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Effect of Silicon Content on the Corrosion Resistance and Radiation-Induced Embrittlement of Materials for Advanced Heavy Liquid Metal Nuclear Systems

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TRP Task 20
Project Title:

Effect of Silicon Content on the Corrosion Resistance and Radiation-Induced Embrittlement of Materials for Advanced Heavy Liquid Metal Nuclear Systems

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AFCI Research Area: **Transmutation Sciences**

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Note: LANL employees do not require funding from UNLV to participate in this project.
ISU employees do not require funding from UNLV to participate in this project.

Abstract

The purpose of this collaborative research project involving the University of Nevada Las Vegas (UNLV), Los Alamos National Laboratory (LANL) and Idaho State University (ISU) is to evaluate the effect of silicon (Si) content on the corrosion behavior and radiation-induced embrittlement of martensitic stainless steels having chemical compositions similar to that of the modified 9Cr-1Mo

steel. Recent studies at LANL involving Alloy EP-823 of different Si content have demonstrated that increased Si content in this alloy may enhance the corrosion resistance in molten lead-bismuth-eutectic (LBE). Since very little data exists in the open literature on the beneficial effect of Si content on the corrosion properties, it seems appropriate to initiate a research project to address this technical issue. This proposal is intended to study the effect of Si content not only on the corrosion resistance but also on the radiation-induced embrittlement of martensitic stainless steels. The susceptibility of these alloys with different Si content to stress corrosion cracking, general corrosion and localized corrosion will be evaluated in the molten LBE and aqueous environments of different pH values using state-of-the-art testing techniques. Testing in the aqueous media is intended to develop baseline data for comparison purpose. Radiation-induced embrittlement of these alloys will initially be studied by irradiating the test specimens with bremmstrahlung gamma radiation from 20-40 MeV electron beams at ISU. These gammas induce (γ, n) reactions in the giant dipole energy region. The principal radiation damage from these irradiations, in turn, stems from the recoiling residual nucleus (with average kinetic energy of approximately 20,000 eV) after the neutrons are emitted. The high penetrability of gammas, whose range is of an order of one meter in steel, ensures that the resulting damage will be uniform over the volume of the sample. The induced activity of these specimens will have very short half-lives (typically minutes) due to the systematics of (slightly) proton-rich nuclei. The resulting radiation-induced hardening can subsequently be evaluated by proper experimental techniques. Later, similar studies can be performed using specimens radiated by neutrons at LANL.

Work Proposed for Year 1 (Fall 2004 –Summer 2005), Goals, and Expected Results:

Four experimental heats of martensitic alloys (similar to Mod9Cr-1Mo) with different Si content (0.5, 1.0, 1.5 and 2.0 weight percent) will be melted by the vacuum-induction melting (VIM) practice at the Timken Research Laboratory (TRL). These heats will subsequently be processed by forging, hot-rolling and cold-rolling, respectively followed by thermal treatments to achieve fully-tempered and fine-grained martensitic microstructures. The thermal treatments to be performed on these alloys will consist of austenitizing, quenching and tempering followed by air-cooling. These heat-treated materials will then used to prepare the desired types of test specimens.

Ambient-temperature mechanical properties will be evaluated by using cylindrical specimens according to the ASTM designation E 8. Microstructural evaluation of all four heats of Mod9Cr-1Mo will be performed by optical microscopy. In order to study the effect of radiation on the tensile and impact properties of the test materials, both cylindrical and Charpy V-notch specimens will be used. The tensile specimens will enable a comparison of mechanical properties including the yield strength (YS), ultimate tensile strength (UTS) and ductility parameters (percent elongation - %El and percent reduction in area - %RA) with and without radiation. The notched Charpy specimens will be tested to determine the impact energy and the ductile-to-brittle transition temperature (DBTT) as a function of the radiation dose. The extent and morphology of failure will be determined by scanning electron microscopy (SEM).

The susceptibility to general and localized (pitting and crevice) corrosion will be determined by using rectangular coupons. The stress corrosion cracking (SCC) susceptibility will be evaluated by using tensile and self-loaded (C-ring and U-bend) test specimens. Both LBE and aqueous environments will be used in the corrosion studies. The critical electrochemical potentials will be determined in the aqueous environments of different pH values as a function of Si content. Fractographic evaluations of all SCC test specimens will be performed by SEM.

Corrosion study using self-loaded specimens in the LBE environment will be performed at LANL. Aqueous corrosion testing, mechanical properties evaluation, impact testing, microstructural and fractographic evaluations will be conducted at UNLV. The test specimens will be radiated at ISU to evaluate embrittlement resulting from radiation-induced hardening of all four heats of these martensitic alloys.

