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Instrumentation of Ysz oxygen sensor calibration in lead-bismuth eutectic

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INSTRUMENTATION OF YSZ OXYGEN SENSOR CALIBRATION
IN LEAD-BISMUTH EUTECTIC

by

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Bachelor of Science
Nanjing University of Aeronautics & Astronautics
1998

Master of Science
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2004

A thesis submitted in partial fulfillment of
the requirement for the

Master of Science Degree in
Department of Electrical and Computer Engineering
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December 2004
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"Instrumentation of YSZ Oxygen Sensor Calibration in Lead-Bismuth Eutectic"

is approved in partial fulfillment of the requirements for the degree of

Masters of Science in Electrical Engineering

Examination Committee Chair

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ABSTRACT

Instrumentation of YSZ Oxygen Sensor Calibration in Lead-Bismuth Eutectic

By

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Although liquid lead-bismuth eutectic (LBE) is a good candidate for the coolant in the subcritical transmutation blanket, it is also 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. Proper formation of the oxide layer critically depends on the accurate measurement and control of the oxygen concentration (tens of ppb levels) in the liquid LBE. An Oxygen Sensor Calibration/Measurement Apparatus is designed and built to deliberately calibrate the Yttria Stabilized Zirconia (YSZ) oxygen sensor. A detailed description of this system with main components and their functions is presented. Some calibration results have been done and is presented and analyzed here. Analysis on the characteristics of this YSZ sensor and the effectiveness of the calibration apparatus are also discussed.
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ACKNOWLEDGEMENTS

I would like to thank Dr. Ning Li, Dr. Wei Hang and Dr. Jingsuo Zhang from Los Alamos National Laboratory for their support and assistance in developing this research project. I would also like to thank my academic advisors Dr. Yingtao Jiang, Dr. Bingmei Fu for providing me the financial support and giving me directions on this undertaking. Special acknowledgements are given to my wife Ms. Hong Chen for her sincere spiritual encouragement and support to my graduate study at University of Nevada, Las Vegas.
INTRODUCTION AND BACKGROUND

1.1 Background

Lead bismuth eutectic (LBE), an alloy with a low melting temperature of 123.5 °C and a high boiling temperature of 1670 °C, has been studied worldwide as a spallation target in Accelerator Driven Systems (ADS) recently, in which high energy protons collide with lead throughout a window to produce 15 to 20 fast neutrons by the spallation reaction. These neutrons can be used either in sub-critical power reactor systems, which present an intrinsic safety quality, or in the long-lived actinides transmutation system in the framework of nuclear waste management. LBE has also been a primary candidate material for nuclear coolant of high-power spallation target in ADS due to its specific thermal-physical and chemical properties, such as the low melting point, high thermal conductivity, low vapor pressure and no violent reaction with air and water [1] [3]. Lead-bismuth has been used successfully as a coolant in submarine nuclear reactors in Russia since 1950s [11]. There has not been any work done in the U.S. on lead-bismuth since then.

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 [22]. In this environment, due to the relatively high solubility of the major alloy components of steel used in
nuclear systems, liquid lead-bismuth can be severely corrosive to steels (via mass
dissolution attack) if no protective means are applied. Corrosion of containment and
structural materials presents a critical challenge in the use of LBE as a nuclear coolant in
ADS and advanced nuclear reactors. This has been widely recognized as one of the
critical issues that need to be resolved in order to ensure adequate and safe operations.
Therefore, knowledge of the characteristics of the flowing-induced and/or enhanced
corrosion is becoming more and more significant in the design and operation of LBE heat
transfer circuits. And the control of oxygen in lead-bismuth eutectic, and in particular the
on-line monitoring of the dissolved oxygen concentration, is then a challenge of both
corrosion control (sufficient dissolved oxygen in liquid LBE to maintain a protective
oxide layer on the surface of the steel carrier to enhance the resistance of the carrier to
corrosion) and quality control (avoid lead oxide precipitation causing slug and circuit
contamination).

One way to reduce corrosion is to protect the structural materials with a stable oxide
layer, because the solubility of the metal oxides in the lead-bismuth eutectic is much
lower than that of the major alloy components of the used steel carriers.

The operating conditions of the lead-bismuth eutectic must help the thermodynamic
stability of the protecting oxide layers. For this reason, a certain activity of dissolved
oxygen must be present in the molten lead-bismuth eutectic. The activity of dissolved
oxygen has to be enough to avoid the thermodynamic decomposition of the protective
oxide layer, but it also has to be lower than the oxygen activity of PbO formation, which
might clog or damage the systems, or which might provide a source of oxygen that
cannot be easily removed [8]. For these reasons, it is necessary to monitor the oxygen
activity in the molten Pb-Bi alloy. Solid-state Yttria Stabilized Zirconia (YSZ) oxygen sensors have been utilized for monitoring dissolved oxygen in molten Pb-Bi. Furthermore, to convert the oxygen partial pressure to oxygen activity in the molten alloy, reliable free energy of formation data and solubility data are necessary. Since the oxygen chemistry is sufficiently well-known, by controlling the temperature and the concentration of oxygen dissolved in liquid LBE, it is possible to maintain a sufficient oxide layer on the surface of the steel containers or carriers to increase the resistance of the structural material to corrosion.

1.2 Knowledge of Lead-Bismuth Eutectics

1.2.1 Thermodynamic Properties of Lead-Bismuth Eutectics

Before trying to resolve this corrosion problem, properties of lead and bismuth eutectic have to be understood very well. Determination of thermodynamic and structural properties of liquid lead-bismuth alloy has been the main subject of numerous investigations using various techniques such as vapor-pressure measurements [17], electro-motive-force measurements [18], mass spectrometry [19], and electrochemical measurement using solid electrolyte [20]. A critical analysis of the earlier studies (before 1973) was presented by Hulgren et al [21]. For current discussion, the alloy with 44.8% Pb and 55.2% Bi is considered to be the lead-bismuth eutectic alloy [35].

To calculate the activity coefficient of the binary solutions, the Krukowski's formulae take the form [35]:

\[
\ln \gamma_1 = w(T)(1 - X_1)^n
\]

\[
\ln \gamma_2 = w(T)[X_2^n - \frac{m}{m-1} X_2^{m-1} + \frac{1}{m-1}]
\]
Where $\gamma_i$ and $X_i$ ($i = 1, 2$) are the activity coefficient and the atom fraction of metal $i$, respectively, function $w(T)$ characterizes the degree of regularity of the system, $m$ is the asymmetry coefficient, and $T$ is the temperature in Kelvin. It was found that Eq.1 applies mostly to the components having the smaller atomic radius in the systems [35]. Then, the activity of metal $i$ is:

$$a_i = \gamma_i X_i$$  \hspace{1cm} (2)

For liquid lead bismuth alloys, it was reported that the exponent $m$ equals to 2 [35]. The function of $w(T)$, independent of the alloy composition, changes for different temperature ranges.

Moser found that in the range of 670~760 K, $w(T) = - [447/T + 0.2025]$, while in the range of 1150~1320 K, Prasad et al. found that $w(T) = - [391.5/T + 0.2693]$ [35]. Therefore, the activity coefficient of Pb and Bi in the liquid alloy can be expressed as the follow formulae:

$$\ln \gamma_{Pb} = w(T)(1 - X_{Pb})^2$$ \hspace{1cm} (3a)

$$\ln \gamma_{Bi} = w(T)(1 - X_{Bi})^2$$ \hspace{1cm} (3b)

1.2.2 Physical Properties of Lead-Bismuth Eutectics

Lead-bismuth eutectics emerges as the leading candidate for nuclear coolant and high-power spallation targets because of its high atomic numbers, and its specific thermal-physical and chemical properties such as the low melting point, high thermal conductivity, low vapor pressure and no violent reaction with air and water [23]. LBE has the exceptional chemical, thermal physical, nuclear and neutonic properties well suited for nuclear coolant and spallation target applications. The liquid binary alloy of lead and bismuth is also thermodynamically near the ideal solution [24].
Density and viscosity are two important physical properties of LBE that are of interest as a nuclear coolant and relevant to corrosion influenced by the hydrodynamic conditions. Both of them are changed with temperature. Generally, the density $\rho$ and the dynamic viscosity $\mu$ can be written as:

$$\rho(T) = (A_\rho - B_\rho T) \times 10^5$$  \hspace{1cm} (4)$$

$$\mu(T) = A_\mu \times 10^3 \exp(E / RT)$$  \hspace{1cm} (5)$$

where $A$, $B$ and $E$ are constant, $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ is gas constant. It was reported for pure lead [26] [27]:

$$A_\rho = 11.4478 \text{ kgm}^{-3}, B_\rho = 0.00131 \text{ kgK}^{-1}\text{m}^{-3}$$

$$A_\mu = 0.5449 \text{ kgm}^{-1}\text{s}^{-1}, E = 7694 \text{ Jmol}^{-1}$$

and for pure bismuth [28] [29]:

$$A_\rho = 11.7393 \text{ kgm}^{-3}, B_\rho = 0.00127 \text{ kgK}^{-1}\text{m}^{-3}$$

$$A_\mu = 0.4380 \text{ kgm}^{-1}\text{s}^{-1}, E = 6432 \text{ Jmol}^{-1}$$

and for LBE [30] [31]:

$$A_\rho = 11.060 \text{ kgm}^{-3}, B_\rho = 0.00122 \text{ kgK}^{-1}\text{m}^{-3}$$

$$A_\mu = 0.4656 \text{ kgm}^{-1}\text{s}^{-1}, E = 6428 \text{ Jmol}^{-1}$$

The kinematic viscosity $\nu$ is calculated as $\nu = \mu / \rho$.

