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Development of an oxygen sensor for molten 44.5% lead–55.5% bismuth alloy

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Abstract

A potentiometric sensor for measuring oxygen activity in molten 44.5% lead–55.5% bismuth alloy is under development. Three parts form this sensor: an In/In_2O_3 reference electrode, a ZrO_2/Y_2O_3 solid electrolyte, and a molybdenum working electrode. The oxygen partial pressure in the melt is calculated applying the Nernst equation to the potential difference measured by the sensor. The minimum oxygen partial pressure detected by this sensor is 10^{-40} bar. The sensor has been calibrated with the following metal/metal oxide mixtures: Pb–Bi/PbO, Pb/PbO, Sn/SnO_2, and Bi/Bi_2O_3. Reproducible measurements of the oxygen pressure of PbO formation have been obtained. The sensor performance has been evaluated in 99.999% N_2 and air (20% O_2) environments. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the problems that can cause the use of the eutectic 44.5% Pb–55.5% Bi alloy as a coolant in the accelerator driven systems (ADS) is the corrosion of the structural materials employed in the circuits. In this environment, corrosion is due to the high solubility of metals in the eutectic Pb–Bi alloy. One way to reduce corrosion is to protect the structural materials with an stable oxide layer, because the solubility of the metal oxides in the eutectic Pb–Bi alloy is much lower than the solubility of the metals.

The operating conditions of the eutectic Pb–Bi alloy must help the thermodynamic stability of the protecting oxide layers. For this reason, a certain activity of dissolved oxygen must be present in the molten Pb–Bi alloy. The activity of dissolved oxygen has to be enough to avoid the thermodynamic decomposition of the protecting oxide, but it also has to be lower than the oxygen activity of PbO formation. The solubility of PbO in the eutectic Pb–Bi alloy is practically negligible and its presence will cause erosion on the structural materials.

For these reasons, it is necessary to monitor the oxygen activity in the molten Pb–Bi alloy. Solid state potentiometric oxygen sensors, based on stabilised zirconia ceramics, have been developed for several applications [1–9], but not for molten Pb–Bi alloys. A similar design can be applied for monitoring oxygen activity in molten Pb–Bi. Using the Nernst equation, the response of these potentiometric sensors is converted to oxygen partial pressure in the molten metal or alloy. To convert the oxygen partial pressure in oxygen activity in the molten alloy, reliable free energy of solvation data is necessary.

In this paper, the results obtained employing a solid state potentiometric sensor as well as the Nernst equation applied are reported. The potentiometric sensor uses a In/In_2O_3 mixture as a reference electrode. Two sets of experiments have been performed: the calibration of the oxygen sensor and the evaluation of the sensor performance.

2. Theoretical development

The oxygen sensor is a galvanic cell formed by:

- an In/In_2O_3 reference electrode;
- a ZrO_2/Y_2O_3 solid electrolyte;
- a molybdenum working electrode.

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The molybdenum working electrode acts as an inert electrode, only for closing the electrical circuit. The real working electrode is the Pb–Bi alloy.

In electrochemical terms, the sensor can be represented by the following equation

$$(\mathrm{In})\mathrm{In_2O_3}, \mathrm{O_2}//\mathrm{ZrO_2}, \mathrm{Y_2O_3}//\mathrm{O_2}, \mathrm{PbO(Pb)}$$

In this electrochemical cell, O^{2-} oxidises to O_2 in the reference electrode, whereas O_2 reduces to O^{2-} in the working electrode. The reactions are

$$\frac{2}{3}\mathrm{In_2O_3} \rightarrow \mathrm{O_2} + \frac{4}{3}\mathrm{In}$$

in the reference electrode, and

$$\mathrm{O_2} + 2\mathrm{Pb} \rightarrow 2\mathrm{PbO}$$

in the working electrode.

The free energy of the electrochemical cell is

$$\Delta G_T = -RT \ln \frac{P_{\mathrm{O_2,RE}}}{P_{\mathrm{O_2,SE}} a_{\mathrm{Pb}}^2},$$

where R is the gas constant, T is temperature in K, $P_{\mathrm{O_2,RE}}$ is the oxygen partial pressure in the reference electrode, $P_{\mathrm{O_2,SE}}$ is the oxygen partial pressure in the working electrode, and a_{Pb} is the lead activity in the molten alloy.

