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著者(和文)	Adhi Pribadi Mumpuni
Author(English)	Pribadi Mumpuni Adhi
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	Pribadi Mumpuni ADHI	指導教員（主）： Academic Supervisor(main)	高橋　実　教授
		指導教員（副）： Academic Supervisor(sub)	加藤　之貴　教授

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Lead-bismuth eutectic (LBE, 44.5 wt% of Pb and 55.5 wt% of Bi) has been proposed as a candidate of coolant of Lead-Bismuth-cooled type fast reactor (LFR) and accelerator-driven system (ADS). Measurement of oxygen concentration in LBE is important in these systems for the suppression of material corrosion and coolant technology. In previous studies, potentiometric oxygen sensors made of zirconia solid electrolyte have been tested for on-line monitoring of oxygen concentration. In the present study, the use of solid Fe/Fe_3O_4 and Ag/air as reference electrode materials was proposed as well as a liquid reference electrode, and the studies were focused on the following characteristics: the stabilization time of oxygen sensor in constant oxygen concentration of air using solid Fe/Fe_3O_4 and liquid Bi/Bi_2O_3 as RE; the performances of the sensors in various oxygen potential of LBE from high to low; and charge transfer reaction rate between liquid Bi/Bi_2O_3 RE and Ag/air RE investigated by means of Electrochemical Impedance Spectroscopy (EIS) in temperature range lower than 450°C.

Zirconia solid electrolyte oxygen sensors were fabricated and characterized for dissolved oxygen in liquid LBE. Three types of reference electrode (RE) materials, i. e., liquid metal Bi/Bi_2O_3, solid powder Fe/Fe_3O_4, and metal-gas Ag/air, were tested for this characterization study. A wire made of Mo or Kanthal was used as electric lead. The oxygen sensor and an electric lead wire was immersed into a working electrode of liquid LBE and cell potential was determined by high impedance electrometer. various Oxygen potential in the working electrode of LBE was controlled by mass-exchanger method where metal/metal oxide powders of PbO, Fe/Fe_3O_4, Cr/Cr_2O_3, and Ti were mixed with LBE. For low oxygen potential test, oxygen concentration in liquid LBE was reduced using the mechanism of an electrochemical oxygen pump (EOP). Charge transfer resistance of oxygen sensor was measured by the electrochemical impedance spectroscopy (EIS) method and the optimum material for RE material of oxygen sensor was determined.

The sensor stabilization time was investigated experimentally in air environment in a temperature range from room temperature to 600°C, where the stabilization time was defined by the time from initial setup condition to the redox equilibrium condition of the internal reference material. A test parameter was the air volumes in the reference compartment of solid powders, i. e. Fe/Fe_3O_4 and Bi/Bi_2O_3. The results demonstrated that reducing the initial air volume in the reference compartment with inert material shortened the stabilization time. It was also found that the stabilization time of oxygen sensor with Fe/Fe_3O_4 was shorter than that of Bi/Bi_2O_3, where the stabilization time was around 10 minutes.

The oxygen sensor with small air inside the solid reference compartment were characterized in liquid LBE environment with high, medium, and low oxygen potential, where the oxygen potential in the LBE was controlled to be equilibrium with the PbO, Fe_3O_4, Cr_2O_3, TiO_2 formation potentials as Mass-exchanger method. The temperatures were varied from 450 – 600 °C.

In cases of high and medium oxygen potential of liquid LBE controlled by PbO and $Fe+Fe_3O_4$ powder, the cell potential of the oxygen sensor agreed well with the theoretical one given by the Nernst equation. When the oxygen sensor with the solid Fe/Fe_3O_4 RE was also tested in low oxygen potential of liquid LBE controlled by $Cr + Cr_2O_3$, the Mass-exchanger method failed to control the oxygen potential at low value in LBE, that is, the result showed lower value than theoretical one with the discrepancy of around 177.44 mV at 450°C. Thus, the oxygen potential was reduced very low value by Ti powder, and the minimum controlled oxygen concentration was 8.36×10^{-19}wt% which is correspond to oxygen partial pressure of 8.83×10^{-50} atm at temperature of 450°C. The results of cell potential obtained by the oxygen sensor with the solid Fe/Fe_3O_4 RE were between the oxide formation potentials of Cr_2O_3 and TiO_2.

The oxygen potential in liquid LBE was lowered by using electrochemical oxygen pump (EOP). Parstat MC as potentiostat was used as an instrument to give external voltage to the EOP cell . The testing temperatures were varied from 450 to 550 °C. Ar and 3%H_2 gas was used as a cover gas inside the

apparatus. The dissolved oxygen potential in liquid LBE was successfully reduced by the EOP method. The result was compared with the previous result of chapter 4. The cell potential obtained was nearly equal to the cell potential obtained in liquid LBE with Ti powder in chapter 4. The oxygen sensor could measure the very low oxygen concentration up to 10^{-19} wt% in liquid LBE at temperature 450°C.

The oxygen sensor with Ag/air RE was tested at low temperature of LBE from 300 to 450°C in liquid LBE equilibrium with PbO formation potential. Ar gas was used as cover gas inside the apparatus. The accuracy of cell potential of the oxygen sensor with Ag/air RE was compared to the oxygen sensor with liquid Bi/Bi_2O_3 RE. Electrochemical impedance spectroscopy (EIS) was used to analyze charge transfer reaction impedance to determine the optimum material of RE.

In the use of Potentiostat Parstat 2273 to perform the EIS, the AC voltage with the amplitude of 500 mV was applied to the oxygen sensor with Ag/Air reference electrode. The AC voltage of 100 mV was applied to the sensor cell for the oxygen sensor with Bi/Bi_2O_3 RE, The impedance response signal was periodically obtained over the frequencies range from 1 to 100 kHz. The result showed that the cell potential of two kind of sensors agreed well with the theoretical one given by the Nernst equation. On the other hand, according to the impedance result, oxygen sensor with Bi/Bi_2O_3 reference electrode had lower impedance than that with Ag/air type reference electrode. Therefore, Bi/Bi_2O_3 was judged as better reference electrode material from a fast response time of the oxygen sensor in a low-temperature range below 450°C.