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

**Shizhong Yang, Ebrahim Khosravi**

**Southern University and A & M Colleg**

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# Outline

- Introduction
- Methods
- TBC for Nb-based Alloy Simulation and Experiment
- 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 $Gd_2Zr_2O_7$ has better corrosion resistance than YSZ.**

# Methods: Interface Energy and Models

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

**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.**

- **$\delta G$ 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 Methods

- **Ab initio potential generating code test.**

$$E_{total}(\rho) = T + \sum_{lm}\int \rho(\vec{r})dv\frac{-e^2 Z_m}{\left|\vec{r}-\vec{\tau}_m-\vec{R}_l\right|}+\frac{1}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}dvdv'+E_{xc}(\rho)+\frac{1}{2}\sum_{mn}\frac{e^2 Z_m Z_n}{\left|\vec{\tau}_m-\vec{\tau}_n\right|}$$

**The kinetic energy term T is expressed as an UBER relation:**

$$T \equiv E_{rep} = \frac{1}{2}\sum_{\substack{i,j \\ (i\neq j)}} \varepsilon d_{ij}^{\,n} \exp\left(-\frac{d_{ij}-d_0}{s}\right)$$

# Molecular Dynamics Methods

- **By fitting the coefficients in UBER relation into the total energy equation, we can calculate the total energy of the system, thus the interatomic potential is known.**

- **Then classical MD could be performed to simulate the physical properties.**

# Current Status

- **The project period: Oct. 2011 ~ Sept. 2013.**
- **Postdoc Oleg N. Starovoytov was working on the project since April 2012.**
- **Nb nanocrystal, $Nb_3Al_2C$ (by MA & arc melting) had been prepared. $Gd_2Zr_2O_7$ corrosive resistance had been tested at LSU TIER.**
- **Y and Mo doped $Nb_2AlC$ MD simulation has been finished.**

# Current Status

- **We have built $Nb_2AlC(001)/Nb(111)$, $Nb_2AlC(001)/Nb(100)$, and $Nb_2AlC(001)/Nb(110)$ Interface. The interface energies calculation is ongoing.**
- **Nb and $Nb_2AlC$ interatomic potentials building is ongoing.**

# 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.

# $Nb_2AlC$ Model (1200K ~ 2100K )

There are 128 Nb atoms (White), 64 Al atoms (gray), 64 C atoms (Black) in the supercell.