Background and Rationale

It is well known that metallic materials can undergo hardening due to their exposure in radiated environments. While the strength of these materials increases, these materials become more brittle with reduced ductility due to this radiation-induced hardening. Since these materials may become radioactive in the presence of high-level radioactive dose, characterization of the metallurgical properties often requires hot cells to isolate researchers from radioactive contamination. In view of this rationale, the materials to be tested in this program will be slightly activated by bremsstrahlung gamma radiation using low-energy electron beams (20 - 40 MeV) such that the half-lives of these radiated materials will be very short, while achieving the radiation-induced hardening within the core of the metal matrix.

The beneficial effect of enhanced Si content on the corrosion resistance of martensitic stainless steel, as evidenced in the LANL study, may be attributed to formation and growth of silicon oxide (SiO_2) film, thus minimizing the dissolution of surface film with increasing Si content. Alloy EP-823 tested so far at UNLV for characterization of metallurgical and corrosion properties possessed Si content ranging between 1 and 1.15 weight percent (wt%). Data obtained on Alloy EP-823 will be used as baseline information. Therefore, it is proposed that martensitic alloys with compositions similar to that of Mod9Cr-1Mo be tested with four different Si contents of 0.5, 1.0, 1.5 and 2.0 wt% to study the effect of incremental Si content on both the corrosion resistance and radiation-induced embrittlement of these alloys. Since all four VIM heats of these alloys will undergo similar thermal treatments prior to the sample preparation, it is obvious that the resultant microstructure can also be analyzed as a function of these four Si contents.

Experimental Procedure

Martensitic alloys of desired chemical compositions will be received from TRL in the form of bars and plates of desired dimensions. The dimensions of these plate materials will be decided based on the type of specimens to be tested. They will be procured in properly heat-treated conditions. All test materials will be austenitized (1850-1900^{o}F) and quenched, followed by tempering (1150-1200^{o}F) to achieve a fully tempered martensitic metallurgical microstructure. Test specimens will be fabricated from these heat-treated bars/plates. The cylindrical tensile specimens will be machined in such a way that the gage section is parallel to the longitudinal rolling direction. Rectangular coupons will be prepared from the plates in the longitudinal direction. SCC testing using C-ring and U-bend specimens will be performed according to the ASTM designations G 38 and G 30, respectively in both LBE and aqueous environments. SCC testing using cylindrical tensile specimens will be conducted in aqueous solutions using both constant-load and slow-strain-rate (SSR) techniques. A strain rate ranging between 10^{-6} and 10^{-7} sec^{-1} will be used during the SSR testing. The susceptibility to general and localized corrosion will be evaluated by immersion of coupons in both LBE and aqueous environments. In addition, electrochemical polarization studies will be performed at a potential scan rate of 0.17 mV/sec using potentiostats to determine the critical potentials (corrosion, pitting and repassivation) in aqueous environments of interest.

V-notched Charpy specimens will be prepared from the plate materials in such a way that the direction of the notch is parallel to the longitudinal rolling direction. The impact energy and DBTT of all four heats of martensitic alloys will be evaluated with and without radiation according to the ASTM designation E 23. Low-level radiation will be applied to both Charpy and tensile specimens to study the radiation effect. The cylindrical tensile specimens will be tested either in an MTS or Instron equipment.

Metallurgical microstructures will be evaluated by optical microscopy. Fractographic evaluations will be performed by SEM. Transmission electron microscopy (TEM) may be used to analyze voids resulting from radiation hardening, if any.

Expected Data

The proposed research program will develop the following scientific/technical information.

- Metallurgical microstructures as functions of Si content and radiation dose
- Mechanical properties (YS, UTS, %El and %RA) before and after radiation
- Impact resistance (impact energy and DBTT)
- Failure stress, ductility (%El and %RA) and threshold stress for SCC
- Corrosion potential, critical pitting potential and repassivation potential
- General corrosion rate versus Si content
- Extent and morphology of cracking (ductile/brittle, intergranular/transgranular)
- Voids due to radiation damage

Research Capabilities at UNLV

The following equipment are currently available in the Materials Performance Laboratory (Room No. TBE B129) and the Materials Testing Laboratory (Room No. TBE B150).