Fig. 1 compares the kinematic viscosity of LBE with those kinematic viscosities of pure liquid lead and bismuth. It is shown that the pure liquid lead has the largest kinematic viscosity during these three materials, while the pure bismuth has the smallest one at the same temperature. This correlation results for LBE agrees very well with the experiment results by IPPE (1995) [32]. All the kinematic viscosities decrease with the increasing temperature.
1.3 Mechanism of LBE Corrosion

Dissolution of the main steel components into the liquid metal is the primary factor causing corrosion of steels in liquid lead bismuth. The main driving force for liquid metal is the chemical potential for dissolution of all solid surfaces in contact with the liquids [33]. The compositional and microstructural changes due to selective dissolution and intergranular corrosion can lead to material failures. The dissolution rate depends on the liquid media, the rate of the surface area of the solid metal to the volume of the liquid metal, the conditions of the surfaces, the content of interstitial impurities such as oxygen and nitrogen in the liquid metal, and the compositions of the solid materials.

There are two basic types of LBE corrosion: uniform and local [35]. Uniform corrosion is characterized by the uniform damage at the surface of the solid phase by the liquid metal. The local corrosion happens when the liquid metal penetrates into the solid metal in the areas where zones with a high density of crystal structure defects reach the surface.
It was found that when liquid metals flow through solid metal/alloy surfaces, corrosion is accelerated by the velocity of liquid metals. This is termed as flow accelerated corrosion (FAC). There are a number of mechanisms for interactions between the flow and the dissolution. The combination of different mechanisms results in four main types of flow accelerated corrosion: mass transport-controlled corrosion; phase transport-controlled corrosion; erosion-corrosion; cavitation-corrosion [36].

1.4 Approaches for Mitigating Corrosion

Early research on LBE nuclear coolant had made significant progress toward identifying the material compatibility issues, but the corrosion problems for steels were not resolved. Some of the findings are briefly listed in the following [11].

Carbon steels are the most corrosion resistant, low alloy steels (<2.25% Cr) are moderately corrosion resistant, and high Cr steels are subject to gross attack; refractory metals (Mo, W and Ta), graphite and some ceramics (alumina, silicon nitride, silica glass and alumina-silica glass) are impervious to LBE attack (but they are not very practical for large installations).

Zr, Ti and Mg additives are variously used as inhibitors with limited but inconsistent success.

Coating the structural materials with nitride or oxide protective films beforehand failed to consistently prevent corrosion.

The second and third findings all point to the use of protective films for corrosion prevention. As is evidenced in the general industrial use of lead, the presence of oxide films on common, inexpensive structural steels result in adequate performance. However, people found experimentally that in more advanced uses of lead or LBE, where long
service life and minimum contamination were required, the chemical conditions made it difficult to maintain and repair a protective oxide film.

Coating the structural materials with nitride or alumina films was tested [11]. However, it is difficult to maintain the integrity of the films since abrasion and cuts take place during handling and installation. The films can further lift, spall, and flake during operation due to differential thermal expansion and other factors. Experiments found severe corrosion when the films failed and no repair mechanism was readily available during testing. Inhibitors are very effective in reducing the corrosion of steel by forming, for example, carbide and nitride films on the steel surface. Zirconium in Bi and LBE is an effective inhibitor against corrosion of low-alloy steels. The required concentration of titanium is slightly more difficult to maintain than that of zirconium. The insoluble films formed on the steel surface by the inhibition process change the rate-controlling step from liquid-phase diffusion to diffusion of the dissolving atoms through the film. However, these films are brittle and tend to spall, bringing fresh surfaces to corrosion. Thus, inhibitors must remain in the liquid at all times to insure restoration of the films in spalled areas [23] [34].

However, if inhibitors are used during the spallation target operations, a variety of spallation products, build up by the interaction of high-energy protons with the target material, will react with the inhibitors in LBE. These reactions may reduce the beneficial effects of the inhibitors [35].

It was found that pre-oxidation of steels would not prevent mass transfer corrosion through oxygen exchange in non-isothermal lead and bismuth systems based on thermodynamic consideration. Fe$_2$O$_4$ based oxide protective film can be reduced by lead
and bismuth if little or no iron exists in the melt, as would be the case when the film shields rather pure lead and bismuth from the substrate Fe. Due to the temperature dependence of this reaction, Fe in lead and bismuth will remain below the equilibrium value in the hottest areas, and gradual removal of oxide layer will ensue. Since this has been observed experimentally, it would appear that using oxide film for protection is not a practical means for preventing corrosion of steels.

However, the kinetics of the above reduction reaction could drastically reduce the Fe transfer rate if the oxygen level is actively maintained at proper levels. Since in Russia's heavy liquid metal coolant technology, the oxygen control technique has been developed and used to form protective oxide layer on steel surface to reduce the corrosion rate.

The active oxygen control technique found that lead and bismuth are chemically less active than the major components of steel, such as Fe, Ni and Cr. Thus, by carefully controlling the oxygen concentration in LBE, it is possible to maintain an iron based oxide film on the surfaces of structural steels, while keeping lead and bismuth from excessive oxidization, which can lead to precipitation contamination. The oxide film effectively separates the substrates from LBE. Once this oxide film is formed on the surfaces exposed to liquid LBE, the direct diffusion of the structural materials becomes negligible because the diffusion rates of the alloying components are very small in oxides, and because the solubility of the metal oxides in the eutectic Pb-Bi is much lower than the solubility of the metals. Furthermore, the resistance of piping can be greatly enhanced [1] [8] [11].
CHAPTER 2

THEORETICAL BACKGROUND

2.1 Thermodynamics of Oxygen in Lead-Bismuth Alloy

The dissolution of oxygen into liquid lead-bismuth alloy can be expressed as the following chemical reaction:

$$\frac{1}{2}O_2 (\text{gas}) = O (\text{alloy})$$  \hspace{1cm} (6)

At equilibrium, the chemical potential of oxygen (gas) is the same as that of oxygen in the alloy. Accordingly, we can have:

$$\frac{1}{2}F_{O_2} = \bar{\mu}_O$$  \hspace{1cm} (7)

where $F_{O_2}$ is the free energy of oxygen, and $\bar{\mu}_O$ is the partial energy of oxygen in the alloy or the chemical potential of oxygen in the liquid. If a standard reference is used (pure $O_2$ at 1 atmosphere), Eq. 7 can be expressed as the following format [35]:

$$P^{1/2}_{\text{O}_2}(\text{gas}) = a_o (\text{alloy}) = \gamma_o X_o$$  \hspace{1cm} (8)

where $P^{1/2}_{\text{O}_2}$ is the partial pressure of $O_2$, $a_o$ is the oxygen activity and $X_o$ is the atom fraction of oxygen in the liquid alloy, respectively, $\gamma_o$ is the activity coefficient.

Normally, another chosen standard state used to describe the oxygen activity in the alloy is often the saturation state, and the activity of oxygen in the liquid lead bismuth at such a standard saturation state can be expressed as the following formula:
where $X_{O,S}$ and $(P_{O,S})^{1/2}$ are the saturation oxygen atom fraction in the alloy and the corresponding partial pressure.

\[ a^*_{O} = \frac{X_{O}}{X_{O,S}} = \frac{r_{O}}{(r_{O,S})^{1/2}} X_{O} = \gamma^*_{O} X_{O} \quad (9) \]

2.2 Solubility of Metals and Oxygen in LBE

Solubility of iron, chromium, and nickel in lead, Bismuth and LBE plays an important role in corrosion phenomena when using such liquid metals/alloys as nuclear coolants. Experiment measurements of solubility of potential containment materials have been carried out since the 1950s. Generally, the solubility in LBE can be expressed as \[ \log C_s = A_1 + B_1 / T \quad (10) \]

<table>
<thead>
<tr>
<th>C_s (wt%)</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>1.53</td>
<td>2.01</td>
<td>-0.02</td>
<td>1.2</td>
</tr>
<tr>
<td>B_1</td>
<td>-843</td>
<td>-4380</td>
<td>-2280</td>
<td>-3400</td>
</tr>
</tbody>
</table>

The solubility of Fe, Cr and Ni in LBE are shown in Fig. 2. The solubility increases quickly with increasing temperature. The solubility of Ni in LBE is much higher than that of Fe and Cr, indicating that Ni content in steel used for containments of LBE needs to be reduced or protected to increase the corrosion resistance.

