Title: OXYGEN SENSORS AND CORROSION WITH OXYGEN CONTROL IN LBE SYSTEMS

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Submitted to: "Sixth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation"
Dec. 11-13, 2000
Madrid, Spain
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In lead-bismuth eutectic (LBE) systems, an effective technique for corrosion prevention is via active control of the thermodynamic oxygen activity (TOA) in the molten metal[1][2]. Because of the relative inertness of Pb and Bi, it is possible to “passivate” the surface of structural steels with a protective “self-healing” oxide film by controlling the oxygen concentration in LBE. In this paper we report the experimental and numerical results from our development of oxygen sensors to measure and control TOA and modeling of corrosion process with oxygen control.

The measurement of the oxygen concentration is accomplished with ceramic solid-electrolyte sensors based on zirconia or thoria. We chose to use a closed rounded cone of the electrolyte with a seal away from the hot metal. These cones are developed for automobile industry and are about 1-2” long, with an integral flange at the base. This shape is strong, suitable for insertion into liquid LBE and has a flanged sealing surface that may be clamped for a high temperature seal.

We have successfully developed an yttrium-stabilized zirconia (YSZ) oxygen sensor with a Bi/Bi$_2$O$_3$ reference electrode in our test LBE system. The sensor is replaceable and uses a graphite gasket on the flange to form a high temperature seal when clamped to the end of a stainless steel fitting. The LBE system has a gas inlet for adding H$_2$ or O$_2$ for control and a continuous oscillating agitation of the liquid metal. We can control the TOA with gas mixtures and measure the resulting voltages, as shown in Figure 1. Using the output voltage as a control parameter we can stabilize the TOA (oxygen concentration) to any given value in the useful range between saturation (precipitation of PbO) and reduction of iron oxides. Polished, electrically isolated stainless steel samples are inserted into LBE at various oxygen concentrations for extended periods during which various electrical characteristics of the stainless steel – LBE interface are recorded for comparison with the resulting surface effects.
The presence of an oxide film on the steel surfaces can drastically reduce the level of Fe at the structure and LBE interface, thus reducing the corrosion rate [2]. In non-isothermal LBE flow systems, Fe from steel is removed from hot legs and transferred to the cold legs where it precipitates as iron oxides. We modeled the corrosion process with oxygen control and compared with corrosion without oxygen.

The transport of Fe in LBE satisfies the convection-diffusion equation. If we assume that convection is dominant in the axial direction and diffusion is dominant in the transverse direction (applicable for most pipe flow configurations), the governing equation becomes:

$$ u(y) \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}, $$

where $D$ is the mass diffusion coefficient. The concentration of Fe at the interface (wall) can be determined by:

$$ c(y = 0) = c_0^e \cdot \frac{4}{3} \exp \left( 4.66 - \frac{29574}{T} \right) $$ (with oxygen control)

or
\[ c(y = 0) = \exp(4.63 - \frac{10085}{T}) \]  
(without oxygen control)

where \( c_{O2} \) is the oxygen concentration in weight percent and \( T \) is temperature in Kelvin.

If we further assume the majority of the diffusion process occurs near wall, as in fully turbulent flows, we can solve the above equation using Fourier transform. The detail of the solution procedure will be reported elsewhere. We found that there is a phase shift of corrosion mass flux profile with respect to the temperature profile. In the case of a single harmonic temperature profile, the maximum corrosion (precipitation) occurs one twelfth of a period ahead of the highest (lowest) temperature.

![Figure 2](image)

**Figure 2.** Temperature distribution and calculated corrosion (precipitation) rates in a materials test loop with oxygen control \((C_{O}=10^{-5}\text{wt}\%)\) and without oxygen.

The analysis is applied to the Materials Test Loop (MTL) under construction at LANL. The MTL consists of a heater, a recuperator and a heat exchanger to set the temperature variations. Figure 2 shows the calculated corrosion/precipitation rate in the loop. As is shown, this rate can be thousands of times lower with oxygen control compared to that without any oxygen in LBE. In this case, the highest corrosion occurs at the end of the heater section where the temperature is the highest. However the highest precipitation occurs at the end of the recuperator, which is at the mid-point of the temperature range.
This model will assist the design and analysis of corrosion experiments, and the design and maintenance of oxygen controlled LBE systems.

Reference:
