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Oxygen Concentration Measurement in Liquid Pb-Bi Eutectic

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Abstract - *Liquid lead-bismuth (Pb-Bi) eutectic (LBE) may see extensive use as a coolant fluid, and perhaps also as a spallation target, in next generation nuclear energy systems. While it is not as reactive as alkali metal liquids, it does present a long term corrosion problem with some materials, notably stainless steels. Mitigation of the corrosion problem may be achieved by producing and maintaining a protective oxide on exposed surfaces, through control of the concentration of dissolved oxygen in the LBE. We have developed an oxygen sensor based on available zirconia-based solid electrolytes used in the automotive industry, which represents a relatively inexpensive source of reproducible and reliable components. We will present the design considerations and characteristics of our sensor unit, and describe its use in the LBE test loop at Los Alamos for measurement and control of dissolved oxygen concentration.*

I. INTRODUCTION

Liquid metals in general are reactive, tending to dissolve, amalgamate or alloy with, other metals. Liquid lead-bismuth alloy is known to be particularly aggressive towards iron and nickel, major components of stainless steels. The long term reliability of piping containing such is determined by its resistance to being dissolved, eroded or corroded by the liquid. This resistance is greatly enhanced if a protective layer of oxide exists on the metal surfaces in contact with the liquid[1]. Monitoring such a layer inside the system is difficult, but the oxygen chemistry is sufficiently well known that if we measure the temperature and the concentration of oxygen dissolved in the liquid lead bismuth, we can control the conditions for maintaining the oxide layer. Extensive work in Russia at the IPPE supports this proposition. Measurements of oxygen levels in the liquid lead-bismuth may be made by measuring the voltage developed across doped zirconia ceramics when a difference in oxygen concentration also exists across them[2]. The material is relatively expensive and construction of reliable temperature-cycling joints is difficult. The automobile industry has many years of experience in these ceramics for exhaust line oxygen sensors. These commercially available elements have many advantages: consistent materials properties; a convenient conical shape; a formed flange for mechanically holding and sealing the element. We describe our initial results using an automobile-style YSZ oxygen sensor unit to measure oxygen levels in a LBE test system as a precursor to use in the large LBE materials test loop at Los Alamos.

II. MATERIALS AND OPERATING PRINCIPLES

The measurement of relative oxygen concentration in liquid metals using solid electrolyte membranes is well established.[3,4] Solid electrolytes are materials which are permeable to specific ions. In the case of a sintered ceramic of zirconia, ZrO_2 , O^{2-} ions may pass through the solid if the temperature is above about 350C. The oxygen ions move by hopping between defect sites.The number and effectiveness of these sites is enhanced by stabilizing (or partially stabilizing) the crystal structure of the ZrO_2 into a cubic or monoclinic structure by the addition of 8-18% yttria, Y_2O_3. This is usually called YSZ or PSZ.

Since charge moves along with the ions, there is also some electrical conductivity at high temperatures. At these high temperatures, it is even possible that electrons from bonding orbitals also become mobile and contribute to the electrical conductivity. This component must be accounted for in any electrical measurements, since it can be confused with the signal from the ionic conductivity.

Oxygen must be converted to ions at one surface, travel through the YSZ and be re-formed into a neutral molecule at the other surface.

$O_2 + 4e^- \leftrightarrow 2O^{2-}$

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 and so a liquid metal does not need the catalytic action of Pt - just as well, liquid LBE dissolves Pt. The liquid metal is therefore a good connection to the PSZ, both for making electrical connection to voltmeters and providing the ions to pass through the PSZ.

The oxygen must have access to the surface of the YSZ. There are two common ways to achieve this: a porous solid film partially covering, and in contact with the surface (Pt, Rh used), or a liquid metal contact where oxygen is mobile in the liquid. An applied current of electrons will attempt to drive ions through the electrolyte, but will not accumulate charges on the surfaces. A measurement of the current can be used to determine the concentration of oxygen – this is called the amperometric mode. If the circuit is open, oxygen moves under the action of the chemical potential difference (from high concentration to low), accumulating charges. This reaches an equilibrium where there is a voltage across the YSZ, but there is no current flowing due to the equal and opposite chemical potential force of the concentration difference. The voltage difference is a measure of the concentration difference – this is the potentiometric mode.

