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Experimental investigation of steel corrosion in Lead Bismuth Eutectic (LBE): characterization, species identification, and chemical reactions

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Abstract:

The goal of the present research is to achieve a basic understanding of corrosion of steels by Lead Bismuth Eutectic (LBE). Liquid LBE is under consideration in the transmuter as both a spallation target and as a blanket coolant. There have been previous studies of LBE, especially by the Russians, who have over 80 reactor-years experience with LBE coolant in their Alpha-class submarine reactors. However, a fundamental understanding and verification of its role in the corrosion of steels is still very incomplete. We have begun a program of post-experiment testing and analysis on steel samples that have been in intimate contact with LBE. We have employed surface analysis techniques, including Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDAX) spectroscopy, and X-ray Photoelectron Spectrometry (XPS). These techniques, applied to the steel surface, have probed the surface morphology, elemental analysis and oxidation states as a function of position. The measurements were made using the facilities at UNLV. Chemical alterations and resulting chemical species are studied at the steel surface. We plan to use micro-Raman and powder X-ray diffraction in the near future. In addition to these well-established laboratory-based instrumentation approaches at UNLV, we have begun to use a state-of-the-art synchrotron-based spectroscopy and microscopy technique, the X-ray fluorescence microprobe at the Advanced Light Source, at Lawrence Berkeley National Laboratory. We have begun to characterize spectroscopically both the LBE and the stainless steel before and after they interact to determine their composition, including minor components such as chromium and nickel. The proposed research moves toward establishing a rigorous experimental database of experimental measurements of LBE and its reactions with steels. Such a database can be used by DOE scientists and engineers in engineering efforts to control, avoid, and/or minimize the effect of corrosion of steels by LBE, under conditions appropriate to the transmuter. One paper has been accepted by the *Journal of Nuclear Materials*. Two graduate students and an undergraduate student are working on the project. One student MS degree is expected in May 2002.

Background and Rationale:

In proposed plans for accelerator transmutation of nuclear waste, intense beams (e.g., up to 45 mA) of medium-energy (e.g., 1000 MeV) protons strike a spallation target, producing neutrons, which sustain fission reactions in the nuclear waste, transmuting it to materials with no radioactivity or radio-isotopes with short half lives. This process places stringent requirements on the materials to be used in the construction of the facility: materials must be capable of withstanding very high neutron fluxes, elevated temperatures, and chemical corrosion. Material science questions may in fact be critical to the feasibility of the entire transmutation project. Materials must be found for a coolant that can conduct away the high heat (Megawatt) load. Materials must also be found to serve as a spallation target, converting the incident proton beam to neutrons. Lead-Bismuth Eutectic (LBE) has been proposed for use in the transmuter, where it can serve two purposes: both as a coolant (removing heat from the nuclear waste) and as a spallation target (generating a neutron flux from the incident proton beam).

The LBE circulates within stainless steel piping and containers. An absolutely critical question is whether LBE can be engineered to be compatible with the stainless steel walls that contain it with sufficient lifetime. The deleterious process is the corrosion of stainless steel that has been in intimate contact with LBE. The 1999 *Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology* lists “Coolant Chemistry and Materials Compatibility” under the Target/Blanket R&D Activities.

The Russians have 80 reactor-years of experience with LBE coolant loops in their Alpha-class nuclear submarines, and they have performed laboratory studies of the reactions of LBE with US steels. Los Alamos scientists have reviewed these studies [He and Li, (2000)], in which several US steels [316 (tube), 316L (rod), T-410 (rod) HT-9 (tube), and D-9 (tube) and one Russian steel EP823 rod)] were corrosion-tested. Los Alamos scientists have built a medium-scale LBE materials test loop (MTL). The Los Alamos loop was first turned on in December 2001, and will be ready to run unattended in April 2002. In addition, UNLV is scheduled to receive an LBE loop from Russia in n the next few months.

