Michigan Ion Beam Laboratory

ANNUAL RESEARCH REPORT

2016

Gary S. Was, Director
Ovidiu Toader, Manager and Research Specialist
Fabian Naab, Research Specialist
Ethan Uberseder, Research Specialist
Thomas Kubley, Research Engineer

2600 Draper Road
Department of Nuclear Engineering and Radiological Sciences
University of Michigan
Ann Arbor, Michigan 48109-2145
mibl.engin.umich.edu

Telephone: (734) 936-0131 Fax: (734) 763-4540

The Annual Research Report

This report summarizes the principal research activities in the Michigan Ion Beam Laboratory during the past calendar year. Eight-five researchers conducted 45 projects at MIBL that accounted for 5625 hours of instrument usage. The programs included participation from researchers at the University, corporate research laboratories, private companies, government laboratories, and other universities across the United States. The extent of participation of the laboratory in these programs ranged from routine surface analysis to ion assisted film formation. Experiments included Rutherford backscattering spectrometry, elastic recoil spectroscopy, nuclear reaction analysis, direct ion implantation, ion beam mixing, ion beam assisted deposition, and radiation damage by proton bombardment. The following pages contain a synopsis of the research conducted in the Michigan Ion Beam Laboratory during the 2014 and 2015 calendar years.

About the Laboratory

The Michigan Ion Beam Laboratory for Surface Modification and Analysis was completed in October of 1986. The laboratory was established for the purpose of advancing our understanding of ion-solid interactions by providing up-to-date equipment with unique and extensive facilities to support research at the cutting edge of science. Researchers from the University of Michigan as well as industry and other universities are encouraged to participate in this effort.

The lab houses a 3 MV Pelletron accelerator, a 1.7 MV tandem ion accelerator, and a 400 kV ion implanter that are configured to provide for a range of ion irradiation and ion beam analysis capabilities. The control of the parameters and the operation of these systems are mostly done by computers and are interconnected through a local area network, allowing for complete control of irradiations from the control room as well as off-site monitoring and control.

In 2010, MIBL became a Partner Facility of the National Scientific User Facility (NSUF), based at Idaho National Laboratory, providing additional opportunities for researchers across the US to access the capabilities of the laboratory.

On December 20, 2013, the lab was closed for a major expansion that includes the addition of a 3 MV Pelletron accelerator, reconfiguration of the accelerator room, establishment of a target room and a control room and coupling of the three accelerators to provide the capability to conduct dual and triple beam ion irradiations. The expansion resulted in a completely refurbished lab consisting of 3 accelerators, 8 beam lines, 5 target chambers and the capability to conduct dual and triple beam irradiations.

Respectfully submitted,

Gary S. Was, Director

2014
RESEARCH PROJECTS

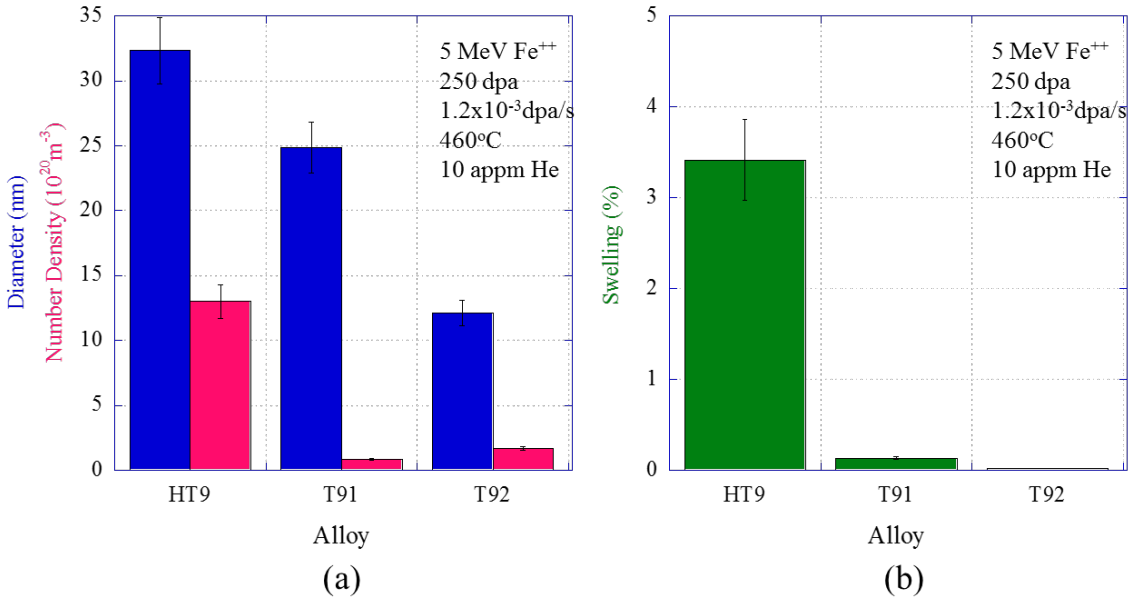
IRRADIATION EFFECTS IN FERRITIC-MARTENSITIC STEELS AT VERY HIGH DOSES

E. Getto, Z. Jiao, K. Sun, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Determining the microstructural behavior of ferritic-martensitic alloys is important for predicting the safety and structural integrity of fast reactors. Self-ion irradiation experiments have been performed on heats of ferritic-martensitic alloys HT9, T91 and T92 to determine void swelling behavior at 460°C up to 650 displacements per atom (dpa). Irradiations were performed with 5 MeV Fe^{++} ions on samples pre-implanted with 10 atom parts per million He and irradiated using a rastered beam with a 3 MV Pelletron accelerator at the Michigan Ion Beam Laboratory. The effects of alloy chemistry and pre-irradiation microstructure on swelling were determined using an Analytic Electron Microscope in STEM mode. The void swelling, dislocation microstructure and secondary phase formation were examined as a function of dose in T91, T92 and HT9.

Swelling was observed in all three alloys up to 250 dpa. A steady state swelling rate of ~0.03%/dpa was determined for HT9, consistent with recent literature results. Swelling resistance was greater in F-M alloys T91 and T92. Swelling was an order of magnitude lower in T91 and two orders of magnitude lower in T92. The decrease in swelling for T91 was primarily due to suppression of void nucleation, rather than void growth, demonstrated by similar void sizes but a tenfold decrease in void density. Precipitation and dislocation microstructures were similar between these three alloys at the doses considered.

This work is supported by TerraPower LLC.



Void diameter (a), number density (a) and swelling (b) in 5 MeV Fe^{++} self-ion irradiated HT9, T91 and T92 pre-implanted with 10 appm He and irradiated at 460°C to 250 dpa.

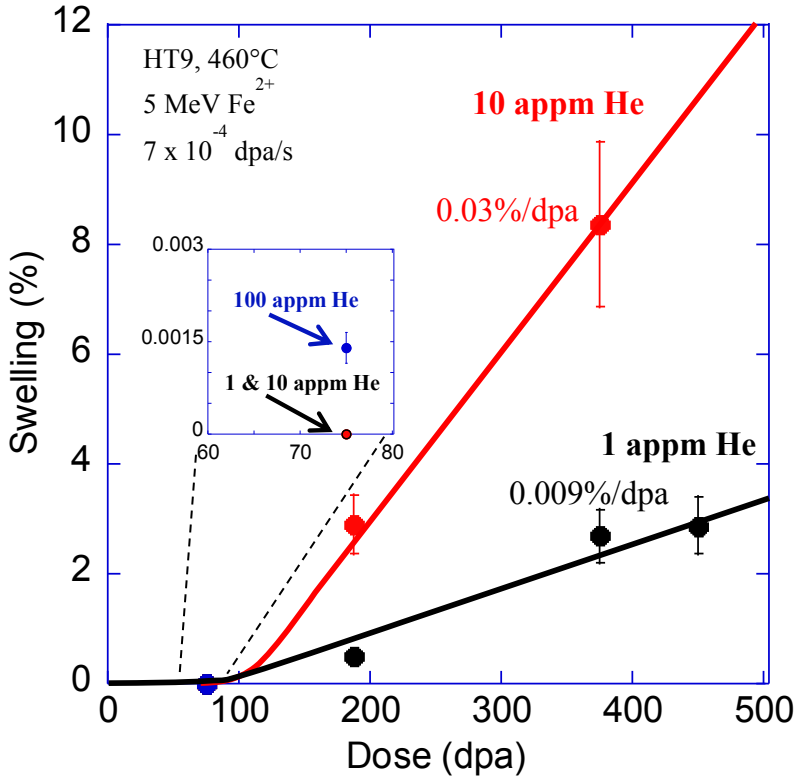
ACCELERATED IRRADIATIONS FOR EMULATION OF HIGH-DOSE MICROSTRUCTURE IN FERRITIC-MARTENSITIC STEELS

A.M. Monterrosa, Z. Jiao, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

The new generation of faster reactors is seeking to push damage levels in structural materials to very high doses, in excess of 500 dpa. Using fast reactors to irradiate materials to such high doses is prohibitively expensive and time-consuming. This project will study how effectively self-ion irradiations can be used to emulate microstructural features (voids and precipitates) seen in neutron-irradiated HT9 and other ferritic-martensitic (F-M) steels.

Self-ion irradiation experiments have been performed on ferritic-martensitic alloys HT9 to determine swelling behavior at 460°C in the range of 75 to 450 dpa with up to 100 atomic parts per million (appm) helium implanted. The irradiations were performed using the 3MV Wolverine accelerator at the Michigan Ion Beam Laboratory. The effects of dose on void swelling were analyzed using a transmission electron microscope in scanning mode (STEM). The size, density and distributions of radiation-induced voids were analyzed through the depth of the microstructure. Swelling rates of 0.03%/dpa and 0.009%/dpa were achieved in 10 and 1 appm He implantation conditions, respectively. Future work will include irradiations of T91 at 420°C in an effort to compare ion irradiation results to neutron irradiated results

This work is supported by DOE NEUP award DE-AC07-05ID14517.



Swelling in alloy HT9 as a function of pre-implanted He content.

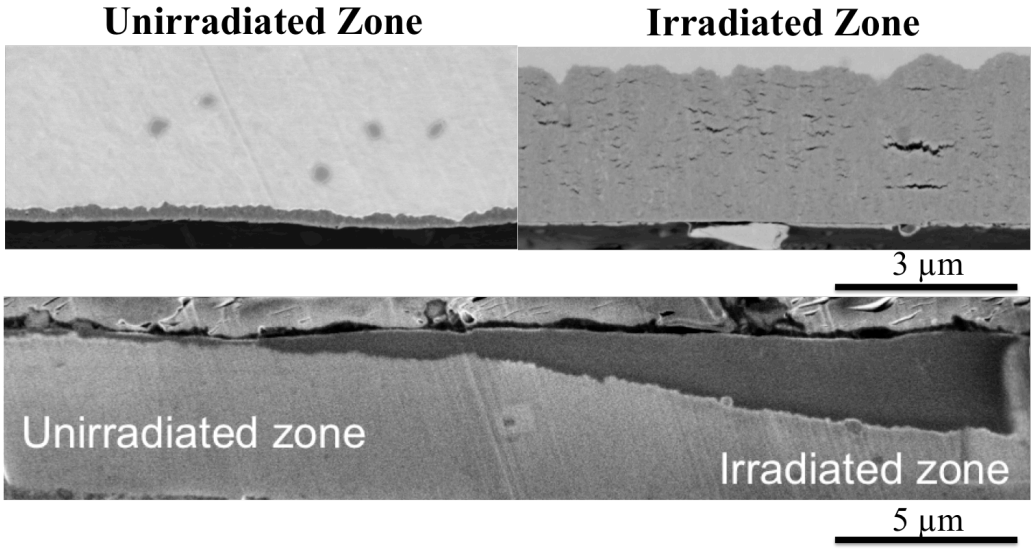
OXIDATION OF ZIRCALOY-4 DURING IN-SITU PROTON IRRADIATION AND CORROSION IN PWR PRIMARY WATER

P. Wang, G. S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

This project aims to understand how radiation affects corrosion behavior of reactor core materials. Studies based on in-pile and out-of-pile weight gain data suggest that neutron radiation has a large impact on the corrosion rate of zirconium alloys during the service. However, only limited data indicates that the radiation effect is large; it causes order of magnitude increases in corrosion rates. This study was focused on the characterization of the oxide film formed on Zircaloy-4 that has been exposed to the PWR primary loop environment (without B and Li addition) during proton irradiation. The oxides and SPPs were characterized for both the irradiated and unirradiated states to understand the effect of simultaneous irradiation during corrosion.

Over the last two years, a number of in-situ proton irradiation-corrosion experiments have been conducted at MIBL on Zircaloy-4. The kinetics and morphology of oxides formed during in-situ proton irradiation–corrosion experiments were analyzed. Experiments were conducted in 320 °C water with 3 wt ppm H_2, while irradiated by a 3.2-MeV proton beam at a current density of 2 $\mu A/cm^2$ producing a damage rate at 4 x 10^{-7} dpa/s. The resulting oxide was compared with reference samples corroded in an autoclave, and literature data found on in-reactor formed oxide. The corrosion rate of the sample irradiated in-situ was 10 times faster than the in-pile corrosion rate. The cracked and porous irradiated oxide consisted of monoclinic equiaxed grains of zirconia with a preferential orientation of the oxide grains. Second phase particles (SPPs) consumed by the oxidation front were rapidly oxidized, but no SPPs were amorphized or dissolved in the metal matrix of the irradiated sample.

This research was supported by the DOE-NEUP, Grant No. DE-AC07-05ID14517, Contract No. 8610-BVW-4300243004, and Consortium for Advanced Simulation of Light Water Reactors (CASL) under U.S. Department of Energy Contract No. DE-AC05-00OR22725.



Backscatter electron image of oxide thickness comparison between a non-irradiated zone and irradiated zone on the 24-h irradiated sample (top). Transition between the unirradiated and irradiated zones (bottom).

DEMONSTRATION OF THE CAPABILITY TO PERFORM MULTI-BEAM ION IRRADIATIONS AT THE MICHIGAN ION BEAM LABORATORY

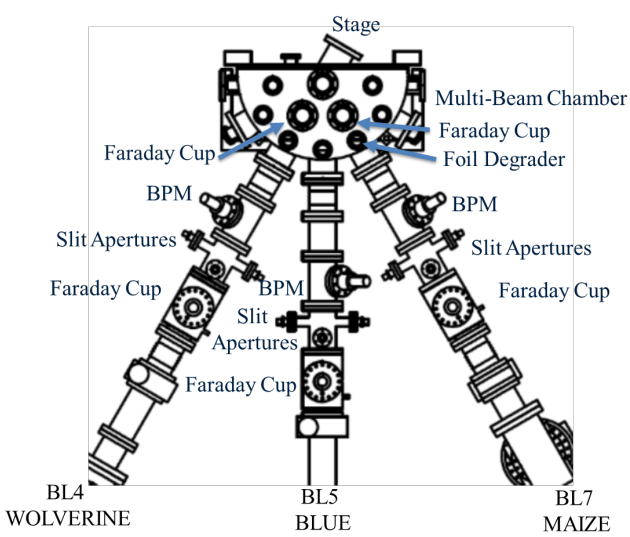
S. Taller, D. Woodley, S. Dwaraknath, Z. Jiao, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

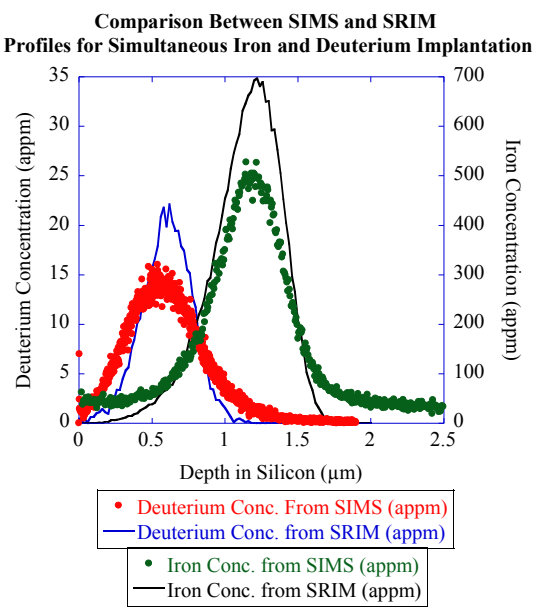
Material lifetime in nuclear reactors is limited by high levels of displacement damage to the microstructure, and by secondary or synergistic effects resulting from the buildup of gas from transmutation. Dual ion beam irradiation can be used as a surrogate for in-reactor irradiations to emulate this process with simultaneous irradiation of both a heavy ion beam and a light ion beam to induce damage and implant gas ions, respectively. This capability was developed at the Michigan Ion Beam Laboratory and a high fidelity demonstration of the efficacy of this technique is required before application to prospective reactor materials.

To demonstrate and benchmark the measurement systems for dual ion irradiations, a 1.34 MeV iron ion beam was defocused and implanted into a silicon wafer from the 3 MV Pelletron accelerator "Wolverine". Simultaneously, a 940 keV deuterium beam from the 1.7 MV Ionex Tandem "Maize" was raster scanned over a 9.8 micron aluminum degrader foil designed for MIBL to reduce the energy and place the implantation peak of the deuterium closer to the surface compared to the implanted iron.

Concentration profiles with depth were measured using dynamic secondary ion mass spectroscopy (D-SIMS) and compared to profiles calculated using Stopping and Range of Ions in Matter (SRIM) for the same measured ion fluence during simultaneous implantation of iron and deuterium. The peaks of the calculated and measured profiles agree for both iron and deuterium, providing confidence in the energy loss calculations in SRIM. The measured peak concentrations are lower, but the integrated area under the profiles are in good agreement, providing confidence in the measurement of the total amount of ions implanted during multi-beam ion irradiations.

This work is supported by the U.S. Department of Energy under grant DE-NE0000639.





The multi-beam chamber used for multi-beam irradiations at MIBL (left). SRIM predicted and SIMS measured concentration profiles with depth into silicon (right).

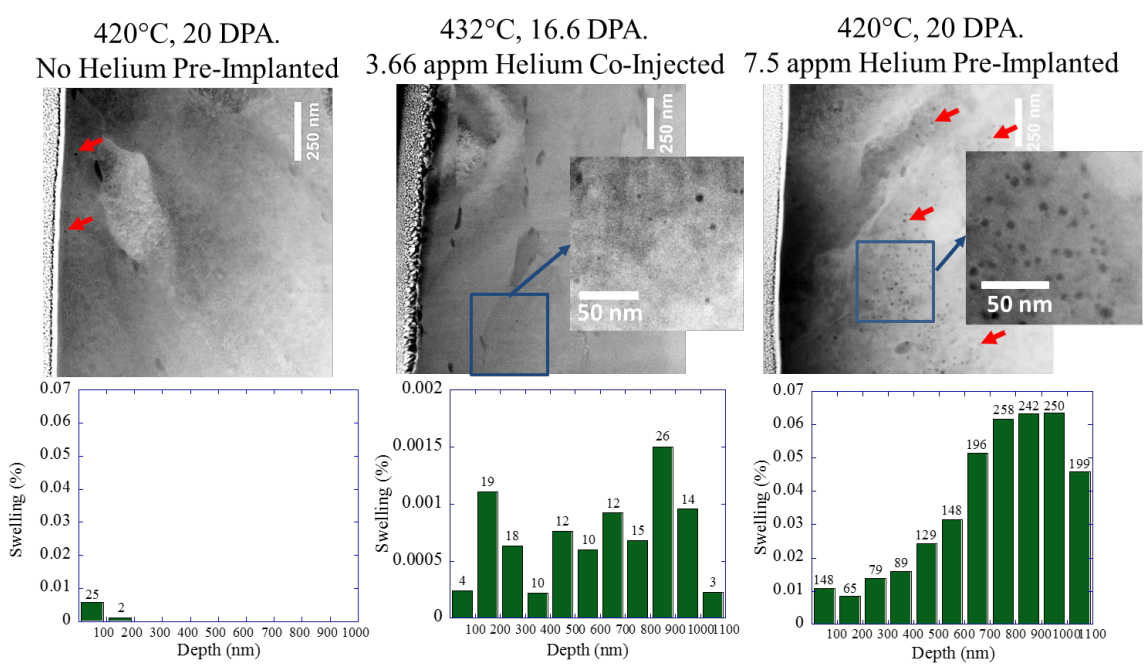
HIGH FIDELITY ION BEAM SIMULATION OF HIGH DOSE NEUTRON IRRADIATION

S.Taller, Z. Jiao, G.S. Was
Department of Nuclear Engineering & Radiological Sciences, University of Michigan

Traditional research efforts to understand radiation-induced processes in materials requires years of comprehensive post-irradiation characterization effort of test reactor produced neutron irradiated material. The same levels of radiation damage can be achieved using heavy ion irradiation under tightly controlled conditions in days or weeks instead of years in a nuclear reactor, albeit with several challenges. The purpose of this work is to address these challenges in using ion irradiation experiments as a surrogacy for neutron irradiation. Several single heavy ion irradiations were conducted for this project at the Michigan Ion Beam Laboratory. Bars of the austenitic steel 800H and a model alloy Fe21Cr32Ni alloy were ion-irradiated using 5 MeV defocused Fe^{++} ions to 1, 10, and 20 displacements per atom (dpa) at 600nm depth, at 440°C. Similarly, bars of the ferritic-martensitic steels T91 and HT9 were ion-irradiated to 1, 10 and 20 dpa using 5 MeV defocused Fe^{++} ions at 470ºC, and to 20 dpa at 420ºC and 440°C.

