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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. The Russians found that the presence of small amounts (ppm) of oxgen in the LBE significantly reduced corrosion. However, a fundamental understanding and verification of its role in the corrosion of steels is still very incomplete. We are carrying out 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), and laser Raman. 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 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 are characterizing spectroscopically the stainless steel before and after interaction with LBE 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. Our first paper was published in the refereed conference proceedings of the ANS. Four graduate students and an undergraduate student are working on the project and a fifth graduate student will be added in year three. The first student MS degree was conferred in December 2002. We are collaborating with LBE experimental efforts at LANL and the proposed LBE Small Experiments Facility at UNLV.

Scientific background:

The UNLV Transmutation Research Program (TRP) is part of the Advanced Fuel Cycle Initiative (AFCI) within the Advanced Nuclear Research Office (NE-20) at DOE. The plans for transmutation of nuclear waste involve the use of reactors or accelerators to transmute spent nuclear fuel, reducing the volume and radiotoxicity of the waste. The transmutation process places stringent requirements on the materials to be used: materials must be capable of withstanding very high particle fluxes, elevated temperatures, and chemical corrosion. Materials must be found for a coolant that can conduct away the high heat load. Materials questions are critical to the feasibility of the entire transmutation project.

Lead-Bismuth Eutectic (LBE) has been proposed for use in the transmuter, where it can serve two purposes: both as a spallation target (generating a neutron flux from the incident proton beam in accelerator-driven systems) and as a coolant (removing heat from the spent fuel, in either accelerator-driven or reactor-driven systems). LBE circulates within stainless steel piping and containers. An absolutely critical question is corrosion in the LBE/stainless steel system. 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 (DELTA loop), and started it up in December 2001. In addition, UNLV has received an LBE loop from IPPE (Russia). Finally, UNLV has planned a LBE Small Experiments Facility, which will enable researchers to perform benchtop experiments using LBE.

In the 1960's, the Russians found that the presence of small amounts (ppm) of oxygen in the LBE significantly reduced corrosion. However, 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 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? What is the oxidation state of each of the elements? 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. LBE research is valuable to transmutation research whether DOE ultimately selects accelerators or reactors for transmutation, because coolants that are compatible with high-energy-spectrum neutrons will be needed elsewhere in the transmutation scenarios and in the DOE complex. More generally, materials questions are important to many parts of the transmutation effort. The behavior of materials subjected to high neutron fluxes at high temperatures is of particular interest.

Research Goals and Objectives:

The goals are:

- To understand the difference in corrosion behavior between different types of selected 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.

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.

Technical Impact:

Although there is vast technical literature about the conventional redox corrosion of steel (e.g., Lai, 1990; Schreier et al., 1994; Schultze, 1997; Talbot and Talbot, 1998), understanding conventional corrosion is not enough to understand the unconventional corrosion of steel by LBE. The proposed work will make a major contribution to the understanding of the mechanism of corrosion in LBE/steel systems. At the meeting of the Liquid Metal Advisory Group (August 1-2, 2002, at UNLV), representatives from LBE groups around the world (e.g., KALLA, MEGAPIE, MYRRHA) agreed on two points: (1) that basic research into corrosion in the steel/LBE system would be valuable to them, but (2) that they were not able to perform such research, because of the stringent timetable for their engineering program.

Research Approach:

Samples have been characterized using a number of experimental techniques. Each technique has its own strength. 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.

(1) Electron Probe Microanalyzer (EPMA). Electron bombardment of the sample produces x-ray fluorescence. This instrument measures the elemental composition as a function of position. It does not reveal the chemical species. This shows the presence of oxides and their spatial distribution, with a spatial resolution of about a micron. Tests have been performed on steel samples, before and after contact between steels and LBE. This allows us to identify the elements present in the samples, and to test models of the chemical reactions that give rise to such species.

(2) XPS/Auger. The sample is illuminated by x-rays, and the resulting photoelectrons are energy-analyzed, revealing the elemental composition as a function of position on the surface. In addition, we can perform "depth profiling" of the sample. by using ion bombardment to strip away the surface of the sample, followed by a subsequent XPS study. This reveals the elemental composition as a function of depth as well. The thickness and composition of the oxide layer is of particular interest. This procedure allows us to obtain data that are relevant to the question of migration of material during the corrosion process. Undergraduate student Denise Parsons has been of great help in the analysis of XPS data. Perry and co-workers have used XPS extensively (Perry et al., 1984; 1985; 1986, 1987; 1992).

(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 new measurements are being performed by graduate student Brian Hosterman in the UNLV physics department. Raman spectroscopy has been used by Perry and co-workers to study the chemistry and bonding of a variety of metals, including uranium (Perry et al. 1993; 1994).

(4) X-ray diffraction. In this techique, a x-ray source (Cu K-α rotating anode) illuminates the sample, and an imaging plate collects the x-ray diffraction pattern, revealing the crystal structure of the sample. These

measurements will be performed in the laboratory of Malcolm Nicol, starting in spring 2003. We plan to analyze powder scraped from the surface. This definitely can give information about the bulk material, and possibly reveal the crystal structure of the oxide layer. It is important to know whether or not the oxide layer is a spinel.