The solubility of a metal in the liquid lead-Bismuth alloys depends on the compositions of the liquid alloy. The dependence of Fe solubility in the liquid lead-Bismuth alloy on the lead content is shown in Fig. 3. For all the temperatures considered,
the Fe solubility decreases with increasing concentration of lead, indicating that the pure lead is less corrosive than LBE. LBE corrosiveness is mainly from the fraction of Bismuth in direct dissolution corrosion. However because the pure lead has higher melting point than that of LBE, a higher operating temperature is needed if lead is used as a nuclear coolant.

From Eq.10, the solubility of oxygen in LBE can be further expressed using the following formula [11]:

$$\log C_o [\text{wt\%}] = 1.2 - 3400/T$$  \hspace{1cm} (11)

Solubility of oxygen in LBE according to IPPE data and Muller's paper is shown in Fig.4. Solubility of oxygen increases quickly with increasing temperature. This demonstrates that the operating temperature will play an important role if LBE is going to be used as nuclear coolant.
2.3 Oxygen Control

2.3.1 Theoretical Calculations for Oxygen Control

Unlike many other liquid metal coolants (Na, Li, NaK, and Pb-17Li), lead and Bismuth are chemically more inert than the major alloying elements in steels (like Fe, Ni, and Cr). This is demonstrated in the molar free energy of formation of the oxides (Fig. 5): the lower the free energy, the easier it is to form the corresponding oxide. It is thus possible to 'passivate' the surface of the structural steels in contact with lead and bismuth by the proper oxygen level control, such that a protective oxide film forms to prevent the steel corrosion, while no excess oxygen is present to contaminate the coolant. For the following thermodynamic calculations, we used the free energy of formation data from the Oxide Handbook [2], and the solubility data from the presentations given by the specialists from the Institute of Physics and Power Engineering (IPPE) [3].
Temperature dependence of free energy formation can be generally expressed as [11].

\[ \Delta F = A_2 + B_2T \]  

(12)

Since Cr has smaller free energy of formation than Fe, Cr$_2$O$_3$ is formed before than Fe$_3$O$_4$ formation. However, the Russian’s experience suggests that Fe$_3$O$_4$ is the base of the protective film [3].

The oxygen control technique promotes the formation of protective oxide layers on steel surfaces to prevent the direct dissolution of metals and the oxide precipitation in the lead and bismuth alloy by carefully controlling the dissolved oxygen concentration in liquid LBE.

Table 2 Free Energy Formation Data (according to Oxide Handbook)

<table>
<thead>
<tr>
<th>$\Delta F (J / mol)$</th>
<th>Bi$_2$O$_3$</th>
<th>PbO</th>
<th>NiO</th>
<th>Fe$_3$O$_4$</th>
<th>Cr$_2$O$_3$</th>
<th>H$_2$O</th>
<th>Na$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>-582070</td>
<td>-220670</td>
<td>-237520</td>
<td>-1108300</td>
<td>-1137700</td>
<td>-245570</td>
<td>-420370</td>
</tr>
<tr>
<td>$B_2$</td>
<td>282.0</td>
<td>101.0</td>
<td>88.04</td>
<td>313.3</td>
<td>260.5</td>
<td>54.45</td>
<td>145.6</td>
</tr>
</tbody>
</table>
The oxygen partial pressure in equilibrium with oxygen saturated in LBE can be calculated through the equilibrium of the following reaction in LBE [35]:

\[ Pb + O_{(g)} = PbO_{(s)} \]  

(13)

At equilibrium

\[
\Delta F_{PbO} = -RT \ln \left( \frac{a_{PbO}}{a_{Pb} a_{O}} \right) = -RT \ln \left( \frac{a_{PbO}}{a_{Pb} P_{O_2}^{1/2}} \right)
\]

(14)

where \( \Delta F_{PbO} \) [J/mol] is the standard free energy of formation of the lead oxide, which can be calculated using Eq. 12.

Then, the oxygen partial pressure can be expressed as:

\[
P_{O_2} = a_{Pb}^{-2} a_{PbO}^2 \exp \left( \frac{2\Delta F_{PbO}}{RT} \right)
\]

(15)

When oxygen is saturated, PbO precipitates from the eutectic and its activity becomes a unit, that is \( a_{PbO} = 1 \). The saturated partial pressure of oxygen is expressed as:

\[
P_{O_2, s} = a_{Pb}^{-2} \exp \left( \frac{2\Delta F_{PbO}}{RT} \right)
\]

(16)

Based on Eqs. 14 and 16, the activity of PbO can be written as:

\[ a_{PbO} = \frac{a_{O_2}}{a_{O_2,s}} = \frac{X_{O_2}}{X_{O_2,s}} = \frac{C_{O_2}}{C_{O_2,s}} \]  

(17)

Correspondingly, the oxygen partial pressure when in equilibrium with oxygen saturated in the pure liquid lead and the pure liquid bismuth alloy can be expressed as [35]:

\[
P_{O_2, s(Pb)} = \exp \left( \frac{2\Delta F_{PbO}}{RT} \right)
\]

(18)

\[
P_{O_2, s(Bi)} = \exp \left( \frac{2\Delta F_{Bi_2O_3}}{3RT} \right)
\]

(19)
Submitted Eqs. 2, 3, 8 and 10 into 16, 18 and 19, the oxygen partial pressure in equilibrium with oxygen saturated in pure lead, pure Bismuth and LBE can be simplified to the following:

\[
P_{O_2,S(Pb)} = \exp\left(\frac{2(-220670 + 101T)}{RT}\right)
\]  
(20)

\[
P_{O_2,S(Bi)} = \exp\left(\frac{2(-582070 + 282T)}{3RT}\right)
\]  
(21)

\[
a_{Pb} = \gamma_{Pb} X_{Pb} = \exp[-(447/T + 0.2025)(1-0.448)^2]0.448
\]  
(22)

\[
P_{O_2,S(LBE)} = a_{Pb}^{-2} \exp\left(\frac{2(-220670 + 101T)}{RT}\right)
\]  
(23)

Temperature dependence of the oxygen partial pressure for saturated liquid lead, Bismuth and LBE is shown in Fig. 6, which indicates that there is no large difference between the oxygen partial pressure for LBE and that of lead.
Meanwhile, to obtain the sufficient oxygen concentration in the liquid LBE to form the protective oxide layer based on Fe$_3$O$_4$, the following reaction occurs on the steel surface:

$$3Fe + 4O(g) = Fe_{3}O_{4}(s)$$ \tag{24}

At equilibrium:

$$\Delta F_{Fe_{3}O_{4}} = -RT \ln \left( \frac{a_{Fe_{3}O_{4}}}{a_{Fe}a_{O}^{3}} \right)$$ \tag{25}

It is well-known that iron is the main composition of the steels that are used for the contraindication of LBE, so it is reasonable to set $a_{Fe} = 1$, and $a_{Fe_{3}O_{4}} = 1$ for continuous films.

Then, the oxygen partial pressure then can be expressed as:

$$P_{O_2} = \exp \left( \frac{\Delta F_{Fe_{3}O_{4}}}{2RT} \right)$$ \tag{26}

Considering the required oxygen partial pressure to form Fe$_3$O$_4$ and PbO, to form a sufficient protective oxide layer on the surface of the steel carrier, oxygen partial pressure must satisfy: $RT \ln P_{O_2} = RT \ln a_{O}^{2} \geq 1/2\Delta F_{Fe_{3}O_{4}}$ in order to main the sufficient protective oxide layer and to avoid any lead precipitation.

Therefore, oxygen partial pressure should be controlled in the following range to form a proper oxide layer:

$$1/2\Delta F_{Fe_{3}O_{4}} \leq RT \ln P_{O_2} \leq 2\Delta F_{PbO} - 2RT \ln a_{Pb}$$ \tag{27}

For pure liquid lead, activity of Pb is unity, i.e. $a_{Pb} = 1$. Then oxygen partial pressure should be controlled in the following range of:

$$1/2\Delta F_{Fe_{3}O_{4}} \leq RT \ln P_{O_2} \leq 2\Delta F_{PbO}$$ \tag{28}
Fig. 7 shows upper and lower oxygen partial pressure limits required to meet the adequate oxide layer to prevent the corrosion problems and also prevent excess oxygen to form PbO precipitation. And for pure lead and LBE, the lower limits of oxygen partial pressure for forming the protective oxide layer are the same.