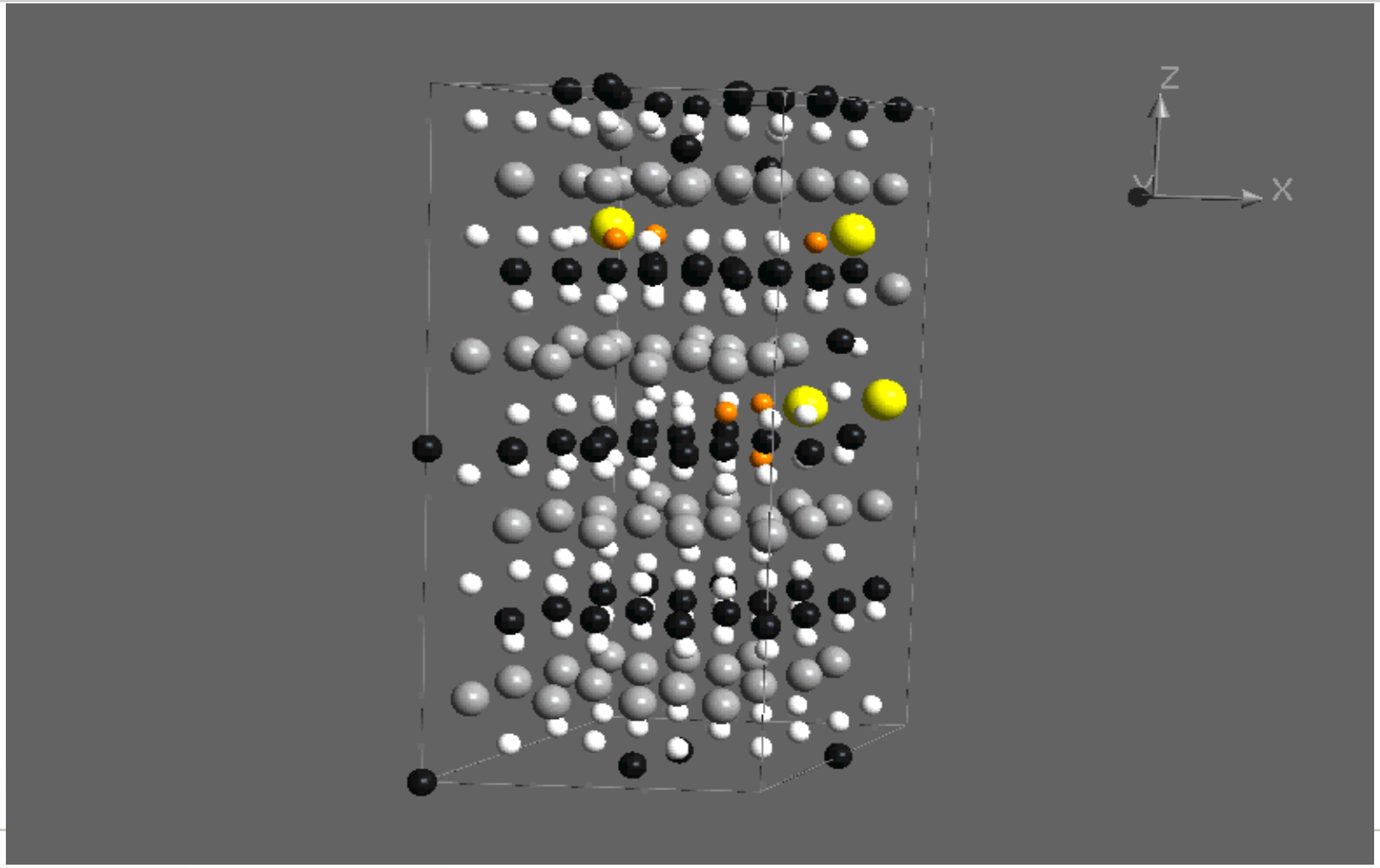
# Y and Mo Doped $Nb_2AlC$ Model

There are 118 Nb atoms (White), 64 Al atoms (gray), 64 C atoms (Black), 6 Mo atoms (Orange), and 4 Y atoms (Yellow) in supercell.

# Oxidation Test on Y and Mo Doped $Nb_2AlC$ Model

There are 118 Nb atoms (White), 64 Al atoms (gray), 64 C atoms (Black), 6 Mo atoms (Orange), 4 Y atoms (Yellow) and 8 O atoms (Red) in the supercell.

