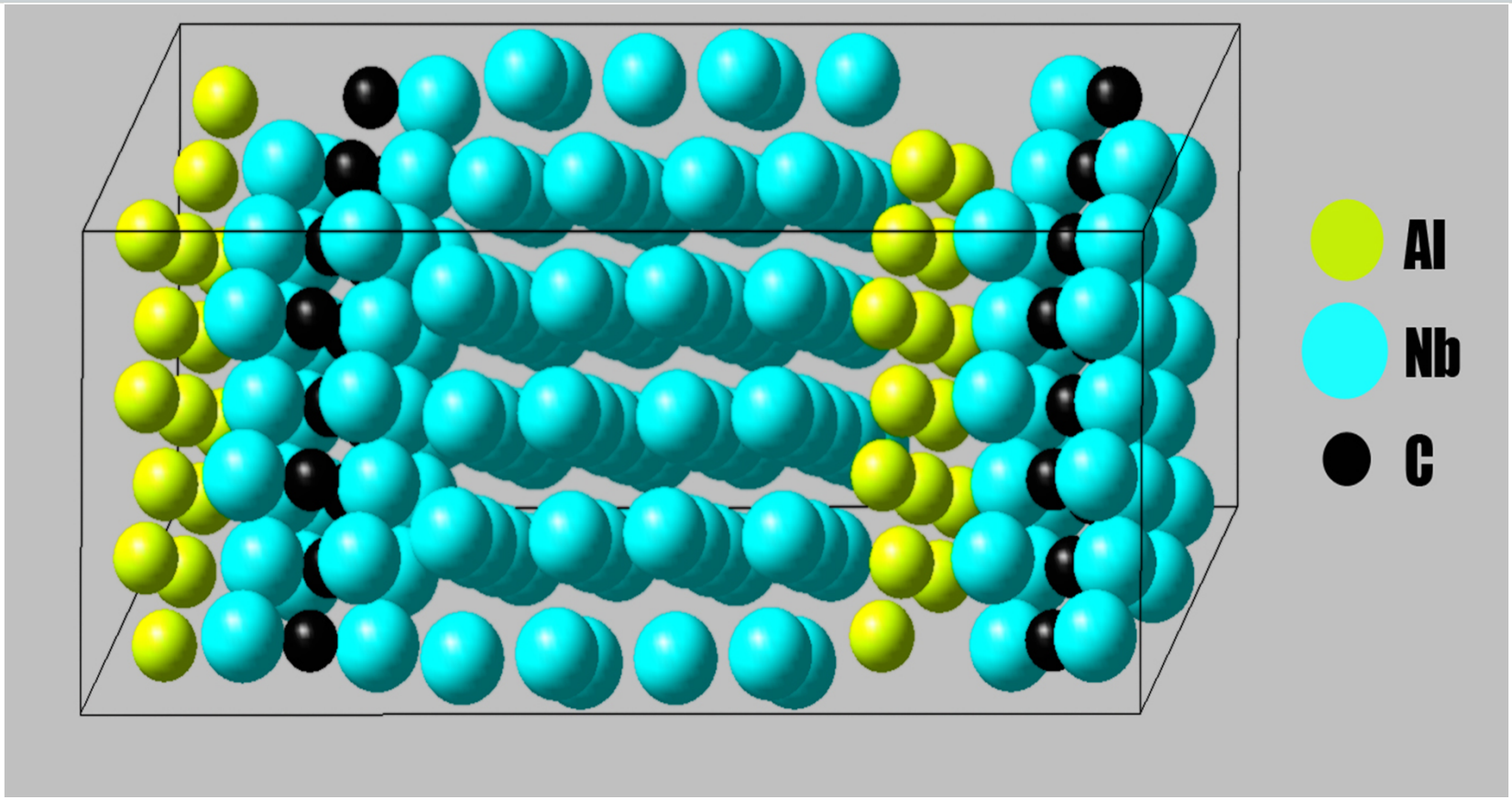
Y and Mo Doped Nb_2AlC MD Simulation Results

(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.