The electrochemical potential of the cell is

$$E = \frac{RT}{nF} \ln \frac{P_{\mathrm{O_2,RE}}}{P_{\mathrm{O_2,SE}} a_{\mathrm{Pb}}^2}.$$

The redox reactions considered are

$$\mathrm{O_2} + 4\mathrm{e^-} \leftrightarrow 2\mathrm{O^{2-}}$$

and the number of electrons involved in both reactions are $n = 4$.

The Nernst equation deducted for the sensor developed is

$$E = \frac{RT}{4F} \ln \frac{P_{\mathrm{O_2,RE}}}{P_{\mathrm{O_2,SE}} a_{\mathrm{Pb}}^2}.$$

The free energy of formation of In_2O_3 can be calculated in the temperature range from 430 to 1000 K using the following expression [10]:

$$\frac{2}{3}\Delta G_{F,\mathrm{In_2O_3}} = -618\,134 + 215.3T \ (\mathrm{J/mol\ O_2}).$$

From this equation, the oxygen partial pressure in the reference electrode ($P_{\mathrm{O_2,RE}}$) can be calculated.

In the case of oxygen saturation in the Pb–Bi alloy, PbO formation will occur. The free energy of formation of PbO can be calculated in the temperature range from 400 to 1000 K with the expression [10]

$$2\Delta G_{F,\mathrm{PbO}} = -437\,440 + 198.7T \ (\mathrm{J/mol\ O_2}).$$

From this equation, the oxygen partial pressure in the working electrode ($P_{\mathrm{O_2,SE}}$) can be calculated.

The free energy of the electrochemical cell in the case of oxygen saturation in the Pb–Bi is

$$\Delta G_T = 180\,694 - 16.62T \ (\mathrm{J/mol\ O_2}).$$

And the electrochemical potential

$$E = -0.468 + 4.31 \times 10^{-5}T \ (\mathrm{V}).$$

At 773 K of temperature, the resulting electrochemical potential is −0.434 V.

3. Experimental

The oxygen sensor is a galvanic cell formed by an In/In_2O_3 reference electrode, a ZrO_2/Y_2O_3 solid electrolyte, and a molybdenum working electrode. A scheme of the sensor is shown in Fig. 1. The reference electrode is closed using high temperature cement. In order to avoid any electrical contact between the sensor and the experimental set-up, the sensor is fitted with a Conax sealing assembly.

Two types of experiments were performed with the oxygen sensor:

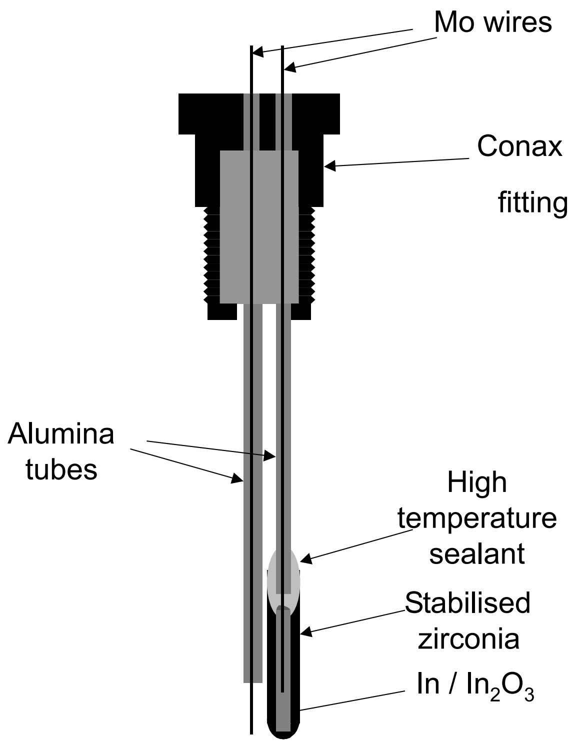

Fig. 1. Scheme of the sensor.

Table 1
Experimental and theoretical electrochemical potentials and oxygen partial pressures at 773 K with different metal/metal oxide mixtures

Mixture	ΔV_{Exp} (V)	$P_{\mathrm{O_2,Exp}}$ (bar)	$\Delta V_{\mathrm{Theor}}$ (V)	$P_{\mathrm{O_2,Theor}}$ (bar)
Pb–Bi/PbO	−0.450	7.9×10^{-19}	−0.434	3.3×10^{-19}
	−0.300	9.6×10^{-23}		
Pb/PbO	−0.350	3.9×10^{-22}	−0.434	6.6×10^{-20}
	−0.260	1.7×10^{-24}		
Sn/SnO_2	0.000	2.8×10^{-31}	−0.080	3.3×10^{-29}
	−0.130	7.1×10^{-28}		

- Calibration of the sensor by measuring the oxygen partial pressures in different metal/metal oxide mixtures. The metal/metal oxide mixtures employed were Pb–Bi/PbO, Pb/PbO and Sn/SnO_2, and the experiments were performed at 773 K. The aim of these experiments was to know the accuracy of the sensor in measuring the oxygen partial pressure of metal oxide formation in the mixtures tested.
- Evaluation of the sensor performance. In these experiments, the response of the oxygen sensor in molten Pb–Bi was analysed when the alloy was exposed at different environments. The environments tested were: 99.999% N_2, air (20% O_2), and alternating N_2 and air.