There are still very important gaps in our understanding of the chemistry of corrosion in the LBE/steel system. For example: what are the chemical species created during the corrosion process? What are the chemical reactions occurring? What is the morphology of the interface at both the macroscopic and microscopic scale? How do these reactions depend on temperature and the presence of trace elements? What is the heterogeneity of the corrosion process in a LBE system? What are the chemical species involved in the reaction as corrosion products? What about oxides of contaminant metal ions that may leach from the stainless steel during the course of the reaction of the LBE at the interface? Which metal ions are involved, and which chemical form do they exhibit? What is the oxidation state of each of the elements? What is the electronic structure of each of the elemental ions? What is the magnetic configuration of each of the appropriate ions? Is there any evidence for passivation at the interface of the reaction of the LBE with the steel substrate?

Answering these questions is necessary in order to understand the corrosion process, and hence to be able eventually to engineer the system in order to control or minimize the various corrosion processes in the LBE/steel system.

Research Objectives and Goals:

The research objectives are:

To elucidate the mechanism(s) and kinetics of corrosion in LBE/steels, which have not been studied in detail.

To determine the signature of the lead oxides, bismuth oxides and other chemical species in samples of steels that have been in intimate contact with LBE.

To determine the forms of solid oxides from corrosion products and lead and bismuth.

To measure the different responses of different kinds of steels to LBE.

The goals are:

To understand the difference in corrosion behavior between different types of select candidate steels.

To determine whether or not particular compositions of steels could be tailored to be especially corrosion-resistant, especially with regard to Si and Al.

To provide an understanding of corrosion of steels by LBE that will allow the realistic formulation of strategies for passivating surfaces, minimizing corrosion, periodically flushing and cleaning of corrosion products, or lengthening service lifetime under realistic conditions.

To advance the overall understanding of corrosion in LBE/steel systems.

Technical Impact

Raman and infrared can differentiate among the different structural phases of elemental oxides in the LBE/steel reaction systems, while, at the same time, giving a lateral mapping of the different species on the surface. X-ray photoelectron and Auger spectroscopy can give valuable information on the oxidation state, chemical state (including species), and the electronic and magnetic configuration of several of the metal ion species as a result of experimental parameters in their spectra. By using Auger transitions observed in the x-ray photoelectron spectra, one can also derive valuable chemical information about the products formed at the LBE/steel interface. Spectroscopic data such as these can be combined with microscopic data, along with x-ray diffraction data, which can be used to fingerprint structural forms of the elemental species formed in the reactions. The proposed work will make a major contribution to the understanding of the mechanism of corrosion in LBE/steel systems.

Research Approach

Samples will be characterized using a number of experimental techniques:

(1) Electron Probe Microanalyzer (EPMA). In this test, a high voltage focused electron beam strikes a solid sample, causing fluorescence in the x-ray spectral region. The x-rays are characteristic of the kind of atom. This instrument is capable of measuring elements from boron (Z=5) through uranium (Z=92). This reveals the elemental analysis as a function of position. It does not reveal speciation; i.e., it does not provide information about the chemical species. This is being performed at UNLV by graduate students Dan Koury and Brian Hosterman under the supervision of John Farley and Allen Johnson with much help from a staff scientist, Dr. Clay Crow, whose formal title is “Instrumental Analyst”. This shows the presence of oxides and their spatial distribution, with a spatial resolution of about a micron. Tests have started on steel samples and LBE samples, before and after exposure contact between steels and LBE. When analysis is complete, this will allow us to identify the elements present in the samples. After analyses, we can formulate hypotheses about the chemical reactions that give rise to such species.

(2) XPS/Auger. In this technique, the sample is illuminated by x-rays, and the resulting photoelectrons are energy-analyzed. Some of the photoelectrons arise from Auger transitions within the sample. Such Auger transitions are characteristic of the element. This measurement will be performed by graduate students Dan Koury and Brian Hosterman, under the supervision of John Farley and UNLV chemistry professor Allan Johnson, who is the UNLV contact person for this instrument. These measurements have already begun. Denise Parsons, an undergraduate student, is of great help in the analysis of XPS data.

(3) MicroRaman system. Raman data are taken from an extremely localized area on the surface of a sample. This Raman spectrum will be indicative of both the chemical species, and, in many cases, the structural polymorph, i.e., different structural phases of the same chemical compounds. This technique has a spatial resolution of a few microns along the surface. The measurements will be performed by graduate students Dan Koury and Brian Hosterman, under the supervision of John Farley and staff scientists at the HiPSEC Materials Laboratory in the UNLV physics department, where this instrument resides. These measurements will start in Spring, 2002.