Since Bismuth has a smaller free energy of oxide formation than that of lead, bismuth oxide will not form until significant amount of lead oxide is already formed on the surface the structural material. Clearly, the above two oxygen partial pressures in the cover gas of a lead and bismuth system define the extremes of the oxygen conditions allowed. If the oxygen partial pressure is too low, then the steel cannot form a sufficient protective oxide film on the surface of the carrier and will be exposed to lead and bismuth and further subject to dissolution and mass transfer corrosion. If the oxygen level is too high, lead oxide will precipitate to contaminate the coolant and degrade the thermal hydraulic performance of the system.
According to Henry's law, \( C_0 \) is the oxygen concentration, \( C_{o,s} \) is the oxygen solubility in lead and Bismuth. Therefore, relationship between the oxygen partial pressure and the concentration can be derived from Eqs. 14 and 17 as:

\[
\ln P_{O_2} = 2(\ln C_0 - \ln C_{o,s}) + 2\Delta F_{PbO}/RT - 2\ln a_{Pb}
\] (29)

Substitute Eq.29 into Eq.28, we find that oxygen concentration in LBE should be kept in the range of:

\[
C_{o,s}a_{Pb} \exp\left(\frac{\Delta F_{Fe_3O_4} - 4\Delta F_{PbO}}{4RT}\right) < C_0 < C_{o,s}
\] (30)

or equivalently oxygen activity of oxygen in LBE should be kept in the range:

\[
a_{Pb} \exp\left(\frac{\Delta F_{Fe_3O_4} - 4\Delta F_{PbO}}{4RT}\right) < a_0^* < 1
\] (31)

Since the liquid metal containing a defined oxygen concentration extends over regions with about 200 °C temperature differences in a liquid metal loop, it is most convenient to us \( C_0/T \) diagrams for determination of the oxygen stability ranges of steel in LBE. Fig. 8 shows that the situation in LBE melt, in which the lowest loop temperature could be around 200 °C. Two boundary curves enclose the limits of the oxygen stability range given by Eq.30.

The upper curve shown in Fig. 8 is \( C_{o,s}(Pb)(T) \) which is the maximum oxygen present in LBE to avoid PbO formation, and the lower one \( C_0(Fe_3O_4)(T) \) shown in Fig. 8 which is the equilibrium concentration of oxygen in LBE in order to maintain a sufficient \( Fe_3O_4 \) oxide layer. For example, such as oxygen control in a temperature region between 350 °C and 550 °C, it is recommended that select the shaded area and end up with a concentration range of \( 1.05 \times 10^{-8} \)–\( 5.5 \times 10^{-5} \) wt% of oxygen. It is obvious that such shaded

19
area can be used to set up the oxygen control limits during the process of experiments, and definitely help people to avoid any insufficient or excess oxygen.

Figure 8. Range between the Solubility Limit $C_{O,S}$ and the Oxygen Concentration at Which Decomposition of Iron Oxide Take Place.

2.3.2 Oxygen Control Strategy

Oxygen sensors used in the LBE loop need to measure oxygen concentration in the range of tens of ppb to a few ppm level. In equilibrium, the partial pressure of oxygen in the cover gas space above LBE equals to that in LBE, when the concentration in LBE is below saturation. In practice, there are two methods to control low oxygen concentrations in the system, such as the Direct Injection of Oxygen and Hydrogen Gases [36], and the Injection of Hydrogen and Water Steam Mixtures [16].

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Direct injection of oxygen and hydrogen gases is previously used to regulate low oxygen concentrations dissolved in LBE liquid because the setup and the procedures of the corresponding experimental apparatus are simple, and input and output are in forms with easy addition of gas supplies without solid residues [36]. It is applicable either as injection into LBE through a bypass loop, or over a flowing LBE pool where the mass exchange rates are favorable. The hydrogen injection line can be used in high flow capacity to clean up oxides and restore the thermal hydraulic performance of the LBE systems after prolonged operations. In this method, hydrogen and oxygen are typically mixed with an inert cover gas, helium or argon, to regulate the pressure, and introduced directly into the system. Excess oxygen reacts with hydrogen to form steam and exits through the exhaust gas line.

However, this method needs the careful design and regulation of the gas line pressures and seals. The low concentration of oxygen in the order of tens of ppb level makes it nearly impossible to supply oxygen at the right level directly. However, hydrogen and water system is used as an alternative to solve this problem. A hydrogen and cover gas (He or Ar) mixture passes through a temperature-controlled water bath to pick up water vapor at the desired levels to acquire the desired oxygen level needed to maintain the sufficient protective oxide layer.

In the reaction of:

$$H_2 + \frac{1}{2}O_2 = H_2O$$

(32)

The reaction equilibrium constant is:

$$K = \frac{P_{H_2O}}{P_{H_2}P_{O_2}^{\frac{1}{2}}} = \exp[-\frac{\Delta F_{H_2O}}{RT}]$$

(33)
It is evident from the above equation, that the ratio of the $H_2$ and $H_2O$ determines the partial pressure of oxygen:

$$\frac{P_{H_2O}}{P_{H_2}} = P_{O_2}^{1/2} \exp\left[-\frac{\Delta F_{H_2O}}{RT}\right]$$ \hspace{1cm} (34)

Given the eq. 27, by controlling the ratio of $P_{H_2O}/P_{H_2}$, we can obtain the desired very low $O_2$ concentration. The resultant hydrogen/steam mixture can either go directly into the LBE system to complete the reaction there, or go through a high-temperature reaction chamber to reach a thermodynamic equilibrium (hence the desired oxygen level) beforehand [36].

According to Eq. 27, $P_{H_2O}/P_{H_2}$ should be controlled in the following range:

$$\frac{1}{4} \Delta F_{FeO_2} - \Delta F_{H_2O} \leq RT \ln\left(\frac{P_{H_2O}}{P_{H_2}}\right) \leq \Delta F_{PbO} - \Delta F_{H_2O} - RT \ln a_{Pb}$$ \hspace{1cm} (35)

Submit Eq.29 into Eq.34, the relationship between $P_{H_2O}/P_{H_2}$ and the oxygen concentration can be described as:

$$\frac{P_{H_2O}}{P_{H_2}} = \frac{c_{O_2}}{c_{O_2,S}} \cdot \frac{1}{a_{Pb}} \cdot \exp\left[\frac{\Delta F_{PbO} - \Delta F_{H_2O}}{RT}\right]$$ \hspace{1cm} (36)

The upper and lower limits of the ratio $P_{H_2O}/P_{H_2}$ are shown in Fig. 9. In the typically operating temperature range (350–550 °C) of an LBE loop, the maximum oxygen concentration in LBE is the oxygen saturation concentration at 350 °C, which is $5.5 \times 10^{-5}$ wt%, corresponding to $P_{H_2O}/P_{H_2} = 10^{4.42}$, the minimum oxygen concentration is the minimum oxygen concentration that the lead oxide film can form at 550 °C which is $1.05 \times 10^{-8}$ wt%, corresponding to $P_{H_2O}/P_{H_2} = 10^{-0.75}$. Taking all of these into account, the reasonable ratio $P_{H_2O}/P_{H_2}$ in the cover gas of LBE loop under the operating temperature range (350–550 °C) can be determined (gray area in Fig. 9).
Figure 9. H₂ and H₂O Mixture for Controlling the Oxygen Concentration Dissolved in Liquid Lead-Bismuth Eutectic.
CHAPTER 3

YSZ OXYGEN SENSOR (OS)

Problem of determining the optimal oxygen concentration is dependent on both the liquid metal and the surface it is in contact with. Many metals are soluble at low concentrations, form intermetallics or amalgamate in this lead bismuth liquid. Surface containing these soluble metals may be protected by an oxide layer, provided that this layer can be maintained by a sufficient oxygen concentration in the LBE. This sets a lower limit on the oxygen concentration in the LBE. An upper limit is set by the constraint that do not wish to have any solid oxides of Pb or Bi formed in the liquid which might clog or damage systems, or which might provide a source of oxygen which cannot be easily removed. Therefore, oxygen sensors are critical to the success of using active oxygen control to mitigate steel corrosion and coolant contamination. The yttria-stabilized zirconia | Bi/Bi₂O₃ sensors developed at LANL are used to fulfill this objective.

3.1 Working Mechanism of Solid Electrolyte

Measurement of relative oxygen concentration in liquid metals using solid electrolyte membranes has been well studied and established [4] [6]. Solid electrolytes are only oxide-ion conducting materials. In the case of a sintered ceramic zirconia, ZrO₂, O²⁻ ions may pass through the solid membrane if they have sufficient thermal energy. The oxygen
ions move by hopping between oxygen vacancy sites. These sites are species-specific—utilized only by oxygen ions. Energy needed to hop between these sites is reduced by stabilizing (or partially stabilizing) the crystal structure of ZrO$_2$ into cubic or monolithic structure through the addition of 8–18% yttria, Y$_2$O$_3$. This is usually called YSZ (Yttria Stabilized Zirconia) or PSZ (Partially Stabilized Zirconia) [6].

Because the hot solid electrolyte membrane is porous to oxygen, an imbalance in the oxygen concentration will cause oxygen to migrate to equalize the concentrations on each side. Oxygen on the higher concentration side will "pick up" two electrons to become ions, travel through the YSZ and re-form into a neutral molecule at lower concentration surface where they will "deposit" two electrons [7].

$$O_2 + 4e^- \leftrightarrow 2O^{2-} \quad (37)$$

Figure 10. Schematic of the Electrochemical Cell in OS.

A metallic connection is used for sourcing and sinking electrons, and chemically catalyzing the reaction (37) shown above. In liquid metals, a certain amount of the dissolved oxygen exists as ions, and thereby liquid metals do not need the catalytic action
of Pt-just as well. The liquid metal is a good connection to YSZ, both for making electrical connection to voltmeters and providing the ions to pass through YSZ [8].

