Sensors and Actuators B 145 (2010) 720–725

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Evaluation of potentiometric oxygen sensors based on stabilized zirconia for molten 44.5% lead–55.5% bismuth alloy

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ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form 11 January 2010
Accepted 16 January 2010
Available online 25 January 2010

Keywords:
Lead–bismuth eutectic
Accelerator driven system
Oxygen sensor

ABSTRACT

A potentiometric sensor for measuring oxygen activity in molten 44.5% lead–55.5% bismuth alloy has been developed at “Institut Quimic de Sarria” laboratories. Three key points are to be considered in the design of this type of sensors for molten metals: (1) the reference system, (2) the solid state electrolyte and (3) the auxiliary electrode submerged in the molten metal. This paper evaluates the response of the sensors using two different reference systems: In/In_2O_3 and Sn/SnO as a Me/MeO reference system and a Pt/air as a gas reference system. All sensors showed a fast response time due to a change in the oxygen concentration of the environment and a good agreement between theoretical and experimental data under oxygen saturation conditions of the molten LBE. A second set of experiments evaluated the possibility of using different metallic materials as auxiliary electrodes submerged in molten 44.5% lead–55.5% bismuth alloy. The following materials were tested in the sensor design: molybdenum, P22 steel, 304 and 316L stainless steels. The sensors performance was evaluated using 90% Ar + 10% H_2, air (20% O_2) and alternating both environments. In all cases, reproducible measurements of the oxygen pressure of PbO formation were obtained.

1. Introduction

Nuclear reactors provide approximately 17% of the world’s electricity [1]. The discharged spent nuclear fuel contains 95% uranium, about 1% transuranic elements (principally plutonium), radioactive fission products and activation elements. Most fission products lose their activity within decades, but a few remain for thousands of years, especially minor actinides (^{237}Np, ^{241}Am, ^{243}Am, ^{243}Cm, ^{244}Cm, ^{245}Cm) and fission products (^{135}Cs, ^{129}I, ^{126}Sn, ^{107}Pd, ^{99}Tc, ^{93}Zr, ^{79}Se). Then, for a sustainable growth of the nuclear industry, it is essential that the management of the spent nuclear fuel gets to be socially, environmentally and financially accepted.

The radioactive by-products of the spent nuclear fuel, even if present at relatively low concentrations, are a hazard to life forms when released into the environment. Then, their disposal requires isolation from the biosphere in stable deep geological formations for long periods of time of up to 1 million years.

One of the possibilities under evaluation for reducing the disposal storage time of the spent nuclear fuel is the use of strategies like partitioning and transmutation [1,2]. Partitioning means to separate the most dangerous elements, essentially those with long half-lives like minor actinides and plutonium, from the spent fuel. In the transmutation scenario the waste separated in the partitioning phase will be burnt in accelerator driven system (ADS) reactors.

In ADS reactors, the long-lived fission products of the spent nuclear fuel can be transmuted, which means that high activity isotopes with high long half-lives can be transformed into others with lower activities and much shorter half-lives. To achieve the transmutation reaction, molten lead–bismuth eutectic (LBE, 44.5% Pb–55.5% Bi) or molten lead can be used as a spallation target and coolant of the reactor.

Oxygen activity and its control is an important parameter in the use of molten LBE or lead as a coolant in ADS reactors. Oxygen concentration in the molten alloy is to be high enough to form and maintain a stable passivation layer on the surface of the structural material. This layer can minimize corrosion problems on the structural materials [3–5]. Below a certain oxygen activity level, the passivation layer may decompose and the base metal of the structural materials may be exposed to the molten alloy [6]. Nickel, chromium and iron, constitutive elements of stainless steels, show a high solubility in LBE [7]. If the structural material is submerged in molten LBE without a passive oxide layer, it will be dissolved by the action of the molten alloy.

High-temperature potentiometric oxygen sensors based on solid state electrolytes (stabilized zirconia) have been developed to measure oxygen activity for different applications [8–11]. These kinds of sensors are oxygen concentration cells. The reference electrode is a known system with a fixed oxygen partial pressure. Stabilized zirconia is used as a solid state electrolyte to separate

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doi:10.1016/j.snb.2010.01.028

the working electrode from the reference electrode. It is important to note that stabilized zirconia is an oxygen specific solid state electrolyte. The different oxygen concentration of the working and reference electrode establishes an electromotive force (emf) in the sensor.

Some of these sensors can be properly modified in order to measure the oxygen concentration in molten lead or molten LBE alloy [12–14]. In this case, LBE is the real working electrode of the sensor, but an inert metallic wire is used in order to close the electrical circuit and it can be considered as the working electrode. Using the Nernst equation, the emf measured for the sensor can be related to the oxygen partial pressure of the molten alloy.

For a complete evaluation and characterization of the oxygen sensors, its main components should be considered in the sensor design [14,15]. They are:

- The reference system which must be stable and has a constant and known oxygen partial pressure.
- The solid state electrolyte (specific for oxygen) employed to separate both electrodes (reference and working electrode).
- The inert metallic material used for closing the electrical circuit (working electrode).

Then, in order to evaluate the sensor performance it is important to know the sensor response using different configurations of the three components mentioned above.

