LA-UR- 10-03191

Title: MaRIE First Experiments Summaries Version: May 9, 2010

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Intended for: MaRIE External Advisory Board (EAB) Meeting
May 25-26, 2010

MaRIE First Experiments
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Microstructure Based Heterogeneity Evolution Leading to Material Phase Transformation and Damage / Failure Events

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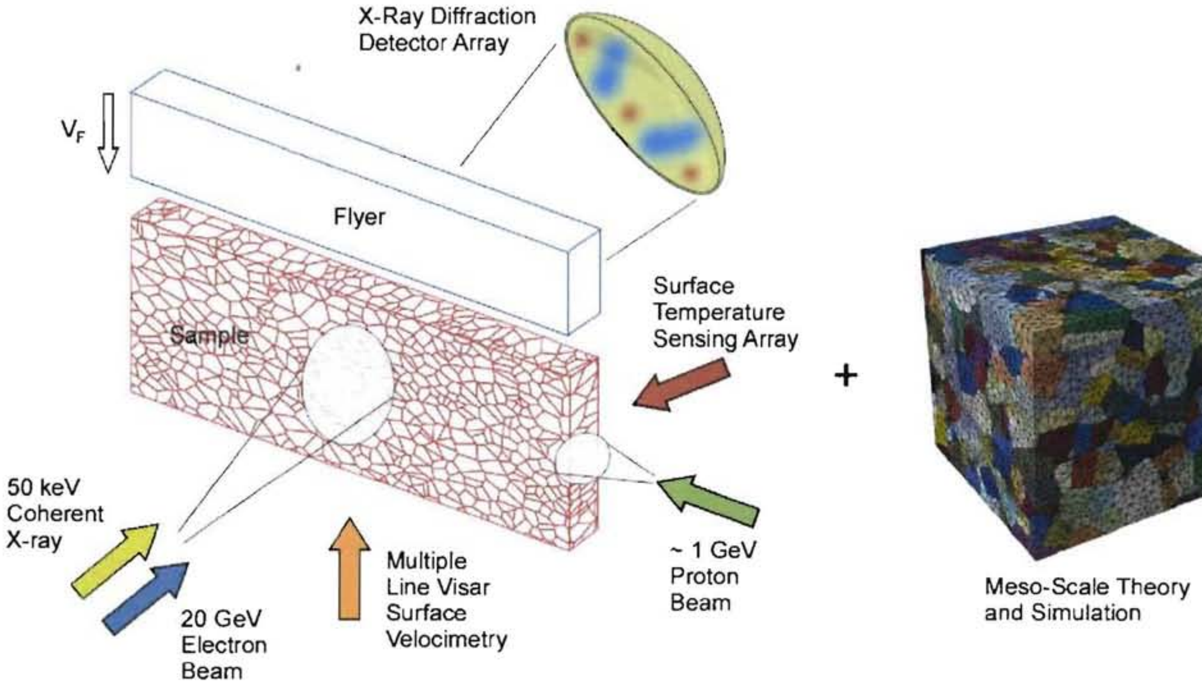
Problem statement

A predictive understanding of microstructure-based heterogeneity and its consequences for materials damage & failure and phase transformation initiation is presently lacking.

Scientific objectives

Most metallic materials used in applications are polycrystalline aggregates – individual single crystals separated by grain boundaries. Most of these materials are either metallic alloys or contain impurities. In either case, there is spatial variability in their chemical composition. These materials also contain dislocations which will be distributed in some way throughout the individual grains and increase in density with deformation and typically form dislocation sub-cell arrangements – producing spatial distribution in dislocation density. Many materials also produce twin or slip band structures with deformation which produce further heterogeneity within individual crystals. The objective of this first experiment is to probe the physics of dynamic solid-solid phase transformation and damage at length scales approaching those at which they nucleate in order to gain a detailed understanding of this process and the influence real material microstructure has on these events. These experiments would simultaneously be simulated by the appropriate modeling tools to further develop these predictive tools and to assist in our interpretation of experimental results.



Envisioned dynamic MaRIE first experiment combined with aggressive theory, simulation, and information sciences development to discover small-scale dynamic phase transformation and damage/failure events.

Experimental details

There are several materials of interest which have a range of Z values from Pu to Al which will determine the sample thickness. The energy level for a coherent X-ray source envisioned for this experiment would be approximately 50 keV. Corresponding transmission direction thickness for the samples are 100 microns for Pu and 2.0 mm for Al. Shock loading of the sample would be achieved by projection of a flyer plate with velocity capabilities in the range of 100 to 1500 m/s. The desired spatial resolution for three-dimensional measurements is 1.0 micron with temporal resolution fast enough for several images during the time a shock wave traverses a grain of material. Line visar measurements would be made on the free surface as would a spatial array of surface temperature measurements. It is also necessary to measure transmitted density profiles in two different directions using both a 20 GeV electron beam (1.0 micron spatial resolution) and a 1 GeV proton beam.

Current landscape

High resolution X-ray diffraction techniques and computed micro-tomography is a well developed experimental tool which has been performed on metallic materials at APS[1]. Computed micro-tomography is also now a readily available tool for use in the materials science laboratory[2]. Recently a program has been initiated to integrate High Energy X-ray Diffraction Microscopy with computed micro-tomography[3] to post analyze damaged plate impact samples. They will also be examining damage evolution in-situ during quasi-static tension. Static high pressure work has been done for years at APS. All of these capabilities are extremely important for advancing our understanding of the performance of materials. However they are not able to probe the in-situ three dimensional evolution of phase transformation and damage processes under dynamic and shock loaded conditions.

R&D needed to enable success as well as roadmap

To perform this first experiment will likely require a transverse and longitudinally coherent source of hard X-rays in a single beam. This source will be used to produce X-ray diffraction imaging in a fashion following the emerging field of ankylography in which a single X-ray beam is passed through the sample and the diffracted image is captured on an Ewald sphere[4]. The captured image is used to reconstruct the spatial structure of the sampled body. The use of a high energy beam to probe a shock loaded sample over a small time interval produces the balancing problem of sampling the greatest amount of mass while preventing significant alteration of the sample. Diffracted image quality will also be determined by the state of the art in X-ray detector technology for both response rate as well as resolution. Producing shock loaded conditions in the imaged material will also require innovative drive technologies for potentially small samples. It is important that these experiments also be performed on samples which have been taken from larger bodies of "real" materials which have experienced practical processing. Once a sample has been taken, it is very important to fully characterize its initial state (e.g. structure, defect distribution, etc.) to as high a resolution possible to enable us to establish credible initial conditions for use in modeling tools from MD to continuum. Developments in our theoretical and simulation tools will also be essential.

Context

This experiment shares similarities in the nature of information needed for an aggregate type material as proposed for "Energetic Materials at MPDH/M4". The same microstructural evolution needs are shared by "Nanoferritic Alloys". Material interests are shared with "Exploring Separate Effects in

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[1] Mat. Sci. Eng. A-Struct. 641, 483 (2008); Appl. Phys. Let. 96, 043122 (2010); Corrosion Sci. 50, 3455 (2008).

[2] Fusion Sci. Tech. 55, 417 (2009)

[3] Hefferan, C.M. et al., Computers, Materials, & Continua, in review.

[4] Nature 463, 214 (2010)

Plutonium". Temperature increases are expected from X-ray probes proposed here and repetition rate concerns are shared with radiation damage experiments.

Influence of Stochastic Explosive Microstructure on Detonation

Joseph T. Mang, Dana Dattelbaum, Dan Hooks, Ralph Menikoff, Ed Kober, Marc Cawkwell, Kyle Ramos, Laura Smilowitz and Darla Thompson, LANL

Problem Statement

The design and application of energetic materials, especially novel energetic materials, is limited by significant gaps in our understanding of properties and processes relevant to their safety and performance, especially in dynamic extremes.

Scientific Objectives

From shock or thermally-driven initiation through the conditions that result in failure, detonation is a chemically-driven event that is highly influenced by the stochastic nature of explosive microstructures, and a wide range of potential stimuli and environments. Most practical applications of energetic materials are guided by insights gleaned through a largely trial-and-error approach, rather than fundamental knowledge of the chemical and physical processes underlying their response. Further, there are national drivers toward insensitive munitions requirements. Challenges associated with designing and qualifying new insensitive explosives are significant.

Over the last century of research, empirical models have achieved adequate fidelity in extrapolating behavior under very tightly controlled engineering scenarios. When applied outside of these scenarios, the predictive capability of these models is extremely limited because they do not capture the specific physics and chemistry that drives the macroscopic response. Plastic bonded explosives (PBXs) are highly heterogeneous materials (Figure 1). For some time, it has been recognized that the shock initiation of PBXs is dominated by formation of "hot spots" or localized regions of high temperature and pressure. To date, no models account for these processes, and there have not been adequate measurements to inform a new generation of models that do capture these processes.

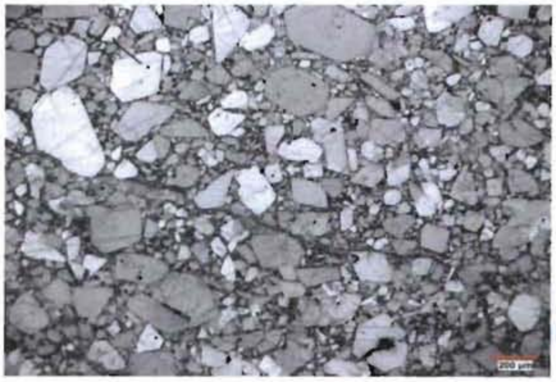

Figure 1. Micrograph of PBX 9501, illustrating the heterogeneous microstructure

The grand challenge for high explosives is thus an ability to quantitatively predict energetic materials performance from chemical composition, thermodynamic properties, and fully-resolved micron-scale structures. "Performance" necessarily must include storage behaviors, mechanical properties, aging and stability, failure, initiation thresholds (sensitivities), initiation mechanisms, and detonation performance characteristics. New data on the scale of this heterogeneous microstructure and the associated improved understanding will help address key scientific needs in order to establish predictive capabilities of the response of energetic materials to a wide range of stimuli with varying temporal, pressure, and temperature characteristics. These needs include deconvolution of the influence of microstructure on the details of hot spot ignition and the relative importance of types of hot spots toward improving our reactive burn models, determination of the links between micro- and chemical structures, reactive burn kinetics and their influence on detonation propagation and failure in complex geometries, and design of an explosive from first principles predictions of thermochemistry and tunable microstructures.

Experimental Details

in situ observations of the evolution of hot spots and mechanical response under dynamic conditions will be made, including experimental environments capable of withstanding and achieving extreme conditions such as the high strain rates encountered under shock compression (up to 10^6 s^{-1}), pressures up to and exceeding ~50 GPa and temperatures of ~3000K with temporal resolution relevant to high explosive reactions over length scales ranging from nanometers to hundreds of microns.

Hot spots, which have many different origins, are responsible for the initiation and detonation properties of solid high explosives. By fabricating explosives with well-defined hot spot features, and conducting experiments at high pressure and temperature on appropriate time scales, with micron-to-sub-micron resolution, we can interrogate details of hot spots such as, their formation, ignition and interactions and thus improve our ability to predict and potentially control hot spots. The understanding of properties such as, critical hot spot sizes, temperatures and pressures as well as the confluence of hot spots leading to initiation and detonation will assist the development of new materials where the material's performance is controlled by induced hot spot nucleation sites.

Current Landscape

Current material models, while performing well within their calibrated regimes, are naturally non-predictive in all situations. Current techniques are incapable of capturing the extremes of temperature and pressure with simultaneous breadth in time and length scales to inform the next generation of microstructure aware models.

R&D Needs/Roadmap

Our goal is to design new explosives with targeted characteristics from first principles with tailored microstructures, and to develop an ability to predict formulation and processing outcomes and their relation to final mechanical properties and performance. Accurate models of the fracture, frictional heat generation, thermal conductivity, phase transitions (melting), chemical reactions, and gas generation occurring during HE reaction are necessary, requiring large-scale three-dimensional simulations with an accurate description of phenomena at interfaces.

Experimentally, we require radiography or imaging techniques with sub-micron resolution with a field of view of several hundred microns and nanosecond time resolution in order to study particle interfaces, single hot spots and interaction of multiple hot spots. Techniques to make in situ measurements of the absolute temperature and density of reacting systems are needed to advance HE EOS understanding.

Context

This work is related to another proposed Marie first experiment considering the consequences of microstructural heterogeneity on failure and damage modes of metals. While the materials of interest (metals vs. high explosives) are quite different, both involve heterogeneous microstructures of similar length scales. Both proposals are interested in microstructural variation as possible nucleation sites for damage and failure.

Predictive Understanding of Fluid/Mineral Interaction in $CaCO_3$ as a f (P,T, X)

D. D. Hickmott, H. Xu, H. Ziock (LANL); A, Kavner (UCLA); R, Hemley (Carnegie)

Problem Statement:

Observe and quantify fluid processes at mineral interfaces at extreme pressure-temperature (P-T) conditions relevant to Earth's interior (e.g., in $CaCO_3$ surfaces and supercritical fluids in the model system H_2O-CO_2-NaCl).

Scientific Objectives:

Processes at mineral-fluid interfaces control a wide-range of phenomena of crucial importance in energy/environmental applications (Figure 1) (Park et al., 2006; BES, 2007). Mineral precipitation/dissolution, colloid formation, contaminant immobilization/mobilization are all determined by interactions at mineral interfaces. Because of the importance of such processes, mineral interfaces have been the subject of a great deal of research using techniques focused on solid interfaces; these techniques include atomic force microscopy (AFM), electron microscopies (SEM & TEM), and advanced synchrotron based methods (x-ray reflectometry, XAFS, etc).

Much less experimental attention has focused on fluid processes at high-P mineral interfaces because relevant techniques (e.g. Sum Frequency Generation – SFG, neutron reflectometry) are not widely available to geochemical researchers nor do they perform well at high pressure.

