Michigan Ion Beam Laboratory
FOR SURFACE MODIFICATION AND ANALYSIS

ANNUAL RESEARCH REPORT

2006

FOR RESEARCH PROGRAMS CONDUCTED IN 2005

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The Annual Research Report

This report summarizes the principal research activities in the Michigan Ion Beam Laboratory during the past calendar year. Twenty-four research programs accounted for 2370 hours of use in 2005. 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 2005 calendar year.

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 1.7 MV tandem ion accelerator, a 200 kV ion implanter and an ion beam assisted deposition (IBAD) system. Additional facilities include a vacuum annealing furnace, a surface profilometry system, and a scanning laser surface curvature measurement system. The control of the parameters and the operation of these systems are mostly done by computers. They are interconnected through a local area network and the world wide web, allowing off-site monitoring and control.

The Industrial Affiliates Program

The Industrial Affiliates Program in Ion Beam Surface Modification was established to provide an organized structure by which improved interaction between industry and the University can occur in the surface modification area.

Respectfully submitted,

Gary S. Was
Director
RBS ANALYSIS OF REACTIVELY SPUTTERED IrO$_2$

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Iridium oxide is of interest as a material for neural stimulating electrodes because of its stability and its ability to inject large amounts of charge when activated. We have used Rutherford backscattering spectroscopy (RBS) to analyze reactively sputtered IrO$_2$ thin films on silicon and sapphire substrates. The IrO$_2$ was sputtered onto 300ºC substrates using a DC magnetron. The RBS analyses showed that the composition of the IrO$_2$ was nearly stoichiometric and uniform through the film. This result was important because we were unable to analyze the film by XPS or Auger sputter depth profiling due to reduction of the IrO$_2$ by the low energy ion sputtering. The RBS confirmed the thickness of the deposited films and revealed that a Ti adhesion layer deposited at the substrate-film interface had been oxidized during the reactive sputter deposition of the IrO$_2$.

This work was supported by Michigan Life Sciences Corridor Grant GR-358.

A representative RBS spectrum of IrO$_2$ on Si with an oxidized Ti adhesion layer. The dots are the data and the line is the fitted simulation.
Conductivity measurements were taken on solid-state thin-film devices after successive proton implantations. The solid-state devices are constructed on glass slides and are composed of 5 nm chromium (thermally evaporated, vacuum), ~100 nm gold (thermally evaporated, vacuum), ~300 nm hydridosilsesquioxane resin (spin coated from methyl isobutyl ketone), and ~100 nm gold cross electrode (thermally evaporated, vacuum). I-V curves taken with a Keithley 236 Source-Measure unit show typical features for this device, including negative differential resistance, hysteresis, and noisiness in the current measured at a ramp rate of 50 mV/s. Current maxima and minima increase after each dose of protons. The proton implantation increases the average conductivity of the devices. The increase in conductivity may be due to the implanted protons acting as dopants that are stabilized within the porous structure of the hydrido-silsesquioxane film. The increase in conductivity may also be due to defects that arise from damage induced by the implantation.
The objective of this research is to determine the corrosion and stress corrosion cracking (SCC) susceptibility of irradiated austenitic alloys in supercritical water. The austenitic alloys used in this study (316L, 690, 800H) have been selected as candidate alloys for the supercritical water-cooled reactor concept due to their good mechanical properties at high temperatures and their low oxidation rates. There is currently a very limited amount of data available on the SCC susceptibility of the materials in supercritical water and even less on the behavior of the irradiated alloys in supercritical water.

Constant elongation rate tensile (CERT) test specimens and transmission electron microscopy (TEM) bars of 316L, 690, and 800H were irradiated with 3 MeV protons at 400°C to a dose of 7 dpa over a period of 9 days. The proton irradiation was used to emulate the neutron damage the materials would encounter in a reactor environment. Hardness measurements were made on the TEM bars before and after the irradiation. The hardness of the alloys increased substantially due to the evolution of the microstructure that occurred in the materials during the irradiation. Beta counting measurements were performed on the samples following the irradiation and they indicated that the samples had been irradiated evenly.

