FINAL REPORT

Project Title: Predictive Characterization of Aging and Degradation of Reactor Materials in Extreme Environments

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Project Objective: Understanding of reactor material behavior in extreme environments is vital not only to the development of new materials for the next generation nuclear reactors, but also to the extension of the operating lifetimes of the current fleet of nuclear reactors. To this end, we propose a suite of unique experimental techniques, augmented by a mesoscale computational framework, to understand and predict the long-term effects of irradiation, temperature, and stress on material microstructures and their macroscopic behavior. The experimental techniques and computational tools will be demonstrated on two distinctive types of reactor materials, namely, Zr alloys and high-Cr martensitic steels. These materials are chosen as the test beds because they are the archetypes of high-performance reactor materials (cladding, wrappers, ducts, pressure vessel, piping, etc.).

To fill the knowledge gaps, and to meet the technology needs, a suite of innovative *in situ* transmission electron microscopy (TEM) characterization techniques (heating, heavy ion irradiation, He implantation, quantitative small-scale mechanical testing, and various combinations thereof) will be developed and used to elucidate and map the fundamental mechanisms of microstructure evolution in both Zr and Cr alloys for a wide range environmental boundary conditions in the thermal-mechanical-irradiation input space. Knowledge gained from the experimental observations of the active mechanisms and the role of local microstructural defects on the response of the material will be incorporated into a mathematically rigorous and comprehensive three-dimensional mesoscale framework capable of accounting for the compositional variation, microstructural evolution and localized deformation (radiation damage) to predict aging and degradation of key reactor materials operating in extreme environments. Predictions from this mesoscale framework will be compared with the *in situ* TEM observations to validate the model.

Summary of Accomplishments of the Project

1. Publications

1. Xiao, X., Chen Q., Yang, Hui, Daun, H. and Qu, J., 2017, "A Mechanistic Model for Depth-Dependent Harness of Ion Irradiated Metals," *J. Nuclear Materials*, Vol. 485, pp. 80-89.
2. Muntifering, B., Fang, Y., Leff, A.C., Dunna, A., Qu, J., Taheri, M.L., Dingreville, R., Hattar, K., 2016, "In situ Transmission Electron Microscopy He+ implantation and Thermal Aging of Nanocrystalline Iron," J. Nuclear Materials, Vol. 482, pp.139-146.
3. Muntifering, B., Juan P.A., Dingreville, R., Qu, J., and Hattar, K., 2016, "In-Situ TEM Self-Ion Irradiation and Thermal Aging of Optimized Zirlo," Microscopy and Microanalysis, Vo. 22 (S3), pp. 1472-1473.
4. Muntifering, B., Dunn, A., Dingreville, R., Qu, J., and Hattar, K., 2016, "In-Situ TEM He+ Implantation and Thermal Aging of Nanocrystalline Fe," Microscopy and Microanalysis, Vol. 21(Suppl. 3), pp 113-114. doi:10.1017/S1431927615001361.
5. Muntifering, B., Blair, S.J., Gong, C., Dunn, A., Dingreville, R., Qu, J., Hattar, K., 2016, "Cavity Evolution at Grain Boundaries as a Function of Radiation Damage and Thermal Conditions in Nanocrystalline Nickel," Materials Research Letters, Vol. 4, pp. 96-103.

2. Experimental component

- Demonstrated using ion beam induced luminescence that both high energy, heavy ions and 10 kV He can be concurrently introduced into the TEM sample location. The alignment of the ion optics has been optimized such that only two to three hours is required before concurrent in-situ ion irradiation TEM (I^3TEM) experiments can be initiated after start-up. **(Quarterly Report on 04/30/2014)**
- Demonstrated the feasibility of doing in-situ heating or quantitative tensile straining during ion irradiation. The former utilizing a combination of the I^3TEM and a hummingbird 2.3 mm heating stage and the later utilizing the I^3TEM in combination with the Hysitron PI-95 and an associated push-to-pull device. Neither has been attempted on the relevant alloys for this project. In addition, quantitative nano-indentation has been demonstrated in a variety of deposited films, but has still not been run in samples prepared from bulk metal alloys. **(Quarterly Report on 04/30/2014)**
- Explored the use of furnace for grain growth and in-situ TEM heating to observe grain growth. **(Quarterly Report on 09/30/2014)**
- Conducted in-situ ion irradiation TEM characterization on a model nanostructured FCC metal (nano-crystalline nickel) samples under successive self-ion irradiation and He implantation in both orders and post irradiation annealing to provide insight on the active mechanisms impacting microstructural changes under separate and combined effects. In addition, the role of oxide modification on the defect evolution within the metal film was identified. **(Quarterly Report on 01/20/2015)**
- Conducted in-situ TEM characterization to elucidate the underlying mechanisms involved

in helium diffusion and cavity nucleation for a wide range of temperatures and implantation conditions. Two types of in-situ TEM experiments were performed: (1) Helium implantation at room temperature followed by annealing to 600˚C, and (2) Helium implantation at elevated temperatures up to 600˚C. These experiments were conducted using in-situ TEM implantation with 10 keV He^+ ions into nano-crystalline iron samples. **(Quarterly Report on 04/20/2015)**