Several dual ion irradiations were performed using 5.0 MeV defocused Fe^{++} ions to damage the material and simultaneously injecting He^{++} ions in a fixed ratio to emulate gas buildup from nuclear transmutation reactions. Bars of 800H, Fe21Cr32Ni, T91, and HT9 were dual ion irradiated to 16.6 dpa with 1.0 atomic parts per million (appm) helium per dpa injected for the austenitic alloys at 446°C and 0.22 appm helium per dpa for the ferritic-martensitic alloys at 406°C and 432°C to compare with multiple conditions from BOR-60. These specimens are being examined with transmission electron microscopy and atom probe tomography to determine the effects of simultaneous helium injection and radiation damage on the irradiated microstructure of these materials.

This work is supported by the U.S. Department of Energy under award DE-NE0000639.



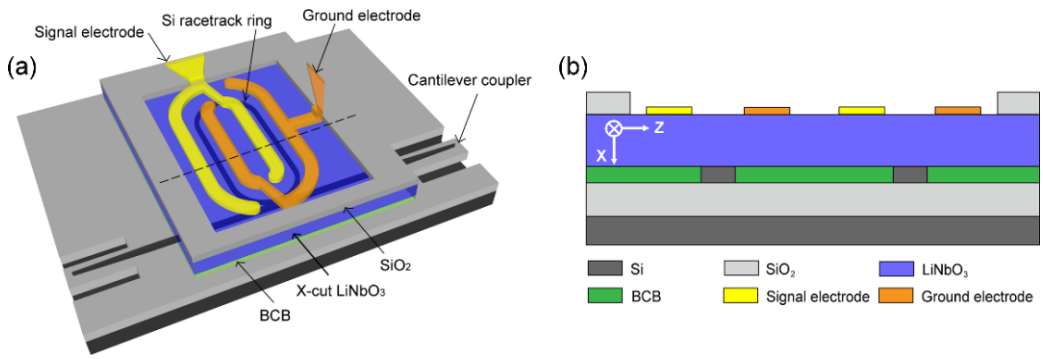
A comparison of High Angle Annual Dark Field STEM images (above) highlighting observed voids and calculated swelling (below) in the ferritic-martensitic steel T91 heat 30176 for single and dual ion irradiation conditions.

ION-SLICED LITHIUM NIOBATE THIN FILMS FOR INTEGRATED OPTICAL MODULATORS

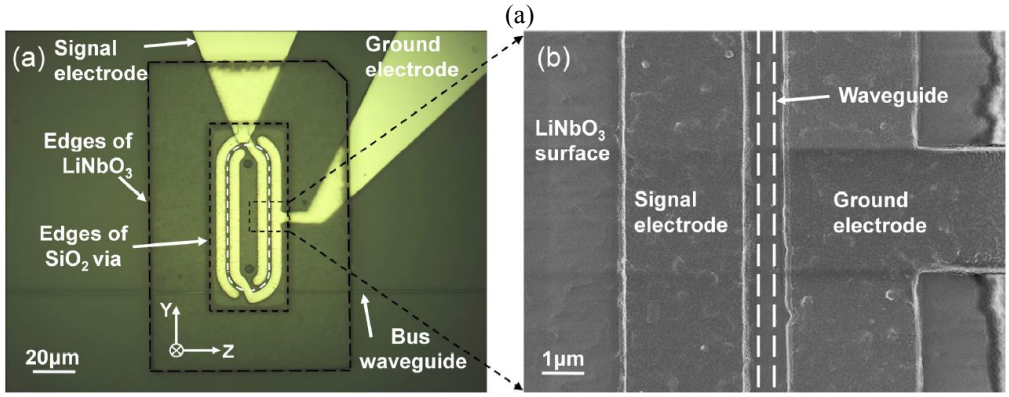
L. Chen, J. Chen, J. Nagy, R. M. Reano
Department of Electrical and Computer Engineering, The Ohio State University

Highly linear optical ring modulators have been developed on a hybrid silicon and lithium niobate ($LiNbO_3$) platform. The modulator consists of a 1 µm thick $LiNbO_3$ film bonded to silicon waveguides via BCB. Electrodes on top of the $LiNbO_3$ are used to modulate 1.55µm light via the r_{33} electro-optic coefficient. Light is coupled on/off the chip with a taped fibers and cantilever couplers. To obtain $LiNbO_3$ thin films, an x-cut $LiNbO_3$ bulk wafer is implanted with He^+ ions with an energy of 380 keV and a fluence of 3.5×10^{16} ions cm^{-2} to form a damaged layer below the top surface. The depth of the damage layer is controlled by the ion implantation energy. The thin film can be patterned and separated from the substrate by thermal treatment.

This work was supported by the Army Research Office (ARO) under grant number W911NF-12-1-0488.



Schematic of hybrid Si/$LiNbO_3$ ring modulator (a). For clarity, the PECVD SiO_2 top cladding layer and electrical contact pads are not shown. Schematic of cross-section of device (b) along dashed line in (a).



Top-view optical micrograph of fabricated device (a). SEM of electrodes (b).

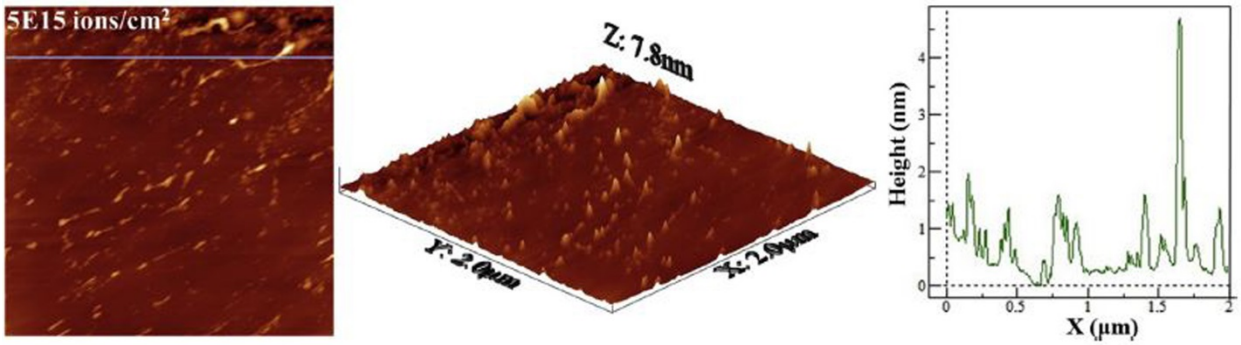
INFLUENCE OF 400 keV CARBON ION IMPLANTATION ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF PMMA

S. Arif[1], M. S. Rafique[2], F. Saleemi[1], R. Sagheer[1], F. Naab[3], O. Toader[3], A. Mahmood[4], R. Rashid[4], M. Mahmood[5]

[1]Department of Physics, Lahore College for Women University, Lahore 54000, Pakistan
[2]Department of Physics, University of Engineering & Technology, Lahore 54000, Pakistan
[3]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[4]National Institute of Lasers and Optronics (NILOP), P.O. Nilore, Islamabad, Pakistan
[5]Department of Metallury & Materials Engineering, Pakistan Institute of Engineering & Applied Sciences (PIEAS), Islamabad, Pakistan

Ion implantation is a useful technique to modify the surface properties of polymers without altering their bulk properties. The objective of this work is to explore the 400 keV C^+ ion implantation effects on PMMA at different fluences ranging from $5x10^{13}$ to $5x10^{15}$ ions/cm^2 using 400 kV NEC ion implanter. The surface topographical examination of irradiated samples has been performed using Atomic Force Microscope (AFM). The structural and chemical modifications in implanted PMMA are examined by Raman and Fourier Infrared Spectroscopy (FTIR), respectively. The effects of carbon ion implantation on optical properties of PMMA are investigated by UV–Visible spectroscopy. The modifications in electrical conductivity have been measured using a four-point probe technique. AFM images reveal a decrease in surface roughness of PMMA with an increase in ion fluence from $5x10^{14}$ to $5x10^{15}$ ions/cm^2. The existence of amorphization and sp^2-carbon clusterization has been confirmed by Raman and FTIR spectroscopic analysis. The UV–Visible data shows a prominent red shift in the absorption edge as a function of ion fluence. This shift displays a continuous reduction in optical band gap (from 3.13 to 0.66 eV) due to the formation of carbon clusters. Moreover, size of carbon clusters and photoconductivity are found to increase with increasing ion fluence. The ion-induced carbonaceous clusters are believed to be responsible for an increase in electrical conductivity of PMMA from $(2.14 \pm 0.06) \times 10^{-10}$ $(\Omega cm)^{-1}$ (pristine) to $(0.32 \pm 0.01) \times 10^{-5}$ $(\Omega cm)^{-1}$ (irradiated sample).

We gratefully acknowledge the kind cooperation of Prof. Gary Was for providing the implantation facilities at University of Michigan Ion Beam Laboratory. S. Arif is thankful to Higher Education Commission, Pakistan for fellowship under the Indigenous Scholarship Program.



Atomic force microscopic (AFM) images (2D, 3D & line profile) of implanted PMMA at an ion fluence of $5x10^{15}$ ions/cm^2

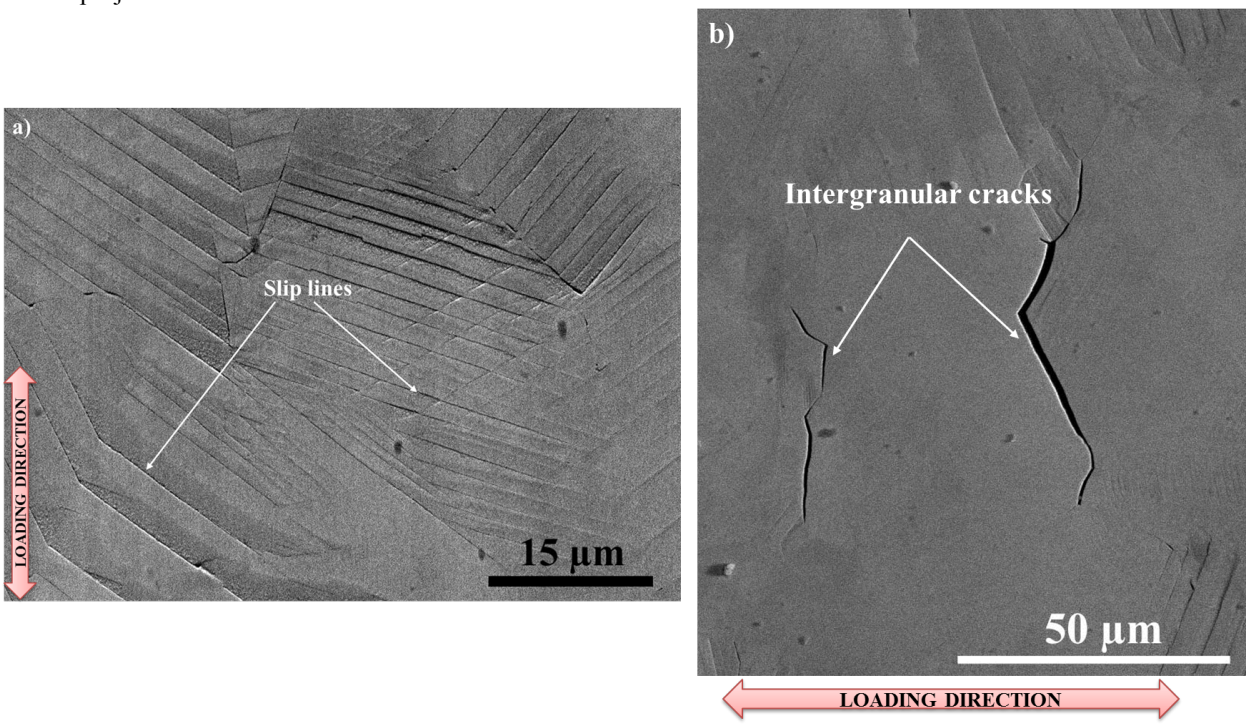
INTERGRANULAR STRESS CORROSION CRACKING (IGSCC) OF IRRADIATED AUSTENITIC STAINLESS STEEL IN PWR ENVIRONMENT

J. Gupta[1,2], B. Tanguy[1], J. Hure[1], L. Laffont[2], M-C Lafont[2], E. Andrieu[2]
[1]CEA Saclay, Department of Materials for Nuclear Applications, Gif sur Yvette, France
[2]Institut CARNOT, CIRIMAT – ENSIACET, Toulouse, France

The objective of this study is to determine the impact of few potential contributors (such as irradiation induced microstructure, strain paths) on the intergranular cracking susceptibility of austenitic stainless steel. The impact of these parameters, individually and in combination, has been previously studied for proton irradiation. This study in particular focuses on the comparison of deformation mechanism of proton and heavy ion irradiated austenitic stainless steel.

To achieve the goal, vibratory polished solution annealed 304 L samples were irradiation using 2 MeV protons at 350 ± 10 °C to 2 dpa K-P at the Michigan Ion Beam Laboratory (MIBL). In parallel, another set of same material samples was irradiated using 10 MeV Fe at 450 ± 20 °C to 5 dpa K-P at JANNuS facility of CEA Saclay. The irradiation induced microstructure was characterized and quantified. Post irradiation, samples were subjected to different loading conditions such as Constant Extension Rate Tensile (CERT) testing, constant loading, cyclic loading. The surface of the strained samples was subsequently characterized using SEM and EBSD to obtain qualitative and quantitative information about the degree of localization and cracking susceptibility for both irradiation conditions.

The authors gratefully acknowledge Dr Ovidiu Toader from MBIL for its assistance in conducting proton irradiations. Support for this research was provided by the CEA RSTB research program within the frame of the R-MATE project.



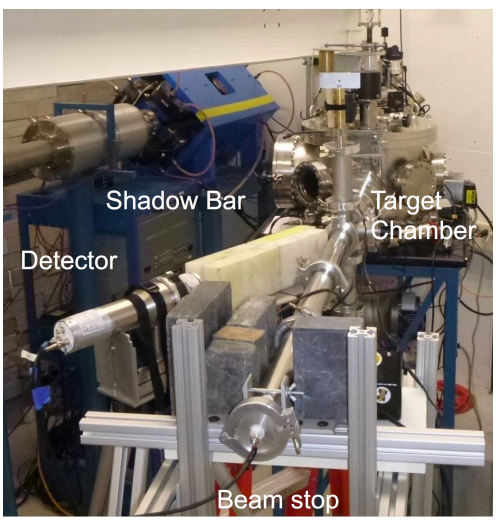
SEM images of the surface of the proton irradiated samples post CERT in simulated PWR primary water environment indicating the presence of a) slip lines and b) intergranular cracks.

2015
RESEARCH PROJECTS

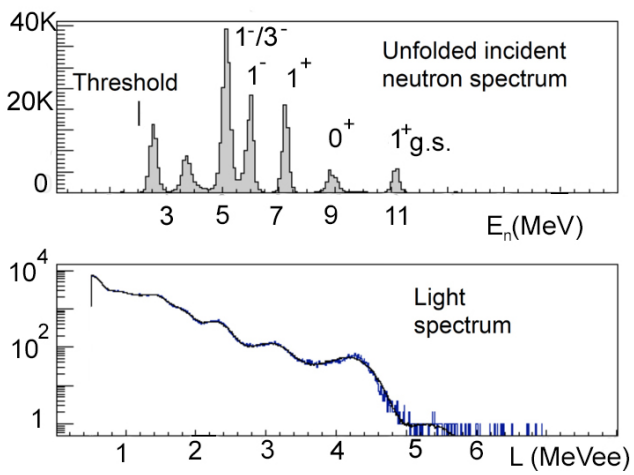
EVALUATION OF DEUTERATED-XYLENE (EJ301D): A NEW, IMPROVED DEUTERATED LIQUID SCINTILLATOR FOR NEUTRON ENERGY MEASUREMENTS WITHOUT TIME-OF-FLIGHT

F.D. Becchetti[1], R.S. Raymond[1], R.O.Torres-Isea[1], A. Di Fulvio[2], S.D. Clarke[2], S.A. Pozzi[2], M. Febbraro[3]
[1]Department of Physics, University of Michigan
[2]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[3]Oak Ridge National Laboratory, Oak Ridge, TN

In conjunction with Eljen Technology, Inc. (Sweetwater, TX) we have designed, constructed, and evaluated at MIBL a 3 in. x 3 in. deuterated-xylene organic liquid scintillator (C8D10; EJ301D) as a fast neutron detector. Similar to deuterated benzene (C6D6; NE230, BC537, and EJ315) this scintillator can provide good pulse-shape discrimination between neutrons and gamma rays, has good timing characteristics, and can provide a light spectrum with peaks corresponding to discrete neutron energy groups up to ca. 20 MeV. Unlike benzene-based detectors, deuterated xylene is less volatile, has a higher flashpoint, and hence is much safer for certain applications. As we demonstrate using the new MIBL 3 MV NEC Pelletron (see figures), neutron reaction measurements can be performed when a bunched and pulse-selected beam (as needed for time-of-flight) is not available. (A paper on this work is being submitted to Nucl. Instrum. Methods)



In-beam set up at UM MIBL NEC tandem accelerator for (d,n) measurements at E_d=6 MeV.



