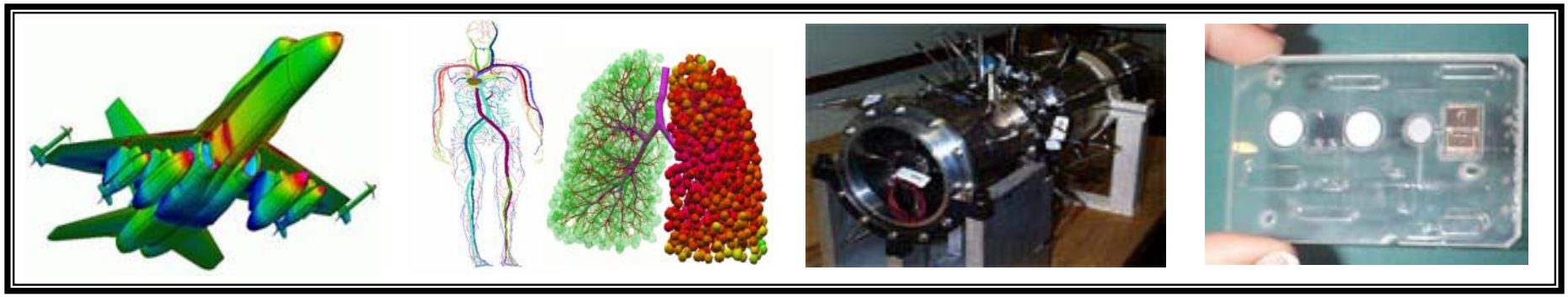
Delivering Breakthrough Solutions

25th Annual Conference on Fossil Energy Materials

Computational Capabilities for Predictive Modeling of Refractory Alloys



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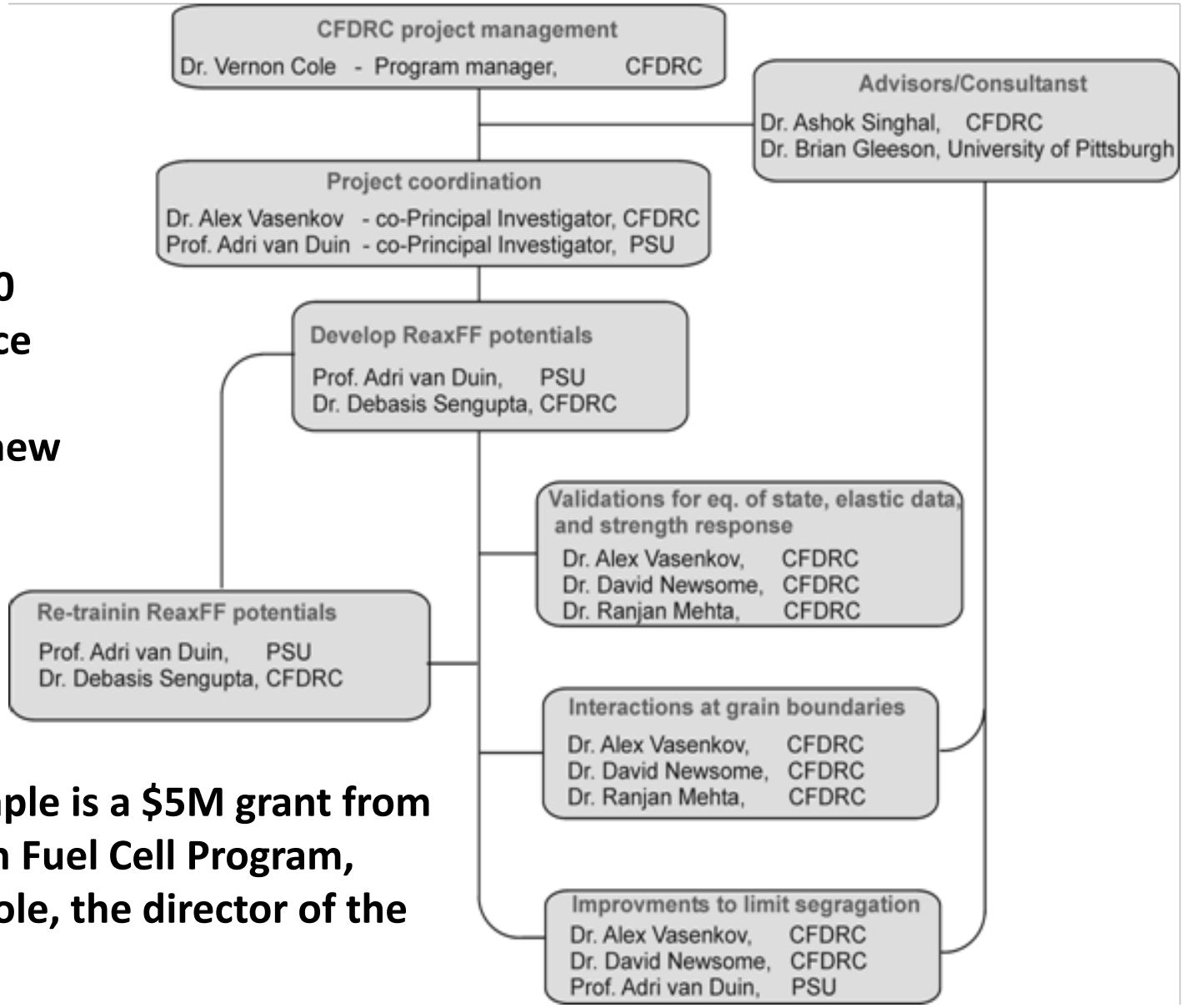
AGENDA

