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Hydrogen-Induced Embrittlement of Candidate Target Materials for Applications in Spallation-Neutron-Target Systems

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To Whom It May Concern:

I have worked with Drs. O'Toole and Roy to identify the R&D needs of the AAA Program and develop the proposal to study hydrogen embrittlement of spallation target materials.

Under proton and spallation neutron irradiation, large quantities of hydrogen and helium are produced in the target materials, along with other products. The production rates are much higher than that in fission or fusion environment, and the effects on materials are expected to be severe. These effects have not been well studied and understood, especially in the temperature range of interest to transmutation applications.

The proposed work will study the effects of hydrogen in candidate alloys for spallation targets (LBE, W-Na or W-H_2O). The effects of different heat treatment will also be investigated. In addition, the experiment can also explore the hydrogen induced or enhanced corrosion. This is an important task to establish the baseline performance before in-proton-beam irradiation of the alloys. I support the scope of work outlined in this proposal.

Yours truly,

Ning Li
AAA Program
Los Alamos National Laboratory

Project Title:
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AAA Research Area: Target / Transmuter

Abstract
The purpose of this project is to evaluate the effect of hydrogen on cracking of candidate target materials for applications in spallation-neutron-target (SNT) systems such as accelerator production of tritium (APT) and accelerator transmutation of waste (ATW). The test materials will undergo appropriate thermal treatments prior to being hydrogen-charged by potentiostatic cathodic polarization technique in a simulated aqueous environment at different temperatures of interest. The specimens, upon completion of testing, will be metallographically examined. Further, the scanning electron microscopy (SEM) will be used to determine the extent and nature of cracking in the specimens tested. The thrust of the proposed testing is to determine the effect of hydrogen on environment-induced cracking of target materials but not to study their radiation-induced damage (radiation hardening).

Work Proposed for Year 1 (Summer 2001-Spring 2002), Goals, and Expected Results
The materials and equipment will be ordered. The materials will be heat-treated and test samples will be machined. Approximately 25% of the experiments will be completed and about 15% of the microscopy will be completed. Monthly contact will be maintained with the LANL collaborator. Brief quarterly reports will be prepared and detailed semi-annual reports will be submitted.

Funding Profile:

Academic Year	**2001-2002**	**2002-2003**	**2003-2004**
Total	$145,759	$136,335	$130,044

Background and Rationale

During his two presentations at the AAA-UNLV Mini-Workshop held at the Harry Reid Center (HRC) on January 18, 2001, Dr. Stuart Maloy of Los Alamos National Laboratory (LANL) identified several research areas in the fields of Material Science and Corrosion Engineering. More recently, Drs. Roy and O'Toole had further interactions with Drs. Maloy and Li to follow-up on the related research topics, and to invite Drs. Maloy and Li of LANL to participate in HRC-sponsored collaborative research at UNLV in areas of Materials Science and Corrosion Engineering, respectively. Drs. Maloy and Li had expressed their willingness to collaborate with UNLV researchers and to actively participate in collaborative materials and corrosion research activities to be pursued at the Mechanical Engineering department of UNLV.

The operating environment of a SNT system can produce a considerable amount of hydrogen, helium and associated environment-induced damage in the target material. Therefore, the test specimens will be cathodically charged in a deaerated (by helium) aqueous environment of interest to evaluate their susceptibility to hydrogen-induced embrittlement (HE) at different temperatures. The test materials will be thermally treated prior to being charged with hydrogen. Thus, in essence, this project will be aimed at evaluating the effect of hydrogen content on the environment-assisted cracking of candidate target materials as a function of metallurgical conditions resulting from different thermal treatments. It is also possible to study the effect of hydrogen on the corrosion resistance of the materials. This study will provide essential information necessary to conduct future in-proton-beam radiation experiment to directly study these effects.

Test Materials

Three martensitic stainless steels, namely HT-9, EP 823 and Type 422 will primarily be tested in this program. Ni-base austenitic Alloy 718 may also be incorporated during the testing if warranted by the AAA program needs.

