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Characterization and re-activation of oxygen sensors for use in liquid lead–bismuth

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A B S T R A C T

Control of oxygen concentration in liquid lead–bismuth is one of the most important tasks to develop accelerator driven systems. In order to improve the reliability of oxygen sensors, re-activation treatments were investigated as well as characterization of oxygen sensors for use in liquid lead–bismuth. The oxygen sensor with a solid electrolyte of yttria-stabilized zirconia and a Pt/gas reference electrode showed almost the same electromotive force values in gas and liquid lead–bismuth, respectively, as the theoretical ones at temperatures above 400 °C or 450 °C. After long-term use of 6500 h, the outputs of the sensor became incorrect in liquid lead–bismuth. The state of the sensor that indicated incorrect outputs could not be recovered by cleaning with a nitric acid. However, it was found that the oxygen sensor became a correct sensor indicating theoretical values in liquid lead–bismuth after re-activation by the Pt-treatment of the outer surface of the sensor.

1. Introduction

Liquid lead and lead–bismuth eutectic (LBE) are promising candidate materials of core coolants and high-power spallation targets of accelerator driven systems (ADSs) for transmutation of radioactive wastes and of coolants of fast reactors. In order to use them in nuclear systems, development of systems for controlling oxygen concentration in lead and LBE is one of important research subjects [1–3]. Liquid LBE is corrosive for steels at high temperatures and likely to cause plugging due to PbO formation at high oxygen concentration. Therefore, it is necessary to mitigate corrosion by means of formation of self-heeling protective oxides above 450 °C in LBE. In addition, it is needed to avoid PbO formation at high oxygen concentration. The active oxygen control within the range between Fe_3O_4 and PbO formation has been proposed from this viewpoint [2–4].

It is essential to measure oxygen concentration correctly in LBE online for the active oxygen control. Oxygen sensors employing yttria-stabilized zirconia (YSZ) and magnecia-stabilized zirconia (MSZ) as a solid electrolyte enable us to measure oxygen concentration in LBE. While oxygen sensors using YSZ as a solid electrolyte and Pt/gas as a reference system are often used in automobile industries, the operating temperature of the sensors is generally rather high. It has been reported that oxygen sensors were used in liquid lead and LBE in Russia where research on nuclear system using them has been conducted for a long-term [1,2]. The special sensor using YSZ as a solid electrolyte and Mo/Bi–Bi_2O_3 as a reference system gave accurate measurement of oxygen concentration and long service lifetime [2]. Recently, oxygen sensors for use in liquid lead and LBE have been manufactured and tested worldwide.

Konys et al. [5,6] showed that YSZ sensors using a Pt/air reference electrode and a Mo/Bi–Bi_2O_3 reference electrode were promising in LBE as a result of tests of sensors using Pt/air, Mo/Bi–Bi_2O_3 and Mo/In–In_2O_3 reference electrodes. Furthermore, it was reported that the Pt/air reference electrode exhibited better reliability and longer lifetime than the Mo/Bi–Bi_2O_3 reference electrode [6]. Courouau et al. [7–9] mainly used the YSZ sensor with the Mo/Bi–Bi_2O_3 reference electrode as a result of tests of several Mo/metal–metal oxide electrodes. Calibration was also conducted for the Mo/Bi–Bi_2O_3 reference electrode sensors manufactured at the laboratory scale [8]. The calibration method firstly proposed by Konys et al. [5] is based on measurement of electromotive force (EMF) of the oxygen sensor following temperature variation under the condition close to oxygen saturation in LBE. The YSZ sensors with the Mo/Bi–Bi_2O_3 reference electrode have been manufactured and used by other researchers [4,10,11]. Although sensors with the Mo/In–In_2O_3 reference electrode have been also developed, the temperature range where measured EMF values agree with theoretical values in the calibration test is very narrow [5,9,12,13]. Furthermore, experience has been reported on use of Russian sensor with the Bi–Bi_2O_3 reference and sensors with the In–In_2O_3 reference in liquid Pb–Bi or liquid Pb [14].

The following two problems are pointed out in case of using the oxygen sensor with the Mo/metal–metal oxide reference

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electrode: this type of sensor often exhibits time drift that EMF values change with increase in service time [3] and measured EMF values disagree with the theoretical ones [5,13]. We have also tested YSZ sensors using Pt/air reference and Mo/Bi–Bi_2O_3 reference electrodes in LBE. Since the Pt/air reference sensor exhibited correct EMF values above 450 °C in LBE, we have used the sensor with the Pt/air reference electrode in LBE as a reliable sensor for a long time. However, we had experience that the sensor with the Pt/air reference electrode also exhibited incorrect EMF values in LBE after long-term use while the reason of incorrect outputs was not clear. In addition, the sensor with the Mo/Bi–Bi_2O_3 reference electrode exhibited different outputs from theoretical ones. According to Courouau [3,9], investigation of the cause of incorrect outputs and the re-activation treatment are important research subjects because time drift and incorrect outputs were often encountered with oxygen sensors.

