5-2005

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X. Wu

Jian Ma
University of Nevada, Las Vegas, jianma@egr.unlv.edu

Yingtao Jiang
University of Nevada, Las Vegas, yingtao@egr.unlv.edu

B. Fu

W. Hang

See next page for additional authors

Instrumentation of YSZ Oxygen Sensor Calibration in Liquid Lead-Bismuth Eutectic

Xiaolong Wu[1], Jian Ma[2], Yingtao Jiang[1], Bingmei Fu[2], Wei Hang[3], Jinsuo Zhang[3], and Ning Li[3]

[1.]Dept. of Electrical & Computer Engineering
University of Nevada, Las Vegas
Las Vegas, NV 89154
USA

[2.]Dept. of Mechanical Engineering
University of Nevada, Las Vegas
Las Vegas, NV89154
USA

[3.] Los Alamos National Laboratory
Department of Energy
Los Alamos, NM 87544
USA

Abstract— **Liquid lead-bismuth eutectic (LBE), a good candidate for the coolant in the subcritical transmutation blanket, is known to be very corrosive to stainless steel that transports it. Such a corrosion problem can be prevented by producing and maintaining a protective oxide layer on the exposed surface of stainless steel. Proper formation of the oxide layer critically depends on the accurate measurement and control of the oxygen concentration in liquid LBE. An oxygen sensor calibration/measurement apparatus thus has been designed and built to deliberately calibrate Yttria Stabilized Zirconia (YSZ) oxygen sensor. A detailed description of this system with main components and their functions is presented. Set of calibration curves of voltage vs. temperature ranging from 350 °C to 550 °C under various oxygen concentrations in liquid LBE for the YSZ oxygen sensors have been obtained, and are presented and analyzed here. Analysis on the characteristics of this YSZ oxygen sensor is also discussed.**

NOMENCLATURE

E : voltage output of the oxygen sensor

E_{max} : maximum voltage output of the oxygen sensor

E_{min} : minimum voltage output of the oxygen sensor

F : Faraday constants, F = 964 85.30929 C/mol

P_{H2} : partial pressure of the hydrogen gas

P_{H2O} : partial pressure of the water steam

P_{O2} : oxygen partial pressure of the working electrode

P_{O2}' : oxygen partial pressure of the reference electrode

R : ideal gas constants, R=8.3144 J $mol^{-1}K^{-1}$

T : the absolute temperature of the melt LBE

a_{Pb} : activity of lead

ΔA_xB_y: free energy of formation of oxide A_xB_y

I. INTRODUCTION

Liquid LBE has been studied worldwide as a spallation target in Accelerator Driven Systems (ADS) recently. LBE has also been a primary candidate material for nuclear coolant of high-power spallation target due to its specific thermal-physical and chemical properties [1]. However, one of the problems using this lead alloy as a coolant in the ADS is the corrosion of the structural materials employed in the circuits. One way to reduce corrosion is to protect the structural materials with a stable oxide layer [10]. Solid-state YSZ oxygen sensors have been utilized for monitoring dissolved oxygen in molten LBE. By controlling the temperature and the concentration of oxygen dissolved in LBE, it's possible to maintain a sufficient oxide layer on the surface of the steel containers. Oxygen required to protect steel surface is established by the control of the ratio between H_2 and O_2 introduced into LBE [6] [9]. It is known that oxygen partial pressure in the gas phase must be higher than that required for oxidation of iron, the main steel component, and lower than that for PbO formation. In terms of free energy of formation of Fe_3O_4 and PbO, this condition is given by [11]

$$1/2\Delta F_{Fe_3O_4} \le RT \ln P_{O_2} \le 2\Delta F_{PbO} - 2RT \ln a_{Pb} \quad (1)$$

Furthermore, P_{H2O}/P_{H2} should be controlled in the following range [11]:

$$\frac{1}{4}\Delta F_{Fe_3O_4} - \Delta F_{H_2O} \le RT\ln(\frac{P_{H_2O}}{P_{H_2}}) \le \Delta F_{PbO} - \Delta F_{H_2O} - RT\ln a_{Pb} \quad (2)$$

In a typical operating temperature range of 350~ 550 °C, the maximum oxygen concentration in LBE is 5.5×10^{-5} wt%, corresponding to $P_{H2O}/P_{H2}=10^{4.42}$; the minimum oxygen concentration is 1.05×10^{-8} wt%, corresponding to $P_{H2O}/P_{H2}=10^{-0.75}$. Taking into account all of these, reasonable to P_{H2O}/P_{H2} ratio in cover gas of LBE loop will be in range of -0.75~4.42.