Types of Testing

The susceptibility to HE will be evaluated by using both smooth and notched uniaxial tensile specimens. The tensile specimens will be pulled in an aqueous environment under either a constant load or a slow-strain-rate (SSR) condition. For constant load testing, a loading device such as a calibrated Proof Ring will be used. For each Proof Ring, a calibration curve generated by the manufacturer will be used to determine the amount of deflection needed to apply the desired load to the test specimen. The determination of cracking tendency using this technique will be based on time-to-failure (TTF). An automatic timer attached to the test specimen will record the TTF. Tensile specimens loaded to desired stress level would provide a fail versus no fail result.

The tensile specimens will be fabricated from heat-treated plate/bar materials in such a way that the gage section is parallel to the longitudinal rolling direction. For constant-load testing, the magnitude of the applied stress will be based on the tensile yield strength (YS) of the test material. The test specimens will be loaded at different percents of YS and the corresponding TTF will be recorded.

During SSR testing, the specimen will be continuously strained in tension until fracture, in contrast to more conventional SCC testing conducted under a sustained load condition. The application of slow dynamic straining (10^{-6} to 10^{-7} sec^{-1}) to the smooth tensile specimen will facilitate cracking in the test materials that may not exhibit cracking under constant load or may take prohibitively long duration for crack initiation. However, the use of a notched tensile specimen may result in fast crack initiation under both constant load and SSR conditions. The smooth tensile specimen in SSR testing may undergo fast failure in a ductile manner if SCC does not occur, or prematurely in a brittle manner if SCC occurs. Prior to being tested in the aqueous environment, a few SSR specimens (both smooth and notched) will be pulled in air to establish baseline data.

It is well known that electrochemistry can play an important role in characterizing the stress corrosion cracking (SCC)/hydrogen embrittlement (HE) behavior of susceptible alloys. Accordingly, at the onset, the corrosion or the open circuit potential (E_{corr}) of the test specimen will be measured in the aqueous environment of interest with respect to a standard Ag/AgCl reference electrode. The specimen will then be strained in the test solution either in a constant load or in a SSR condition using either a Proof Ring or a mechanical testing machine (Instron or MTS) with or without a controlled electrochemical potential (E_{cont}). The magnitude of E_{cont} will be selected based on the measured E_{corr} value (cathodic versus E_{corr}). This cathodic (negative) potential (E_{cont}) will be applied potentiostatically during the entire straining period. Two graphite rods will be used as cathodes during the potentiostatic polarization of the tensile specimen (anode). A three-electrode polarization technique will be used.

For conventional SCC tests under static loading condition, the cracking susceptibility will be expressed in terms of a threshold stress (σ_{th}) below which cracking does not occur during arbitrary test duration, or the TTF at a given applied stress. With SSR tests, however, similar approaches cannot be used since the test specimen is subjected to a continuously changing stress during straining. Therefore, the cracking tendency will be characterized by a number of readily measurable and quantifiable parameters obtained from the load-deflection curve and the examination of the broken test specimen.

Since environment-assisted cracking is usually associated with relatively little macroscopic plastic deformation during crack growth, the ductility parameters such as the percent elongation (%El) and the percent reduction in area (%RA) are very useful in characterizing the cracking susceptibility. In addition, the true fracture stress (σ_f) obtained from the load-deflection curve and the final specimen dimension is useful in expressing the extent of cracking tendency.

Secondary ion mass spectrometry (SIMS) will be used to analyze the hydrogen content resulting from the cathodic potentiostatic polarization. Optical microscopy and scanning electron microscopy (SEM) will be used to characterize the extent and morphology of cracking in all materials tested. Energy dispersive spectroscopy (EDS) will be used to detect and identify chemical species present in the vicinity of cracks.

Test Conditions

All three martensitic stainless steels will be received in the form of both bar and plate. This group of materials is called martensitic because they are capable of changing their crystal structure upon heating and cooling. They can be quench hardened to fully martensitic structures without any retained austenite. These plates and bars will be austenitized in the temperature range of 1900 to 2000^{o}F for 1 hour followed by a water/oil quench. These martensitic structures are very hard and brittle. Therefore, these quenched materials will further be tempered at 1200^{o}F for 1, 1.5 and 2 hour(s) followed by air-cooling. All test specimens will be fabricated from these quenched and tempered stainless steels.

