Task 13

Developing a Sensing System for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic

Y. Jiang and B. Fu

BACKGROUND

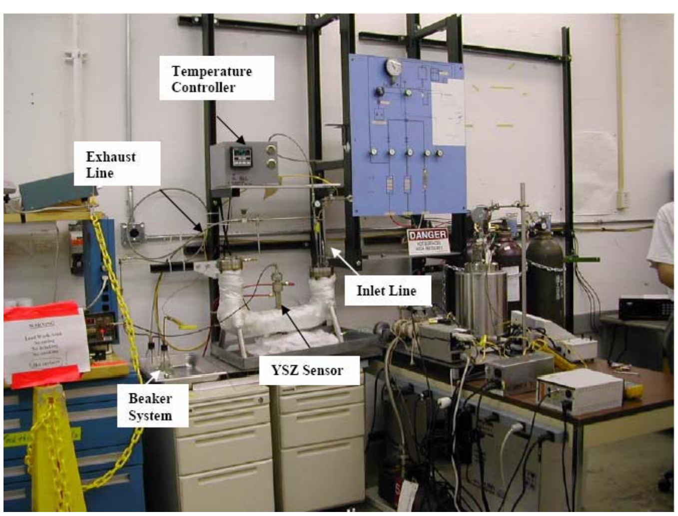
Although liquid lead-bismuth eutectic (LBE) is a good candidate for the coolant that can be employed in a subcritical transmutation blanket, it is known to be very corrosive to stainless steel, the material used in the containment structure. To mitigate this problem, trace levels of oxygen can be introduced into the system, causing the formation of a protective oxide layer at the interface between the LBE and steel. The proper formation of this oxide layer largely depends on the accurate measurement and subsequent control of the oxygen concentration in liquid LBE.

Yttria Stabilized Zirconia (YSZ) oxygen sensors, using molten bismuth saturated with oxygen as the reference, have been utilized to accurately measure the concentration of oxygen dissolved in LBE. By measuring the voltage difference across the YSZ sensor, the oxygen concentration in test solutions can be determined relative to that in the reference solutions (the potentiometric method). The theoretical model for calculating oxygen concentration based on voltage measurements from YSZ sensors in static conditions is well understood. The real world performance of these systems, however, is less predictable.

RESEARCH OBJECTIVES AND METHODS

The research objectives of this project were as follows:

- To generate calibration curves of voltage versus oxygen concentration for the YSZ oxygen sensor system under various temperatures in liquid LBE.
- To determine the sensor characteristics of the YSZ sensor system.
- To determine oxygen dissolving rates in LBE under different temperatures in vitro.
- To study the effects of unwanted electrical conductivity, contributed by the mobility of the electrons at high temperatures, for more accurate oxygen measurement.
- To study alternative and promising oxygen measuring methods.



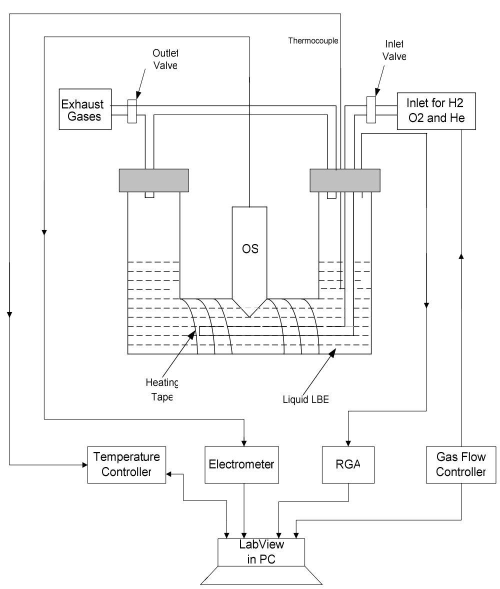
The first sensor calibration experimental setup.

RESEARCH ACCOMPLISHMENTS

The first experimental set up consisted of a temperature controlled U-shape container, gas supplies and exhaust, a residual gas analyzer (RGA), a high-impedance electrometer, and a PC for data acquisition. The container is tightly sealed from the outside atmosphere using a conflat flange except for gas inlet and outlet, and openings for insertion of thermocouple or RGA signal wire. Flexible heating tapes around the container heated the liquid metal to the required temperature under the control of a temperature controller. Meanwhile, the thermally insulated container is placed on a rocker to provide fluid motion that promotes mixing and homogenization of oxygen concentration in LBE.

Although some calibration results were obtained using this setup, it had several shortcomings. For instance, it was impossible to heat the system to reach the desired high temperature (up to 750 ^{o}C). In addition, direct injection of O_2/H_2 method adopted in this system is unlikely to produce a required extremely low oxygen level (ppm to tens of ppb) in liquid LBE. These problems in part were solved by developing a new apparatus. Some noticeable features of this apparatus were:

- Instead of using a steel tube, this apparatus incorporates a cylindrical crucible made of Magnesia Stabilized Zirconia (MSZ), and the liquid LBE is contained in this MSZ crucible. MSZ was chosen because of its desirable material properties.
- The MSZ crucible sits on a stainless steel beaker. The beaker acts as a pressure boundary, and it can distribute the weight of the molten metal and crucible to the outer support. Back-up materials are used to fill the gap between the inner crucible and beaker.



