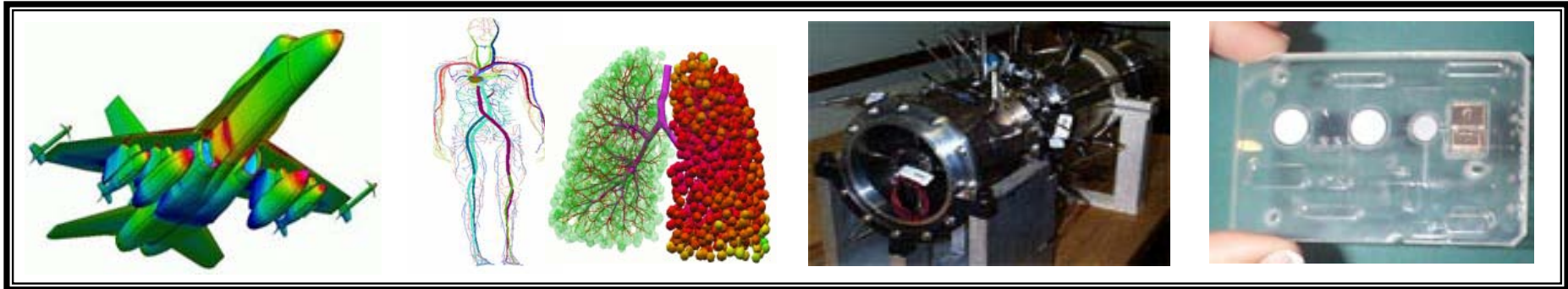


Ab Initio and Multi-Scale Study of Alloy Systems



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DE-FE0005867 award
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AGENDA

- INTRODUCTION
- APPROACH
- REAXFF DEVELOPMENT
- REAXFF MOLECULAR DYNAMIC MODELING
- QUESTIONS AND DISCUSSION

INTRODUCTION

CFD Research Corporation

Advanced Technology and Service Company

- Supporting Federal Agencies and global businesses since 1987
- Over 70% staff with advanced degrees
- 50+ patents (awarded & pending)

CFDRC develops cutting-edge technologies and provides innovative solutions for:



Energy & Materials



Biomedical & Life Sciences



Aerospace & Defense



HQ – Huntsville, AL



Bio-Laboratories
HAIB, Huntsville, AL



Engineering T&E
Scottsboro, AL

Gov't Sites

MSFC, Huntsville, AL
USAARL, Ft. Rucker, AL

Why CFDRC? *Valuable Technology Partner*

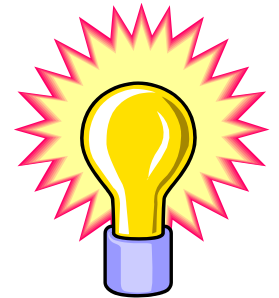
Pioneering Physics-based Simulations

Coupled Multi-physics, Multi-scale, Multi-fidelity simulations of fluid, thermal, chemical, mechanical, electrical and biological phenomena for real world applications.



Better insights and better decisions for:

- new concepts and designs
- improved operations and safety
- reduced development time and cost



Complimentary Design, Fabrication, T&E Expertise and Facilities for:

- Combustion, Propulsion and power systems
- Biomedical and Energy devices

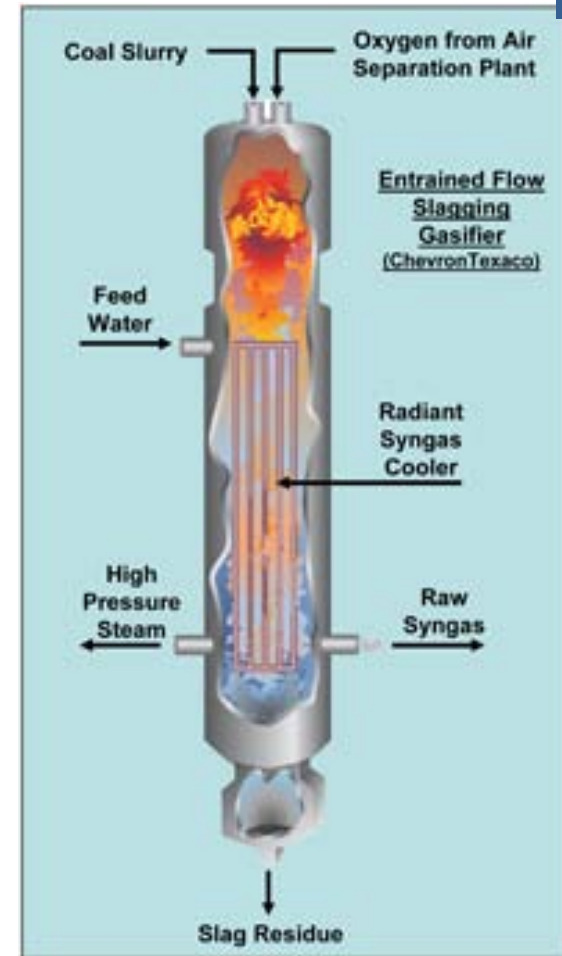


Facilitates better products & better systems.

MATERIALS FOR A CLEAN ENERGY ECONOMY

- New materials with micro-to-nano features (e.g., grain shape and size distribution, grain boundary character, grain orientation, and texture) are of vital importance for a clean energy economy.
- However, the current trial-and-error material development methodology is expensive (> \$10M) and time consuming (10 to 20 years).
- Activity and excitement over new materials have enhanced, driven by government investment (<http://www.whitehouse.gov/blog/2011/06/24/materials-genome-initiative-renaissance-american-manufacturing>).
- Increasing trend is to use the advances in multi-scale simulations and high-throughput screening.
- CFD Research Corporation (CFDRC) and Pennsylvania State University (PSU) have teamed in this project to develop, demonstrate, and validate computational capabilities for predictive analysis of interactions at the grain boundary of refractory alloys.

- High-chromia refractories could last ~ 3.5 years in a slagging coal gasifier under optimum conditions (Fahrion et al 1999).
- However, commercial gasifiers must often use suboptimal feed stocks and operating conditions, and the refractory lifetime is often reduced to < 1.5 years (Stiegel et al 2006).
- The expense of refractory replacement in a large-scale gasifier can exceed \$1 M (Stiegel et al 2006).
- One of the most frequently cited R&D needs is improvement of fundamental understanding of refractory alloy degradation mechanism.



REFRACTORY ALLOYS AND SLAG COMPOSITION

- Majority of reported refractory alloys utilized in a slagging coal gasifier are chromia (Cr_2O_3) and alumina (Al_2O_3) based refractories.
- Chrome oxide materials showed low chemical solubility in gasifier slags by forming high melting spinels/solid solutions with iron oxides (Bennett 2007 and Kim et al 2008).
- In the past, non-chromia refractory compositions did not show comparable performance to high chrome oxide refractory materials.
- Only a few materials (ZrO_2 etc.) have the potential to resist slag corrosion as good as chrome oxide.

	Datong ash	Chromia refractory
SiO_2	55.2	8.3
Al_2O_3	19.0	24.6
Fe_2O_3	15.4	0.7
CaO	6.2	1.8
Cr_2O_3	–	52.7
ZrO_2	–	9.4
MgO	1.0	0.4
MnO	0.3	–
Na_2O	0.5	1.0
K_2O	1.4	–
TiO_2	0.8	1.8
P_2O_5	0.2	–
SUM	100	99.9

Component	Wt %
Cr_2O_3	92
Al_2O_3	4.7
P_2O_5	3.3

Component	Wt%
SiO_2	47
Al_2O_3	25
Fe_2O_3	17
CaO	6
MgO	1
Na_2O	1
TiO_2	1
K_2O	2

• Refractories and ash (wt %), Kim et al 2008

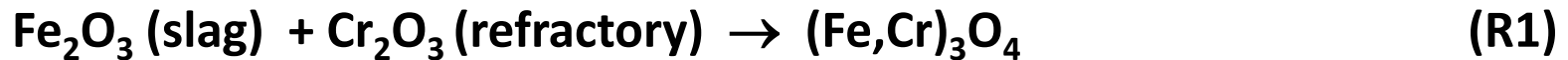
• Refractories and ash, Besmann 2008

FAILURE MECHANISMS OF SLAGGING COAL GASIFIER

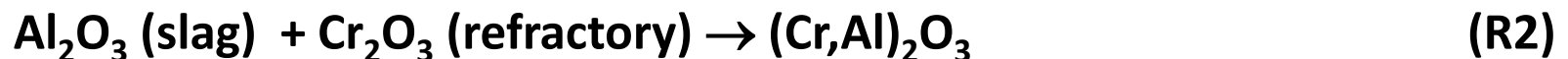
- Slagging coal gasifier typically operates at high temperature (1300–1600 C) and pressure (2–3 MPa) conditions (Williford et al 2008).
- Industrial refractories have a finite amount of porosity, including initial flaws and joints between bricks.
- These defects are responsible for penetration of the slag into the interior of the refractory by permeation and infiltration mechanisms assisted by the pressure gradients within the gasifier, along with capillary and diffusive intrusion mechanisms.
- The thermal–chemical–mechanical interactions between the refractory and slag result in degradation by corrosion, erosion, cracking, and spalling.

