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Developing a sensing system for the measurement of oxygen concentration in Liquid Pb-Bi Eutectic

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Developing A Sensing System for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic (Year III Renewal)

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Project Summary

Although liquid lead-bismuth eutectic (LBE) is a good candidate for the coolant in the subcritical transmutation blanket, it is known to be very corrosive to stainless steel, the material of the carrying tubes and the containers. Such a corrosion problem can be prevented by producing and maintaining a protective oxide layer on the exposed surface of stainless steel. The proper formation of this oxide layer critically depends on the accurate measurement and control of the oxygen concentration in the liquid LBE. YSZ (Yttria Stabilized Zirconia) oxygen sensors, using molten bismuth saturated with oxygen as the reference, have been utilized to measure the concentration of oxygen dissolved in the liquid LBE. In the first two years (5/2002-4/2004), calibration of oxygen sensors was performed using the experimental setup located in LANL. A set of calibration curves at temperature ranging from 300 ^{0}C to 500 ^{0}C has been obtained. A new experimental apparatus has been built up for calibration at higher temperature (500^{0}C-700+^{0}C). On the basis of the theoretical predictions, this new apparatus is currently being re-engineered to combat some problems originally unperceived at the early design phases. More experimental results will be generated using this new setup after finishing the re-engineering.

The proposed specific aims in the third year are:

1. To complete and fully test the new oxygen control and measurement apparatus;

2. To employ a more precise H_2/H_2O steam injection strategy for oxygen control instead of previous method of direct injection of O_2;

3. To continue the sensor calibration by using our new setup at higher temperature ranges (500 ^{0}C to 700+^{0}C);

4. To continue the numerical simulation of the oxygen concentration distribution in the liquid LBE for the new setup;

5. To determine oxygen dissolving rates under various conditions through numerical simulation and experimental measurement.

Background and Significance

Lead bismuth eutectic (LBE) has been a primary candidate material for high-power spallation neutron target and nuclear coolant due to its thermal-physical and chemical properties, such as low melting point, high thermal conductivity, and low vapor pressure. As LBE is very corrosive to common steels used in nuclear installation, a protective oxide layer on the interface between LBE and the steel, generally, is applied by controlling the oxygen activity and concentration [5]. The stainless steel test tube contains soluble metals, such as Fe, Ni, Pt, Zr, and Au, which may be protected by an oxide layer, provided that layer can be maintained by a sufficient concentration of oxygen in the LBE. This sets a lower limit on the oxygen concentration in the LBE. An upper limit is set by the constraint that any solid oxides of Pb or Bi will not be formed in the liquid which might clog or damage the systems [2], or which might provide a source of oxygen that cannot be easily removed [7]. Determination of the optimal oxygen concentration has been widely recognized as one of the critical issues that need to be resolved before the general use of LBE coolant is accepted [5]. Accurate quantification and control of oxygen concentration in a non-isothermal liquid LBE flow loop under high temperature and highly turbulent flow conditions is the first step towards the solution of this critical issue.

The oxygen concentration can be measured using following methods: gas chromatography, spectrum analysis, fiber optic fluorosensor, or electro-chemical measurements [3][4][13]. Among these methods, the most widely used are electro-chemical ones, such as the Galavani cell and Zirconia-based methods. Under the high temperature (350+^{0}C) environment as in the case of the LBE test loop in LANL, an YSZ (Yttria Stabilized Zirconia) type sensor is currently designed to measure the oxygen levels [3][6]. **Figure 1** shows the schematic drawing of this YSZ sensor [9]. The outside of the sensor is immersed in LBE, with an unknown oxygen concentration, and the inside contains liquid metal (Bi) with a known dissolved, also saturated, oxygen concentration [6].

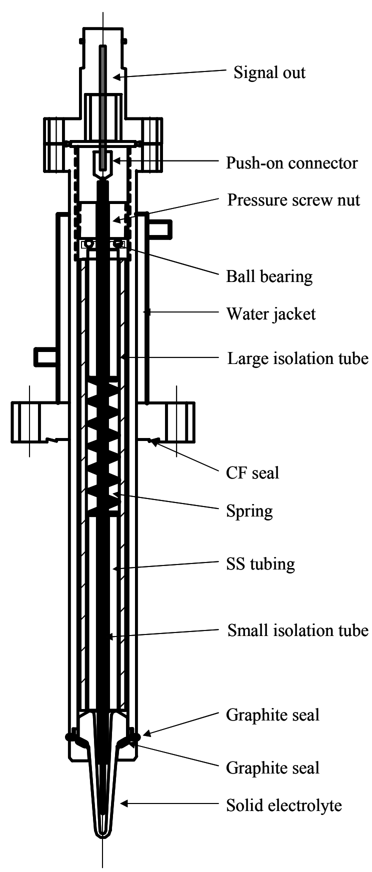

Fig. 1 Schematic Drawing of the YSZ Sensor used in Our Experiment

Due to the oxygen concentration difference in oxygen-saturated bismuth reference and the liquid LBE, there exists a chemical potential difference, resulting in the flow of oxygen ions and accumulation of charges. When it finally reaches equilibrium, there is an electromagnetic force (EMF) across the sensor. The EMF is the measure of the oxygen concentration difference. Of the system filled with Pb, PbO, oxygen permeable solid electrolyte, Bi and Bi_2O_3 (saturated-exposed to the air), the reaction is