This research is supported by the U.S. Department of Energy under NERI grant DE-FC07-05ID14664.
INTERACTION OF GRAIN BOUNDARY CHARACTER AND IRRADIATION ASSISTED STRESS CORROSION CRACKING

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Modification of the distribution of grain boundary character has been widely investigated as a means of decreasing susceptibility to intergranular stress corrosion cracking and this investigation examines the relationship between grain boundary character and the factors responsible for Irradiation Assisted Stress Corrosion Cracking (IASCC) in stainless steel. As part of this ongoing work, samples of high carbon type 304 stainless steel were irradiated with 3.2 MeV protons at the Michigan Ion Beam Laboratory at 360°C and to a dose of 1 dpa and 3 dpa.

Experimental work in progress on these specimens focuses on two areas. Initiation of intergranular stress corrosion cracking in the irradiated surface and characterisation of the cracked grain boundaries by electron backscatter diffraction (EBSD). Particular attention will be paid to crack ‘bridging’ features, which have been attributed to special grain boundary character and have a mechanical shielding effect on the crack tip strain [1,2]. Secondly, characterisation of radiation induced segregation by high resolution energy dispersive spectroscopy (EDX) and nanoSIMS (high resolution secondary ion mass spectroscopy) will be conducted to study the relationship between segregation and grain boundary character. The effects of annealing the irradiated samples will also be investigated.

This work has been supported by British Nuclear Fuels Ltd (BNFL) as part of the University of Manchester Materials Performance Centre Research Alliance.

SEM Image of Intergranular crack in proton irradiated 304 stainless steel. Tested above yield under high temperature/pressure autoclave conditions after irradiation.

WAFFER BONDING FOR ION-CUT SYNTHESIS

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Ion implantation plus thermal annealing often leads to the formation and coalescence of gas bubbles which may be used for integrating heterogeneous materials by means of transferring thin layers of one material onto another. For example, when an ion-implanted substrate is bonded to another substrate and subsequently thermally annealed, bubble formation and coalescence often lead to fracture of the original substrate just below the interface. To date, the sole role of implanted ions has been to induce the formation and coalescence of gas bubbles. Our group recently reported the formation and blistering of a layer of luminescent GaN-rich nanostructures, using N ion implantation into GaAs, followed by high temperature rapid thermal annealing.

We are adapting this concept to achieve simultaneous nanostructure synthesis and layer transfer, a process termed “ion-cut-synthesis.” For this purpose, we are exploring methods for glass-mediated bonding of GaAs to other semiconductor and ceramic materials that can in turn withstand subsequent high-temperature annealing. For example, previous attempts at GaAs/Si integration include using methylsiloxane spin-on glass layers or PECVD SiO₂. We have achieved GaAs/Si bonded heterostructures with methylsilsesquioxane (MSSQ) spin-on glass with and without PECVD SiO₂ layers at annealing temperatures as high as 385°C.

The quality of bonding may be described by the toughness, a measure of the energy required for fracture. We have recently set up an IR microscopy system for ‘wedge tests’, in which a wedge is inserted at the interface between two bonded wafers, and the resulting crack length is related to the toughness. Preliminary estimates of the toughness of spin-on glass bonded GaAs/GaAs interfaces are similar to literature reports. We are endeavoring to optimize bonding parameters to maximize the interface toughness, with the goal of achieving a thin layer of nanostructured material on alternative substrates. This is part of an effort to develop integration methods for a variety of technologies including optoelectronics and photovoltaics.

This work was supported in part by the National Science Foundation Graduate Research Fellowship Program and the University of Michigan Rackham Graduate School.

Schematic of the ion-cut-synthesis process: the ion implanted GaAs is bonded to a new substrate (left); following thermal annealing, the GaAsN nanostructure layer forms and splits from the GaAs substrate, and the layer transfer is accomplished (right).

In an effort to understand the effect of helium on the irradiated microstructure, the ferritic/martensitic steel T91 was implanted to three helium concentrations of 720 appm, 1260 appm and 1800 appm. The alloy with and without helium pre-implantation was irradiated with 2.0 MeV protons to doses of 2.2, 7 and 9.2 dpa, respectively, at 450°C. The irradiated microstructure, consisting of dislocation loops and bubbles, was characterized using transmission electron microscopy (TEM). Helium was found to play a crucial role in bubble nucleation. Small bubbles/voids were found in helium pre-implanted samples. No voids were observed in irradiated samples without helium pre-implantation.

The average dislocation loop size is the largest in samples without helium and it decreases slightly as the helium concentration increases. He bubbles induced by helium-implantation may act as defect sinks and impede the growth of dislocation loops. No significant effect of irradiation on dislocation loop size was observed regardless of helium concentration, but loop density increases by about a factor of 2 between 2.2 and 9.2 dpa.