SLAG/REFRACTORY INTERFACE REACTIONS

- Slag penetration and chemical corrosion are the primary causes for refractory degradation in a gasifier (Bennett, et al., 2007 and Kim et al. 2008).
- Dominant reaction product at the slag/refractory interface $(\text{Fe,Cr})_3\text{O}_4$ is formed as a result of the following reaction:

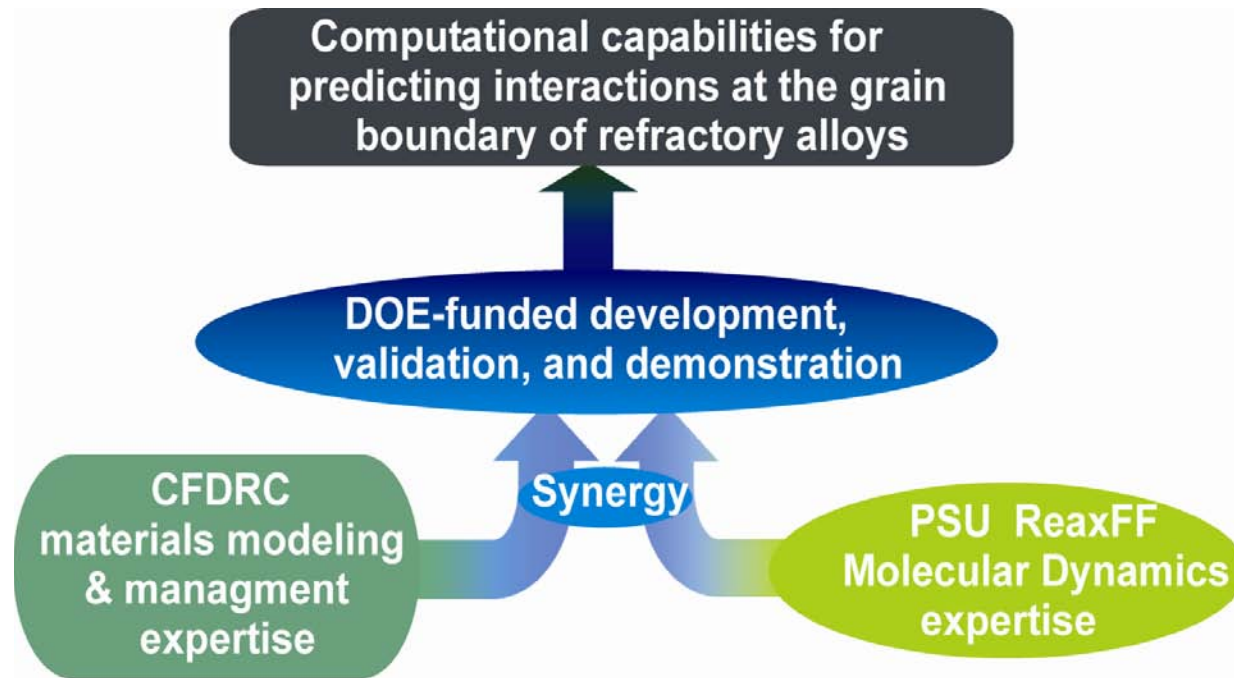


- Once Fe in the slag is depleted, Al_2O_3 in the slag interacted with Cr_2O_3 :



- It was found that the densified large Cr_2O_3 grains were less affected by the reaction (R2) than the Cr_2O_3 small particles observed in the refractory alloys before the tests.

OVERALL PROJECT OBJECTIVES

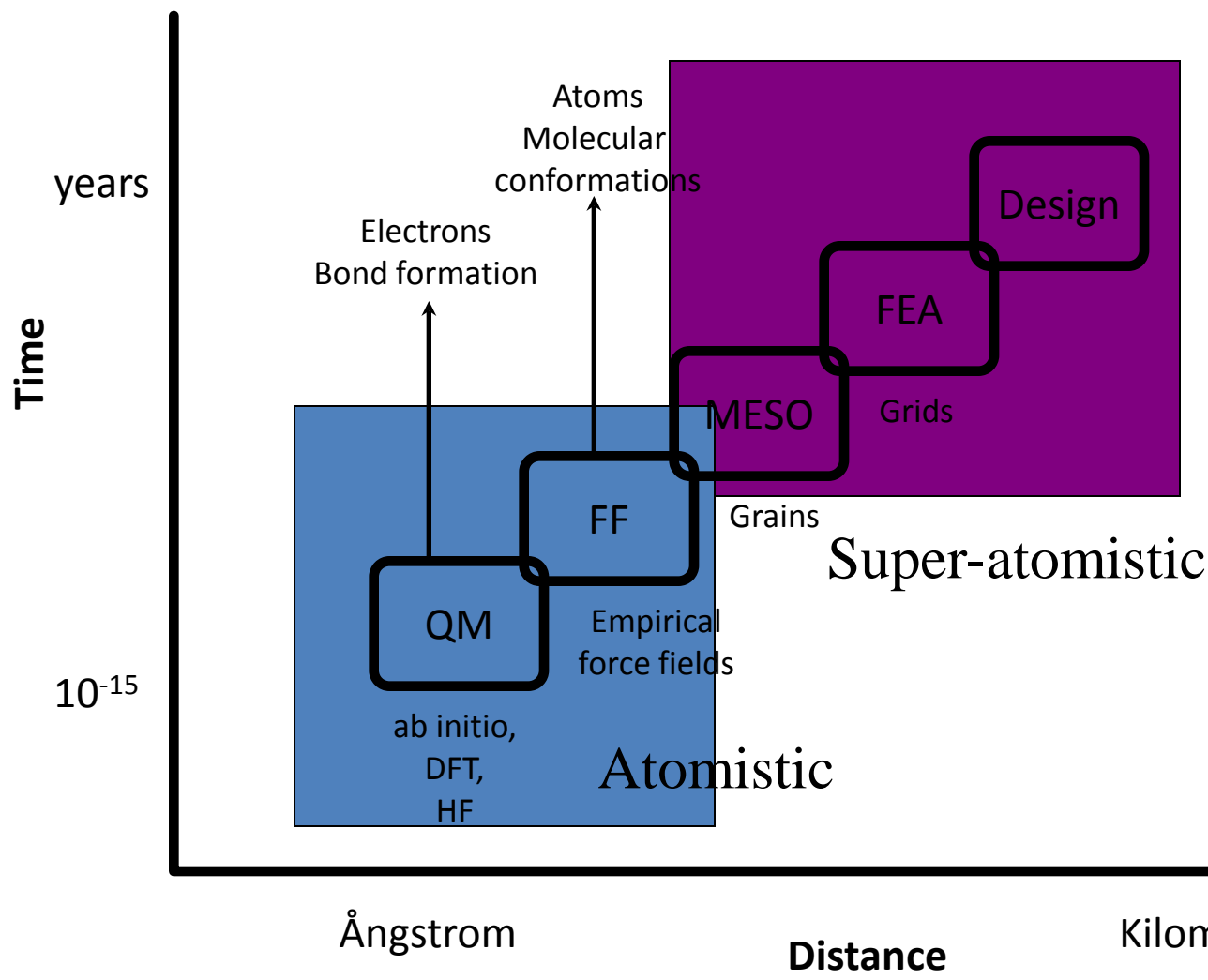


- The overall objectives of the proposed project are:
 - Develop computational capabilities for predictive analysis of grain boundary interactions using large-scale ReaxFF-Molecular Dynamics (MD) simulations
 - Assess degradation mechanisms, and
 - Design approach to limit segregation at the grain boundaries of refractories for coal gasification and related processes