$$Pb + \tfrac{1}{3} Bi_2O_{3(Bi)} = PbO_{(Pb)} + \tfrac{2}{3} Bi \qquad (1)$$

The transport of ions in above reaction is a thermally activated process, which does not become feasible until the temperature of the solid electrode is greater than ~350 ^{0}C. Above this temperature, the potential difference across the electrode is calculated from the Nernst equation [8],

$$E = E^0_{PbO} - E^0_{Bi_2O_3} - \frac{RT}{2F} \ln \frac{a^{2/3}_{Bi} a_{PbO}}{a_{Pb} a^{1/3}_{Bi_2O_3}} = \frac{1/3 \Delta F^0_{Bi_2O_3} - \Delta F^0_{PbO}}{2F} - \frac{RT}{2F} \ln a_{PbO} \qquad (2)$$

which assumes (i) a perfect porous membrane, (ii) perfect electron transfer at interfaces, (iii) pure ionic conduction, and (iii) no ohmic contributions (zero current). Here $E^0_{PbO} - E^0_{Bi_2O_3}$ is the difference in the free energies of formation of the bismuth and lead oxides at the temperature T; F and R are the Faraday and ideal gas constants, respectively; T is the absolute temperature; and a_x is the activity of species X. The values for the free energies are available in the Oxide Handbook [7]. The activity of species X is related to the corresponding oxygen concentrations according to Henry's law.

In addition to the temperature threshold (~350^{0}C), applying Eq. 2 to measure and control the oxygen concentration in the liquid LBE, requires that the oxygen concentration must be within two limits, in order to maintain a sufficient oxide protective layer. The lower limit on the oxygen concentration in the liquid LBE, below which steel corrosion takes place, corresponds to the maximum value of EMF, E_{max}. After substituting parameters obtained from the Oxide Handbook Handbook [7], we have

$$E_{max} = 8.17 \times 10^{-5} T + 0.431 [V] \qquad (3)$$

The upper limit is set by the concern that we do not wish to have any solid oxides of Pb or Bi formed in the liquid, which might clog or damage the system, or might provide source of oxygen that cannot be easily removed. This corresponds to the minimum value of EMF, E_{min}. Again, from the Oxide Handbook [7] for those parameters, we have

$$E_{min} = -3.63 \times 10^{-5} T + 0.138 [V] \qquad (4)$$

According to [4], it appears that the optimal to run the system is near the cold-trap condition. This implies that we should operate with E_{min} at the coldest part of the system, where T = T_c. After using the oxide Handbook data [7], we have

$$E(T) = -3.63\times10^{-5}T - 0.199 + \frac{0.337T}{T_s}[V] \quad (5)$$

where $T_s = T_c$ is the saturation temperature for oxygen.

Research Objectives and Goals

- To obtain calibration curves of YSZ sensor in terms of voltage vs. different oxygen concentration under various temperatures (350^0C – $700+^0$C) in the liquid LBE using both the apparatus developed in UNLV and another system developed in LANL;
- To fully characterize the YSZ sensor system;
- To determine oxygen dissolving rate in the liquid LBE under various conditions;
- To search for alternative materials to be used as solid electrolytes O_2 sensor;
- To search for alternative oxygen measuring methods;
- To determine import corrosion parameters and search for the new anti-corrosion methods in the LBE environment using the new setup.

Accomplishments in Previous Years (5/2002-4/2004)

Calibration of Sensor Characteristics

Sensitivity

We tested the characteristics of the YSZ oxygen sensor using the previous setup located in LANL [15]. **Figure 2** shows the sensitivity curve of an YSZ sensor at 420^0C. The dashed and dotted lines are theoretical results for the minimum and maximum values of EMF when the oxygen levels are desired (Eqs. 3 and 4). That the voltage response curve is within the predicted limits indicates that this YSZ type sensor has adequate sensitivity for our purpose.

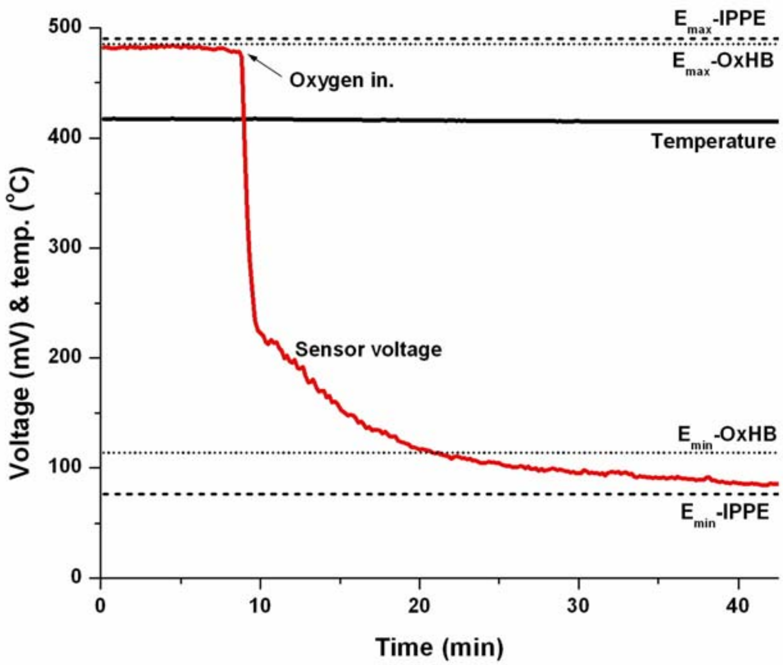

Fig. 2 Dynamic range of the YSZ sensor

Response Time

Figure 3a shows the voltage response of our oxygen sensor in a test loop. From the experimental data, we have observed that:

- When oxygen is introduced into the liquid LBE, the YSZ sensor shows immediate response and the voltage reading decreases transiently;
- When hydrogen is introduced into the liquid LBE, the YSZ sensor responses slowly and the voltage reading increases gradually.