- Introduction to the project.
- EOS and elastic modulus of molybdenum.
- Molybdenum and nickel oxidation mechanisms.
- Sulfur agglomeration.
- Summary and future plans.

TEAM

- **CFDRC has over 20 years of experience developing and commercializing new technologies.**

- **Most recent example is a $5M grant from the DOE Hydrogen Fuel Cell Program, managed by Dr. Cole, the director of the proposed work.**



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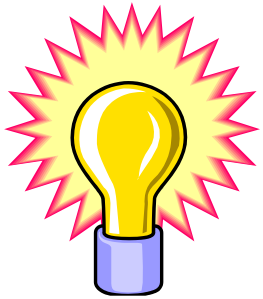
- reduced development time and cost



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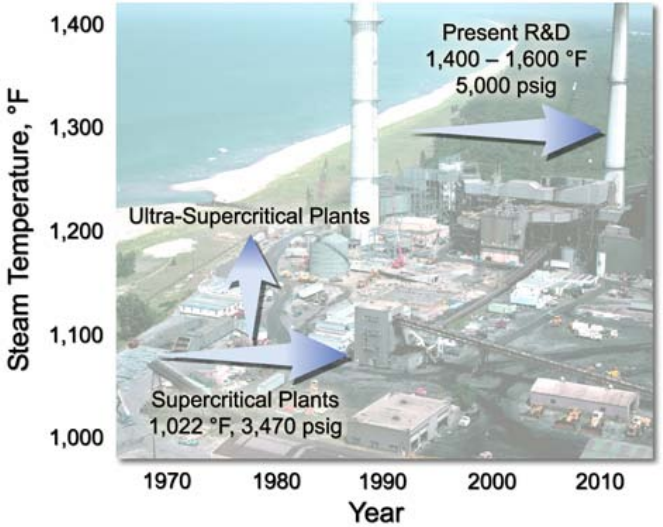
COMPUTATIONAL DESIGN OF REFRACTORY ALLOYS FOR ENERGY APPLICATIONS