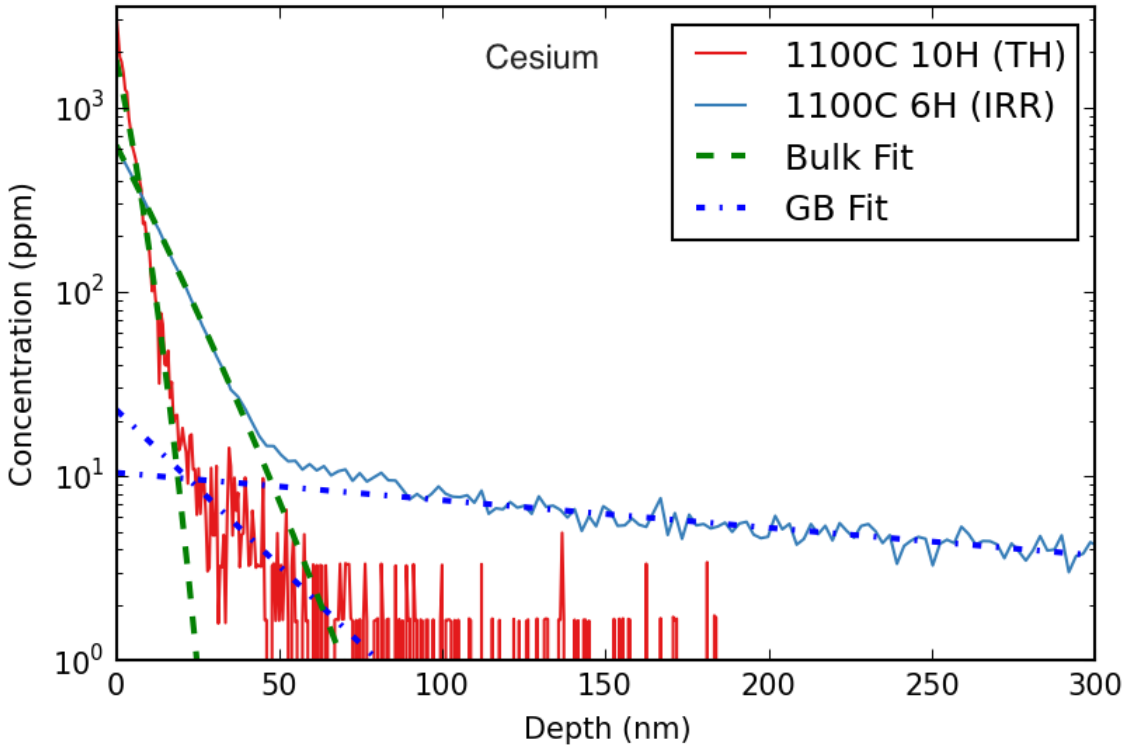
Unfolded incident neutron energy spectrum (25 degs. lab) for $^{13}C(d,n)^{14}N$ at E_d=6 MeV. Levels in ^{14}N attributed to individual states or doublets energies in ^{14}N are indicated.

RADIATION ENHANCED DIFFUSION OF CESIUM IN SILICON CARBIDE

S. Dwaraknath, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

This work focused on identifying the mechanism for cesium, europium and strontium diffusion into silicon carbide (SiC) under ion irradiation conditions in support of TRISO fuel licensing and the very high temperature reactor (VHTR) program. High temperature multi-layered diffusion couples were constructed consisting of a SiC substrate, a thin layer of pyrolytic carbon (PyC), followed by a final coating of SiC. The PyC was ion implanted with strontium to a fluence of 10^{16} cm^{-2} at the Michigan ion beam laboratory (MIBL) using the 400 keV ion implanter. The implanted fluence was verified by Rutherford backscattering spectroscopy (RBS) performed at MIBL. The diffusion couples were ion irradiated at MIBL between 900ºC and 1100ºC for 6 hours to a total dose of 10 dpa as calculated by SRIM using the quick calculation mode. The figures shows a comparison of the thermally annealed and ion irradiated cesium concentration profile in SiC. Ion irradiation greatly enhanced cesium diffusion along both bulk and grain boundary paths.

This work is supported by the Department of Energy under NEUP Contract #00103195



Concentration vs. depth profile for cesium diffusion in SiC. The thermally annealed concentration profile is plotted in red while the ion irradiated profile is plotted in blue. Both bulk and grain boundary diffusion were identified and fit in these concentration profiles. Ion irradiation greatly enhanced both processes.

IRRADIATION EFFECTS IN FERRITIC-MARTENSITIC STEELS AT VERY HIGH DOSES

E. Getto, Z. Jiao, K. Sun, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

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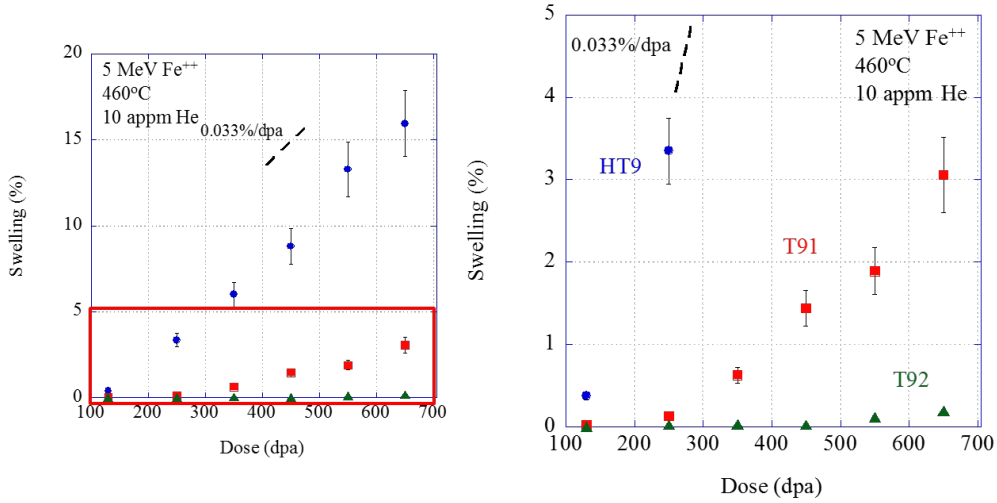
A steady state swelling rate of 0.037%/dpa was determined for HT9. Swelling resistance was greater in F-M alloys T91 and T92. By 650 dpa, T91 had reached a swelling rate of 0.01%/dpa. The decrease in swelling for T91 was primarily due to suppression of void nucleation, rather than void growth. T92 was still within the nucleation regime with swelling below 0.2%, with voids that had not grown appreciably, indicating suppression of both nucleation and growth. Analysis of additional heats of T91 indicated that alloy was not the primarily determining factor of swelling resistance.

Formation of rod-like M_2X precipitates was observed at 250 dpa. They appear to inhibit void nucleation, but do not affect void growth. Formation of these precipitates during the steady state swelling regime (as in for HT9), did not appear to affect steady state swelling rate, but they appear to strongly inhibit void nucleation if swelling has not reached the steady state swelling regime as in T91 and T92. No dependence of void swelling on lath length or width was observed.

This work is supported by TerraPower LLC.



Void swelling evolution in 5 MeV Fe^{++} self-ion irradiated HT9, T91 and T92 preimplanted with 10 appm He and irradiated at 460°C. The lower swelling alloys are highlighted in the right hand graph.

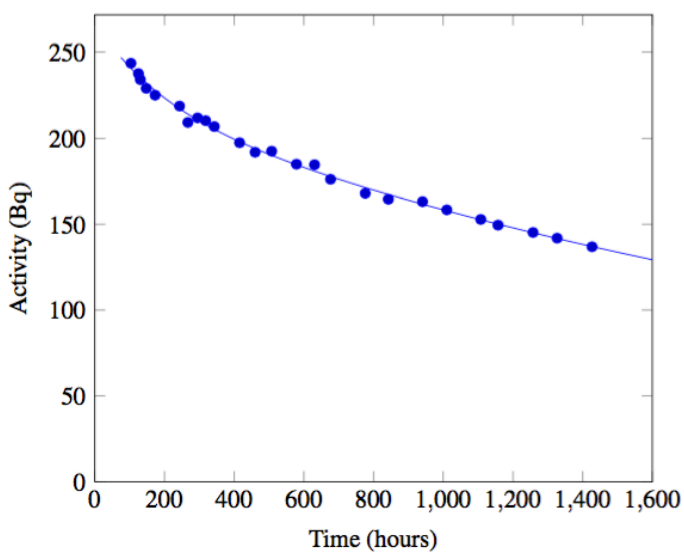
GRAIN ORIENTATION EFFECT ON IRRADIATION ACCELERATED CORROSION OF 316L STAINLESS STEEL

R.D. Hanbury, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Accelerated corrosion in an irradiated environment is a poorly understood phenomenon, but it is a critical component of irradiation assisted stress corrosion cracking (IASCC). This project aims to study the mechanics of corrosion under irradiation on 316L samples. Previous work has shown that the oxide structure can be affected by the orientation of the underlying grain. Grain orientation, along with corrosion behavior, may be significantly changed by deformation. Prior irradiation accelerated corrosion (IAC) experiments at MIBL required hydraulically deformed materials to withstand the pressure differential between the beamline and the corrosion cell. With the higher energy capabilities of MIBL, up to 6 MeV protons can be used with a thicker, undeformed sample while still penetrating to the metal-water interface.

One preliminary experiment has been performed at MIBL to address issues related to excessive proton activation and sample deformation. A 316L stainless steel sample was irradiated with a 5.8 MeV proton beam to 0.1 dpa. The radioactive decay of the sample is being monitored after irradiation and is plotted in the figure below. Future work will mitigate activation and deformation of the sample and examine the oxide film structure over various grain orientations.

This research is supported by EDF.



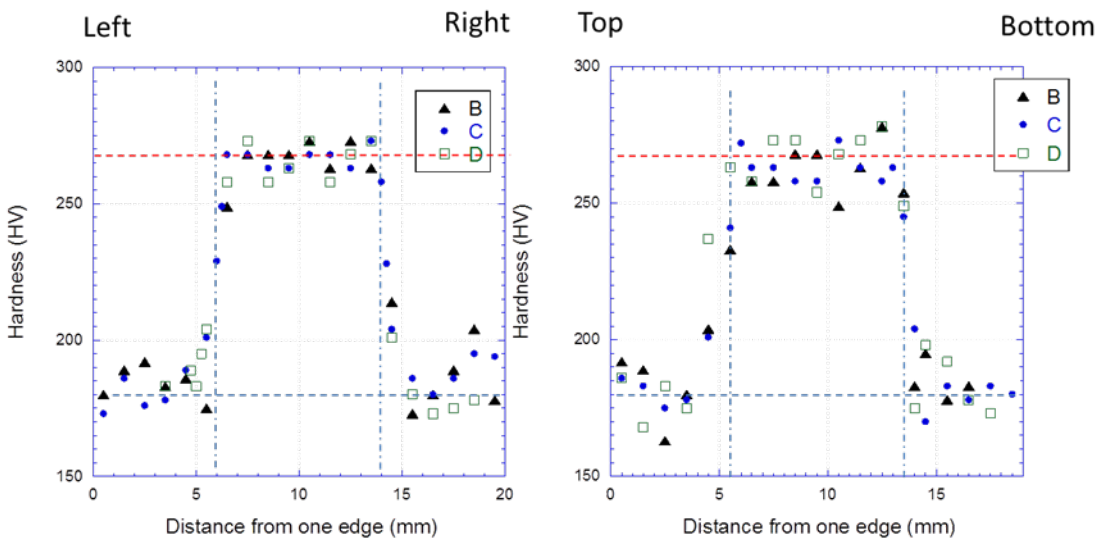
Decay curve for alloy 316L after irradiation with 5.8 MeV protons to 0.1 dpa.

PROTON IRRADIATION BENCHMARK EXPERIMENT

Z. Jiao, P. Roy, F. Naab, O. Toader,
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

A proton irradiation was conducted after the beamline reconstruction (BL2) at MIBL in 2014. This irradiation was conducted using the same alloy (CP304) at the same irradiation conditions (Temperature: 360°C; Irradiation dose:1dpa; Proton energy: 3.2MeV) as a previous proton irradiation prior to the beamline reconstruction. The purpose was to ensure that proton irradiation can be properly conducted after beamline reconstruction and that it produces the same irradiation damage (using irradiation hardening as the measure) as seen in the previous irradiation. In addition, irradiation hardening (correlates to irradiation damage) was used to verify if the dose was correct (indirectly) and if the irradiated area was uniform and well aligned.

The proton benchmarking irradiation was successful with excellent agreement in irradiation hardening with previous irradiation before the beamline reconstruction. The irradiated area was also in reasonable agreement with the set slit opening indicating that the divergence of beam from the slit to the sample is small. Temperature control was excellent and the beam was overall stable with a few beam drops.



Hardness profile across the sample surface from both left to right and top to bottom. The green and red horizontal dashed lines indicate the unirradiated and irradiated hardness from the previous irradiation. The vertical dashed lines show the width of the 8mm opening to which the slits were set.

ESTABLISHING A CAUSE-AND-EFFECT RELATIONSHIP BETWEEN LOCALIZED DEFORMATION AND IASCC

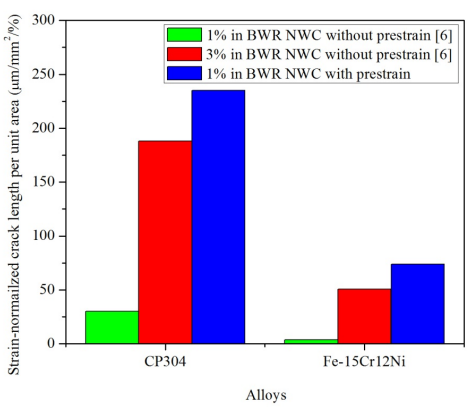
Z. Jiao[1], J. Hesterberg[1], G.S. Was[1], P. Chou[2]
[1]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[2]Electric Power Research Institute

Irradiation assisted stress corrosion cracking (IASCC) is the primary form of core component cracking in boiling water reactors. It is also an issue of growing importance in pressurized water reactors. This project aims to establish direct evidence of a cause-and-effect relationship between localized deformation and IASCC, aided by improved methods for quantifying crack initiation, and to develop an understanding of how localized deformation leads to IASCC.

IASCC susceptibility of a commercial grade alloy CP304 and a high purity alloy Fe-15Cr12Ni was examined. Both alloys were irradiated to 5 dpa at 360°C using 2 MeV protons. Multiple steps of straining in argon and in simulated BWR NWC were performed. It was found that a water environment was necessary for IASCC crack initiation of CP304 and Fe-15Cr12Ni at 288°C. The alloys did not crack when strained in pure argon up to 3.4% and 3.6% plastic strain, respectively. Cracking only occurred when a portion of that strain was conducted in simulated BWR NWC.

The cause-and-effect relationship between localized deformation and IASCC was not established. It would need a much more detailed analysis of the stress state including both the normal stress resulting from the applied stress and the contribution of the dislocation channel to be able to understand the role of localized deformation. Some grain boundaries may need a large contribution from dislocation channels while some other may need minimal. Characterization of the channel height alone is simply not enough for understanding the role of localized deformation.

Support for this research was provided by the Electric Power Research Institute (EPRI) through contract EP-P35203/C15971.



Strain-normalized crack length per unit area of CP304 and Fe-15Cr12Ni (360°C:5dpa) with or without prestrain in Ar.

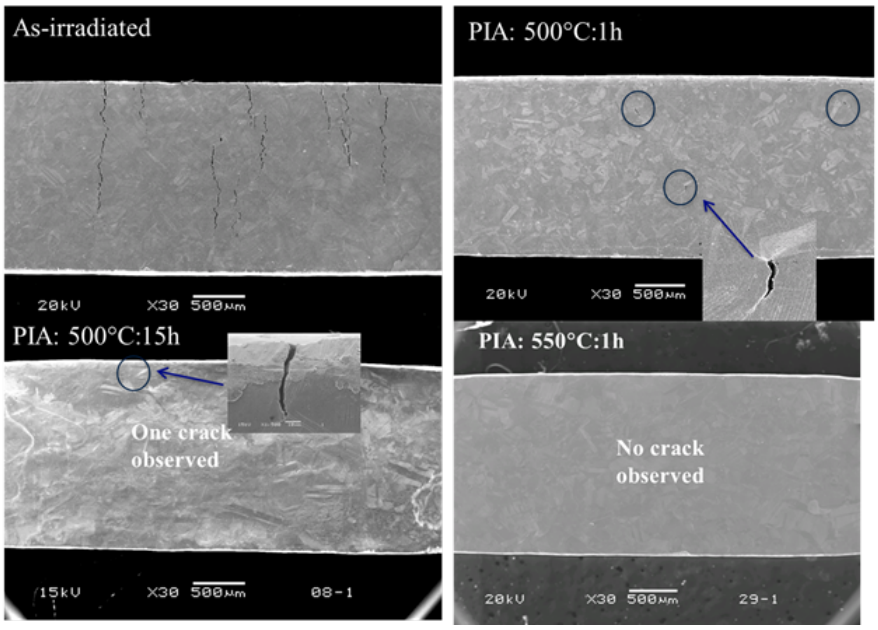
POST-IRRADIATION ANNEALING AS A MITIGATION STRATEGY FOR IASCC IN AUSTENITIC STAINLESS

Z. Jiao[1], J. Hesterberg[1], G.S. Was[1], P. Chou[2]
[1]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[2]Electric Power Research Institute

Irradiation assisted stress corrosion cracking (IASCC) is the primary form of core component cracking in boiling water reactors. It is also an issue of growing importance in pressurized water reactors. Post-irradiation annealing (PIA) has been demonstrated as a potential mitigation method for IASCC in stainless steels in a few studies. This project is intended to understand the mitigation mechanism of PIA using a proton-irradiated austenitic stainless steel.

Commercial grade 304SS that is susceptible to IASCC in simulated BWR environment was selected for this study. Samples were irradiated to 10 dpa using 2 MeV protons at 360°C at Michigan Ion Beam Laboratory (MIBL). PIA was performed in a vacuum furnace at temperatures 500-600°C and CERT test was conducted in BWR NWC water. IASCC susceptibility was significantly mitigated after PIA at 500°C for 1h and fully removed after PIA at 500°C for 15h or 550°C for 1h. PIA appeared to not only reduce the number density of cracks but also the ability of cracks to propagate (average crack length). PIA mitigated the degree of localized deformation in dislocation channels. The fraction of large dislocation channels dramatically dropped in the PIA samples that showed resistance to IASCC.

Support for this research was provided by the Electric Power Research Institute (EPRI) through contract EP-P39425/C17515.



Comparison of cracking susceptibility of CP304, as-irradiated (360°C:10dpa) and after PIA at different conditions, in simulated BWR NWC environment after 10% plastic strain.

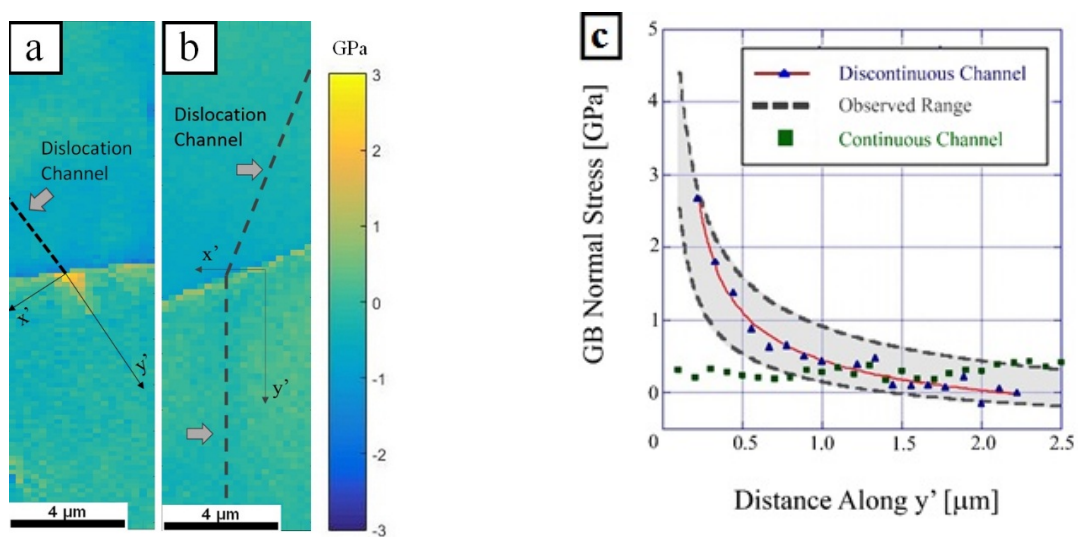
LOCALIZED DEFORMATION AND INTERGRANULAR FRACTURE OF IRRADIATED ALLOYS UNDER EXTREME ENVIRONMENTAL CONDITIONS

D.C. Johnson[1], G.S. Was[1], B. Kuhr[2], D. Farkas[2], R. Mo[3], I.M. Robertson[3]
[1]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[2]Department of Materials Science and Engineering, Virginia Tech University
[3]Department of Materials Science and Engineering, University of Wisconsin

The project is a collaboration between the University of Michigan, University of Wisconsin, and Virginia Tech University with the purpose of determining the role of localized deformation in austenitic steel during irradiation assisted stress corrosion cracking (IASCC). Samples are being irradiated at the University of Michigan and strained in constant extension rate tensile (CERT) tests to study the cracking behavior. Atomistic models of the experiments are being developed by Dr. Farkas' group at Virginia Tech University, and irradiated samples will be strained in-situ in a TEM by Dr. Robertson's group at the University of Wisconsin.

