

# **Role of Microstructure on Fuel Performance: Macroscale Insights from Atomic-resolution Simulations**

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Nuclear fuel in service is a unique environment of high temperature, high stress, irradiation and ever changing chemistry and microstructure. The insights that can be obtained by atomic-level simulation into the complex chemical and microstructural phenomena that take place in both the fuel pellet and the clad are illustrated.

With respect to fuel the issues, we illustrate insights from atomistic simulations of defect energetics, evolution and thermal transport properties. Specifically, we have used atomic-level simulation methods to determine the interaction of metallic fission products with the core of edge dislocations in  $\text{UO}_2$ . Detailed analysis shows that the trends in segregation energy can be understood in terms of bulk behavior and continuum elasticity, opening up an efficient method for rapidly generating databases of segregation properties for input to mesoscale codes. We also analyze the results of molecular dynamics simulation of void formation in  $\text{UO}_2$  in the bulk and close to a grain boundary. The microstructural evolution during burnup, results in a progressive degradation in the thermal transport properties. We present the results of thermal conductivity calculations within the lattice dynamics framework in  $\text{UO}_2$  using electronic-structure calculations for the interatomic force constants. Comparison of the phonon lifetimes with the recently measured lifetimes is provided. We have also performed large scale molecular dynamics (MD) simulations to determine the effects of microstructure – grain boundaries and dislocations - on the thermal conductivity of  $\text{UO}_2$ . We show how insight from such simulations can be integrated into the FRAPCON fuel performance code

Finally, in the context of clad, we have developed a charge-optimized many-body (COMB) potential for the  $\text{Zr-ZrO}_2\text{-ZrH}_x$  system. We perform classical molecular dynamics simulations showing the initial corrosion behavior of three low-index zirconium surfaces via the deposition of  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules. The basal (0001) surface shows greater resistance to oxygen diffusion than the prismatic surfaces. Nanoindentation simulations on both basal and prismatic  $\text{Zr}$  and  $\text{ZrO}_2/\text{Zr}$  provide insights into unit mechanisms associated with the deformation of clad.

## Interatomic potentials accuracy: how do they bridge the scales? U-Mo fuel case

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Perspective reliable multiscale models of radiation damage in nuclear fuels should bridge a gap between atomistic level dynamics and kinetic rate theory (or phase field theory) at mesoscopic level. Radiation defects evolution models comprised of millions of atoms are required to resolve essential physical effects (point defects clustering, interaction with dislocation loops, grain boundaries etc). Empirical potential models are the main tool for transferring to the meso-level the peculiarities of atomic interactions that can be captured only using sophisticated quantum methods. That is why the accuracy of the interatomic potentials is of utmost importance for predictive modelling and simulation of nuclear fuels.

We have built a set of interatomic potential models targeted at the description of U-Mo fuels. The developed central symmetric EAM many-body potential models have been shown to provide decent accuracy for pure Mo [1], pure U [2] and U-Mo alloys [3]. Recently an angular dependent ADP model for the U-Mo alloy has been built as well. All potentials are constructed using force-matching method and fitted to the values of ab initio interatomic forces, energies and stresses. As a question of verification we discuss the loss of information at the corresponding “data transfer” between quantum and classical levels. The validation and application of the resulting models include the following issues:

1. Structure of  $\alpha$ -U,  $\gamma$ -U, bcc Mo, U<sub>2</sub>Mo compound and U-Mo alloys.
2. Elastic constants, melting temperatures, thermal expansion and isotherms of U-Mo and the Grüneisen parameter for liquid and solid U.
3. Point defect formation energies, diffusion mechanisms and diffusivities.

We discuss a consistent way to include FPs in the U-Mo model and present the simulation results on Xe diffusion and bubble formation. We also consider how the resulting MD models bridge the gap to the level of rate theory [4].

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[2] D.E. Smirnova et al. “Interatomic potential for uranium in a wide range of pressures and temperatures,” J. Phys.: Cond. Mat. **24** (2012) 015702.

[3] D.E. Smirnova et al. “A ternary EAM interatomic potential for U–Mo alloys with xenon,” Model. Sim. Mater. Sci. Eng. **21** (2013) 035011.

[4] A.V. Yanilkin et al. “Atomistic simulation of clustering and annihilation of point defects in Molybdenum,” Defect and Diffusion Forum **323-325** (2012) 95.