# $Nb_2AlC$-Y-Mo



# 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.

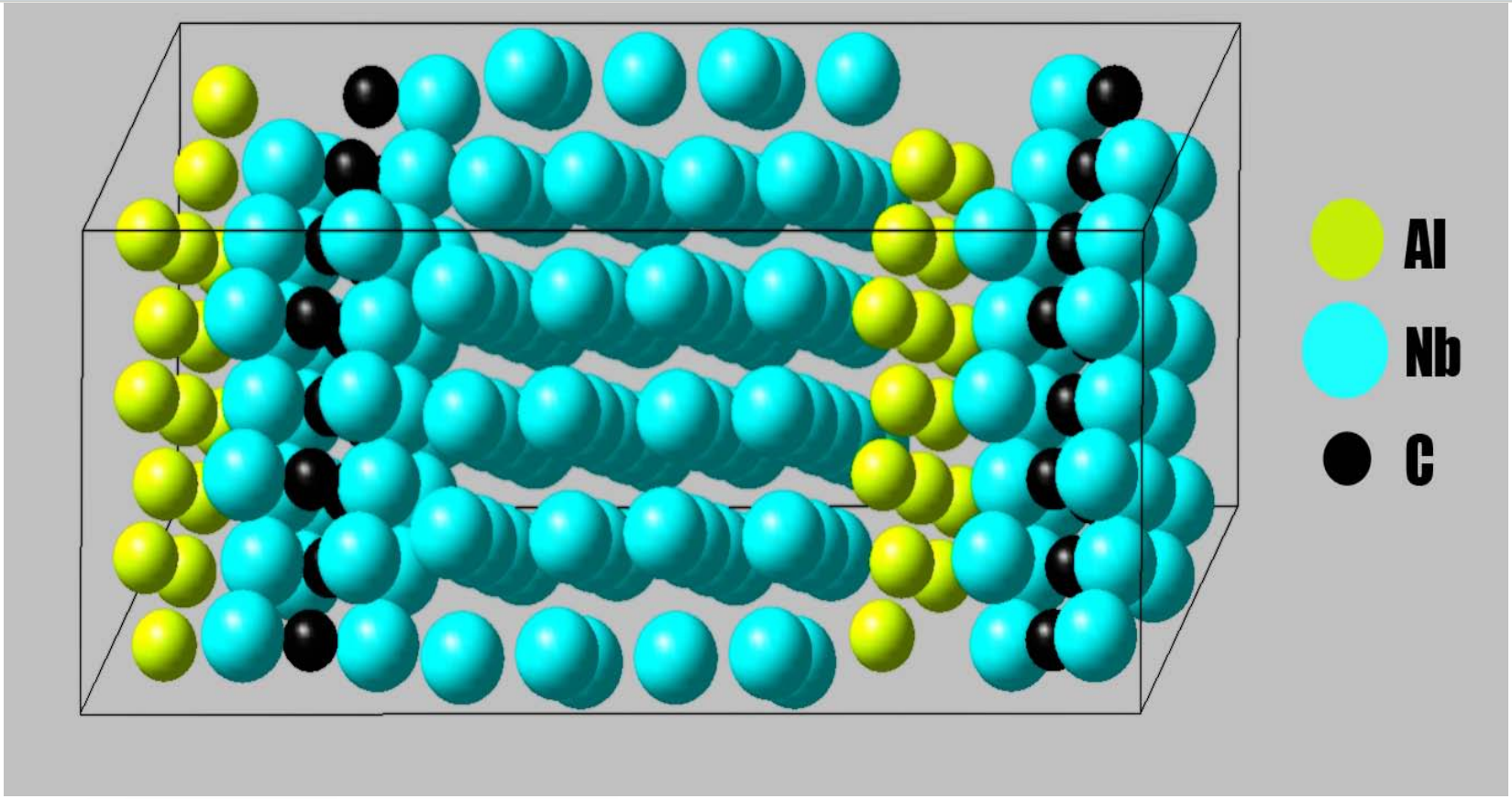
# Y and Mo Doped $Nb_2AlC$ MD Simulation Results