This year, a set of samples was been irradiated using 2 MeV protons in the Tandem Accelerator located in the Michigan Ion Beam Laboratory. Tensile samples from this irradiation will be used to quantify the stress component normal to grain boundaries at discontinuous dislocation channel – grain boundary interaction sites, which will be related to cracking. Samples will be strained in high temperature argon (288°C) to produce many dislocation channels. These channels are either arrested at the grain boundary or transmit into the adjacent grain. In both cases, residual elastic stress values will be calculated using High Resolution Electron Backscatter Diffraction. The component of stress normal to the grain boundary at these interaction sites will be determined and compared between the two types of interactions. Once stress has been characterized, the samples will be strained in water, and cracking behavior will be characterized, with respect to the known stress levels in the dislocation channel/grain boundary intersections.

This research has been supported by the Basic Energy Science office of the U.S. Department of Energy under grant DE-FG02-08ER46525.



Stress profile near a discontinuous channel (a) and near a continuous channel (b). GB normal stress has been plotted as a function of distance from the GB in both cases (c)

A STUDY ON IRRADIATION HARDENING OF HIGHLY IRRADIATED RPV STEELS USING PROTON IRRADIATION

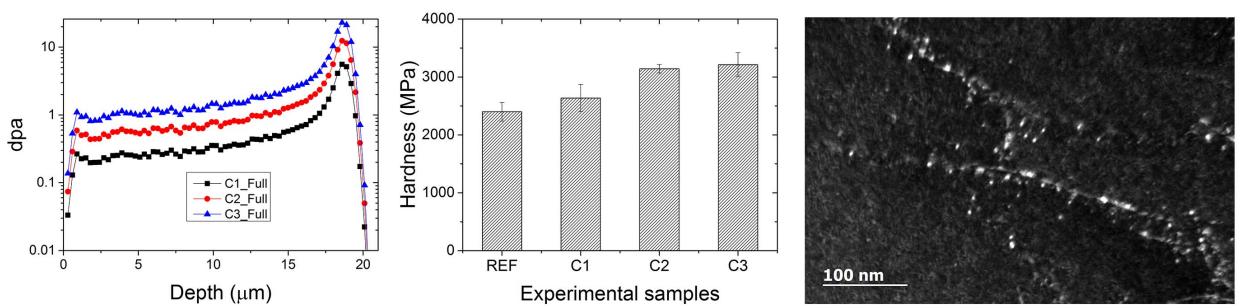
H-.H. Jin, E.S. Ko, S. Y. Lim, J.H. Kwon
Nuclear Materials Safety Research Division, Korea Atomic Energy Research Institute

A key research has been launched to understand radiation-induced hardening and embrittlement of reactor pressure vessel (RPV) steels. The materials investigated in this research are commercial RPV steels used for Korean nuclear reactors. Proton irradiation was performed using the 3 MV Pelletron accelerator at the Michigan Ion Beam Laboratory of the University of Michigan. The energy of the protons used for irradiation was 2 MeV. The irradiation temperature was set to 300 °C ± 10 °C. Before proton irradiation, the surfaces of the specimens were mechanically wet-polished using SiC sandpaper (No. 400–No. 2400) and diamond suspensions. Fine polishing was conducted using colloidal silica to reduce surface damage.

We prepared proton-irradiated RPV steel samples with different radiation doses, approximately 2 x 10^{18} (C1), 4.5 x 10^{18} (C2) and 8.3 x 10^{18} (C3) p/cm^2. The radiation damages in displacement per atom (dpa) of the two samples were calculated with the Stopping and Range of Ions in Matter (SRIM) 2008 program using displacement energy of 40 eV in 'full cascade' mode. The level of radiation damage was calculated to be only half of these values if the 'quick calculation' mode is used.

Micro-hardness measurements were conducted for each proton irradiated RPV sample with nano indenter system (CSM, NHT2). It is clearly shown that the micro-hardness value increases with proton irradiation doses. Currently, we have been performing micropillar compression tests for the evaluation of the yield strength of the proton irradiated samples. In parallel, we have been conducting analytical TEM analysis and 3D-APT analysis for the characterization of irradiation induced defects, clusters and precipitates to reveal primary sources for the significant hardening developed after proton irradiation.

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2012M2A8A4025886).



SRIM calculation result (left) and micro hardness results (center) of proton irradiated samples.
Dark field TEM image showing irradiation induced defects formed around dislocation in the C3 sample (right).

PERFORMANCE EVALUATION OF Fe-Cr-Al ALLOY SURFACE COATING ON ZIRCALOY 2 IN HIGH TEMPERATURE STEAM AND BWR-NWC SIMULATED ENVIRONMENT WITH AND WITHOUT IRRADIATION DAMAGE

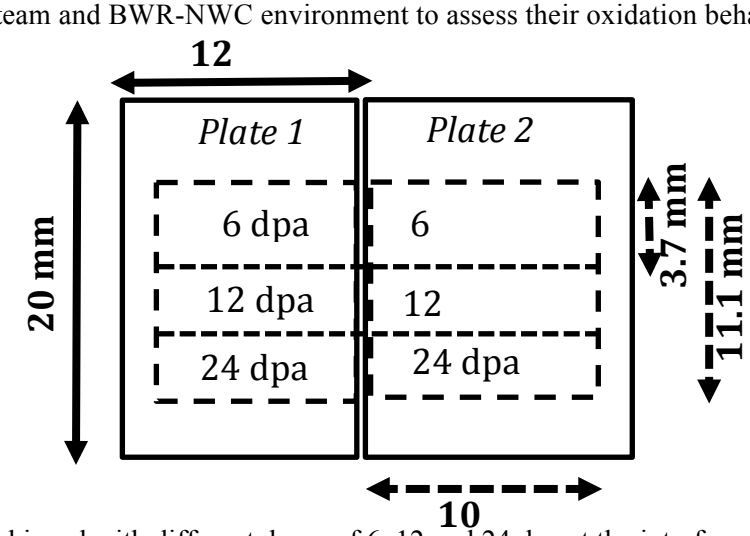
G. S. Was, K. K. Mandapaka
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

As a consequence of 2011 Fukushima Dai-ichi accident, the thrust in the nuclear industry is to develop advanced accident tolerant fuel (ATF) clad materials. An ATF clad material is expected to have enhanced oxidation resistance as compared to zirconium alloys in accident conditions, while performing satisfactorily in normal reactor operating conditions. Worldwide, there have been two different approaches; (a) development of new oxidation resistant alloys, and (b) application of surface coatings over the existing Zr-alloy cladding. The objective of this project is to develop iron-chromium-aluminum (Fe-Cr-Al) surface coatings over Zircaloy-2 and evaluate their performance in high temperature steam as well as in boiling water reactor (BWR) normal water chemistry (NWC) environment. In this context, Fe-Cr-Al coatings of different compositions were deposited over Zircaloy-2 by magnetron sputtering technique. The coatings were approximately 1.3 mm thick. The aim was to evaluate the coating performance before and after irradiation. Irradiation of the coated surfaces was carried out in the Michigan Ion Beam Laboratory (MIBL). Two types of irradiation experiments were conducted; (a) irradiation with 1 MeV protons at a temperature of 360 °C, and (b) irradiation with 8.5 MeV Fe^{3+} ions at 360 °C.

The proton irradiation was carried out to achieve a damage of 6 dpa at the interface of Fe-Cr-Al coating and Zircaloy-2 plate. The temperature and vacuum pressure were stable through the experiment. A beam current of ~25 mA was achieved and was stable during the experiment.

The irradiation with 8.5 MeV Fe^{3+} ions was aimed at achieving three different doses in three regions of the coated Zircaloy-2 plate. A stage current of ~200 nA was achieved and temperature was stable. The irradiation was performed in three stages with suitable opening of apertures so as to achieve a cumulative dose of 24 dpa at the bottom one-third, 6 dpa at the top one third and 12 dpa in the middle. This resulted in plate samples of 10 mm x 3.7 mm region irradiated to 6, 12 and 24 dpa each as shown in the figure below.

These irradiated Fe-Cr-Al coated Zircaloy-2 plates, along with unirradiated samples, will be exposed to high temperature steam and BWR-NWC environment to assess their oxidation behaviour.



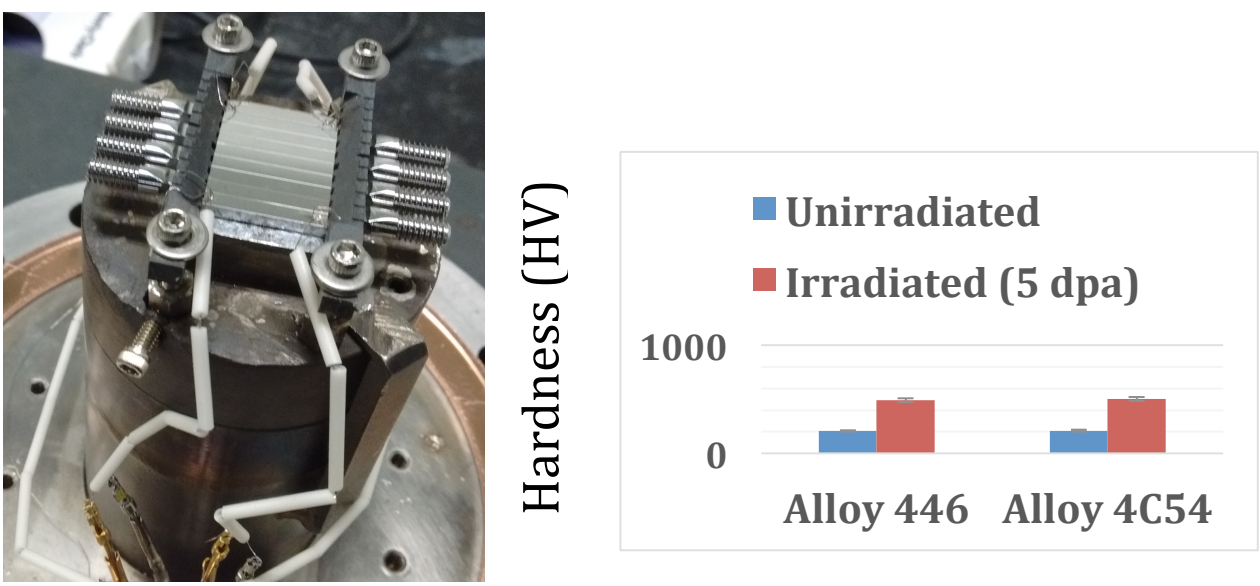
Irradiated zones achieved with different doses of 6, 12 and 24 dpa at the interface of FeCrAl coating and Zircaloy-2 using 8.5 MeV Fe^{3+} ions at 360 °C.

IRRADIATION ASSISTED STRESS CORROSION CRACKING (IASCC) AND HIGH TEMPERATURE OXIDATION BEHAVIOR OF ALLOY 446 AND ALLOY 4C54

G.S. Was, K.K. Mandapaka
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

The research work carried out in this project is a part of a project aimed at development of advanced alloys for accident tolerant fuel (ATF) clad application. In this context, three different alloys; alloy 33, alloy T91 and APMT were studied in previous years. The IASCC behavior and oxidation performance was demonstrated to be best in the case of APMT alloy. In continuation of this project, a number of new candidate alloys are being investigated for ATF clad application. Two alloys currently being studied for this purpose are alloy 446 and alloy 4C54. Both of these alloys are ferritic and have high amount of Cr (~ 25 %). A systematic investigation has been initiated to assess their IASCC and oxidation behavior in boiling water reactor (BWR) normal water chemistry (NWC) environment at the University of Michigan.

Both alloys 446 and 4C54 were subjected to irradiation using 2 MeV protons at a temperature of 360 °C. A total area of 18 mm x 10 mm was irradiated, which included two tensile specimens of each alloy, three TEM bars of alloy 446 and 2 TEM bars of alloy 4C54. The arrangement of specimens on the irradiation stage is presented in the figure on the left. A total dose of 5 dpa was achieved through the irradiation. A stable beam current of ~ 32 mA was achieved on the stage. The temperature and pressure throughout the irradiation experiment remained stable. A considerable hardening was observed on both the alloys as a result of irradiation up to 5 dpa. The irradiation hardening as measured on irradiated TEM bars is presented in the figure to the right. The irradiated tensile specimens of both alloys will be subjected to stress corrosion cracking (SCC) tests in BWR-NWC simulated environment. TEM bars will be used for microstructural investigation.



Irradiation stage with tensile specimens and TEM bars of alloy 446 and 4C54 (a), hardness values for both alloys before and after irradiation (b).

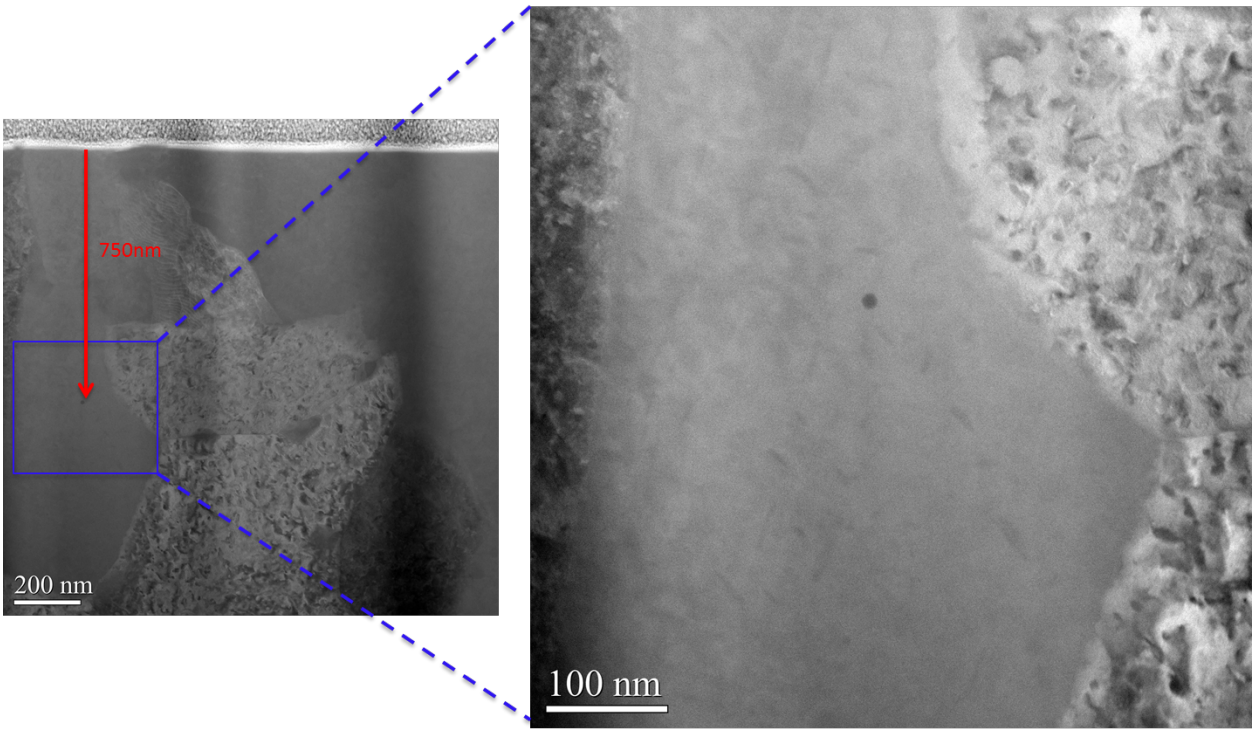
ACCELERATED IRRADIATIONS FOR EMULATION OF HIGH-DOSE MICROSTRUCTURE IN FERRITIC-MARTENSITIC STEELS

A.M. Monterrosa, Z. Jiao, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

The new generation of faster reactors is seeking to push damage levels in structural materials to very high doses, in excess of 500 dpa. Using fast reactors to irradiate materials to such high doses is prohibitively expensive and time-consuming. This project will study how effectively self-ion irradiations can be used to emulate microstructural features (voids and precipitates) seen in neutron-irradiated HT9 and other ferritic-martensitic (F-M) steels.

Self-ion irradiation experiments have been performed on ferritic-martensitic alloys T91, HT9, and 14YWT to determine swelling behavior at 420°C, at doses of 40 and 80 dpa with up to 10 atomic parts per million (appm) helium implanted. The irradiations were performed using the 3MV Wolverine accelerator at the Michigan Ion Beam Laboratory. The effects of dose on void swelling were analyzed using a transmission electron microscope in scanning mode (STEM). At these doses, no voids were observed in the analysis area of 500-700nm. However, voids were observed in regions just beyond the analysis area (deeper than 700nm). This suggests that higher doses will result in the presence of voids in the valid swelling region. Future work will include irradiations of T91 at 420°C in an effort to compare ion irradiation results to neutron irradiated results

This work is supported by DOE NEUP award DE-AC07-05ID14517.



Voids observed just beyond the analysis region in HT9 irradiated at 420 ºC:80 dpa:10He.

PROTON IRRADIATION UNDER AN APPLIED STRESS TO STUDY THE COUPLING BETWEEN IRRADIATION CREEP AND ACCELERATED GROWTH IN Zr ALLOYS

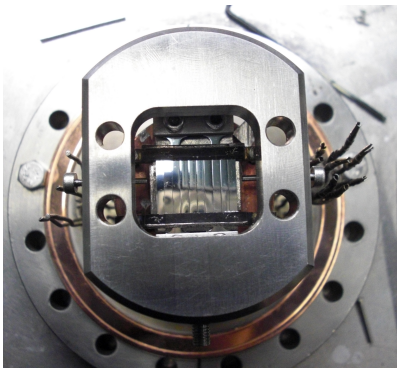
F. Onimus[1], O. Toader[2], N. Gharbi[1], D. Gilbon[1], J.-P. Mardon[3]
[1]CEA–DEN, Section for Applied Metallurgy Research, 91191 Gif-sur-Yvette, Cedex, France
[2]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[3]AREVA NP SAS Fuel Business Unit 10, Rue Juliette Recamier 69456, Lyon Cedex 06, France

Recrystallized zirconium alloys are used as cladding and structural components materials for the Pressurized Water Reactor (PWR) fuel assemblies. Under neutron irradiation, they undergo deformation and especially irradiation growth which takes place in the absence of any applied stress. This phenomenon, referred as "stress-free" growth, accelerates for high irradiation doses. The breakaway growth is correlated to the formation of a specific irradiation defect: the c-component dislocation loops.

Some industrial feedbacks on the in-service behavior of PWR fuel assemblies suggest that a coupling between axial irradiation-induced creep and irradiation growth could exist. Since these two phenomena have significant impact on fuel assembly performance, a possible interaction between them should be taken into consideration to design it properly.

The aim of the present work is to investigate the impact of a macroscopic stress, applied under irradiation, on the evolution of c-loop microstructure and, therefore, on the resultant "stress-free" growth deformation.