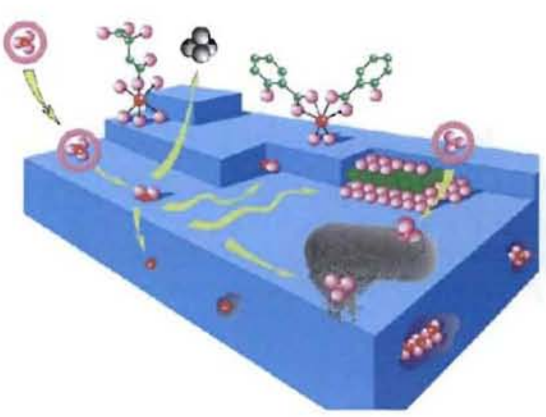

Figure 1: Schematic of processes at mineral-fluid interface including biotic interactions, sorption/ desorption, phase growth and boundary layer formation

$CaCO_3$ (polymorphs include vaterite (hexagonal), calcite (rhombohedral), aragonite (orthorhombic)) is an extremely important phase in a wide-range of Earth/energy /environmental applications and Earth processes. Sorption on calcite has been postulated as a method of contaminant/ radionuclide immobilization, calcite colloids may be crucial in plutonium mobilization in some environments, calcite buffers the pH of aqueous fluids preventing contaminant mobilization, and, most importantly, precipitation/ dissolution of calcite is a key process that will occur during the geologic sequestration of CO_2. $CaCO_3$ also represents a model mineral system for a range of carbonates (magnesite, dolomite, siderite) that are important within the deep Earth. Calcite surface properties have been widely studied (e.g. Reeder 1996; Geissbuhler et al., 2004). Interestingly, there is a significant (up to a factor of 10), difference in the sorption behavior of a number of cations on different growth faces of calcite (e.g. Reeder, 2006). For example, Mn and Sr are differentially enriched in {0112} faces in calcite compared to {1014} faces when calcite in precipitated from aqueous solutions (Reeder 1996). This implies a strong difference in the interface structure and cation binding forces and suggests that there may also be differences in fluid properties adjacent to the different crystal/growth faces. This opens the possibility that surface energies and therefore reaction driving forces and kinetics may be tailored by manipulating preferred orientations and sample microstructures for carbonate-fluid systems.

Carbonates represent a crucial system in which interface/fluid interactions, including chemistries and kinetics, can be probed as a function of differing surface structures within the same crystal structure (calcite crystal faces) and between differing surface structures between crystal structures of the same composition (calcite vs. aragonite vs. vaterite) as a function of P-T and fluid composition. By comparing different structures with identical compositions an understanding of fluid/interface processes independent of bulk compositional control will be obtained and compared with molecular dynamics (MD), density functional theory (DFT) or other computational chemistry results.

Experimental Details:

The main objective of the proposed experiment is to observe and quantify the interactions between $CaCO_3$ surfaces and supercritical fluids in the model system H_2O-CO_2-NaCl. Specific objectives include: 1) to determine the structure and energetics of $CaCO_3$/fluid interfaces as a function of fluid composition, P (atm to 2 GPa), and T (room T to calcite melting); 2) to examine mineral/mineral interfaces as a function of P, T and fluid composition in polycrystalline aggregates; 3) to perform MD and DFT calculations relevant to the observed results; and 4) ultimately to upscale and incorporate these data and models into flow and transport simulations of Earth processes. We anticipate the following experimental tasks:

Synthesis

1) Obtain large calcite, vaterite, and aragonite crystals. Cut/cleave these along relevant crystal/cleavage faces and polish these to angstrom-scale smoothness. These materials will be characterized for bulk and interface properties (e.g. composition using electron microprobe, structure using X-ray diffraction, surface structure/roughness using AFM and neutron/x-ray reflectometry). Polycrystalline samples will be produced by grinding and sintering – to produce homogeneous, low-strain aggregates.

Extreme Environment

2) A special high-P solid-liquid interface cell will be constructed with sapphire windows. The high-energy coherent x-rays to be produced in MaRIE should be able to penetrate such a cell with acceptable transmission. This cell would allow experiments to 100 MPa. (Figure 2)
3) A hydrothermal diamond anvil cell (DAC) accommodating either single crystal or polycrystalline samples will be designed & constructed allowing the P range to reach the conditions of the lower crust (~2 GPa).

Measurement

4) H_2O/CO_2/NaCl mixtures of known composition would be loaded (condensed) into P vessels. A series of coherent x-ray imaging and x-ray probe experiments will be completed:
   a. Fluid/calcite interface structure determination adjacent to calcite {1014} and {0112} at ambient P-T conditions using coherent x-ray imaging over a range of fluid compositions. Resolutions of imaging should be at the nm scale and will provide information on growth processes and sorption.
   b. Fluid/calcite interface structure determinations adjacent to calcite {1014} and {0112} at elevated P-T conditions (to 2 GPa and calcite melting T).
   c. X-ray probes of the interfaces in 4(a) and 4(b) using EXAFS/XANES and resonant X-ray reflectivity.
   d. Similar experiments to 4(a) through 4(c) above for vaterite and aragonite (over the relevant phase stability ranges).
   e. Studies of polycrystalline calcite buried interfaces and defects as a function of P-T-X.

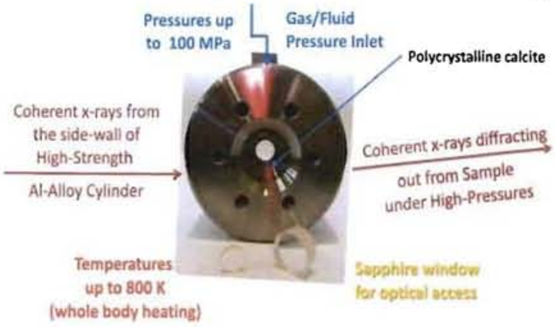

Figure 2 –Schematic of high-P experimental cell and coherent x-ray beam access

> Because the wetting behavior (surface free energies) of calcite/fluid varies over the experimental conditions of interest, fluids would range from fully wetting, to filling grain edges to being confined in grain corners.

In future phases of experiments, similar investigations would be extended to other geologically relevant phases (SiO_2, muscovite, etc) and polycrystalline aggregates of such phases, and a wider range of fluid compositions (various solutes). In addition, MD and/or DFT modeling of the experimental results will be integrated with experimental results.

Current Landscape: A first-ever coherent x-ray imaging experiment in a DAC was reported at the 2009 AGU meeting. Yang et al. reported on data obtained at LCLS on nanocrystalline gold to several GPa. The high energy (50 keV) high-brilliance coherent x-rays proposed for MaRIE would allow higher-z materials to be used for P cells (x-ray energies above the absorption edges of many metals) as well as improved transmissivity through diamond.

R&D Roadmap:

In the short term, experiments on single crystal calcite surfaces at moderately elevated P and T could be attempted using x-ray reflectivity or neutron reflectometry. This would initiate development of relevant P cells and provide the first-ever direct insights into geological material interfaces at elevated Ps in the presence of fluids.

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Three-Dimensional Measurements of Turbulence in Shocked Fluids to Mach 15

Malcolm J. Andrews, Kathy Prestridge, Robert Gore, Chris Tomkins, Fernando Grinstein, James Fincke, LANL; Oleg Schilling, LLNL; Joseph Katz, John Hopkins University; David Youngs, AWE.

Problem Statement

A predictive understanding of turbulence, especially "material mixing" phenomena relevant to stockpile certification, is presently lacking.

Scientific Objectives

Turbulence underpins much of modern technology (e.g. combustion, heat transfer, aerodynamics, energy generation, and Inertial Confinement Fusion - ICF), environmental processes (climate, oceans), and biological functions (blood flow, laboratory mixers). Our choice of a "material mixing" problem associated with high Mach (Ma) number shocks reflects important broad classes of applications, with billion dollar impacts, specifically Predictive Science for Stockpile Stewardship, and ICF design and problem resolution. We would expect that progress with this experiment will also lead to advances across an even broader set of applications that include: combustion and turbulent mixing problems at high density ratios (gas/liquid), and the development of advanced diagnostics for turbulence measurement, and validation of advanced models for turbulent mixing for application to gas/liquid problems, e.g. ocean modeling, sprays, cavitation, and multi-phase flows.

The present route for stockpile stewardship relies on advancing predictive science that, in-turn, demands an understanding of shock-driven turbulent mixing processes. The first experiment described below would address some of the hardest turbulent mixing problems in stockpile science. Variable material (density) flows incorporate a broad class of fluids mechanics that generally considers mixing between different fluids, with different densities. The scalar (density) difference does dynamically effect the flow (e.g. buoyancy); typified in our case by Rayleigh-Taylor (RT - buoyancy driven) mixing, and Richtmyer-Meshkov, (RM - shock-driven density interfaces), see Fig. 1.

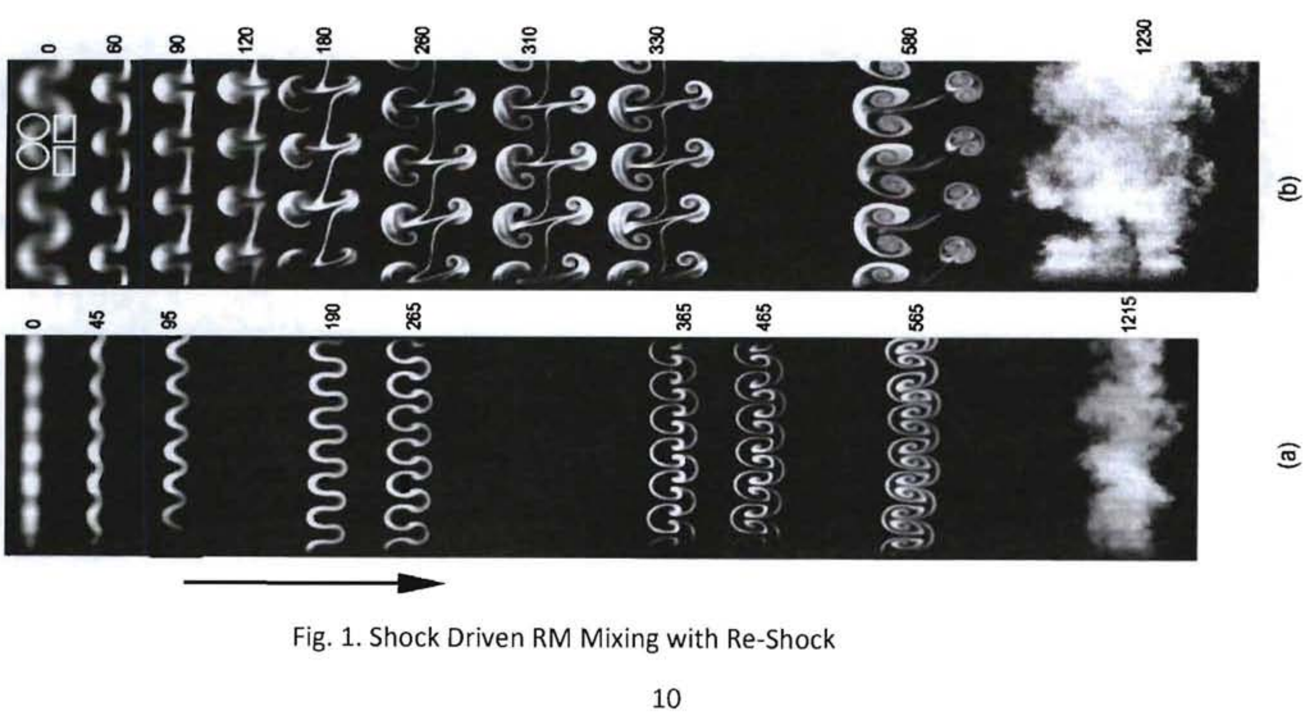


Fig. 1. Shock Driven RM Mixing with Re-Shock

At the present time it is not clear at what point RM mixing processes become Ma dependent, but it is believed to be around Ma~4. Moreover, it is not clear what modifications need to be made to existing (and forthcoming) turbulence models to capture high Ma effects. Indeed, the physics at Ma~10 suggests ionization and change of phase, coupled with the possibility of mix "shocklets" that may substantially enhance the turbulence.

The objective for this first experiment is to obtain high fidelity, simultaneous, 3D velocity and scalar fields for RM (with re-shock) up to Ma ~ 15. Such data would provide validation of existing models, and modification of those models to incorporate new physics and mixing mechanisms.

Experimental Details

We anticipate two related experiments: 1) an optical diagnostic experiment that would operate to Ma ~ 6 (hereafter termed Ma6), shown in Fig. 2, and employs Particle Image Velocimetry (PIV) and Laser Induced Fluorescence (LIF) to simultaneously probe the mixing volume; and, 2) an explosive based pRad experiment that would seek to operate within the range 6 < Ma < 15, and obtain similar velocity and density profiles (hereafter termed Ma15), illustrated in Fig. 3.

The optical experiment Ma6 has the advantage of: building on current advanced diagnostics that we might reasonably expect to improve over the next 15 years; using known technologies to build and validate a new facility (this could take 10 years); and, be substantially less expensive than the high Ma pRad experiment. The pRad experiment Ma15 would build on current efforts to investigate high Ma RM mixing, but would take advantage of on-going and planned MaRIE improvements that might include: multiple axes for 3D measurements; higher spatial and time resolutions (to obtain molecular mix measurements); and, introduction of multi-probe techniques to obtain PIV type measurements of velocity fields.

Current Landscape

The Ma15 apparatus is modeled after the current Multi-Shocked-Fluid (MSF) experiment at pRad. The MSF is similar to the Ma15 shown Fig. 3, and takes advantage of the pRad powder gun to launch a flyer that leads with Ma~9 shock that then interacts with the He/SF_6 or an He/Xe interface.

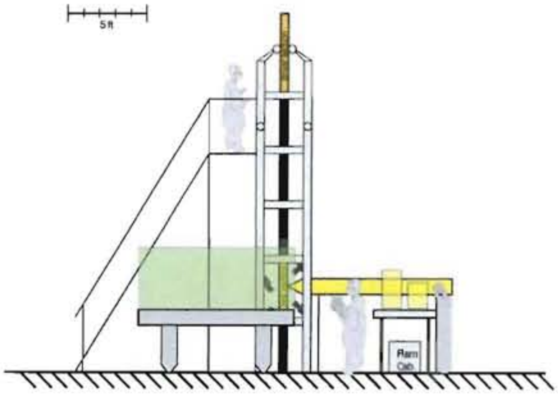


Fig 2. 0 < Ma < 6 Pressure Driven Shock Tube

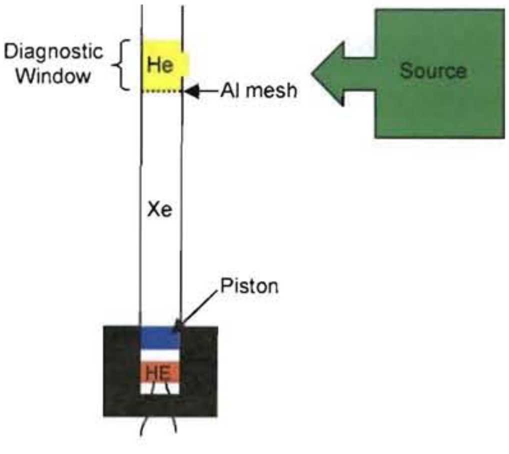


Fig 3. 6 < Ma < 15 HE Driven Shock Tube

The detailed scientific functional requirements for the Ma15 experiment may be found in the First Experiments Report, but key length and time scales resolutions are 1.28μm and 0.03μs.