4. Results and discussion

4.1. Calibration of the sensor

In order to calibrate the sensor, the oxygen partial pressure of metal oxide formation in different metal/metal oxide mixtures at 773 K was measured. These mixtures were obtained by two different ways:

- mixing directly the metal and the oxide,
- generating the oxide on the molten metal by passing a current of air.

The mixtures tested mixing the metal and the oxide were Pb–Bi/PbO, Pb/PbO and Sn/SnO_2. The results obtained with these mixtures are summarised in Table 1.

A good agreement between experimental and theoretical data is observed in the mixtures Pb–Bi/PbO and Sn/SnO_2. In both cases, the range of the experimental data includes the theoretical values. Overpotential (−0.450 V for Pb–Bi and −0.130 for Sn) is recorded in both mixtures. Oxygen partial pressures calculated from experimental data are of the same order than those obtained from theoretical data.

In the Pb/PbO mixture the agreement between experimental and theoretical data is no so good. The minimum potential recorded, −0.350 V, can be included in the range of potentials obtained with the Pb–Bi/PbO mixture, but the highest potential obtained, −0.260 V, is out of this range. The difference between the potentials recorded in Pb and in Pb–Bi can be attributed to the different physical properties of the pure metal and the eutectic alloy. For example, the temperature of fusion is 327 °C for Pb and 123.5 °C for eutectic Pb–Bi. The difference between physical properties can affect to the oxygen solubility in Pb and in Pb–Bi at the experiment temperature (500 °C).

The results obtained generating the oxide on the molten metal by passing a current of air are summarised in Table 2.

Again a good agreement between experimental and theoretical data is obtained in the Pb–Bi/air and Sn/air mixtures. Overpotential is also recorded in these experiments. In the case of Pb–Bi/air, the difference between theoretical and experimental potentials is only of ±35 mV. Oxygen partial pressures calculated from experimental data are of the same order than those obtained from theoretical data.

Table 2
Experimental and theoretical electrochemical potentials and oxygen partial pressures at 773 K with different metal/air systems

Mixture	ΔV_{Exp} (V)	$P_{\mathrm{O_2,Exp}}$ (bar)	$\Delta V_{\mathrm{Theor}}$ (V)	$P_{\mathrm{O_2,Theor}}$ (bar)
Pb–Bi/air	−0.466	2.1×10^{-18}	−0.434	3.3×10^{-19}
	−0.390	2.1×10^{-20}		
Pb/air*	−0.015	7.1×10^{-29}	−0.434	6.6×10^{-20}
Sn/air	−0.150	2.3×10^{-27}	−0.080	3.3×10^{-29}
Bi/air	−0.380	2.4×10^{-21}	−0.545	5.4×10^{-17}
	−0.300	1.9×10^{-23}		

In the Pb/air mixture, a lack of agreement between experimental and theoretical data is observed. At the end of this experiment, Pb was totally oxidised.

In the Bi/air mixture, the agreement between experimental and theoretical data is no so good as in Pb–Bi/air and Sn/air mixtures. The difference between experimental data obtained in Bi and in Pb–Bi can be attributed to different physical properties at the experiment temperature—$T_{\text{fusion,Bi}} = 271$ °C in front of $T_{\text{fusion,Pb–Bi}} = 123.5$ °C—and to the formation of a spongious oxide on the Bi surface that can difficult the contact between the air current and the molten metal.

4.2. Sensor performance

The sensor performance has been evaluated measuring the oxygen partial pressure in molten Pb–Bi exposed to the following environments:

- 99.999% N_2,
- air (20% O_2),
- alternating air and N_2.