In this study, the characteristic of the YSZ sensor with the Pt/air reference electrode is investigated through calibration tests in gas with constant oxygen concentration and in LBE. Furthermore, effectiveness of re-activation treatments is studied for the oxygen sensor that exhibited incorrect outputs.

2. Theory

An electrochemical galvanic cell using YSZ as an electrolyte is represented as follows:

Po_2(reference)//YSZ//Po_2

where Po_2 (reference) is the oxygen partial pressure at the reference electrode and Po_2 is the oxygen partial pressure at the working electrode. The EMF is formed across the solid electrolyte between the different oxygen partial pressures. The EMF, E is expressed as follows according to the Nernst equation:

$$E = \frac{RT}{4F}\ln\frac{P_{O_2}(\text{referece})}{P_{O_2}} \tag{1}$$

where R is the gas constant, T temperature and F the Faraday constant. When the gas containing a given oxygen concentration is used at the reference electrode side, the oxygen partial pressure at the working electrode, Po_2 can be calculated using the Eq. (1).

The oxygen activity, a_o in equilibrium with an oxygen pressure Po_2 is written assuming that dissolution of oxygen into LBE obeys the Henry's law:

$$a_o = \gamma_o C_o = \frac{C_o}{C_o^s} = \left(\frac{P_{o_2}}{P_{o_2}^s}\right)^{\frac{1}{2}} \tag{2}$$

where γ_o is an activity coefficient, C_o the oxygen concentration in LBE, C_o^s the saturated oxygen concentration in LBE and $P_{o_2}^s$ the oxygen concentration in gas in equilibrium with oxygen-saturated LBE. The activity a_o becomes unity when the oxygen dissolved in LBE attains the level of saturation (C_o=C_o^s). The saturated oxygen concentration in LBE is calculated using the following Orlov's equation [1]:

$$\log C_o^s\ (\text{wt}\%) = 1.2 - \frac{3400}{T} \tag{3}$$

Oxygen sensors using YSZ as a solid electrolyte and Pt/gas or Mo/Bi–Bi_2O_3 as a reference system were used in this study. When measurement was conducted in LBE, air was used as the reference gas in Pt/gas reference system. The 304SS rod was used as an electrode immersed in LBE. Therefore, the system for measurement in LBE is represented by Pt/air//YSZ//LBE/SS or Mo/Bi–Bi_2O_3//YSZ//LBE/SS. The relationship between the EMF and the oxygen concentration in LBE has been calculated for these two reference electrode sensors using standard Gibbs energy of PbO and Bi_2O_3 [6,7]. The equation derived by Courouau et al. [7] was used in this study.

For Pt/air reference sensor

$$E_{\text{Saturation}} = 1.129 - 5.858\times10^{-4}T \tag{4}$$

$$E = 0.791 - 4.668\times10^{-4}T - 4.309\times10^{-5}T\ln C_o \tag{5}$$

For Mo/Bi–Bi_2O_3 reference sensor

$$E_{\text{Saturation}} = 0.128 - 6.368\times10^{-5}T \tag{6}$$

$$E = -0.210 + 5.538\times10^{-5}T - 4.309\times10^{-5}T\ln C_o \tag{7}$$

3. Experimental procedure

3.1. Oxygen sensor

While YSZ sensors with the Pt/gas reference electrode and the Mo/Bi–Bi_2O_3 reference electrode were prepared, the former was mainly used in this study. The Pt/gas reference sensor made by Sukegawa Electric Co., Ltd. was the one-end closed YSZ tube with outer diameter of 15 mm and inner diameter of 11 mm. Fig. 1 shows the schematic drawing and the appearance of the Pt/gas reference sensor. The Pt/gas reference system was put inside the YSZ tube. In addition, platinum paste was painted on the lower part of the outer YSZ surface to measure oxygen concentration in gas. The Mo/Bi–Bi_2O_3 reference sensor was a sensor using the one-end closed tube of YSZ with the sizes of 8 mm in outer diameter, 5 mm in inner diameter and 300 mm in length. The Mo/Bi–Bi_2O_3 reference electrode was made inside the YSZ tube. The ratio of Bi and Bi_2O_3 was 9:1 in weight. The upper part of the YSZ tube was sealed using alumina cement. Our sensor with the Mo/Bi–Bi_2O_3 reference electrode was similar to the Mo/Bi–Bi_2O_3 reference sensor manufactured in other institutes [6,8,10].

3.2. Procedure and apparatus

Tests in this study consist of calibration tests of oxygen sensors and re-activation treatments of a sensor indicating incorrect outputs. The following two methods were employed for calibration of oxygen sensors: (1) comparison between measured EMF values and theoretical ones using two kinds of gases with different oxygen concentrations for the reference electrode and the working electrode, and (2) comparison between measured EMF values and theoretical ones in LBE with the parameter of temperature under the condition close to oxygen saturation in LBE. The latter method has been often employed as a calibration test in LBE [5,8].