Figure 3b shows the sensor response to the temperature change. The response is simultaneously.

Reversibility

Figure 4 shows the reversibility of the sensor with respect to temperature. Although hysteresis exists in the response during the reversing temperature process, it is within 25% for the temperature range of interest.

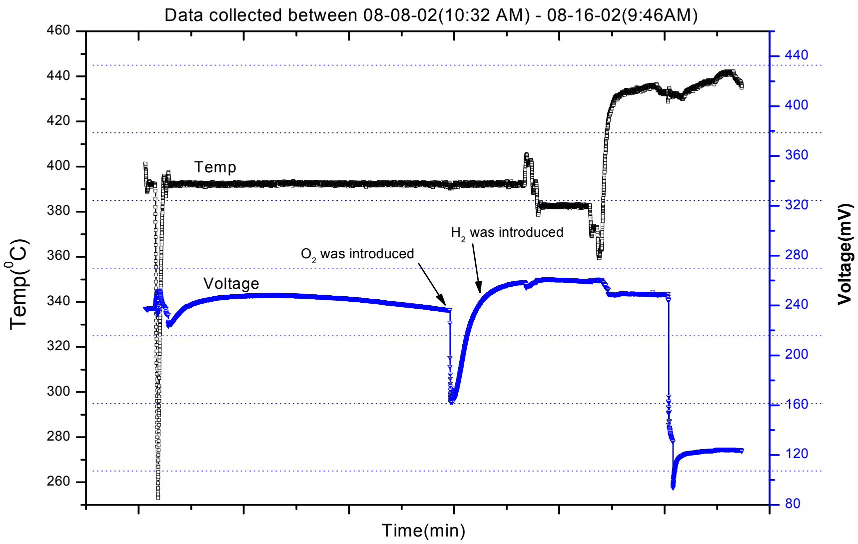

Fig. 3a Voltage Response of an YSZ Oxygen Sensor to Hydrogen and Oxygen

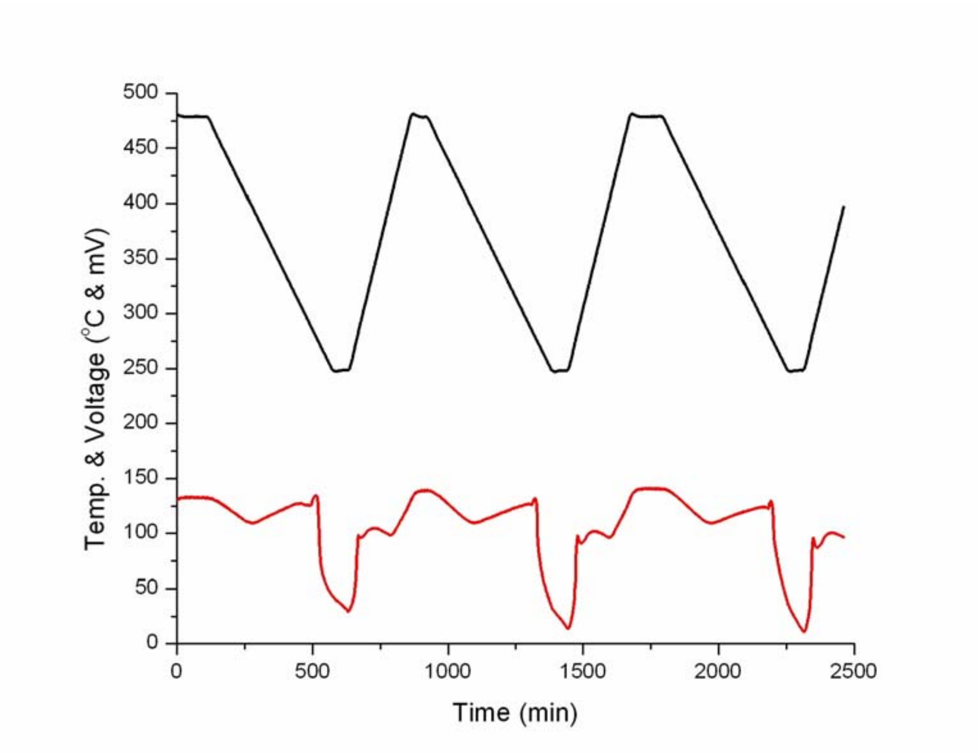

Fig. 3b Voltage Response of an YSZ Oxygen Sensor vs. Temperature change

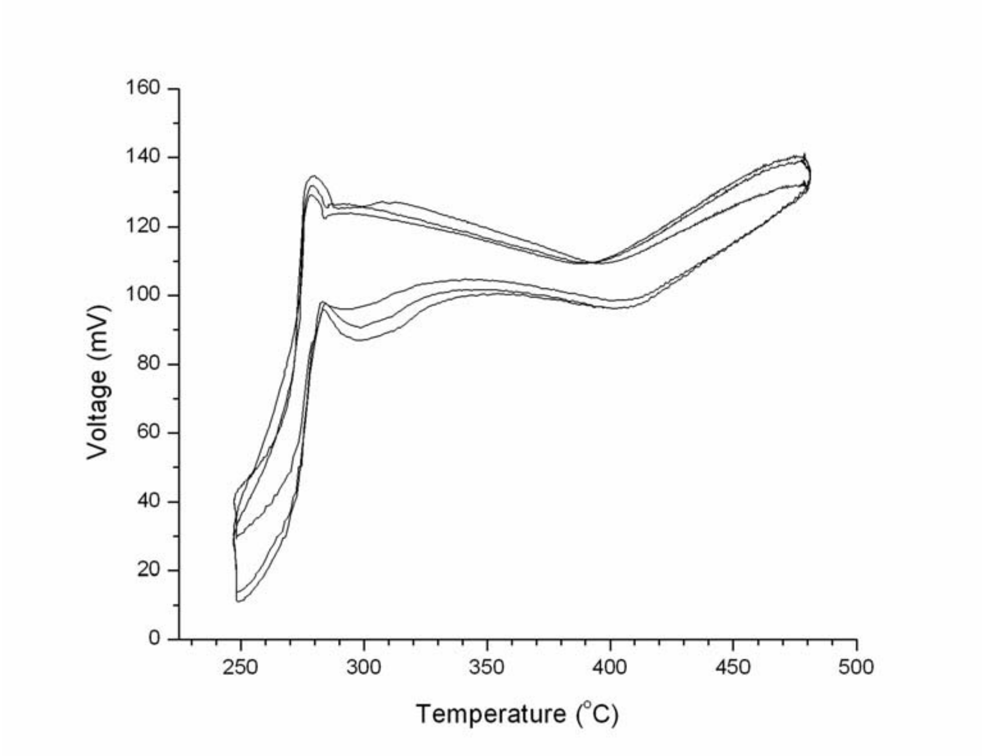

Fig. 4 Reverse response of an YSZ sensor as a function of temperature

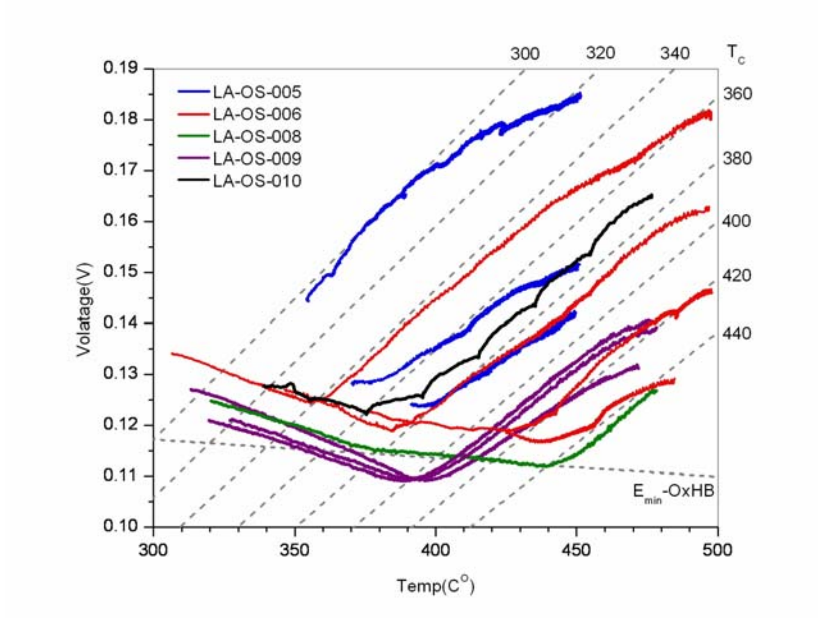

Fig. 5 Comparison of the sensor response with the theoretical results

Consistency

Figure 5 shows the response curves for five YSZ sensors. Comparison of these curves with theoretical results (the dashed lines, Eqs. 4 and 5) indicates:

- The slopes of experimental and theoretical curves are almost identical, ranging from 0.33 to 0.5. This confirms that the YSZ sensors are of high sensing quality;
- Being almost consistent with the theoretical results, the turning points shown on the experimental curves for the sensor 006 (red), 008 (green) and 009 (purple) indicate the regions at which the oxygen saturation occurs;
- Overlapping in the response curves of different sensors indicates the consistency in the sensors of the same design.

Design of a New Apparatus for the Sensor Calibration and Test