- Characterized radiation induced damage in 316L stainless steel under a heavy ion irradiation and helium implantation. The microstructural evolution as a result of heavy ion induced displacement damage and helium implantation was studied on 316L stainless steel with Au^{3+} and He^+ ions. Both concurrent and sequential irradiation and implantation was performed to elucidate the role of helium in defect evolution and the synergist effects of helium implantation and displacement damage. **(Quarterly Report on 07/20/2015)**
- Experimental characterizations were conducted based on jet polishing TEM samples of HT9, 304 stainless steel, and zirconium alloys: (1) Characterization of the effect of hydrogen isotopes on cascade damage in model FCC materials such as Nickel; (2) Characterization of the dynamic evolution of dislocation loops during annealing in model BCC materials such as iron; and (3) Experimental validation of theoretical predictions of dose and dose rate on mechanical properties by performing nano-indentation to characterize hardness as a function of dose and dose rate. **(Quarterly Report on 10/20/2015)**
- Conducted experimental characterization of radiation induced damage in zirconium alloys under self-ion irradiation and thermal aging. TEM samples of zircaloy 4 and optimized zirlo were prepared and the in-situ TEM experiments were conducted to investigate ion irradiation induced high damage levels and post irradiation thermal aging effects corresponding to the long term reactor conditions. **(Quarterly Reports on 01/20/2016 and 04/20/2016)**
- As control experiments, nano-indentations of both unirradiated zircaloy 4 and optimized zirlo samples were conducted based on a hysitron triboindenter with a Berkovich indenter tip. Material properties of unirradiated zircaloy 4 and optimized zirlo, such as modulus and hardness, were extracted from the measured force-depth curves. **(Quarterly Reports on 04/20/2016 and 07/20/2016)**
- Performed both nano- and micro-indentation tests (continuum stiffness measurement (CSM)) to investigate the irradiation dose effect on the material properties of both zircaloy 4 and optimized zirlo. Samples were polished for both nano- and micro-indentation experiments. For the polished samples, partial masks were used to cover one half part of the polished surface of each sample. The other half of the uncovered surface was treated by self-ion irradiation with different radiation doses. Then, both nano- and mirco-indentation experiments (based on iNano® and iMicro® Nanoindenters, respectively) were performed on both unirradiated and irradiated regions of zircaloy 4 and optimized zirlo samples to explore the hardening effect of irradiation. **(Quarterly Reports from 07/20/2016 to 07/20/2017)**
- Conducted in-situ experimental characterization of the evolution of self-ion irradiation induced damage in zirconium alloys during indentation measurement. Optimized zirlo

samples were firstly polished and treated by self-ion irradiation with different radiation doses. In-situ focused ion beam (FIB) lift-out was then conducted for the preparation of in-situ nano-indentation TEM samples. Finally, in-situ nano-indentation tests were conducted in a Hysitron PI-95 picoindenter in TEM for the direct observation of the distributions and evolutions of irradiation caused damage in the samples. **(Quarterly Report on 09/15/2017)**

2. Modeling component

- Developed a mesoscale stochastic hardening model for the modelling of mechanical response dependence of irradiation dose on polycrystals for BCC systems. Defects (dislocation loops and stacking fault tetrahedras) found in these irradiated materials are treated stochastically based either on dispersed barrier model, Friedrich, Kroupa, Hirth and Bacon models. Experimental considerations and results from cluster dynamics are used for the choice of defects generated (SIA dislocation loops vs. vacancies), their associated size and strength are determined randomly and vary with the irradiation dose. The statistical approach relies on repeated three dimensional mesoscale simulations for different physical realizations of irradiated microstructures to study the mechanical response of irradiated polycrystalline materials. The model was validated by the Cu single crystal experimental data. **(Quarterly Reports from 04/30/2014 and 09/30/2014)**
- Developed a spatially resolved stochastic cluster dynamics (SRSCD) model that is coupled the mesoscale stochastic hardening model with cluster dynamics as an alternative to describe radiation-induced defect evolution in metals. The stochastic nature of the method allows SRSCD to model more chemical species and more mobile defects than rate theory methods without loss of computational efficiency. **(Quarterly Reports from 04/30/2014 and 01/20/2015)**
- Built a chemo-mechanics framework that governs the kinetic process of microstructure evolution driven by both radiation damage and mechanical loading at elevated temperature. A stress-dependent chemical potential is being developed for clusters of interstitial vacancies/atoms. Based on the model, the interaction between defect diffusion and mechanical stresses was investigated. **(Quarterly Reports from 04/30/2014 and 01/20/2015)**
- Coupling of simulated results for radiation defect accumulation using spatially resolved stochastic cluster dynamics (SRSCD) with a crystal plasticity model including radiation-induced hardening, and results were fit to experimental results as a proof-of-concept of the ability to use multi-scale modeling to predict mechanical hardening of irradiated metals. **(Quarterly Report on 01/20/2015)**
- Simulation of helium implantation and subsequent defect accumulation in iron were performed using spatially resolved stochastic cluster dynamics (SRSCD). Various hypotheses regarding the interaction of helium with SIA loops and vacancies have been investigated to elucidate the active mechanisms, and the results are compared with experimentally observed trends. **(Quarterly Report on 04/20/2015)**