The high concentration side electrode becomes positively charged (lost electrons) and the low concentration side electrode becomes negatively charged (collects the electrons as ions become molecules again). The voltage, measured with an “infinite” impedance voltmeter so that no charge leaks off the electrodes into the meter, is then a measure of the concentration difference.

In this potentiometric mode, the equilibrium voltage associated with the charge buildup will be an indicator of the ratio of the concentrations (actually the Henrian activities) of oxygen on each side of the electrolyte. With an appropriate electrode connected to the surfaces, this voltage may be measured with a high impedance voltmeter. In air, porous platinum electrodes which allow oxygen to reach the surface and catalyze the reaction which converts oxygen molecules into ions are used. The reference concentration is then the partial pressure of oxygen in atmospheric air. A more stable reference is the equilibrium concentration of oxygen dissolved in a liquid at its saturation concentration, maintained by being in contact with the solid oxide. Commonly used systems are indium/indium oxide and bismuth/bismuth oxide, where the equilibrium looks like

$$2Bi_{(liquid)} + 3\ (1/2\ O_2) \leftrightarrow Bi_2O_{3(solid)}$$

The transport of ions is a thermally activated process which does not become feasible until the temperature of the solid electrolyte is greater than about 350C, which is in the operating temperature range of the LBE loop system. Above this temperature the voltages corresponding to various oxygen activity (α concentration) ratios are calculable from the Nernst equation (1) which assumes: a perfect porous membrane, perfect electron transfer at interfaces, and cannot deal with offsets due to interface resistance.

$$V = E_0 - (RT/2F) \ln (A1/A2)$$

$A1 = a_{Bi}^{2/3} / a_{Bi2O3}^{1/3}$ and $A2 = a_{Pb} / a_{PbO}$ where a_X is the activity of X.

For LBE saturated with oxygen (in equilibrium with solid oxides) and using a reference of liquid Bi/Bi_2O_3 , the expected voltage at 400C is 0.11volts . If instead an air reference is used with a platinum electrode, the expected voltage is 0.79 volts.

III OXYGEN SENSORS

The problem of determining the optimal oxygen concentration is dependent on both the liquid metal and the the surface it is in contact with. The liquid metal is a Pb-Bi eutectic, LBE (55% Bi, MP 127C). Many metals are soluble at low concentrations , form intermetallics or amalgamate in this liquid, among them Fe, Ni, Pt, Zr, Au and also graphite (solubility in Bi: $\log(wt\%C) = -360/T - 3.17 \sim 2 * 10^{-4} wt\%$ near 400C). Refractories such as Ta, Mo are essentially insoluble in this temperature range.

Surfaces containing these soluble metals may be protected by an oxide layer, provided that layer can be maintained by a sufficient concentration of oxygen in the LBE. This sets a lower limit on the oxygen concentration in the LBE. An upper limit is set by the constraint that we 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[5].

III.A. Practical considerations for the sensor

For LBE the entire system will be maintained at elevated temperatures in the range 300C-500C. Most metals will oxidize in air at these temperatures, stainless steel will acquire a brown oxide and any compressed same-metal joints will have a chance of binding, copper may entirely transform into CuO, a black, flaky oxide. Beyond ceramics, few insulating materials survive this temperature range, and metal and electrical contacts must be welded, brazed or mechanically clamped. Connections made to stand-off a distance from heated components may be cool enough for solder, plastics and o-ring seals to survive. Ceramics, including YSZ often have poor responses to thermal shock and are mechanically brittle, but they are hard (RC= 68-72, cf SS ~ 17) and have high yield strengths. Machining must be done with diamond grinding tools. Mechanical support of a YSZ membrane with one side in the liquid LBE and the other exposed to atmosphere or another liquid metal is also a problem. Differential expansion (SS =16, YSZ=8 (*1e-6/K)) may crack ceramic to metal seals, or clamped ceramic elements, particularly thin plates. Seals must keep LBE from leaking and function at 300-500C. To clamp and seal a parallel sided cylinder closed tube (commonly available form of YSZ) or a flat plate is a tricky task at high temperatures.