The procedure and conditions of tests are shown in Fig. 2 and Table 1, respectively. Test 1 is a calibration test for the Pt/gas reference sensor using two kinds of gases with different oxygen concentrations. 10.45%O_2–He gas was used as reference gas and 502 ppmO_2–He gas as working gas. The temperature range was 350–600 °C and the temperature was kept for about 24 h to investigate change of the EMF values at each temperature.

In test 2, the above-mentioned calibration test in LBE was conducted for the sensor after test 1. A thin PbO film was observed on the surface of the liquid LBE with pure Ar cover gas at 450 °C. In addition, EMF measurements were performed in oxygen-unsaturated LBE after Ar–H_2–H_2O gas bubbling and Ar–4%H_2 gas bubbling.

The Pt/gas reference sensor examined in tests 1 and 2 exhibited good performance and has been used in LBE for about 6500 h. In test 3, calibration was conducted in LBE for the Pt/gas reference sensor after long-term use and a new Mo/Bi–Bi_2O_3 reference sensor. An apparatus made of 304SS was used in test 3 in consideration of practical use for LBE systems.

Since the Pt/gas reference sensor exhibited much higher EMF values than theoretical ones in test 3, re-activation treatments of

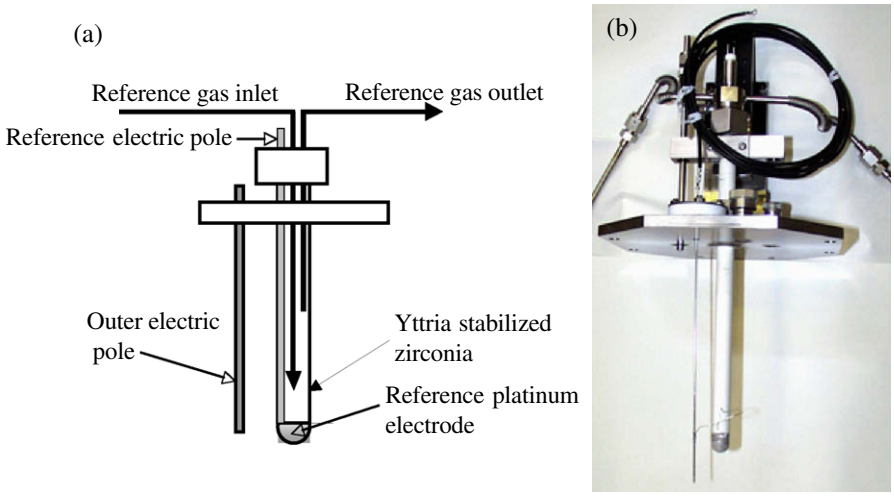

Fig. 1. Schematic drawing (a) and appearance (b) of the YSZ oxygen sensor with Pt/gas reference system.

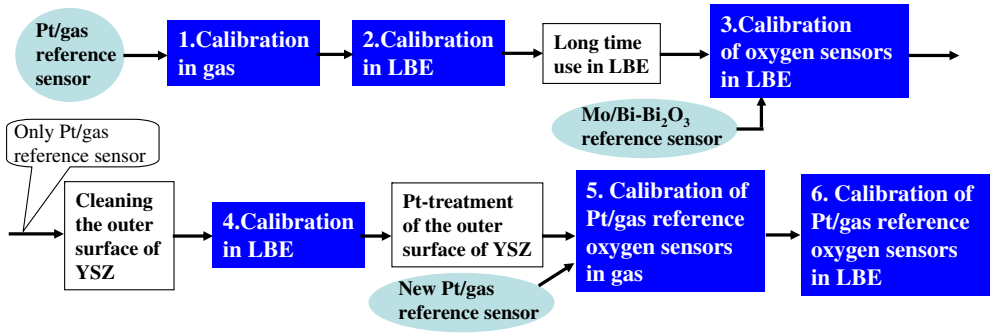

Fig. 2. Procedure of tests in this study.

Table 1
Test conditions of oxygen sensors.

Test No.	Sensor type	New or used	Outer Pt-treatment	Cleaning by HNO_3	Measured environment	Temperature range (°C)
1	A	New	○	–	Gas	350–600
2	A	New	○	–	LBE	355–555
3	A	Used	–	–	LBE	300–500
	B	New	–	–		
4	A	Used	–	○	LBE	350–500
5	A	Used	○	–	Gas	337–558
	A	New	○	–		
6	A	Used	○	–	LBE	314–550
	A	New	○	–		

A: Pt/gas reference.
B: Mo/Bi–Bi_2O_3 reference.

the sensor were tried. In test 4, calibration in LBE was conducted for the Pt/gas reference sensor after the cleaning the outer surface of the YSZ with a nitric acid.

In test 5, calibration was performed in gas for the Pt/gas reference sensor that exhibited much higher EMF values than theoretical ones in LBE. The Pt-treatment was made on the outer surface of the YSZ for calibration in gas. In this test, air was used at the inner reference electrode side and 504 ppmO_2–He gas was used at the outer working electrode side. Furthermore, the newly manufactured Pt/gas reference sensor was also tested in gas.