This year, 2 MeV proton irradiations were performed in March 2015 up to 8 dpa and in July 2015 up to 5 dpa at 350°C on the same M5 samples, therefore reaching a final dose of 13 dpa. Two tensile test samples were added to the usual 8 TEM bars. The first irradiation was performed using the usual procedure without any applied stress. At this irradiation dose, c-component loops are known to have nucleated in the material. For the second irradiation step, a device especially designed for this experiment was used to apply a tensile stress on the two tensile test samples. Thanks to this procedure the influence of the stress on the growth of the c-component loops can be studied. The specimens were heated up to 250°C and a tensile test was applied out of the chamber. Then the holder was installed and the irradiation started with a careful monitoring and control of the temperature on the surface of the samples. The final dose of 13 dpa was successfully achieved and the samples were dismounted. No problem was detected after irradiation. Especially we noticed that the stress was clearly still applied on the tensile test samples.



Original device designed by the CEA team in order to apply stress on two samples during proton irradiations at the MIBL.

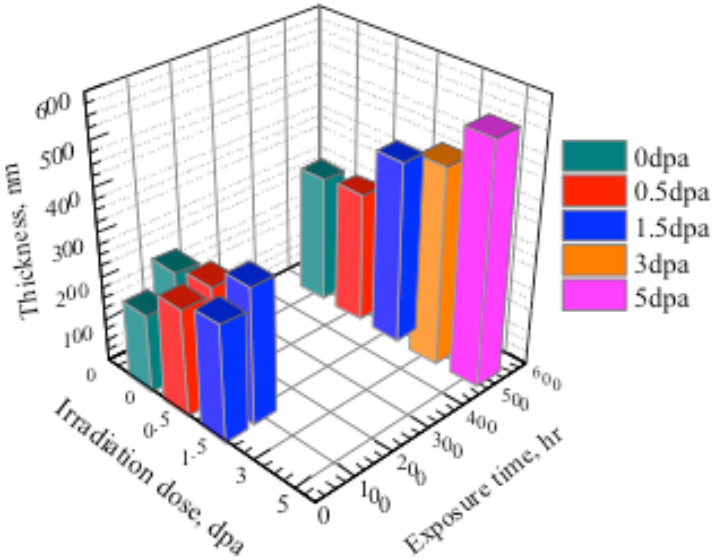
IRRADIATION ASSISTED CORROSION AND STRESS CORROSION CRACKING OF NUCLEAR GRADE STAINLESS STEELS

Q.J. Peng[1], P. Deng[1], E-H. Han[1], C. Sun[2], Y.K. Bai[2]
[1] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
[2] State Nuclear Power Research Institute, Beijing 102209, China

In recent years, environmental degradation of materials in nuclear power plants has been investigated extensively in China. However, due to the capacity limitation of the experiment facilities, there is still a lack of the investigation of the environmental degradation of core structural materials under the synergic effect among irradiation, high temperature water corrosion and stress. By utilizing the advanced ion beam research facilities of Michigan Ion Beam Laboratory, this program investigates the irradiation assisted corrosion and stress corrosion cracking of domestically-fabricated nuclear grade stainless steels, with main focuses on: 1) Irradiation assisted corrosion of 304 stainless steel in simulated primary water; 2) Irradiation assisted stress corrosion cracking of 304 stainless steel in simulated primary water; 3) Effect of annealing on irradiated microstructure and property of 308 stainless steel. Through these research works, it is expected to provide proofs for the validity of domestically-fabricated nuclear grade stainless steels for the fabrication of core structures.

Three proton irradiation experiments were conducted to doses of 1, 3 and 5 dpa at 360°C at MIBL during 2015 and the corrosion and SCC experiments are currently being conducted at the Institute of Metal Research in China.

This work is supported by the International S&T Cooperation Program of China under grant 2014DFA50800.



Thickness of the oxide scale on 304SS as a function of irradiation dose and exposure period. The exposure experiments were conducted in simulated primary water at 320°C. Surface of the bar before the exposure was polished using 40nm-colloidal silica slurry. The thickness of the oxide scale was assessed by the half-height of O in the depth profile obtained by XPS analysis.

IRRADIATION ACCELERATED CORROSION OF 316L STAINLESS STEEL

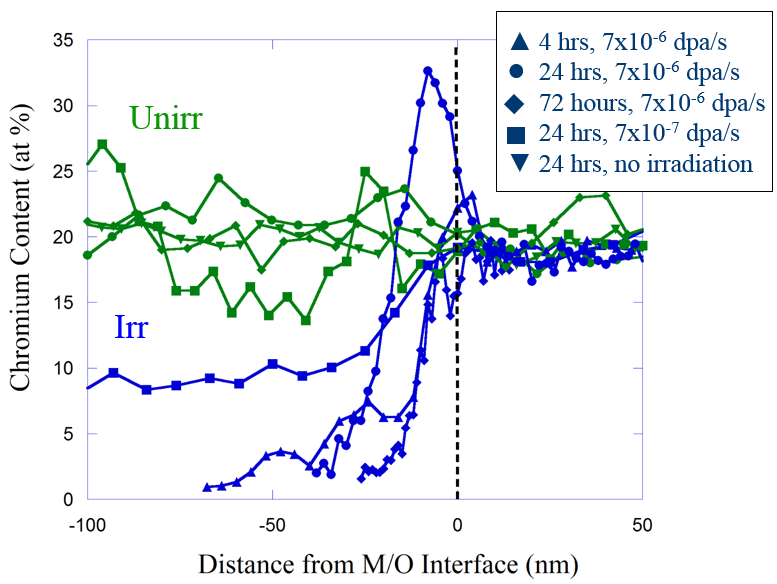
S. S. Raiman, G. S. Was,
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Corrosion of stainless steel components is an important factor in environmentally assisted cracking in nuclear reactor core components. Several factors can affect the rate of corrosion of stainless steel core components, and radiation is among the least understood. Previous works have found that radiation can significantly accelerate the corrosion rate of stainless steel in high temperature water.

A 3.2-MeV proton beam was used to irradiate 316L stainless steel samples while they were simultaneously exposed to simulated PWR conditions to examine the effect of radiation on corrosion. The proton beam was transmitted through the 37 µm thick sample which served as a "window" into a corrosion cell containing flowing 320˚C water with 3 wppm H_2.

Irradiation was found to have several effects on the morphology and composition of the oxide film. Among them, irradiated oxides were found to be depleted in chromium when compared to unirradiated oxides. The graph below shows chromium profiles across the metal-oxide interface of irradiated oxides, and a large decrease in chromium can be seen in the irradiated specimens.

This research is supported by the U.S. DOE and EDF.



STEM-EDS chromium profiles taken across the metal-oxide interface of irradiated and unirradiated areas of samples irradiated for 4, 24, and 72 hr at damage rates of 7 x 10^{-6} or 7 x 10^{-7} dpa/s in 320˚C water with 3 wppm hydrogen. A sample exposed to the same conditions for 24 hrs with no irradiation is also shown.

MICROSTRUCTURE EVOLUTION OF NICKEL BASE ALLOY SUBJECTED TO PROTON IRRADIATION

M. Song, M. Wang, G. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

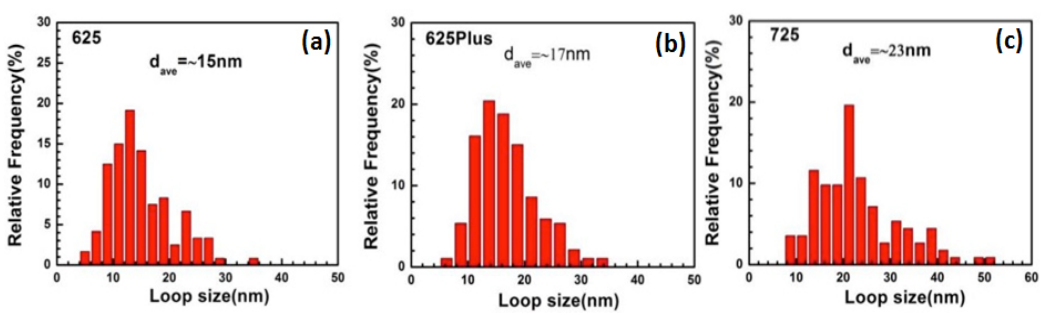
The life extension of current existing reactors and design of next generation nuclear reactors require advanced materials that can maintain structural integrity in harsh radiation environments. However, most in-core structures were built with austenitic stainless steels, which are susceptible to degradation at a relative early time during service. Thus, replacement components may become a necessity. The Advanced Radiation Resistant Materials (ARRM) project is aimed at identifying promising candidate alloys that can replace austenitic stainless steels, which suffer from serious irradiation-assisted stress corrosion cracking in light water reactors environments. Thus, reactors can operate with better efficiency and lower costs of maintenance and repair.

Several nickel base alloys are irradiated by proton to 5 dpa at 360°C as listed in the table. Dislocation loops were observed in all these alloys. Smallest loops are observed in alloy 625. The loops with larger size are observed in alloy 725. The loop density is on the order of $10^{22}/cm^3$. Alloy 625 and alloy 625Plus have a similar density of dislocation loops and both of which is higher than alloy 725. The loop size is believed to be determined by the stacking fault energy. Lower stacking fault energy encourages the formation of larger loop due to the larger separation distance between the partial dislocations. More characterization work will be completed in future.

The ARRM project is supported by EPRI (contracts 10002164 and 10002154) and DOE (contract 4000136101).

Proton irradiations completed at MIBL

Materials	Dose	Temperature (°C)
Alloy 625	5 dpa	360
Alloy 625Plus	4.15 dpa	360
Alloy 725	5 dpa	360



Statistical study of the dislocation loops in (a) alloy 625 (b) alloy 625 Plus and (c) alloy 725. The largest loop size occurs in alloy 725. These alloys are irradiated at at 360°C to about 5 dpa by proton.

MICROSTRUCTURE RESPONSE OF THERMO-MECHANICALLY TREATED ALLOY 718 IRRADIATED BY PROTON

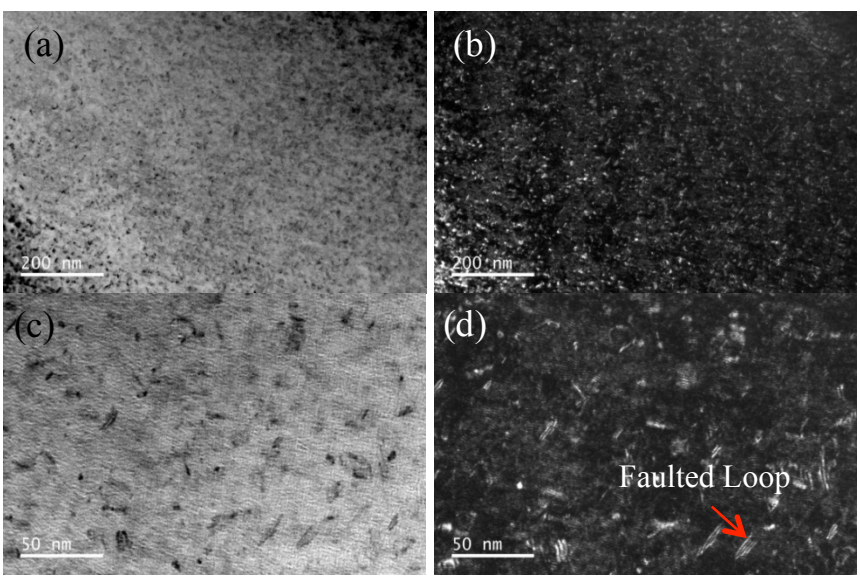
M. Song[1], M. Wang[1], G. Was[1], C.Silva[2], J. Busby[2]
[1]Department of Nuclear Engineering and Radiological Sciences, University of Michigan
[2]Materials Science and Technology Division, Oak Range National Laboratory

Alloy 718 is a precipitation-hardened nickel-based super-alloy which derives its strength from nano-sized γ' and γ'' precipitate, even at elevated temperatures. It has been widely applied in the aerospace industry and nuclear power plants especially pressurized water reactors (PWRs). In PWRs, the components made of alloy 718 include hold-down springs and fasteners. However, the traditional heat treatment procedures for high creep strength application may not be optimized for application in PWRs, which is in the intermediate temperature range with corrosion and irradiation environment. A sub-optimal treatment or processing can lead to assembly failure and fuel failures.

In this project, a wide range of alloy 718 subjected to different thermo-mechanical treatments (TMT) was examined to optimize the condition for various application in PWRs. Proton irradiation up to 4 dpa was performed in selected conditions. A comprehensive characterization is desired for the microstructure response of those TMT processed 718 alloys.

The figure shows black dot damage following irradiation to 0.05 dpa, which become white contrast under the dark field condition (part b). A closer examination was carried out at higher magnification in (c) and (d). Faulted loops were observed in this alloy in the dark field image (d). These loops are around 30 nm in size. Further characterization work will be done in future.

This work is supported by Electric Power Research Institute (EPRI).



TEM images of alloy 718 subjected to proton irradation at 360°C to 0.05dpa. This alloy is heat treated at 1093°C for 1h, and double aged at 718°C and 621°C for 8 h.

HELIUM BUBBLE EVOLUTION IN A Zr-Sn-Nb-Fe-Cr ALLOY DURING POST ANNEALING: AN In-Situ INVESTIGATION

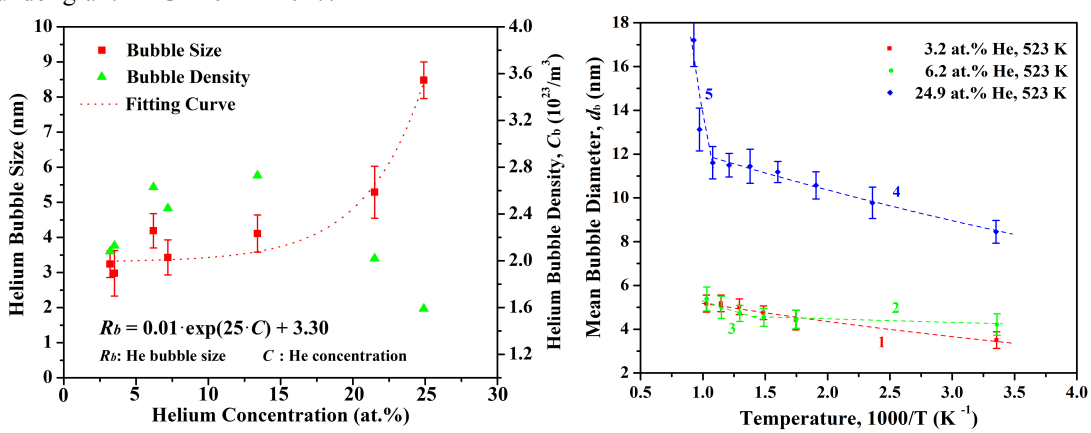
H. H. Shen[a,b], K. Sun[a] and X. T. Zu[b]
[a] Department of Materials Science and Engineering, University of Michigan
[b] School of Physical Electronics, University of Electronic Science and Technology of China

Zirconium and its alloys have been chosen as the fuel cladding, pressurize pipe and structure materials in the nuclear reactor primarily for their very low thermal neutron absorption cross section, good mechanical property and corrosion resistance. The formation of helium bubbles is considered to be detrimental to the mechanical performance of Zr alloys. This work focuses on the growth behaviors of helium bubbles in a helium ion implanted Zr-Sn-Nb-Fe-Cr alloy with respect to the helium fluence and subsequently annealing procedure were investigated by *in-situ* transmission electron microscopy study.

Helium implantation was conducted at the Michigan Ion Beam Laboratory at the University of Michigan. The implantations were performed at the energy of 400 keV. The irradiation temperature was kept at 523 K, and the helium fluence was 0.5×10^{17} He^+/cm^2, 1.0×10^{17} He^+/cm^2 and 5.0×10^{17} He^+/cm^2 resulting in a helium concentration of 3.2%, 6.2% and 24.9% at the projected depth of 1120 nm. The TEM sample of Zr-Sn-Nb alloy used in this investigation was prepared by an advanced FIB Lift-out method working in a Helios 650 Nanolab workstation.

In the as-implanted sample, the measured size distributions of the helium bubbles are consistent with the simulated helium concentrations. Moreover, the average size of the helium bubbles increases with the increase of the helium concentration obeying an exponential relationship. Alternatively, the He bubble concentration increases with the increase of the He concentration from $2.08 \times 10^{23}/m^3$ for 3.2 at.% He to $2.73 \times 10^{23}/m^3$ for 13.4 at.% He, and decreases to $1.59 \times 10^{23}/m^3$ for 24.9 at.% afterwards. The decrease of He bubble concentration with He concentration is mainly attributed to the coalescence of smaller He bubbles. The *in-situ* heating study performed in a transmission electron microscope indicates that the mean size of the helium bubbles increase slowly below 923 K and dramatically above 923 K. The coarsening of the He bubbles in the alloy obeys the migration and coalescence mechanism.

This work is supported by the Fundamental Research Funds for the Central Universities of Ministry of Education of China under grant ZYGX2012YB017.



The average helium bubble size and bubble density of the specimens changing with the helium concentration at the projected depth (left). Temperature dependencies of mean bubble size for specimens with different helium concentration (right).

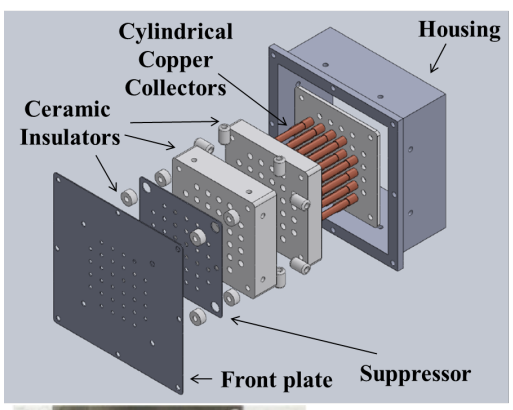
A MULTI-PINHOLE FARADAY CUP DEVICE FOR MEASUREMENT OF DISCRETE CHARGE DISTRIBUTIONS OF HEAVY AND LIGHT IONS

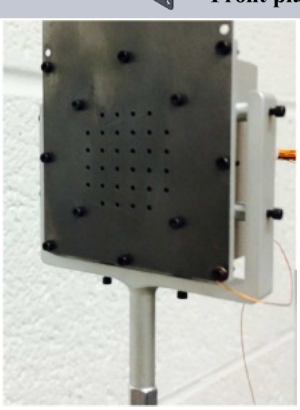
P.K. Roy[1], S. Taller[2], O. Toader[2], F. Naab[2], S. Dawarknath[2], G.S. Was[2]
[1]Los Alamos National Laboratory
[2]Department of Nuclear Engineering & Radiological Sciences, University of Michigan

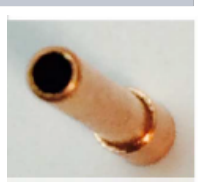
Nuclear reactor lifetimes are limited by materials degradation from radiation damage and other environmental factors. Heavy ion irradiations have been successful in emulating microsctructural features of materials in reactor. The measurement of uniformity of the heavy ion distribution over the material specimens is necessary to quantify the dose of these experiments. To provide a better description of the beam charge density profile, a multi-pinhole Faraday cup (MPFC) was designed, fabricated and tested for the Michigan Ion Beam Laboratory (MIBL) under relevant ion beam conditions.