APPROACH



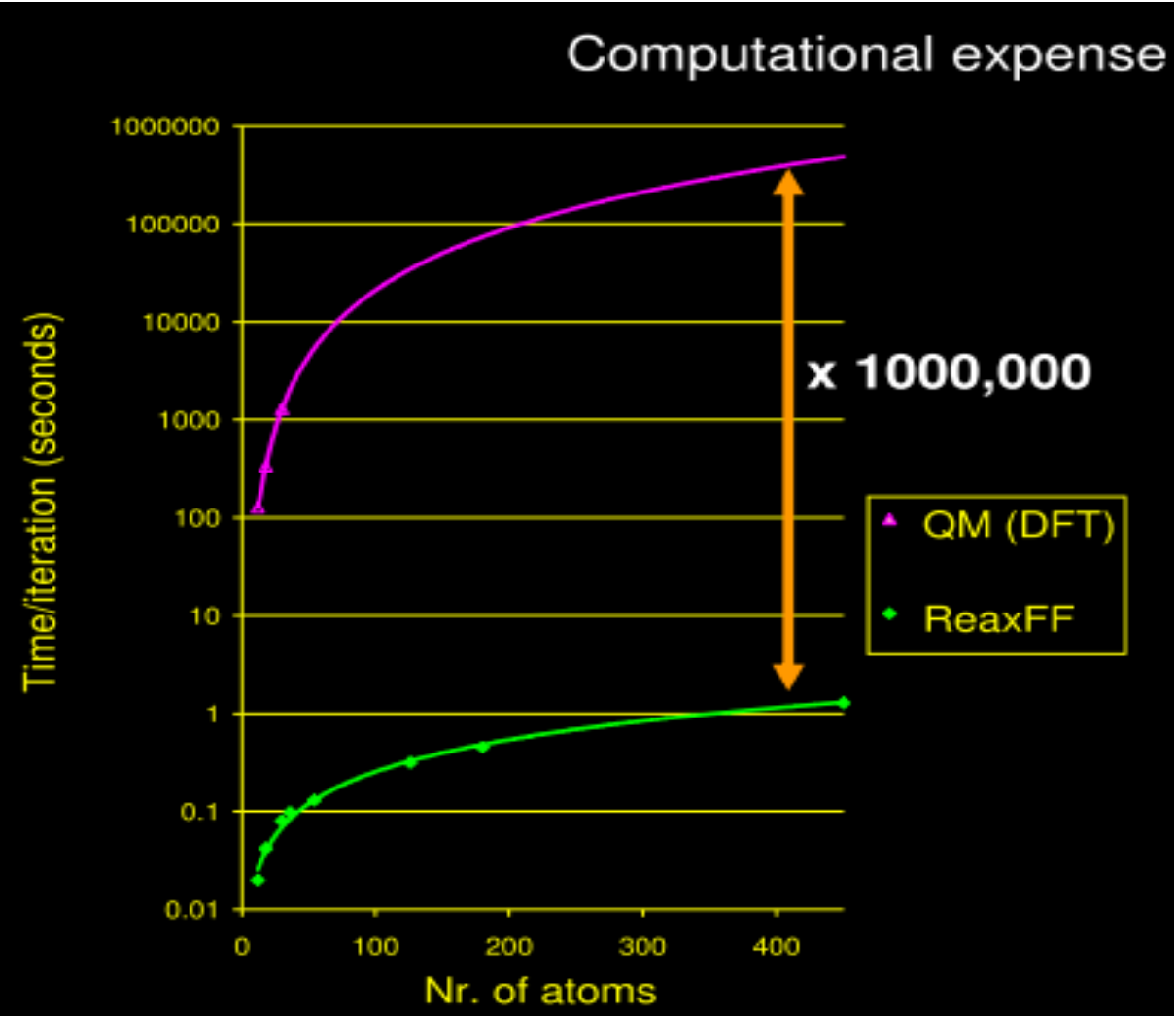
MULTISCALE MODELING FRAMEWORK



- QM methods:
- Fundamental
 - Expensive, only small systems
- FF methods
- Empirical; need to be trained
 - Much cheaper than QM, can be applied to much larger systems



REAXFF REACTIVE FORCE FIELD METHODOLOGY



REAXFF FORCE FIELD DEVELOPMENT



Method: Plane-wave Basis Density Functional Theory (DFT)

- All calculations were performed using **VASP 5**
- 0 K electronic structures were calculated by solving the Kohn-Sham equation using plane-wave basis set.
- Structures were optimized by decoupling the quantum representation of electrons from the classical representation of nuclei (Born-Oppenheimer approximation).



More calculation details:

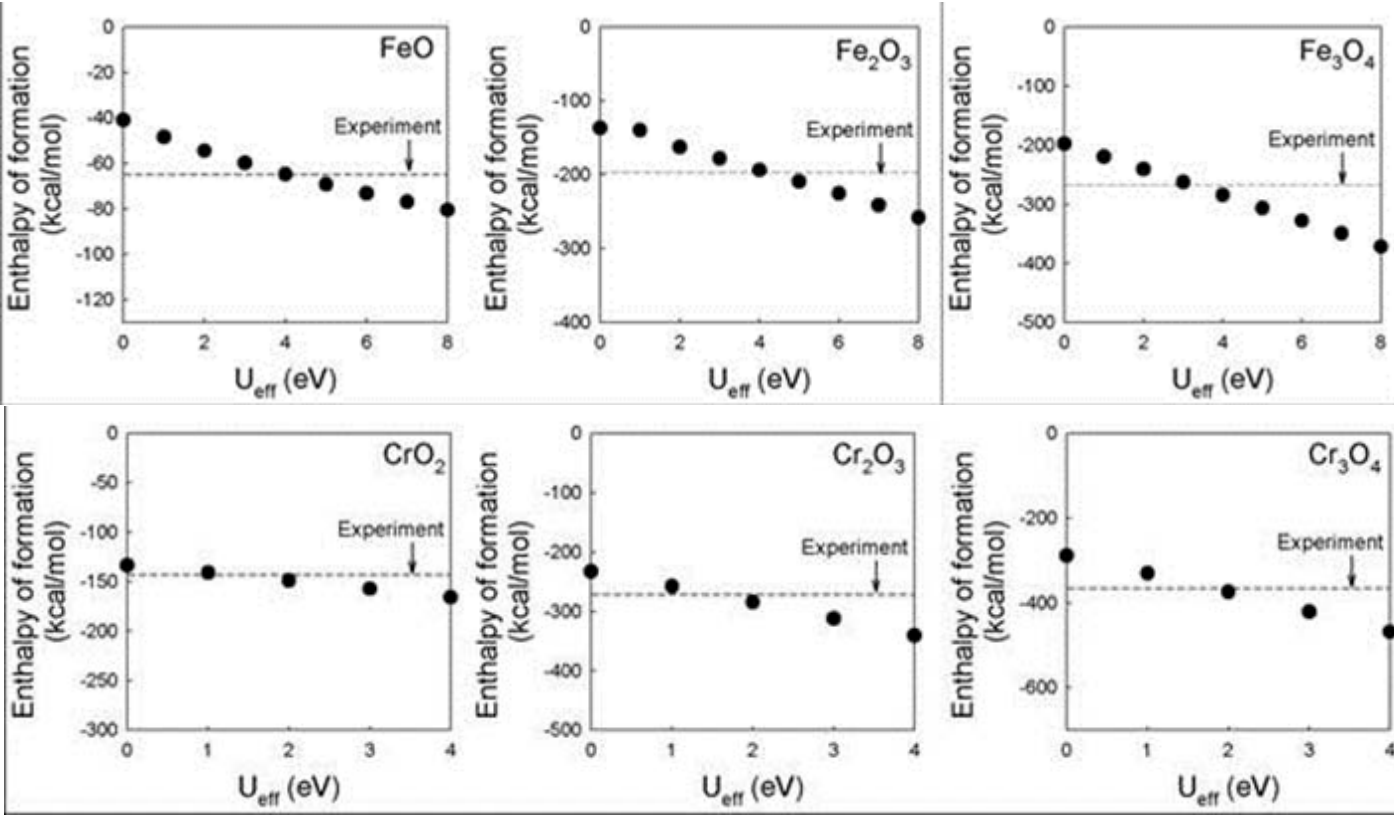
- Projector-augmented-wave (PAW) method for ion-electron potential
- Perdew-Burke-Ernzerhof (PBE) exchange correlation functional
- Plane-wave cut off energy of 400 eV (standard for oxides and sulfides)
- Interval in momentum space for k-point sampling: $0.20 \text{ \AA}^{-1} - 0.25 \text{ \AA}^{-1}$
- Spin polarization considered for all calculations

DFT+U STRUCTURE-ENERGY APPROACH

- DFT is capable of producing reasonably accurate predictions for electronic and structural properties of many materials systems
- Traditional DFT with simple delocalized exchange-correlation functional from LDA or GGA does not properly describe partially filled d- or f-orbital electron configurations
- For example, DFT predictions for iron oxide and chromium oxide were found to be off by about 100 kcal/mol
- A cost-effective approaches to take the strong correlation effect into account is DFT+U method
- Idea is to add an explicit correction to the localized electronic states by including the on-site Coulomb interaction of the semi-core level such as d- or f-orbital
- In such an approach, a multi-orbital mean-field Hubbard-type potential called the U-potential is added to the original density functional Hamiltonian

