The performance of Pt/air oxygen sensors in stagnant Pb-Bi eutectic at high temperatures (Postprint)

Authors: WANG Yan-Qing, HUANG Qun-Ying, WU Bin, ZHANG Min, WU Xin, GAO Sheng

Date: 2023-06-18T00:00:00+00:00

Abstract

Oxygen control technology is a critical issue for compatibility of candidate structural materials with liquid lead-bismuth eutectic (LBE) in accelerator driven systems. Performances of a self-developed Pt/air sensor and another one from Karlsruher Institute of Technology (KIT) were tested in stagnant oxygen-saturated liquid LBE. Calibrations showed that the trend and values of corrected electromotive force (EMF) of the self-developed sensor, with a bias voltage of 20 mV, were consistent with theoretical results above 425 ℃, and similar results were obtained in cross-calibration test with EMF value of KIT sensor as reference. In stability test at 450 ℃ for 100 hours, the KIT sensor performed better than the self-developed one, which showed signal fluctuations. Both sensors exhibited quick response to temperature variations in the responsiveness test.

Full Text

Preamble

The Performance of Pt/Air Oxygen Sensors in Stagnant Pb-Bi Eutectic at High Temperatures

WANG Yan-Qing (王艳青),[1,2] HUANG Qun-Ying (黄群英),[1,2] WU Bin (吴斌),[2,†] ZHANG Min (张敏),[1,2] WU Xin (武欣),[2] and GAO Sheng (高胜)[2]

[1]University of Science and Technology of China, Hefei 230027, China
[2]Institute of Nuclear Energy Safety Technology, Chinese Academy of Sciences, Hefei 230031, China

(Received January 22, 2014; accepted in revised form March 18, 2014; published online December 16, 2014)

Oxygen control technology is a critical issue for compatibility of candidate structural materials with liquid lead-bismuth eutectic (LBE) in accelerator driven systems. Performances of a self-developed Pt/air sensor and another one from Karlsruher Institute of Technology (KIT) were tested in stagnant oxygen-saturated liquid LBE. Calibrations showed that the trend and values of corrected electromotive force (EMF) of the self-developed sensor, with a bias voltage of 20 mV, were consistent with theoretical results above 425 °C, and similar results were obtained in cross-calibration test with EMF value of KIT sensor as reference. In stability test at 450 °C for 100 hours, the KIT sensor performed better than the self-developed one, which showed signal fluctuations. Both sensors exhibited quick response to temperature variations in the responsiveness test.

Keywords: Lead-bismuth eutectic, Oxygen sensor, Calibration, Electromotive force
DOI: 10.13538/j.1001-8042/nst.25.060602

Introduction

Driven by the need for candidate materials for spallation neutron targets and coolant in accelerator driven systems (ADS), lead-bismuth eutectic (LBE) has been studied widely due to its favorable thermophysical and chemical properties. However, liquid LBE is corrosive to structural materials at high temperatures and may cause plugging due to the formation of lead monoxide (PbO). For compatibility of materials with LBE, oxygen contents in LBE should be maintained within certain margins to form protective oxide films on the surface of structural materials and to prevent the formation of PbO [1–7]. As accurate oxygen content measurement is a prerequisite for oxygen control technology, oxygen sensors play a critical role in an active oxygen control system (OCS). In lead or LBE systems, yttria-stabilized zirconia (YSZ) or magnesia-stabilized zirconia (MSZ) are employed as solid electrolytes for oxygen sensors [8], with YSZ being more widely used [1, 3, 9]. It is generally accepted that Russian scientists paved the way for the development of oxygen sensors and oxygen control technology [6, 8]. The oxygen sensors developed in Russia are accurate in measuring oxygen content, with long service lifetimes [10].

Oxygen sensors have been studied extensively. Konys et al. found that oxygen sensors with Pt/air reference electrodes showed better reliability and longer lifetimes than those with Bi/Bi_2O_3 reference electrodes, based on tests carried out in the CORRIDA loop and other devices at the Karlsruher Institute of Technology (KIT) [2, 11]. Courouau et al. developed oxygen sensors with Bi/Bi_2O_3 reference electrodes [3, 12, 13]. Kurata et al. studied Pt/air and Bi/Bi_2O_3 reference sensors and found that electromotive force (EMF) values of both sensors could be corrected by subtracting a certain bias voltage, though the physical meaning of the bias voltage was not entirely clear [8]. It is necessary to verify the performance of a newly assembled oxygen sensor before its use in a liquid LBE system, to ensure high accuracy, reproducibility, long-term stability, and short response time [14].