Oxygen must have access to the surface of the YSZ. A common way to achieve this is to insert the sensor into loop, so that only the zirconia electrolyte is in contact with oxygen molecule present in liquid LBE. Due to the oxygen concentration difference between oxygen-saturated bismuth reference and liquid, there exists a chemical potential difference resulting in the flow of oxygen ions (from high concentration to low), accumulating charges. When it finally reaches equilibrium, there is an EMF (electromagnetic force) across the YSZ, but there is no current flowing due to the equal and opposite chemical potential force of the concentration difference. The EMF is the measure of the oxygen concentration difference.

The high concentration side electrode becomes positively charged (lose electrons) and the low concentration side electrode becomes negatively charged (collects electrons). The voltage, measured with an “infinite” (10^{11} Ohm) input impedance voltmeter so that no charge leaks off the electrodes into the meter, is then a measure of the concentration difference. In this mode, the equilibrium voltage associated with the charge built up will be an indicator of the ratio of the concentrations of oxygen on each side of the electrolyte.

3.2 Reference of the Oxygen Sensor

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

\[ P'_o, \text{ora'}_o // \text{solid electrolyte} // O, PbO(\text{liquid metal}) \]

(38)

where superscript prime denotes the reference, and the solid electrolyte is typically YSZ. For fixed oxygen activity or partial pressure of the reference, pure oxygen (\( P'_o = 1 \)) or air
(\(P_{O_2}^0 = 0.21\), the standard state is pure \(O_2\) at 1 atmosphere) as gas reference or metal/metal oxide buffers such as In/In\(_2\)O\(_3\), Bi/Bi\(_2\)O\(_3\), Sn/SnO\(_2\), Cu/Cu\(_2\)O and many other so-called coexistence electrodes of these types have been used worldwide.

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 oxygen sensor will be immersed in liquid LBE with an unknown oxygen concentration. The inside must be exposed to the reference with a known oxygen concentration.

If the inside is coated with porous Pt, we then can use the reasonable stability of the concentration of atmospheric oxygen \(~21\%\) as a reference. This has the advantage of being able to be mounted at any angle, and the disadvantage of requiring a vent to the atmosphere, and of having a reference where local concentration variations may occur.

Mounted vertically, the inside of the cone may contain other liquid metals, such as Bi or In, and no Pt coating is needed. If Bi is in equilibrium with chunks of its solid oxide, the dissolved oxygen in the liquid (Bi and Bi\(_2\)O\(_3\)) will have a known saturation value, depending on the temperature. This saturation value can serve as a good reference. The advantages of using liquid metal saturated with bismuth oxide are having a stable reference and not needing a vent to atmosphere. A disadvantage is the need for a vertical mounting to contain the liquid.

3.3 Sensor Design

The automobile industry has spent decades working with YSZ to make reliable oxygen sensors for exhaust gas monitoring application. This form has a number of advantages: they have conical shape, with a rounded end, which can contain a liquid
metal electrode inside; they have a well machined flange at the base of the cone which affords the opportunity to clamp a removable seal tightly to the sensor; they can come with platinum electrodes already coated with connecting strips.

Oxygen sensor used in our experiments is manufactured by Delphi, a GM spinoff company. We have special ordered elements without Pt coating. The conical material with a rounded end, as shown in Fig. 11, is the sensing element of the oxygen sensor which is made of Yttria Stabilized with Zirconia (YSZ).

![Figure 11. Schematic Drawing of the Oxygen Sensors Used in Current Experiments.](Image)
If for any reason the sensor, or any seal in the module should break and allow liquid LBE out of the normal flow of the loop, LBE must be contained and any potential flow paths minimized. Design or procedures thus will minimize the possibility of any brittle section being subjected to thermal shocks.

In addition, sensor and seals have a good life expectancy under operating conditions and thermal cycling of the loop. Provision should be made to replace sensor elements without major cutting or welding operations. The sensor module should be made with materials and thickness that will be not be adversely affected by the temperature in the loop or deteriorated by prolonged contact with liquid LBE [8].

OS, shown in Fig.11 was developed to measure the dissolved oxygen concentration in liquid lead bismuth. The sensor element has a graphite seal at the bottom of the tube so that it protrudes into the LBE flow. This sealing can keep LBE from leaking into the sensor and make OS function at 350–550 °C or higher [37]. The interior of the tube has several concentric tubes of stainless steel and alumina ceramic. This serves several of the following purposes:

I. The space inside the tube is almost entirely filled, leaving the smallest gaps for LBE leak paths;

II. The inner tubes serve as push rods between the sensor support ring and the tube tip, and between sensor and sensor support ring; and

III. The ceramic insulates the innermost tube and connection wire (made of Ta, insoluble in most liquid metals).

A standard vacuum flange with copper gasket 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 feedthrough 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 feedthrough to a liquid reference through a Ta wire to the center of the ceramic tube.

A stainless steel water jacket surrounds the tube near the flange end. This provides protection against leaks by freezing any liquid LBE that may, in an abnormal circumstance, find its way into the tube. It also keeps the connection end cool so that the BNC cable fitting (inevitably containing plastics) will not be adversely affected by the high heat transferred from the dissolved liquid LBE with temperature up to 550 °C or higher.

3.4 Sensor Signal

In the reference electrode, the reaction is:

\[ 2Bi + 3O = Bi_2O_3 \]  \hspace{1cm} (39)

For the equilibrium state, the oxygen partial pressure can be expressed as:

\[ (P_{O_2})^{1/2} = \exp \left( \frac{\Delta F_{O_2}}{RT} \right) \]  \hspace{1cm} (40)

At the working electrode, the oxygen partial pressure can be calculated from Eq. 15. The potential difference across the electrode is calculated from the Nernst equation [35], which assumes:

(i) a perfect porous membrane;
(ii) perfect electron transfer at interfaces;
(iii) pure ionic conduction; and
(iv) no ohmic contributions (zero current).

\[ E = \frac{RT}{4F} \ln \left( \frac{P_{O_2}}{P_{O_2}} \right) \]
Where:

(i) $P_{O_2}^0$ refers to the oxygen partial pressure of the reference electrode;

(ii) $P_{O_2}$ refers to the oxygen partial pressure of the working electrode;

(iii) $F$ and $R$ are Faraday and ideal gas constants, respectively ($R = 8.3144 \, J \, mol^{-1} \, K^{-1}$ and $F = 96485.30929 \, C/mol$);

(iv) $T$ is the absolute temperature.

These activities are assumed to be simply related with the corresponding oxygen concentrations by Henry's law. The values for the free energies were taken from the Oxide Handbook [2].

Substituting Eq. 17 into Eq. 40, the EMF can be expressed as:

$$C_0 = C_{O,s} \exp\left[\frac{1}{RT} \left( -2FE + \frac{1}{2} \Delta F_{Bi,O_2} - \Delta F_{PbO} \right) + \ln a_{pb} \right]$$

(42)

Furthermore, we can get the relationship between the voltage output and the oxygen concentration in LBE:

$$E = \frac{RT}{2F} \left( \frac{\Delta F_{PbO}}{3RT} - \frac{\Delta F_{PbO}}{RT} - \ln\left( \frac{C_0}{C_{O,s}} \right) + \ln a_{pb} \right)$$

(43)

Therefore, oxygen concentration dissolved in LBE melt can be determined from the EMF reading of the YSZ oxygen sensor. In order to maintain the sufficient protective oxide layer and to prevent the precipitation of lead oxide, the real voltage of the sensor should in the following range considering Eq.30:

$$\frac{RT}{2F} \left( \frac{\Delta F_{Bi,O_2}}{3RT} - \frac{\Delta F_{PbO}}{RT} + \ln a_{pb} \right) < E < \frac{RT}{2F} \left( \frac{\Delta F_{Bi,O_2}}{3RT} - \frac{\Delta F_{PbO}}{4RT} \right)$$

(44)
By Substituting the free energy of oxide formation and lead activity into Eq. 44, two limits of sensor voltage output can be described as these:

\[
E_{\text{max}}^{(Fe,O)} = 8.123 \times 10^{-5} T + 0.4304[V] \quad (45)
\]

\[
E_{\text{min}}^{\text{PbO}} = -7.264 \times 10^{-5} T + 0.142[V] \quad (46)
\]

Because of the turbulent mixing flow in the typical lead and bismuth coolant systems, it is the oxygen concentration rather than the oxygen activity that is constant throughout. More likely than not, the oxygen in the melt is in equilibrium with the oxygen in the cover gas at the coldest part of the system. Since the oxygen sensors usually do not work reliably till well above 360 °C for the lack of sufficient oxygen diffusion in the solid electrolyte at low temperatures, it would be useful to map out E vs. T regions for the existence of proper conditions throughout the systems. This would ensure that through measuring the oxygen concentration at a workable temperature and location where we can detect possible coolant contamination conditions at the coldest part where oxygen sensors may not work properly. Conversely, we can also detect possible corrosion conditions at the hottest part where it is difficult to insert oxygen sensors, such as in a spallation target, or in reactor cores.

