Performance of Oxygen Sensors with Solid Fe/Fe$_3$O$_4$ and Liquid Bi/Bi$_2$O$_3$ Reference Electrode in Liquid LBE

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The performance of the oxygen sensors with solid and liquid type reference electrodes (RE) was investigated in the liquid lead-bismuth eutectic (LBE). The oxygen potentials in the LBE were made equilibrium with the formation potentials of PbO and Fe$_3$O$_4$ at 450°-600°C. The stabilization time to an equilibrium condition of the RE of solid type RE was shorter than liquid type RE, and both of the sensors performed well in the liquid LBE.

**Keywords:** Solid electrolyte oxygen sensor, Lead-bismuth eutectic, Reference electrode

1. Introduction Various solid electrolyte oxygen sensors have been developed for measurement of oxygen concentration in a liquid Pb-Bi coolant of fast reactor [1]. A sensor with solid type reference electrode (RE) has some advantages compared to that with liquid RE [2]. However, the stabilization time of solid RE and liquid RE must be made clear. The stabilization time means the time required for the internal reference material to reach the redox equilibrium condition from initial setup condition. The purpose of the present study is to investigate the stabilization time of RE and the cell potential (E) of oxygen sensor under steady state condition with the oxygen potential corresponding to the formation potential of PbO and Fe$_3$O$_4$.

2. Experimental Conditions Two types of RE material were used, liquid Bi/Bi$_2$O$_3$ RE and solid Fe/Fe$_3$O$_4$/gas RE. Magnesia stabilized zirconia (MSZ) was used as solid electrolyte material. Fig. 1 shows the schematic drawings of fabrication of the oxygen sensor with solid Fe/Fe$_3$O$_4$/gas and liquid Bi/Bi$_2$O$_3$ RE. The details of fabrication of the oxygen sensor have been explained in the previous work [3]. The experimental conditions were summarized in Table 1. The oxygen potentials in LBE were controlled to be equilibrium with the PbO and Fe$_3$O$_4$ formation potentials using the mass-exchanger method. The details of this method to control the oxygen potential have been explained in the previous work [3].

<table>
<thead>
<tr>
<th>Reference Electrode Type</th>
<th>Temperature (°C)</th>
<th>Equilibrium oxygen potential in LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Fe$_3$O$_4$</td>
<td>450 - 600</td>
<td>PbO</td>
</tr>
<tr>
<td>Bi/Bi$_2$O$_3$</td>
<td>450 - 600</td>
<td>Fe$_3$O$_4$</td>
</tr>
</tbody>
</table>

3. Results and Discussion In the beginning the sensors were tested from initial setup condition to 550°C in liquid LBE to see the stabilization time of the oxygen sensor. The liquid of Bi/Bi$_2$O$_3$ type RE needed a longer time to reach an equilibrium condition compare to the solid Fe/Fe$_3$O$_4$ type RE. The oxygen saturated liquid Bi RE could not achieve the equilibrium condition within a short period probably because the effective area of gas phase for the equilibrium reaction of the liquid reference was smaller than that of the solid powder reference. Fig. 2 shows the results of measured cell potential from experiment and the theoretical calculation for oxygen sensor with Fe/Fe$_3$O$_4$ and Bi/Bi$_2$O$_3$ RE. The data shown in Fig. 2 were the average data for the last 1 hour after the steady state condition was attained. In LBE equilibrium with PbO and Fe$_3$O$_4$ formation potential, the oxygen sensor could attain steady state condition for each temperature. The discrepancy between experimental data and theoretical calculation was small. Therefore, both of the RE materials can be used in oxygen sensors in liquid LBE at temperature 450°C - 600°C.

4. Conclusion The stabilization time to an equilibrium condition of the RE of solid Fe/Fe$_3$O$_4$ RE was shorter than liquid Bi/Bi$_2$O$_3$ RE. However, after the steady state condition attained both of the sensors performed well in the liquid LBE at the temperature of 450°C - 600°C.

**References**