ENTHALPIES OF FORMATION FOR FeOx AND CrOx

- DFT+U structure-energy calculations for FeOx and CrOx systems were performed in this project
- Enthalpy of formation based on DFT+U formalism with varying the effective U potential in range of 0-8 eV for iron oxide structures and 0-4 eV for chromium oxide structures were obtained



• Calculated enthalpies of formation for iron oxide crystals

• Calculated enthalpy of formation calculated for chromium oxide crystals

- To determine the effective U potential which would give the best predictions for oxide crystals we formulated a simple optimization function:

$$\lambda(U_{\text{eff}}) = \left[\Delta_{\text{err}}^{\text{X1}}(U_{\text{eff}}) \right]^2 + \left[\Delta_{\text{err}}^{\text{X2}}(U_{\text{eff}}) \right]^2 + \left[\Delta_{\text{err}}^{\text{X3}}(U_{\text{eff}}) \right]^2$$

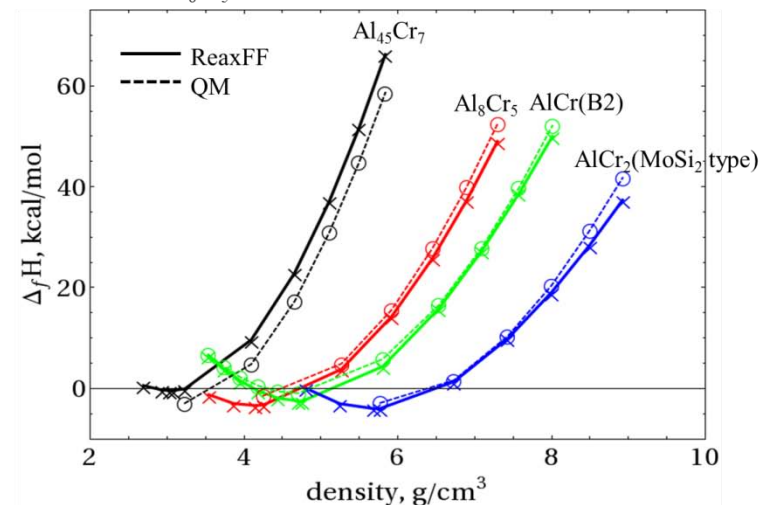
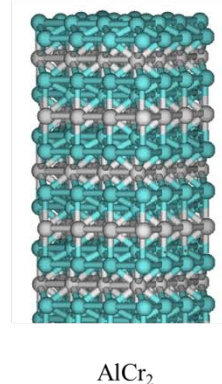
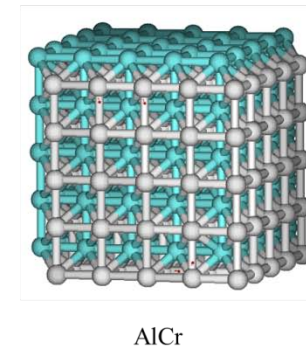
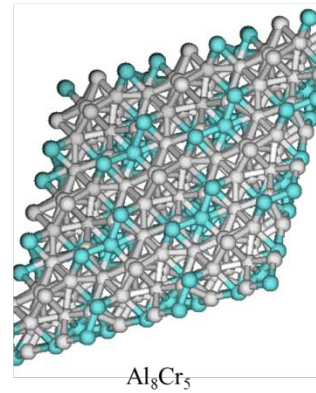
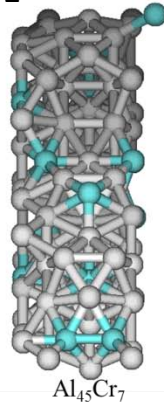
Here,

- $\Delta_{\text{err}}^{\text{X}}$ - Difference between theoretical and experimental enthalpies of formation for crystal X
- X1, X2, and X3 - FeO, Fe₂O₃, Fe₃O₄ for iron oxide, and CrO, Cr₂O₃, Cr₃O₄ for chromium oxide
- U_{eff} - Effective U potential which minimizes the optimization function (3.6 eV for iron oxide and 2.0 eV for chromium oxide)

- Determined U_{eff} potentials value were applied to all DFT (+U) calculations to produce EOS data for the Fe-O/Cr-O binary systems as well as the Fe-Cr-O ternary systems.

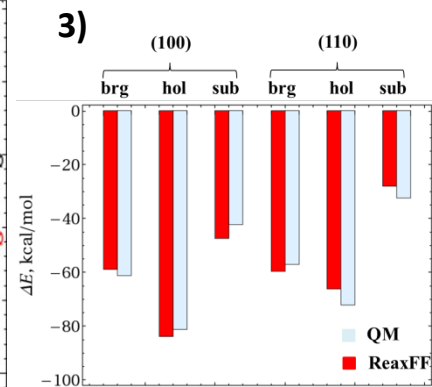
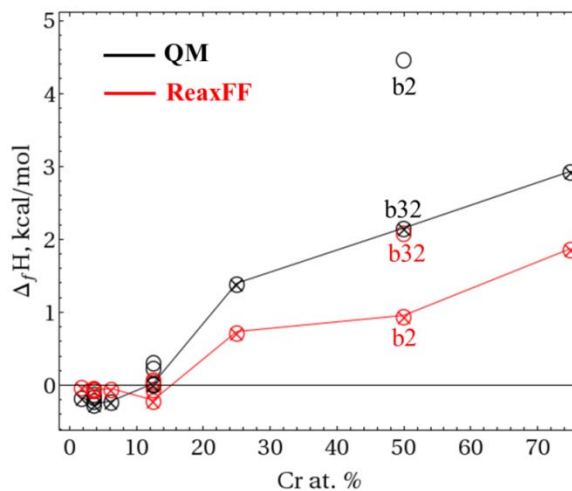
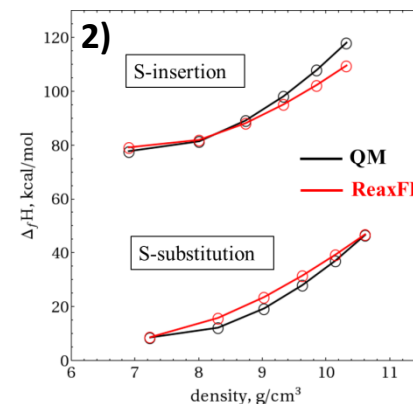
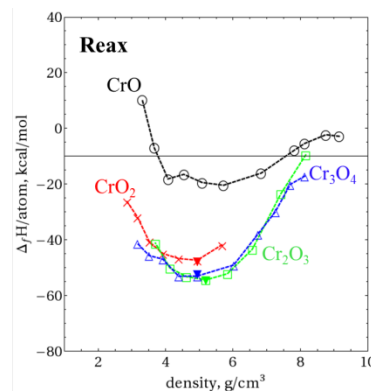
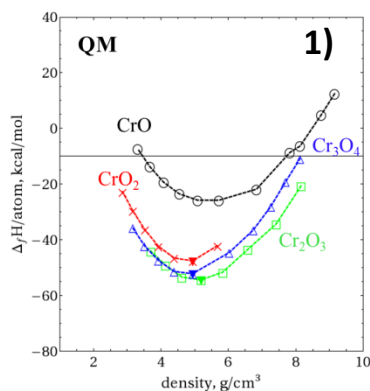
HEAT OF FORMATION FOR AL/CR-ALLOYS

- Al/Cr alloys improve the high-temperature oxidation resistance and mechanical properties
- For example, small amount of AlCr_2 in Al matrix can improve the corrosion resistance and hardness
- ReaxFF was trained against the QM for various Al/Cr (e.g., $\text{Al}_{45}\text{Cr}_7$, Al_8Cr_5 , $\text{B}_2\text{-AlCr}$ and MoSi_2 type AlCr_2)
- The Al/Cr bond and van der Waals parameters were tarined against the energy-volume relationship over a wide range of volume
- Heats of formation for the Al/Cr phases were well reproduced in ReaxFF



REAXFF FORCE FIELD DEVELOPMENT FOR Cr-O/S/Fe

- The force field was directly derived from QM including 1) EOS for various oxide phases of Cr/O, e.g., Cr(II)-, Cr(III)-, Cr(IV)- and Cr(II,III)-oxide, 2) S-insertion/substitution into bcc-Cr and 3) S-binding energies on Cr(100, 110). (Cr-surface energies, Mulliken charges and Fe/Cr₂O₃ system were also added to the training set (data not shown).
- Sulfur occupying Cr-site is more stable than the interstitial sulfur.
- The formation of Fe/Cr binary alloys at low Cr-conc. is favorable, while it is not at high Cr-conc.