(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.

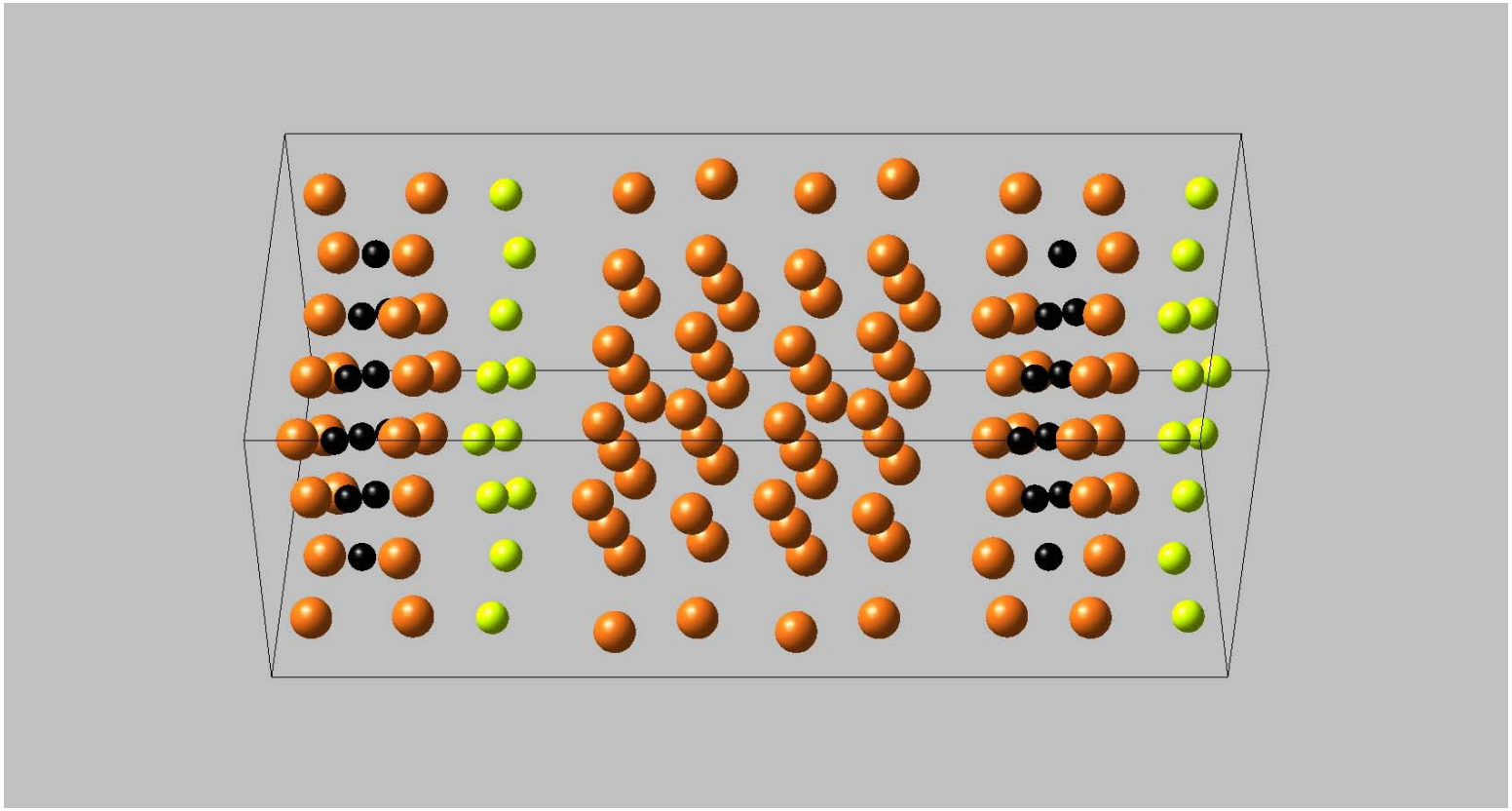
(2). Y and Mo doping enhanced the oxidation resistance capability of the $Nb_2AlC$ by forming strong Al-O and Y-O bonds;