As shown in the figures below, helium was found to promote swelling in T91. The swelling increases with helium concentration. Irradiation may not be essential for void nucleation. However, when combined with helium pre-implantation, irradiation plays a role by assisting void growth and promoting swelling.

Support for this research was provided by the Department of Energy under contract # 73713-001-03 8T.
POLYMER EVOLUTION OF A SULFONATED POLYSULFONE MEMBRANE AS A FUNCTION OF ION BEAM IRRADIATION FLUENCE

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Ion beam irradiation was used to modify the surface of a sulfonated polysulfone water treatment membrane. A beam of 25 keV H\(^+\) ions with three irradiation fluences (1×10\(^{13}\), 5×10\(^{13}\), and 1×10\(^{14}\) ions/cm\(^2\)) was used for membrane irradiation. ATR-FTIR analyses were performed on the virgin and irradiated membranes in order to determine the changes to chemical structure incurred by ion beam irradiation. The results show that some of the sulphonic and C-H bonds were broken and new C-S bonds were formed after irradiation. AFM analyses show that membrane roughness decreased after irradiation. A significant increase in flux after ion beam irradiation was also observed, while the amount of cake accumulation on the membrane was decreased after ion beam irradiation. Hyrophobicity, pore size distribution and selectivity of the membrane were not affected by ion beam irradiation.

This project was funded by the National Science Foundation grant CTS 03-31778.

ATR-FTIR Spectra for the Virgin and irradiated membranes with ion fluences of 1×10\(^{13}\), 5×10\(^{13}\), and 1×10\(^{14}\) ions/cm\(^2\).
Roughness analysis of the virgin and irradiated membranes after filtration.

Flux vs. time of virgin and irradiated membranes.
Dilute nitride semiconductor alloys have shown significant promise for a wide range of applications including long-wavelength light-emitters, high-performance electronic devices, and high efficiency solar cells. To date, literature reports of dilute nitride semiconductor alloys have presented substantially lower electron mobilities than those of (In)GaAs. Furthermore, for (In)GaAsN alloys, the electron mobility and optical emission efficiency have been reported to decrease as the N incorporation increases. Recent calculations suggest that in addition to the strong scattering from isolated substitutional nitrogen atoms, random nitrogen clusters may also substantially affect the mobility [1]. Although these clusters are statistically rare, they give rise to very strong resonant electron scattering. To study the scattering from N complexes with a resonant energy level near the Fermi energy, we are using gated-Hall measurements of modulation-doped GaAsN-based heterostructures. We are studying structures with a range of N compositions in the triangular quantum well containing the two-dimensional electron gas (2DEG). In all cases, we quantify the N concentration in simultaneously grown bulk layers using nuclear reaction analysis, with the $^{14}\text{N}(d,\alpha)^{12}\text{C}$ reaction. For the transport measurements, a gate voltage applied with respect to the 2DEG allows us to shift the Fermi energy of the electron gas without affecting the energy of the resonant scattering levels. When the energy of the resonant defect levels associated with the N clusters are close to the Fermi energy, varying the Fermi energy by a small amount is expected to significantly change the scattering rate due to such resonant levels. For example, the Figure presents mobility vs. carrier concentration data for a modulation-doped heterostructure with $[N]=0.08\%$ GaAsN, in comparison with corresponding experimental and calculated values.

This work has been supported in part by the NSF, AFOSR, DOE, and TRW.

Electron mobility as a function of carrier density measured at 4K for control and dilute nitride 2DEG samples. The linear least-squares fits are made to the initial data points. The mobility of the control sample follows a power law, indicating that the dominant scattering mechanism is remote ionized impurity scattering, while the mobility of the dilute nitride sample flattens out for carrier densities above $2\times10^{11}\text{ cm}^{-2}$, indicating significant scattering from short-range neutral sources, such as substitutional nitrogen defects. Fahy’s calculations [1], shown for $x=0.1\%$, assume all N substitutes for As, and include the resonant scattering contribution from N clusters. The GaAsN channels for Mouillet[2] and Fowler[3] contained 0.05$\%$ and 0.1$\%$ N, respectively.