The expectation for developing anti-corrosion strategies in the nuclear plant is at temperature 800+^{0}C. Although our YSZ sensor shows high quality from 300^{0}C to 500^{0}C as described above, we need to design a new apparatus that can create higher temperatures because the highest temperature in the previous setup is only 500^{0}C. In the second half of the fiscal year 2002-2003 to the first half of the fiscal year 2003-2004, we developed a new apparatus, as illustrated in **Fig. 6**, to test and calibrate the sensor at temperature above 500^{0}C and up to at least 700^{0}C. After the completeness of the manufacturing, this apparatus was shipped to LANL in Aug. 2003 and currently under testing. In this system,

- The liquid LBE is contained in a magnesia stabilized zirconia (MSZ) inert crucible, which sits in a stainless steel beaker. The beaker acts as a pressure boundary, and it distributes the weight of molten metal and crucible to the outer support. Back-up materials are used to fill the gap between the inner crucible and the beaker;
- A stirring unit made of Silicon Nitride ceramic (Si_3N_4) is incorporated to mix gases with the liquid LBE.
- The crucible is heated using a Watlow™ heat jacket.
- Two Norcal™ CF flanges, mounted on the top of the bucket and the vacuum feedthrough usage, are tightly sealed to ensure a vacuum environment;
- Two watch windows, located on the top of the flanges, have been added to monitor the activity inside the crucible;
- Two sensors are used to measure the oxygen concentration at the same time. In this way, we may check the consistency of the sensor units;
- Residual Gas Analyzer (RGA) is incorporated to the system to monitor the partial pressure of the gases inside the system. With this device, we can immediately check a sudden/obvious leakage inside the system;
- All the output data are collected and recorded through a DAQ system and a voltmeter with 10^{11} Ω input impedance.