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

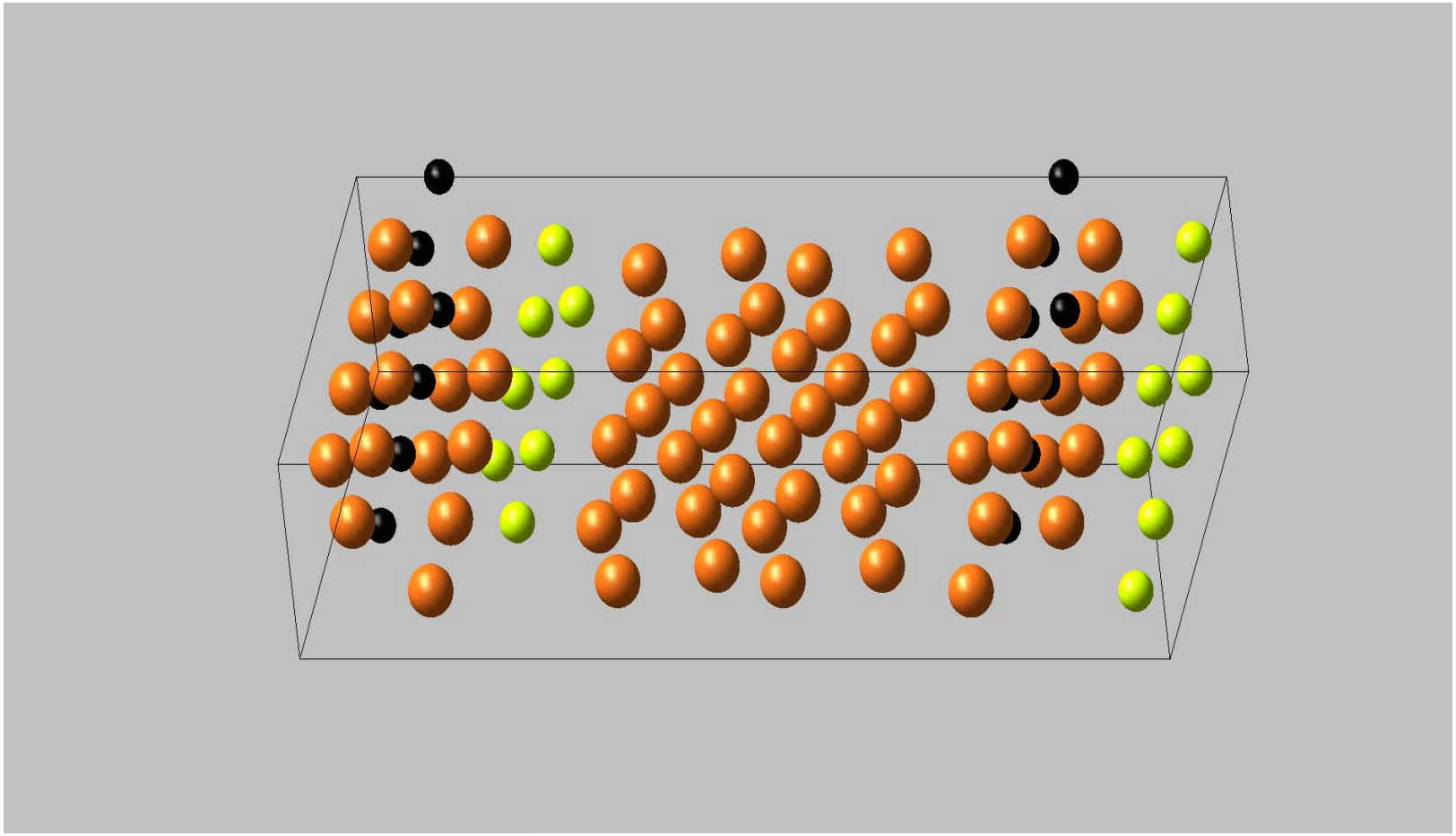
# $Nb_2AlC(001)/Nb(111)$ Interface



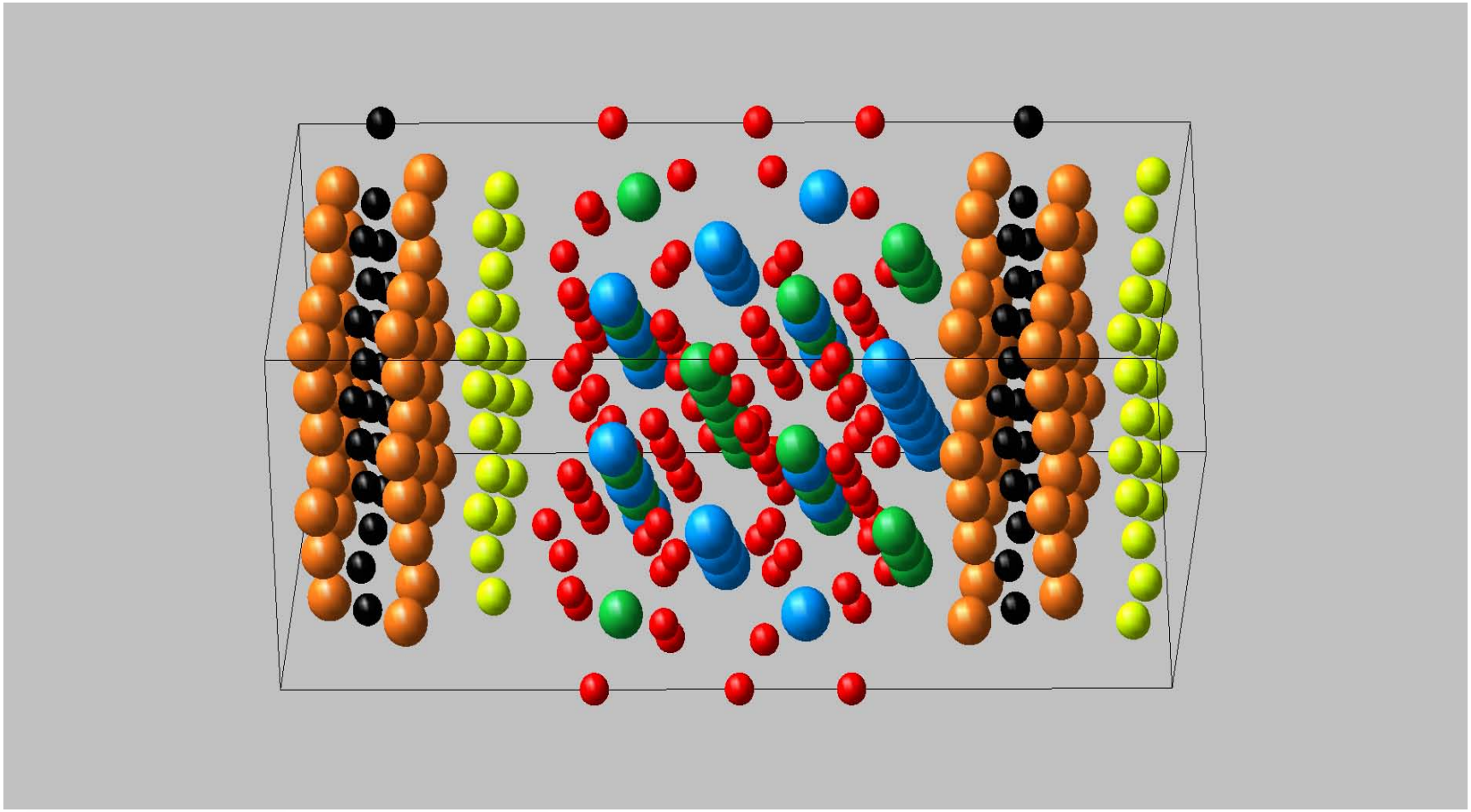
# $Nb_2AlC(001)/Nb(110)$ Interface



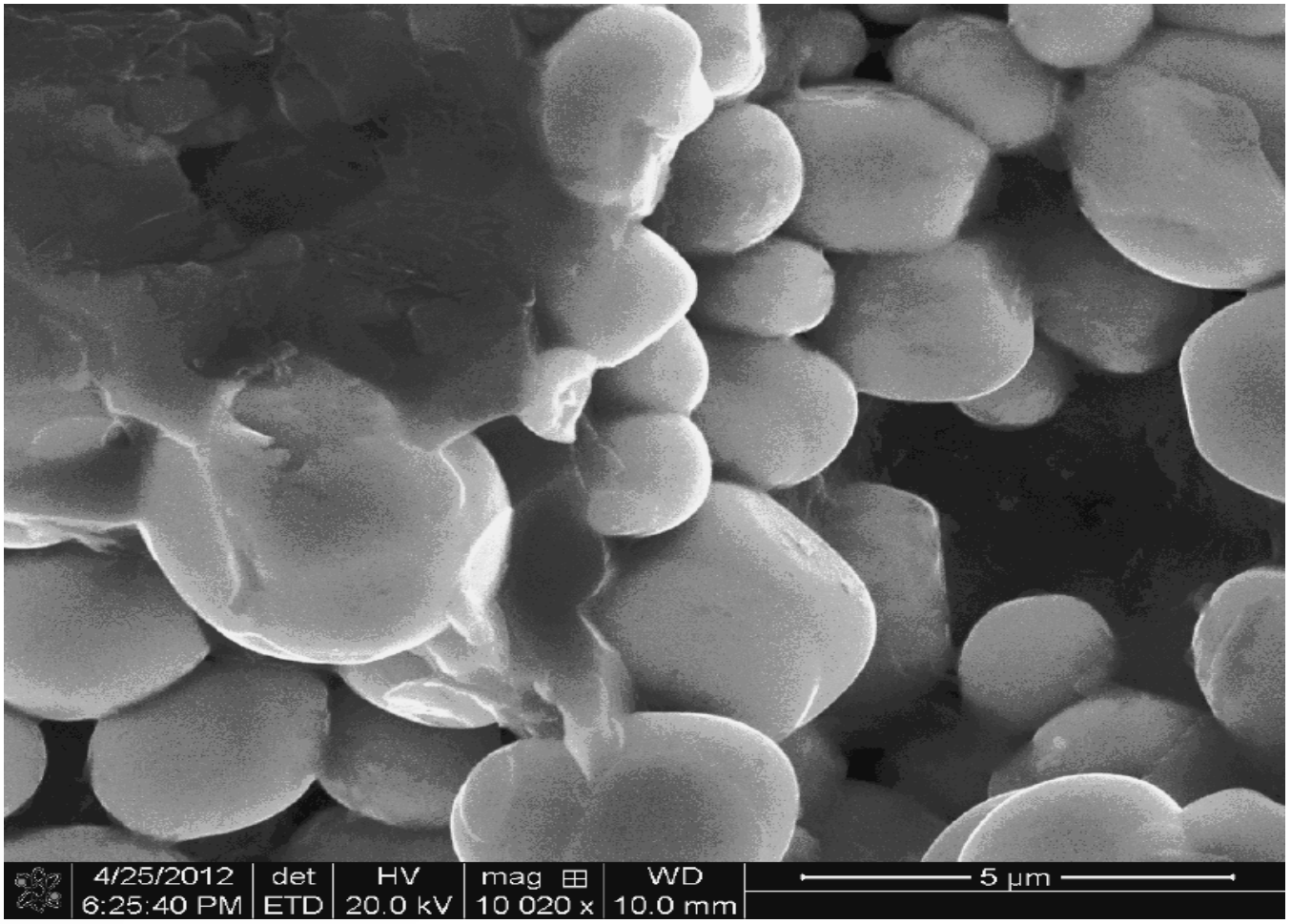
# $Nb_2AlC(001)/Nb(100)$ Interface



# $Gd_2Zr_2O_7(100)/Nb_2AlC(001)$ Interface



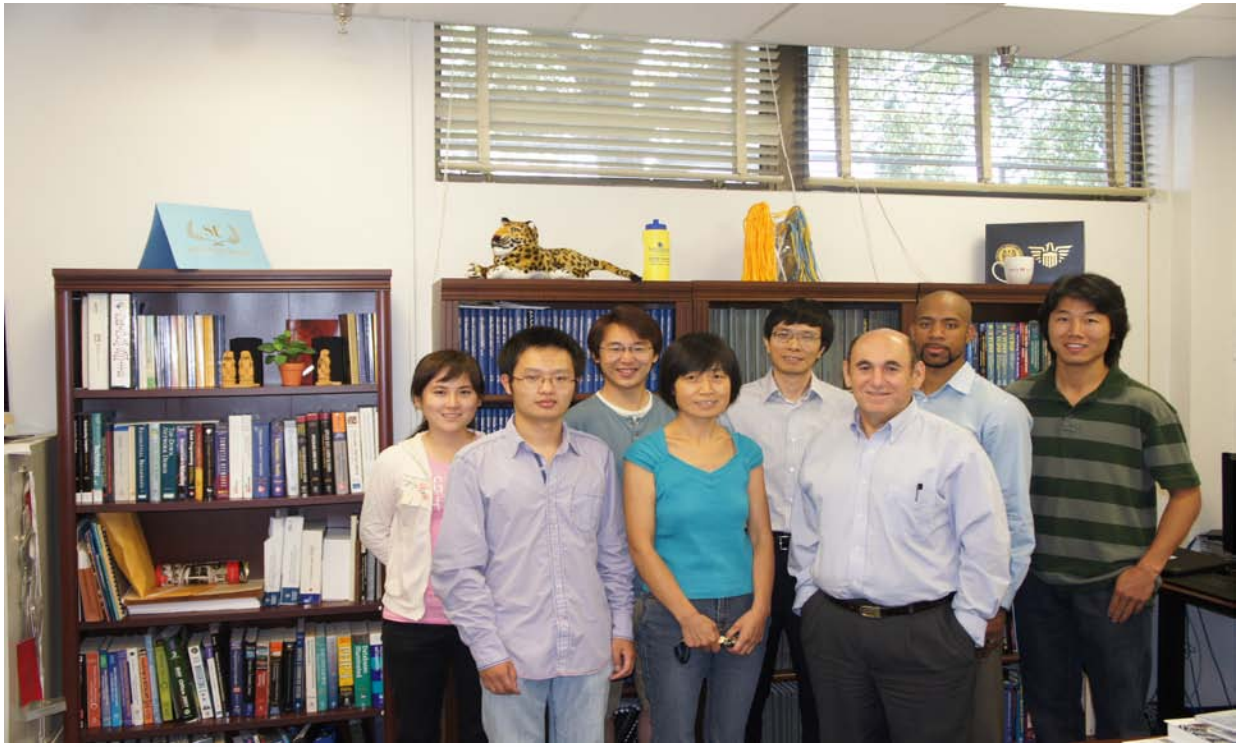
# SEM of $Nb_3Al_2C$



# Future Work

1. $Nb_2AlC$/Nb and $Gd_2Zr_2O_7$/$Nb_2AlC$ interface energy calculation (with and without Y/Mo doping).
2. *Ab initio* interatomic potentials building for $Nb_2AlC$/Nb system.
3. HPC MD simulation on $Nb_2AlC$/Nb and $Gd_2Zr_2O_7$/$Nb_2AlC$ to finalize the stable structures.
4. TGA and DSC experimental verification on the screened candidates.

# HPC Group at SUBR



Front left to right: Zhao, Bai, and Khosravi
Back left to right: Yao, Lei, Yang, Baham, and Guo

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