The automobile industry has spent decades working with YSZ to make reliable oxygen sensors for exhaust gas monitoring. The forms they produce have a number of advantages: they are conical, with a rounded end, which means they can be removed from solidified LBE, and 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. We use elements manufactured by Delphi, a GM spinoff company. We have special ordered elements with no Pt coatings and with Pt coatings on the inside only. The cost is approximately $8 each. The sensors actually operate at temperatures above 360C as figure 1 indicates: the despite an offset, the behavior of the sensor only agrees with a Nernst equation prediction above 360C.

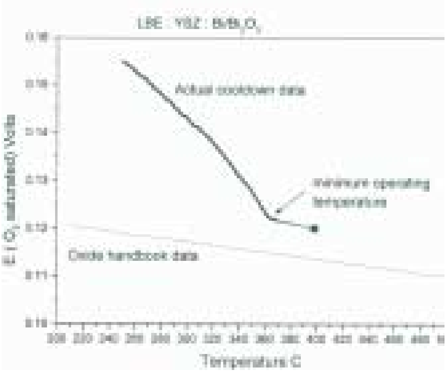

Fig. 1. Operating temperature for the YSZ sensor

The zirconia ceramic used as the sensor element is a strong but brittle material. 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, the LBE must be contained and any potential flow paths minimized. Design or procedures should minimize the possiblility of any brittle section being subjected to thermal shocks.

The sensor and seals should 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 thicknesses that will not be adversely affected by the temperatures in the loop or be deteriorated by prolonged contact with liquid LBE.

III.B. Reference oxygen concentrations

Since we only measure relative concentrations, we must have a stable, known oxygen concentration to measure against. The outside of our conical sensor will be immersed in the LBE with an unknown oxygen concentration. The inside must be exposed to the reference. If the inside is coated with porous Pt, we 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 disadvantages of requiring a vent to the atmosphere (potential LBE leak path), and of having a reference where local concentration variations may occur.

Mounted vertically, the inside of the cone may contain another liquid metal and no Pt coating. If the liquid metal, such as In or Bi (must have a low melting point) is in equilibrium with chunks of its solid oxide, the dissolved oxygen in the liquid will have a known saturation value, depending on the temperature. This saturation value is a good reference. Advantages are a stable reference and no vent to atmosphere needed, a disadvantage is the need for vertical mounting to contain the liquid.

III.C. Design

The design was developed to accommodate the requirements listed above and is shown in figure 2. A stainless tube penetrates the loop pipework and is welded in place. The sensor element has a graphite seal at the bottom of the tube so that the cone protrudes into the LBE flow. The interior of the tube has several concentric tubes of stainless steel and alumina ceramic. This serves several purposes: the space inside the tube is almost entirely filled, leaving the smallest gaps for LBE leak paths; the inner tubes serve as push rods to compress the graphite gasket material between the sensor support ring and the tube lip, and between the sensor and the sensor support ring; the ceramic insulates the innermost tube and the connection wire (made of Ta, insoluble in most liquid metals), so they can both be used as electrical connections. A standard vacuum flange with copper gasket is welded to the top end. A mating flange seals, and 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 to a liquid reference through a Ta wire down the center ceramic tube, or to the Pt metal coating connection through the innermost tube and a spot welded Ta wire to the BNC feedthrough.

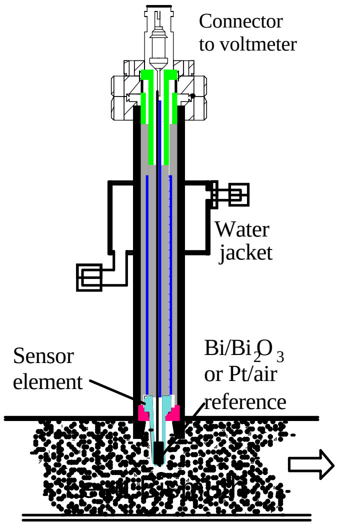

Fig. 2. The oxygen sensor in place in the pipework.

A stainless steel water jacket surrounds the tube near the flange end. This provides protection against leaks by freezing any liquid LBE which may, in an abnormal circumstance, find its way into the tube. It also keeps the connection end cool so that BNC cable fittings (inevitably containing plastics) are not affected by the heat.