Au-Pt alloys from Delphi Co. are being treated for use in an exhaust gas sensor electrode. Heat treatments were conducted to optimize the Au-Pt electrode function done in the vacuum furnace at MIBL. The figure below shows how the surface composition of the Au-Pt electrode is affected by the temperature according to the time of the heat treatment. Post-treatment surface composition measurements were done at MSU by means of EDX. Analyzing the Au composition at the surface the researchers at Delphi decided that the optimum temperature is 700°C. More sensors were treated this year at this temperature for time intervals between 2 and 6 hours.

Amount of gold on the surface as a function of annealing time and temperature.
Rutile-TiO$_2$ is a potential transparent conducting oxide (TCO) semiconductor. Density functional theory calculations predict that Bi dopants can form additional partially occupied bands below and above the TiO$_2$ valence band due to the hybridization of Bi 6s with O 2p. This could either result in a metallic or degenerated p-type electronic behavior in Bi doped TiO$_2$ thin films.

In our work, Bi-doped rutile-TiO$_2$ thin films were deposited on (110), (101) TiO$_2$ and r-plane sapphire substrates by pulsed laser ablation from 5%~40%Bi-doped TiO$_2$ targets. The films’ structure qualities were studied by X-ray diffraction, cross-section and high resolution TEM. Energy-dispersive spectra (EDS) and Rutherford Backscattering Spectrometry (RBS) were performed to verify the existence of Bi atoms and the concentration in the films according to different deposition conditions (see table below). Electrical transport properties were studied by Hall-measurements. Pure TiO$_2$ thin films are n-type while p-type conductivity is observed in some Bi doped TiO$_2$ thin films with small mobility values of 0.5~1 cm$^2$/Vs. This could be due to structural defects introduced during the growth by large-size Bi atoms. The films deposited on TiO$_2$ substrates are more conductive ($\rho$=10$^{-5}$~10$^{-3}$ Ohm-cm) compared to those deposited on r-plane sapphire ($\rho$=10$^{-1}$~10$^{-2}$ Ohm-cm). Either as n- or p-type, Bi-doped TiO$_2$ turns out to be a promising transparent conducting oxide.

### Bi concentration in TiO$_2$ films for various deposition conditions.

<table>
<thead>
<tr>
<th>Target Doping (% at.)</th>
<th>Dep. Temp (°C)</th>
<th>Bi in film (% at.)</th>
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<tr>
<td>5</td>
<td>700</td>
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NANO-THERMOMETRY: TRANSMISSION ELECTRON MICROSCOPY OF FEMTOSECOND LASER IRRADIATED CO/SI MULTILAYER THIN FOILS

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Our work seeks to use nanoscale multilayer film systems for assessment of laser modifications induced by high intensity, ultrafast lasers. Pre-thinned foils composed of amorphous silicon and polycrystalline cobalt were irradiated using femtosecond pulse-length lasers at fluences sufficient for ablation (material removal). The film thickness were measured by Rutherford Backscattering Spectroscopy (RBS) performed at the Michigan Ion Beam Laboratory (MIBL). The resultant ablated hole and surrounding vicinity was studied using transmission electron microscopy to determine modifications to the structure. Evidence of cobalt silicide formation was observed within a 3 micron radius of the laser hole edge by use of selected area electron diffraction (SAED). In addition, elongated grains of crystalline silicon was observed within 500 nm of the laser hole edge, indicating melting of the amorphous silicon and heat dissipation slow enough to allow recrystallization. This initial work demonstrates the use of pre-designed nanostructured multilayer systems as a method for nanoscale profiling of heat dissipation following pulsed laser irradiation.

TEM micrographs of the vicinity of a laser hole edge ablated using 930 mJ/cm². Three zones are discernible: elongated grains of recrystallized silicon, cobalt silicide formation with dislocations, nanocrystalline cobalt unreacted with surrounding silicon.
Hall thrusters are electrostatic engines developed in the 60s in the Soviet Union. Because of their high efficiency and potential long lifetime, a great deal of interest exists in their use on a variety of space applications. The cubic phase of boron nitride (c-BN) presents certain advantages as a cold cathode field emitter for electric propulsion: it is chemically inert, it has outstanding mechanical and thermal properties and it has a low work function.

Thin films of c-BN 150nm thick were deposited on a Si (001) substrate using nitrogen plasma assisted sputtering. Since the material is a wide band gap semiconductor, the conductivity of the film had to be increased in order to achieve a good field emission. To achieve that, the film was implanted with a dose of $10^{13}$ cm$^{-2}$ of CO$_2$ at the Michigan Ion Beam Laboratory.