According to Eq. 43:

\[
E = \frac{RT}{2F} \left( \frac{\Delta F_{\text{PbO}}}{RT} - \frac{\Delta F_{\text{PoO}}}{RT} - \ln \left( \frac{C_o}{C_{O,5}} \right) + \ln a_{\text{Po}} \right)
\]

\[
= E_{\text{min}} - 2.303 \frac{RT}{2F} (\log C_o - \log C_{O,5})
\]

\[
= 4.644 \times 10^{-5} T - 0.195 - 9.924 \times 10^{-5} T \log C_o \quad (47)
\]

The maximum voltage output of sensor corresponds to the minimal oxygen
concentration in LBE that forms the minimal iron oxide ($Fe_3O_4$) protective layer on the LBE carrying tube, while the minimum voltage output of sensor corresponds to the maximum saturated oxygen concentration in LBE that the lead oxide starts to precipitate.

Figure 12 shows those maximum and minimum voltage outputs, meanwhile it also shows the voltage output changes with temperature under different constant oxygen concentration in LBE. This can be used for calibration the lower oxygen concentration dissolved in LBE later. Figure 13 also shows those maximum and minimum voltage outputs, and also shows the voltage output changes with temperature corresponding to different oxygen concentrations, which are almost close to the saturated condition. These
constant oxygen concentration plots can be used for calibration of the upper and lower oxygen limits later.

![Graph showing sensor voltage outputs vs. temperature]

Figure 13. Maximum and Minimum Sensor Voltage Outputs to Maintain a Sufficient Oxide Layer on the Surface of the LBE Steel Carrier according to Eqs. 45, 46 and 48.

3.5 Oxygen Sensor Calibration Strategies and Procedures

Although the theoretical model for calculating oxygen concentration based on voltage measurement of YSZ oxygen sensor in static conditions is well understood, there is an urgent and strong need to obtain a complete set of calibration curves for YSZ sensor systems under various temperature and flow conditions in LBE environment due to device and material imperfectness as well as the unwanted mobility of the electrons at high temperatures. Current research efforts, therefore, is aimed at filling the gap of sensor calibration/validation and further developing new sensors for oxygen concentration measurement in a nuclear environment.
Oxygen sensors used in LBE technology need to measure oxygen concentration in LBE in the range of a few ppb to ppm, and in the temperature range from 350–550 °C even higher in the future plan.

There are different methods that can provide cross sensor calibration and/or validation of the YSZ oxygen sensor. The most convenient way is to use the saturation and oxide dissociation limits for the oxygen sensor calibration. When oxygen dissolved in liquid LBE reaches the oxygen solubility limit, the measured oxygen activity will reach a “fixed” point. If this happens during addition of oxygen, the continued addition of oxygen will not change the activity (excess oxygen goes into solid lead oxides, or slag). If the LBE temperature decreases slowly, oxygen activity will follow the solubility change, since solubility decreases with the decreasing temperature. Knowing the solubility of oxygen dissolved in LBE (IPPE data), one can obtain a group of temperature dependent calibration curves of sensor voltages [8].

Meanwhile, similar “fixed” point is reached when oxygen is depleted to such a low level that the oxide on structural material starts to dissociate. In the case of steels, the first limit is for magnetite (Fe₃O₄). Upon reaching that point, further slow injection of hydrogen into LBE will not change the oxygen activity until the corresponding surface oxygen is gone. Increasing temperature will force the oxygen activity to follow the temperature dependent dissociation limit. By measuring several dissociation limit determined oxygen activity, e.g. by using different pure materials (Fe, Ni, Cr, etc) and their oxides in contact with LBE, it is theoretically possible to calibrate oxygen sensors since the dissociation limits can be determined from free energy of formation of the oxides.
Since oxidation and reduction kinetics are relatively slow if LBE is in an inert and hermetically sealed container, it is possible to fix the oxygen concentration and vary the LBE temperature to obtain calibration curves between the saturation and dissociation limits.

It is also useful to cross-calibrate sensors of different reference electrodes, e.g. Bi/Bi$_2$O$_3$, In/InO$_2$, or Pt/air, and in gas and LBE.

Currently, we are focusing on the calibration using the oxygen saturation limit. This saturation calibration is based on the comparison of the voltage measurements (E) with the expected theoretical e.m.f. (Eth). The use of the graphical representation shown in Fig. 13, where the voltage is expressed versus temperature and the oxygen concentration as a parameter, is most useful to achieve the comparison.

For the slightly under-saturated oxygen solutions, a singular point should appear when decreasing the temperature during the process of the oxygen sensor calibration. This indicates exactly the moment when the solution becomes saturated in oxygen: the saturation temperature is then exactly defined (we can find this saturation temperature from the turning point in Fig. 13). As the oxygen concentration is linked to the saturation temperature by equation (48), the oxygen concentration $C_0$ dissolved in the solution is then exactly known, assuming a constant oxygen concentration during the process of the experiments. Those constants previously defined in Eqs. 45&46 can then be adjusted later.

When repeating this kind of temperature decrease for different similar oxygen sensors and for different oxygen concentrations, mean values can be figured out for all the
parameters. We can achieve our more practical, more precise experimental relations for the sensor voltage.
CHAPTER 4

EXPERIMENTAL SETUP AND RESULTS

Several designs so far have been used to calibrate this YSZ oxygen sensor system. Each of them and the corresponding experiments results will be described in detail here. Advantages and disadvantages of each design will also be addressed.

4.1 Previous Experimental Setup and Experiment Results

4.1.1 Apparatus Description

Calibration of oxygen sensors was performed at Los Alamos National Laboratory (LANL) using the experimental set up shown in Fig.14. This oxygen sensor calibration system consists of a temperature controlled LBE 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 a gas inlet and outlet and several other openings for insertion of thermocouple or RGA signal wires. Flexible heating tapes around the SS tube are used to heat up the liquid metal to the required temperature controlled by a temperature controller. The container is thermally insulated and placed on rocker to provide a fluid motion that promotes mixing and homogenization of oxygen concentration in LBE. Fig. 15 shows the entire system of this setup. Controlled quantities of 6% \( \text{H}_2 \) and \( \text{O}_2 \) in He are introduced into the system via a solid state mass flow controller (MKS Multi
Gas Controller 647C) in all SS systems. The exhaust line includes a HEPA filter to trap particles (especially lead oxide), and a vacuum oil trap for residual vapors.

![Diagram of experimental setup]

Figure 14. Previous Experimental Setup in LANL.

The sensor output is fed through a BNC cable to a high impedance electrometer (Keithley 6514 Electrometer). Computer based data acquisition software/LabVIEW is 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 pressure of all gases present in the system, and monitor the system tightness.
Direct injection of oxygen and hydrogen is employed to adjust the required oxygen concentration in LBE, estimated from the oxygen sensor readings and the Nernst equation.

Then the container is closed by turning off both the inlet and outlet valves. A waiting period allows for equilibration between the residual cover gas and the dissolved oxygen in LBE. After the electrometer reading becomes stable, the temperature is gradually reduced via the control of the Omega temperature controller. Meanwhile, it keeps recording the sensor voltage output. This procedure produces calibration curves first following the constant oxygen concentration lines, then reaching the oxygen saturation.
point. According to the oxygen solubility data, the measured saturation point is used to determine when the PbO starts.

4.1.2 Calibration Results

The experiment was conducted by initially setting up the temperature of the system up to 500 °C, and oxygen concentration to a certain under-saturation condition. The apparatus was then closed. After a waiting time, the oxygen activity reached a "fixed" point, and started to slowly decrease the temperature by 10 °C for every 20 minutes. The temperature of the system and the sensor voltage signal were recorded by LabVIEW for each time interval. The procedure was repeated for various oxygen concentrations.

Figure 16. Calibration Curves Obtained in Summer, 2002 using Sensor A.

Fig.16 shows the calibration results from oxygen sensor A. After some initial transients, voltage-temperature curves first follow constant oxygen concentration lines according to the Nernst equation, then turn to the concentration saturation line. These curves display a linear trend with slopes close to the theoretical values. A singular point

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appears when the line reaches the oxygen concentration saturation line, this indicates the moment when solution becomes oxygen saturated: each saturation temperature is then defined.

![Graph showing calibration curves obtained in Summer, 2002 using Sensor B.]

**Figure 16.** Calibration Curves Obtained in Summer, 2002 using Sensor B.

In order to compare calibration data with the theoretical predictions, the saturation limit and several constant concentration lines are plotted in Fig.s 16&17. Constant concentration curves are labeled by $C_0$. Repeating the same procedures described above but using a different YSZ oxygen sensor B, similar calibration results have been obtained shown in Fig. 17. Due to insufficient waiting time to let oxygen activity to reach a "fixed" point before the temperature starts to decrease, the linear tread of these curves are not as good as those of oxygen sensor A. Fig.18 combined the calibration results from these two oxygen sensors together. It is obvious that their curve slopes are almost the same, both in the range from 0.33 to 0.5. This indicates that the YSZ oxygen sensors we
used, are of high sensing quality under our experimental conditions, and there are no significant differences from sensor to sensor. The turning points on the curves clearly depict the region at which the solution becomes saturated in oxygen. These analyses suggest that the experimental results are consistent with our theoretical predictions. The overlapping of the calibration curves indicates the consistency of the sensors of the same design.