In test 6, the calibration test in LBE was conducted for both Pt/gas reference sensors after the test in gas. The sensors were soaked into liquid LBE as the state of Pt-treatment on the outer YSZ.

An apparatus for corrosion tests in LBE [15] was used for calibration tests of oxygen sensors except for test 3. The apparatus was composed of a quartz pot. The He gas containing a certain content of oxygen was passed in the pot for the calibration test in gas. 7 kg of LBE was put into the pot and melted under Ar cover gas with purity of 99.9999% for the calibration test in LBE. The chemical compositions of LBE were 55.60Bi–0.0009Sb–0.0002Cu–0.0001Zn–0.0005Fe–0.0007As–0.0005Cd–0.0001Sn–Bal.Pb (wt.%).

The temperature of the YSZ surface near the working electrode was measured using a thermocouple couple in the calibration test in gas. The outer working Pt/gas electrode for tests in gas was made by the Pt-treatment composed of painting platinum paste on the outer YSZ surface and baking. An electrometer with high impedance of $10^{14}\ \Omega$ was used for measurement of the EMF.

4. Results and discussion

4.1. Characteristics of Pt/gas reference sensor

Fig. 3 shows the relationship between the EMF and temperature in test 1. The theoretical line calculated from Eq. (1) is also drawn in this figure. The EMF values approach the theoretical line of the Nernst relation.

Fig. 4 shows results in test 2. Open circles indicate EMF values measured in oxygen-saturated LBE with pure Ar cover gas. The theoretical line calculated from Eq. (4) for the oxygen-saturated LBE is written with a thick solid line. The measured EMF values are almost on the theoretical line for the oxygen-saturated LBE above 450 °C. From the measured EMF value at 550 °C, it is estimated that the oxygen concentration in the LBE is about 10^{-3} wt%. The measured EMF values are much lower than the theoretical line below 400 °C. Furthermore, the measured EMF value attained the stable one in LBE above 450 °C in short time. In addition, solid triangles indicate EMF values measured in LBE after Ar–H_2–H_2O gas bubbling. These data were obtained in oxygen-unsaturated LBE. The theoretical lines calculated from Eq. (5) are drawn for the EMF values of oxygen concentrations of 10^{-3}–10^{-10} wt% in LBE. Regarding EMF values measured in LBE after Ar–H_2–H_2O gas bubbling, the slope and the magnitude above 450 °C are identical with the expected values for LBE with dissolved oxygen concentration of about 3×10^{-5} wt%. A solid square shows the EMF value measured in LBE after Ar–4%H_2 gas bubbling. Oxygen concentration of 10^{-9} wt% in LBE can be measured using the Pt/gas reference sensor. Konys et al. showed validation of oxygen sensors from calibration tests in saturated and unsaturated LBE [5]. On the basis of the results obtained in test 2, it is found that the Pt/air reference sensor enables us to measure oxygen concentration in LBE above 450 °C.

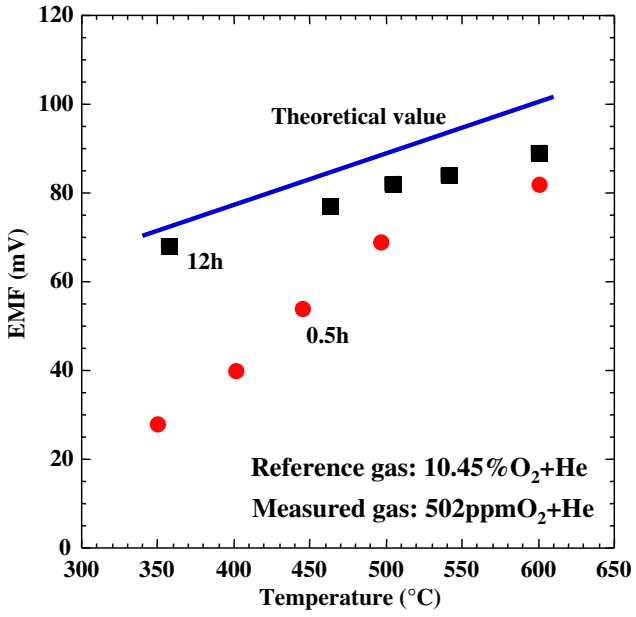

Fig. 3. Relationship between EMF and temperature measured in gas using Pt/gas reference sensor (test 1).

Fig. 5 shows the appearance of the oxygen sensor after the test in LBE. Since much LBE adheres to the YSZ surface of the sensor, it is found that the YSZ surface is wet well with liquid LBE.

4.2. Comparison test of Pt/gas reference and Mo/Bi–Bi_2O_3 reference sensors in LBE

In test 3, the comparison test was conducted in LBE for the Pt/gas reference sensor after long-term use and the Mo/Bi–Bi_2O_3 reference sensor.