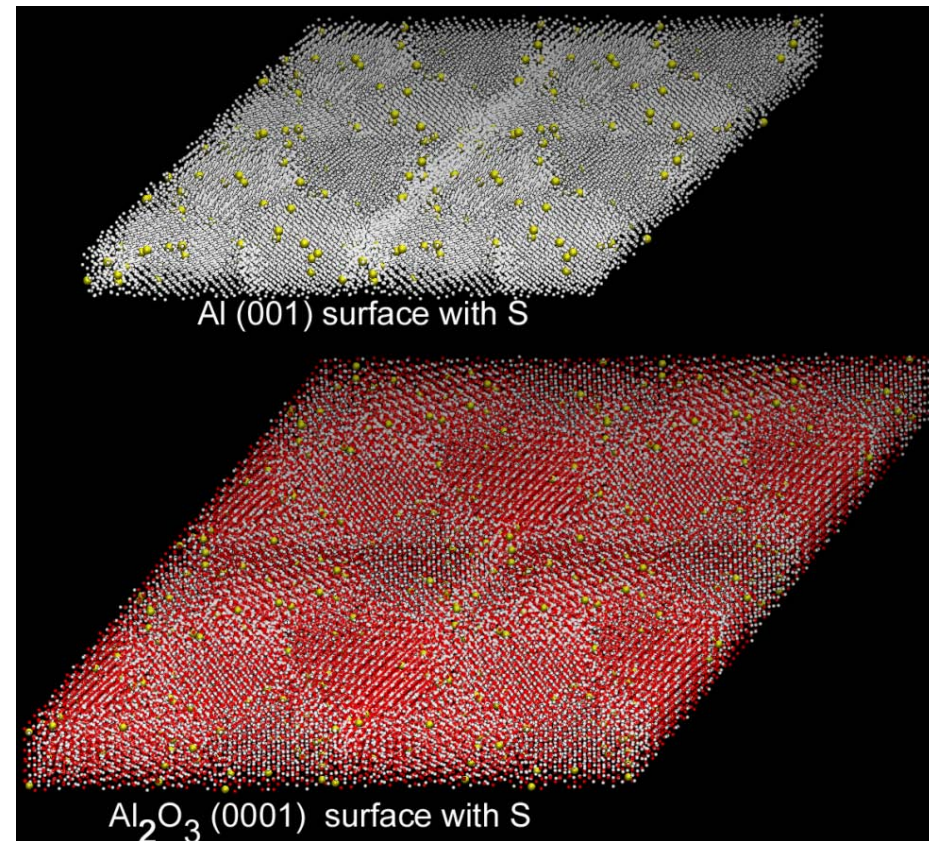


REAXFF MOLECULAR DYNAMIC MODELING



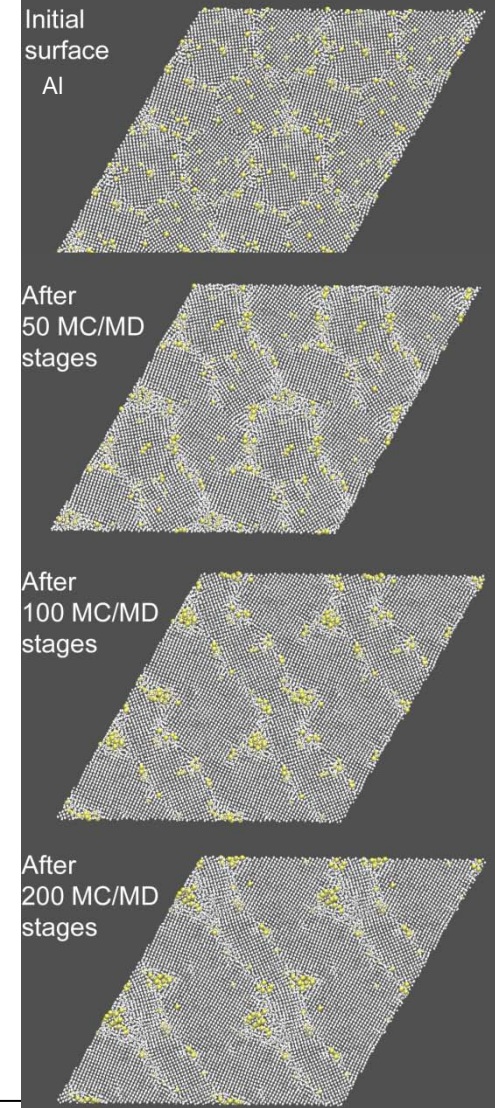
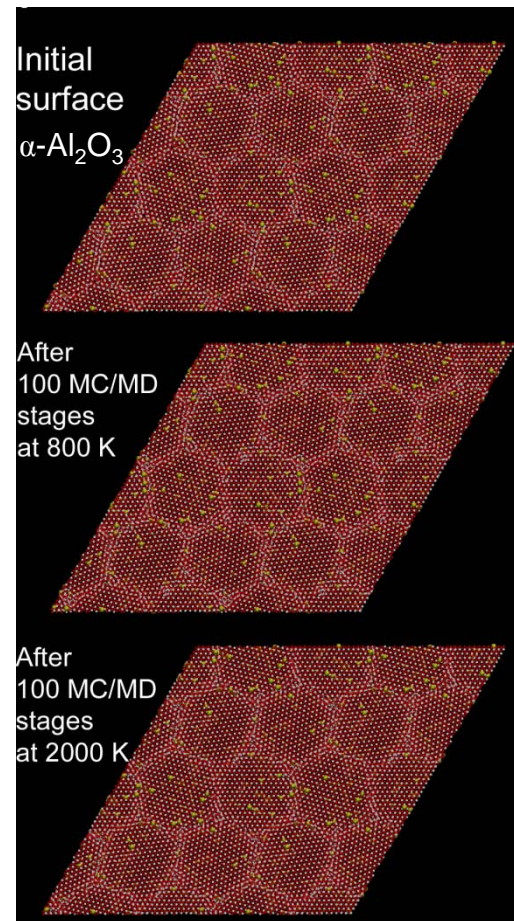
SULFUR DIFFUSION AND SEGREGATION IN FCC Al AND α -Al₂O₃

- Sulfur is a common impurity in metal alloys
- It tends to segregate to the grain boundaries leading to the grain boundary embrittlement
- Structures for FCC Al and α -Al₂O₃ with grain boundaries and Al-S substitutional defects were created
- To represent random orientation of realistic grain structures, each grain was rotated from the original direction by 0, $\pi/8$, $\pi/4$, and $3\pi/8$ (in radian) in xy-plane
- The z-direction of the crystal corresponded to (001) direction for FCC Al and (0001) direction for α -Al₂O₃
- 1 at% of sulfur defects were introduced to the grain structure by randomly assigning Al-S substitutional defects to the grain structures with given defect concentrations

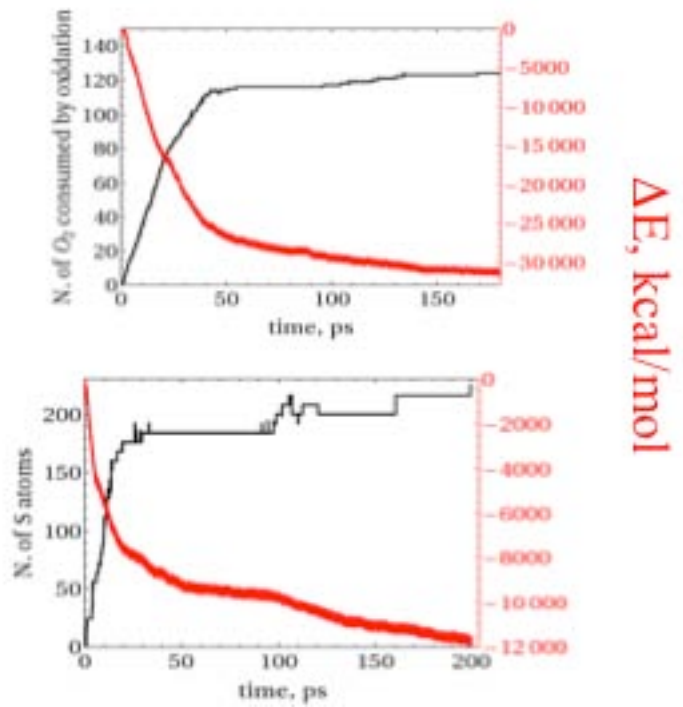
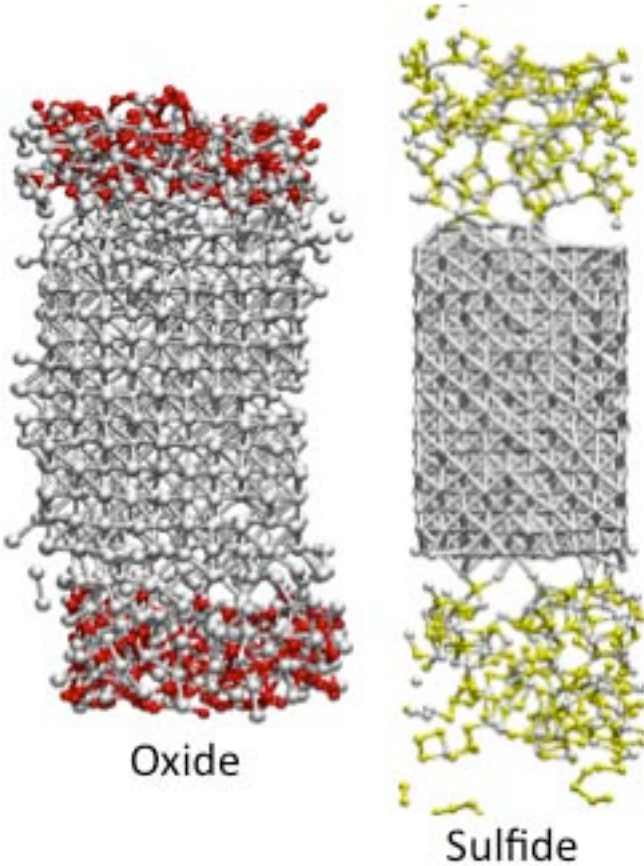