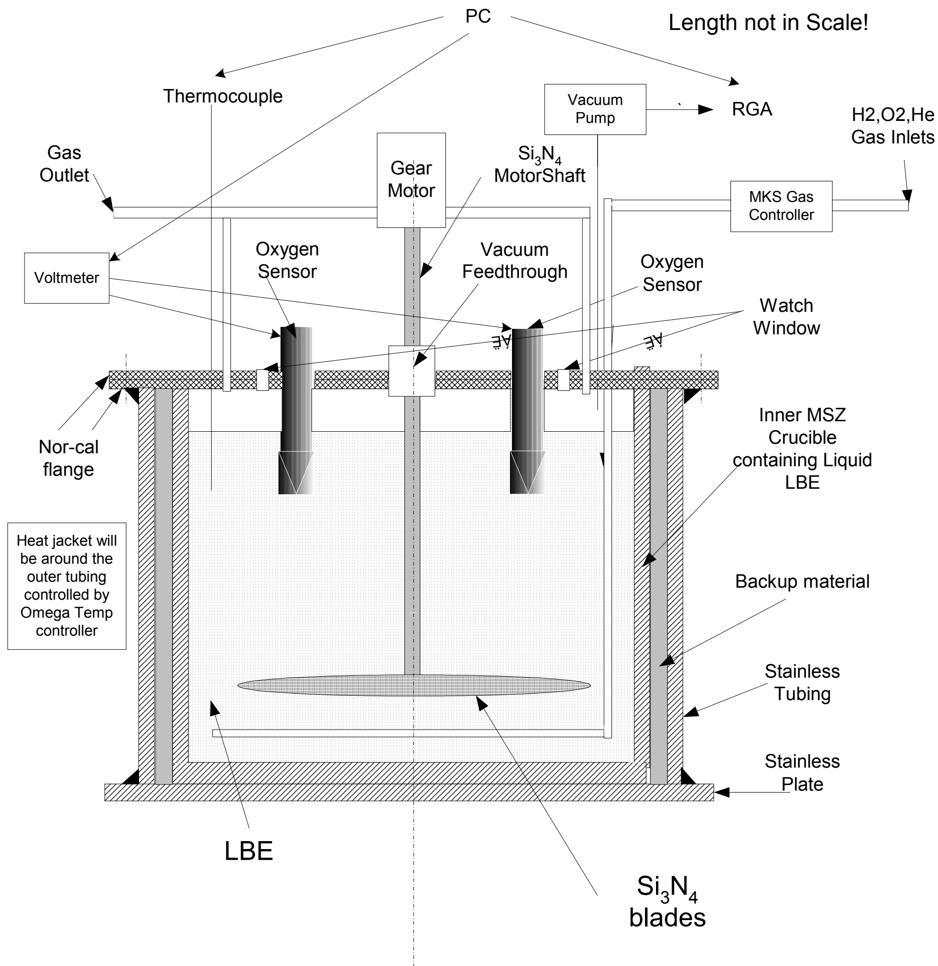

Fig. 6 Schematic drawing of the new apparatus with a stirring system and an inner ceramic crucible.

Enhancement of Oxygen Transfer in LBE by Natural Convection

When testing the new apparatus, we found that the stirring bar made of Si_3N_4 was rather fragile and the motor needed careful installation and maintenance. A new strategy for oxygen mixing by using natural convection was developed through theoretical simulating [16]. The schematic of simplified apparatus geometry with three temperature boundary conditions is shown in **Fig.7**. **Figure 8** shows the corresponding oxygen concentration contours in the container at various times. For condition (a) of higher temperature at the bottom and lower temperature at the top, it is hard for oxygen to be transferred to the top region of the container where the sensors are located; for condition (b) of higher temperature at the sides and lower temperature at the ends, it is hard for oxygen to be transferred to the center of the container; and for condition (c) of higher temperature at one side and lower temperature at the other side, oxygen is well transferred to all over the space in the container.