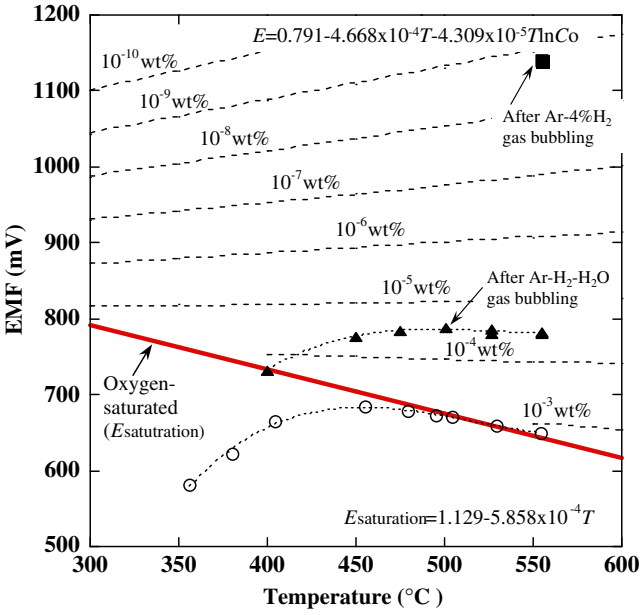

Fig. 4. Relationship between EMF and temperature measured in LBE using Pt/gas reference sensor (test 2).

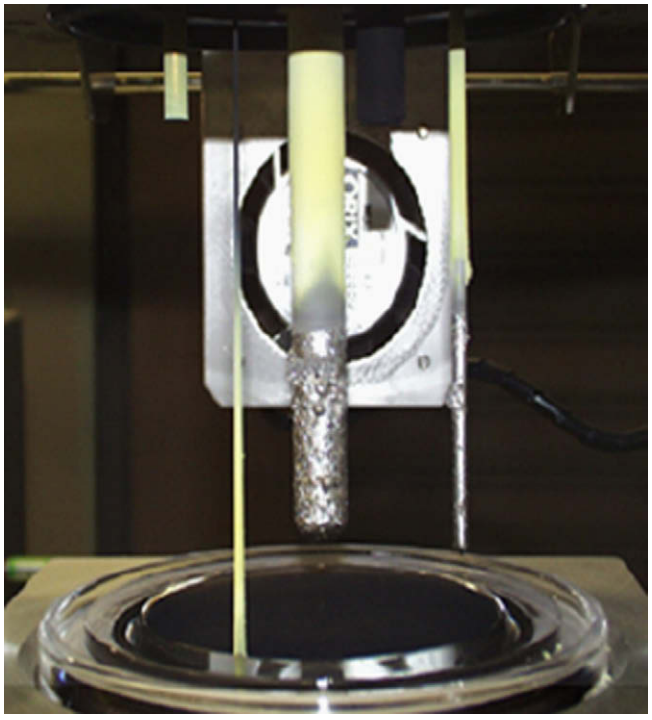

Fig. 5. Appearance of the Pt/gas reference sensor after measurement in LBE.

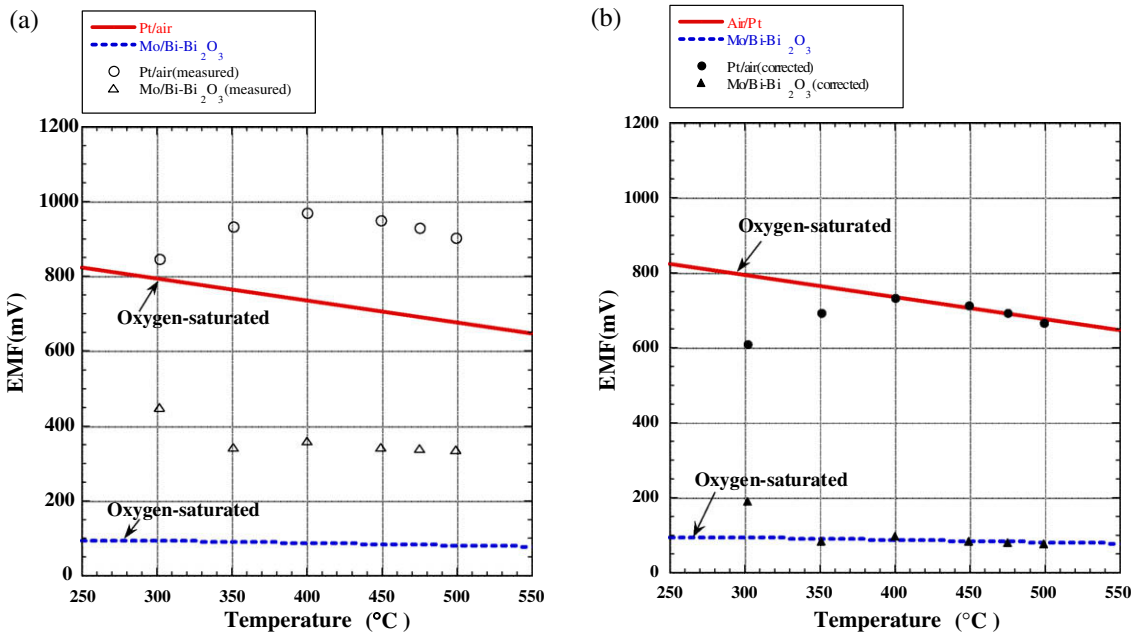

Fig. 6. Relationship between EMF and temperature measured in LBE using Pt/gas reference and Mo/Bi–Bi_2O_3 reference sensors (test 3): (a) measured EMF and (b) EMF after correction.