R&D Needed

R&D is needed to develop a $0 < Ma < 6$ vertical shock tube, and similarly $6 < Ma < 15$ facility, that aside from being appropriately diagnosed must also meet access, maintenance, and safety requirements. We anticipate a staged development over the next 15 years starting with our present MSF HE shock tube, and progressively adding capability and diagnostics. Included in the development are advanced spectroscopies and optical diagnostics, in particular: 3-D high precision optical laser diagnostics; 3-D PIV for velocity fields; 3-D Planar Laser Induced Fluorescence (PLIF) for density fields; Rayleigh scattering (materials); Raman (species); and, Coherent Anti-Stokes Raman Spectroscopy - CARS - (species, temperature). We also expect to make use of pRad (3D density fields in thin/thick dense materials), X-rays (3D density fields in thin dense materials), and Phase Contrast Imaging (density measurements).

Context

Our "turbulence" phenomena and associated data involve statistical averages either over an ensemble average of separate experiments, time, or space. Thus, our requirements include the ability to collect simultaneous (or almost simultaneous) measurements over either extended run times (perhaps up to several seconds), or sample depth (perhaps up to 1m). It is the need for ensembles, compared with "single shots", that makes "turbulence" a unique challenge for MaRIE.

Irradiation Stability of Structural Nanocomposites

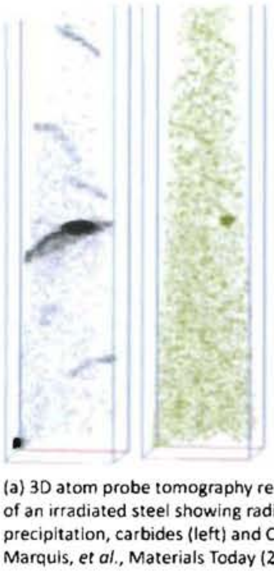
Amit Misra, Mike Nastasi, Alfredo Caro, Yong Wang, Stuart Maloy (LANL); Lumin Wang (University of Michigan); Mitra Taheri (Drexel University); Mark Kirk (ANL); Xinghang Zhang (Texas A&M); Jie Lian (RPI); Peter Hosemann, Brian Wirth (UC-Berkeley); Mike Demkowicz (MIT); Srinivasan G. Srivilliputhur and Raj Banerjee (University of North Texas); Pascal Bellon and Bob Averback (University of Illinois); Yuntian Zhu (North Carolina State University); Dhriti Bhattacharya (ANSTO, Sydney).

Problem Statement

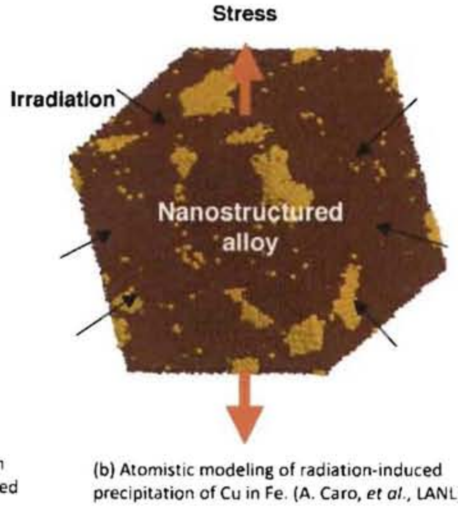
Fundamental understanding of the mechanisms that impart morphological and chemical stability in nanomaterials will lead to the development of radiation-tolerant nuclear energy materials with predictable and controlled performance at irradiation extremes.

Scientific Objectives

The key objective is the development of fundamental understanding of interface-driven morphological and phase instabilities in advanced nanomaterials. Irradiation may cause phase instability via one or more of the following effects: (i) crystal to amorphous transformations or from one crystal structure to another, (ii) redistribution of solute atoms in an alloy leading to dissolution of fine precipitates, or nucleation of new precipitates or enrichment (segregation) or depletion of solutes at boundaries, or (iii) morphological changes such as grain coarsening or spheroidization of layered structures.



(a) 3D atom probe tomography reconstruction of an irradiated steel showing radiation-induced precipitation, carbides (left) and Cu (right). E. Marquis, *et al.*, Materials Today (2009).



(b) Atomistic modeling of radiation-induced precipitation of Cu in Fe. (A. Caro, *et al.*, LANL).

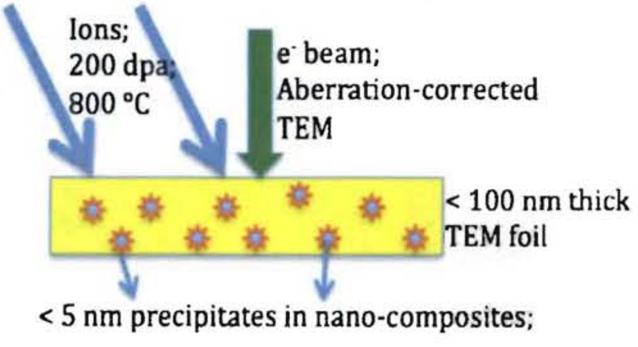
As an example, consider the case of oxide particles less than 5 nm in diameter in a ferritic steel matrix. The specific science issue is: *what is the mechanism of phase instability of nano-composites and what is the stability limit under extreme irradiation conditions*? Similar science issues are applicable to a much broader class of nanomaterials. Measurements are needed on phase stability (changes in morphology and chemistry) of the nano-features as a function of irradiation dose at a given temperature. *In situ* measurements that allow the characterization of dynamics of phase instabilities are needed to integrate experiments with multi-scale modeling.

Experimental Details

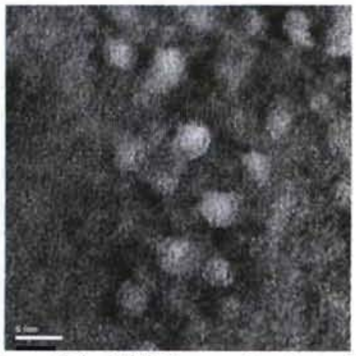
First experiment: *in situ* ion irradiation in an aberration-corrected TEM

Current status: *In situ* experiments in a TEM capture dynamics typically at rates of 30 frames/second but the defect evolution starts at sub-ps time scale. Also, sub-Å resolution is needed to resolve interface chemistry at the atomic scale, as opposed to defect clusters on the scale of 1 nm that is achieved currently. This represents a significant gap between experiments and modeling. Molecular dynamics simulations can reveal radiation-induced point defect (resolution of single vacancies and interstitials) interactions with interfaces at sub-pico to nano-seconds, but experiments only resolve defect clusters (≈ 1 nm diameter) at time scales on the order of 1/30 second.

Proposed first experiment: A significant development is appearing which can have great impact on experimental work in irradiation effects at the 1 Å scale. This is the coming development of doubly aberration corrected (spherical and chromatic aberrations) electron microscopes with expanded accessible volume for *in situ* ion irradiation (1,2 or 3 beams) combined with well controlled specimen environment (temperature, stress, gas or liquid) and space for additional measurement techniques (laser based, x-ray, physical properties) beyond just the electron beam techniques (which will be quite powerful in itself: energy filtering, analytical probes, tomography, etc). To achieve this expanded space for *in situ* experiments will compromise the ultimate spatial resolution, but only to 1 Å. Useful temporal resolution for the study of dynamic processes should also be extended down to milli-sec or better over the next decade. The proposed first experiment (see schematic) is *in situ* irradiation studies in an aberration corrected TEM using up to 3 ion beams for precise control of dpa-to-implanted gas ratio. Heavy ions will be used to create damage (up to 200 dpa or less; at temperatures ranging from liquid N_2 to 800 °C) while additional ion beams will be used to implant controlled amounts of helium and/or hydrogen. Such real time experiments will help validate predictions from multi-scale models. *Ab initio* and MD simulation methods will provide insight on the defect (radiation-induced)-interface interactions. The information from the atomistic models will be incorporated into phase field and KMC models to study phase stability at higher length and time scales.



Schematic of the *in situ* ion irradiation experiment to study phase instabilities at interfaces in nano-composites.



High-resolution TEM image showing < 5 nm oxide precipitates in nano-ferritic alloy U14Y WT (D. Bhattacharyya, *et al.*, LANL).

Proposed follow-up experiment: Neutron irradiation with *in situ* XRD & *post-mortem* TEM characterization

Ion beam irradiation experiments will provide guidance on the promising radiation-tolerant nanocomposites. However, the ion irradiation spectrum and damage rates differ from neutron irradiations. Thus, it is important to subject selected promising bulk nano-composites to neutron irradiation to study phase stabilities and damage evolution in reactor-like extreme irradiation conditions. For a given promising material system, the ion irradiation experiments performed on it, coupled with theoretical analyses and simulation, may provide an estimate of the neutron irradiation conditions that may be of interest to explore. During neutron irradiation, *in situ* XRD may be used to probe damage evolution and supplemented with post-irradiation TEM. Given the fact that neutron irradiations could run for years, probing the structural evolution *in situ* during irradiation is crucial to save time and also reduce, where possible, the extent of post-irradiation experiments on radioactive samples.

Current landscape

The development of new nanocomposite materials for nuclear reactors may not be possible until a facility such as MaRIE is built to understand the stability of bulk nanocomposites in neutron-reactor-like extreme environments in terms of helium to dpa ratio, total dpa, dose rate, temperature, etc. In addition, by adding the capability of measuring structural changes *in situ* under ion irradiation, one can couple the microstructures produced under irradiation with the changes in mechanical behavior. Note that MaRIE will allow fundamental studies of phase stability in novel structural nanocomposites through the use of in situ ion irradiation capabilities to measure structural changes under irradiation. Such capabilities are NOT available at test reactors (e.g., ATR, HIFR) that simply provide a source to neutron irradiate engineer materials. On the other hand, the current light sources such as LCLS do not have neutron irradiation capabilities. Regarding *in situ* ion irradiation in a TEM, current facilities such as ANL (operated part-time) do NOT have the spatial resolution of aberration-corrected TEM for elucidating subtle changes in chemistry and structure at Å-scale. Furthermore, there is no current facility that co-locates within the same complex the following capabilities: *in situ* ion irradiation in TEM, neutron irradiation with *in situ* XRD, and material synthesis, property measurements and materials theory/modeling to allow an integrated effort in radiation damage research.

R&D needed to enable success

A two-step approach is proposed. First, *in situ* ion irradiation in an aberration-corrected TEM to study the unit processes at accelerated dpa and identify radiation-tolerant nanomaterials without having to wait for decade-long neutron irradiations. Second, neutron irradiation (including *in situ* measurements) of the most promising radiation-tolerant nanomaterials for fundamental studies of stability under extreme neutron environments.

For scientific exploration with the sole objective of studying a certain phenomenon (e.g., irradiation-induced solute redistribution), ion irradiation may suffice (ion-solid interactions research community). However, if the long-term objective is to develop and qualify new materials for nuclear reactor applications (nuclear reactor community), then the "first" experiments with ion irradiation will be used to guide "second" experiments with neutron irradiation.

Context

The research proposed here is closely related to the first experiments being proposed by Hosemann, Maloy *et al.* to study the effect of irradiation on mechanical properties of radiation-tolerant nanocomposites and to activities on synthesis of nanocomposites (Mara)

Fission Gas Bubbles and Concomitant Swelling in UO_2 Nuclear Fuel

Los Alamos National Laboratory (PI: K. Sickafus), *Institute for Transuranium Elements, Karlsruhe, Germany* (PI: T. Wiss), *CNRS, SPMS-Ecole Centrale Paris, Chatenay-Malabry, France* (PI: G. Baldinozzi), *Bhabha Atomic Research Centre (BARC), Mumbai, India* (PI: S. Kailas), *Central Research Institute of Electric Power Industry (CRIEPI), Tokyo Japan*, (PI: M. Kinoshita), *Florida State University, Tallahassee, FL* (A. A. El-Azab), *Arizona State University, Phoenix, AZ* (PI: P. Peralta)

Problem Statement Gas bubbles cause swelling which severely limits the service life of a fuel pellet. If we can understand and control fission gas bubble formation, we should be able to greatly extend the life expectancy of nuclear fuel in a light water reactor.

Scientific Objectives

Our goal is to reveal microstructural evolution and concomitant swelling due to fission gas bubble nucleation and growth during the burning of a UO_2 nuclear fuel pellet. Our first experiment is designed to achieve this goal under relevant fuel irradiation conditions, especially exposure to high temperature and high temperature gradient, but under conditions that will not involve significant actinide fissioning (the latter produces additional chemical effects, as well as undesired sample radioactivity and consequent sample-handling problems). In other words, we desire to simulate a burning nuclear fuel without actually burning the fuel.

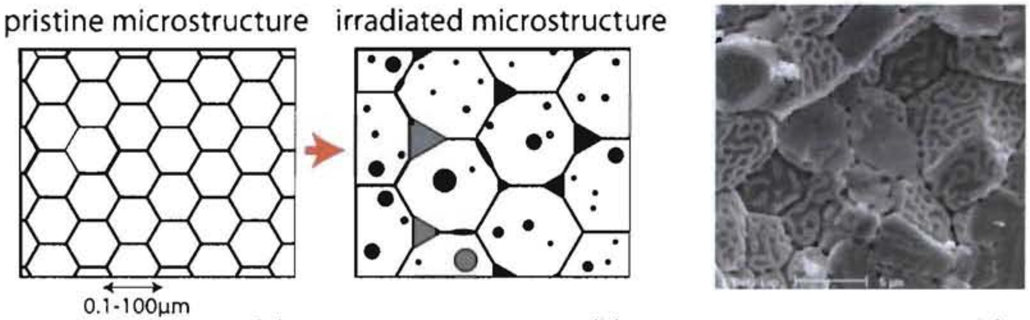


Figure 1. (a) (b) (c)

Perform *in-situ* and *ex-situ* characterization of microstructural evolution in UO_2 due to: (1) high temperature and high temperature gradients; (2) radiation damage; and (3) the incorporation of gaseous fission products (namely, xenon, Xe). Experiments require resolving evolutionary microstructural effects at nm, μm, and mm length scales, over times ranging from hours to weeks. Experiments will be complemented by atomistic and higher scale computational methods, in order to predict microstructural evolution (grain growth, pore migration, etc.) and especially the nucleation and growth of fission gas bubbles,as well as concomitant swelling and micro-cracking effects.