SULFUR DIFFUSION AND SEGREGATION IN FCC Al AND α -Al₂O₃ (CONT.)

- Large-scale ReaxFF-MC/MD calculations were performed for constructed FCC Al and α -Al₂O₃ structures
- S tends to segregate, especially at the boundaries, in a good agreement with the literature trends
- Snapshot obtained after 100 MC/MD stages demonstrates that several grain boundaries are dissolved due to the segregation of S in small clusters
- In contrast, the simulations performed for α -Al₂O₃ demonstrated the absence of substantial S diffusion and segregation
- According to thermodynamics it is nearly impossible to replace oxygen – metal bonds by sulfur – metal bonds
- Also, there is no free space at an intact α -Al₂O₃ lattice for segregation of the big negatively charged sulfur



COMPARISON OF Al-OXIDE VS. Al-SULFIDE GROWTH



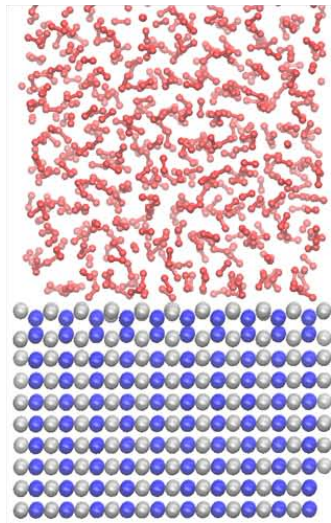
- Oxidation results in a dense oxide, sulfide growth gives a low-density interface
- Oxidation is significantly more exothermic than sulfide growth



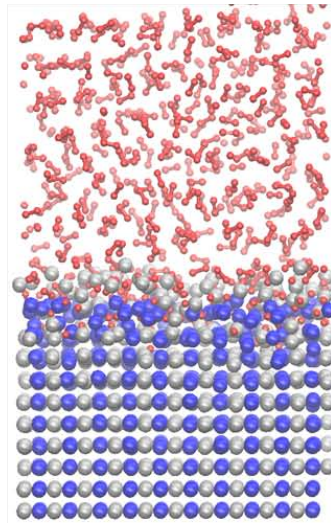
PROTECTIVE OXIDE LAYER FORMATION IN Al-BASED ALLOYS

- Oxide scale nucleation starts with the growth of less stable alumina phase (dominantly θ - Al_2O_3)
- ReaxFF-MD/MC calculations were used to understand the mechanism of oxide nucleation on NiAl
- Separation between aluminum-rich and nickel-rich regions begins as early as about 10 ps
- After about 50 ps, a thin aluminum oxide film with a small fraction of nickel oxide clusters is formed

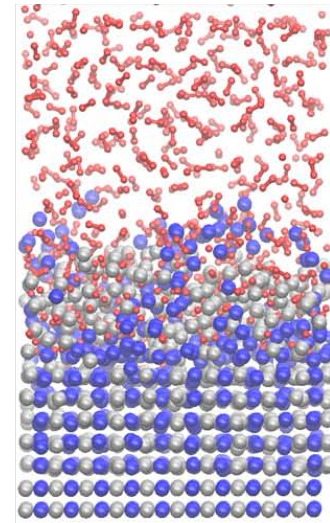
- This is a clear trend to quickly form protective aluminum oxide layers on top of the alloy surfaces



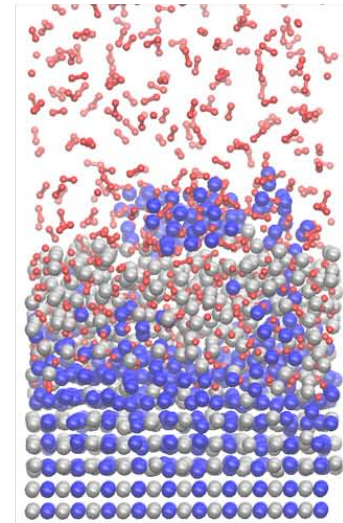
0.1 ps



1 ps



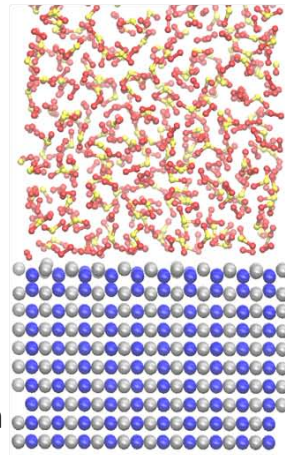
10 ps



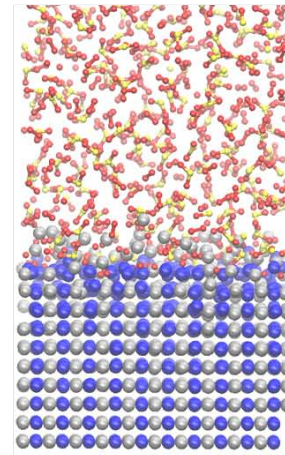
50 ps

PROTECTIVE OXIDE LAYER FORMATION IN Al-BASED ALLOYS (CONT.)

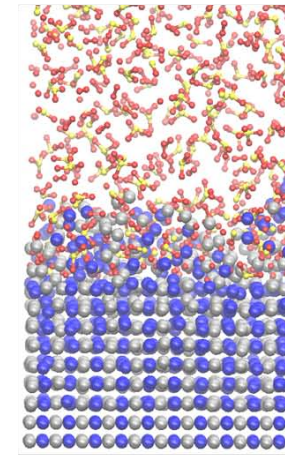
- There are noticeable differences when SO_2 is introduced to the same oxidation environment
- First, rate of overall oxidation becomes noticeably slower and the resulting depth of oxygen penetration differs by over two atomic layers after 50 ps
- Second, there is not as distinctive separation between the nickel-rich and the aluminum-rich region in the oxidized surface area compared to the oxygen-only case
- Such difference is attributed to the strong S-O bond in SO_2 molecules even after SO_2 surface adsorption
- Unlike the O-O bond in O_2 which almost immediately dissociates on a metal surface, S-O bond in SO_2 hardly dissociates and eventually blocks the diffusion pathway of nearby oxygen atoms as well as Ni and Al atoms drifting to the surface
- As such, the rate of initial penetration by oxygen atoms in the slab surface is significantly slowed down by adsorbed SO_2 atoms
- At the same time, the atomic diffusion of Ni and Al atoms are also slowed down so that the effective phase separation between nickel oxide and aluminum oxide is inhibited