II. OXYGEN SENSOR

A. *Solid Electrolyte Materials and Operation Principles*

Measurement of relative oxygen concentration in liquid metals using solid electrolyte membranes is well established [2][3]. Solid electrolytes are materials permeable to specific oxygen ions. In the case of a sintered ceramic zirconia, ZrO_2, O^{2-} ions may pass through solid from high concentration side to low concentration side if they have sufficient thermal energy. Oxygen ions move by hopping between oxygen vacancy sites. Energy needed to hop between these sites is reduced by stabilizing (or partially stabilizing) the crystal structure of ZrO_2 by addition of 8-18% yttria [2].

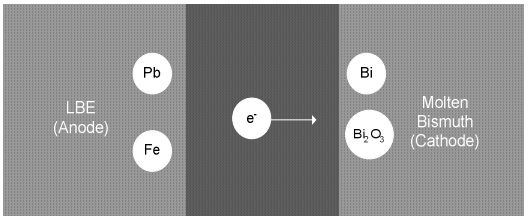

Fig. 1. Schematic of the Electrochemical Cell in OS.

Because the hot solid electrolyte membrane is porous to oxygen, an imbalance in oxygen concentration will cause oxygen to migrate so as to equalize concentrations on each side. Oxygen on higher concentration side will "pick up" two electrons to become ions, travel through the YSZ and re-formed into a neutral molecule at lower concentration surface [3]. This process is shown in Figure 1.

$$O_2 + 4e^- \leftrightarrow 2O^{2-} \quad (3)$$

A metallic connection is used for sourcing and sinking electrons, and chemically catalyzing the reaction shown above. In liquid metals, a certain amount of the dissolved oxygen exists as ions. The liquid metal is a good connection to YSZ, both for making electrical connection to voltmeters and providing the ions to pass through YSZ [3].

In electrochemical terms, oxygen sensor can be represented by the following equation:

$$P'_{O_2} ora'_o // solid\ \ electolyte // O, PbO(liquid\ \ metal) \quad (4)$$

where superscript prime denotes the reference, and the solid electrolyte is typically YSZ. Since we only want to measure the relative oxygen concentrations, we must have a stable, known oxygen concentration reference to measure against. The outside of the conical sensor will be immersed in LBE with an unknown oxygen concentration. If Bi is in equilibrium with chunks of its solid oxide, the dissolved oxygen in the liquid (Bi and Bi_2O_3) will have a known saturation value, depending on the temperature. This saturation value will serve as a good reference.

Due to the oxygen concentration difference in oxygen-saturated reference and liquid LBE, there exists a chemical potential difference, resulting in the flow of oxygen ions, and accumulating charges. When it finally reaches equilibrium, there is an EMF (electromagnetic force) across. EMF is the measure of the oxygen concentration difference [7].

B. Oxygen Sensor Design

Oxygen sensors used in experiments are manufactured by Delphi [5]. The conical material with a rounded end, as shown in Fig.1, is the sensing element of the sensor made of YSZ.

Oxygen sensor shown in Fig.2 has a graphite seal at the bottom of the tube so that it protrudes into the LBE flow. The interior of the tube has several concentric tubes of stainless steel and alumina ceramic. A standard vacuum flange is welded to the top end. A mating flange seal via a spring and the first inner tube, compresses the support ring gasket. A second flange with a high temperature BNC feed through also seals with a copper gasket and through a spring and the innermost tube presses the sensor onto its gasket. Electrical connections are made via the BNC feed through to a liquid reference through a Ta wire down to the center of the ceramic tube [7].

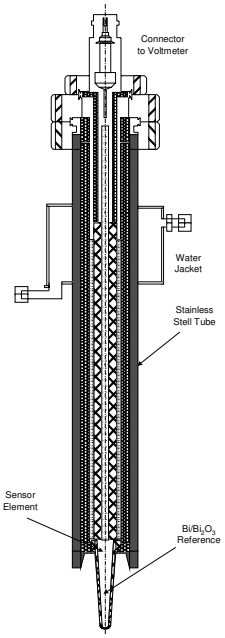

Fig. 2. Schematic Drawing of an Oxygen Sensor.

C. Oxyen Sensor Signal

In the reference electrode, the reaction is:

$$2Bi + 3O = Bi_2O_3 \quad (5)$$

Potential difference across the electrode is calculated from the Nernst equation, which is

$$E = \frac{RT}{4F}\ln\left(\frac{P'_{O_2}}{P_{O_2}}\right)$$

$$= \frac{1}{2F}\left(\frac{1}{3}\Delta F_{Bi_2O_3} - \Delta F_{PbO} - RT\ln a_{PbO} + RT\ln a_{Pb}\right) \quad 6)$$

These activities are assumed to be simply related with corresponding oxygen concentrations by Henry's law. Therefore, oxygen concentration dissolved in LBE melt can be determined from the EMF reading of the YSZ Oxygen Sensor. Two limits of sensor voltage output can be described as [11]:

$$E_{\max}^{(Fe_3O_4)} = 8.123\times10^{-5}T + 0.4304[V] \quad (7)$$

$$E_{\min}^{PbO} = -7.264\times10^{-5}T + 0.142[V] \quad (8)$$

The maximum voltage output of YSZ Oxygen Sensor corresponds to minimal oxygen concentration in LBE that forms minimal iron oxide Fe_3O_4 protective layer on the LBE carrying tube, while the minimum voltage of YSZ Oxygen Sensor corresponds to the maximum saturated concentration in LBE that lead oxide starts to precipitate. Figure 3 shows those maximum and minimum outputs, as well as shows

output changes with temperature under different constant oxygen concentrations in LBE.