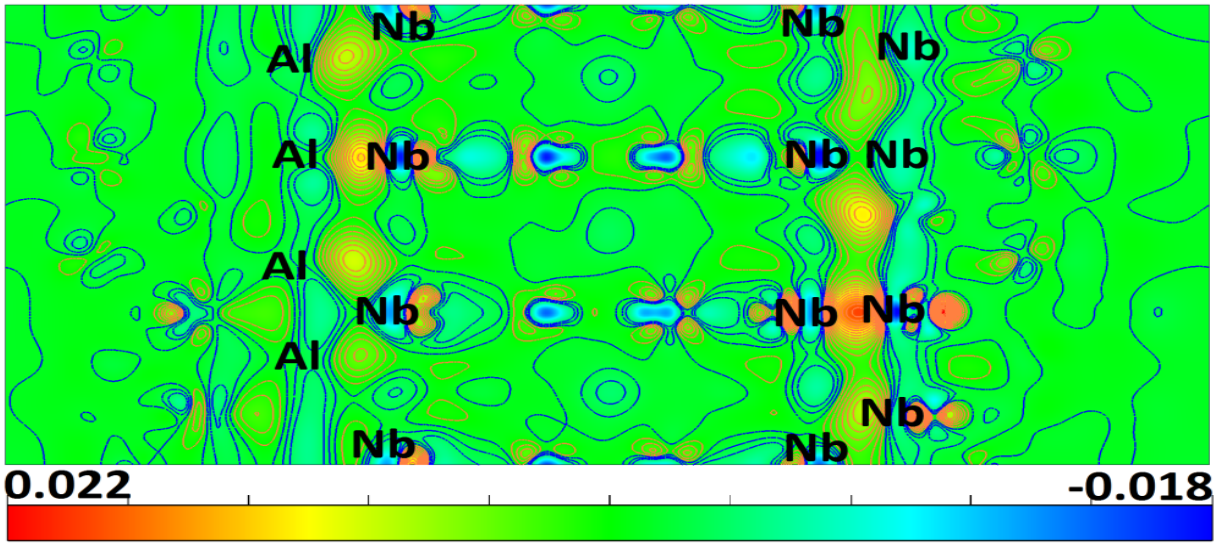
(2). Y and Mo doping enhanced the oxidation resistance capability of the Nb_2AlC by forming strong Al-O and Y-O bonds;

(3). The doping also enhances the inter-layer bonding and thus improves the high temperature mechanical property.