## **Atomistically-informed cluster dynamics modeling of void and loop nucleation in irradiated UO<sub>2</sub>**

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A novel Cluster Dynamics (CD) model that describes the nucleation and evolution of defect clusters in oxides systems has been developed. The model has been used to predict clustering of vacancies and interstitials into voids and dislocation loops, respectively, in irradiated UO<sub>2</sub>. The model reproduces well a range of experimental data on nucleation and growth behavior and its temperature dependence. A very important feature of this model is its ability to predict the off-stoichiometry (or composition) of defect clusters, allowing, in turn, for the tracking of off-stoichiometry of the matrix. The effect of migration energy of point defects on the concentration and average size of voids has been studied. Also, the effect of irradiation conditions such as irradiation temperature, irradiation dose and dose rate on clusters concentration and composition has been investigated. The preliminary results show that Frenkel defects, as opposed to Schottky defects, dominate the nucleation process in irradiated UO<sub>2</sub>. Vacancy clusters tend to grow mainly by absorbing oxygen vacancies and the migration energy of uranium vacancies is the rate limiting energy in nucleation and growth of voids. The results also show that, in a stoichiometric UO<sub>2</sub> under irradiation, vacancy clusters (voids) tend to have both hypo- and hyper-stoichiometric composition with a higher fraction of hyper-stoichiometric composition clusters. A hyper-stoichiometric cluster composition indicates that the matrix would become oxygen rich even if the initial state is perfectly stoichiometric.

## **Radiation growth in Zr under Frenkel-pair produced irradiation**

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Existing theory explains radiation growth of hcp Zr under 1 MeV electron irradiation by the diffusion anisotropy of self-interstitial atoms (SIAs), assuming isotropic diffusion of vacancies. Recent density functional theory (DFT) study suggests preferential in-basal-plane diffusion for both vacancies and SIAs. Kinetic Monte Carlo calculations of the point defect diffusion at temperatures from 200 to 1100K, performed using the DFT data on the migration, are presented. The ratio of diffusion coefficients parallel and perpendicular to the basal planes, i.e. the diffusion anisotropy, is found to be higher for vacancies than SIAs at temperatures below ~900K. With these data the theory predicts existence of a crossover temperature somewhere between 600 and 800K, depending on the dislocation bias (which is defined by the relative strength of point defect interaction with the dislocation stress field), below which the diffusion anisotropy difference between point defects does not account for observations. It is speculated that small SIA clusters with higher diffusion anisotropy may determine the observed growth in Zr.

## Challenges in energy applications of non-stoichiometric complex perovskites

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Two ABO<sub>3</sub>-type perovskite solid solutions (BSCF: Ba<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub> and LSCF: La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub>), mixed ionic – electronic conductors, recently have attracted a lot of attention because of a wide range of potential applications in modern technologies, e.g. gas separation membranes, solid oxide fuel cells (SOFC), etc. The use of SOFC for electricity supply in space stations poses a question of materials radiation stability. Clearly, radiation defects, first of all oxygen vacancies and antisite defects in perovskites, affect many properties and worsen performance of the perovskite materials in specific applications.

In this study, we present results of first principles calculations of the perfect BSCF and LSCF crystals, the crystals containing basic point defects (cation and anion vacancies, cation exchange, and antisite defects), disorder (Frenkel and Schottky), and a set of relevant solid-solid solution reactions [1,2]. Our DFT modeling reveals that oxygen Frenkel defects, full Schottky disorder and partial Schottky disorder accompanied by the growth of a new phase (e.g. a parent perovskite) all have relatively low formation energies and are favorable. The obtained cation exchange energies are very low for both the A- and B- sublattices of the perovskite structure; this leads to a formation of new phases or interphases.

We explored and analyzed in great detail the oxygen vacancy formation energies in the cubic and hexagonal phases of BSCF and demonstrated that a high concentration of vacancies (oxygen non-stoichiometry), in fact, serves as a stabilizing factor that governs the preference of the cubic phase over the hexagonal phase. We also discuss peculiarities of the oxygen vacancy diffusion in BSCF and LSCF. We established that the A/B-site cation size mismatch in BSCF leads to the unusually low oxygen vacancy formation energy, which causes a considerable non-stoichiometry, and facilitates vacancy migration with a prominent charge transfer at the transition state. The smaller mismatch between A- and B-site cations in LSCF results in twice higher vacancy formation energy and higher migration activation barrier, which give rise to a smaller oxygen vacancy concentration and thus a slower oxidation reaction, as compared to BSCF.