The susceptibility to HE will be evaluated by subjecting the thermally treated tensile specimens to cathodic charging in a deaerated (by helium) acidic brine (NaCl solution) at temperatures ranging from ambient (25^{o}C) to elevated temperatures (up to 120^{o}C). The strain rate used during the SSR tests will range from 10^{-6} to 10^{-7} sec^{-1}. The pH of the test solution will range between 2 and 3. Duplicate specimens of each material will be tested under each heat-treat and electro-chemical conditions.

Expected Data

The proposed experimental program will generate the following data:

- Corrosion potential (E_{corr})
- Failure load (P_f)**
- True fracture stress (σ_f)**
- Threshold stress for cracking (σ_{th})**
- Percent elongation (%El)**
- Percent reduction in area (%RA)**
- Time-to-failure (TTF)**
- Hydrogen content evaluated by SIMS
- Metallurgical microstructures evaluated by optical microscopy
- Fracture Characteristics evaluated by scanning electron microscopy

**Versus E_{cont}

The resultant data will enable a mechanistic understanding of the HE process in candidate target materials under the synergistic influence of applied tensile stress and the corrosive media with or without the presence of hydrogen. Others may eventually utilize these data in developing and validating the hydrogen-induced degradation models for target materials used in transmutation processes.

Research Capabilities at UNLV

Some of the research facilities needed to pursue this project are available at UNLV except for the SIMS and the corrosion test equipment identified in Table 1. The corrosion testing equipment is listed in this proposal for information purposes only. The equipment is not included in this research project proposal budget. The UNLV AAA Ad Hoc Committee on Infrastructure will be reviewing and making equipment-funding recommendations in the near future. The UNLV AAA Finance Advisory Committee, which authorizes UNLV AAA funding, has already determined that this equipment will be a high priority for the Infrastructure Committee. The cost estimates are listed here to provide detailed information to these committees. Short delays in obtaining this equipment may not have an impact on the progress of this project because there will be time-intensive materials acquisition and sample preparation tasks during the first few months.

Table 1: Corrosion Testing Equipment Needs for this Project*

Description	Cost
Potentiostat (2)/Corrosion Software	$34,000
Electrochemical Cells/Electrodes	$2,000
Water Bath/Glass Test Cells	$5,000
SSR Testing System with Corrosion Resistant Cells	$80,000
High Resolution Optical Microscope and Accessories	$45,000
Proof Rings/Assemblies (6)	$23,200
Computer Hardware for 2 Different Test Systems	$6,000
Laboratory Ventilation	$10,000
Utility Connections	$3,500
TOTAL EQUIPMENT COST	***$208,700***

*These costs are being requested through the Research Infrastructure Augmentation funds of the UNLV AAA University Participation Program and are intentionally excluded from the proposed budget for this project.

Heat Treatment Facilities

Two high temperature furnaces are available:

1) Lindberg Furnace
   The maximum temperature is 1200 ^{o}C (2200 ^{o}F). The working dimensions are 15” x 7.5” x 5.5”.

2) Thermodyne Furnace
   The maximum temperature is 1200 ^{o}C (2200 ^{o}F). The working dimensions are 6.5” x 4.5” x 4.5”.

Machine Shop

The UNLV College of Engineering has a machine shop with two vertical mills, two lathes, a welding station, and a variety of band saws, shear breaks, and drill presses. None of this equipment is automated so we have developed good working relationships with several local machine shops. There are several good local shops with CNC, EDM, water jet, and laser cutting capabilities that can be contracted at reasonable rates. Ray Kozak, the graduate student on this project, teaches our machine shop classes and has worked with several of the local machine shops and material suppliers on previous projects.

Microstructural Analysis

The UNLV Mechanical Engineering Department has a photomicroscopy lab with two 3-wheel sample polishing stations along with a sample potting machine and sanding wheels. The lab has a Unimet Unitron 8644 Inverted Metallurgical Microscope with 800X magnification equipped with a digital camera and computer for recording micrographs. The lab also has a Leco M-400A microhardness tester, several Wilson and Clark Rockwell hardness testers, and a Beuler sample mounting press.

However, the metallographic laboratory needs to be upgraded with a high-resolution optical microscope and accessories to perform microstructural characterization planned in this project. Analyses of hydrogen content by SIMS can be performed at LANL.