The relationship between the measured EMF and temperature is shown in Fig. 6(a). In the same way as Fig. 4, the theoretical lines calculated from Eq. (4) for the Pt/air reference sensor and from Eq. (6) for the Mo/Bi–Bi_2O_3 reference sensor in the oxygen-saturated LBE are drawn in this figure. It is a surprise that the measured EMF values in LBE with Ar cover gas are much higher than each theoretical line of oxygen-saturated LBE because oxygen concentration in calibration tests using LBE with Ar cover gas has been constantly in a range of 10^{-4}–10^{-3} wt.%. Therefore, it is necessary to examine whether EMF values measured by both sensors in test 3 showed correct oxygen concentration or not. Since Ar cover gas does not contain a reducing gas component, it is considered that fresh LBE used in test 3 contained oxygen of 10^{-4}–10^{-3} wt.%. In the case of the Pt/air reference sensor of Fig. 6(a), the slope of the relationship between the EMF value and temperature is similar to that of the theoretical line above 400 °C. Similar trend is also observed in the case of the Mo/Bi–Bi_2O_3 reference sensor above 350 °C. These results suggest that oxygen concentration in LBE used in test 3 was close to saturated oxygen concentration.

If LBE is oxygen-saturated, it is considered that both sensors exhibited high EMF outputs including somewhat bias voltage. Courouau et al. showed time drift of Mo/metal–metal oxide electrode sensor and presented several hypotheses to explain the cause of the time drift: alteration of the interface of the electrode(working or reference) by oxide deposition, reaction with LBE or the liquid metal reference, or alteration of YSZ affecting eventually the electrode potential [3,9]. When the magnitude of the effect on the electrode potential is constant, the alteration can produce constant bias voltage. It may be possible to modify the EMF values by subtraction of somewhat bias voltage. As a trial, corrected EMF values were calculated by subtraction of 240 mV from the measured value for the Pt/air reference sensor and of 260 mV from the measured value for the Mo/Bi–Bi_2O_3 reference sensor although physical meaning of the values of the bias voltage was not clear. The relationship between corrected EMF values and temperature is shown in Fig. 6(b). Agreement of the corrected EMF values of both sensors with each theoretical line of oxygen-saturated condition for the Pt/air reference sensor and for the Mo/Bi–Bi_2O_3 reference sensor suggests existence of bias voltage independent of temperature above 400 °C. From these results, it is judged that the high EMF values of both sensors are caused by the addition of bias voltage to the true EMF value.

There were various surface conditions on the YSZ of the sensors after the tests in LBE. Fig. 7 depicts photos of the Mo/Bi–Bi_2O_3 reference sensors after comparison tests in LBE. While the YSZ surface was often wet as shown in the 2nd run of Fig. 7, it was not wet sometimes, in particular at low temperatures. The black soot of Pb and Bi deposited on the YSZ surface after the 1st run shown in Fig. 7. Both sensors with Pt/gas and Mo/Bi–Bi_2O_3 reference electrodes exhibited higher EMF values by above 200 mV than the theoretical ones above 400 °C in all cases after the comparison test.

While the conclusion that both sensors exhibited incorrect outputs containing bias voltage in test 3 was drawn, the following three issues should be considered: (1) what is the cause of the incorrect outputs? (2) can the correction method by bias voltage be used generally? (3) can the sensor that exhibited incorrect outputs be re-activated? Regarding the cause of incorrect outputs, some suggestion is shown in experiments of 4.3 although it was difficult to search for the cause from the viewpoint of interface phenomenon between YSZ and LBE in this study. The cause of time drift which has been often observed with various oxygen sensors is still a point to be further studied. Both sensors exhibited higher EMF values by about 250 mV in LBE than theoretical ones in the calibration tests using the apparatus made of 304SS in test 3 and a quartz pot. Unfortunately, values of bias voltage varied from 200 mV to 260 mV in repeated calibration tests. Therefore, it is generally difficult to employ the correction method by the constant bias voltage. Regarding re-activation of the oxygen sensor, it is tried in Section 4.3 for the Pt/gas reference sensor that got to exhibit incorrect outputs in LBE after long-term use.