All the field emission measurements were done under high vacuum (~$10^{-8}$ torr or better). An electrode consisting of a glass slide covered with ITO was used to apply the bias, separated by the sample with kepton foil 25 microns thick. The voltage was varied between -400V and 400V and emission was observed at voltages greater than 250V.
NANO-FIBERS FORMED IN Ge AND GaSb BY ION IRRADIATION

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Fabrication of one-dimensional nano-structures such as nanowires or nanotubes has become the focus of intense studies worldwide due to their unique properties and potential applications in electronic and optoelectronic nanodevices. In our study, self-assembly nanofibers formed by 30 keV focused Ga⁺ ion beam irradiation on the surface of Ge and GaSb to fluences of $1.3 \times 10^{16}$/cm² and $6.5 \times 10^{15}$/cm², respectively. In order to determine the relation between ion energy and length of nanofibers, we implanted 150 keV Kr⁺ in Ge and GaSb to the same fluences as Ga⁺. The ion implantation was conducted at room temperature using Varian 200 implantor at Michigan Ion Beam Laboratory (MIBL) of University of Michigan.

The free-standing nano-fiber on the surface of Ge and GaSb irradiated by Kr⁺ were observed, as the cross-sectional TEM images shown in the figure below. The highly ordered nanofibers were parallel to the ion projected direction, i.e., normal to the surface, with the uniform intervals of 20-30 nm. The length of the nanofibers was 50-60 in Ge and it even reached 1.1 µm in GaSb. A high density of nano-voids was observed in the fibers and the substrate beneath the fibers to approximate 50 nm in Kr⁺-implanted Ge. In the bottom of fibers of GaSb, the cellulosic structure can still be observed. Cavities due to agglomeration of vacancies generated by ion irradiation are responsible for the formation of nanofibers.

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Nanofibers in Kr⁺-irradiated Ge (a) and GaSb (b) with an energy of 150 keV to the fluences of $1.3 \times 10^{16}$/cm² and $6.5 \times 10^{15}$/cm², respectively.
INCORPORATION OF A HYDROGEL ONTO PLATINUM ENDOVASCULAR COILS FOR THE TREATMENT OF ANEURYSMS

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Tim Becker and Kaylan Brakora, Neural Intervention Technologies

Vascular defects such as aneurysms are life threatening, and can be difficult to treat with surgery. Platinum endovascular coils are commonly used to occlude aneurysms without surgery. The packed coils form a tight mesh in the aneurysm that eventually excludes the placement of additional coils, limiting the aneurysm occlusion volume to roughly 30%. Such low occlusion volumes are unstable, and can result in aneurysm regrowth and a persistent life threatening condition. Incorporating an expandable hydrogel coating on the platinum coils could dramatically increase the aneurysm occlusion volume, and increase the stability of the treated aneurysm. When hydrated, the coating will expand to increase the diameter of the coil. The hydrogel coating must be stable enough to withstand the bending and shear forces associated with microcatheter delivery, must be flexible enough to bend with the coil, and the hydrogel/platinum adherence must be strong enough that the coating does not peel off the coil. Ion implantation may be able to produce a stable hydrogel/platinum interface without adversely affecting the flexibility or expandability of the hydrogel coating.

A range of implantation settings was evaluated to determine the dose and energy that maximizes adhesion, flexibility, and coating expansion. Several coated coils were too burnt or brittle from ion implantation to give useful data. Optimized settings showed rehydration expansions between 1.07 -1.47x the dehydrated diameter (see figure below), which can dramatically improve aneurysm occlusion volumes.

This work was funded by a grant from the Michigan Economic Development Council to the University of Michigan Neural Engineering Laboratory and Neural Intervention Technologies (NIT). Additional funding was provided through a Small Business Innovation Research grant to NIT.

Ion implanted hydrogel coated coil. Dehydrated (A), Hydrated (B).
THE EFFECT OF Zr AND Hf ADDITIONS ON RADIATION-INDUCED GRAIN BOUNDARY SEGREGATION IN AUSTENITIC STAINLESS STEELS

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In this work, austenitic stainless steels are modified with additions of the oversized atoms zirconium or hafnium to examine their role in mitigating radiation damage. Some previous work has shown the beneficial effect of Zr or Hf additions in reducing both radiation-induced grain boundary segregation (RIS) and susceptibility to irradiation assisted stress corrosion cracking (IASCC). This work will further develop previous studies by looking at higher doses of 3, 7 and 10 dpa. Irradiations are performed using 3.2 MeV protons at a temperature of 400°C.