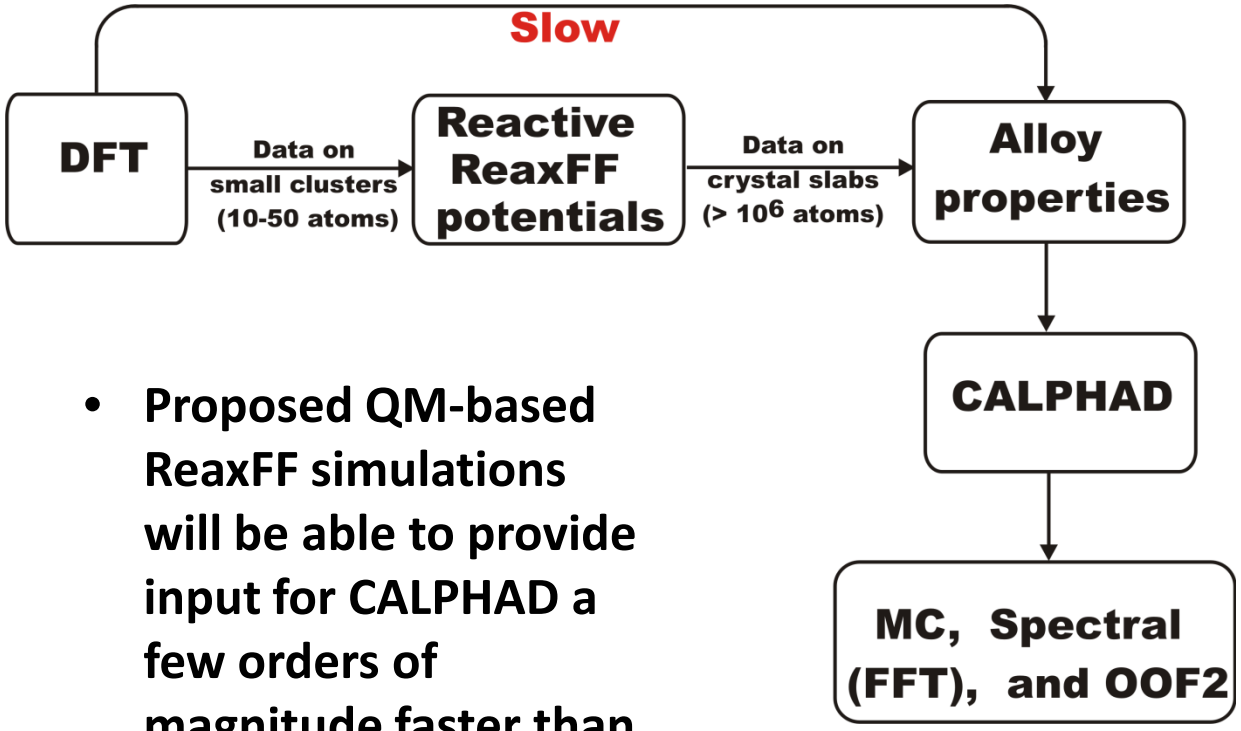
- **Novel materials such as refractory alloys that can withstand extreme conditions are dominant themes in the materials development.**
- **Currently, the alloy development remains slow because it is driven by trial-and-error experimental approach.**
- **Atomistic simulations has the potential to accelerate alloy design through the prediction of mechanical properties and corrosion resistance of new materials (Albany NETL group - Drs. Doğan and Gao).**