IV. MEASUREMENTS

The loop and the liquid LBE will be maintained at ground potential as best as possible, so that the shell of the BNC feedthrough, connected by welds, will be a good ground and will be the voltage reference for measurement of the charge accumulated at the inside electrode. The inside electrode, either Pt or liquid Bi, is connected to the center conductor of the BNC. A standard BNC cable will take this signal to the input of a 10^{14} Ω input impedance electrometer. The low impedance analog output from these instruments will be taken to a digitizing input to be read by the computer control system.

There are four places in the loop pipework where sensors are inserted, two near the hottest and two near the coldest parts of the loop. This is important since the oxidation chemistry varies with the temperature and we need to maintain protection for the entire loop by controlling the oxygen level in the lead bismuth to appropriate levels. This control is a feedback process where oxygen is added or removed from the liquid by introducing gases into the flow through the cover gas system. Adding hydrogen gas will tend to remove dissolved oxygen from the fluid in the form of water vapor, while adding oxygen gas adds dissolved oxygen. Figure 3. shows the voltage response of one of our sensors in a test apparatus. An argon/6% hydrogen gas was bubbled through the system until the voltage stabilized, near 0.45V, below the expected limit for dissolving oxygen from iron oxide. This flow was maintained as a Argon/6%Oxygen gas mixture was added to the flow. The voltage responded almost immediately and leveled out near the saturated value within minutes. Removing the oxygen flow showed a slow recovery to the cleaned state, taking about 18 hours. The cleanup process is much less efficient than the oxidation process, suggesting that initially clean LBE would be advantageous. Also it seems that the values we calculated via the Nernst equation are close, but not entirely accurate, suggesting the importance of calibration.

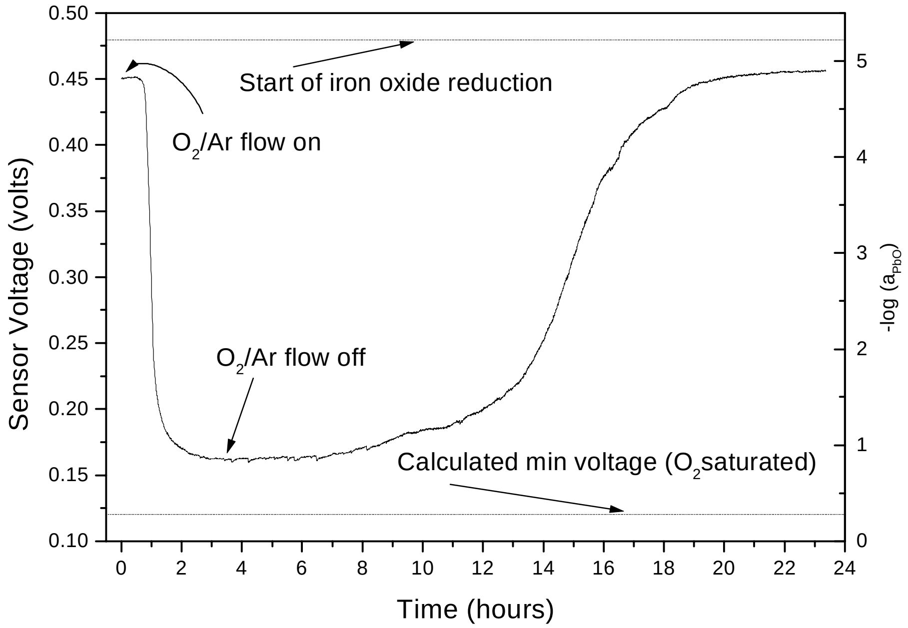

Fig. 3. Voltage response of the sensor to hydrogen and oxygen gas flows.

V. CONCLUSIONS

We have verified the performance of automobile industry YSZ oxygen sensors in liquid LBE. They offer a number of advantages over the usually available forms of YSZ, in the ease of making replacable seals and the availability of industry-produced porous Pt coatings. The calibration of the sensors is an issue which can be covered by using known thermochemical oxide data for several fixed states at known temperatures. This sensor design will be used in the Los Alamos LBE materials test loop for oxygen level control.

ACKNOWLEDGEMENTS

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