The response of the oxygen sensor in 99.999% N_2 is shown in the first part of Fig. 2. This figure shows the

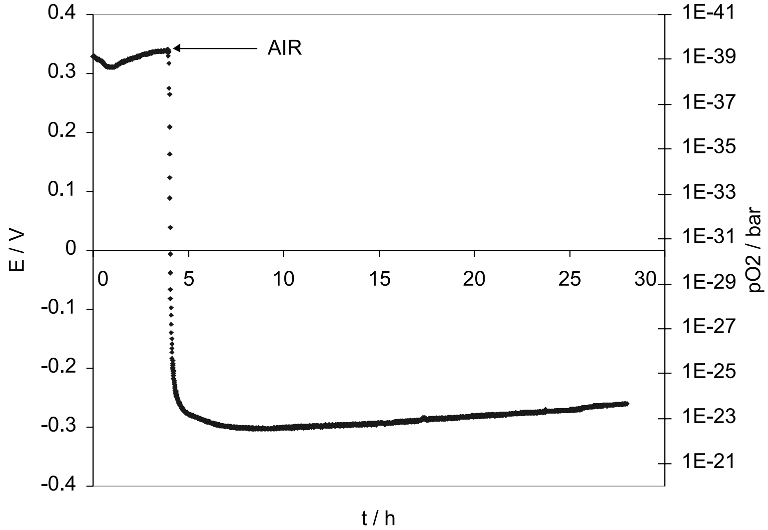

Fig. 2. Potential of the sensor and oxygen partial pressure of molten Pb–Bi at 773 K in high purity N_2 and air.

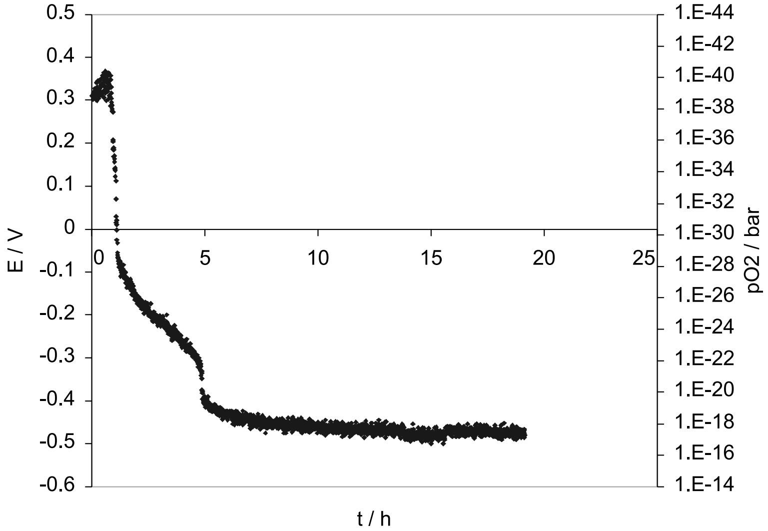

Fig. 3. Potential of the sensor and oxygen partial pressure of molten Pb–Bi at 873 K in air.

potential of the sensor and the partial pressure of oxygen at 773 K, when the Pb–Bi alloy was exposed to high purity N_2 and in air. During the first part of the experiment, when the liquid alloy was exposed to N_2, the electrochemical potential of the sensor was 0.336 V, which means an oxygen partial pressure of 4.8×10^{-40} bar. This value is the minimum oxygen pressure that the sensor can detect.

When the molten Pb–Bi at 773 K was exposed to air, the potential of the sensor evolved rapidly to −0.298 V (Fig. 2). This potential corresponds to an oxygen partial pressure of 1.8×10^{-23} bar, which is of the same order than the oxygen partial pressure of PbO formation at 773 K (3.3×10^{-19} bar). The same behaviour was observed when the temperature was increased to 873 K (Fig. 3). The stabilised potential recorded was −0.409 V, which means an oxygen partial pressure of 3.7×10^{-17} bar.

In order to evaluate the sensitivity of the sensor to changes in the environment, some experiments at 773 K alternating air and N_2 were performed (Figs. 4 and 5). When after 47 h of experiment in air, the environment was changed to high purity N_2, the potential of the sensor quickly evolved to 0.387 V. This shift in the potential indicates that the sensor exhibits a good response to changes of the environment. This result also shows that the PbO layer formed on the surface of the molten Pb–Bi does not form a closed environment and it does