- Twelve Cortest Constant Load Testing Fixtures (Proof Rings – 7,500 lb Load Capacity)
- Four Cortest SSR Test Frames (Constant Extension Rate Test Fixture - 7,500 lb Load Capacity)
- Twelve High-Temperature (120^0C) Corrosion-Resistant Test Vessels (Hasteloy C-276)
- One High-Temperature (500^0C) Corrosion-Resistant Autoclave (Hasteloy C-276) with Lid having Electrochemical Connections
- Two EG&G Model 273A Potentiostats, and one EG&G eight-channel multiple potentiostat
- One Blue-M 1200^0C Heat Treatment Furnace
- High – Temperature Water Bath and Mettler Electronic Balance, one each
- Twelve Custom Luggin Probes for Polarization under Controlled Electrochemical Potential
- One 1000X Resolution Leica Optical Microscope with Digital Image Capture
- Buehler Sample Preparation Accessories – Isomet 4000 Linear Precision Saw, Abrasimet 2 Abrasive Cutter, Ecomet 6 Variable Speed Grinder/Polisher with Automet 2 Power Head
- One High-Temperature (1000^0C) Furnace with Inert Gas Purge for Tensile Properties Evaluation in Association with an MTS Axial/Torsional Test System (50,000 lb Load Capacity)

<u>Additional Heat Treatment Facilities</u>
Two high temperature furnaces are available:

1) Lindberg Furnace
The maximum temperature is 1200 ^{0}C (2200 ^{0}F). The working dimensions are 15” x 7.5” x 5.5”.

2) Thermodyne Furnace
The maximum temperature is 1200 ^{0}C (2200 ^{0}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, drill presses and a CNC that has just been installed in TBE.

Mechanical Testing

The UNLV College of Engineering has a 55 kip Axial/Torsional Servo hydraulic MTS Materials Testing System. The machine has hydraulically controlled actuator with 5.5" of stroke and approximately 55^{O} of angular rotation. It also has a hydraulic grip supply and two different hydraulic grips: a set of 55 kip axial/torsional collet grips and a set of 27 kip wedge grips. The axial motion can be controlled by force, displacement, or an external signal such as a strain gage. The torsional motion can be controlled by torque, angular position, or an external signal. The machine is equipped with an 8-channel signal-conditioning box from the Measurements Corporation for monitoring strain gages, extensometers, and other sensors. Signals from this box are processed directly by the MTS control software programs TestStar and TestWare SX. Other accessories for this machine include: digital longitudinal and transverse extensometers and a digital deflectometer. This machine has been used for tensile, torsion, flexure, and compression testing of metals, polymer composites, and polymer foams.

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. 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 has currently being developed.

Transmission Electron Microscopy

A transmission electron microscope (TEM) has recently been installed at the Harry Reid Center, which is currently operational for metallurgical analyses.

Research Capabilities at ISU

The Idaho Accelerator Center at Idaho State University (ISU) provides opportunities for nuclear physics research and development to university, industrial, and governmental organizations. The center combines accelerators owned by the U.S. Department of Energy and the state of Idaho with the university's facilities and the technical expertise of university faculty and researchers. The IAC's mission is to conduct and to promote research and development in radiation science and accelerator applications. The laboratory creates partnerships with scientists and engineers in government, university and the private sector designed to lead to new advances and practical applications in nuclear and radiation science. The Center occupies some 16,000 square feet of laboratory space on the Idaho State University campus, including the new Accelerator Center Building completed in October 1998, which houses Center operations and the major electron Linear Accelerator (LINAC). Center management is in the hands of a director and two part-time associate directors. Proposals for accelerator and facilities usage and advice on operations are given by a Users Advisory Group comprised of representatives from the university and national laboratories. Strategic direction and peer review is given by the Advisory Board, a group of nationally prominent scientists, public policy and business leaders.

The Center has available the following accelerators:

1. A 30 MeV electron linac which can produce 10 to 50 ps, 10nC pulses in the short pulse mode. The energy range in this mode is 0.5 to 28 MeV. Long pulses to 4 microseconds are also available. Repetition rates are to 360Hz. Beam energy spread can be as small as 0.5%. Three beam ports are available.
2. Two Van de Graaff type positive ion accelerators one is equipped for materials analysis studies (back-scattering, PIXE, channeling, etc.). The other Van de Graaff is principally for variable energy neutron production, using (p,n) and (d,n) reactions.
3. A mobile, variable energy (2-12 MeV) electron linac for photo-nuclear studies and applications.
4. A 6 MeV electron linac, equipped for radiation effects studies can deliver high radiation dose rates with precision dosimetry.
5. An 18 MeV electron linac for photo-nuclear studies.
6. A field portable 4MeV electron linac for radiography and neutron generation.
7. A large-scale industrial Scientific Measurements Systems x-ray tomography system, which can be equipped with 450keV or 4MeV x-ray source.
8. Two electron linacs (20 and 40 MeV) dedicated to high dose-rates for radiation effects studies. These will be the primary radiation-damage accelerators for this research.