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

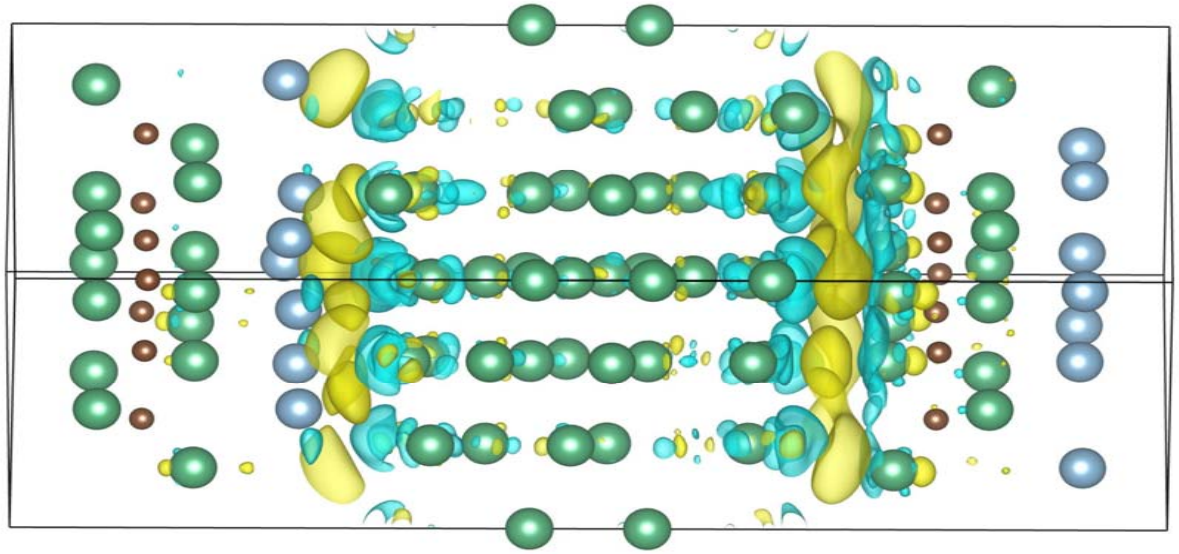


Charge Density of $Nb_2AlC(001)/Nb(111)$ Interfaces



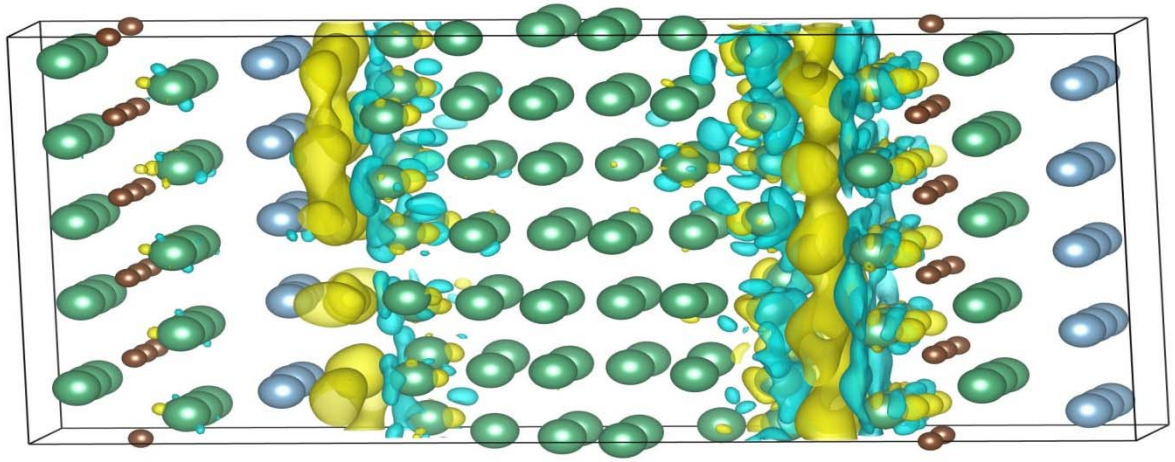
(110) plane difference charge density contours of $Nb_2AlC(001)/Nb(111)$ interfaces showing partial covalence Al-Nb bondings and metalic Nb-Nb bondings in the two interfaces. The orange lines and red areas stand for charge accumulation while the blue lines and areas stand for charge depletion.

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



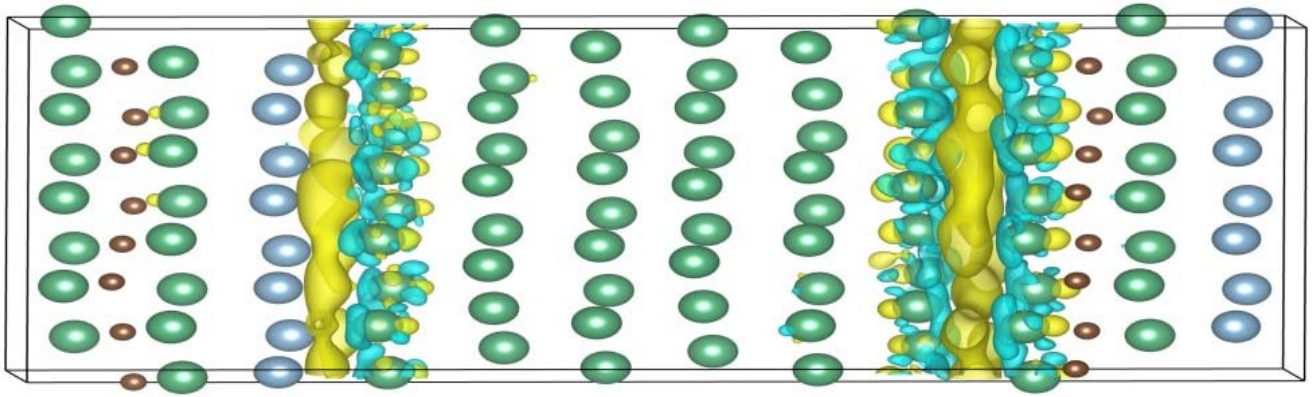
3D difference charge density contours of $Nb_2AlC(001)/Nb(111)$ interfaces. The brown balls stand for C, the light blue balls for Al, and the light green balls for Nb atoms. The charge accumulation areas are marked in yellow while the charge depletion areas in blue.