(5) The four techniques mentioned so far employ laboratory instruments at UNLV. In addition, we plan to perform tests using synchrotron radiation (SR)-based x-ray fluorescence (XRF), a sensitive analytical technique capable of providing direct quantitative information on chemical compositions. The x-ray fluorescence technique will give a detailed mapping (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} g) level, one of the most sensitive of spectroscopic techniques. Dale Perry and co-workers (Perry *et al.*, 1997) has used this technique to map different metals such as calcium, nickel, and potassium, for example, in films of complex quaternary metal oxides.

The data are analyzed and compared with the predictions of models. Fortunately, Los Alamos scientists Ning Li and his postdoc Jinsuo Zhang (He, Li, and Mineev, 2001; Li, 2002) have developed a model for corrosion in the steel/LBE system. 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. Our results are presented at scientific meetings, incorporated into student theses, and published in the peer-reviewed scientific literature. Dale Perry, an expert in the field, is of great help to the graduate students in the analysis portion of the work.

Progress achieved in Year Two

Human resources:

At the beginning of year 2, there were two graduate students in the project: Dan Koury and Brian Hosterman. A third physics graduate student, Umar Younas, was admitted to the graduate program in physics in January 2003. A fourth graduate student, Julia Manzerova, was admitted to the graduate program in chemistry in January 2003. Thus, during the second year, the number of graduate students doubled from two to four.

In addition, 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. 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:

We have investigated the composition of oxide layers in 316, 316L, and similar alloys exposed to oxygen controlled LBE at IPPE using the technique of XPS/sputter depth profiling. Superficially, we observed that the lead and bismuth was confined to the surface of the oxide – there was little or no penetration of the coolant into the protective oxide layer. We found two forms of oxide layer – on 316 and the other alloys we found a complicated structure, with a surface composed primarily of iron oxide and an underlying oxide with both chromium and iron (work is currently underway to determine if this is a physically mixed oxide or a chemical (i.e. spinel) mixed oxide). Interestingly, on the 316L sample we observed a simpler chromium oxide layer on the metal substrate, similar to what is observed in the uncorroded starting materials. The 316L sample showed an order of magnitude lower loss of weight and an order of magnitude lower oxide thickness as compared to all of the other samples corroded at the same time.

Imaging the oxide layers of the 316 and 316L samples showed a fairly uniform 10 µm thick oxide layer in the 316 samples and a ~1 µm thick oxide in the 316L samples. The bottoms of the etch pit were optically examined and the 316L was seen to have a "patchy" bottom – as if the oxide layer in the 316L was failing locally, to create a region of deeper oxide in the failure region, as compared to the smooth bottom of the etch pits on 316 stainless.

In searching the literature, we found that these kinds of structures have been seen with oxidation of austenitic steels in other environments, including gas phase oxidation. Baer et. al.(1971) found that the tendency to form the pure chromium "protective" oxide was dependent on oxygen concentration, steel grain size, and surface contamination of the steel (in particular the amount of carbon and sulfur). This dependence of corrosion behavior on surface preparation is highlighted by a recent study of 316LN (Carbucicchio et al. 2002) corrosion by oxygen-controlled lead where they found the "complex" oxide structure, with the additional complication of lateral heterogeneity of the oxide layer over the sample. These results are in contrast with what we see from the material exposed at IPPE and is not unexpected from the literature.

Fulfillment of Milestones for Second Year (June 1, 2002 - May 30, 2003):

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.

These milestones have been fulfilled.

Deliverables for Second Year:

- **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.

- **Collaboration with LBE loop project at UNLV**. An LBE loop is scheduled to arrive at UNLV from Russia. We will collaborate with that project.

- **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).

- **Data** to be incorporated into student theses.

All of these deliverables have been delivered. One deliverable remains.

- **Manuscript submitted** to peer-reviewed scientific journal by May 30, 2003 for publication. A manuscript, "Spectroscopic and Microscopic Investigation of the Interaction of Lead-Bismuth

Eutectic (LBE) with 316 and 316L Stainless Steel at Elevated Temperatures", by Koury, Farley, Perry, and Johnson, will be submitted to the refereed *Journal of Nuclear Materials* before May 30, 2003.

Master's Thesis:

Dan Koury, "Investigation of the Corrosion of Steel by Lead-Bismuth Eutectic using Scanning Electron Microscopy and X-Ray Photoelectron Microscopy," Physics Department, December 2002.

Presentations:

"Surface Studies of Corrosion of Stainless Steel by Lead-Bismuth Eutectic," D. Koury, B. Hosterman, J. W. Farley, D. L. Perry , D. Parsons, J. Manzerova, and A. L. Johnson. Invited talk delivered by Allen Johnson. Meeting: *VIII Simposio en Fisica del Materiales*, sponsored by Universidad Nacional Autonoma de Mexico, Centro de Ciencias de la Materia Condensada, Jan. 22-24, 2003, Ensenada, Mexico.