4.3. Re-activation treatments and calibration test of the Pt/gas reference sensor

Fig. 8 shows the results of test 4 after the cleaning with a nitric acid. The Pt/gas reference sensor after the washing exhibits higher EMF values by about 220 mV than theoretical line of oxygen-saturated LBE above 450 °C. Therefore, it is not capable of recovering

Fig. 7. Photos showing appearance of the Mo/Bi–Bi_2O_3 reference sensor after measurement in LBE.

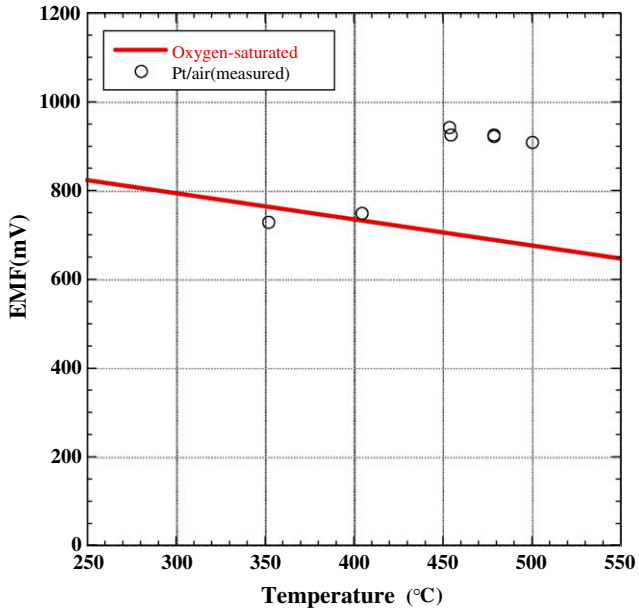

Fig. 8. EMF measurement in LBE using the Pt/gas reference sensor after cleaning with a nitric acid (test 4).

Fig. 9. Appearance of the YSZ surface of the Pt/gas reference sensor after test 4 in LBE.

the ability of the Pt/gas reference sensor by the method of cleaning with a nitric acid. Fig. 9 depicts the appearance of the YSZ surface after the test in LBE. While the LBE adheres to some areas, other lower areas are not wet well with LBE.

The results of test 5 in gas are shown in Fig. 10. The old Pt/gas reference sensor that exhibited the incorrect outputs in LBE indicates the EMF values almost equal to the theoretical ones calculated from Eq. (1) above 450 °C. The following three causes are considered for the poor condition of the sensor that exhibited the incorrect outputs in LBE: (1) failure or degradation of the inner Pt/gas reference system, (2) alteration of YSZ itself and (3) alteration of the outer YSZ surface in contact with LBE. If the cause of the incorrect outputs is failure or degradation of the inner Pt/gas reference system or alteration of YSZ itself, then the old sensor exhibits incorrect outputs in gas. Since the old sensor exhibits correct outputs in gas, the cause of the incorrect outputs seems to be alteration of the outer YSZ surface in contact with LBE. In addition, the EMF values measured using the new Pt/gas reference sensor is almost equal to the theoretical ones above 450 °C.

Results in test 6 are shown in Fig. 11. The old sensor after the Pt-treatment exhibits the EMF values almost equal to the theoretical line of oxygen-saturated LBE above 450 °C. Furthermore, the new Pt/gas reference sensor after the Pt-treatment also indicates similar behavior. Considering these points into account, the Pt-treatment, which enables us to measure oxygen concentration in gas, seems to play a useful role for measuring oxygen concentration in LBE. The following dissociation reactions occur at the YSZ surface in measurement of oxygen concentration using YSZ:

For measurement in gas

$$O_2 \rightarrow 2O^{2-} \tag{8}$$

For measurement in LBE

$$[O]_{LBE} \rightarrow O^{2-} \tag{9}$$

The Pt electrode made on the YSZ surface has catalytic characteristics in gas for dissociation reaction of Eq. (8) and enables us to measure oxygen concentration at lower temperatures. The YSZ interface becomes the activated state due to assistance of the Pt electrode after attaining electrochemical equilibrium under a gas environment. The role of the Pt electrode is a little different in LBE. There are two possibilities: improvement of wetting and formation of activated YSZ surface. It is known that dissolution of Pt on YSZ

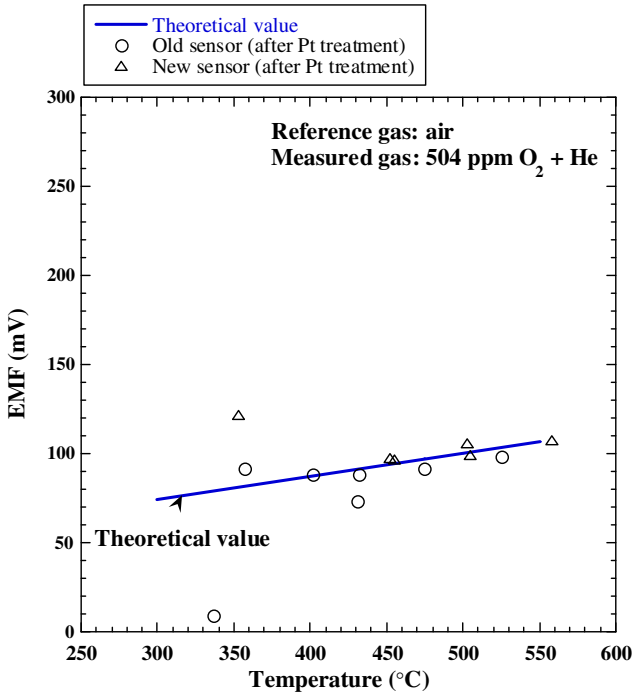

Fig. 10. Relationship between EMF and temperature measured in gas using Pt/gas reference sensors after Pt-treatment (test 5).