The Center has available a wide range of nuclear detector types, including neutron detectors, and supporting electronics. Custom electronics and mechanical design and fabrication are available.

Research & Applications

Current research activities include:

Radiography, tomography and nuclear techniques for NDE/NDA.
Industrial and agricultural applications of accelerator-produced radiation.
Ion and photon beam analysis for environmental and mineral extraction needs.
Radiation science in medicine; radioisotope production, accelerator based neutron sources
BNCT and other forms of neutron therapy.
Instrument and radiation detector testing for weapons surety studies and other applications.

Education

The Idaho Accelerator supports educational activities at all levels of ISU's academic areas, including:

Physics
Health Physics
Engineering
Waste Management
Geology
Biological Sciences
Health Sciences

Facilities and services

Two other IAC facilities on campus house positive ion accelerators, scanners, imaging facilities, and support services. This arrangement provides a venue for convenient, inexpensive proof of principle testing, integrated demonstrations, and basic research. The broad range of ongoing scientific and engineering activities facilitates collaboration from a variety of private, university and governmental agencies, while providing an academic research environment with all the amenities of a university.

The Center can provide in house expertise in:

Neutron and photon transport calculations using various codes including MCNP, and ACCEPT.
Neutron spectroscopy using various detector types
A wide range of nuclear and radiation measurements
Precision dosimetry for gamma radiation and neutrons

Research Capabilities at LANL

Los Alamos National Laboratory (LANL) has a molten Lead Bismuth Eutectic (LBE) testing facility that will be used to evaluate the susceptibility of the test materials to SCC in the molten LBE.

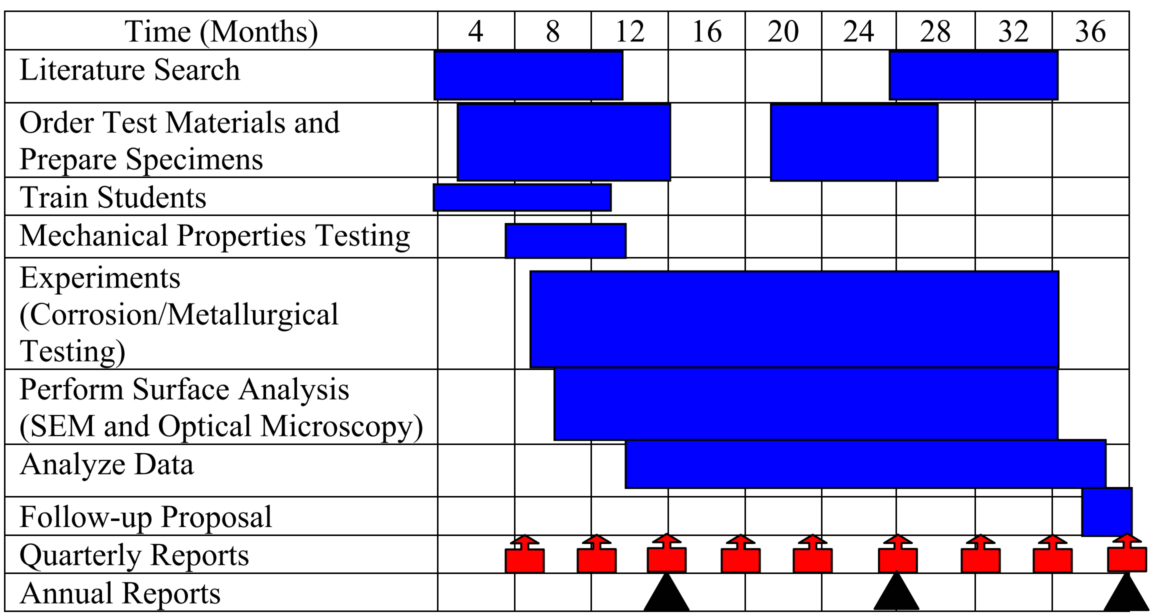
Project Timeline

Timeline Narrative

The proposed research is planned for three years, commencing in the fall of 2004. Initial tasks will be performing literature search in relevant areas and ordering test materials from TRL. Heat treatment will be performed in Materials Performance Laboratory (MPL). Subsequently, different types of test specimens will be manufactured at reliable machine shops according to the specified drawings. Various types of testing will be performed to study the effect of Si and radiation Embrittlement. The tested specimens will be cut to desired sizes for performing metallographic and fractographic studies using optical microscopy and SEM. The UNLV research team (Faculty and Students) will visit ISU to radiate test specimens. In addition, the research team will visit LANL to coordinate insertion of test specimens into the LBE loop. Emphasis will be placed to define a set of realistic research objectives for two graduate students to develop and pursue their thesis topics for doctoral studies.