Experimental Details

Fig. 1 shows the details of our first experiment. Fig. 1a shows a schematic diagram of a UO_2 microstructure before irradiation (i.e., before fuel service in a reactor core). The microstructure consists of grains with average diameters ranging from 0.1 – 100 μm, depending on fuel fabrication procedures. Fig. 1b shows a schematic diagram of a UO_2 microstructure following irradiation, wherein grains have grown considerably in size, compared to the pristine microstructure. In addition, fission gas bubbles of various sizes have precipitated in the bulk of the grains (shaded microstructural features), as well as along grain boundaries and at grain triple junctions. Fig. 1c (courtesy of T. Wiss, ITU, Germany) is a scanning electron micrograph showing a UO_2 fracture surface following fuel service to a typical "end-of-life" burnup. Notice the remnants of "worm-like" fission gas bubbles along the previously un-fractured grain boundaries.

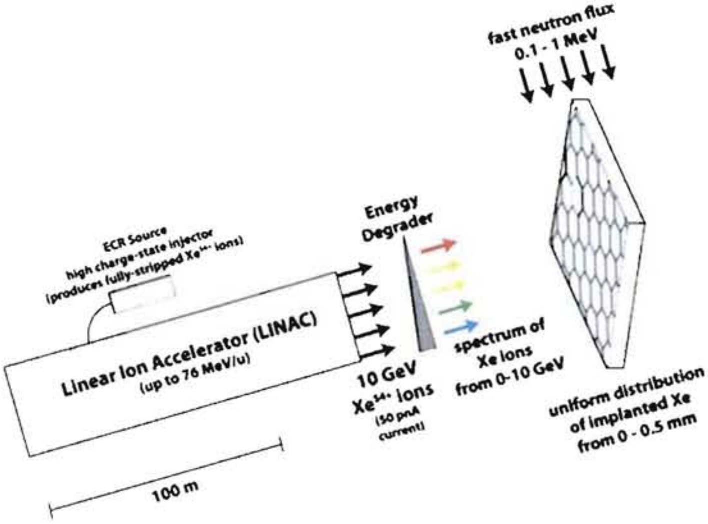


Figure 2.

We will use a high-energy (10 GeV) ion accelerator plus an *energy degrader* to implant our UO_2 sample (0.5 mm thick) with a uniform concentration of Xe ions (Fig. 2). Xe is intended to represent a fission product, specifically the most prevalent gaseous fission product formed during fissioning of uranium. So, essentially, this experiment is designed to monitor microstructural evolution in UO_2 while only one fission product (Xe) is incorporated into the material. The Xe implantation will occur at high temperature (~1000°C plus a large temperature gradient) over a long period of time ($\sim 1 \times 10^6$ s or nearly two weeks), so as to simulate the microstructural evolution that occurs in a real, burning UO_2 fuel, as Xe atoms migrate to nucleate and grow fission gas bubbles.

Current landscape

Microstructural analyses of irradiated UO_2 fuel are typically performed *post-mortem* (post irradiation examination or PIE) following "in-pile" irradiation in the core of a nuclear reactor. PIE of in-pile irradiated nuclear fuel is woefully inadequate to reveal the underlying atomistic and microstructural mechanisms responsible for the swelling, micro-cracking, and ultimate failure of nuclear fuel at moderate to high burnups. Too many mechanisms contribute to the microstructural evolution of "real" burning nuclear fuel, and the excessive radioactivity of irradiated UO_2 make detailed analyses of irradiated UO_2 nearly impossible. Our "reductionist" first experiment will help to isolate the most important mechanisms responsible for swelling-induced nuclear fuel failure (namely, fission gas bubble nucleation and growth).

R&D Requirements

We require detailed theoretical examinations of fission gas bubble nucleation and growth as a function of varying fuel microstructural parameters (e.g., average grain size and grain size distribution, initial fuel pellet porosity, residual stress, and fuel composition including impurities). We require preliminary fission gas implantation experiments using existing high-energy ion accelerators. These existing ion accelerator facilities tend to provide fairly low ion currents compared to our MaRIE requirement (50 particle nA beam current). Nevertheless, we can learn a great deal regarding the embryonic stages of fission gas bubble nucleation and growth using existing ion accelerators. Our proposed MaRIE experiment, on the other hand, will allow us to observe and characterize microstructural changes typical of nuclear fuel at high burnups.

Context

This first experiment is closely related to proposed MaRIE first experiments regarding: (1) thermal transport in irradiated nuclear fuel; (2) microstructural changes in nuclear clad material; and (3) the role of interfaces in irradiation-induced microstructural evolution.

In situ Mechanical Testing of Structural Materials in a Fusion/Fission Relevant Spectrum

P. Hosemann, S.A. Maloy, J. Van den Bosch, A.T. Nelson, LANL

Problem Statement

An efficient irradiation capability with state of the art diagnostics is essential to fulfill the Nation's energy needs and allow faster materials licensing and development for nuclear applications.

Scientific Objectives

In order to reduce greenhouse gas emission and ensure energy security for the Nation's future, nuclear power need to play a larger role in future energy solutions. To address this goals in the near term, the US must engage in the following activities:

1. Extend the lifetime of the present reactor fleet out to 80 years.
2. Build new light water reactors (LWR)
3. Close the fuel cycle and build fast spectrum transmutation systems

All of these activities may be completed with the present qualified materials but there are significant advantages to developing and qualifying new advanced materials. In order to accelerate materials development and materials testing, sufficient materials testing capabilities need to be provided in a relevant neutron spectrum and He/dpa ratio. Performing additional measurements under irradiation allows one to obtain data which cannot be obtained after irradiation and will help the simulation efforts and validate the models.

1. Performing characterization measurements in situ on a proposed fuel/clad system to determine the stress state of the cladding under relevant reactor irradiation conditions without actually building a new test reactor. This reduces the time needed to test fuels by a factor of 2-3.
2. Performing critical mechanical property measurements (creep, fatigue and fatigue crack growth) on advanced materials while under irradiation to measure the relevant changes in mechanical properties for qualifying these materials or developing improved materials.
3. These experiments performed in combination with ion beam irradiations under controlled conditions allow one to screen numerous new potential alloys to accelerate the development of advanced nuclear materials.
4. By performing measurements under controlled irradiation conditions of flux, temperature, transmutation gas production and stress critical data is obtained for development and validation of models for understanding and predicting radiation effects in materials.

Experimental Details

Performing stress and strain measurements on an actual fuel cladding tube and measuring creep and fatigue on samples under irradiation are unique measurements that can only be performed under irradiation because the stress state on the cladding is only present under irradiation and creep and fatigue are strongly controlled by irradiation. These measurements provide critical data on the conditions experienced by a cladding allows licensing new materials fast and efficiently for the use in a nuclear environment (fission and fusion) while gaining scientific insight of how the irradiation induced creep and cracking formation take place. A wide post irradiation characterization using new tools like Local Electron Atom Probe, small scale mechanical testing, micro diffraction, Transmission electron microscopy and in situ materials testing, etc. allow one to obtain a complete microstructural description of the samples tested in the beam.

Experiment 1) Measuring creep or fatigue under irradiation: In order to be able to qualify new materials for the use in nuclear applications uniform irradiations on specimens qualified to ASTM standard specimens must be performed. These samples can be creep as well as fatigue. The defects created during irradiation strongly affect creep and fatigue in materials, requiring these measurements to be made under irradiation. Local strain measurements provide an understanding of where and why localized failure occurs in the material. A setup as shown in figure 1a) allows also studying more complicated components such as the effect of radiation and stress on welds..

Experiment 2) fuel in clad: When a fuel is irradiated in a uniform neutron flux, a strong thermal gradient occurs across the cladding outside and the fuel inside. This leads to internal thermal stress. While the radiation and the stress can lead to creep in the actual component knowledge of the actual temperature and stress gradient throughout the entire assembly is important in order to improve the fuel and cladding design (Figure 1b) and develop models to predict and understand clad failure from irradiation.

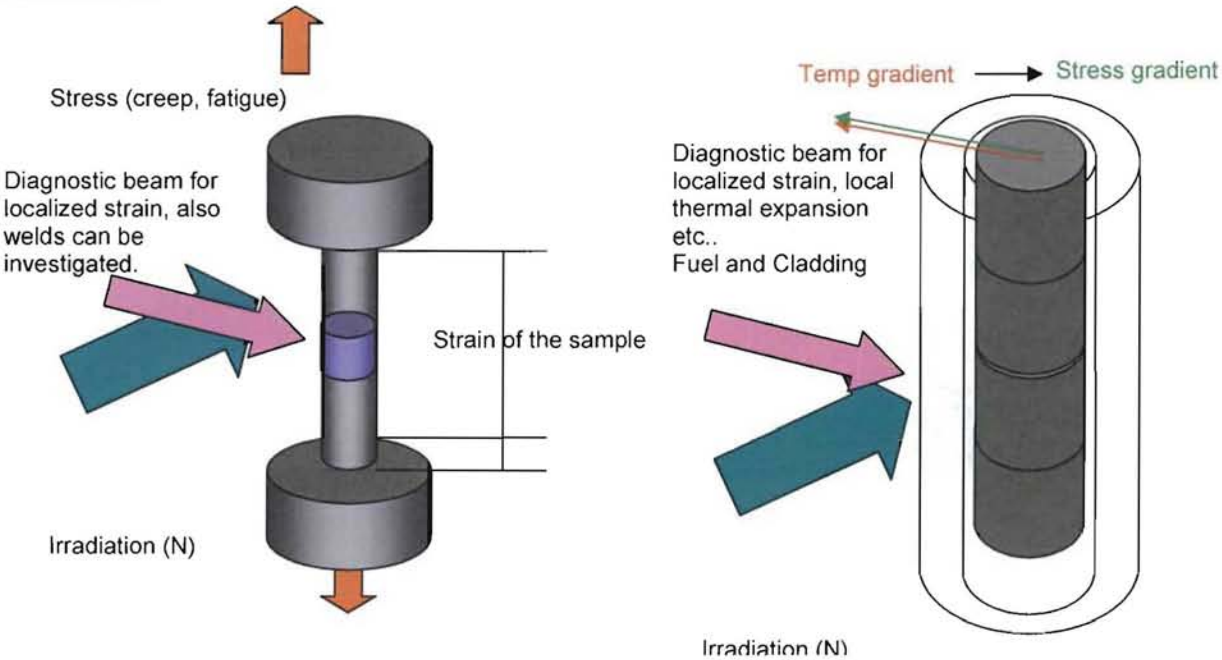


Figure 1: Setup to measure creep in the radiation environment while investigating localized strain (a).Test setup for measuring localized stress under irradiation on a fuel rod with cladding (b)

Current Landscape

Currently there are no irradiation facilities in the US with a fast neutron spectrum. Only in Russia (Bor 60 and BN 600) a fast neutron spectrum is readily available. Other irradiation facilities do not have an extensive in-situ measurement capability and or a fast neutron spectrum

R&D Needs/Roadmap

Design the proper test stages and transfer tools for in situ measurement. Ensure robust and open access of people and sample to facility. Develop models using design data allowing us to license future reactors faster while studying the basic mechanism of radiation induced defect evolution in stress and temperature fields leading to better models and a comprehensive understanding of the materials in question

Context

Placeholder We will get design data allowing us to license future reactors faster while studying the basic mechanism of radiation induced defect evolution in stress and temperature fields leading to better models and a comprehensive understanding of the materials in question

Inside a Nuclear Fuel: Measurements of Temperature, Microstructure, and Thermal Transport

Marius Stan, Michael Furlanetto, Vincent Yuan, Filip Ronning, Don Brown, Kenneth McClellan, Richard Mason, Bogdan Mihaila, Sven Rudin, Alfredo Caro (LANL), Todd Allen (U. Wisconsin), Donald Olander (U. C. Berkeley), Sidney Yip (MIT), Simon Phillpot (U. Florida), Anter El-Azab (Florida State U.), Zi-Kui Liu (PennState), Dieter Wolf (INL), Theodore Besmann (ORNL), Shenyang Hu (PNNL), Christine Gueneau (CEA, France), Rudy Konings (ITU, Germany), and Toru Ogawa (JAEA, Japan)

Problem Statement: Creating, by design, a high-thermal conductivity nuclear fuel, capable of sustaining high temperatures and high burnup levels is a grand challenge.

Scientific Objectives: Thermal conductivity (λ) is a measure of how fast the heat generated during the nuclear reaction is transported through the fuel element to the coolant, for further use in generating electricity. A decrease in λ can slow down the heat release and overheat the fuel element. Fig. 1 shows that the thermal conductivity of the widely used nuclear fuel uranium oxide (UO_2) significantly decreases with both external temperature and burnup (time in the reactor)[5]. The cause of the decrease is unclear but thought to be related to temperature and radiation effects on the UO_2 microstructure. For example, Fig. 2 shows that fission gas bubbles accumulate in UO_2 fuel that was irradiated in a Pressurized Water Reactor (PWR)[6]. Unfortunately, a direct correlation between the observations in the two figures is impossible at this time. To establish such a correlation one has to go inside the fuel.

The scientific objectives of this experiment are:

- Measure, *in situ,* the time evolution of temperature at specific locations inside the fuel and characterize the microstructure (grain size distribution, fission gas bubble location, size, and shape) at the same times and locations.
- Study the influence of neutron irradiation and thermal gradients on the internal temperature and microstructure and develop a model of the thermal conductivity of the fuel.

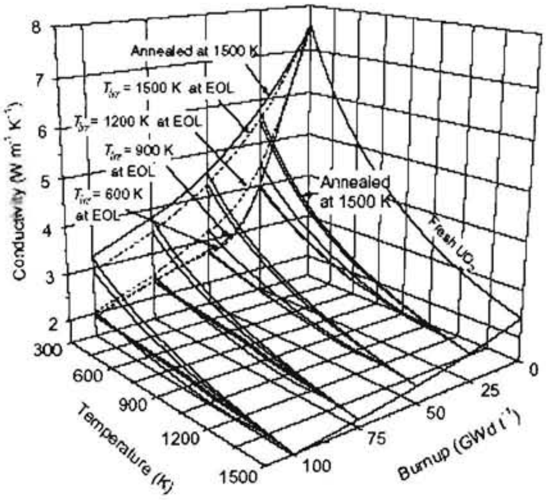


Figure 1. Thermal conductivity of UO_2 as function of external temperature and burnup for irradiation temperatures ranging from 600 K to 1500 K, after annealing (thermal treatment) at 1500 K and at the end-of life (EOL) of the fuel.