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



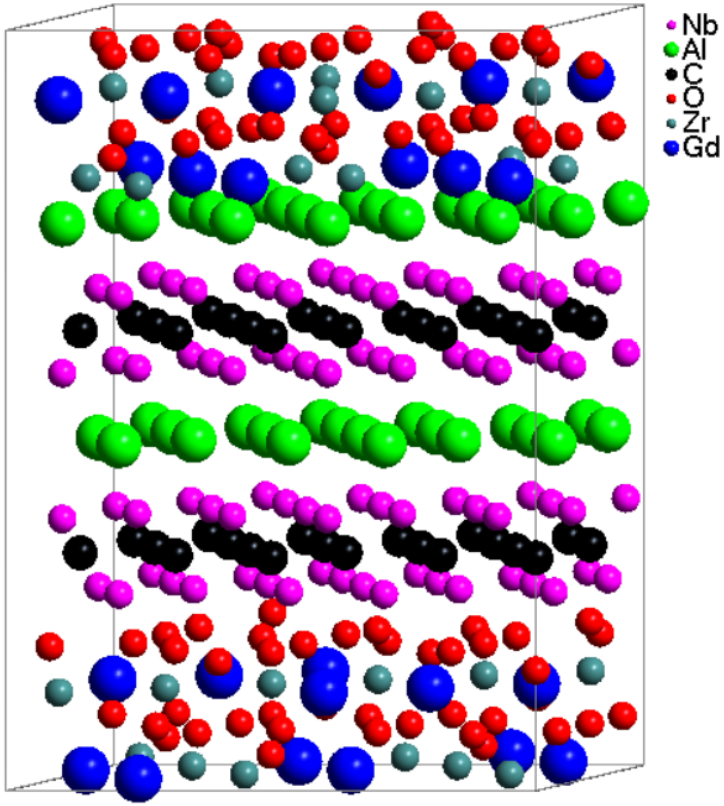
3D difference charge density contours of $Nb_2AlC(001)/Nb(001)$ interfaces.