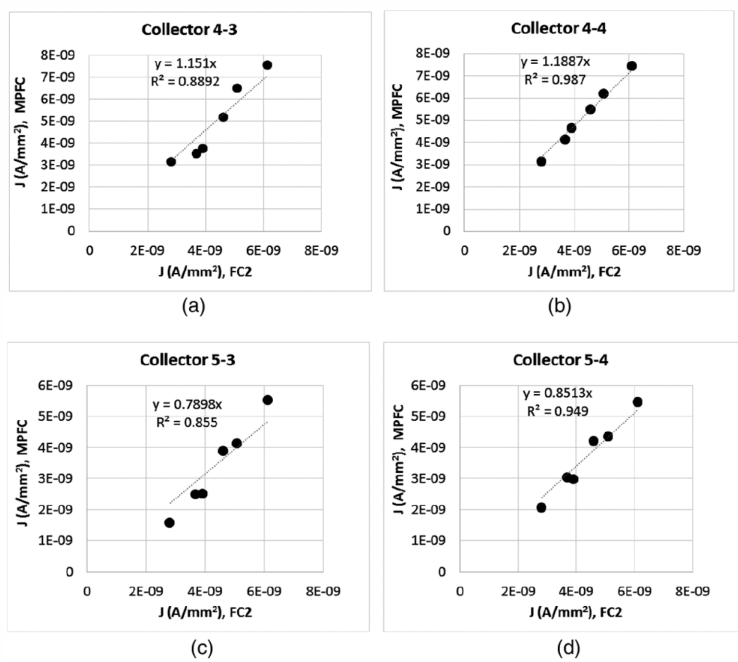
The MPFC consists of a grounded front tantalum plate, a negatively biased tantalum suppressor plate, and 32 copper pin collectors in a 4mm x 4mm center-to-center array with 1mm hole diameter opening. Tantalum was selected for the plates because of its ability to withstand heat dissipation from the ion beam, its low sputter yield, and its high melting temperature. The collector cups have been designed with a length of 1.96cm and an inner diameter of 0.25cm. This high aspect ratio provides effective geometric suppression of secondary electrons. The MPFC was connected to a data collection system consisting of a multiplexer, picoammeter for current collection, and digital control system designed in National Instruments LabVIEW 2013.

When placed in a diagnostic section at the downstream end of a beam line, the MPFC device collectors in the beam area responded in a linear manner to variation in the total ion beam current. The measurements correlate with the current density of traditional suppressed Faraday cups. The MPFC is able to detect a raster scanned ion beam and a defocused ion beam. Initial results provide confidence that the collectors are able to sample charged particle distributions in a discrete form within a given geometrical resolution.









An expanded schematic of the MPFC (top left), with the physical device fully assembled and a single collector shown (bottom left). The current densities measured by the MPFC are comparable to a traditional suppressed Faraday cup (above, right) for four collectors.

RADIATION RESISTANCE OF NOVEL ODS ALLOY

S. Teysseyre
Idaho National Laboratory

This project aims to develop advanced materials with improved radiation performance by tuning the chemical composition of the nanoclusters of an Oxide Dispersion Strengthened (ODS) ferritic alloy. The steel class chosen for this project (ODS) is already considered for advanced reactors (Generation IV reactor designs, fast and fusion reactors) and as a future material for current light water reactor designs (ARRM program).

A novel Oxide Dispersion Strengthened (ODS) ferritic alloy was developed at the Center of Advanced Energy Studies (CAES). Preliminary results suggest that the path chosen also provides the benefit of a significant improvement in the mechanical performance for the class of material considered. In order to confirm that this material is a promising candidate for nuclear application, it is necessary to prove that these oxide particles remain stable under irradiation.

Nine heats of material were created at CAES using spark plasma sintering. The composition include reference alloys ODS ($Fe/Cr/Al/Y_2O_3$ and $Fe/Cr/Mo/Y_2O_3$) and those alloys with two types of additives ($Fe/Cr/Al/Y_2O_3/YSZ$, $Fe/Cr/Al/Y_2O_3/Ti$, $Fe/Cr/Al/Y_2O_3/Ti/YSZ$, $Fe/Cr/Mo/Y_2O_3/YSZ$, $Fe/Cr/Mo/Y_2O_3/Ti$, $Fe/Cr/Mo/Y_2O_3/Ti/YSZ$). Specimens from six heats were irradiated at the Michigan Ion beam Laboratory with 5MeV iron ion to about 100 dpa at a temperature of ~400ºC. The specimens were sent to CAES where the irradiated microstructure will be characterized.

This irradiation was supported by the Nuclear Science User Facilities.

AN INVESTIGATION INTO THE MICROSTRUCTURAL EVOLUTION OF BINARY ZIRCONIUM ALLOYS WHEN SUBJECTED TO PROTON-IRRADIATION

M. Topping, M. Preuss
University of Manchester, England

Zirconium (Zr) alloys are widely used in light water reactors for nuclear fuel assemblies and structural components. The safe operation of these assemblies requires dimensional stability to ensure that both sufficient coolant flow is provided to the fuel rods and that the control rods can be inserted as and when required. However during their operational lifetime these fuel rods are prone to dimensional changes, which can lead to bowing and buckling. This phenomenon is known as irradiation induced growth (IIG).

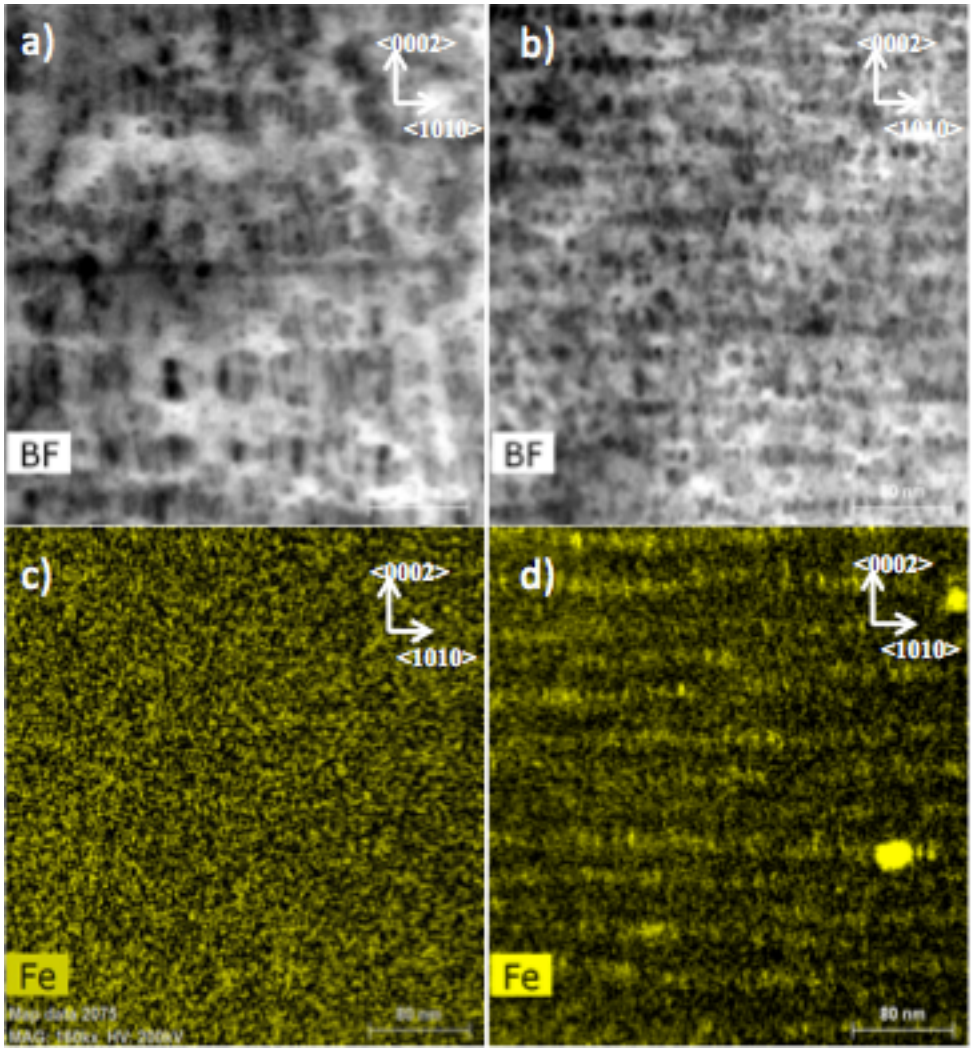
The main cause of IIG is believed to be dislocation loops that form during irradiation. There are two main types of dislocation loop formed, <a>-loop and <c>-loop dislocations. <a>-loop dislocations form on prismatic planes and have been found to form at low doses, whereas <c>-loops form on the basal plane of the hexagonal close packed (hcp) crystal structure and are only seen at higher doses. It is believed that the <a>-loops are responsible for the initial growth and that the <c>-loops are responsible for the delayed breakaway growth.

Experimental binary alloys have been made by Westinghouse to investigate the effect of a single alloying element had on the evolution of dislocation loops during irradiation. Iron (Fe) is present in all commercial Zr alloys so binary Zr-0.1Fe, Zr-0.6Fe and Zr-0.8Fe alloys were irradiated. Niobium (Nb) is also an interesting alloying element as commercial alloys containing Nb have exhibited lower levels of IIG. All these alloys were proton-irradiated to 3 and 5dpa. Previous irradiations carried out at MIBL has yielded a large test matrix of dpa levels (0.2 – 5dpa) are available for study.

Scanning Transmission Electron Microscopy (STEM) studies have been carried out using an G2 80-200Kv spherical aberration-corrected FEI Titan microscope. This microscope is fitted with the FEI ChemiSTEM^{TM} system. This is comprised of four windowless energy dispersive spectroscopy (EDS) detectors in close proximity to the sample. The ChemiSTEM^{TM} coupled with the aberration corrector allows for high resolution spectral imaging.

An example of how the irradiations carried out at MIBL have helped with the understanding of how Fe effects dislocations can be seen in the figure that depicts the comparrision of <a>-loops in Zr-0.1Fe and Zircaloy-2 (5 and 4.7dpa respectively) in a BF-STEM image. The difference in size and ordering of these loops has been attributed to Fe segregation seen in Zircaloy-2. This shows that Fe segregation leads to smaller, more ordered <a>-loops. There is more Fe available in the matrix in the irradiated Zircaloy-2 sample as secondary phase particles are dissolving due to the irradiation damage.

To investigate these ideas further a proposal for time at the Diamond Light Source Synchrotron Facility at the start of 2016. Measurement of diffraction patterns with a high enough quality for particle size, volume fraction and anisotropic x-ray line broadening analysis, excellent angular resolution and low background, is achievable using a high-resolution powder diffraction beamline and a multi-analysing crystal detector. For reliable analysis of dislocation loops, we aim to record over a wide enough range of the diffraction spectrum to include higher order peaks such as the (0004) and (0006) reflections.



All images taken at 11-20 zone axis depicting <a>-loops. a) BF-STEM image of 5dpa Zr-0.1Fe. b) BF-STEM image of 4.7dpa Zircaloy-2. c) Fe map of Figure1a [noise]. d) Fe map of Figure1b.

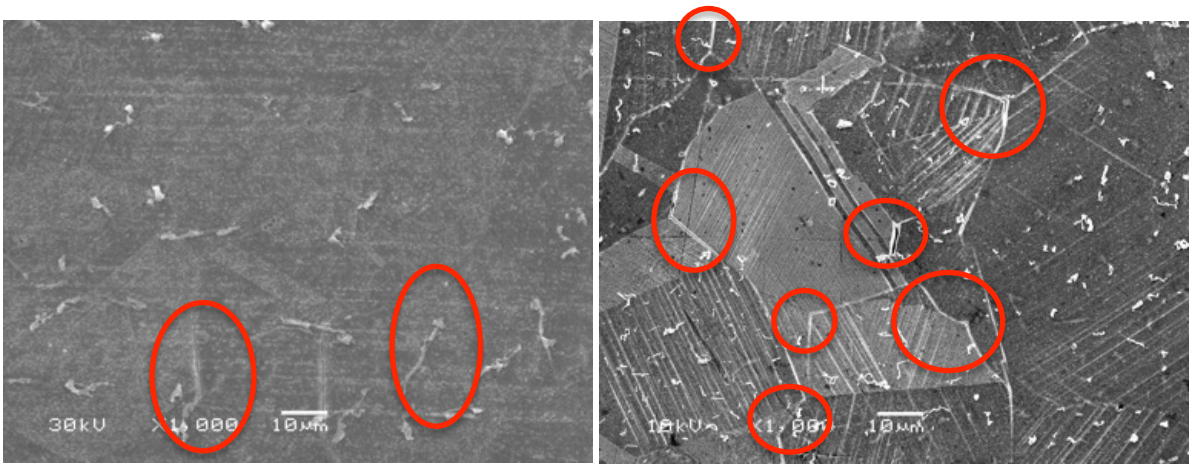
IRRADIATION ASSISTED STRESS CORROSION CRACKING BEHAVIOR EVALUATION OF NICKEL BASE ALLOYS IN LIGHT WATER REACTORS (LWRS) ENVIRONMENT

M. Wang, M. Song, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

This project focusing on evaluating the Irradiation Assisted Stress Corrosion Cracking (IASCC) behavior of thirteen candidate alloys in light water reactor environments, including four nickel base alloys (Alloy 625, Alloy 625Plus, Alloy 725, Alloy 625DA). Nickel base alloys usually have exhibited good resistance to corrosion and SCC, however, no data exists on their susceptibility to IASCC.

Four tensile and three TEM samples of each alloy were irradiated 2 MeV protons to a dose of 5 dpa at a temperature of 360°C. The tensile samples were used to evaluate IASCC behavior and the TEM ones were used for microstructural characterization. CERT tests were conducted at a strain rate of 1×10^{7} s^{-1} in both PWR (320°C PWR primary water with 1000 ppm B as H_3BO_3, 2 ppm Li as LiOH, and 35 cc/kg H_2) and BWR (288°C simulated BWR normal water chemistry) environments to a fixed strain. Cracking was characterized by the crack density, crack length and crack length per unit area on the irradiated surface.

This research is supported by Department of Energy (DOE) and Electric Power Research Institute (EPRI).



SEM micrographs of alloy 725 strain to about 4% in BWR NWC environment, unirradiated area (left) and irradiated area (right). Cracks are highlighted in red circle.

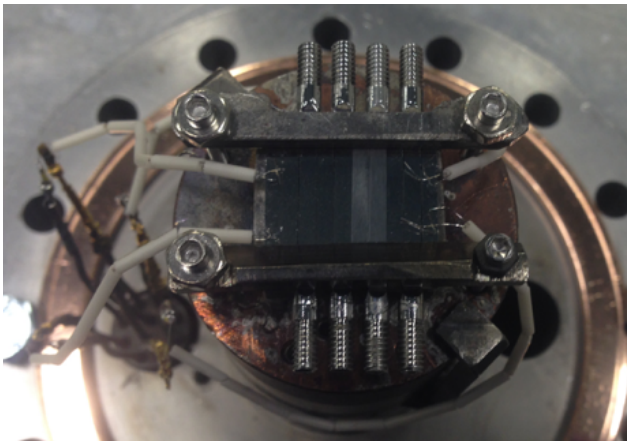
IRRADIATION ASSISTED STRESS CORROSION CRACKING BEHAVIOR STUDY OF ALLOY 718

M. Wang, M. Song, G.S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

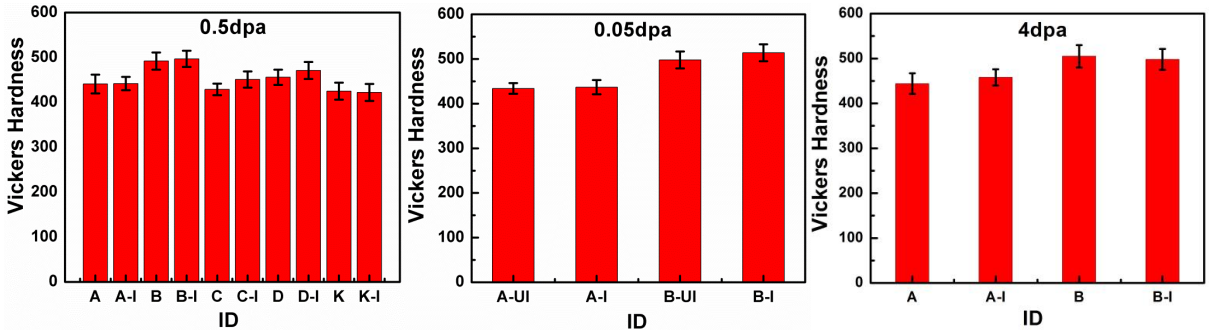
This project focusing on studying the Irradiation Assisted Stress Corrosion Cracking (IASCC) behavior of Alloy 718 in PWR primary environment. Alloy 718 is a nickel-base, precipitate-hardened superalloy is used in PWR fuel assembly components because of its significant strength and resistance to irradiation-induced crack growth and corrosion.

The stress corrosion cracking (SCC) behavior of alloy 718 subject to different thermal mechanical histories was studied in both the irradiated and non-irradiated conditions. Four tensile and three TEM samples were irradiated 2 MeV protons to doses of 0.05 dpa, 0.5 dpa, and 4 dpa at a temperature of 360°C. The tensile samples were used to evaluate IASCC behavior and the TEM ones were used for microstructural characterization.

This research is supported by Electric Power Research Institute (EPRI).



Irradiation stage of alloy 718 (0.05 dpa) prior to irradiation.



Vickers Hardness Measurement pre- and post-irradiation of different doses.

INITIAL TESTS FOR INVESTIGATION OF SHADOW CORROSION ON ZIRCALOY-2 COUPLED WITH INCONEL 718 USING IN-SITU PROTON IRRADIATION-CORROSION EXPERIMENT

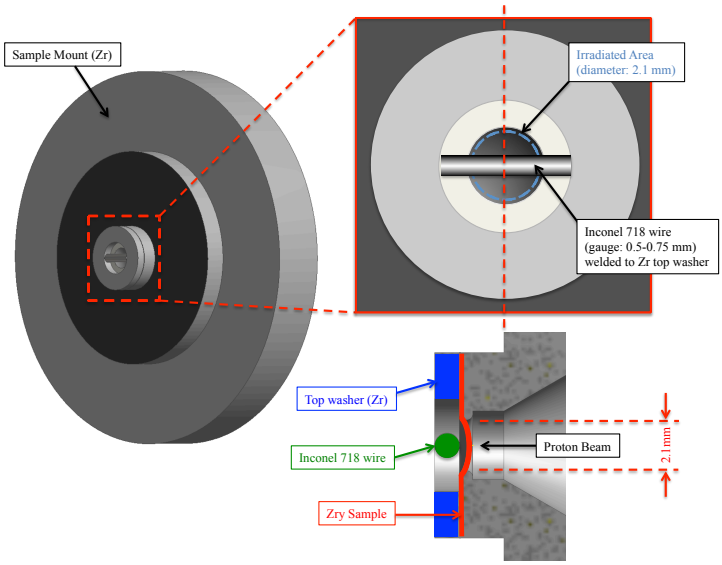
P. Wang
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Shadow corrosion (SC) is a form of accelerated corrosion on Zircaloy components at locations in close proximity to dissimilar metals, such as stainless steels and Inconel. It has been observed only in boiling water reactor (BWR) environments. Many BWRs have experienced shadow corrosion-induced channel bow issues. In order to mitigate these operational issues, the mechanism needs to be understood in detail.

Several mechanisms have been proposed to explain the shadow corrosion mechanisms, and the majority of them are related to electrochemical nature of the Zircaloys. However, shadow corrosion was only observed on reactor exposed samples, this leads to the development of possible mechanisms by which radiation assist the shadow corrosion process, (1) increase the conductivity of the oxide film on Zr alloy, (2) increase the conductivity of the water by creating radiolysis product.

The objective of this experiment is to determine whether in-situ proton irradiation-corrosion experiment can be used as a tool to investigate shadow corrosion effect on Inconel 718 coupled Zircaloy-2 samples. 3.2 MeV proton beam at a current density of 2μA/cm^2 was used to irradiate a 50μm Zr sample at 320˚C, in pure water with 200 ppb of dissolved oxygen at a pressure of 1900 psi.