Based on the above-discussed results of first principles calculations of the defect formation and migration energies, as well as oxygen atom and molecule adsorption on perovskite surfaces, we calculated the diffusion-controlled kinetics of oxygen reduction reaction (ORR) as a function of adsorbed oxygen and surface vacancy concentrations [3]. This allowed us to determine *the rate-determining steps* (which is important for improvement of fuel cell and permeation membrane performances) and suggest interpretation of available experimental data.

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[2] M. M. Kuklja, E.A. Kotomin, R.Merkle, Yu. A. Mastrikov, J. Maier, *Phys. Chem. Chem. Phys.* **15** (2013) 5443 (a review article).

[3] Yu. A. Mastrikov, R. Merkle, E. Heifets, E.A. Kotomin, J. Maier, J. Maier, *J. Phys. Chem. C* **114** (2010) 3017.

## **First principles study of anisotropy of point defect diffusion barriers in HCP Zr**

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The radiation growth of Zr is observed not only under neutron irradiation but also under ~1 MeV electron irradiation and the neutron. To explain this it is natural to assume that the diffusion anisotropy of single self-interstitial atoms (SI) (preferentially along the basal planes) is higher than that for vacancies. We used density functional theory (DFT) approach to find the lowest in energy SI configuration of SI and analysed large set of possible transition barriers between these configurations together vacancy transition barriers. We demonstrated that the lowest barrier corresponds to two transitions 1) between basal octahedral (BO) and basal split (BS) configurations, and 2) BO and octahedral (O) configuration. Between the last two barriers the in basal one (BO to BS) is slightly lower and corresponds to longer “jump”. Thus, it was demonstrated that in-basal plane jumps are the most favorable for both vacancies and SIAs, so that both defects exhibit anisotropic diffusion, predominantly parallel to the basal planes.

## **Radiation damage evolution in nanostructure materials**

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As the materials in nuclear reactors, both fission and fusion, experience ever increasing radiation damage due to a desire to maximize efficiency, the need to design materials that can withstand that damage becomes ever more pressing. One proposed avenue for mitigating that damage is through the use of nanostructure materials where the high density of interfaces can enable the enhanced recombination of the defects. Here we present combined experimental and theoretical studies of radiation damage evolution within nano composites, focusing on composites containing oxide phases. We first examine how the defect kinetics and thermodynamics within the constituent phases influence the damage evolution in the composite, independently of the structure of the interfaces themselves. Atomistic results are used to parameterize reaction-diffusion models of the composite under irradiation. We find that the damage evolution is very sensitive to the defect properties within these phases with different damage evolution regimes possible depending on the relative kinetics and thermodynamics of defects. We then examine how the atomic structure of the interfaces in oxide/ oxide composites further modifies the evolution of radiation damage within these materials. We find that there can be a complex interplay between the structure of the interface and the evolution of defects produced under irradiation. Finally, using a combination of atomistic and phase field simulations, we examine the evolution of the chemistry of a multicomponent nanocomposite under irradiation and how factors such as the interfacial structure, the characteristic length scale, and the chemistry of the alloy itself can be used to control the redistribution of the various chemical species under irradiation. Together, these studies elucidate the effect of nanocrystalline microstructure on the overall radiation damage response of the composite and provide insights into the design of advanced radiation tolerant materials.

## ***Ab initio* prediction of point defect properties in materials for energy production**

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In materials science, defects may be unintentionally created and have detrimental effects, e.g. during crystal growth or in harsh environments found in electronic devices in satellites, optical fibers in nuclear plants. They can also be introduced deliberately into a material to engineer its electrical, transport, or optical properties (e.g. semiconductor junctions ensuring charge separation in photovoltaic cells or transparent conducting oxides used as electrodes). Despite their technological importance, defects are difficult to characterize experimentally. Quantum mechanical first principles calculations offer a complementary description. However, first principles calculations for defects are still challenging for several reasons: The structural models required for a converged description of a defect contain a large number of atoms and therefore make a quantum mechanical calculation computationally very expensive. Furthermore, the point defect properties are strongly affected by the exchange-correlation approximation employed in the calculations.

In this presentation, I will present recent advances on the effect of the exchange-correlation approximation choice on the defect properties. The talk will focus on hybrid functionals and on the so-called GW [1] and Random-Phase [2] approximations of the many-body problem.

The results will be exemplified with two relevant materials for the energy production: SiC for the nuclear industry [3] and ZnO for the photovoltaic applications [4].

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