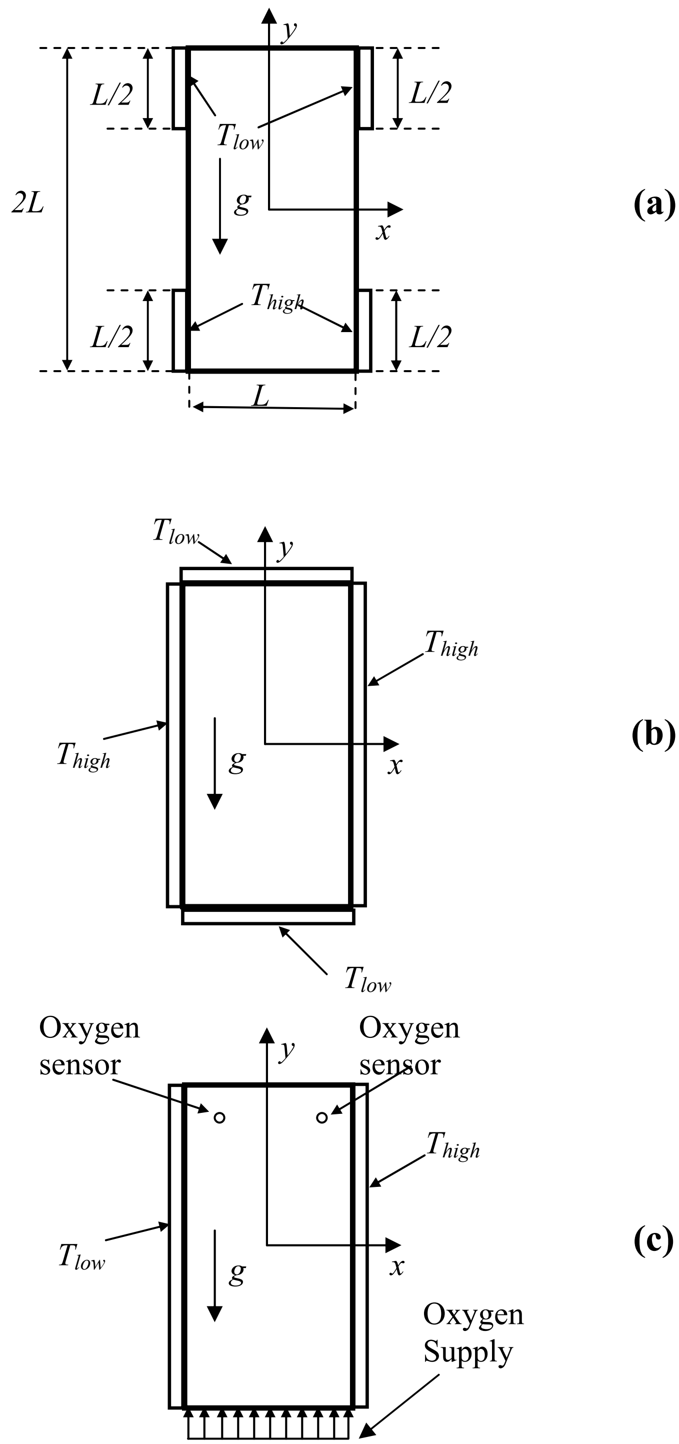

Fig. 7 Schematic of the simplified apparatus with three temperature boundary conditions. Several heaters are set on the wall of the container with low or high temperatures. Insulation conditions are applied to places without heaters. LBE fills up entire space of the container and oxygen input is from the bottom. Two sensors are located in LBE at the upper region.

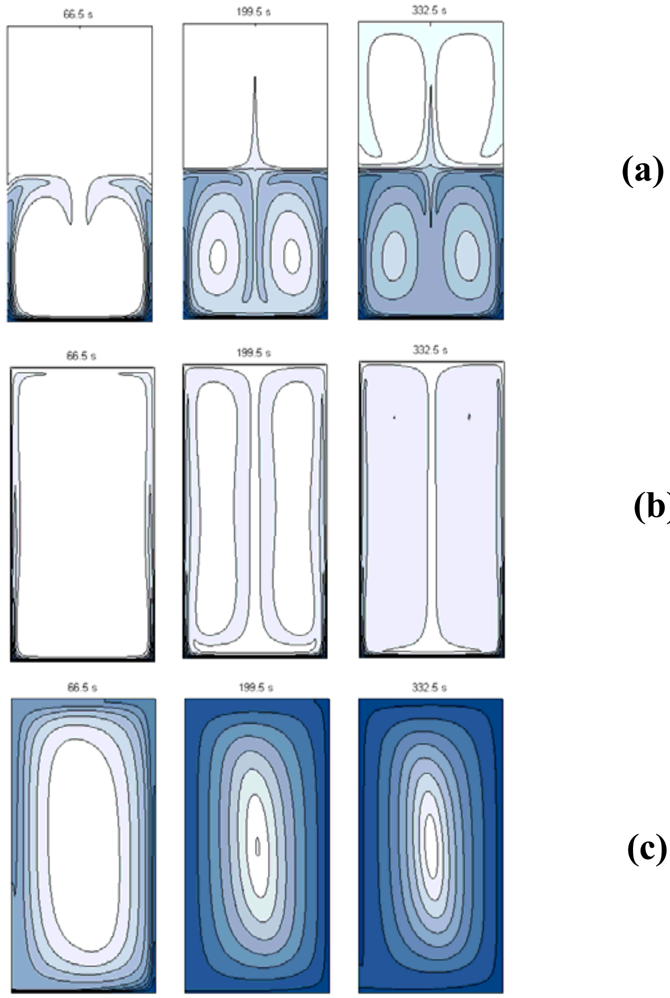

Fig. 8 Oxygen concentration contours in the container under three corresponding temperature boundary conditions shown in **Fig. 7**.