- Implemented the chemo-mechanical formulation into a simulation code by using a hybrid finite element and finite difference approach. The formulation is valid for concentrations that are well below the maximum and for small strains. Initial results show that the approach captures both stress and diffusion, as they can be seen to evolve together during the simulation. They also suggest that the coupling is stronger in one direction than in the other. The defects induce large stresses, whereas stress has a relatively weak effect on diffusion given the current formulation and simulation problem. **(Quarterly Reports on 04/20/2015 and 10/20/2015)**
- Using the SRSCD code, the hardening effect of heavy ion-irradiated iron was investigated by simulating cascade damage in bulk iron at a variety of dose rates and temperatures. The subsequent damage produced was then upscaled into the iMPALE code developed at Sandia to estimate the hardening induced by that damage. Results of previous studies performed as a part of this project were used to calibrate these hardening simulations. Dose rate and temperature were both predicted to have a significant impact on hardening. **(Quarterly Report on 07/20/2015)**
- As a multi-scale damage accumulation tool, the spatially resolved stochastic cluster dynamics (SRSCD) was used to simulate radiation damage over a wide range of dose rates and temperatures. Dose rate effects on hardening were simulated and compared with experimental results. The relationship between dose rate and temperature was predicted for a range of rates, and a tool was developed to help design experiments. **(Quarterly Report on 10/20/2015)**
- Conducted modeling of the evolution of defect distribution in irradiated metals. The clustering terms were added into the diffusion rates in the chemo-mechanical model to separately track the size and concentration of individual defects as well as the clusters that they form over time. The addition of a dissociation rate enables the clustering model can account for both growth and decay of defect clusters. The growth of large clusters outward, over multiple volume elements, in areas with large stress gradients was modeled. The disclination structural unit model was also incorporated in order to model defect segregation along grain boundaries. By comparing the results with and without the self-stress effect, the strength of the two-way interaction between diffusion and stress was investigated. **(Quarterly Reports on 10/20/2015 and 01/20/2016)**
- Developed finite element models based on the strain gradient plastic theory and the classical plastic theory to simulate the nano-indentation of irradiation zirconium alloys with and without size effect, respectively. **(Quarterly Report on 04/20/2016)**
- Developed an analytical model for the indentation size effect in irradiated materials. A mechanistic model, which is capable of capturing the indentation size effect, the ion irradiation induced damage gradient effect, and the effect of unirradiated region acting as a soft substrate, was developed for modeling the depth-dependent hardness in ion irradiated metallic materials. Calibrations of the developed model were conducted with available experimental data. **(Quarterly Reports on 04/20/2016 and 10/20/2016)**
- Extended the previously developed chemo-mechanical model which considered the two-way coupling between mechanical stress and defect concentration to finite deformation formulation to simulate the behaviors of defect clusters over a longer time period and with

finer spatial resolution. The chemo-mechanical diffusion formulation used in the model was updated to capture not only the effects of intrinsic stress and eigenstrain, but also to simulate the void denuded zones observed near grain boundaries. Based on the model, radiation-induced segregation has been simulated for vacancies and self-interstitial atoms (SIAs) near a selected group of point defect sinks in iron, such as edge dislocations, disclination dipoles, and tilt grain boundaries. The effects of stress field on the behaviors of different defects, i.e., vacancies and self-interstitial atoms, were compared. **(Quarterly Reports on 07/20/2016 and 10/20/2016)**

- Simulations were conducted to study the segregation of vacancies and self-interstitial atoms (SIAs) in Fe near edge dislocations and grain boundaries based on the chemo-mechanical model which considered the two-way coupling between mechanical stress and defect concentration. In the model, a modified chemical potential was developed to model diffusion under the influence of an intrinsic stress field, and the stress field was influenced by the eigenstrains from the defects. In addition, a mean field rate theory was incorporated to model the clustering and recombination of defects. **(Quarterly Report on 01/20/2017)**
- The previously developed chemo-mechanical model which considered the two-way coupling between mechanical stress and defect concentration was extended to couple with phase-field approach in which dislocations are treated as perfect defect sinks. In the updated model, periodic boundary conditions for displacements were implemented, allowing grain boundaries and other defect sinks to be accurately simulated using a single unit cell. Based on the extended model, studies were conducted to investigate the radiation-induced segregation (RIS) around grain boundaries, dislocation loops, lone edge dislocations, and lone disclination dipoles. **(Quarterly Reports on 04/20/2017 and 07/20/2017)**