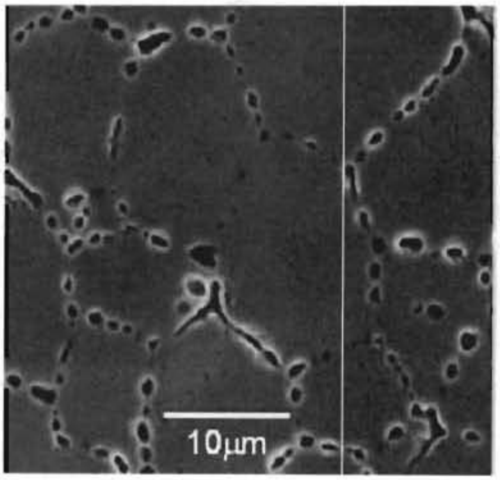


Figure 2. Fission gas bubbles in UO_2 fuel irradiated in a PWR, at a burnup level of 25GWd/t. The sample was annealed at 1275 °C for 5 hours.

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[5] C. Ronchi, *et al.* J. Nucl Mater., **327** (2004) 58-76.

[6] I. Zacharie, *et al.* J. Nucl Mater., **255** (1998) 92-104.

Achieving the objectives will enable the design of nuclear fuels with optimal composition and microstructure, capable of maintaining high thermal conductivity at high external temperatures and high burnup levels.

Experimental Details: We will perform *in situ* measurements of the temperature profile at specific locations inside a UO_2 sample, at various temperatures and neutron irradiation levels (Fig. 3). The external temperatures (T_{hot} and T_{cold}) are measured using a pyrometer while the internal temperatures are measured using implanted markers and Neutron Resonance Spectroscopy[7]. The microstructure is characterized using in-situ Neutron Diffraction coupled with Thermal Microscopy or Synchrotron 3-D Tomography. The thermal conductivity model is developed based on the **simultaneous** characterization of the internal temperature and microstructure evolution during neutron irradiation and external temperature excursions.

Notations:
d = dose
T = temperature
t = time
r = radial position in the sample
α = thermal diffusivity
C_p = specific heat
ρ = density
λ = thermal conductivity, $\lambda = \alpha C_p \rho$
∇ = mathematical gradient
q = heat source (fission)

The heat transport equation:
$\partial T / \partial t = \nabla(\alpha \nabla T) + \alpha q / \lambda$
is used to calculate λ.

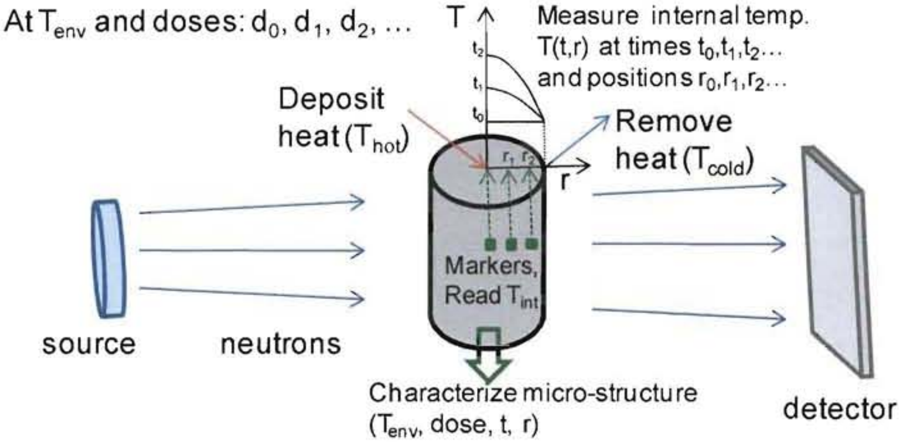

Figure 3 Experimental setup. The UO_2 sample is 10 mm length and 10 mm diameter. The space between markers is 1 mm.

Current Landscape: Common measurements of thermal conductivity involve the laser flash technique[8]. In this technique a laser deposits heat on one side of a thin, rectangular sample (2 mm) to create a temperature gradient used to calculate an average, "effective" λ. The method does not provide information about λ inside the sample and does not correlate λ with the local microstructure.

R&D Roadmap: We expect that advances in techniques that couple neutron, ion, and photon sources will allow us to characterize temperature and microstructure inside a solid with time resolutions of 100 ps and space resolutions of 10 μm. Using *in-situ* experiments over long irradiation times and during sudden cooling-heating regimes we will develop microstructure-informed models of the thermal conductivity of UO_2, UO_2-PuO_2, UO_2-ThO_2, and new, innovative fuels. The measurements and models will be used to inform and validate meso-scale (e.g. Phase Field) simulations of microstructure

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[7] V. W. Yuan, *et al.*, Phys. Rev. Let, **94** (2005)125501-125504.

[8] M. Amaya *et al.*, J. Nucl. Mater. **396** (2010) 32-42.

evolution[9] and continuum (e. g. Finite Element) simulations of heat transport in the fuel element[10]. This integrated approach will assist the discovery and design of fuels with improved properties[11].

Context: This experiment is coordinated with the following MaRIE first experiments: (1) Fission gas bubbles and concomitant swelling in UO_2 nuclear fuel); (2) Microstructural changes in nuclear clad material; and (3) The role of interfaces in irradiation-induced microstructural evolution.

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[9] S.Y. Hu *et al.*, J. Nucl. Mater. **392** (2009) 292–300.

[10] B. Mihaila *et al.*, J. Nucl. Mater, **394** (2009) 182-189.

[11] M. Stan, Materials Today, **12** (2009) 20-28.

In situ x-ray Methods to Examine Radiation Damage in Passive Oxide Films and its Influence on Corrosion Mechanisms

Scott Lillard, Christopher Taylor, Los Alamos National Laboratory, Los Alamos, NM; *Gary Was,* University of Michigan, Ann Arbor, MI; *Peter Andresen,* GE Global Research, Niskayuna, NY

Problem Statement

The high temperatures, chemically aggressive coolants and high radiation fluxes associated with the next generation of fast reactors pose a major challenge for the development of new structural materials resistant to irradiation assisted corrosion and irradiation assisted stress corrosion cracking (IASCC).

Scientific Objectives

The radiation assisted transport of defects though the bulk oxide and the coalescence of these defects and/or alloying additions from the bulk alloy at the metal oxide interface influences passive oxide breakdown and repair and ultimately the susceptibility of the material to irradiation assisted corrosion and irradiation assisted stress corrosion cracking (IASCC). We propose to use *in situ* grazing x-ray diffraction (GXRD) and x-ray adsorption near edge structure (XANES) experiments at to uncover the fundamental physics of oxide transport which will allow new approaches for the design of materials resistant to irradiation assisted corrosion.

Experimental Details

In these experiments, single crystal iron (Fe) and alloy surrogate samples (Fe-Cr, Fe-Cr-Mo) will be placed in a cell that would allow simultaneous exposure to a corrosive and a neutron irradiation environment. The environment in this First Experiment would be an aqueous solution that would also act as a coolant and provide neutron moderation, however, other gaseous environments could also be investigated. To interrogate the structure and composition of the passive film on this sample we propose to use high intensity x-rays from a free electron laser (XFEL, Figure 1) to generate GXRD and XANES data. Here the x-rays will impinge the surface at angles of 0.5° or less. At this angle surface features such as passive oxide films on the order of a few nm to several 100 nm in thickness are fully penetrated by the x-ray beam. These data will provide passive oxide structure information as a function of dose. By studying the structure of the absorption coefficient (in the x-ray adsorption fine structure) around 50 eV of the edge the data are chemically specific. This is referred to as XANES and will provide data on oxide chemistry (e.g. composition) as a function of dose.

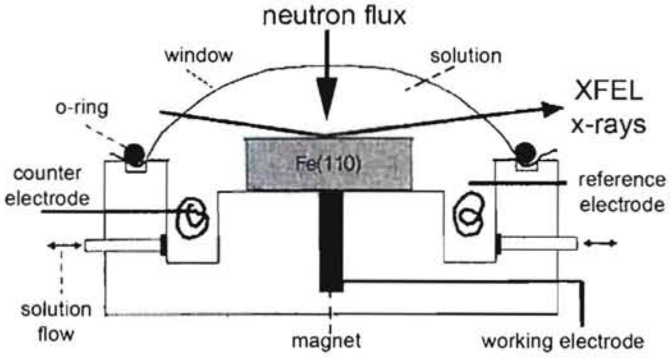


Figure 1 Diagram depicting what a GXRD/XANES electrochemical cell at F^3 may look like. (Adapted from: Davenport, *J. Electrochem. Soc.*, **147**, 2162 (2000).

Two First Experiments will be conducted: *steady state* and *transient* experiments. In the *steady state* experiment, we will use GXRD to calculate the structure factor of the passive film over the irradiation period thus quantifying the amount of disorder in the passive film as a function of dose. In addition to

GXRD, we will also use XANES data to quantify changes in the chemical composition of the film as a function of dose, for example, as might result from the preferential transport of alloying additions.

In the *transient experiments*, the passive film will be removed during the irradiation period via a physical or electrochemical "scratch" exposing a bare surface. This would be done at an electrochemical potential where passive film would reform quickly (seconds). During the repassivation transient we would again use GXRD structure factor data taken at time intervals on the order of 10's of microseconds to evaluate the role of radiation damage on film growth and the ability the materials to self-heal, for example, at a crack tip (Fig. 2).

Current Landscape

Ion irradiation provides opportunities for simulating the interaction of the components of reactor environments (radiation, stress, temperature, aggressive media). In these experiments, controlled environmental cells are coupled to accelerator beamlines to study the interaction of the environment and irradiation on structural materials. Corrosion at the substrate-environment interface is studied in real time by numerous electrochemical techniques. With respect to dose, light ions can be used to reach doses up to ~10 dpa in several days. However, the depth of penetration is low (tens or micrometers) which puts unrealistic limitations on electrochemical cell construction. Heavy ion irradiation can reach several hundred dpa in a matter of days but the penetration depth is much less. Finally, as it relates to simultaneous high intensity light source interrogation of passive films, there are no facilities in the world that permit GXRD/XANES of passive films during ion beam irradiation.

Context

In the film rupture SCC mechanism, cracking initiates with passive film rupture followed by very high dissolution rates and, correspondingly, high crack advance rates. Passive film rupture may be influenced by many factors including radiation-induced disorder (*steady state experiments*) which may increase film strain or promote hardening. During the propagation stage of SCC the crack tip must propagate faster than the oxide film can repassivate the surface (Fig. 2). Thus, if irradiation decreases the ability of the metal surface to repassivate (*transient experiments*) increased SCC propagation will result. Finally, the research proposed here is complimentary to the First Experiment proposed by Hosemann and Maloy *et al.* to study the effect of irradiation on mechanical properties of structural materials. In that experiment they propose to measure the stress on samples locally (1-2 um resolution) as a function of dose to investigate the mechanism of radiation hardening and the resulting increase in susceptibility to cracking.

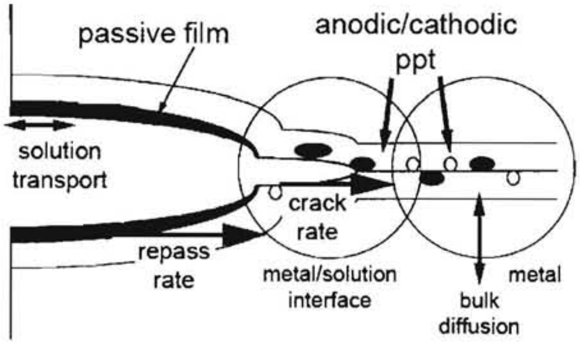


Figure 2 Diagram depicting the processes that may go on during IASCC. (Adapted from: Ballinger, in Environmental Induced Cracking, Gangloff/Ives eds. NACE 1990.)

Understanding Emergent Phenomena in Complex Materials

A.J. Taylor, G. Rodriguez, S. Trugman, Q. Jia, D. Yarotski, S. Conradson, X. Zhu, R. Prasankumar (LANL), Keith Nelson (MIT), David Hilton (University of Alabama, Birmingham), Richard Averitt (Boston University), Elbert Chia, (Nanyang Technological University, Singapore), Jure Demsar (University of Konstanz), Kenneth Burch (University of Toronto) Hae Ja Lee (LCLS, SLAC National Laboratory), Diyar Talbayev (Yale University)

Problem Statement

Conceptually new approaches are required to understand the emergent physics that evolves over multiple length and time scales and to use this knowledge to design materials with entirely new, or significantly improved, functionalities.

Scientific Objectives

Emergent properties in novel materials appear as a result of competing interactions. These interactions produce a delicate balance between states with very different properties, e.g. charge ordered, magnetic, ferroelectric, and superconducting, and provide the enabling ingredients for new physics and functionalities. However, emergence cannot be predicted within presently available frameworks. If we are to move beyond observation of materials properties towards control of materials functionality, we need to understand fundamentally the role of competing interactions in producing emergent behavior.

The power of ultrafast spectroscopic techniques lies in their ability to temporally resolve phenomena at the fundamental timescales of atomic and electronic motion and to unravel the competing degrees of freedom that ultimately determine mechanism, functionality, and ultimately emergence. The sub-10-fs temporal resolution, combined with spectral selectivity spanning the far-infrared to the x-ray regimes enable studies of charge, spin and lattice dynamics, and more importantly, of the dynamics of the coupling between these degrees of freedom. Advanced, high-brightness x-ray sources offer new opportunities for direct probing of the lattice, as well as the valence charge density on ultrafast and ultrasmall scales. This new experimental capability provides fundamental insights important for learning how coherent quantum control techniques might yield novel materials through the creation of non-thermally accessible states. The resultant detailed understanding of the properties of materials on an ultrafast time scale will then enable a robust rational basis for the design of new materials with desired functionalities.

Experimental Details

We propose a three-stage suite of experiments to achieve the goal of understanding the role of competing interactions leading to emergent phenomena in complex materials.

- Unravelling the coupled interactions in complex oxides with various functionalities using the ultrafast spectroscopy appropriate to the functionality.
- Using this knowledge designing new materials that optimize a particular functionality and completely characterizing the coupled interactions that yield its functionality.
- Implementing coherent control techniques on these materials ultimately to access non-thermally accessible states.

The materials systems to be studied and controlled are epitaxial nanocomposite complex oxides (see Figure 1) with architectures that both layered laminar-like, and vertically aligned nanocomposites. By varying the nanostructure of the constituent phases, we will place in close physical proximity materials with different ordered phases, such as

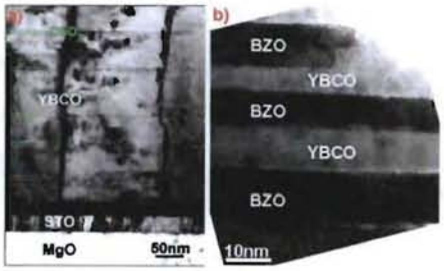


Fig. 1 Transmission electron microscope images of a pulsed laser deposition (a) $YBCO/CeO_2$ multilayer on MgO substrate with a $SrTiO_3$ buffer layer and (b) self-assembled $YBCO/BaZrO_3$ multilayer film.

superconducting (SC) and antiferromagnetic (AFM), superconducting and ferromagnetic (FM), and ferroelectric (FE) and ferromagnetic in order to elucidate and control the factors that promote coupling or competition between different order parameters. Once competing interactions are understood in the relatively well-understood oxide materials, we will explore the same issues in actinides and layered intermetallics to understand the role of f-electron physics in these competing interactions.