Scanning Electron Microscopy (http://www.unlv.edu/Colleges/Sciences/Geoscience/EMIL.htm)

The UNLV Geosciences Department has a JEOL-5600 Scanning Electron Microscope (SEM). It is optimized for imaging micron to millimeter scale topographic detail of solid materials. Resolution of up to 50 nm at 100,000 times magnification is possible. The SEM is equipped with a BSE detector and an Oxford ISIS EDS system, capable of semi-quantitative analysis (± 10%). The topographic and compositional images can be processed directly on the screen to show pseudo-color and critical point measurement of features. The images can also be combined, allowing for easy comparison of samples or different magnifications. The manual stage can accommodate four 1-cm diameter samples or one sample up to 3.2-cm diameter. The SEM and EDS are controlled by two networked Windows 95 operating systems allowing for intuitive, simple operation.

The UNLV Geosciences Department also has the JEOL-8900 Electron Probe Microanalyzer (EPMA). It is optimized for quantitative, non-destructive chemical analysis of solid materials on a micron scale. Four fully automated wavelength dispersive spectrometers (WDS) are equipped with 2 crystals each and are capable of quantifying elements ranging from boron to uranium. Concentrations of at least 0.10 wt % can be measured to within ±1% of the measured abundance. In addition, elements present in smaller concentrations can be measured with somewhat less precision. The energy dispersive spectrometer (EDS) collects a full spectrum of x-rays at once and is capable of rapidly qualifying up to 8 elements at one time. Both EDS and WDS can also be used to obtain high-precision x-ray maps and line scans of spatial variation in chemical composition. The instrument is also equipped with backscattered electron, secondary electron, and cathodoluminescence detectors capable of producing "real time" images, or automated images in tandem with x-ray mapping to further characterize the area of interest. A fully automated stage, capable of holding up to nine one-inch round samples (or six petrographic sections) has reproducibility of less than one micron. Unmounted samples up to 15 cm in diameter can also be accommodated. The EPMA is controlled by a graphical user interface on a HP-UX UNIX workstation. These two instruments are available as a user facility. A fee structure is currently being developed.

Project Timeline

<u>Timeline Narrative</u>

The proposed research is planned over three years, starting in Summer 2001. Raymond Kozak is a Ph.D. level graduate student so he will be expected to work on a longer, more complex problem. In addition, Mark Jones will be pursuing a M.S. degree on a related project. Initial tasks will be ordering bar and plate stock materials and equipment. The UNLV research team (faculty and students) will visit LANL during the first quarter to meet with our collaborators, refine our testing plan, and learn about related projects at Los Alamos. A primary goal early in the project will be to define a set of realistic objectives for Raymond Kozak for his doctoral thesis.

The plate and bar stock will be heat treated at UNLV and machined into test samples at UNLV or at a local machine shop. Corrosion testing will begin when all necessary equipment have been procured and installed, and the samples have been machined. Optical microscopy and SEM will be used to evaluate the tested samples. The effect of hydrogen content on the cracking susceptibility will be evaluated. Attempts will be made to correlate the resultant cracking parameters to the microstructures for the different stainless steels and heat treatments.

Brief quarterly reports will be prepared and detailed semi-annual reports will be written. It is anticipated that Raymond Kozak will complete a substantial part of the experimental work toward his doctoral degree by the end of the second year of this project. He may continue some experimental work during the third year of this project. A two-year schedule is shown in Table 2.

Table 2: Three-Year Research Plan

Time (Months)	3	6	9	12	15	18	21	24	27	30	33	36
Literature Search												
Order Materials												
Order Equipment												
Set-up Laboratory												
Heat Treat Materials												
Machine Samples												
Train Students												
Perform Experiments												
Perform Microscopy												
Perform SEM												
Data Analyses												
Follow-up Proposal												
Quarterly Reports												
Semi-Annual Reports												

Year 1 Milestones (Assuming a start date of May 15, 2001)

- (August 2001) All material and equipment has been obtained.
- (December 2001) Heat Treatments have been completed, sample machining has started.
- (February 2002) HE testing has started.
- (May 2002) Microscopy and SEM have started, data analysis has started, Year 1 report is submitted.