Having worked on heavy liquid metal (HLM) technologies for over ten years [15–21], the FDS team is now studying key technologies for liquid LBE loops named KYLIN series, focusing on material corrosion, thermal-hydraulics, oxygen measurement and control, and related areas [22–24]. For oxygen measurement, two Pt/air sensors—the self-developed Sensor 1 and Sensor 2 from KIT—were tested in oxygen-saturated liquid LBE. The accuracy of Sensor 1 was evaluated and cross-calibrated with the EMF values of Sensor 2, and the stability and responsiveness of both sensors were also tested.

II. Methods

A. The Oxygen Sensor

Electrochemical oxygen sensors are based on EMF measurement at null current for a galvanic cell built with a doped zirconia solid electrolyte, which conducts oxygen ions specifically [25]. A Pt/air reference oxygen sensor with YSZ as solid electrolyte is illustrated schematically in Fig. 1 [Figure 1: see original paper] [9, 24, 26]. The oxygen partial pressure in the reference electrode ($pO_{2,\mathrm{ref}}$) is higher than the partial pressure of dissolved oxygen in LBE (pO_2). The oxygen ions (O^{2-}) move through the solid electrolyte toward the LBE side, and electrons are transferred back to the reference side through connecting wires, thus forming an EMF across the solid electrolyte, which can be measured by a high-impedance electrometer [25, 27] with impedance > 1 GΩ in general [1].

The cell can be expressed in the following form [27]:

$$(-)SS|Pb, PbO|YSZ|Pt, O_2|SS(+)$$

The left side represents the oxidation process: $Pb + O^- \rightarrow PbO + 2e^-$. The right side represents the reduction process: $O_2(g)/2 + 2e^- \rightarrow O^-$. The total reaction is $Pb + O_2(g)/2 \rightarrow PbO$.

B. EMF of Oxygen Sensor

According to the Nernst equation, the EMF value of an oxygen sensor is expressed as [6]:

$$E = (RT/4F)\ln(pO_{2,\mathrm{ref}}/pO_2)$$

where E is in V and T is in K (being so throughout the text), $R = 8.31451\,\mathrm{J/(mol\cdot K)}$ is the ideal gas constant, and $F = 96485.31\,\mathrm{C/mol}$ is the Faraday constant. The $pO_{2,\mathrm{ref}}$ is given at a certain temperature, and pO_2 can be calculated by Eq. (5).

Inserting the values of R and F into Eq. (5) yields:

$$E = 2.1543 \times 10^{-5} T \ln(pO_{2,\mathrm{ref}}/pO_2)$$

For Pt/air sensors, the reference oxygen partial pressure is determined by the volume concentration of oxygen in air (generally 20.946 vol%), giving $pO_{2,\mathrm{ref}}/p^{\Theta} = 0.20946$, where p^{Θ} is standard atmospheric pressure. Substituting Eq. (7) into Eq. (6) yields:

$$E = [-3.3677 - 2.1543 \ln(pO_2/p^{\Theta})] \times 10^{-5} T$$

The oxygen partial pressure above saturated LBE, $pO_{2,s}$, and the oxygen partial pressure above unsaturated solutions, pO_2, can be calculated by Eqs. (9) and (10) [28]:

$$pO_{2,s}/p^{\Theta} = \exp[25.624 - (52341/T)]$$

$$pO_2/p^{\Theta} = C_O^2 \exp[13.558 - (32005/T)]$$

where C_O is the oxygen concentration in wt%. Substituting Eqs. (9) and (10) into Eq. (8), respectively, gives [28]:

$$E_{\mathrm{th}} = 1.1276 - 5.8568 \times 10^{-4} T$$

$$\log C_O = -3.2837 - (6949.8 - 10080E)/T$$

where E_{th} is the theoretical EMF for oxygen-saturated LBE.

C. Experimental Apparatus and Procedures

Figure 2 [Figure 2: see original paper] shows the schematic diagram and photograph of the experimental apparatus. It consists mainly of a gas control system, an experimental tank with three positions for installing oxygen sensors, and a data acquisition (DAQ) system.

Oxygen sensors were mounted onto the tank (Fig. 2(b)), the tank's air tightness was checked, and the LBE was melted. The oxygen sensors were then inserted approximately 30 mm into the liquid LBE by depressing the bellows. EMF values of the oxygen sensors and the temperature of LBE were recorded by the DAQ system using LabVIEW.

An Ar+2%O_2 gas mixture was introduced continuously into the tank as cover gas at a flow rate of 10 mL/min, and the oxygen partial pressure of this mixed gas was higher than the oxygen pressure required for PbO formation in liquid LBE [29]; therefore, the liquid LBE was saturated with oxygen.