For our 'first experiments' we will achieve intrinsic control and manipulation of competing interactions by designing and synthesizing layered complex oxide nanocomposites using ferroelectric (FE) $BaTiO_3$, ferromagnetic (FM) $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), and high-temperature superconducting (HTS) $YBa_2Cu_3O_7$ (YBCO) materials as the functional components. Using the broken symmetry at controlled interfaces between these materials as a way to perturb the subtle balance between competing processes, we expect to produce materials with emergent properties significantly different from those of the constituents. Through a closely coupled synthesis, characterization and theoretical effort (Fig.2), we will use advanced ultrafast spectroscopic techniques to investigate the character of competing spin, charge, and lattice interactions in these oxides as a function of material composition and excitation format. Complementary to these intrinsic emergent phenomena in such nanocomposites, we will pursue extrinsic control of functionality via excitation with shaped ultrafast optical pulses. This research will result in a new experimental and theoretical framework for understanding and controlling the competing interactions to yield a nontrivial, coherent response with both spatial and temporal signatures. Our initial efforts will focus on the magnetoelectric (ME) effect (FE/FM interfaces) and unconventional superconductivity (SC/FM and SC/FE interfaces) as the most representative and prototypical emergent phenomena.

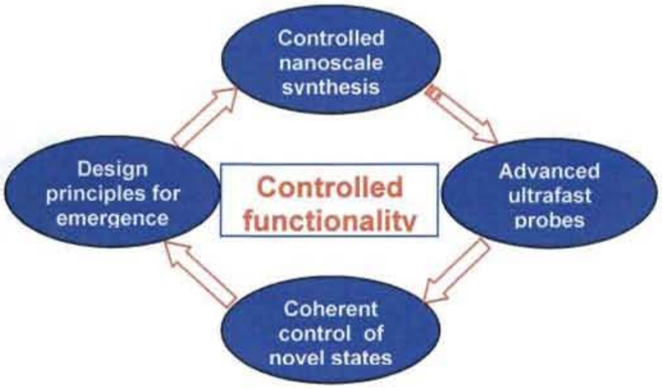


Fig. 2: Elements of approach to 1st experiments towards understanding and controlling emergent phenomena

Ultrafast excitation (pump: ω_1 in Fig. 3) of the electronic system using visible or near-infrared pulses will be complemented by ultrafast far-infrared excitation of phonon or magnon modes. Advanced ultrafast spectroscopic probes (ω_2 in Fig. 3) will be used to characterize the dynamics of a specific functionality of the material following excitation. To probe the charge order we will use a broadband (0.3-30 THz) ultrafast THz probe with coherent detection that will enable determination of the dynamic complex conductivity over the probe's bandwidth. THz spectroscopy also enables tracking of the superfluid and quasiparticle dynamics in a superconductor. To explore the spin dynamics ultrafast x-ray magnetic linear dichroism, an element-specific technique sensitive to both ferro- and antiferromagnetism, will be used and the element specificity will particularly useful in isolating the response of the interface. Ultrafast x-ray diffraction will be used to characterize the lattice dynamics. Ultrafast angle-resolved photoemission spectroscopy (ARPES) with 10-nm spatial resolution will be used to elucidate the dynamic electronic structure on the nanoscale, enabling the observation of the dynamics of spatial inhomogeneities

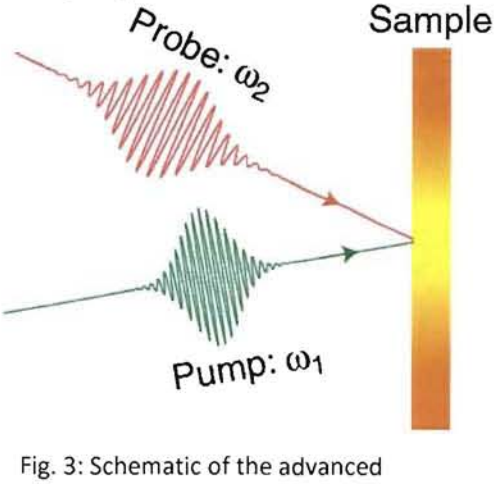


Fig. 3: Schematic of the advanced ultrafast spectroscopies for elucidating competing interactions. The pump will excite either carriers or magnons or phonon modes. Proposed probes range from THz to x-rays, revealing carrier, spin or lattice dynamics, as well as band structure evolution.

produced by competing interactions. To understand the emergent functionality in these nanocomposite materials we will produce an excitation in one constituent material and probe its effect either selectively at the interface or across the interface in the other constituent. These experiments will provide unprecedented insight into the competition mechanisms among the spin, charge and lattice degrees of freedom to directly identify routes for optimizing nanocomposite functionalities. Finally, coherent control methods will be used to create non-thermally accessible transient states with further optimized functionality. For example, coherent magnons or phonons will be generated in the FM or FE layers and their effect on the gap in the SC layer will be optimized through properly shaped excitation pulses. Mixed Ginzburg-Landau models will be used to interpret and predict responses.

Current Landscape

We note that the ***integration*** of the materials synthesis, nanoscale characterization and complex materials theory and modeling proposed for M4 combined with the advanced ultrafast spectroscopic capabilities produced by MPDH will be required for the success of the proposed experimental series. This is not a capability available or proposed elsewhere. The understanding gained from this set of experiments is essential for the goal of controlled functionality of emergent properties, those which hold the most promise for providing us with transformational materials to solve our problems in energy and national security.

R&D Roadmap

To enable such an ambitious suite of integrated experiments, teams should be formed, perhaps under the auspices of the new BES call for "Discovery and Development of New Materials," to attempt such an integrated approach to materials discovery enroute to controlling materials functionality. Such teams should include synthesis, advanced characterization and theory and modeling members, working on the same materials, preferably in one location, with the goal of developing a predictive capability.

Further, the ultrafast x-ray spectroscopies (ultrafast ARPES, x-ray diffraction, and magnetic dichroism) described in this experiment are either in a very preliminary stage or not developed at all. Over the next five to ten years developing these capabilities, in conjunction with the theoretical tools to interpret their output, on materials systems of increasing complexity and with increasing experimental sophistication will be essential to the success of this experimental series.

Context

The proposed scientific issues in this experiment are closely related to those in the first experiments on "Superconductors by Design" and "Making Every Photon Count." Further, there is synergy in the ultrafast spectroscopic techniques developed for this experiment and other experiments such as: "Process Aware Materials Performance," and "Understanding hot spot physics on length and time scales relevant to high explosive initiation."

Achieving Practical High-Density Energy Storage Through New Support/Catalyst Electrode Systems

T. Mark McCleskey, Anthony Burrell, Albert Migliori, Fernando Garzon, Neil Henson, Piotr Zelenay (LANL), Digby Macdonald (Penn State), Pradeep Haldar (CNSE Albany)

Problem Statement

Transformational research is needed to replace platinum with a less expensive alternative for current fuel cells, and to tackle the grand challenge of electrochemical reduction of carbon dioxide to enable a carbon neutral fuel cycle.

Scientific Objectives

One of the great challenges in the next decades will be the effective storage of electrical energy to match the growing supply of intermittent renewable energy sources such as wind and solar with electrical demand. Chemical bonds are the densest form of energy storage outside of nuclear materials. Storage of electrical energy in chemical bonds, *via* electrosynthesis, will be required on a scale that cannot be considered if precious metals such as iridium and platinum are required. Efficient electrosynthesis requires a conductive support to transfer electrons, a catalyst to lower activation barriers (overpotentials), a high-surface-area architecture to maximize the reaction kinetics, and support/catalyst combinations with long lifetimes in pH and electric field extremes. Currently, electrode systems used in the electrolysis of water and fuel cells are focused on activated carbon supports, having a complex and often ill-defined architecture, modified with platinum catalysts. Diminishing improvements have been made in reducing the platinum content, but there is little room for further advancement. The exploration for non-precious metal catalysts has been an active area of research for many years with occasion promising results, but nothing has matured into an efficient operating device. The key challenge to more rapid progress is to develop a theoretical framework that can effectively predict material properties beyond known materials that we have made. To accomplish this goal requires:

- Flexible rapid synthesis of well-defined materials to systematically explore a range of materials
- Characterization of nucleation and growth processes during synthesis as porous substrates are prepared and catalysts are deposited within pores
- Real time characterization in extremes to understand catalyst agglomeration over time and nucleation on growth of corrosion at the substrate surface

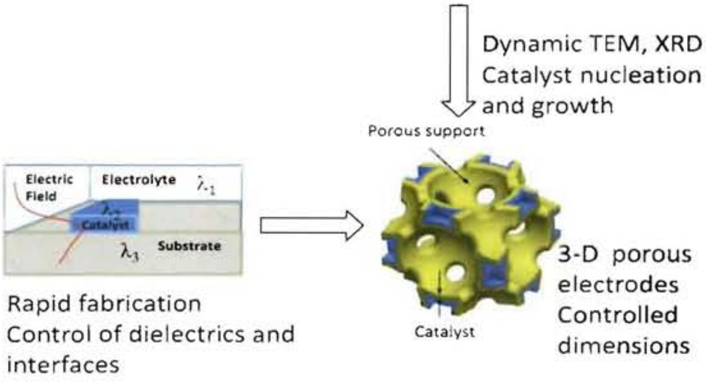
The need for an integrated, systematic approach that MaRIE would provide is recognized in the BES report on energy storage: "*A systematic, highly coordinated research effort in which synthesis is strongly coordinated with modeling and the characterization of novel materials with controlled and optimized pore structures, tailored surface functionality, and nanostructured architectures is critically needed to elucidate these fundamental atomic- and molecular-level issues... Combining the power of new computational capabilities and in situ analytical tools could open up entirely new avenues for designing novel multifunctional nanomaterials with the desired physical and chemical properties, leading to greatly enhanced performance.*" MaRIE will provide an integrated materials discovery facility designed to integrate rapid flexible synthesis and *in situ* characterization with theoretical models to push the envelope of directed synthesis and provide complex 3-D composite materials. In addition the high energy X-rays at the MPDH facility will provide a way to probe the catalyst structure directly in the complex chemical extremes of an operating device. The goal is to advance our understanding of the complex interactions at surface interfaces to enable the design of new more efficient devices.

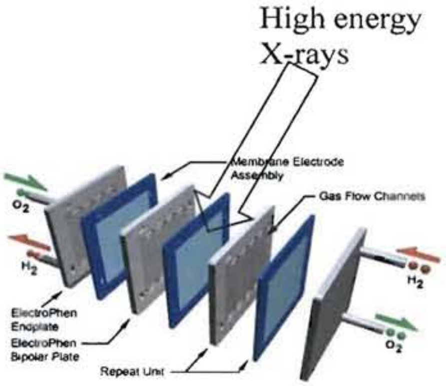
Experimental Details

MaRIE will transform advances in new materials through an integrated approach where control science is achieved by bringing together

1) Improved theoretical models to predict band gaps, density of states and chemical potentials at the catalyst surface where support, catalyst and electrolyte interfacial interactions can dominate the performance
2) Controlled synthesis of materials with systematic, well-defined changes in composition and architecture that include catalyst dimensions comparable to De Broglie wavelengths up to 10 nm and porous substrate dimensions of 5 nm to microns
3) Characterization of materials structure and properties across length scales from nano to micron including detailed resolution of buried interfaces and their evolution in extremes of chemical pH, electric fields.

The MaRIE facility will provide the integrated tool needed to explore fundamental electrode substrate interactions via electric field, NMR and optical probes at the charged double-layer interface during electrochemistry to benchmark theory. Using a combination of fabrication/lithography, thin film growth, single crystal growth and chemical synthesis it will be possible to rapidly explore new combinations of patterned thin catalysts on a variety of well defined conductive substrates. The combined capabilities will allow one to systematically vary the dielectric constants of the catalyst, substrate and electrolyte. These fundamental efforts will advance theoretical codes to predict catalyst substrate combinations with desired band gaps and surface chemical potentials. New catalyst substrate combinations predicted by theory will then be tested on flat surfaces. Bulk porous 3-D structures will be prepared using template chemical and bio-inspired synthesis. Catalysts will be deposited in a controlled manner within the 3-D structure with the help of *in situ* diagnostics such as dynamic TEM and time resolved XRD to observe the nucleation and growth process. Detailed characterization using high energy X-rays that can penetrate the 150 micron scale porous electrodes without damaging the material will enable movies to be made of catalyst evolution in the pH and electric field extremes. Watching the catalyst and support structure dynamically will expose for the first time how the catalyst agglomerates and degrades over time and how corrosion of the electrode nucleates and grows leading to device failure. These results will enable advance design of electrodes with longer lifetimes and improved performance.





In situ monitoring of catalyst evolution within the 150 mm membrane

Current Landscape

The current state of the art relies on advances, such as Nocera et al.'s discovery of a new Co catalyst that appears to serve as an effective anode for water splitting, by accident. This catalyst was discovered during electrochemical experiments when it precipitated onto the electrode surface. Experiments at APS have shed some light on the material in terms of a potential active molecular species, but little is known about the micron(s) thick film on the electrode surface. Results at current light sources are giving valuable information on the ensemble average and have the potential to shed light on individual particles at a given time, but it is not possible to watch the evolution and performance of a single catalyst particle. Time resolved information on the size of a single catalyst particle over time would give insight into the mechanism of how catalyst particles change and eventually fail over time.

R&D Roadmap

Experiments on arrays of identical catalysts deposited on a well defined conductive surface at LCLS, and APS would be a step toward identifying the mechanism of catalyst evolution. By watching the spots of catalysts on a surface before and after cycling it should be possible to determine if the catalyst particles are migrating on the surface. Combining confocal imaging and surface probe microscopy such as Raman and AFM would allow one to begin to correlate reactivity with catalyst/surface/electrolyte interfaces. Key to both of these is the preparation of well defined 2-D systems as opposed to the ill-characterized complex 3-D systems typically studied.