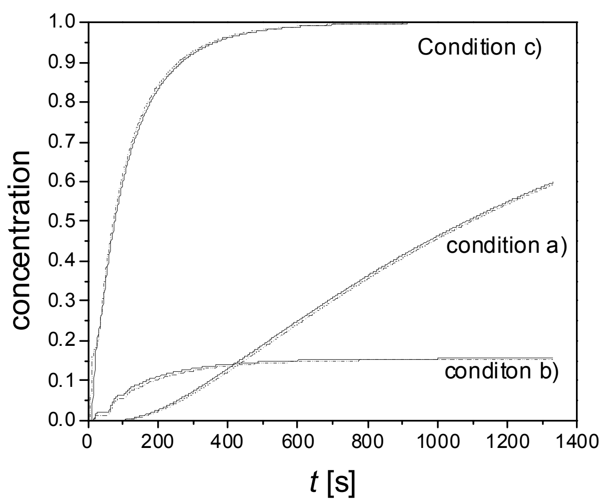

Fig. 9 Time increase of oxygen concentration at two sensor locations under three corresponding temperature boundary conditions shown in **Fig. 7**.

Figure 9 shows the time increase of oxygen concentration at the sensor locations under conditions (a), (b) and (c). We can see that it takes ~600 s (10 min) to reach the oxygen equilibrium at 98% and 15% of input oxygen concentration under conditions (c) and (b), respectively. It seems that condition (a) will not lead to concentration equilibrium in a short time. Compared to ~70,000 hr by pure diffusion, natural convection due to temperature gradients under conditions (b) and (c) will greatly enhance the oxygen transfer for our purpose.

Proposed Work in Year III

In the third year (5/2004-4/2005), after careful re-engineering, the new experimental apparatus [14], will be used to test and calibrate the YSZ sensor at higher temperatures (500^0C-$700+^0$C). The specific tasks are: (1) We will apply a better heating and mixing method for the new apparatus based on the theoretical modeling and numerical simulation. (2) We will use a new H_2/H_2O steam inlet system for more precise and easier oxygen control. (3) We will add a more sophisticated residual gas analyzer and a data acquisition (DAQ) system. (4) We will continue the theoretical modeling and numerical simulation using FLUENT for the determination of the dissolved oxygen concentration distribution in the LBE under various conditions. (5) We will determine the oxygen dissolving rate in LBE under various temperatures by comparing the theoretical predictions with the measured oxygen concentration data.

<u>Apparatus Re-engineering and Sensor Calibration and Test at Higher Temperatures</u>

The new apparatus shown in **Fig. 6** has been shipped to LANL and is currently under careful re-engineering. In general, in this system,

- The liquid LBE will not be contained in a magnesia stabilized zirconia (MSZ) inert crucible. Rather, the crucible will be replaced with a stainless steel container. Use of MSZ material was initially considered to prevent solubility effects from metallic component of the liquid, thus help eliminate the contamination problem. However, past lab operation shows the opposite direction, and subsequently, this crucible-based design is under careful revision.

- On the basis of theoretical modeling and simulation, the heating and temperature control system will be re-developed.
    - In order to enhance the oxygen transport in the fluid of LBE, at least two sets of temperature control should be used. This is a significant departure from the original design using a stirring unit to mix gases with the liquid LBE.
    - In order to obtain the response of oxygen sensor at high temperature (700+ °C), a new heating method will be used.
    - In order to actively control the temperature, the cooling system will be developed along with the control of the heating.
    - An alarming system, as well as an on-line monitoring or control system through the Internet, will be developed. The oxygen sensor test or

calibration may be continued during the evenings when the system is unattended.

- Two watch windows will be maintained and they are located on the top of the flanges to monitor the activity inside the stainless steal container.
- Two sensors are continued to be employed to measure the oxygen concentration simultaneously. In this way, signal responses obtained from the two readings may be cross-checked. In particular, we plan to
  - calibrate the sensors operating in two temperature regions: the high temperature region (600^0C – 700+ ^{0}C) and the low temperature region (350^0C-600 ^{0}C). Lifetime of the sensors operating in these regions will be thoroughly determined through intensive lab testing.
  - try several other types of sensors for low concentration of oxygen in liquid metal at high temperatures.
  - find the self-compensation mechanism for accurate oxygen-concentration measurement at different initial conditions.
- Residual Gas Analyzer (RGA) is also incorporated to the system to monitor the partial pressure of the gases inside the system. With this device, we can immediately check a sudden/obvious leakage inside the system.
- Commission an integrated system for oxygen concentration measurement.
  - A functioning computerized oxygen sensor calibration and test system will integrate the low level oxygen input system with the temperature control system and the heating-system. That is, all the output data are collected and recorded through a DAQ system, and an alarming system shall be triggered to shut down the system when any event deemed to be irregular occurs in the apparatus.

New Oxygen Control Method

The low concentration of oxygen in LBE is in the order of tens of ppb, making it nearly impossible to directly supply oxygen to its desired level. As a better alternative, a hydrogen and water steam system (H_2/H_2O steam) will be used. This method is based on the following principle.