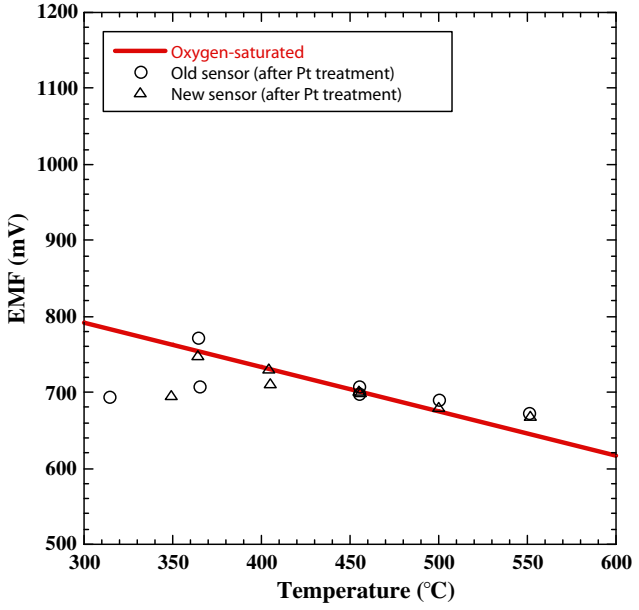

Fig. 11. Relationship between EMF and temperature measured in LBE using Pt/gas reference sensors after Pt-treatment (test 6).

brings improvement of wetting of the YSZ surface by LBE. Once the YSZ surface is activated in gas by the Pt electrode, the activated state of the YSZ surface will continue in LBE. The activated YSZ surface will be useful to promote dissociation reaction of Eq. (9).

The YSZ surface has been often wet with LBE even in the case where the Pt/gas reference sensor exhibits the incorrect EMF outputs in LBE. On this basis, the surface wetting with LBE is a necessary but not sufficient condition for the EMF measurement in LBE using the YSZ sensor. The simple wetting seems to be not sufficient to attain the electrochemical equilibrium at the interface between the YSZ and LBE. When there are highly catalytic electrodes to promote dissociation reaction of Eq. (9) in LBE, it will be possible to conduct measurement of oxygen concentration in LBE with high reliability at low temperatures. Recently, Goto et al. [16,17] developed Ir–C composite and Ru–C composite electrodes which could operate in a gas environment at temperatures below 300 °C due to the excellent catalytic activity. The YSZ oxygen sensors with Ir–C composite and Ru–C composite electrodes have possibility to measure the oxygen concentration in LBE accurately and with high reliability at low temperatures.

From results obtained in Sections 4.2 and 4.3, re-activation instead of the correction by taking into account the bias voltage is recommended for the Pt/gas reference sensor that got to exhibit incorrect outputs. Time drift has been often observed with Mo/metal–metal oxide reference sensors [3,9]. It is also possible as shown in this study that time drift occurs even with the Pt/gas reference sensor known as a reliable oxygen sensor. For this reason, it is important to conduct calibration tests periodically in LBE and gas in order to enhance the reliability of oxygen sensors used in LBE.

5. Conclusions

The calibration tests were conducted in gas and LBE for the oxygen sensor with YSZ as a solid electrolyte and Pt/gas as a reference system. Furthermore, some re-activation treatments were made for the Pt/gas reference sensor that got to exhibit the incorrect EMF outputs. The obtained results were as follows:

(1) The Pt/gas reference sensor exhibited the EMF values almost equal to the theoretical ones in gas and LBE at temperatures above 400 °C or 450 °C in the apparatus made of quartz. The lower limit of operating temperatures changed somewhat. It took time to attain the stable EMF value below 500 °C in the case of measurement in gas.

(2) Both of the Pt/gas reference sensor after long-term use and the Mo/Bi–Bi_2O_3 reference sensor exhibited higher EMF values by about 250 mV than theoretical ones in LBE in the apparatus made of 304SS. The phenomenon was caused by bias voltage of more than 200 mV. The state of the oxygen sensor that indicated incorrect outputs could not be recovered by cleaning the outer YSZ surface with a nitric acid.

(3) The Pt-treatment made on the outer YSZ surface of the Pt/gas reference sensor produced the EMF values almost equal to the theoretical ones above 450 °C in gas and LBE. The Pt-treatment is a good method to re-activate the sensor in LBE.

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