Context

This first experiment has overlap in the areas of 1) rapid high quality synthetic requirements for practical superconductors by design for energy security 2) fabrication and architectural control for cost-effective photovoltaics based on functionally integrated nanostructures and *multifunctional materials*: correlated multiferroics, new photonic materials 3) ability to probe buried interfaces with temporal resolution common to dynamic experiments. The same capability that allows for subgranular resolution of phase/structure with micron depth penetration and ps temporal resolution for dynamic experiments, will also allow one to watch the grains at a buried interface boundary as a device operates in extremes. Currently it if observed catalyst growth over time (and loss of performance) occurs as catalyst particles migrate on the surface and coalesce or if the particles slowly dissolve and re-precipitate on another catalyst particle. Depending on the mechanism the strategy for developing longer lived system is dramatically different. In one case limiting catalyst movement on the surface would be a key factor and in the other case control of the nucleation and growth sites is the critical factor.

Cost-effective Solar Energy Conversion based on Functionally Integrated Nanostructures

Milan Sykora, Alp Findikoglu, Jennifer Hollingsworth, Tom Picraux, Victor Klimov, Ian Campbell, Darryl Smith, Sergei Tretiak, Andrei Piryatinski (LANL), Paul Alivisatos (UC Berkeley), Michael Graetzel (EPFL), Martin Green (U. New South Wales), Tom Meyer (UNC Chapel Hill).

Problem Statement

Development of efficient, low-cost solar energy conversion devices based on functionally integrated nanostructures using known and inexpensive materials and fabrication processes.

Scientific Objectives

Although much effort has been dedicated over the past fifty years to the development of solar energy conversion technologies the most efficient devices available today remain either too inefficient or to expensive to compete with conventional energy sources. One possible path to necessary breakthroughs leads through exploitation of unique properties of nanoscale materials, which possess a combination of electronic and optical properties absent in bulk semiconductors or molecules. In spite of significant recent progress in our understanding of isolated nanostructures the cost effective integration into functional, efficient solar energy conversion device remains a major challenge.

The development of efficient nanomaterials-based solar energy conversion device is unlikely to be accomplished relying on traditional characterization tools tailored to study properties of bulk materials. To achieve revolutionary breakthroughs, development of new tools is needed, which will allow mapping of materials properties with sub-10 nm spatial resolution and real time monitoring of charge formation, transport and extraction with nanometer, picosecond resolution, in an operating device. The scientific objective of the research performed in this section is to develop low-cost solar energy conversion devices using nanostructures, functionally integrated with the aid of new, nanoscale characterization tools.

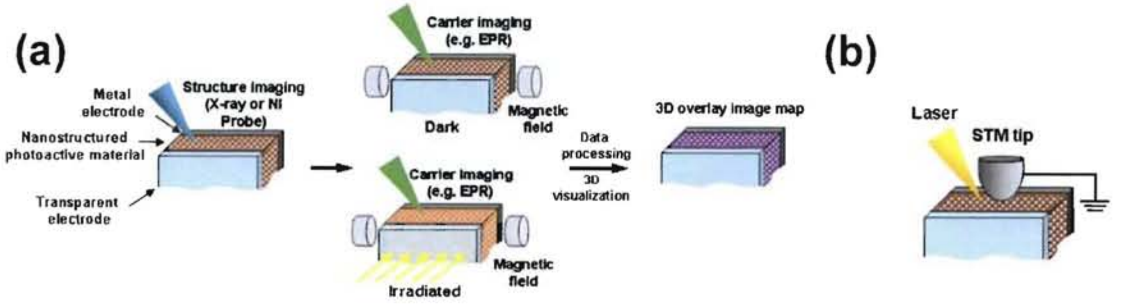


Figure 1. (a) Schematic diagram of a process used to generate 3D structure/carrier distribution image map in a cross-section of an example nanomaterial-based photovoltaic device. (b) Scheme of the approach to use 2D carrier map using Light-Modulated STM.

Experimental Details

A schematic diagram of the experimental approach used for characterization of nanomaterials based PV device is shown in Figure 1. A nanotomography 3D image of a PV device cross-section is initially generated using e.g., X-ray and neutron probe beams. When used in concert these techniques provide complementary information based on distinct sensitivity to materials with different chemical composition (e.g., metal oxides can be imaged with higher contrast with neutrons than x-rays). The result is a 3D nanometer-scale structural map of the photoactive material as well as the interfaces with the charge-collecting electrodes. Next, the carrier density imaging is performed in "dark" and irradiated device, first in cw and then in time-resolved mode, in which the delay between the activation light and the probe are systematically varied. Various methods will be investigated to optimal carrier map imaging. One potentially powerful technique is Electron Paramagnetic Resonance imaging (EPRI). The high sensitivity of EPRI to unpaired electrons and their specific environments is an important advantage in imaging the carrier formation centers, transport paths and potential formation of carrier traps and pools. To achieve high spectral and image resolution the use of high magnetic fields is required. In the final stage of the experiment, the information obtained in materials imaging and carrier imaging stages is digitally processed to generate 3D overlay image map correlating structural and electronic properties of the device. The 3D structure/carrier map is used as guide in device structure optimization.

Current landscape

Sub-micron 3D imaging of material properties by number of techniques has enjoyed tremendous progress in recent years mainly due to advances in digital imaging systems. In terms of materials structure imaging, currently the x-ray tomography provides highest spatial resolution, reaching pixel size <10 nm, with field of view ~10-200μm. The neutron imaging/tomography, limited by the efficiency of neutron beam focusing is currently reaching ~10μm resolutions, which is currently insufficient for nano-imaging. A sub-10 nm 3D structural imaging is also currently possible with electron tomography. The carrier imaging options are currently much more limited. While EPRI made significant progress in recent years, particularly using Pulsed-Gradient Spin Echo techniques, best spatial resolution is on the order of ~10-100μm. The temporal resolution is in nanoseconds. The optical imaging techniques, while providing sub-picosecond temporal resolution, suffer either from poor spatial resolution (~10μm for optical microscopy) or depth profiling limitations (Near field techniques). Recently, a first 2D map of carriers in an operating p-n junction PV device was generated using novel, Light-Modulated Scanning Tunneling Microscopy (LM-STM) approach. Although, this method was first demonstrated on bulk PV device the ~10nm spatial resolution makes it a suitable tool for studies of nanomaterials-based PV.

R&D needed to enable success.

Although the 3D carrier imaging techniques, currently do not have sufficient spatial resolution to yield carrier maps on sub-micron scale, rapid development of the EPRI and other techniques is likely to yield nanoscale resolutions within few years. In the short-term, in our first experiment, we will combine 3D material imaging using x-ray and electron beam tomography with 2D carrier map imaging using LM-STM. While 3D information will be limited, using this approach we can generate important initial insights about correlation between materials structure and carrier formation and diffusion pathways from mapping studies of materials with various structures and compositions. The first experiment studies will provide opportunity to develop the integrated structure/carrier density mapping tool with the flexibility to upgrade its capability with the progress in the EPRI and Neutron Tomography.

One of the important requirements for the success in the device development effort is the availability of an integrated facility with the combination of tools needed for components synthesis, fabrication of devices, characterization of components and devices. Particular focus is on wet chemical approaches to nanomaterials and low-cost fabrication methods.

Context.

The research proposed here is closely related to the first experiments proposed by T Mark McCleskey on energy storage and by A.J. Taylor on Understanding Emergent Phenomena in Complex Materials.

Developing Practical Superconductors by Design

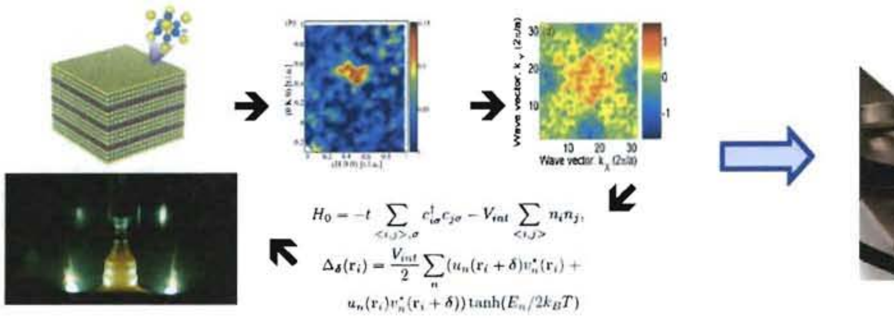
Joe Thompson, Eric Bauer, Cristian Batista, Leonardo Civale, and Alp Findikoglu

Problem Statement

Integrate theory, modeling, and simulation with materials-driven research and broad-based characterization, to "discover by design" practical superconductors for real-world energy applications, thus replacing the serendipitous discovery approach of the past.

Integrate:
- **precisely-controlled** synthesis
- **broad-based** characterization
- **experiment-coupled** theory

for Practical Superconductors by Design



$$H_0 = -t \sum_{<i,j>,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} - V_{int} \sum_{<i,j>} n_i n_j,$$

$$\Delta_\delta(\mathbf{r}_i) = \frac{V_{int}}{2} \sum_n (u_n(\mathbf{r}_i + \delta) v^*_n(\mathbf{r}_i) + u_n(\mathbf{r}_i) v^*_n(\mathbf{r}_i + \delta)) \tanh(E_n/2k_B T)$$

Scientific Objectives

The discovery of practical superconductors with higher operating temperatures (distinct from superconducting transition temperature T_c), higher current-carrying capabilities, and easier manufacturability than what are currently available would have a disruptive effect on a broad range of energy technologies, especially in production, storage, transmission, and use of electrical energy. The proposed research will emphasize underlying physical and chemical principles that will direct the design of new practical superconductors. Specific design principles are beginning to emerge to guide this approach (Fig. 1). The transition temperature in three diverse classes of unconventional superconductors (heavy-fermion, cuprate, and FeAs compounds) shows linear correlation with the characteristic energy scale of antiferromagnetic fluctuations, spanning three orders of magnitude in energy. One important goal of this project is to understand more fully this guiding principle and discover additional unifying concepts that limit more tightly the expansive phase space of possible materials. New characterization tools with nm-scale spatial resolution and fs-scale temporal resolution are needed to unravel the competing interactions that give rise to high T_c. Practical superconductors should operate at liquid nitrogen temperature or higher, have more three-dimensional character than cuprate superconductors, and have mechanical properties that are compatible with wire or tape production. The newest family

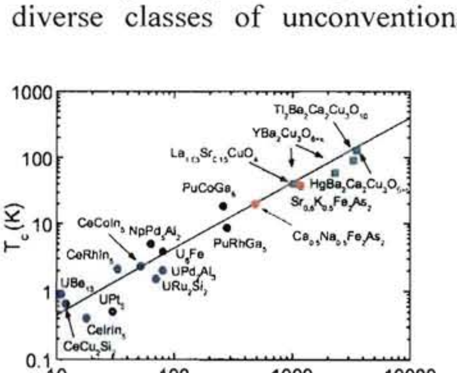


Fig. 1 Transition temperature T_c of unconventional superconductors vs characteristic spin fluctuation energy T_{sf}.

of compounds based on FeAs holds promise in this regard because they are intermetallic (i.e., easily formable), are less anisotropic than cuprate superconductors, and exhibit unconventional superconductivity with potentially high transition temperatures. Diagnostic capabilities to not only understand the underlying physics but also assess the quality of these superconductors in practical form are needed.

Experimental and Theoretical Details

New synthesis tools, such as single-crystals by e-beam float zone growth, will be essential to synthesize "neutron-size" (i.e., from mm^3 to cm^3) single-crystals of new intermetallic superconductors in extremes of temperature and pressure (up to 2500°C and up to 6 GPa). In addition, atomic-precision synthesis of intermetallic films by MBE, with controlled strain, dimensionality, and defects will allow one to go beyond the limitations of bulk phase equilibria, to extend phase boundaries and microstructures, and to design "built-in" functionality. The in situ measurement tools required to provide real-time feedback for synthesis/processing optimization must be developed. Because the electronic spin degrees of freedom play a fundamental role in unconventional superconductivity, it is crucial to measure the spin excitations near and inside the superconducting phase. Integrated experimental capabilities such as inelastic neutron scattering at low temperatures (down to 0.1K), and high magnetic fields (up to 30 T) and high pressures (up to 3 GPa) would have a large impact on theoretical efforts for identifying the underlying mechanism of superconductivity and the variables of the spin excitation spectrum that are correlated with the critical temperature. As essential complements to the measurement of spin excitations, a suite of thermodynamic and transport measurements needs to be performed at extremes of very low temperatures (down to 0.1 K), high pressures (up to 3 GPa) and magnetic fields (up to pulsed-300 T) to unravel the complex, coupled spin-charge-lattice state from which superconductivity develops. New spin-sensitive and multi-scale experimental methods, sensitive to intrinsic inhomogeneity in real space and momentum space on the nm scale, such as spin-resolved STS, ARPES, dHvA, will reveal additional crucial information. Similarly, in situ structural characterization tools to assess the degree of crystalline anisotropy as well as mechanical response are needed.

Current Landscape

There is a growing realization in the US and elsewhere of the need for new superconductors with improved performance capabilities. As a result, distributed efforts are beginning to form that contain elements of a more comprehensive approach. The Energy Frontier Research Center on Emergent Superconductivity (BNL & ANL) is one example. The convening power (co-location of expertise in synthesis, characterization and theory; co-location of unique experimental capabilities – Lujan and NHMFL) of MaRIE will allow further integration and the intimate coupling of theory, synthesis, and characterization that is needed to shorten substantially the time scale for the discovery of new superconductors with desired functionality.

R&D Roadmap

MaRIE will have co-located and integrated capabilities in synthesis (growth of bulk crystals and MBE films), characterization (STS, high magnetic fields for dHvA, neutrons for inelastic scattering and pdf measurements as well as thermodynamic and transport measurements), and theory. Materials synthesis and characterization capabilities will use extremes of pressure, temperature, and magnetic field to learn what optimizes T_c and J_c. A powerful strength of MaRIE is co-location and integration of wide range of capabilities that will be necessary to develop materials by design, for example enabling rapid turn around in broad-based characterization of spin, charge and lattice degrees of freedom of new materials and ability to provide quick feedback to synthesis and theory.

Context

The proposed first experiment "Practical Superconductors by Design" and another first experiment "Understanding Emergent Phenomena in Complex Materials" are closely related in terms of the underlying physics and in the use of theoretical and dynamic characterization tools. This experiment, with its emphasis on designing of superconductors for practical and efficient use of electrical energy, also complements other energy-related first experiments on "Energy Storage" and "Make Every Photon Count." Further, there are common needs for characterization tools to be developed for these experiments in wide-ranging areas, such as high spatial- and temporal-resolution optical, electrical, x-ray, and neutron beams and detectors.