(4) X-ray diffraction. In this technique, a x-ray source (copper K-, rotating anode) illuminates the sample, and an imaging plate collects the x-ray diffraction pattern. We can scrape a sample of powder from the surface, and perform x-ray diffraction on the powder. This reveals the crystal structure of the sample. These measurements will be performed by graduate students Dan Koury and Brian Hosterman, under the supervision of John Farley and UNLV physics professor Malcolm Nicol, in whose laboratory this instrument resides. These measurements will start in spring 2002.

(5) The four techniques mentioned so far employ laboratory instruments at UNLV. In addition, we plan to perform tests using synchrotron-based x-rays. Synchrotron radiation-based (SR) x-ray fluorescence (XRF) will be used, because it has been proved to be a sensitive analytical technique capable of providing direct quantitative information on chemical compositions. The x-ray fluorescence technique will give a detailed mapping (with a 1 micron resolution) of the heavy metal ions being studied. The sensitivity of the synchrotron x-ray fluorescence microprobe for many metals can approach the femtogram (10^{-15}) level, one of the most sensitive of spectroscopic techniques that can be employed in conjunction with microscopic imaging. Synchrotron-based x-ray fluorescence microprobe techniques have been used by Dale Perry and co-workers Perry *et al, Appl. Spectrosc.*, **51**, 1781(1997)] to map different metals such as calcium, nickel, and potassium, for example, in films of complex quaternary metal oxides.

We wish to emphasize that these experimental techniques have already proven productive in the hands of Perry and co-workers. The proposed research uses the techniques of x-ray fluorescence (XRF) spectromicroscopy, x-ray photoelectron (XPS), and Auger electron spectroscopy (AES) to study the metal ions and their reaction chemistry. Perry and co-workers (*Inorg. Chim. Acta (Chemistry of the f-Block Elements), 127,* 229(1987); *J. Mat. Sci. Lett., 5,* 384(1986); *Inorg. Chim. Acta (Chemistry of the f-Block Elements), 127,* 229(1987); *J. Appl. Phys. 78*, 5356(1995)) have used XPS to study several metal ion systems, along with combined XPS/AES (*Applications of Analytical Techniques to the Characterization of Materials*, D. L. Perry, Plenum Press, 1992), along with lead and oxides and associated compounds (*J. Vac. Sci. Technol. A, 2*, 771(1984)). Raman spectroscopy has been used by the same group to study the chemistry and bonding of a variety of metals, including uranium (*Spectrochimica Acta 49A,* 975(1993); *50A*, 757 (1994)).

After taking the data, the analysis phase begins. Of course data alone, without the necessary analysis or interpretation, cannot yield scientific understanding. Typically the analysis and interpretation phase takes much longer than the actual data taking. The analysis and interpretation are intended to yield a consistent picture of the chemical species present and their spatial heterogeneity, the chemical reactions occurring in the LBE/steel system, and the dependence of the chemical reactions upon composition, temperature, and time. When the analysis and interpretation is complete, we will submit the results for presentation at scientific meetings, incorporation in student theses, and publication in the peer-reviewed scientific literature. Dale Perry, an expert in the field, will be of great help to the graduate students in the analysis portion of the work.

Progress achieved in the first eight months

Human resources: This project began in June 2001. Progress has been rapid in the first eight months. The research group has come together rapidly. At the beginning of June 2001, there were two only members of the group (John Farley and Dan Koury). Brian Hosterman enrolled in the graduate program in fall 2001. UNLV Chemistry Professor Allen Johnson joined the group in fall 2001. His expertise on the XPS was absolutely crucial in getting the XPS experimental apparatus up and running, and keeping it running.

The XPS effort has benefited from the efforts of an undergraduate student, Denise Parsons, who has a wealth of experience for Los Alamos at the Yucca Mountain Project (and previously at the Nevada Test Site). She is working with us analyzing the XPS results. She was particularly helpful in preparing the presentation at the winter ANS meeting in Reno. We are very pleased to be able to give her the opportunity to continue to pursue this kind of research.