"Surface Studies of Corrosion of Steel by Lead-Bismuth Eutectic" by Daniel Koury, Allen L. Johnson, Brian Hosterman, Denise Parsons, Dale L. Perry, and John W. Farley, Poster presentation at FACSS 2002 (29th Annual meeting of the Federation of Analytical Chemistry and Spectroscopy Societies), Oct. 13-17, 2002, Providence RI. Presented by Dale Perry

"Surface Studies of Corrosion of Steel by Lead-Bismuth Eutectic," D. Koury, B. Hosterman, D. Perry, D. Parsons, J. Manzerova, and A. L. Johnson, Poster presentation, Semi-annual meeting, Advanced Fuel Cycle Initiative, U. S. Department of Energy, Albuquerque, NM, January 22-24, 2003.

Conferences Attended:

John Farley attended the DOE Nanoscale Science Research Centers Workshop in Washington DC, Feb 26-28, 2003.

Liquid Metal Target Advisory Group meeting, August 1-2, 2002, UNLV. Attended by John Farley, Allen Johnson, Dale Perry, Dan Koury, Brian Hosterman, Julia Manzerova, and Denise Parsons.

Student ANS meeting in April in Berkeley. Students attending include Dan Koury, Brian Hosterman, Julia Manzerova, Denise Parsons, Umar Younas

ANS meeting, San Diego, CA, June 2003. Farley and Johnson will attend.

Honors and Awards:

Dale Perry, Adjunct Professor of Physics and Senior Scientist at Lawrence Berkeley National Laboratory, traveled to Denver on Feb 13-18 to be honored as a Fellow of the American Association for the Advancement of Science (AAAS).

Other accomplishments in Year Two:

Strengthening samples preparation facilities in materials science at UNLV

During Year Two, we found that we needed an improved way of cutting the steel samples in order to prepare them for analysis. A metallographic cutoff saw was purchased for that purpose. This enables us to measure the oxide thickness by making a cross-sectional cut. Collaboration with scientists at Los Alamos (especially Dr. Stuart Maloy) was very helpful.

An optical microscope was purchased for surface analysis, complete with digital camera, computer, and color printer. The microscope was installed in February 2003, and the computer is on order. It has a translation stage with digital read out for making accurate distance measurements on steel samples.

Statement of Work for Year Three:

During the first two years of this project, it has been demonstrated that high quality data can be obtained from our laboratory. We are now comparing our data with the predictions of models of corrosion. The use of rigorous, high-quality samples for determining chemical species in the corrosion of the lead-bismuth eutectic chemistry is extremely important, with their unequivocal identification being of paramount importance. The chemistry of lead and the other minor constituents (such as transition metal ions) of the stainless steel samples used in the LBE technology have previously been shown to be extremely complex. One of the Principal Investigators in this work (D. L. Perry) has demonstrated that even seemingly simple binary oxides such as lead (II) oxide, PbO, are far more complex than they at first seem (Perry *et al.*, 2002). By synthetic and mechanical handling differences, he has shown that the two forms of the compound easily can be interconverted between each other.

(1) Depth profiling with the XPS will continue to be used to examine steel samples. Other steels such as D9, HT9, T410 will be examined. More resources will be put into maintenance of the XPS machine, because during the second year there was heavy use of the XPS. The XPS has been down at times.

(2) Raman measurements will be made. Raman measurements are essential to measurement of speciation. The chemical species needs to be known in order to model the corrosion process. Knowing the elemental composition alone is not enough. Graduate student Brian Hosterman has obtained an excellent Raman spectrum of a standard sample of Fe_2O_3 (red iron oxide).

(3) Samples before and after benchtop LBE experiments will be examined using the LBE Small Experiments Facility. The research using the LBE Small Experiments facility is being proposed separately. The schedule for the proposed LBE Small Experiments laboratory is uncertain because the room has to be renovated, there must be a health and safety plan carried out, etc. Several groups will be collaborating in designing experiments for the LBE Small Experiments Facility.

(4) The new photoacoustic infrared microscope in the UNLV Chemistry Department will be used to make measurements. UNLV Chemistry Professor Dave Hatchett is in charge of this microscope, which allows vibrational characterization, even of opaque samples.

(5) Collaboration with LBE research efforts will be continued. These include: (a) other LBE efforts at UNLV (e.g., the effort in hydrodynamic flow simulations by Samir Moujaes), (b) DOE scientists at Los Alamos (especially Ning Li of Los Alamos and his postdoc, Jinsuo Zhang) and elsewhere, and (c) international LBE partners working on projects such as KALLA, MEGAPIE, MYRRHA, IPPE.

Deliverables for Year Three:

Continued collaboration with the national DOE project.

Continued collaboration with the LBE loop project at UNLV.

Continued collaboration with the LBE modeling effort and Small Experiments Facility at UNLV.

Progress Reports at regular intervals (currently monthly)

Manuscript submitted to peer reviewed journal by May 2004.

Master's thesis. Brian Hosterman, "Laser Raman Spectroscopic Study of Corrosion of Steel by Lead-Bismuth Eutectic", expected May 2004.

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