- The crucible is tightly sealed with a metallic flange, with only a few openings left for gas inlets and outlets.
- A stirring unit is employed in order to mix the gases with the molten metal. The stirrer is made of Silicon Nitride (Si3N4) ceramic. Silicon Nitride has high temperature strength, creep resistance,

oxidation resistance, and it is not wetted by any molten metal. On top of those, compared to many other ceramic materials, Si_3N_4 has good mechanical strength.

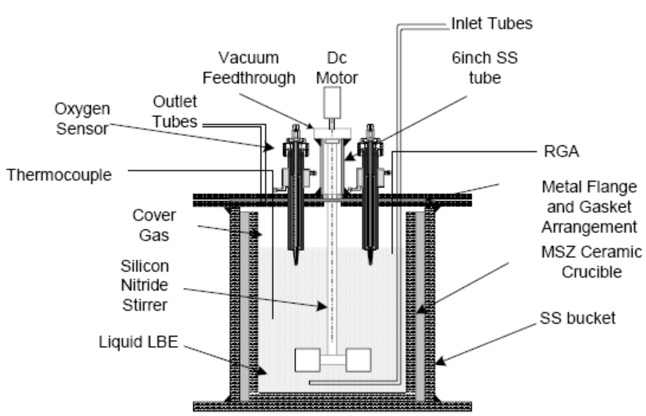
Oxygen Sensor Calibration Results

Calibration curves were obtained from two oxygen sensors. After some initial transients, voltage-temperature curves first follow constant oxygen concentration lines according to the Nernst equation, and then turn to the concentration saturation line.

The slopes of experimental and theoretical curves are almost identical, ranging from 0.33 to 0.5. This indicates that the YSZ sensors are of high sensing quality. Overlapping of the calibration curves for the two sensors indicates consistency in the sensors of the same design.

Experimental results show that tantalum oxidizes at high temperature around 480^{o}C after running for a certain amount of time. This directly causes tantalum wires to lose electrical conductivity, and consequently, the sensor fails to provide meaningful signal output. This effect was demonstrated. In the first trial experiment cycle, molybdenum, stainless steel (SS) and tungsten were tested for this purpose. When introducing hydrogen and helium mixture into the system to clean excessive oxygen in the LBE container, it was found that Mo responds a little faster than SS.

It had been suspected that different combinations of Bi or Bi_2O_3 may have affected the sensor response. During Phase III of this project, several experiments were performed and it was determined that there are no evident effects on the sensor response. Experiment results further confirmed that even a small amount of residual oxygen inside sensor tubes will be sufficient for Bi to be oxidized.



Schematic of the second sensor calibration experimental setup.

Commercial FEM (finite element method) software, FEMLAB was used to simulate the oxygen dissolving process and the distribution in liquid LBE for the new system under three different boundary conditions. Simulation results show that the oxygen concentration distributes evenly in the whole flow field due to the strong convection flow in LBE. These simulation results with the experimental measurements help to not only determine the oxygen dissolving rate and the diffusion coefficient under different temperatures, but also provide suggestions for better experimental design.

TASK 13 PROFILE

Start Date: May 2002
Completion Date: May 2005

Theses Generated:

Ramkumar Sivaraman, M.S., Department of Electrical and Computer Engineering, "Calibration of YSZ Sensor for the Measurement of Oxygen Concentration in Liquid LBE," December 2003.

Xiaolong Wu, M.S., Department of Electrical and Computer Engineering, "Instrumentation of YSZ Oxygen Sensor Calibration in Lead-Bismuth Eutectic," December 2004.

Journal Article:

J. Ma, P. Guo, J. Zhang, N. Li, B. Fu, "Enhancement of Oxygen Transfer in Liquid Lead and Lead-Bismuth Eutectic by Natural Convection" *International Journal of Heat and Mass Transfer*, Vol. 48 (13), p. 2601-2612, January 2005.

Conference Proceedings:

X. Wu, J. Ma, Y. Jiang, B. M. Fu, W. Hang, J. S Zhang, and N. Li, "Instrumentation of YSZ Oxygen Sensor Calibration in Liquid Lead-Bismuth Eutectic," *Proc. of 2005 IEEE International Symposium on Circuits and Systems*, May, 2005.

X. Wu, R. Sivaraman, N. Li, W. Hang, T. W. Darling, Y. Jiang, W. Yim, B. M. Fu, "Design of an Oxygen Sensor Calibration/ Measurement Apparatus for the Liquid Lead-Bismuth Eutectic System," *Proc. of 2003 Annual Meeting*, San Diego, CA, June 1-5, 2003.

X. Wu, R. Sivaraman, N. Li, W. Hang, T. W. Darling, Y. Jiang, W. Yim, B. M. Fu, "Calibration of YSZ Sensors for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic," *Proc. of 10th International High-Level Waste Management Conference*, Las Vegas, March 30-April 3, 2003.

Research Staff

Yingtao Jiang, Principal Investigator, Assistant Professor, Department of Electrical and Computer Engineering
Bingmei Fu, Assistant Professor, and Woosoon Yim, Professor, Department of Mechanical Engineering
Jian Ma and Peng Guo, Post Doctoral Research Associates, Department of Mechanical Engineering

Students

Xiaolong Wu, Ramkumar Bhavani Sivaraman and Yi Lu, Graduate Students, Department of Electrical and Computer Engineering
Shahidur Rahman and Bin Chen, Graduate Students, Department of Mechanical Engineering

Collaborators

Ning Li, LBE Project Leader, and Wei Hang, Research Scientist, Los Alamos National Laboratory