The technical results can be summarized as follows:

Results obtained using SEM/EDAX

Studies on 316 stainless steels have shown amorphic oxidation buildup on steel surfaces. SEM imaging reveals significant differences in oxidation buildup between samples exposed for different times and for different steels. Oxide thickness measurements agree fairly well with the Russian reports. EDAX has revealed significant amounts of oxygen and iron in the top several microns of the oxidation layer as compared to the unoxidized steel. On the other hand, very little chromium, if any, is seen in the EDAX data but is presumed to be present at a greater depth than SEM can probe.

Future studies planned are SEM investigations of alternative steel candidates, EDAX studies of their corrosion, investigation of ion milled and sectioned samples, and studies of samples generated by the US test loops at LANL and the one planned for UNLV.

Results obtained using XPS

Surface contaminants are present and dominate the spectra of the as-received 316 and 316L samples, as expected since XPS is sensitive to the top several layers of atoms, in comparison to EDAX which probes hundreds to thousands of atomic layers deep. Investigations using sputter depth profiling quickly removed the surface constituents and revealed enhancement of iron and oxygen in the corrosion layer as compared to the starting steel, in agreement with the EDAX data. Further depth profiling showed a changing iron content on a background of constant corrosion layer composition. Preliminary oxidation state analysis of the corrosion layer on 316 steel indicates that the ratio of iron oxides also change as a function of depth. This leads to the hypothesis that there is a considerable amount of iron oxides in the surface and near-surface regions (~10 um depth) and that the changing iron composition with depth indicates a chemically dynamic system, perhaps with iron migrating from the steel to form the corrosion layer. Chromium in the corrosion layer is much weaker than in the starting steel. So far, our results agree well with those in the literature.

Future studies planned are deep sputter profiling of the current steels to determine the fate of the surface chromium oxide layer and to calibrate the depth profiling. Alternative candidate steels will be investigated, as well as samples from local test facilities.

Contacts are in place to use small spot XPS analysis (using the Advanced Light Source at LBNL) to investigate chemical states of regions in the 2-10um size regime. Some exploratory work suggested that silicon may be forming inclusions. This kind of information will be useful in determining the cause of the formation of "islands" in the initial corrosion of the steels. Allen Johnson performed some preliminary work at the ALS beamline 7.3.1.2 this fall, using microXPS.

Capabilities at the University, Los Alamos, and Lawrence Berkeley Lab (Advanced Light Source)

Electron Probe Microanalysis facility. UNLV. Geosciences. Clay Crow, instrumental analyst and contact person

MicroRaman system. UNLV. HiPSEC Materials Laboratory, Physics Dept. Malcolm Nicol, faculty contact person.

X-Ray diffraction system. UNLV. Laboratory of Physics Prof. Malcolm Nicol.

XPS/Auger. UNLV. Housed at DRI; UNLV Chemistry Prof. Allen Johnson, contact person

X-ray fluorescence microprobe. ALS Beamline 10.3.1. Dale Perry, contact person.

A wide variety of standalone equipment, Lawrence Berkeley National Laboratory. Dale Perry, contact person.

Lead-Bismuth Eutectic (LBE)/steel Materials Test Loop (MTL), at Los Alamos. Ning Li, contact person.

Project Timeline: Progress achieved during the first year (2001-2002)

Timeline narrative

The original (Feb, 2001) proposal described a research program that will take three years to complete. The original proposal contained timeline describing the expected technical results, milestones, and deliverables for the **first year only**. This is a brief review of the progress achieved so far in the first eight months of the first year.

Proposed: The two graduate students will become familiar with LBE, its scientific literature, and the major pieces of scientific instrumentation.

Achieved: The two graduate students are familiar with LBE and with three of the major pieces of scientific instrumentation: SEM, EDAX and XPS. A critical review of the scientific literature on LBE is underway.

Expected technical results for the first year

Proposed: Documentation of the chemical forms and states of elements in various candidate steels of interest; understanding of the exact composition of the steels.

Understanding of the different lead oxide phases in precipitation.

Understanding of the different bismuth oxide phases in precipitation.

Preliminary determination of the metal oxide phases formed in LBE/steel reactions.