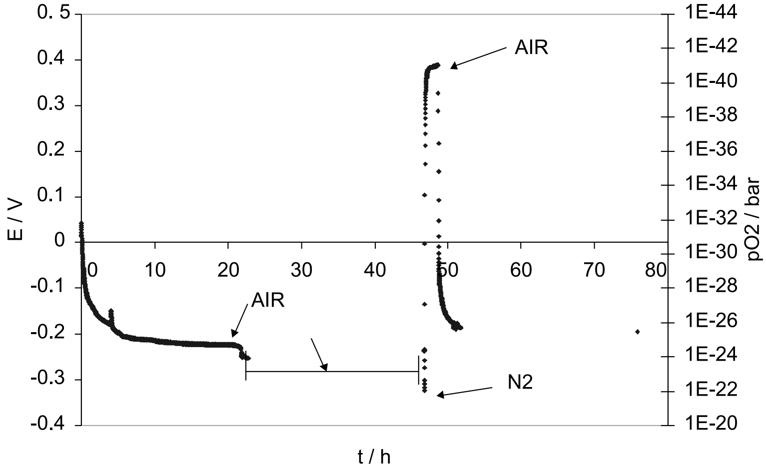

Fig. 4. Evolution of the potential of the sensor and the oxygen partial pressure of molten Pb–Bi at 773 K in air and N_2.

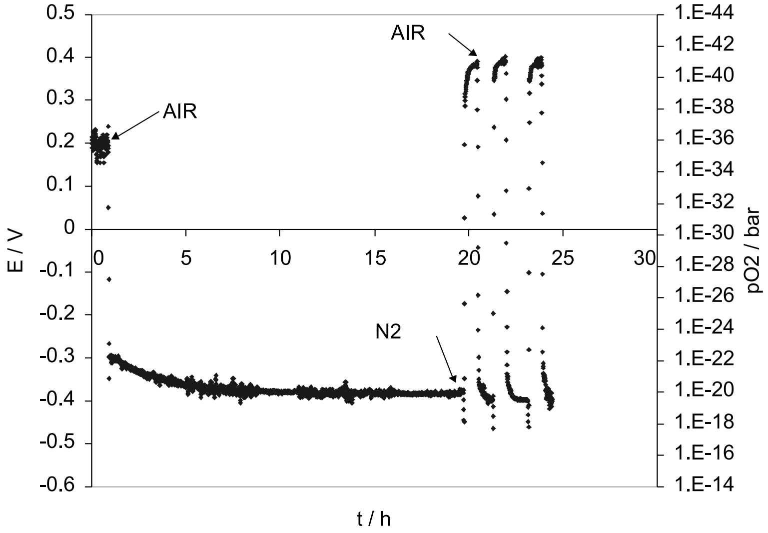

Fig. 5. Evolution of the potential of the sensor and the oxygen partial pressure of molten Pb–Bi at 773 K in alternating currents of air and N_2.

not avoid the contact between the liquid alloy and the environment.

The same behaviour was observed after 20 h of experiment at 773 K in air, when the currents of high purity N_2 and air were alternated (Fig. 5). The potential of the sensor shifted from −0.330 V in air to 0.360 V in N_2. The sensor followed quickly the several changes of the environment, and the values of the potential in air and in N_2 were well reproduced. The sensor also stabilised the potential so quickly.

All the characteristics shown in this part demonstrates that this potentiometric oxygen sensor is suitable to monitor the oxygen partial pressure in the eutectic Pb–Bi alloy.

5. Conclusions

1. A potentiometric sensor for measuring oxygen activity in molten metals has been developed. There is a good agreement between theoretical and experimental data of oxygen activity measured by the sensor in mixtures of Pb–Bi/PbO and Sn/SnO_2.
2. There is also a good agreement between theoretical and experimental data of oxygen activity measured by the sensor in molten Pb–Bi and Sn in contact with air.
3. There is a rapid response of the sensor by changing the oxygen partial pressure over liquid Pb–Bi: in a few minutes the potential value goes from 400 mV (in N_2) to −400 mV (in air).

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References

[1] C.B. Alcock, Rev. Int. Hautes Temper. Refract. 28 (1992–1993) 1.
[2] K. Kukiola, C. Wagner, J. Electrochem. Soc. 104 (1957) 379.
[3] J. Pratt, Metall. Trans. A 21A (1990) 1223.
[4] T. Etsell, C.B. Alcock, Solid State Ionics 34 (1981) 621.
[5] C.B. Alcock, Can. Met. Quart. 10 (1971) 257.
[6] P. Roy, B. Bugbee, Nucl. Technol. 39 (1978) 216.
[7] A. Mortimer, G. Reed, Sens. Actuators B 24 & 25 (1995) 328.
[8] A. Seidl, G. Müller, J. Electrochem. Soc. 144 (1997) 3243.
[9] A. Seidl, G. Müller, J. Electrochem. Soc. 141 (1994) 2564.
[10] I. Barin, Thermochemical Data of Pure Substances, VCH, Weinheim, 1989.