This research was supported by the AREVA Germany, Contract No.GF01/1015054405, AREVA ref: FE-15-01478.



Geometry of the sample and sample mount and positioning of the 718 wire for the shadow experiment.

OXIDATION OF Fe-Cr-Al ALLOYS IN SIMULATED PWR ENVIRONMENTS DURING IN-SITU PROTON IRRADIATION

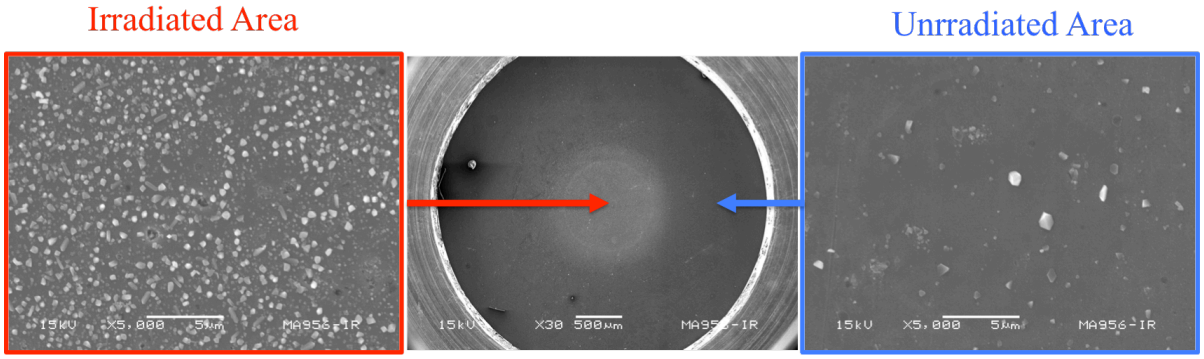
P. Wang, D. Bartels, G. S. Was
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Following the high oxidation rate of fuel rods during the Fukushima Daiichi nuclear accident in 2011, the emphasis for nuclear fuel R&D activities has shifted to the development of accident-tolerance of LWR fuel. FeCrAl alloys were selected as one of the candidate materials for Accident-Tolerant Fuel application due to their excellent high temperature (1200˚C) corrosion resistance in steam, greater strength, and resistance to stress corrosion cracking. However, their general corrosion resistance is borderline and more importantly, no data exist on whether the iron-base alloys being considered for fuel cladding for ATF fuel are susceptible to irradiation-accelerated corrosion. There is also a lack of understanding of the mechanisms by which corrosion such corrosion rates are accelerated to be of any predictive value to the ATF program.

The objective of this work is to assess the corrosion behavior of ATF candidate iron-based alloys under normal LWR operating conditions consisting of high temperature, relevant water chemistry and irradiation.

Corrosion experiments on 30 µm thick FeCrAl alloy MA956 samples were conducted in high purity water at 320˚C containing 3 appm H_2 during irradiation with 3.2 MeV protons to evaluate the effect of irradiation on the corrosion behavior. The thin sample acts as a "window" to allow protons to fully penetrate and deposit their energy in water to induce radiolysis while creating displacement damage in the metal. Results of oxide film characterization via TEM and Raman spectroscopy will be combined data on corrosion rate to determine the effect of irradiation on corrosion.

This research was supported by the DOE-NEUP, Contract No. DE-NE0008272.



SEM image of oxide surface comparison between irradiation area and unirradiated area on the 24-h irradiated MA956 sample, noticed that higher particle density was observed in the proton irradiated area, indicating higher corrosion rate must be present during proton irradiation.

DOSE RATE EFFECT ON CORROSION AND HYDROGEN PICKUP FACTION OF ZIRCOLOY-4 IN DEUTERATED PWR PRIMARY WATER USING IN-SITU PROTON IRRADIATION-CORROSION EXPERIMENTS

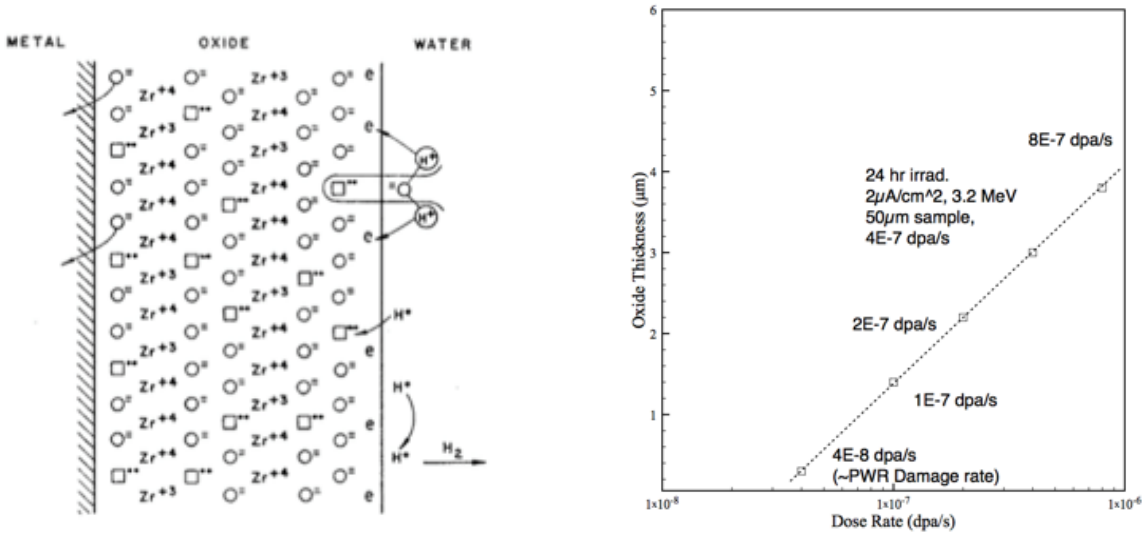
P. Wang, G. S. Was
Department of Nuclear Engineering & Radiological Sciences, University of Michigan

This project aims to understand how irradiation dose rate affects corrosion and hydrogen pickup behavior of zirconium alloy under PWR conditions. Previous study on in-situ proton irradiation-corrosion had indicated that dose rate was thought to be an acceleration factor for enhanced corrosion. Hence, a detailed study of corrosion rate as a function of dose rate was proposed this year. Furthermore, the hydrogen loss through the thin zirconium sample to the beamline vacuum will be addressed by applying a hydrogen permeation barrier layer (e.g. Al_2O_3 or Al-Cr-O layer) to the vacuum side of the sample. Deuterium oxide (D_2O) will be used as corrosion medium, and SIMS will be used to determine the deuterium pickup and distribution.

This study will focus on the characterization of the oxide film formed on Zircaloy-4 that has been exposed to the PWR primary loop environment (without B and Li addition) during proton irradiation in deuterated water. The oxides morphology and microstructure will be characterized as a function of dose rate.

Experiments will be conducted in 320 °C deuterated water with 3 wt ppm H_2, while irradiated by a 5.4 -MeV proton beam at a current density of 2 μA/cm^2 producing a damage rate at 4 x 10^{-7} dpa/s. The resulting oxide will be compared with the results obtained from the reactor-irradiated oxides (from collaborator at Univ. Manchester, UK).

This research was supported by the Consortium for Advanced Simulation of Light Water Reactors (CASL) under U.S. Department of Ene rgy Contract No. DE-AC05-00OR22725.



Schematic of zirconium oxidation and hydrogen pickup mechanism (left), proposed irradiation plan for variable dose rate experiment to study the influence of dose rate on corrosion kinetics (right).

HIGH DOSE ION IRRADIATION OF CNS-I AND CNS-II STEELS

X. Wang, G.S. Was, L.M. Wang
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Core internal components of advanced reactor concepts and fusion reactors will face high radiation doses of 200 dpa or above. Cladding and duct in the traveling wave reactor will experience doses up to 600 dpa. Ferritic-martensitic (F-M) steels are candidate structural materials for these high dose reactor applications because of their swelling resistance under irradiation. CNS I and CNS II are two types of reduced-activation F-M steels developed at the Institute of Nuclear Materials, University of Science and Technology Beijing (USTB). To study the radiation effects, ion irradiation is often used as a surrogate for neutron irradiation. The bulk CNS-I and CNS-II samples were pre-implanted with 10 or 100 appm helium at room temperature using a 400kV ion implanter in the Michigan Ion Beam Laboratory (MIBL) at the University of Michigan. After helium implantation, ion irradiations were performed up to 375 dpa and 450 dpa using a 1.7 MV tandem accelerator or a 3 MV Pelletron accelerator at MIBL using 5 MeV Fe++ ions in raster-scanned mode at a temperature of 460℃.

Fig. 2 shows the swelling results of CNS I and II in the region 500-700nm irradiated to 375 and 450dpa. Swelling values, void density and void mean diameter are shown beneath the under-focused TEM images. Compared to the 188 dpa data reported earlier [1], the swelling of CNS I increased to 8.0% and 5.7% at 375dpa for 10 and 100 appm helium samples, respectively. At 450 dpa, it increased to 8.9% at 10 appm helium and to 5.7% at 100 appm helium. Compared to the 188 dpa data reported earlier, the swelling of CNS I increased to 8.0% and 5.7% at 375dpa for 10 and 100 appm helium samples, respectively. At 450 dpa, it increased to 8.9% at 10 appm helium and to 5.7% at 100 appm helium.

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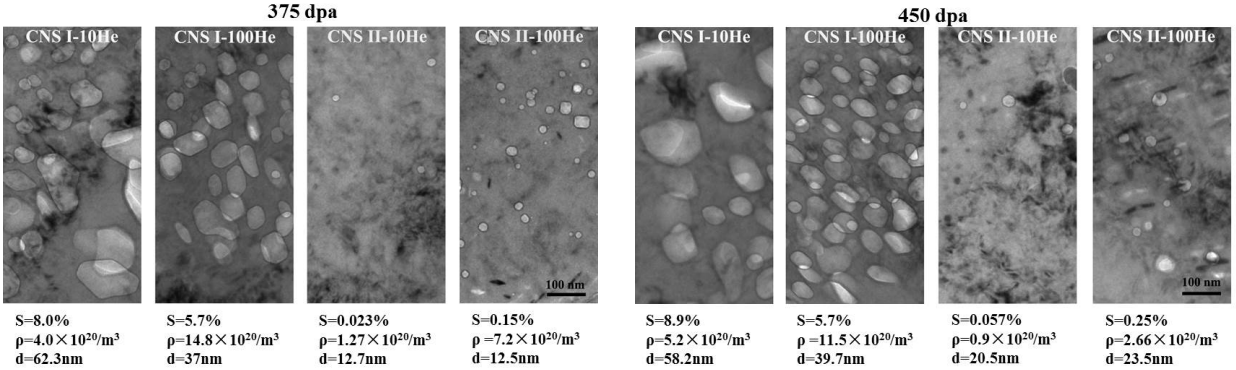
This work has been supported by China General Nuclear Power Group.



Swelling results of CNS pre-implanted with 10 appm and 100 appm helium irradiated to (a) 375 dpa and (b) 450 dpa with 5 MeV Fe++ at 460°C.

EVALUATION OF CHARGED PARTICLE IRRADIATIONS ON FE-9%CR ODS STEEL

M. J. Swenson, J. P. Wharry
Department of Materials Science and Engineering, Boise State University

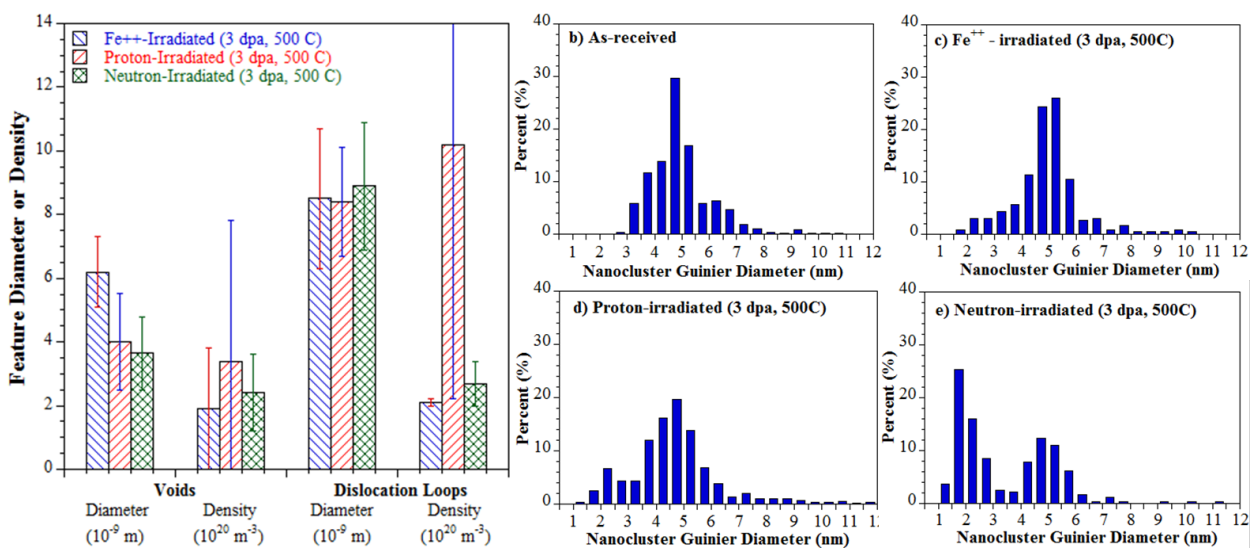
Although charged particles are commonly used to simulate neutron irradiation, the irradiation dose rate, damage cascade morphologies, and depth profiles all differ widely between protons, self-ions, and neutrons. Understanding the implications of these differences is key to using ion irradiation techniques to assess the long-term viability of materials for advanced reactor systems. In particular, this project focuses on a model Fe-9%Cr oxide dispersion strengthened (ODS) alloy.

Specimens were irradiated at MIBL to 3 dpa at 500°C with either 5.0 MeV Fe^{++} self-ions (~10^{-4} dpa/sec) or 2.0 MeV protons (~10^{-5} dpa/sec), and compared to earlier fast neutron irradiations in the Advanced Test Reactor (~10^{-7} dpa/sec). The irradiated microstructure was characterized using transmission electron microscopy (TEM) and atom probe tomography (APT), and was compared to the as-received sample.

TEM results show that grain size, dislocation line density, and carbide precipitates remain unchanged and the size and number densities of dislocation loops and voids were consistent across all irradiating particle types. These results suggest that at TEM resolution, the neutron-irradiated microstructure in Fe-9%Cr ODS can generally be replicated using either self-ion or proton irradiation carried out at identical doses and temperature.

APT analysis enabled characterization of the oxide nanoclusters. Self-ion and proton irradiation led to decreases in the average nanocluster size by ~0.9-1.2 nm. However, neutron irradiation induced a more significant decrease in nanocluster size by more than 2.5 nm. The evolution of the particle size distributions and number density of the nanoclusters suggests partial irradiation-induced dissolution of the nanoclusters, but the extent of dissolution varies with irradiating particle.

This research was sponsored in part by the US Nuclear Regulatory Commission Grant NRC-HQ-84-14-G-0056 and by the US DOE, Office of Nuclear Energy under DOE Idaho Operations Office Contract DE-AC07-05ID14517, as part of the ATR National Scientific User Facility.



Measured size and number density of a) voids and dislocation loops; Particle size distributions of oxide nanoclusters for b) as-received, c) Fe^{++}-, d) proton- and e) neutron-irradiation at like dose and temperature (3 dpa at 500°C).

RADIATION EFFECTS ON THE SIC/STEEL INTERFACIAL REACTION

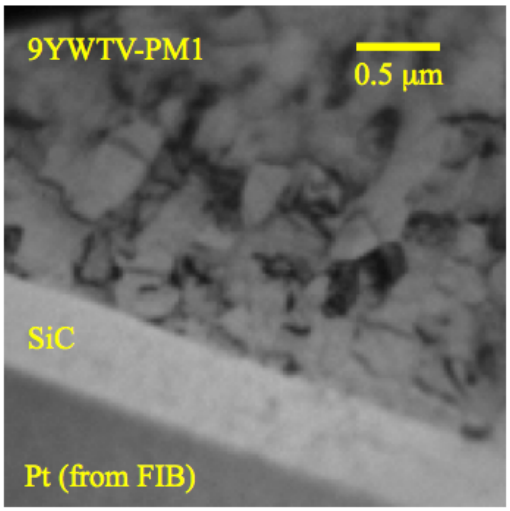
M. L. Lepule, J. P. Wharry
Department of Materials Science & Engineering, Boise State University

Silicon carbide (SiC) is a promising material for nuclear applications due to its desirable intrinsic properties including chemical and environmental inertness, irradiation stability, and high-temperature performance. However, integration and joining of SiC with metallic structures, specifically Fe-based alloys, remains a practical engineering challenge. SiC and metallic Fe undergo a solid state chemical reaction at their interface, which weakens the joint and makes components more susceptible to failure. Diffusion and mechanical bonding techniques have been demonstrated for joining SiC with Fe, but these techniques require the use of interlayers of Cr, Cu, and/or W, to minimize the SiC/Fe interfacial reaction. But the use of interlayers results in stress concentrations, and also limits scalability and manufacturing of complex structures. As an alternative, this study hypothesizes that radiation induced segregation (RIS) – a phenomena which causes preferential segregation of alloying species such as Cr, W, and Si, to grain boundaries and the surface of Fe-Cr alloys – can also inhibit the SiC/Fe interfacial reaction.

In this project, we are focusing on nanostructured ferritic bcc oxide dispersed strengthened (ODS) steels 9YWTV-PM1 and 9YWTV-PM2, both containing ~9 wt% Cr, ~0.5 wt% Cu, and ~1 wt% W. The alloys were both irradiated at MIBL at 500°C with 2.0 MeV protons and 5.0 MeV iron ions. The proton irradiations were carried out to 1 and 7 displacements per atom (dpa) and Fe^{++} to 1, 3, and 100 dpa.

Our future work involves coating the irradiated samples with SiC using the radio frequency magnetron sputtering at temperatures ranging 25-475°C. Cross-sectional transmission electron microscopy (TEM) will be used to quantify the extent of RIS and interfacial reaction as a function of irradiation dose and reaction temperature.

This research was sponsored in part by US Nuclear Regulatory Commission Grant NRC-HQ-84-14-G-0056 and by the National Aeronautics and Space Administration (NASA) Idaho Space Grant Consortium.



Cross-sectional TEM image of 9YWTV-PM1 with SiC deposited at 300°C.

DEFECT DRIVEN METALLIC OXIDES FOR RECHARGABLE LITHIUM ION BATTERIES

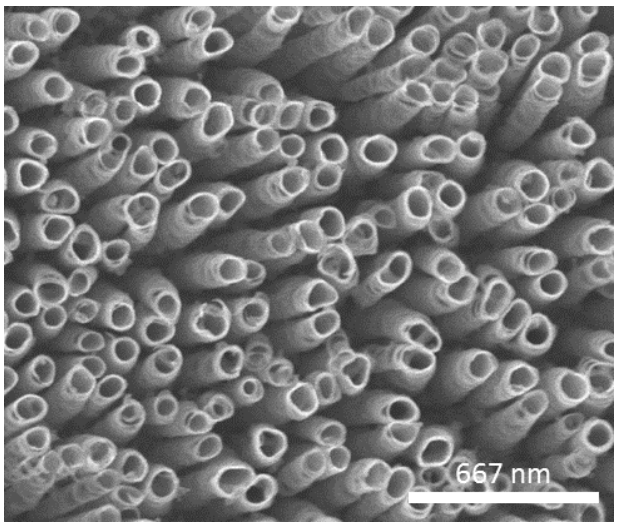
K. Smith, J. P. Wharry, H. C. Xiong, D. P. Butt
Department of Materials Science and Engineering, Boise State University

Rechargeable lithium-ion batteries have transformed the portable electronics industry and are considered amongst the most promising electrochemical energy storage methods for electric vehicles and renewable energy systems. As society shifts further towards clean and renewable energy sources, energy storage becomes evermore critical. Nanostructured titanium dioxide (TiO_2) is a promising electrode material for rechargeable Li-ion batteries because of its improved electrochemical reactivity with lithium compared to bulk TiO_2. However, researchers have yet to achieve the theoretical charge storage capacity of 1.0 Li/Ti at room temperature. Previous work has demonstrated that TiO_2 nanotubes with cation vacancies exhibit desirable short- and long-range order to promote lithium ion intercalation and charge storage. In addition, synthetic methods of doping and ion implantation can induce defects, which enhance the charge storage capacity of metal oxides. This project hypothesizes that irradiation can produce intentional defects in nanostructured crystalline TiO_2 electrode materials, thereby enhancing the electrochemical performance of the TiO_2 electrode in a Li-ion battery.