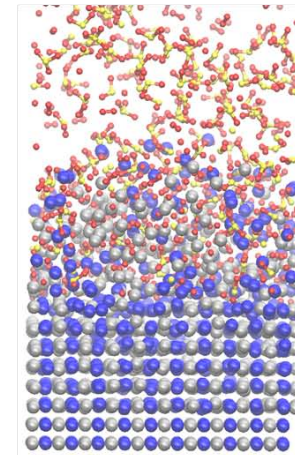
0.1 ps



1 ps

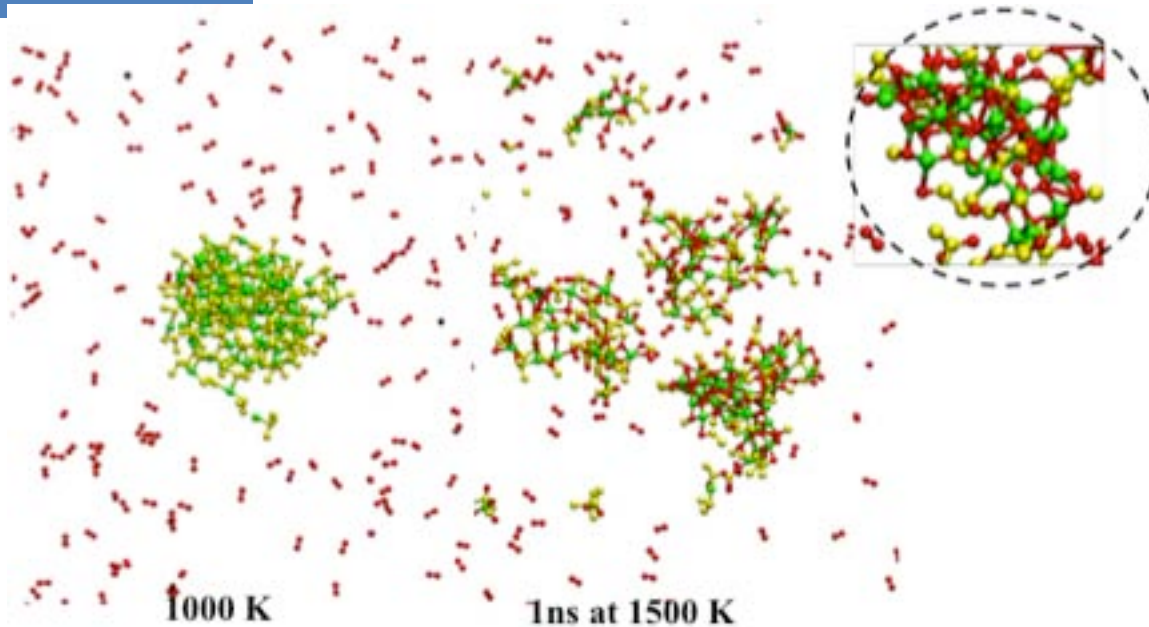


10 ps

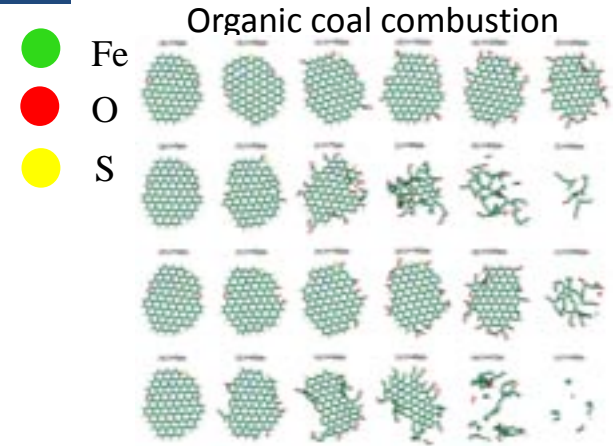


50 ps

SIMULATIONS ON PYRITE OXIDATION AT T=1500K TOWARDS COAL COMBUSTION

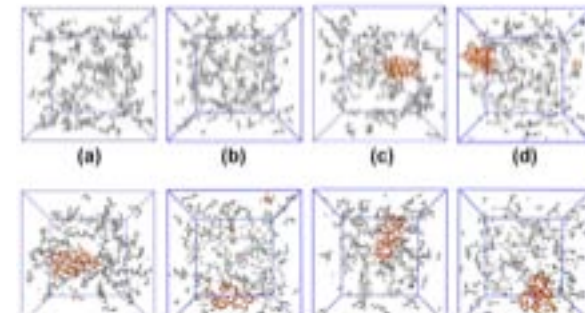


Fe-Al-O fragments : $Fe_7S_{11}O_9$, $Fe_3S_8O_6$, $Fe_{19}S_{58}O_{47}$, $Fe_{34}S_{37}O_{51}$, $Fe_{24}S_{48}O_{50}$,
 $Fe_9S_{13}O_{22}$, FeS_3O_3 , $Fe_2S_5O_6$, FeS_6O_2 , FeS_2O_5 , SO



Castro, van Duin et al. Comb.Flame 2012

Si

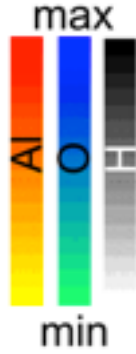


Castro and van Duin Comb.Flame 2013

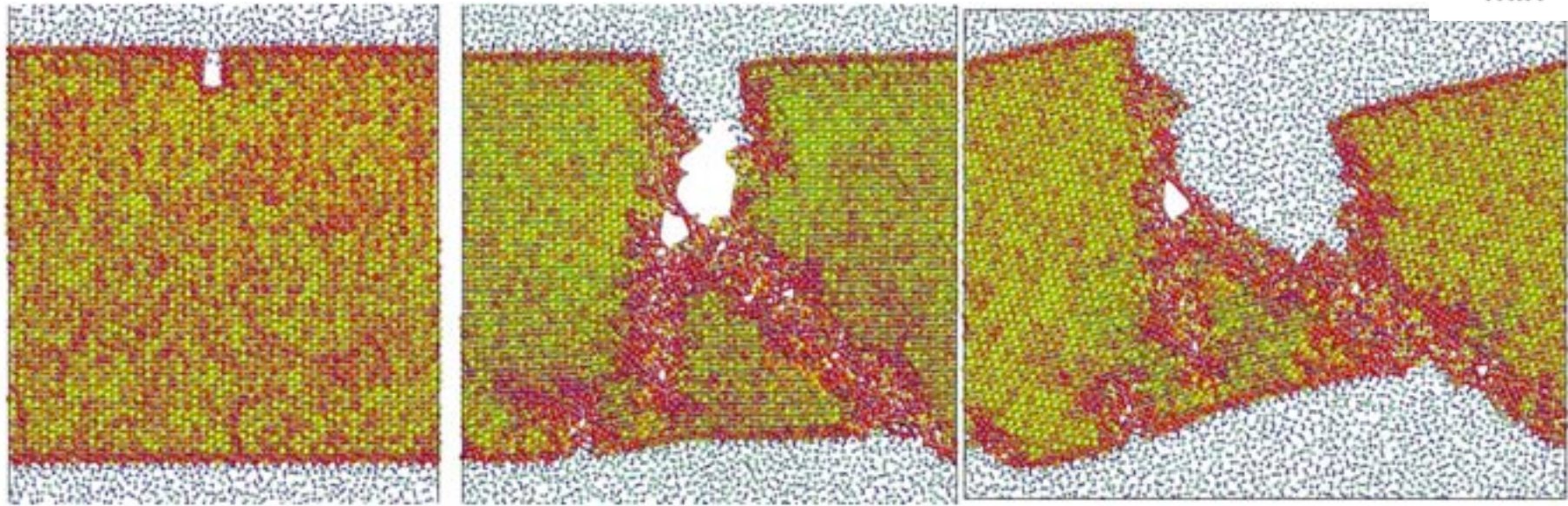
- Pyrite is an important inorganic component of coal materials
- We can now simulate both the organic and inorganic coal components
- Next step – complete coal (silicates/pyrite/organic) combustion