Brief quarterly reports and detailed annual reports will be written. Efforts will be made to prepare technical papers and present them in conferences followed by subsequent publication in journals. It is anticipated that the two graduate students will be able to complete their doctoral degree by the end of third year of this project. It is also expected that a follow-up proposal will be submitted by the end of the third year. A three year schedule is shown in Table 1.

Table 1: Three-Year Research Plan



Year 1 Milestones (Assuming a start date of September 01, 2004)

- (September 2004): Initiate materials procurement (TRL).
- (November 2004) Heat treatments have been completed, sample machining has started.
- (December 2004) Testing initiated.
- (February 2005) Metallographic / Fractographic evaluations initiated.
- (August 2005) Prepare first year draft report.

Deliverables

- **Train Graduate Students:** The primary deliverable will be to train two graduate students in a field relevant to the national AFCI program needs. An undergraduate student will also be added to train in relevant technical areas.
- **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.
- **Progress Reports:** Brief reports indicating progress will be provided every month, quarter, and year.
- **Bi-Annual Reports:** Written reports detailing experiments performed, data collected, and results to date to support Semi-Annual Review presentations and reports.
- **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.

Roles and Responsibilities

UNLV Researchers

As Principal Investigator (PI), Dr. Roy will take the lead in the overall coordination of this project. He will assume responsibility for many different aspects of this project to ensure that all desired tasks are accomplished in a timely and cost-effective manner. He will train both graduate students for performing the various research tasks, supervise the preparation of their thesis, and provide them with an interdisciplinary working environment so that they can make steady progress towards their research goals. As their supervisor, Dr. Roy himself will not perform the related research work but will ensure that high quality work is performed by these students through continuous guidance and consultation in areas of metallurgy, mechanics, thermal treatment, corrosion science, fractography and fabrication techniques. He will also be responsible for specifying and ordering test materials from prospective vendors. The graduate students will conduct and monitor the related experimental work, and will record all test data in the scientific notebooks under the supervision of the PI. Dr. Roy will analyze the resultant data, and will subsequently outline the follow-up experimental work to be performed by the graduate students. He will also prepare the interim and final reports.

ISU Collaborators

Dr. Doug Wells, Associate Professor at ISU/IAC will be responsible for arranging the radiation experiments of the desired test specimens at ISU that will undergo comprehensive metallurgical testing (Tensile/Charpy) at UNLV. Also, he will be involved in direct interaction with UNLV faculty/students on a routine basis.

LANL Collaborators

Drs. Stuart Maloy and Ning Li at LANL will be responsible for coordinating the corrosion testing involving self-loaded test specimens in the molten LBE environment. They will also evaluate the overall test data as they become available.

Condensed Matter and Thermal Physics Group
MST-10, Mail Stop K764
PH: 665-6677 FX: 667-7443

Date: February 17, 2004

From: Ning Li, Ph.D.
Project Leader, LBE Technology Development, AFCI
Subject: Support Statement

To Whom It May Concern:

This letter is provided in support of the proposed project "**Effect of Silicon Content on the Corrosion Resistance and Radiation-Induced Embrittlement of Materials for Advanced Heavy Liquid Metal Nuclear Systems**", for which I'll serve as a national lab collaborator.

Through the recent experimental investigations at LANL, MIT and other international organizations, the effect of Si on enhancing corrosion resistance of steels in LBE is becoming evident. So far we have been testing Fe-Si, Fe-Si-Cr alloys aiming to understand the mechanisms. Modifying qualified US/European/Japanese nuclear-grade steels (e.g. Mod9Cr-1Mo) with Si addition and testing the changes in corrosion resistance along with mechanical properties and radiation damages had become a top-priority task for AFCI/Gen IV LFR lead-alloy materials R&D.

I have discussed the program priority with Prof. Roy, and helped modified the scope and material candidates accordingly. Within the LANL project, we're beginning to implement development and testing tasks that can be very synergistic with the proposed task. In addition, the collaboration with IAC to irradiate with the electron-beam facility, although not as prototypic, provides rare opportunity to irradiate specimens in contact with LBE. This proposed project meets the UNLV TRP objectives, with substantial additional value for the US DOE Gen IV Program as well. I will strongly support this project.

Yours sincerely,

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(Ning Li)