For this project, we grew anatase TiO_2 nanotubes on titanium foil. The nanotubes were irradiated at MIBL with 400 keV protons to doses of 0.14 and 0.4 displacements per atom (dpa) at room temperature. The irradiated foils were then placed into lithium ion coin cell batteries, and their electrochemical behavior was recorded. Initial results suggest some irradiation-induced changes in the capacity of the batteries, but the mechanisms for these changes have not yet been confirmed.

Future work involves testing for repeatability as well as using heavier ions (e.g. Ni^+, Nb^+) to conduct simultaneous irradiation and doping. We will also irradiate single-crystal anatase and rutile TiO_2 in order to provide insight into the mechanism of irradiation effects on electrochemical performance.

This work is supported by the National Science Foundation, through award number DMR-1408949.



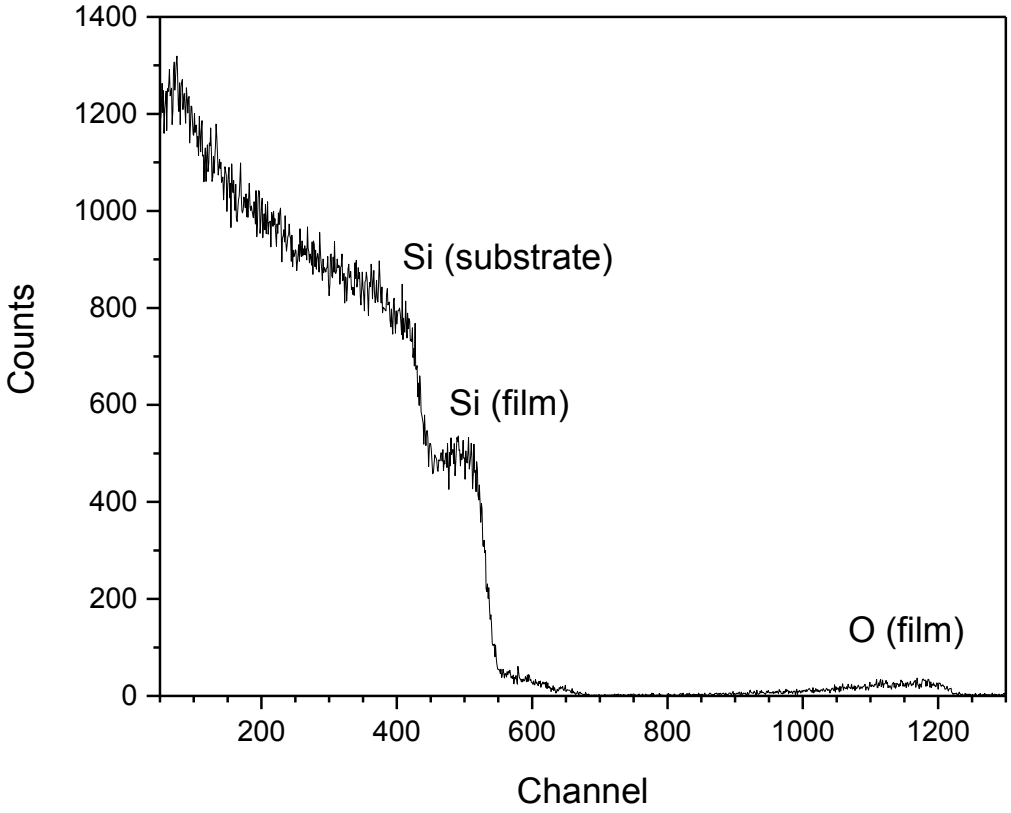
Scanning electron microscope image of TiO_2 nanotubes on Ti foil substrate.

NUCLEAR REACTION ANALYSIS IN THE STUDY OF OXIDATION OF SiC

B. Wing,
Department of Materials Science and Engineering, University of Michigan

This work involves high temperature exposure of silicon carbide (SiC) in oxidizing environments. As such, it is important to determine the thickness of the oxide coating formed on the surface of the SiC. The first attempt to measure oxide thickness was done in an SEM. The results from the SEM indicated that the oxide layer was not uniform, and determining a characteristic thickness was not possible through SEM.

We therefore turned our attention to nuclear reaction analysis. This technique is able to examine a much larger area and determine the average oxide thickness more easily. With the assistance of Dr. Fabian Naab, the sample was placed in a deuterium ion beam with an accelerating voltage of 877 keV. The detection angle is set to 150°. The data was post-processed with the assistance of Dr. Naab.



NRA/RBS spectrum of the SiC sample with the thin oxide layer on the surface.

IRRADIATION ASSISTED STRESS CORROSION CRACKING (IASCC) OF 316 STAINLESS STEEL IN PRIMARY WATER

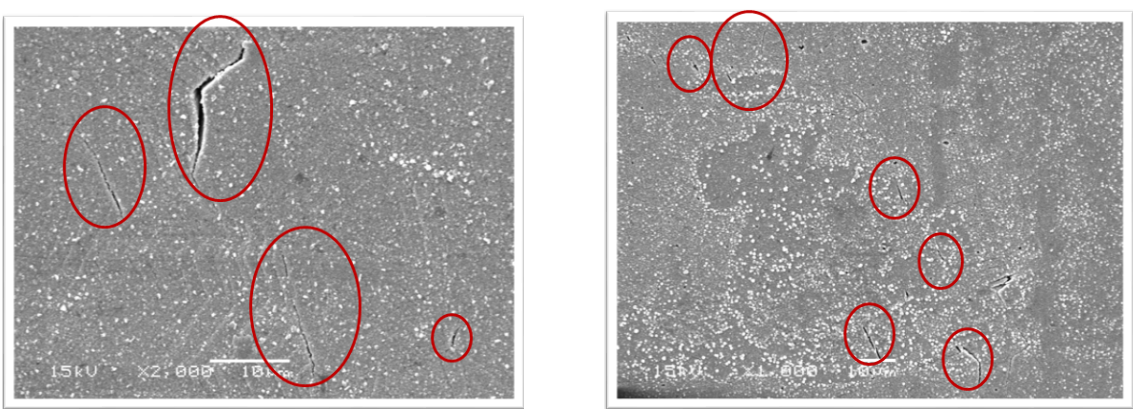
T.-N. Yang, L.M. Wang
Department of Nuclear Engineering and Radiological Sciences, University of Michigan
Shanghai Nuclear Engineering Research and Design Institute

Stainless steels are known to be susceptible to IASCC in light water reactor conditions. Intergranular cracking has been observed in both BWR (normal water chemistry and hydrogen water chemistry) and PWR conditions. Proton irradiation has been shown to be effective in replicating the cracking behavior of neutron irradiated components in reactors. Cracking susceptibility can be assessed by conducting constant extension rate tests on proton irradiated stainless steels in the appropriate environment after irradiation. The material used in this experiment is Chinese made 316 Stainless Steel, provided by Shanghai Nuclear Engineering Research and Design Institute.

Two irradiations were conducted using 2MeV protons to different doses, 1.0 and 5.0 dpa respectively. A total of 8 Constant Extension Rate Test (CERT) samples were irradiated along with 8 TEM bars for hardness and microstructure analysis. Irradiation was conducted at 360 $\pm$ 10 °C with a dose rate of approximately 1 x 10^{-5} dpa/s. Nine areas of interest were set up within the irradiated region for each sample. After irradiation, the samples were set aside for the short-lived isotopes to decay. Beta counting was performed after irradiation to confirm samples were being irradiated evenly.

The hardness measurement performed before and after irradiation provides quick analysis on the changes of mechanical property due to irradiation. CERT testing was conducted at a strain rate of 3 x 10^{-7} s^{-1} in ~320°C PWR primary water with 1000 ppm B as H_3BO_3, 2 ppm Li as LiOH, and 35 cc/kg H_2 overpressure. Step straining was performed to examine the cracking density for various conditions. Some examples of cracks on the irradiated surface are shown below; cracks are circled in red.

This work is supported by the Shanghai Nuclear Engineering Research and Design Institute.



SEM images on 5 dpa (left) and 1 dpa (right) CERT sample surface with 3.5 % and 3 % of plastic strain.

HELIUM BUBBLE EVOLUTION IN ION IRRADIATED Al/B_4C METAL METRIX COMPOSITE

F. Zhang, L.M. Wang
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

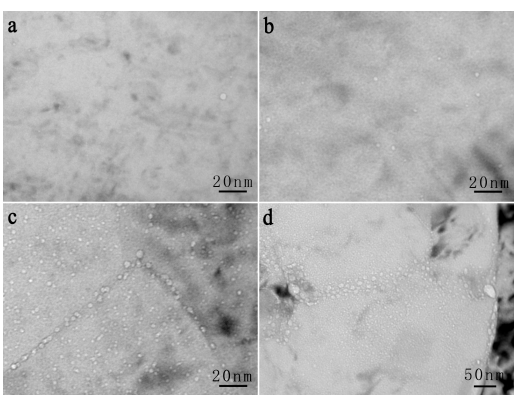
Al/B_4C metal matrix composite (MMC) is an important neutron absorbing material used in both wet storage pools and dry storage casks of spent nuclear fuel for preventing criticality. Al/B_4C MMC can effectively absorb fast and thermal neutrons, because of the high neutron absorption cross-section of ^{10}B through the $^{10}B(n, \alpha)^7Li$ transmutation reaction for a wide energy range of neutrons.

Helium behavior in Al/B_4C metal matrix composite with two different sets of ion irradiation conditions has been investigated by transmission electron microscopy. Helium bubbles in Al were found to be much larger than those in B_4C after a helium fluence of 1.5×10^{17} ions/cm^2 at the room temperature. Also, bubbles at grain boundaries and their vicinity in aluminum are faceted. With additional proton irradiation, a bubble denuded zone along the aluminum grain boundary appears.

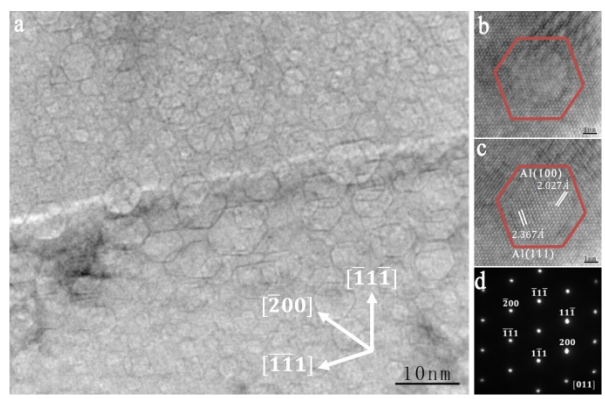
This work has been supported by the US DOE NEUP Program under the contract No. DE-AC07-05ID14517.

Two sets of ion irradiations

	Ions	Fluence, ions/cm^2	Irradiation direction
Irradiation A	400 keV He^+	1.5×10^{17}	→
Irradiation B	400 keV He^+	1.0×10^{16}	→
	1.5 MeV H^+	2.2×10^{19}	↓



Helium bubbles in Al matrix with increasing helium concentrations, (a) 0 appm, (b) 10^2 appm, (c) 10^3 appm, (d) 10^4 appm. (a) ~ (c) were taken from the sample after ***Irradiation B***, and (d) was taken after ***Irradiation A***. Bubble denuded zone with width of ~10nm is visible and outlined in black in (c).

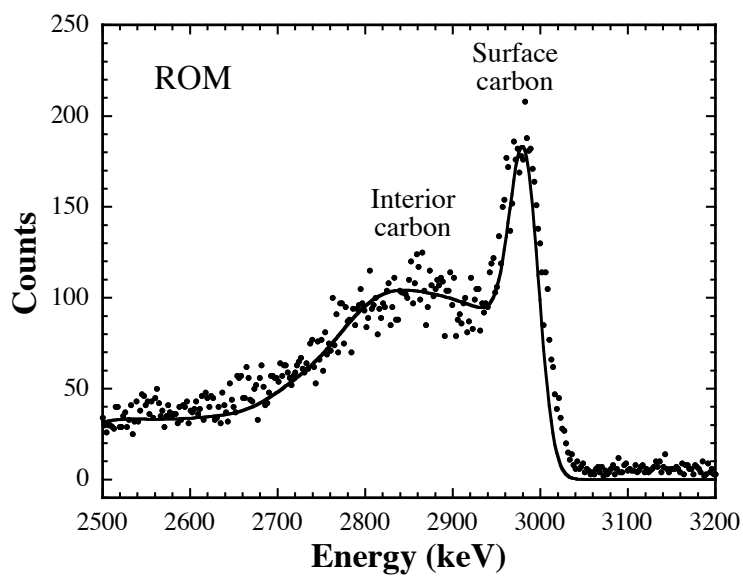


(a) TEM images showing preferential orientations for faceted bubbles grown in Al after ***Irradiation A***. Through-focus HRTEM images (b and c) show contrast of a faceted bubble in the nether Al grain of (a). (d) is SAED pattern of the nether Al grain of (a).

CALIBRATION FOR IR MEASUREMENTS OF CARBONATE IN APATITE BY NUCLEAR REACTION ANALYSIS

Y. Zhang[1], K. Clark[1], and F. Naab[2]
[1]Department of Earth and Environmental Sciences, University of Michigan
[2]Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Apatite is a widely distributed accessory mineral in igneous rocks. One special aspect of apatite is that it can hold almost all volatile elements in its structure, including H (in the form of OH^-), C (in the form of CO_3^{2-}), S (in the form of SO_4^{2-}), F^-, and Cl^-. Hence, apatite may be used as an indicator of the magmatic volatile environment during apatite formation. To realize this potential, it is necessary to measure the volatile components accurately. Carbonate in apatite can be present in two different sites and several vibrational bands of carbonate in apatite can be detected by infrared (IR) spectroscopy in tiny samples with high sensitivity and precision. However, IR can only provide peak intensities. To convert the intensities to absolute concentrations, it is necessary to calibrate the IR technique against absolute concentrations. Nuclear Reaction Analysis (NRA) is used to determine absolute C concentrations in apatite. The nuclear reaction is $^{12}C(d,p)^{13}C$ (i.e., $^{12}C + {}^2H \rightarrow {}^{13}C + {}^1H$). A high-energy beam of deuteron (^2H) particles bombards the target material (polished apatite crystal). As the particles enter the target, some ^2H particles react with the target nucleus (^{12}C), converting the target nucleus to a new nucleus (^{13}C) and releasing a reaction product (^1H) with a specific amount of energy, which is detected in the NRA spectrum at different energy channels. The number of counts at each channel number is proportional to the concentration of the target after a matrix correction for the stopping powers. Figure 1 shows two NRA spectra of an apatite crystal. The accuracy of the NRA method has been verified by the measurement of a calcite mineral with known carbon concentration. The NRA data are used to calibrate the IR method for the analysis of carbonate in apatite.



NRA spectrum showing the analysis of C in an apatite crystal from the Royal Ontario Museum. The increased counts from 2500 to 2950 reflect the C concentration in the interior of the sample. The spectrum is fit using known apatite composition and basic principles of nuclear reactions, leading to a C concentration of 1800 ppm.

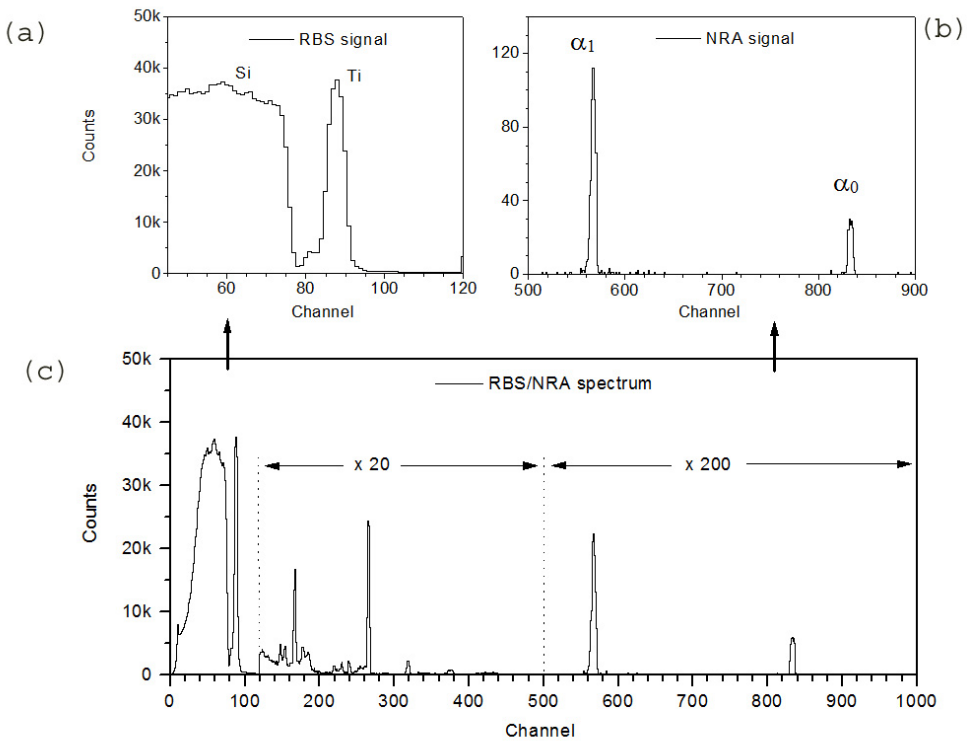
2015 TEACHING

NERS 425 LABORTORY ON NUCLEAR REACTION ANALYSIS

O. Toader, F. Naab, M. Atzmon
Department of Nuclear Engineering and Radiological Sciences, University of Michigan

For the NERS 425 course, students conducted an experiment to determine the stoichiometry of a Ti_xN_y sample using the reaction between a deuterium particle and a nitrogen nucleus: $N^{14}(d,\alpha)C^{12}$. Nuclear reaction analysis (NRA) is a well-established surface analysis technique. In this method, an energetic particle (deuterium – produced by the Tandem accelerator at MIBL) interacts with the nucleus of an N atom (from the target) to give a reaction product (α particle) that can be measured. The students also use the backscattered yield from an RBS experiment to determine the amount of Ti in the sample by implementing simulation codes like RUMP or SIMNRA with the given experimental spectrum.

This year the experiment was successfully carried out by all the section of the NERS 425 class. During the first meeting of this class, and prior to the experiment, a short tutorial was given to the students on the accelerator, electronics, detectors, software, and vacuum components. After that, they worked independently in a few groups with just the basic support from the MIBL staff (required in the setup of the ion beam and the collection of the spectra). The students decided on a few parameters of the experiment (beam energy, time for spectrum acquisition, etc.) and after that each group obtains spectra similar to the ones in the figure.



Details of the RBS spectrum (a), the NRA spectrum (b), and typical NRA spectrum for the TiN film obtained during class (c). Conditions: beam energy: 1.4 MeV D^+, solid angle 5 msr., detector angle 150°.

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