Deliverables

- **Collaboration with DOE project:** Monthly communications (by phone or in person) with National Project collaborator and/or technical lead to update on progress, discuss problems, and allow for re-focusing if necessary to address shifts in direction by the National Project.
- **Ph.D. Degree:** Raymond Kozak will have completed or be very close to completion of his degree by the end of the third year.
- **M.S. Degree**: Mark Jones will complete his degree by the end of the second year.
- **Progress Reports:** Brief reports indicating progress will be provided every quarter (to support DOE AAA quarterly meetings).
- **Bi-Annual Reports:** Written reports detailing experiments performed, data collected and results to date.
- **Final Report:** Written report detailing experiments performed, data collected, results, and conclusions to be submitted at the end of the project.
- **Project Samples:** For archival purposes, samples generated during the experimental campaigns will be turned over to the National Laboratory partner. For experiments where multiple samples were prepared, only one sample will be turned over. This sample archive will allow the Project researchers (either from the National Laboratories or UNLV or other academic partners) to re-examine samples as necessary, either in support of this work or for use in other research projects.

Personnel Responsibilities

Role of the Students

The graduate students will be given a significant amount of the responsibility for this project. Raymond Kozak (Ph.D. student) and Mark Jones (M.S. student) have a significant amount of experience machining test samples, polishing samples for microscopy, and conducting mechanical testing experiments. They will need training in the areas of heat treating, preparing the corrosion test vessels, and preparing and analyzing samples for Scanning Electron Microscopy. The faculty investigators will provide this training. Both of these students have taken several courses in metallurgy, mechanics, experimental mechanics, and manufacturing.

Each student will prepare a prospectus for their thesis or dissertation within the first 3 months of the project clearly delineating their individual research objectives. The M.S. project will focus on the HE studies involving smooth tensile specimens. The Ph.D. project will focus on the advanced level understanding of HE phenomenon through extensive testing and analysis of failed notched specimens and development of related failure mechanisms involving synergistic effects of material, environment, and applied stress.

An undergraduate research assistant will also be hired to help with this project. It is important to involve undergraduates with research so that they are exposed to research opportunities. This student will help with heat treatments, machining, testing, and microstructural analysis as needed.

Role of the Faculty

The primary responsibility of the faculty members on this project is to train students for performing the various research tasks, supervise the writing of their thesis/dissertation, and to provide them with an interdisciplinary working environment. Dr. Roy is currently an adjunct faculty member of the Mechanical Engineering Department and is the leading candidate for a new faculty position within the department. This position will be partially funded by the state of Nevada and the AAA program. The faculty members will assume responsibility for various aspects of the project to ensure that the students make steady progress towards their research goals. The faculty will not be doing the research for the students but will ensure that high quality work is accomplished in a timely manner. Each of the faculty advisors has unique expertise in one or more fields related to this project. The faculty will also be learning from each other.

As the lead PI, Dr. Roy will spend 25% of his time in this project. He will work in close association with Dr. O’Toole in areas of mechanical aspects related to the SSR testing unit. Dr. Roy will be responsible for specifying and ordering test materials from prospective vendors. The students will be included in this process from the beginning. Drs. O’Toole and Roy will perform ordering of the test equipment and setting-up of the laboratory jointly. During the initial phase of this project, Dr. Roy will train the graduate students in areas of electrochemical test techniques, heat-treating practices, microstructural and fractographic analyses. Later, Drs. O’Toole and Roy will train the graduate students on the practical aspects of performing the HE experiments using the SSR method. Dr. Roy will take the lead in specifying and ordering the test specimens from an outside vendor. Dr. Roy will work closely with the graduate students and other supporting staff within the UNLV infrastructure to ensure that the desired data are generated in a timely manner. The graduate students under the direct supervision of both Drs. O’Toole and Roy will record all test data in the scientific notebooks. Drs. Roy and O'Toole will jointly perform data analyses and prepare the interim and final reports. Dr. Hatchet will be responsible for the electrochemical testing and microstructural evaluation. Dr. Wang will be responsible for analyzing the mechanical aspects of fractography. It should suffice to state, that all faculty members would work in close association with graduate students, both in experimental and analytical activities.