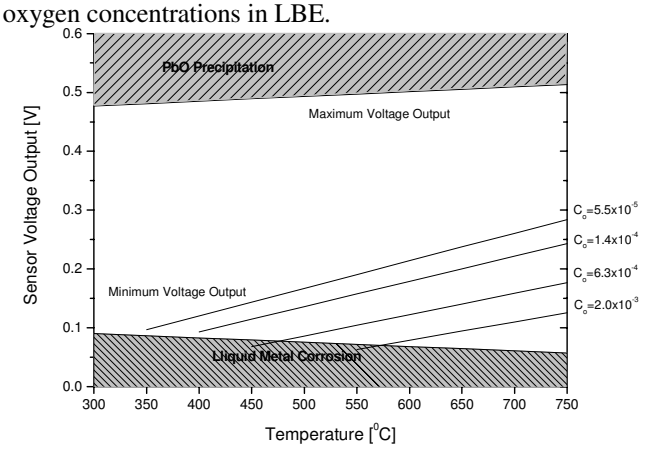

Fig. 3. Maximum and Minimum Sensor Voltage Output to Maintain a Proper Oxide Layer.

III. EXPERIMENTAL SETUP AND RESULTS

A. *Apparatus Description*

Calibration of Oxygen Sensor has been performed using the experimental set up shown in Fig.4. This Oxygen Sensor calibration system consists 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. This SS U-shape container is tightly sealed from outside atmosphere using conflat flange except for gas inlet and outlet and other several openings for insertion of thermocouple or RGA signal wire. Flexible heating tapes around the SS tube were used to heat up the liquid metal up to the required temperature controlled by a temperature controller. The container is thermally insulated and placed on rocker to provide fluid motion that promotes mixing and homogenization of oxygen concentration in LBE [7] [11].

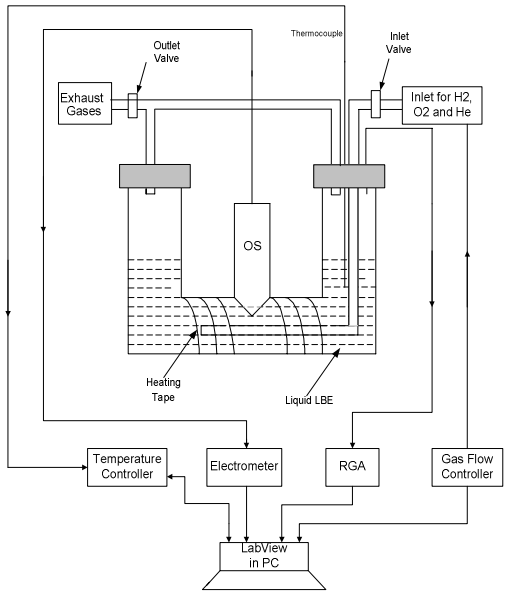

Fig. 4. Experimental Setup. (OS: YSZ Oxygen Sensor).

Controlled quantities of 6% H_2 and O_2 in He are introduced into system via a solid state mass flow controller (MKS Multi Gas Controller 647C) in all SS system. The exhaust line includes a HEPA filter to trap particles, and a vacuum oil trap for residual vapors. Sensor output is fed through a BNC cable to a high impedance electrometer (Keithley 6514 Electrometer). Computer based data acquisition software/LabVIEW was utilized to continuously record the temperature inside the LBE loop and sensor signal output. A Residual Gas Analyzer is also connected to the system to continuously monitor the partial pressures of all gases present in the system, further to monitor the system tightness.

B. *Calibration Results*

Experiment is conducted by initially setting up temperature of the system to 500 ^oC, and oxygen concentration to a certain under-saturation condition. The apparatus is then closed. After a waiting time until the oxygen activity reaches a "fixed" point, we start to slowly decrease temperature by 10 ^oC for every 20 minutes. Temperature and sensor voltage signal were recorded by LabVIEW for each time interval. This procedure was repeated for various oxygen concentrations.