![Calibration Results from Oxygen Sensors A & B.](image)

In the oxygen-saturated domain, for sensor A, the variation between the experimental result and the theoretical prediction 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 some characteristic differences still exist between them even if both have the same design mechanism. This can partly be due to
assembly issues and slightly different experiment condition. Also each sensor is slightly different even though each follows the same assembling procedures.

4.1.3 Sensor Characteristics

The following sensor characteristics are usually expected for liquid metal electrochemical oxygen sensors: accuracy, reproducibility, Response time to changes about operating conditions, large operating temperature and oxygen concentrations range, limited or no time drift, long service life, mechanical resistance, and limited sensor to sensor differences.

![Figure 19. Voltage Response of an Oxygen Sensor vs. Temperature Change.](image)

Calibration experimental results, shown in Fig.s 16 & 17, demonstrate linear trend close to the theoretical predictions even though there exists a 5~10 mV difference between the turning point and the saturation line. Both oxygen 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%).

![Figure 20. Response time to Temperature Changes using Sensor A.](image)

Fig.19 shows the reproducibility of the YSZ oxygen sensor with respect to temperature change under this set of experiments. Although some hysteresis exists in the response time domain during the reversing temperature change process, it is within 25% for the temperature range of interest. This might be due to two major factors: the oxygen sensor's response time (including the intrinsic oxygen sensor response time and the oxygen sensor thermal response time), and the response time of the oxygen present in liquid LBE.
Response time is excellent as no significant delay in temperature or oxygen concentration changes are detected (shown in Fig.s 19&20). Fig.20 shows the voltage response of oxygen sensor to temperature change is really fast. And Fig.21 shows that how the oxygen sensor response when oxygen mixture is introduced following by hydrogen dilution. From the experimental data, it was found that: (i) when oxygen gas is introduced into the liquid, the voltage response of oxygen sensor responds immediately and decreases very quickly; however, (ii) when hydrogen is introduced into the liquid, the voltage responds very slowly. Furthermore, experimental results show that the cleanup process is much less efficient than the oxidation process, suggesting that initial cleaning of LBE will be advantageous.

Current experiments are run between 350~550 °C. Experiment data showed that oxygen sensor responses well under this range. LBE coolant applications in Russia suggest high temperature usage, YSZ oxygen sensors will be tested at higher temperature up to 800 °C in the coming experiment schedule. Current available technology proves that it is easy to heat the liquid LBE up to 800 °C. However, experience strongly suggests that new signal wires that can stand high temperature with good electricity conductivity and no excess oxidation be exploited and tested first in the future.

The oxygen concentration range is controlled between $1.05 \times 10^{-8} \sim 5.5 \times 10^{-5}$ wt%, where the operating conditions are kept in the very low oxygen concentration thanks to a very efficient air tight system applied after hydrogen reduction. Even at this very low level and although the physical meaning of such a low oxygen concentration is not obvious, the sensors operate normally and give a very stable output, showing absolutely no time drift up to now.
Figure 21. Response Time to Oxygen or Hydrogen Introduction using Sensor A.

Our experiment experience tells us that this sensor will continue to work unless the signal wire is extremely oxidized and loses electrical conductivity. A difference in the output of 2 sensors (meter to meter difference from 0 to 10 mV) was observed (Fig.s 16&17).

4.1.4 Disadvantages of the Previous Experimental Setup

Even some good calibration results have been obtained and some sensor characteristics have been tested under this experimental setup, the following shortcomings have been observed during the process of the experiments:

- Heating tapes wrapped around the stainless steal container can only heat the liquid LBE up to 480 °C. Such temperature is lower than expected operating temperature range (up to 800 °C);
• The oxygen concentration is controlled using the direct injection of $O_2/H_2$. This control method is unlikely to produce a required extremely low oxygen level (ppm to tens of ppb) in liquid LBE and is difficult to record this low concentration;

• The liquid LBE is contained in a stainless steel vessel. We anticipate that some contamination already exists in the vessel. In addition, there are no watch windows attached to the vessel to monitor the processes inside;

• The experiment has been troubled by the gas leakage. The source of leakage remains undetected.

4.2 Current Experimental Setup and Experiment Results

All aforementioned problems have been partially rectified in the new experimental design described in the following.

4.2.1 Experimental Setup

The current setup, shown in Fig. 22, incorporates a crucible type design instead of a steel tube as discussed in the previous section. The liquid LBE is contained in a cylindrical crucible made of Magnesia Stabilized Zirconia (MSZ), which sits on a stainless steel beaker. The beaker acts as a pressure boundary, and distributes the weight of the molten metal and crucible to the outer support. Also, MSZ has a few promising properties, like high thermal shock resistance, insolubility in molten metals and non-wetting characteristics, which makes it ideally suitable for our operation. The crucible is tightly sealed with a metallic flange, with only a few openings left for gas inlets and outlets. Back-up materials are used to fill the gap between the inner crucible and beaker. A stirring unit is employed in order to mix the gases with the molten metal. The stirrer is
made of Silicon Nitride (Si$_3$N$_4$) ceramic. Silicon Nitride has high temperature strength, creep resistance, oxidation resistance, and is not wetted by any molten metal. The material also has good mechanical strength compared to many other ceramic materials. Our later real experiments show that this Magnesia Stabilized Zirconia crucible still has some apparent corrosion. Even experiments in the MIT group show this material works pretty well under their experiment situation. And the Silicon Nitride (Si$_3$N$_4$) ceramic stirrer has a strength design problem and was broken twice, further showing that this stirrer design is not practical. Later we changed the MSZ crucible to SS, and used natural convection to mix oxygen dissolved in the crucible [38].

Figure 22. Schematic Description of Apparatus under Construction.
Two oxygen sensors will be simultaneously used to measure oxygen concentration, further to check sensor to sensor differences in the same experiment conditions. Two watch windows are used for continuous monitoring the inside oxidization process.

![Operating Window of Residual Gas Analyzer](image)

Figure 23. Operating Window of Residual Gas Analyzer.

The electric heating jacket that surrounds the steel tube containing LBE heats up the LBE up to the required preset temperature controlled by an Omega temperature controller. A Residual Gas Analyzer (RGA) is utilized to continuously analyze the kind of gases in the cover gas area inside the LBE steel tubes and monitor the partial pressure of all gases present in the system in order to test the system tightness. Fig.23 shows the detailed running window of this gas analyzer. Fluctuation of nitrogen gas shown in the chart indicates some leakage exists. Because during the normal experiment situation we
only introduce a hydrogen or oxygen mixture with helium, any nitrogen fluctuation
definitely comes from leakage somewhere in the system. In this way, it is easy for people
to determine whether the whole system is tightly sealed.

Figure 24. Operating Window of DAC System.

A computer-based Data Acquisition and Control (DAC) system reads the data
collected by the oxygen sensors and thermocouple simultaneously. The DAC system is
written in LabVIEW, a widely accepted standard for data acquisition languages and
instrument control software. Fig.24 demonstrates the running window of this system. The
analog voltage signals from the sensors and thermocouple are fed to the LabVIEW
interface board that converts the analog signal to digital signals interpreted by the
LabVIEW software. A LabVIEW program, which is shown in Fig.25, has been written
in order to collect the data at regular intervals of time, and to view them in the form of graph plotted against time, through which we would be able to determine the oxygen sensor response for various levels of oxygen concentration. The collected data is stored in text file format for later processing. The sensor output is fed to the high impedance electrometer in order to view any instant changes in the sensor signals.

Figure 25. LabView Source Code used to Report the OS Output and Temperature.

4.2.2 Experimental Results and Analysis

Sensor characteristics are further tested with this new experimental apparatus. Different conducting wires and different references have been tried to decide which combination will provide the best sensor response. Some experimental results and discussions will be described in detail here.
Experimental results show that Tantalum oxidizes at high temperature around 480 °C after running for a certain time. This directly causes Tantalum wire to lose the electrical conductivity and the sensor no longer to respond to any operating condition change. In our first trial experiment cycle, molybdenum, SS and tungsten have been tested for this purpose. The corresponding experimental results are shown in Fig.26. Molybdenum and SS wires with the same reference, Bi only, are tested under the same experimental conditions. When introducing hydrogen and helium mixture into the system to clean excessive oxygen in the LBE container, Mo responds a little faster than SS. And Mo gives a faster response to temperature reduction than SS. Even through Mo sensor wire shows a better response than SS wire under this case, it still needs more experiments to compare Mo with SS and other conducting wires due to current limited experimental results.

Figure 26. Mo and SS Conducting Wires were Tested under the Same Condition.
Figure 27. Tungsten Wire with Different Contents of Bi$_2$O$_3$ to Test Reference’s Influence.