Increase in Steam Temperature and Pressure in Coal-Fired Power Plants

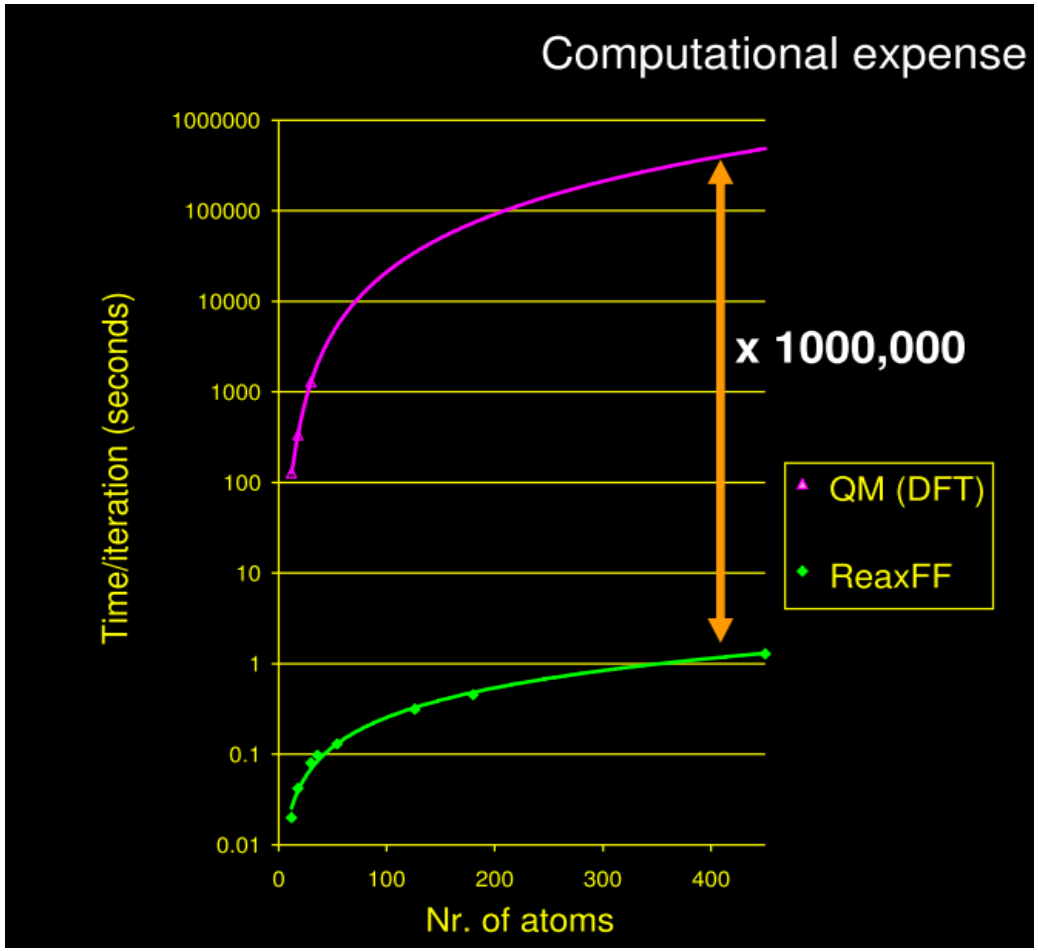
COMPUTATIONAL DESIGN OF REFRACTORY ALLOYS FOR ENERGY APPLICATIONS

- The success of atomistic simulations critically depends on the fidelity of a specific model of interatomic interactions.
- CFDRC teamed with Penn State University in this effort to develop predictive Quantum Mechanics (QM) based reactive ReaxFF potentials (force fields) to be used in atomistic-based design of new refractory materials.
- Proposed QM-based ReaxFF simulations will be able to provide input for CALPHAD a few orders of magnitude faster than traditional QM calculations based on the Density Functional Theory (DFT).