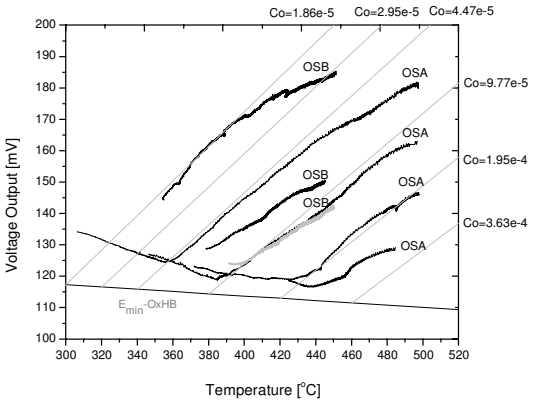

Fig.5. Calibration Results from Sensors A & B.

Figure 5 shows the calibration results from Sensors A & B. It finds after some initial transients, voltage-temperature curves first follow constant oxygen concentration lines according to Nernst equation, then turn to concentration saturation line. These curves display linear trend with slopes close to the theoretical values. A singular point appears when turn to the oxygen concentration saturation line, this indicates the moment when solution becomes oxygen saturated. Due to insufficient waiting time to let oxygen activity to reach a "fixed" point before the temperature starts to decrease, the linear tread of the curves from Sensor B are not as good as those of Oxygen Sensor A. It's clear that their curve slopes are almost the same, both in the range from 0.33 to 0.5. This indicates the YSZ sensors we used are of high sensing quality under our experimental conditions. The turning points on the curves clearly depict the region at which the solution becomes saturated in oxygen.

Overlapping of the calibration curves indicates consistency of the sensors of the same design.

In the oxygen-saturated domain, for sensor A the variation between the experimental result and the theoretical predication is limited to about +5mV. However, for oxygen Sensor B the variation between the experiment result and the theoretical prediction is about +10 mV or even higher. This shows that there still exit some characteristic differences between them even they both have the same design mechanism. This is partly due to the variations of assembly issues

C. *Sensor Characteristics*

Following sensor characteristics are usually expected for liquid metal oxygen sensors: accuracy, reproducibility, time to response to changes about operating conditions, large operating temperature and oxygen concentrations range, limited or no time drift, long service life, mechanical resistance, limited sensor to sensor differences. Figure 5 demonstrates linear trend close to the theoretical predictions even there exists 5~10 mV difference between the turning point and the saturation line. Both Sensors A and B indicate good accuracy of the oxygen sensor under such a low oxygen concentration level (1.05×10^{-8} ~ 5.5×10^{-5} wt%).

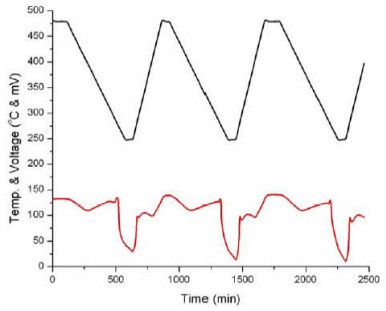

Fig. 6. Voltage Response of Sensor vs. Temperature Change.

Figure 6 shows the reproducibility of sensor with respect to temperature under this set of experiments. Although hysteresis exists in the response time during the reversing temperature change process, it is within 25% for the temperature range of interest. This might be due to two major factors: sensor's response time and response time of the oxygen in liquid LBE. Figures 5 shows voltage response of oxygen sensor to temperature change is really fast and has linear trend. And figure 7 shows that how oxygen sensor response when oxygen is introduced following by hydrogen dilution.

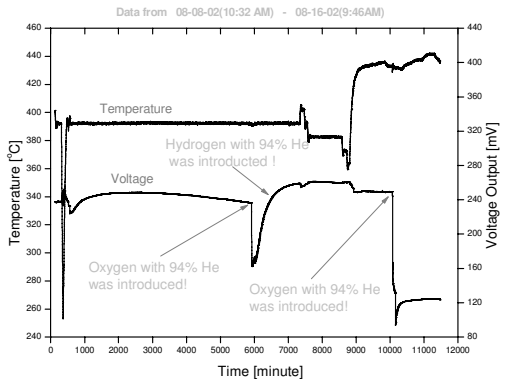

Fig.7. Time to Response to Oxygen Concentration Chantge

IV. CONCLUSION

An YSZ oxygen sensor calibration/measurement apparatus has been designed and built to deliberately calibrate the sensor to be used in LBE. Current experiments have been operating between 350 ^{o}C and 550 ^{o}C. Experiment data showed that oxygen sensor responses well under this temperature range. YSZ oxygen sensors will be tested at higher temperature up to 800 ^{o}C in the coming experiment schedule. Current available technology proves that it's easy to heat the liquid LBE up to 800 ^{o}C. However, experience strongly suggests that new signal wires that can stand high temperature with good electricity conductivity and with no excess oxidation need to be exploited and tested first prior to the filed deployment.

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