As to the reaction of

$$H_2 + \tfrac{1}{2}O_2 = H_2O \qquad (6)$$

the reaction equilibrium constant is determined by

$$K = \frac{p_{H_2O}}{p_{H_2}p_{O_2}^{1/2}} = \exp[-\frac{\Delta F^0_{H_2O}}{RT}] \qquad (7)$$

Here, ΔF_{H2O} is the free energies of formation of the water at the temperature T. It is evident from the above equation that the ratio of the partial pressures of H_2 and H_2O determines the partial pressure of oxygen.

$$P_{O_2}^{1/2} = \frac{P_{H_2O}}{P_{H_2}} \exp[-\frac{\Delta F_{H_2O}^0}{RT}] \quad (8)$$

From Eq. 8, we can easily apply reasonable levels of H_2 and H_2O steam. By controlling the ratio of P_{H2O}/P_{H2}, we thus can obtain the desired extremely low O_2 concentration. The resultant hydrogen/water steam mixture can either go directly into the LBE system to complete the reaction there, or pass through a high-temperature reaction chamber to reach a thermodynamic equilibrium (hence the desired oxygen level) beforehand [9][10].

Theoretical Modeling and Numerical Simulation

Self-written codes and commercial software FLUENT, will continue to be used to simulate the oxygen dissolving process and distribution in liquid LBE under various temperature conditions. Comparing the numerical simulation results with experimental measurements will not only help us determine oxygen dissolving rates under different temperatures, but also provide suggestions for better experimental design. Furthermore, simulation will be helpful to estimate when to start the actual experiment after the gases are introduced into the system.

Technical Impact

LBE is a promising candidate for a spallation target and coolant for the subcritical transmutation blanket. Accurate measurement of the oxygen concentration is critical to the US DOE TRP program for active control of the corrosion and erosion of transport carriers. After successfully completing this project, we will acquire valuable knowledge on the design and calibration of the oxygen sensor systems to be used in the LBE environment and will obtain the sensing characteristics of the YSZ sensor at temperature ranging from 350^0C-$700+^0$C. In addition, this research effort will build up a solid foundation for future development of the new oxygen sensing systems. Furthermore, the apparatus and sensing systems developed in this project can be used to measure many important parameters in corrosion process and to test other anti-corrosion methods.

In concert with the UNLV's strategic goal to build a nationally competitive nuclear engineering program, two graduate students and one research scientist will be properly trained at the home institute and LANL. Their research endeavor will lead to theses and publications.

Capabilities at UNLV

Personnel

Prof. Bingmei Fu is an Assistant Professor of Department of Mechanical Engineering at the University of Nevada, Las Vegas. She received her B.S and M. Eng. in Modern Mechanics and Mechanical Engineering in 1985 and 1988, respectively, from University of Science and Technology of China. She obtained her Ph. D. in Mechanical

Engineering in 1995 from the City University of New York. From 1995 to 1998, she was a NIH postdoctoral fellow in School of Medicine, University of California at Davis. Her research interests include modeling transport phenomena in biology and medicine, and in traditional engineering environment; quantitative fluorescence photometry, confocal microscopy and video microscopy for investigating mechanisms of microvessel permeability related diseases such as tumor metastasis, edema, thrombi and osteoporosis; seat shock isolation for military vehicles; and optimization of thermal design for computer microprocessor packaging. Her diverse research projects have been supported by National Institutes of Health (NIH), NSF (CAREER), NASA, DOE, ARL, UNLV and private companies.

Prof. Yingtao Jiang is an Assistant Professor of the Department of Electrical and Computer Engineering at the University of Nevada, Las Vegas. He received his B. Eng. degree in Biomedical Engineering and Electronics at the Chongqing University, Chongqing, China in 1993, and M. A. Sc. degree in Electrical Engineering at Concordia University, Montreal, Canada in 1997. Dr. Jiang completed his Ph. D degree in Computer Science at the University of Texas at Dallas in 2001. His research interests include algorithms, VLSI architectures, and circuit level techniques for the design of DSP, networking, and telecommunications systems, computer architectures, and designs of sensor-based data acquisition systems.

Collaborators Dr. Ning Li, Dr. Wei Hang, and Dr. Jinsuo Zhang in LANL have extensive expertise in the proposed research areas and general knowledge in instrumentation and theoretical modeling.

<u>Resources</u>

There are lab spaces in LANL for the proposed experimental work. We are expecting lab space in UNLV in two years. The personnel in this project have access to the engineering machine shops located in UNLV and LANL. These machine shops are equipped with modern machinery and certified technicians. The team in UNLV has a Sun Workstation and a Pentium computer. All PI's have their own offices. Research scientists/assistants share departmental offices (TBE-B113 and B311) and have access to various computers in the departments and Origin 2000 supercomputing machine in the college.

Project Timeline with Milestones and Deliverables

<u>Timeline Narrative</u>

The proposed research is planned to cover one year, starting on May 1, 2004. Research will be conducted with close interaction with appropriate personnel at LANL.

<u>Milestones</u>

- Re-engineer and test the new setup (5/15, 2004);

- Continue theoretical simulation based on the new setup (July 2004);
- Calibrate the YSZ oxygen sensors using the re-engineered apparatus at low temperature range (350^0C - 500^0C) (July, 2004);
- Calibrate the YSZ oxygen sensors using the re-engineered apparatus at high temperature range (500^0C - 700+^{0}C) (November, 2004);
- Compare the numerical simulation results with experimental data to determine oxygen dissolving rates (January, 2005);
- Study alternative approaches for the measurements of oxygen concentration in LBE (March, 2005);
- Preparing the final report (May, 2005).

Deliverables

In addition to the monthly, quarterly, semi-annual, and final reports, researchers expect to publish the results of this project at the appropriate technical conferences and journals (three proceeding papers have been finished so far from the previous support). This project will lead to two Ph. D. dissertations and one M. Sc. thesis (finished in Dec., 2003) from the graduate students participating in this project.

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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)