CRACK PROPAGATION IN WATER/AL-OXIDE INTERFACE



Maximum principal stress distribution



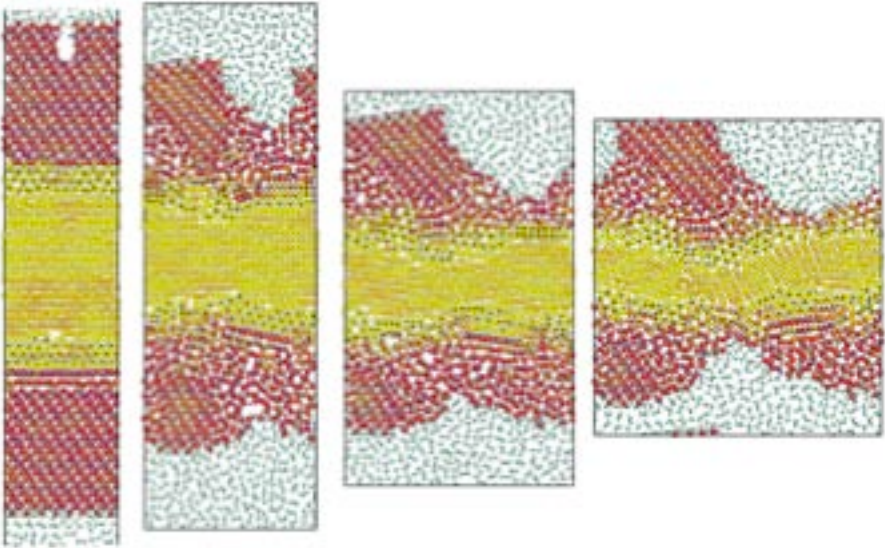
0

6

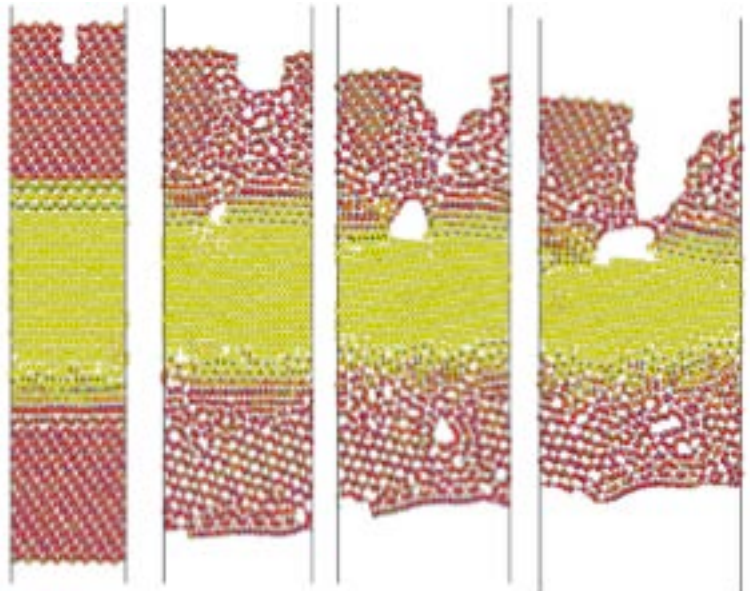
- 20,000 atoms, LAMMPS/ReaxFF, 4 processors
- Water assists in the crack propagation by transforming the oxide into a weaker hydroxide
- Water front trails after the crack – related to high strain rate

WATER EFFECT ON CRACK PROPAGATION IN A Al-OXIDE/Al-METAL INTERFACE

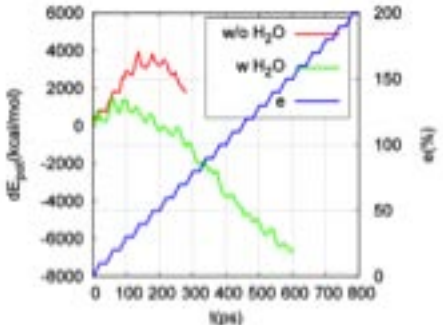
With water



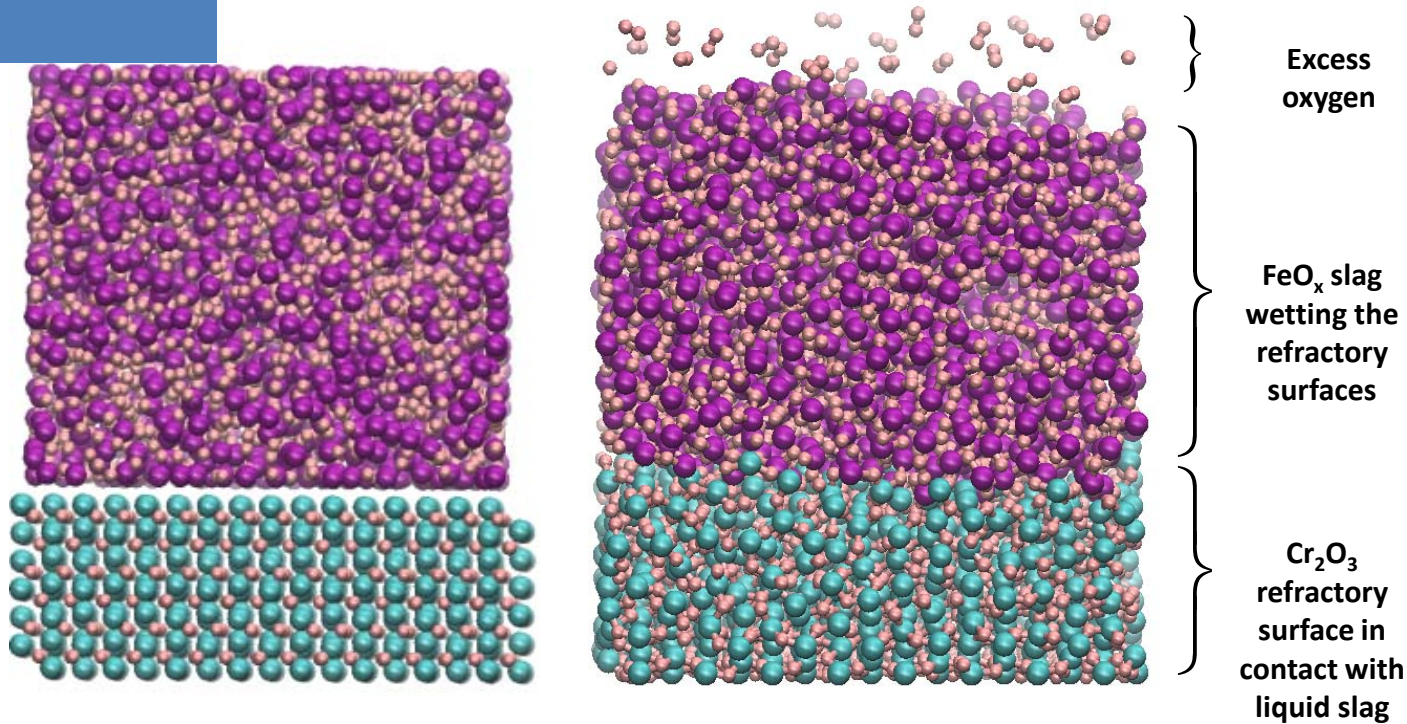
Without water



- 20,000 atoms, LAMMPS/ReaxFF, 4 processors
- Without water – brittle crack propagation; with water: ductile
- Presence of water makes crack propagation exothermic

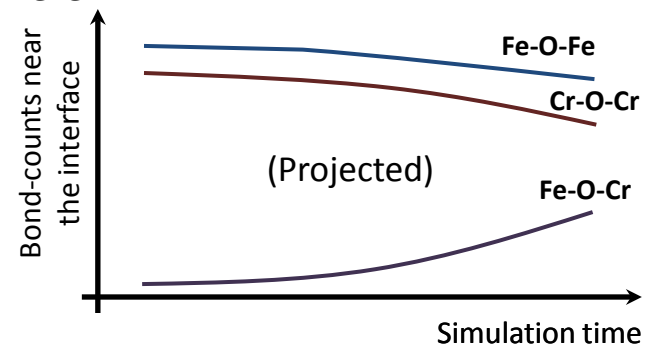


MODELING DEGRADATION AT Cr_2O_3 (REFRACTORY)/ FeO_x (SLAG)



Reactive MD simulation of refractory/slag interface at high temperature (2000 K)

- ReaxFF force field developed for Fe-Cr-O ternary systems were used to model the refractory/slag interface
- Nucleation and/or growth of any Fe-Cr-O complexes at the interface would indicate the degradation of refractory surface by the slag phase:



CONCLUSIONS



CONCLUSIONS

- ReaxFF potentials for Cr/Fe/Al/O/S interactions relevant to many industrially important alloys (i.e., steels, refractory alloys) were developed
- First-principles energetics data from QM calculations were used to evaluate the ReaxFF parameters
- QM calculations were performed using DFT+U approach applicable to systems with partially filled d- or f-orbital electron configurations
- Oxidation energies for different iron oxide crystals (Fe, Fe₂O₃, and Fe₃O₄) and chromium oxide crystals (CrO₂, Cr₂O₃, and Cr₃O₄) were analyzed to find the proper +U correction potentials
- Developed ReaxFF potentials for Cr-Fe alloy are reliable to the scale of 3 kcal/mol per atom for energy formation and correctly describe the thermodynamics of various structures

CONCLUSIONS (CONT.)

- Developed force fields were used to provide substantive insights to many important research questions
- Analysis of diffusion dynamics of Al adatoms on BCC Fe and Fe/O surface revealed that exchange diffusion is more favored for the Fe/O surface than for the Fe surface
- Modeling NiAl alloy surface oxidation demonstrated important role of sulfur surface segregation
- Rate of oxidation became noticeably slower and the resulting depth of oxygen penetration differed by over two atomic layers after 50 ps of simulations with and without SO₂
- This was attributed to the strong S-O bond in SO₂ molecules
- Large-scale ReaxFF-MC/MD calculations demonstrated the dissolving of grain boundaries due to sulfur segregation in FCC Al
- In contrast, the absence of substantial S diffusion and segregation for α -Al₂O₃ was demonstrated

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