The effect of irradiation on grain boundary segregation in stainless steels is linked to the flow of point defects toward grain boundaries. Zr or Hf atoms in solution act as point defect sinks to enhance recombination and reduce point defect flow, reducing the degree of segregation at grain boundaries. The figure shows the amount of grain boundary Cr depletion and Ni enrichment for a reference 316SS alloy and four other alloys, two each containing different concentrations of Zr or Hf. In general, alloys with oversized solute additions show substantial decreases in RIS, especially at the lowest dose of 3 dpa, but continuing even up to 10 dpa for the Zr alloys.

The goal of this work is to develop more radiation-tolerant structural materials for the nuclear industry. The role of oversized solutes in mitigating RIS and reducing IASCC could help to extend reactor component lifetimes and increase safety in nuclear systems.

This research was supported by the U.S. Department of Energy under grant DE-FG07-03ID14542. The research was performed under appointment to the Naval Nuclear Propulsion Fellowship Program sponsored by Naval Reactors Division of the U.S. DOE.

Reduction in Cr depletion (left) and Ni enrichment (right) in 316 ss containing Zr and Hf additions following irradiation with 3.2 MeV protons at 400°C to 3, 7 and 10 dpa.
ANALYSIS OF HYDROGEN CONTENT
IN DIAMOND-LIKE COATINGS

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The Michigan Ion Beam Laboratory has contributed critically to the development of diamond-like-carbon coatings for dry machining applications at GM R&D. In this project many DLCs were profiled for hydrogen content using Elastic Recoil analysis and Rutherford Backscattering Spectroscopy. Below are graphs of a hydrogen recoil spectrum for one of the samples and the elemental distribution near the surface.

A spectrum of hydrogen recoils from a diamond-like coating.

Elemental distribution near the surface of a diamond-like coating.
The goal of this project is to utilize both experiments and computer simulations to understand the effects that helium and hydrogen have on irradiation damage occurring in single crystal bcc (body centered cubic) iron.

A series of irradiations were carried out with 1 MeV protons and 2.3 MeV He\(^{2+}\). Thirteen samples were proton irradiated as follows: 0.03 dpa at 573K (2), 0.3 dpa at 573K (2), 0.03 dpa at 723K (2), 0.3 dpa at 723K (1), 3 dpa at 573K (3), and 3 dpa at 723K (3). The low dose (0.03 and 0.3 dpa) specimens were previously implanted with helium ranging from 0.3 to 45 appm. The high dose specimens were also pre-implanted with 30 or 450 appm helium. A representative irradiation with helium and protons is shown in the figure below. The combination of both irradiations using helium and protons giving a systematic matrix of four values of helium to damage ratios: 0, 10, 150, and 75000 appm/dpa at temperatures of 573K or 723K. The values of 10 and 150 appm/dpa were chosen since these values are consistent with what is observed in fusion and spallation systems, respectively.

Following the irradiations, the specimens will be analyzed via positron annihilation spectroscopy and transmission electron microscopy. The experimental results will also be compared to the computational results.

This work was supported by Los Alamos National Laboratory under grant 81862-001-04 and under a Department of Energy UNERI grant DE-FC07-05ID14665.
The objective of this study is to determine the surface film characteristics of several different experimental magnesium alloys after exposing them to the corrosive environment of automotive coolants, including ethylene glycol, aqueous solution of ethylene glycol and water, and other liquids being considered for coolants in magnesium engine blocks. The experimental magnesium alloys have been developed for high temperature creep resistance, but their corrosion behavior in the engine coolant environment has not been studied in detail. Rutherford Backscattering Spectroscopy (RBS) is used for the assessment of surface films that develop as a result of corrosion. An understanding of the chemical make up of the surface film and its effect on the corrosion reaction is essential for further consideration of these alloys in engine block applications.

The work completed thus far involves pure magnesium and magnesium alloy AZ91D. Specimens of these materials were exposed to aqueous electrolytic solution of pH4 and containing 5 wt.% NaCl. Using the RBS spectra, it was possible to identify that the film deposited on the surfaces of these specimens contained Mg, O and possibly H (see the figure below). Samples of Mg, MgO and Mg(OH)$_2$ were used to generate reference RBS spectra that were used for comparison purposes. Future work will involve the reference magnesium alloys exposed to the coolant environment.