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



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

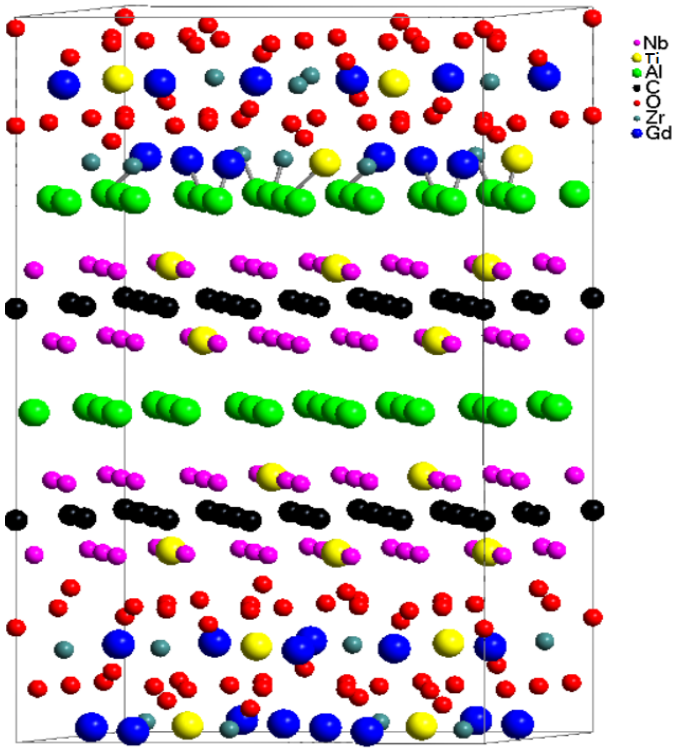
$Gd_2Zr_2O_7/Nb_2AlC$ Interface



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.

Ti doped $Gd_2Zr_2O_7/Nb_2AlC$ Interface Model



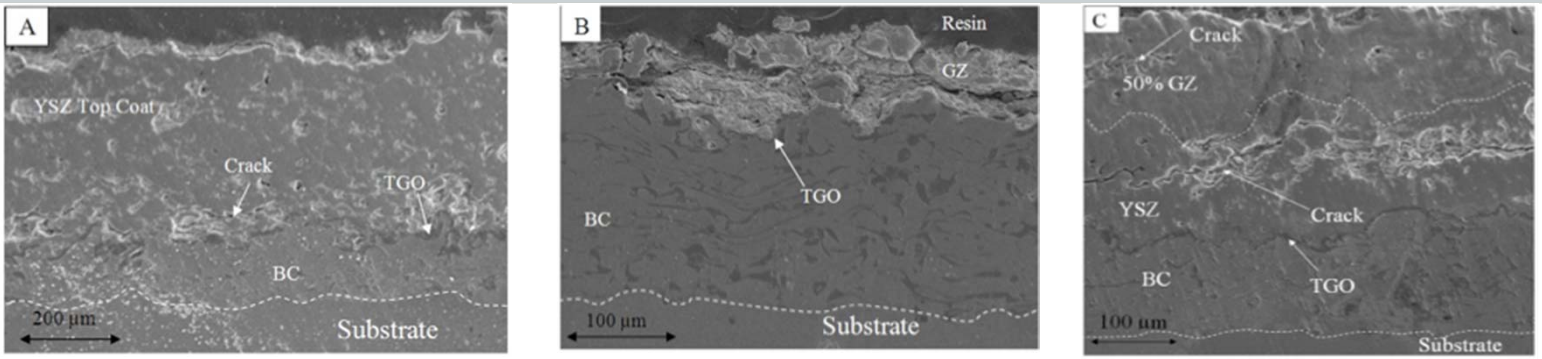
292 atoms in total and (Nb+Ti)–80, Al–40, C–40, Gd–24, (Zr+Ti)–24 and O-84.

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

Ti Doped $Gd_2Zr_2O_7/Nb_2AlC$ 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 strain/stress.

$Gd_2Zr_2O_7$ and YSZ Thermal Cycling



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

SEM Micrographs of Cross-Section of Coatings after Thermal Cycling at 1100°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 meets the expectations, as the thermal cycling performance is similar to those of YSZ TBCs.

$Gd_2Zr_2O_7$/YSZ Compress/Decompress at LBNL BL-12-2-2 (a summary)

1. To understand the phase stability of $Gd_2Zr_2O_7$/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 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).
- "Catalytic reactions on the open-edge site of nitrogen-doped carbon nanotubes as cathode catalyst for hydrogen fuel cells", F. Gao, G.L. Zhao, and S. Yang, ACS Catalyst **4**, 1267 (2014).
- "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 ZrO_2-Ta_2O_5 compound in Na_2SO_4-V_2O_5 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_2AlC/Nb and doped $Gd_2Zr_2O_7$/Nb_2AlC 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.

Acknowledgement

- **Project manager: Richard Dunst**
- **Graduate students: Lei Zhao, Jialin Lei, Daniel Hart, and Cheng Guo; undergraduate student: Michael Jackson and Megan Jones.**
- **Postdocs: Drs. Liuxi Tan, Oleg Starovoytov.**
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