Achieved: Important progress towards this goal has been achieved. Our conclusions are incorporated into the presentation made by our group at the Winter ANS meeting (September, 2001) and into the manuscript accepted by *J. Nuclear Materials*.

Milestones proposed for first year (June 1, 2001- May 30, 2002)

Familiarization with the major pieces of equipment at UNLV by graduate student Dan Koury (September, 2001). The second graduate student, Brian Hosterman, will start at UNLV in September, 2001.

This milestone has been met. Brian Hosterman arrived at UNLV and is doing well.

Familiarization with the scientific literature of LBE by both graduate students (December, 2001).

The students are becoming familiar with the scientific literature, primarily articles in the *Journal of Nuclear Materials.*

Take preliminary measurements of LBE and appropriate steels and products formed in the reaction between LBE and steels (March, 2002).

This milestone has been met ahead of schedule.

Study of the different phases produced, depending on the results from the previous point (May 30, 2002).

We already have some data addressing this question.

Deliverables for the first year

Collaboration with DOE project: Monthly communication with phone or email with Dr. Ning Li, National Project collaborator to update on progress, discuss problems, and allow for re-focusing if necessary to address shifts in direction by the National Project.

We are collaborating with Dr. Ning Li, and also with other Los Alamos scientists involved in the LBE project.

Progress Reports: Brief reports indicating progress will be provided every quarter (to support DOE AAA quarterly meetings).

First Manuscript submitted to peer-reviewed scientific journal May 30, 2002 for publication.

Our first manuscript was submitted in Fall, 2001, ahead of schedule. It has been accepted by the *Journal of Nuclear Materials*.

Data to be incorporated into student theses.

Data has been obtained that will be part of the MS thesis of graduate student Dan Koury expected for May, 2002.

Project Timeline for the second year (June 1, 2002 - May 30, 2003)

Expected technical results for the second year

The various types of data will yield the elemental composition of the samples and the spatial distribution of elements, both before and after corrosion.

The working hypothesis of the proposed research is that trace amounts of oxygen in LBE are important in the corrosion processes in bismuth-lead eutectics and their interaction with steels and other system components. Metal oxides may be formed as a result of leaching of the contaminant parent metal from the steel matrix as coolant contaminant.

Accordingly, we expect to learn the chemical species present and their spatial heterogeneity, the chemical reactions occurring in the LBE/steel system, and the dependence of the chemical reactions upon composition, temperature, and time.

Examination of LBE/steel surface using Raman spectrometer at UNLV.

Determination of vibrational frequencies from our Raman data, other published experimental data, and calculated values in the literature.

Interpretation of Raman vibrational frequencies of the LBE/steel samples in terms of possible chemical species present, in conjunction with Raman data from the literature on high-quality pure standards.

Experimental study using XRD (x-ray diffraction) to probe the LBE/steel system, either by using powder diffraction of the corroded material, or by using X-ray diffraction of the bulk material. This experimental technique may or may not yield useful for these samples. We will find out.

<u>Milestones for second year (June 1, 2002 - May 30, 2003)</u>

Familiarization with Raman spectrometer system by graduate students

Testing of scientific hypothesis about nature of corrosion process in LBE/steel system.

Examination of more LBE/steel samples having undergone different exposure conditions.

<u>Deliverables for second year</u>

> **Continued collaboration with the DOE project**. Monthly communication by phone or email with Dr. Ning Li, National Project collaborator to update on progress, discuss problems, and allow for re-focusing if necessary to address shifts in direction by the National Project.
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> **Collaboration with LBE loop project at UNLV**. An LBE loop is scheduled to arrive at UNLV from Russia. We will collaborate with that project.
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> **Collaboration with LBE modeling effort at UNLV**. Two UNLV faculty members from Mechanical Engineering (Y. T. Chen, Samir Moujaes) have proposed a modeling study of the hydrodynamics of LBE flow. If they are funded, we will collaborate with them.

Progress Reports: brief reports indicating progress will be provided every quarter (to support DOE AAA quarterly meetings).

Second manuscript submitted to peer-reviewed scientific journal by May 30, 2003 for publication.

Data to be incorporated into student theses.

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