2. Experimental

The first aspect considered in the sensor design in this work has been the reference system used. These systems have to be capable of maintaining a constant oxygen partial pressure. The following reference systems have been evaluated using the sensor design proposed (see Fig. 1):

- In/In_2O_3 (In and In_2O_3 both 99.999% supplied by Alfa Aesar).
- Sn/SnO (Sn and SnO both 99.999% supplied by Alfa Aesar).
- Gas reference system: Pt/air.

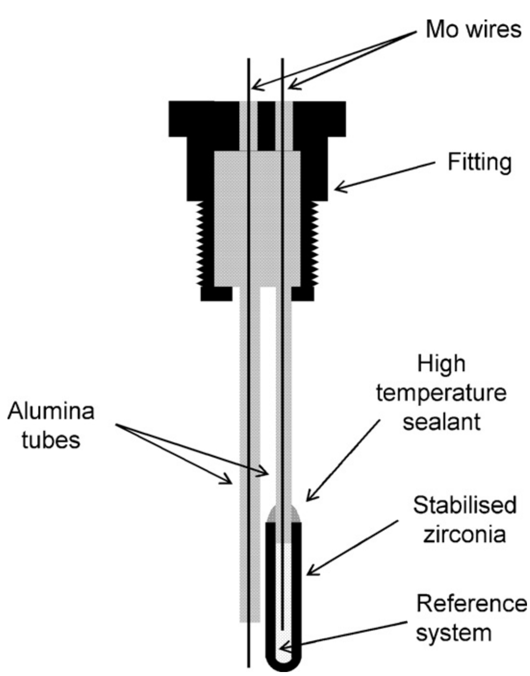

Fig. 1. Sensor design for molten LBE alloy.

In the experiments with Me/Me_2O_n reference systems, magnesia stabilized zirconia (3 mol%) (Ferrotron) has been used as solid state electrolyte and molybdenum wire has been used as inert electrode in the molten LBE. In Pt/air experiments, yttria stabilized zirconia (8 mol%) (Friatec) has been used as solid state electrolyte.

The second point has been the use of different materials as working electrode in the sensor design (see Fig. 1). For this purpose, sensors have been fabricated using In/In_2O_3 as reference system and ZrO_2/MgO as solid state electrolyte. The following metallic materials were tested as working electrodes in molten LBE:

- Molybdenum 99.999% (Alfa Aesar).
- P22 low carbon steel.
- 304 stainless steel (Goodfellow).
- 316L stainless steel (Goodfellow).

In a previous work [15], the solid state electrolyte used in the sensor was evaluated. Two different solid state electrolytes were compared: ZrO_2/Y_2O_3 and ZrO_2/MgO. It was concluded then that from a practical point of view, either zirconia/yttria or zirconia/magnesia could be used as a solid state electrolyte for oxygen potentiometric sensors applied to LBE.

In this paper, the experiments were performed measuring the emf of the sensors in molten LBE using covering gases with different oxygen contents: 90% Ar + 10% H_2, high purity Ar (99.999%, $[O_2] < 2$ vol.-ppm) and air (20% O_2). Air was selected to assure oxygen saturation in molten LBE in a short period of time.

All the tests were performed under static conditions in an autoclave. The LBE was contained in a ceramic crucible. This experimental set-up allowed working with controlled environments. The temperature of LBE was measured using a thermocouple connected to a temperature controller that regulated an electrical heater. The emf given by the sensor was measured by a digital voltmeter ($R_i = 10^{13}\ \Omega$) and the data were stored in a computer. The area of the sensors immersed in the molten LBE was 3.1 cm^2 (1 mm wall thickness). The oxygen partial pressure in the molten lead was calculated using the measured emf of the sensors as explained in previous papers [14,15].

3. Results and discussion

3.1. Evaluation of the reference system

3.1.1. Gas reference system: Me/Me_2O_m

Figs. 2 and 3 show the response of the sensor using In/In_2O_3 and Sn/SnO reference systems in molten LBE at 773 K. Molyb-

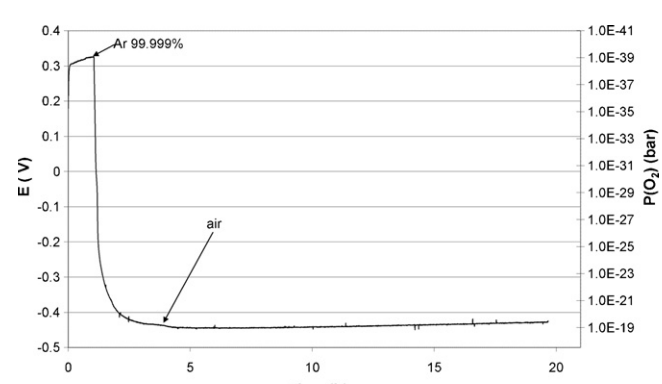

Fig. 2. Electromotive force of the sensor vs. time using In/In_2O_3 reference system, ZrO/MgO as solid state electrolyte and molybdenum wire as auxiliary electrode in the LBE. Tests were performed at 773 K using Ar 99.999% and air as covering gases.