III. Results and Discussion

A. Calibration

An oxygen sensor should be calibrated to verify whether its EMF output is accurate [9]. Calibration was carried out in oxygen-saturated LBE at 370–540 °C [25]. As shown in Fig. 3 [Figure 3: see original paper], the measured EMF data of Sensor 1 (E_{S1}) were lower than the theoretical prediction (E_{th}, oxygen-saturated) [28], but it can be seen that above 425 °C the E_{S1} variation trend is consistent with E_{th}, indicating that Sensor 1 did not work reliably below 425 °C. Similar results have been reported [6, 8]. This was caused by insufficient diffusion rate of oxygen ions in the solid electrolyte at low temperatures [30], which increases cell irreversibility, making Eq. (5) no longer applicable to the cell [6]. For LBE in oxygen-saturated conditions, a bias voltage can be considered [8]. The bias voltage was 20 mV at temperatures above 425 °C, and E_{S1} was measured again. Fig. 3 shows that the corrected EMF data of Sensor 1 ($E_{S1\text{-corrected}}$) agree well with E_{th} above 425 °C. The deviation of E_{S1} can be related to the electrolyte conduction properties, alteration of the electrode/electrolyte interface, and resistance of the Pt/air electrode. Sensor 1 was cross-calibrated with Sensor 2, which had been calibrated at KIT and serves as a suitable reference. Fig. 3 also shows the EMF data of Sensor 2 (E_{S2}) and $E_{S1\text{-corrected}}$. They are consistent with each other above 425 °C, similar to the results using E_{th} as reference.

The relative errors of $E_{S1\text{-corrected}}$ are shown in Fig. 4 [Figure 4: see original paper]. Referenced against E_{th} and E_{S2}, the maximum and minimum errors were −3.6% at 370 °C and 0.063% at 518 °C, and −5.0% at 370 °C and −0.27% at 518 °C, respectively. Therefore, the accuracy of $E_{S1\text{-corrected}}$ is assessed to be within $±$5% relative error.

Based on these results, Sensor 1 (with a bias voltage of 20 mV) was suitable for measuring dissolved oxygen concentration (C_O) in LBE above 425 °C, and the corresponding oxygen concentrations calculated with Eq. (12) [29] confirmed these points (Fig. 5 [Figure 5: see original paper]). The oxygen concentrations calculated using $E_{S1\text{-corrected}}$ ($C_{O,S1\text{-corrected}}$) and E_{S2} ($C_{O,S2}$) as input variables are consistent with the theoretical saturated oxygen contents ($C_{O,\text{oxygen-saturated}}$) calculated with EMF from Eq. (11) as input variables.

B. Stability Test

Checking the stability of an oxygen sensor under specific conditions is essential for practical application [12, 31]. Stability tests of Sensors 1 and 2 were carried out in stagnant oxygen-saturated LBE at 450 °C for 100 h. As shown in Fig. 6 [Figure 6: see original paper], the averaged EMF was (0.683 ± 0.020) V and (0.706 ± 0.002) V for Sensors 1 and 2, respectively, while the calculated EMF was 0.704 V at 450 °C. The temperature fluctuation during the 100 h was $±$2 °C (Fig. 6(b)). The results show that Sensor 2 performed well in the test, comparing the experimental and theoretical EMF values [31]. For Sensor

1, large fluctuations were observed during the 100 hours; however, with a bias voltage of 20 mV, the mean EMF value (0.703 V) agrees well with the theoretical value of 0.704 V.

C. Responsiveness Test

Response time to changes in operating conditions is important for oxygen sensors used in LBE [14, 25]. Fig. 7 [Figure 7: see original paper] shows the response test results of Sensors 1 and 2 with three stages of heating (see the dashed line in the figure). Both sensors exhibited fast response (Fig. 7(a)), with no significant delay relative to temperature variations initially from 386 °C, 409 °C, and 426 °C, respectively. According to Eq. (11), for oxygen-saturated LBE, EMF decreases with increasing temperature, and EMF results of both sensors followed this trend.

Figure 7(b) shows temperature fluctuations with peaks due to the inertia of the heating cell of the experimental tank, but temperatures stabilized at approximately 409 °C, 426 °C, and 443 °C, respectively. From Fig. 7(a), only at the first peak of each heating stage did the EMF values of both sensors decline clearly, and small temperature disturbances over relatively short periods did not change the oxygen concentration of LBE immediately. Comparing the time required for initial sensor response at the three heating stages, faster responses were observed at higher starting temperatures.

IV. Conclusion

Two Pt/air reference electrode oxygen sensors (Sensor 1, self-developed; and Sensor 2, from KIT) were tested in stagnant oxygen-saturated liquid LBE. The sensor performances are summarized as follows:

(a) In the calibration test, the corrected EMF data of Sensor 1 with 20 mV bias voltage showed consistency with theoretical results and the EMF data of Sensor 2 at temperatures above 425 °C. The calculated oxygen contents confirmed these findings.