Figure 28. Tungsten Wire with Different Content of Bi$_2$O$_3$ to Test Reference’s Influence.
During the normal experiments condition, we only use Bi$_2$O$_3$ as the reference with known oxygen concentration. Meanwhile, we doubted different combinations of Bi or Bi$_2$O$_3$ might have some effects on sensor output. Therefore, several experiments to prove these doubts have been performed. In Fig.s 27 & 28, tungsten wire using different Bi$_2$O$_3$ contents show almost the same voltage output. This obviously proves Bi or Bi$_2$O$_3$ will have no evident differences from oxygen sensor reference. Experiment results further confirm our assumption that even a little oxygen residing inside sensor tubes will be sufficient for Bi to be oxidized. Fig.27 also demonstrates the oxygen sensor under the new setup has good response to temperature change.

![Figure 29. Thick Lead Oxide Layer on the Surface of LBE after Open to Air.](image)

During the process of experiments, we change sensors occasionally. This means the surface of the LBE liquid has to touch air directly during the process of changing sensor and later sealing. If this process takes too long, a thick lead oxide layer forms on the surface of the LBE liquid. This is shown in Fig.29. The surface of the oxygen sensor will
be immediately blocked by the lead oxide when the oxygen sensor is inserted into the liquid LBE again. This causes the oxygen sensor not to respond anymore later. This phenomenon can also be found in the following Fig.30.

Experiments also shows that the oxygen sensor wire will lose the electricity conductivity after a certain running time (shown in Fig.30). This strongly suggests that new signal wires that can stand high temperature with good electricity conductivity and no excess oxidation to be exploited and tested first in the future.

Figure 30. Sensor Wire Lost the Conductivity after Running a Certain Time.

4.3 Material Test Loop and Experiments Data

Beside the previous described two experiment setup, LANL also built one large LBE Material Test Loop (MTL) to study the materials behavior in a flow of melt LBE. In this loop, the melt LBE is in a dynamic flow condition, providing more uniform oxygen
distribution in liquid than the previous setup. A brief description of the loop with main components and their functions is going to be presented here. Some experimental data will be presented and analyzed.

4.3.1 Description of Material Test Loop

MTL is shown in Fig. 31. It is a closed loop consisting of a pump, piping, heat exchangers, and tanks. During the process of the operation, LBE is melted in the Melt Tank and transferred by gas pressure into the Sump Tank. A centrifugal pump submerged in the liquid metal in the Sump Tank circulates the fluid through the loop. After leaving the Sump Tank, liquid LBE travels up to the recuperator’s shell side, where fluid’s temperature is increased by 500 °C. A magnetic flow meter is placed on the long vertical pipe leading from the recuperator’s shell side to the heated section at the bottom of the loop. Band heaters cover the next five horizontal tubes. There the fluid’s temperature is raised another 500 °C. Then the liquid goes up through a narrower vertical Test Section (one inch nominal diameter) and through the tube side of the recuperator where its temperature is reduced by 500 °C. After leaving the recuperator, the fluid flows to the Heat Exchanger where its temperature is again reduced by 500 °C. The fluid leaves the Heat Exchanger through the bottom outlet, goes down through the vertical pipe, turns and returns to the Sump Tank through the bottom inlet. Several pipes are built into the loop to allow the bypass of the recuperator, Heat Exchanger or the Sump Tank. The pump used in MTL is a standard mechanical pump manufactured for lead smelting industry. It is a centrifugal pump with an 8.5 inch impeller. The impeller is submerged in liquid LBE during operation. It is driven by a 25 horse power electric motor and is capable of 58
GPM maximum flow in the loop. The motor is coupled to the impeller by a long vertical shaft.

Figure 31. Drawing of Material Test Loop (MTL).

The pump was built by LaBour Pumps. The recuperator is a standard shell and tube heat exchanger where both the hot and the cold fluids are liquid lead bismuth at different...
temperatures. The Heat Exchanger is a special IPPE design. It consists of several concentric tubes with water as the cooling fluid. Water is separated from the loop fluid by an annulus filled with lead-bismuth. This intermediate fluid can be moved up and down inside the annulus by moving the inside cylinder that works as a piston. When brought all the way up it leaves the intermediate lead-bismuth at the bottom of the outer cylinder thus reducing the heat exchanging capacity of the apparatus to minimum. When the piston is lowered to the very bottom the intermediate fluid is pushed up into the annulus thus increasing the heat exchanging area and the heat exchanger capacity. Approximately 8000lb (3400kg) of LBE is used in the loop. The loop is surrounded by an enclosure.

4.3.2 Experimental Data Analysis

One oxygen sensor (marked as OS103) is placed at the loop inlet, one (OS101) is placed at the beginning of main heat section, and another (marked as OS102) is located at the test section. During the operation, the temperatures at the three locations are different (the temperature at OS102 is the highest and that at OS103 is the lowest), while the oxygen concentrations should be the same due to the fully turbulent flow. Therefore, the output signals should be linear in temperature at a fixed time.

As discussed earlier, the oxygen sensors for LBE systems must have sufficiently fast response time to the operation conditions changing for the proper control of the oxygen level. For the sensor itself, there are two main factors contributing to the response time: heat transfer and oxygen transfer in the ceramic element. These factors result in the temperature/oxygen concentration change in the sensor behind that of the LBE and a new reaction equilibrium that also takes some time. For constant oxygen concentration (0.35 ppm), the response time of OS101~103 to the local temperature changes are shown in
Fig. 32 (a)–(c). It is shown that the response time to temperature changes is excellent without significant time delay.

Figure 32(a). Dynamic Response of the Oxygen Sensor (OS101) to Temperature Change.

Figure 32(b). Dynamic Response of the Oxygen Sensor (OS102) to Temperature Change.
Figure 32(c). Dynamic Response of the Oxygen Sensor (OS103) to Temperature Change.

The response time to H$_2$/He injection during cleaning process of DELTA Loop is shown in Fig.s 33&34. Since H$_2$/He injection reduces the oxygen level, such response time is to oxygen concentration change at constant temperature. The OS103 output turn to increase at the beginning H$_2$/He injection faster than the other two oxygen sensors and there is no significant time delay. The OS101 responded with a little delay. There is also a time delay for OS102. This can be explained due to the gas transport in the liquid LBE. Since the OS103 is placed near the inlet of the loop, it responded immediately after the H2/He injection. The figure also shows that OS103 responds more sensitively than OS102, which is because the hydrogen is consumed by reacting with oxygen during its transport in the flowing LBE. After H$_2$/He is closed, the voltages drop suddenly and then the decreasing rates become slow. The slow rates correspond to the dissociation of the surface oxide because the oxygen activity is lower than that for oxide formation after
long-term injection of H\textsubscript{2}/He. If no new oxygen is supplied, the surface oxide will continue to dissociate until reaching a new equilibrium at the liquid/oxide surface. Such a process is pretty long and should be paid more attention to a practical lead-alloy system.

Figure 33. Response Time of the OS to H\textsubscript{2}/He Injection.

Figure 34. Response Time of the OS to H\textsubscript{2}/He Injection.
CHAPTER 5

CONCLUSION AND DISCUSSION

Current experiments are run between 350–550 °C and at very low oxygen level (1.05×10⁻⁸ ~ 5.5×10⁻⁵ wt%), the YSZ oxygen sensors operate normally and give a very stable output, and exhibit a good response to operating conditions changes such as temperature and oxygen concentration. A difference in the output of 2 sensors (meter to meter difference from 0 to 10 mV) was observed. It has to be understood somehow in order to be able to reduce or cancel that effect, and it could be strongly affect the accuracy. The oxygen concentration range is controlled between 1.05×10⁻⁸ ~ 5.5×10⁻⁵ wt%, where the operating conditions are kept in the very low oxygen concentration thanks to a very efficient air tight system applied after hydrogen reduction. Even at this very low level and although the physical meaning of such a low oxygen concentration is not obvious, the sensors operate normally and give a very stable output, showing absolutely no time drift up to now.

Different experimental apparatuses have been designed and tested. Experimental data collected from these apparatuses shown YSZ oxygen sensor has good response to operating condition changes without any significant delay. The advantages and disadvantages of each apparatus have been analyzed and methods have been utilized to minimize these disadvantages.
LBE coolant applications in Russia suggest high temperature usage, YSZ oxygen sensors will be tested at higher temperature up to 800 °C in the coming experiment schedule. Current available technology proves that it is easy to heat the liquid LBE up to 800 °C. Our experiments tell us that this YSZ oxygen sensor will continue to work unless the signal wire is extremely oxidized and loses electrical conductivity. This strongly suggests that new signal wires that can stand high temperature with good electricity conductivity and no excess oxidation to be exploited and tested first in the future. We also found that there will exist a thick lead oxide layer on the surface of the LBE liquid during the process of changing sensors. The surface of the oxygen sensor will be immediately blocked by the lead oxide when the oxygen sensor is inserted into the liquid LBE again. This prevents the oxygen sensor from responding.
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