This work is supported by the United States Automotive Materials Partnership (USAMP) under a grant provided by the U.S. Department of Energy.

RBS spectrum obtained with AZ91 magnesium alloy exposed to an aqueous solution of pH4 and containing 5 wt.% NaCl.
Localized deformation (induced by low stacking fault energy (SFE) and/or irradiation damage) may play a key role in IASCC susceptibility of stainless steels. Three model alloys (UHP-304:E, 304+Si:H, and 304+Cr+Ni:L) having a spread in SFE and previously measured susceptibility in simulated LWR environments were selected for this study. Two batches of samples were irradiated with 3.2-MeV protons at 360°C to 1.0 and 5.5 dpa respectively, and then incrementally strained in 288°C Ar atmosphere to 3%, 7% and 12%. After each strain level, channel height, width and spacing were quantified. As shown in the figure below, the degree of localized deformation at 3% strain in both 1.0 and 5.5 dpa samples was considerably higher in alloys H and E than in alloy L, consistent with the cracking at 5.5 dpa where alloys E and H failed via IG cracking while alloy L was resistant to cracking. The degree of localized deformation, which is affected by irradiation dose and SFE, is closely related to the observed IGSCC.

Support for this research was provided by the Cooperative IASCC Research (CIR) program.

Average channel strain in alloys H, E and L at doses 1.0 and 5.5 dpa.
Barium strontium titanate (Ba$_{x}$Sr$_{1-x}$TiO$_{3}$), a ferroelectric material, is used for making novel tunable microwave circuits, because its dielectric constant can be varied under DC electric field. Its high dielectric constant (hundreds) makes it suitable for device and circuit miniaturization. The ratio between barium and strontium is an important parameter in characterizing material and electrical properties. Rutherford backscattering spectrometry (RBS) was used to characterize a of Ba$_{0.5}$Sr$_{0.5}$TiO$_{3}$ on platinized sapphire (see figure). Results indicated that the Ba:Sr stoichiometry was 1.14:1 which was slightly off the target stoichiometry of 1:1, indicating a need for process optimization.

RBS spectrum for BST thin film on platinized sapphire.
Ferritic-martensitic (F-M) alloys have been identified as candidate core structural alloys in the supercritical water reactor (SCWR). Preliminary studies have shown that F-M alloys experience high corrosion rates in pure SCW. They generally exhibited low susceptibility to SCC, although HT-9 has shown evidence of IGSCC in SCW. The effect of irradiation on SCC of F-M alloys is unknown. Hence an understanding of the effects of irradiation on the structure and chemistry of F-M alloys and how these changes can lead to IASCC is important. The purpose of the current study is to investigate the effect of irradiation on SCC of F-M alloys for use as structural materials in the SCWR.

Irradiations were conducted on F-M alloys HCM12A, T91 and HT9 at 400-500°C to doses of 3 and 7 dpa using 2 MeV protons. Following irradiation, constant extension rate tensile (CERT) tests were conducted in SCW at 400°C and percent ductility and reduction in area were measured along with analysis of the irradiated and fracture surfaces. Results were also compared with the unirradiated condition. HT-9 had the lowest values of reduction in area and strain to failure among all the alloys thus exhibiting maximum ductility degradation. Figure 1 shows the plot of stress vs. strain for F-M alloy HT-9 tested in deaerated SCW at 400°C for three conditions: unirradiated, irradiated to a dose of 7 dpa at 400°C and irradiated to a dose of 7 dpa at 500°C. The stresses for the two irradiated samples are higher than the unirradiated one, with the sample irradiated at 400°C having higher values of stresses than the one irradiated at 500°C, though lower total and uniform elongation. Cracking analysis showed that only HT9 displayed evidence of intergranular cracking. For both irradiation temperatures the number of cracks and maximum crack depth was more than those found on the unirradiated sample (Figure 2).

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IRRADIATION EFFECTS ON MICROSTRUCTURE AND STRESS CORROSION CRACKING RESISTANCE OF AUSTENITIC CANDIDATE ALLOYS FOR THE SUPERCRITICAL WATER COOLED REACTOR

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Proton irradiations were conducted to determine the microstructure induced in alloys 304L, 316L and 690 and to determine the influence of irradiation on the alloys stress corrosion cracking behavior in conditions relevant for the supercritical water reactor concept. Irradiation was conducted using 3.2 and 2 MeV protons to a dose of 7 dpa at 500°C. SCC experiments on the irradiated specimens were conducted in constant extension rate tensile (CERT) mode in deaerated supercritical water (SCW) at 500°C. Radiation induced hardening and the irradiated microstructure (loop size and density and void size and density) were characterized post irradiation. The stress corrosion cracking susceptibility was characterized by the amount of cracking (crack density, crack length per unit area) and by the nature of the cracking.