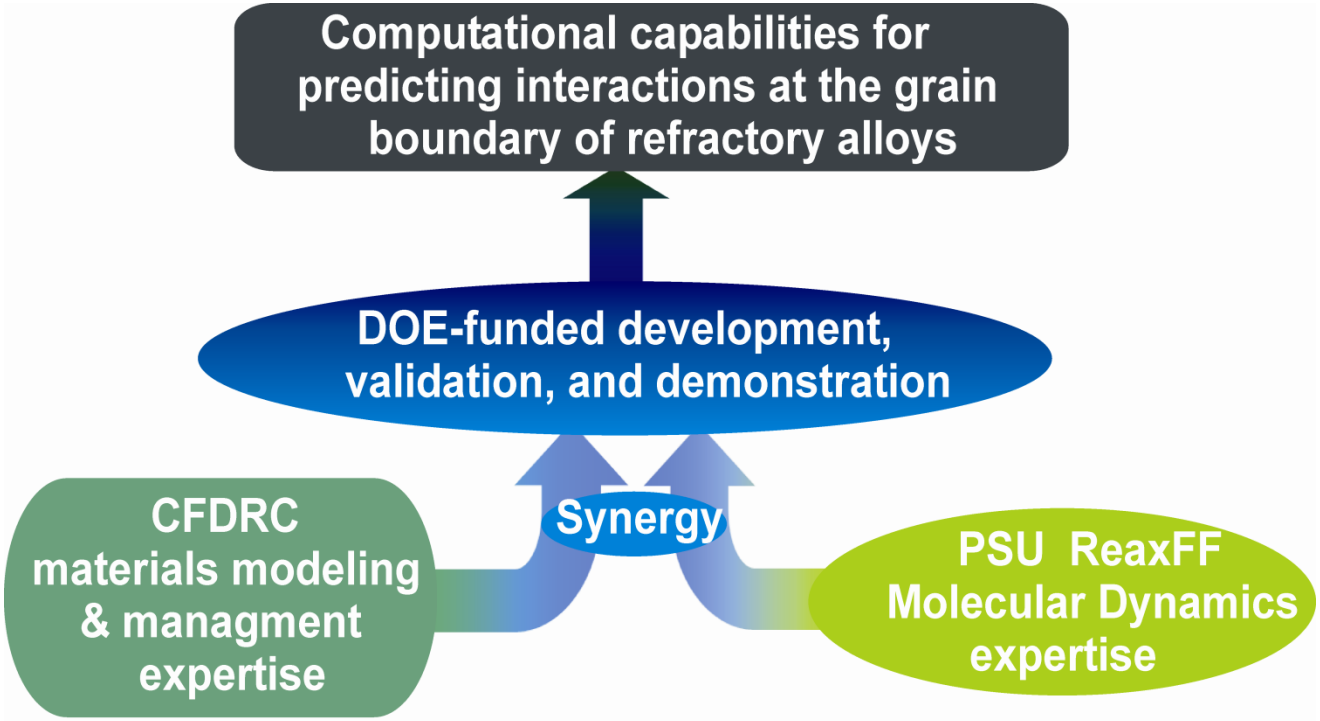


INNOVATIVE QM BASED REAXFF FORCE FIELDS

- ReaxFF offers a compromise between high-level QM description and computational speed.
- ReaxFF can be used for atomistic simulations of large systems with up to 1,000,000 atoms.
- Unlike conventional non-reactive force fields, ReaxFF contains information on both alloys mechanical properties and chemical corrosion reactions with oxygen, hydrogen sulfide, etc.



OVERALL PROJECT OBJECTIVES



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

PROJECT RISKS AND THEIR MITIGATION

- There are manageable risks associated with the proposed research and development.
- Most notably, we recognize that the size- and time-ranges of the atomistic simulations do not yet provide a seamless match with the experimental resolution.
- In the case of large mismatch in simulation and experimental resolution, we will employ complementary computational tools including accelerated MD, kinetic Monte Carlo, and parallel replica methods.
- Simulations will be directed toward in-depth understanding of fundamental mechanism of segregation at the grain boundary.
- Another technical risk is in the development of Quantum Mechanics based ReaxFF potentials for chromium, the major element missing from the current library of ReaxFF potentials for simulations of refractories.
- The risks associated with this development are mitigated by
  - Reported ReaxFF descriptions for a number of elements in the periodic table closely related to chromium, including molybdenum and vanadium,
  - Proven strategy for the ReaxFF potential development, and
  - Clearly defined individual steps in the development plan.

PROJECT RISKS AND THEIR MITIGATION (CONT.)

- Given the complexity of the interactions at the grain boundary of chromia and alumina based refractories, we anticipate that the initial ReaxFF force fields will make unexpected, and possibly erroneous predictions.
- We will validate these initial force field predictions by performing QM-based analysis of reaction energies and barriers associated with the ReaxFF-predicted processes.
- This QM/ReaxFF feedback loop will be continued until the high-temperature ReaxFF predictions are fully validated by QM calculations.
- On the whole, we are confident that the probability for the success of the proposed research is very high.
- This assessment is based on the proven expertise of CFDRC in materials modeling and 20 years experience in managing projects of similar size and complexity, as well as Prof. Adri C.T. van Duin's demonstrated expertise in the development and application of ReaxFF potentials.

SUMMARY

- **Feasibility of training ReaxFF potentials by gradually increasing QM-based training set was demonstrated.**

- **ReaxFF predictions within MD framework were found in an excellent agreement with (1) High temperature shock compression measurement data in the pressure range of 0-350 GPa, (2) Literature density in the temperature range of 300°K to 1500°K, and (3) Literature Young's modulus in the temperature range of 300°K to 1500°K.**

- **It was found that Mo oxidation proceeded at a significantly higher rate than the oxidation of Ni slab and involved large heat release resulting in surface melting.**

- **Following trends were identified from modeling H_2S/Mo interactions: (1) H_2S consistently diffused into Mo and MoO_3 slabs and decomposed there to form S and H, (2) Mo-Mo metal bonds were replaced by S-Mo bonds leading to S agglomeration in the slab, and (3) H preferably desorbed from Mo slab and formed gaseous H_2.**

FUTURE WORK

- **Future work objectives are as follows:**
  - **Demonstrate the feasibility by reproducing trends observed for elemental segregation and reactions at the grain boundaries of Al_2O_3 based refractories;**
  - **Develop ReaxFF potentials for predictive MD modeling of interactions with impurities at the grain boundary of Cr_2O_3 based refractories;**
  - **Validate ReaxFF potentials against literature data for equation of state and elastic data;**
  - **Demonstrate the feasibility to reproduce major reaction pathways during interaction of slag with refractories in a typical slagging gasifier environment;**
  - **Determine mechanisms of segregation at the grain boundary of Cr_2O_3/Al_2O_3 based refractories and validate the predictions against the literature results;**
  - **Identify approaches to limit sulfur segregation at the grain boundaries of $Cr_2O_3/Al_2O_3/P_2O_5$ refractory.**

CONTACT INFORMATION

- Industry and academia representatives are encouraged to contact

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