Process-Aware Materials Performance: Nanostructured Ferritic Alloys

Nate Mara (LANL, MPA-CINT), I. Beyerlein (LANL, T-3), M. Demkowicz (MIT), R. Hackenberg (MST-6), P. Hosemann (MST-8), C. Koch (N. Carolina State), Amiya Mukherjee (UC Davis)

Problem Statement:

Direct observation of defect-interface interactions, and nucleation and growth phenomena in nanostructured alloys will facilitate the mechanistic understanding necessary to develop and validate physics-based, multi-scale predictive models, forming the scientific foundation for a process-aware materials performance approach to design radiation-resistant structural materials.

Scientific Objectives:

Currently, lead candidate materials for application in extreme irradiation environments include Oxide Dispersion Strengthened (ODS) / Nanostructured Ferritic Alloy (NFA) steels, chosen for their ability to mitigate damage caused by irradiation-induced defects, and high strength and microstructural stability over a range of elevated temperatures. [1] These favorable characteristics are attributed to the high density of (1-5nm diameter) nanoparticulate oxides distributed through the matrix, providing interfacial content for recombination and annihilation of radiation-induced point defects, He trapping, as well as impedance of dislocation motion. Despite their promise in nuclear applications (especially as cladding), a lack of fundamental understanding of key atomic-level processes encountered during synthesis and service such as defect-interface interactions, nucleation and growth of nanodispersed oxides in a metallic matrix, and corrosion phenomena have limited the development of this class of materials from widespread application and certification for use in nuclear reactors.

If successful, MaRIE will give the capability to:

- ***Resolve the evolution and detailed structure of interfaces*** between oxide particles and metal matrix in which they are embedded. This will require understanding the effects of synthesis routes on interfacial structure. NFA processing currently consists of dissolution of oxide powders into the Fe matrix via ball milling, and subsequent powder consolidation and thermomechanical processing to achieve the desired dispersion of nanoscale oxide content. Due to the chemical complexity of the interfaces involved, their atomic arrangement may form numerous hitherto unresolvable atomic configurations or complexions [2, 3]. These in turn may be sensitive to the exact composition of the matrix alloy as well as to that of the particles themselves and are likely to change with varying temperatures and stress states. Nanometer-level 3-dimensional spatial resolution is required to distinguish interface complexions from the formation of second phase embryos through their growth based on interface thickness and chemistry. While much can be gained from F^3's ability to irradiate specimens under a wide range of conditions, and M4's ex-situ characterization capability (see Misra 1st experiment), capturing the transient interfacial response to changing environments such as temperature and strain occurs on time scales approaching picoseconds, not exceeding microseconds. Therefore, chemical and crystallographic data, as well as atomic displacement vectors at similar time and spatial lengthscales is required.
- ***Measure time-dependent radiation response*** of material in the proximity of oxide particle interfaces. Depending on the nature of the interaction between radiation-induced point defects and oxide interface, zones denuded of radiation damage may form in the vicinity of the oxide particles in ODS steels. The same is true for He formed in a fast neutron or proton environment where interfaces can act as "He traps", creating He-free regions adjacent to the interface. The extent of these zones as well the type of radiation damage of which they are denuded (e.g.

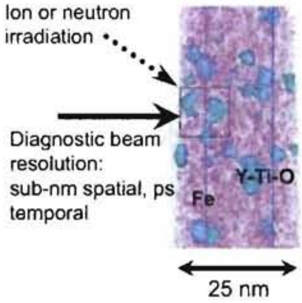
isolated point defects or defect clusters like dislocation loops, gas-filled bubbles, stacking fault tetrahedral, or He bubbles) depends strongly on the irradiation conditions as well as the mechanisms of interaction between the radiation-induced defects or defect clusters and the oxide particle interfaces. Irradiation experiments similar to those outlined by Misra *et al.* will provide a crucial first step towards this goal, especially given improved temporal resolution (<milliseconds) in the TEM.

- ***Scrutinize oxide interface-dislocation interactions***, including pinning, cutting, bowing, and accumulation of geometrically necessary dislocations (GNDs) under conditions of severe plastic deformation. Due to high rates of dislocation recombination at high plastic strains, an accurate representation of the instantaneous dislocation densities during deformation requires continuous, time resolved measurement of these densities at time scales dictated by the rates of dislocation generation and annihilation, which may vary by many orders of magnitude depending on strain rates (creep to shock) and temperature (athermal conditions to melting). Transient phenomena like strain bursts associated with dislocation avalanches may occur on nanosecond time scales or shorter.
- ***Detail the full lifetime of oxide particles from synthesis to service.*** The synthesis of ODS steels relies on processing techniques that drive the material far from thermodynamic equilibrium. The way in which the oxide particles in ODS steels form under these conditions is a subject of ongoing debate that may be resolved with appropriate *in situ* investigations. In service, ODS steels are driven far from equilibrium in ways whose effect on the oxide particles requires fine spatial and temporal resolution to study. Exhaustive characterization of the role of particle-matrix interfaces in interacting with the externally applied conditions may help to elucidate this question.

Experimental Details: In order to address the scientific issue of predicting microstructural evolution during processing and performance of NFA materials under conditions similar to those found in a nuclear reactor, we propose two related sets of experiments:

1.) ***Probe nano-precipitate nucleation and growth during synthesis.***
2.) ***Investigate the stability of nano-precipitates/Fe matrix interfaces and their interaction with radiation and stress-induced defects.***

The majority of experiments will involve material synthesis in M^4, irradiation under a variety of conditions in F^3, and subsequent ex-situ microstructural characterization in M^4 using available techniques (TEM, XRD, SANS, SAXS, positron annhilation spectroscopy). The results from these studies will set the groundwork for targeted *in-situ* measurements using 3-dimensional diagnostic probes appropriate for the length and time scales proposed (sub-nm, picoseconds to microseconds) over sample volumes of $\sim 1\ \mu m^3$. The local atomic structure, chemistry, and real-time atomic displacement vectors will be determined *in-situ* during critical synthesis steps such as ball milling, sintering/consolidation, and thermomechanical processing. The evolution of bi-phase interfaces and their response to stress, temperature, and changes in stress state will be evaluated. Once these interfaces have been synthesized and characterized, small scale in-situ ion irradiation creep experiments will reveal interface stability under irradiation and loading conditions that will expose the interface content to defects similar to those found in a nuclear reactor, albeit at higher dose rates to minimize experiment duration. The in-situ probe, similar to that described for examining phase transformations during processing, will now be the interrogation tool for determining interface-defect interactions, both with mechanically induced (e.g. dislocation loops) and radiation induced defects (e.g. Frenkel pairs, interstitials, He-bubble formation). The results of these two studies will form the basis for a predictive atomistic model to enable the design of appropriate interface content for maximum damage mitigation in a reactor environment. Extension of these atomistic models to feed higher-scale models capable of handling synthesis routes such as rolling and extrusion (Visco-Plastic Self-Consistent, Dislocation Dynamics) will be required. To validate models at the fuel-cladding or full-scale component level, in-situ creep experiments will be carried out using neutron irradiation at dose levels of ~20 dpa/year for a duration of weeks. For these experiments, the same diagnostic probes will be applied periodically to examine the defect-interface interactions as the microstructure evolves, and validate the ion irradiation experiments under conditions similar to those actually encountered during service in a nuclear reactor.



Atom probe micrograph of MA-957 nanoferritic alloy, with Fe atoms shown in pink, and other atoms (Ti, Y, O) shown in blue. Experiments such as second phase evolution under stress or temperature transients that mimic processing conditions reveal their effects on final interfacial structure. Addition of concurrent ion beam or neutron irradiation at appropriate stress and temperature conditions provides for investigation of interfacial structure under extreme nuclear reactor environments.

Current Landscape: Current experimental and computational capabilities do not allow for the detailed, spatially- and temporally-resolved interrogation necessary to understand interfaces in NFA steel under driven conditions, which may include radiation, plastic deformation, thermal spikes and gradients, or combinations thereof. A recent DOE report has identified ways in which dramatic advances in supercomputing may enable the breakthroughs in modeling of chemically complex interfaces like those found in NFA steels [4]. To motivate and validate such modeling efforts, experimental facilities capable of interrogating material behaviors *in situ* on the comparable length and time scales—nanometers and microseconds—will be needed.

R&D Roadmap:

Concerted efforts into studying defect/interface interactions at irradiation and mechanical extremes (e.g. the Center for Materials at Irradiation and Mechanical Extremes, Lead: Nastasi) provide the opportunity to develop predictive models at the atomistic level that are validated by small-scale experiments. However, in order to model material response at far from equilibrium conditions during processing of NFA's and the subsequent irradiation of fuel-cladding assemblies, a link between atomistic interfacial modeling and larger-scale modeling such as VPSC is needed. Additionally, preliminary radiation damage studies can be carried out using ex-situ methods coupled with appropriate radiation conditions utilizing the Materials Test Station at LANSCE.

Context:

The first experiments outlined above are oriented towards in-situ measurements, however, the vast majority of experiments to solve the relevant scientific issues encountered during processing and service will be conducted ex-situ. Given M^4's extensive synthesis and characterization facilities, it is uniquely equipped to determine the effects of synthesis pathways on interfacial content, with F^3

providing the irradiation conditions for studying the performance of these newly formed interfaces under appropriate service conditions.

The diagnostic probes proposed for this first experiment will apply to other first experiments (Pu processing, etc) currently under development. While the intent of this first experiment is focused on process-aware materials performance for NFA materials, the capabilities developed here will apply to a much broader user base outside the nuclear energy community. Specific applications include processing methodologies where manipulation of nucleation and growth phenomena is key to the final microstructure and its properties (welding, casting, precipitation strengthening, film growth, nanotube/nanowire growth, etc).

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[2] S. J. Dillon, M. Tang, W. C. Carter, and M. P. Harmer, Acta Mater. **55** (2007) 6208.

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Exploring Separate Effects in Plutonium

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Problem Statement

We need to understand the impact of primary manufacturing compositional and processing changes on plutonium alloy microstructure and properties which ultimately affect physics and engineering performance.

Scientific Objectives

For ^{239}Pu in solid form (i.e., elemental, alloyed or in compounds) the experimental challenge is to separate the intrinsic physical, metallurgical, chemical, and mechanical properties from those effects induced by self-irradiation and daughter product in growth. Decoupling these effects and examining them in isolation would offer a substantial advancement in the understanding of the physics, metallurgy, and chemistry of plutonium. As a first experiment, we propose the utilization of the ^{242}Pu isotope in well-characterized unalloyed and alloyed metals and compounds in neutron and X-ray studies of in situ U and He ion beam implantation experiments:

- to allow tunable systemic studies - a greater capacity for experimental variable evolution and control (i.e., self-irradiation damage and aging, defect creation, etc.);
- to enable operations which are more efficient, less costly, and offer more experiment flexibility; and
- to generate well-characterized samples of known damage and pedigree for physics performance experiments (i.e., EOS, spall strength, ejecta, etc.) and engineering performance experiments (i.e., corrosion, phase stability, etc.) .

These experiments are dependent on utilization of the ^{242}Pu isotope as it is essentially non-radioactive ($\tau_{1/2}$ = 375,000 years) and non-fissile for low energy neutrons which makes it attractive for neutron scattering experiments. Although there is a recognizable difference in the nuclear physics of these isotopes, the physics and chemistry of the ^{242}Pu electrons and associated electronic structure and metallurgy is identical with that of ^{239}Pu; but less disrupted with a lower rate of self-irradiation damage and daughter product ingrowth.

Experimental Details

As a first experiment, we propose the utilization of the ^{242}Pu isotope in well-characterized unalloyed and alloyed metals and compounds in neutron and X-ray studies of in situ U and He ion beam implantation experiments. Manually controlled irradiation damage resultant from U and He collision cascades would be characterized in a tunable manner by exposing samples of ^{242}Pu to U or He ion implantation beams and monitored damage evolution and growth in situ both crystallographically with coincident neutron or X-ray diffraction spectroscopy and macroscopically with dilatometry. (See Fig.1.) These experiments would be conducted on variable temperature stages to enable insitu thermal recovery and phase transformation studies to be conducted as well. X-ray transmission capabilities could be utilize for Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy to obtain atomic pair distribution functions (PDF) as necessary to resolve nearest neighbor and next-nearest neighbor distances and to uniquely identify atomic positions and discern crystallographic changes. The results from these experiments would be integrated with results from Molecular Dynamics models not only to baseline plutonium crystallographic, metallurgical, and thermophysical properties necessary to define interatomic potentials, but to customize experimental conditions to suit theoretical limitations.

Current Landscape

Currently, there are no facilities capable of conducting such an integrated series of experiments. However, ^{242}Pu alloys and compounds have been and continue to be utilized in neutron diffraction experiments at LANL and is an essential component of the recently developed LANL Plutonium Science and Research Strategy Plan. Also, for economic and hazard reduction reasons, ^{242}Pu is being considered for shock experiments at the LLNL National Ignition Facility in a joint collaboration of LLNL and LANL. These and similar studies and experimental activities will provide a foundation on which to develop MaRIE first experiments described here.

R&D Needs/Roadmap

The broader impact of these MaRIE first experiments and the resultant technology are significant. As innovative ideas translate into mature capabilities, other capabilities could be employed in situ to include mechanical and elastic properties determination and thermo-mechanical processing simulations. Scientific use of these materials would not end with these experiments as samples of ^{242}Pu alloys and compounds which have been dosed and examined nondestructively could then be fabricated into samples for high explosive, electromagnetic, or laser driven shock experiments to examine changes in equation of state and strength and damage properties resultant from microstructural changes. These experiments would also be utilized to elucidate the as of yet unresolved mechanisms which drive the polymorphic phase transformations in elemental plutonium. Phase boundary variation which has historically been associated with impurities and inherent stress due to large unit cell volume variations are likely impacted by self-irradiation damage and daughter product ingrowth. For high temperature (i.e., $T \approx 0.8T_m$) technologically related experimental activities such as those exploring casting and welding, the replacement of ^{239}Pu with ^{242}Pu may be of little consequence other than minimizing radiological hazards. However, for experiments which are thermo-mechanical history dependent or strongly dependent on initial conditions, it is crucial to separate intrinsic elemental characteristic from temporal radioactive decay processes and products.

Current and planned supporting efforts include:

- Actinide Science LDRD-DR Grand Challenge:

Understanding 5f Electrons of Plutonium, Hydrogen Effects in Pu, etc.

- LANL Plutonium Science and Research Strategy Plan
- NNSA Dynamic Plutonium Experiments Program Strategic Plan
- Dynamic Compression Collaborative Access Team (DC-CAT) at the APS

Context

This first experiment is closely related to proposed MaRIE first experiments in nanostructured ferritic alloys due to similar needs of processing and characterization capabilities proposed at M4 facilities and high explosives and compression dynamics due to similar needs of fast diagnostic capabilities proposed at MPDH facilities.