(b) In the stability test, Sensor 2 performed well, and the corrected EMF value of Sensor 1 was in accord with the theoretical value at 450 °C, though its signal fluctuations were somewhat large.

(c) In the responsiveness test, both sensors exhibited quick response to temperature variations, with faster sensor response observed at higher starting temperatures.

The results showed that Sensor 1 was suitable for measuring dissolved oxygen concentration in LBE above 425 °C. How to reduce signal fluctuation during long-term service and further study response performance are important issues to be addressed in future work. The primary LBE charge/discharge operation and circulation in the KYLIN-II loop has recently succeeded, and testing of self-developed Pt/air reference oxygen sensors in this loop is currently in progress.

Acknowledgements

The authors thank Dr. JIANG Zhi-Zhong of the FDS team and Mr. HE Long-Hai of Anhui Institute of Optics and Fine Mechanics, CAS, for useful discussions.

References

[1] Schroer C, Konys J, Verdaguer A, et al. J Nucl Mater, 2011, 415: 338-347.
[2] Schroer C, Wedemeyer O, Konys J. Nucl Eng Des, 2011, 241: 4639-4646.
[3] Courouau J L, Trabuc P, Laplanche G, et al. J Nucl Mater, 2002, 301: 53-59.
[4] Rivai A K, Kumagai T, Takahashi M. Prog Nucl Energ, 2008, 50: 575-581.
[5] Zhang J S and Li N. J Nucl Mater, 2008, 373: 351-377.
[6] OECD. Handbook on lead-bismuth eutectic alloy and lead thermal hydraulics and properties, materials compatibility, technologies, 2007.
[7] Arkundato A, Su' ud Z, Abdullah M, et al. Ann Nucl Energy, 2013, 62: 298-306.
[8] Kurata Y, Abe Y, Futakawa M, et al. J Nucl Mater, 2010, 398: 116-121.
[9] Gabriele F D. Protocol and standards for HLM technology elements testing. FP7-249677-HeLiMnet, 2012.
[10] Shmatko B A and Rusanov A E. Mater Sci+, 2000, 36: 689-692.
[11] Konys J, Muscher H, Voss Z, et al. J Nucl Mater, 2004, 335: 249-252.
[12] Courouau J L. J Nucl Mater, 2004, 335: 254-259.
[13] Courouau J L, Deloffre P, Adriano R. J Phys IV, 2002, 12: 141-148.
[14] Wu X L. Master Thesis, University of Nevada, Las Vegas, 2008.
[15] Wu Y C, Huang Q Y, Zhu Z Q, et al. Chin J Nucl Sci Eng, 2009, 29: 161-169. (in Chinese)
[16] Wu Y C and FDS Team. Nucl Fusion, 2007, 47: 1533-1539.
[17] Wu Y C and FDS Team. Fusion Eng Des, 2007, 82: 1893-1899.
[18] Wu Y C and FDS Team. J Nucl Mater, 2007, 367: 1410-1415.
[19] Gao S, Zhang M L, Zhu Z Q, et al. Chin J Nucl Sci Eng, 2007, 27: 51-54. (in Chinese)
[20] Huang Q Y, Gao S, Zhu Z Q, et al. Fusion Eng Des, 2009, 84: 242-247.
[21] Huang Q Y, Li C J, Li Y F, et al. At Energ Sci Technol, 2007, 41: 397-406. (in Chinese)
[22] Zhu L L, Bai Y Q, Chen Z, et al. Chin J Nucl Sci Eng, 2010, 30: 333-337. (in Chinese)
[23] Wu Y C, Huang Q Y, Bai Y Q, et al. Chin J Nucl Sci Eng, 2010, 33: 238-243. (in Chinese)
[24] Wang G Y, Bai Y Q, Gao S, et al. Chin J Nucl Sci Eng, 2012, 32: 165-169. (in Chinese)
[25] Foletti C, Gessi A, Benamati G. J Nucl Mater, 2008, 376: 386-391.
[26] Ghetta V, Fouletier J, Henault M, et al. J Phys IV, 2002, 12: 141-148.
[27] Muscher H, Konys J, Voss Z, et al. Measurement of oxygen activities in eutectic lead-bismuth by means of the EMF method, FZKA 6690, 2001.
[28] Schroer C and Konys J. Physical chemistry of corrosion and oxygen control

in liquid lead and lead–bismuth eutectic. FZKA 7364, 2007.
[29] Colominas S and Abella J. Sensor Actuat B-Chem, 2010, 145: 742–746.
[30] Li N. J Nucl Mater, 2002, 300: 73–81.
[31] Schroer C, Wedemeyer O, Konys J. Nucl Eng Des, 2011, 241: 4639–4646.

Note: Figure translations are in progress. See original paper for figures.