Microstructure analysis shows that the loop and void sizes are considerably lower for alloy 304L compared to alloy 316L, whereas the density is higher. Alloy 690 irradiated up to 7 dpa exhibits lower loop and void sizes and higher densities than 316L. The stress-strain curves obtained show that all irradiated alloys exhibited a decrease in the failure strain compared to the unirradiated condition and that the amount of cracking greatly increase with dose (see figure below). Alloy 304L is more susceptible to cracking than is alloy 316L in both the unirradiated and irradiated conditions. In the irradiated condition, alloy 690 is more susceptible to IGSCC than the stainless steels. This is surprising given that in the unirradiated state, alloy 690 is relatively resistant to IGSCC in SCW.

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![Average crack length per unit area measured on the gage surfaces of the samples after the CERT test performed in pure 500°C supercritical water.](image-url)
ENHANCED REMOTE DATA ACQUISITION AND INSTRUMENT CONTROL CAPABILITIES AT MIBL

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Having the capability to control and observe experiments from a remote location has several benefits, including the ability to track and to assist in solving most of problems that might arise. The best way to remotely control and monitor activity during an irradiation experiment is via the World Wide Web, using a method that is browser and computer independent and with software easily available on the market. In the last several years, researchers and groups of researchers outside of the university have been requesting time in the facility to conduct irradiations. However, since there is not student who “owns” the research, the current mode of operation used in student-based research at U-M is unworkable. During 2005 MIBL staff, with feedback from students and users, has enhanced the remote monitor and control capability by using a combination of commercial software packages (Labview and Appletview). During an experiment, most of the parameters could be accessed and monitored remotely by simply reaching a web site.

The following capabilities are currently active: the Torvis ion source is fully controllable and the irradiation stage terminal is being monitored (TC temperature, chamber pressure, irradiation dose, stage current and Stinger (thermal imager) temperature values). The data is fed in real time to a web site and can be accessed from anywhere. Due to the fact that the application is Java based the access is platform independent (Windows, UNIX and Mac). Work had begun in 2005 to extend the remote capabilities to include: the control of the heating source and of the air flow (cooling the stage), Faraday cup on/off control, gate valves in/out control (to separate areas of the beam line in case of vacuum failure), RBS remote monitoring and web-cam monitoring of the MIBL with the idea of easing the remote troubleshooting and surveillance by the MIBL staff.
ZnO is an attractive semiconductor oxide for short-wavelength light-emitting devices due to its large exciton binding energy (60 meV). Because the core of such light-emitting device is a p-n junction, the synthesis of both n-type and p-type high-quality ZnO epilayers is a requirement. ZnO is asymmetric and intrinsically n-type therefore the synthesis of robust and reliable p-type ZnO films is a major challenge, which limits its use for optoelectronic applications. Our research focuses on the fabrication and characterization of p-type epitaxial ZnO films. We have first demonstrated the reliable p-type conductivity of nitrogen-doped ZnO epitaxial films, grown on (0001) sapphire substrates, with a hole concentration of up to \(10^{17}\) cm\(^{-3}\). Due to its ability to pick out light elements, nuclear reaction analysis (NRA) was used to measure the nitrogen and hydrogen concentration in the films. The film thickness was obtained by profilometry and measurement of the step height. These two measurements were performed at the Michigan Ion Beam Laboratory (MIBL). We have also demonstrated p-type conductivity in phosphorus-doped epitaxial ZnO thin films with a hole concentration up to \(10^{18}\) cm\(^{-3}\) and have fabricated ZnO p-n homojunctions on Zn-terminated (0001) ZnO wafers. In this work, we used Rutherford backscattering spectrometry (RBS) at the MIBL to evaluate the phosphorus doping amount in the films. We are currently investigating the electroluminescence of our ZnO homojunctions.

Semi-log NRA plot of a p-type nitrogen-doped ZnO thin film obtained from the \(^{14}\text{N}^{12}\text{C}\) reaction.
PAPERS AND PRESENTATIONS

Publications


Presentations


