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Effect of the presence of In and Sn in the oxygen chemistry in molten 44.5% lead–55.5% bismuth alloy

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Abstract

The oxygen activity and its control is a key parameter in the use of molten lead–bismuth eutectic LBE in accelerator-driven systems (ADS) reactors. The presence of pollutants in the molten alloy, such as metallic impurities dissolved from the structural material or from other sources, can modify the oxygen chemistry in the molten alloy. For this reason, the oxygen activity in molten LBE has been studied under the presence of In and Sn as a metallic impurities. All the experiments were performed with a shift of the covering gas from a reductive environment (Ar + 10% H_2) to air (20% O_2). These covering gas conditions were used to enable measurement of the electrochemical potential of the sensor in a low oxygen environment and under oxygen saturation conditions of the molten alloy (Me/LBE). All of the tests were performed at 500 °C and in stagnant conditions in an autoclave.

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1. Introduction

Oxygen activity and its control is a key parameter in the use of molten LBE in ADS reactors. Oxygen concentration in the molten alloy should be high enough to form and maintain a stable passivation layer on the surface of the structural material. This layer can minimize the corrosion problems on the structural material [1–3]. If the oxygen activity drops bellow a certain level, the passivation layer may decompose and the base metal of the structural material might be exposed to the molten alloy [4]. Nickel, chromium and iron, as constitutive elements of stainless steels, show a high solubility in LBE [5]. 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.

The presence of pollutants in the molten LBE, such as metallic impurities dissolved from the structural material (Ni, Cr or Fe) or from other sources, can affect its physical and chemical properties. Since oxygen plays a key role in the safety of the reactor, it is important to know if the presence of these metallic impurities modifies the oxygen chemistry in the molten alloy.

The first impurities studied are In and Sn. Possible sources of these impurities can be the electrochemical oxygen sensors, that use these metals as components of the reference systems. In future works, the effect of Ni, Cr and Fe will be studied.

2. Theoretical development

The potentiometric oxygen sensor can be described as an oxygen concentration cell [6]. It can be represented electrochemically by the following expression:

$$O_2(P_1)//ZrO_2, MgO//O_2(P_2) \quad (P_1 < P_2), \tag{1}$$

where P_1 and P_2 are the oxygen partial pressures in the reference system and in the working electrode, respectively, and ZrO_2, MgO is the solid electrolyte, selective to oxygen. This electrochemical cell must have metallic electrodes,

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which can be inert metals, e.g. Pt, or metals which compose the reference or the measured systems.

The electrochemical potential of the sensor can be calculated using the Nernst equation,

$$E = -\frac{RT}{nF}\ln\frac{P_2(O_2)}{P_1(O_2)}, \tag{2}$$

where R is the molar gas constant, T the temperature (expressed in K), n is the number of electrons involved, F is the Faraday constant, and $P_1(O_2)$ and $P_2(O_2)$ are the oxygen partial pressures in the reference system and in the working electrode, respectively.

In this cell, the redox reaction to consider is

$$O_2 + 4e^- \leftrightarrow 2O^{2-}, \tag{3}$$

where the number of electrons involved per oxygen molecule is $n = 4$.

For a metal impurity to influence the LBE chemistry, it must have the following properties:

- It must be soluble in molten LBE.
- The free energy of formation of the corresponding metallic impurity oxide per oxygen mol should be more negative than the free energy of PbO formation. That means that the solubility limit of oxygen in molten LBE can be affected by the presence of the metal impurity.

This implies that, under oxygen saturation condition of the working electrode (metallic impurity/LBE), lead cannot be oxidized to form PbO but the metallic impurity can be oxidized to form Me_2O_m. This system, can be outlined electrochemically by the following equation:

$$(In)In_2O_3, O_2(P_1)//ZrO_2, MgO//O_2(P_2), Me_2O_n, \tag{4}$$

where In, In_2O_3 is used as the reference electrode.

In this cell, the reaction which takes place in the working electrode is the metallic impurity oxidation:

$$\frac{4}{m}\cdot Me + O_2 \rightarrow \frac{2}{m}\cdot Me_2O_m. \tag{5}$$

The free energy of reaction in the working electrode is

$$\Delta G_r = \frac{2}{m}\cdot\Delta G_{Me_2O_m} = -R\cdot T\cdot \text{In}\left(\frac{1}{a_{Me}^{4/m}P_{O_2,ind}}\right) \tag{6}$$

and the Nernst equation for this system is,

$$E = \frac{RT}{nF}\text{In}\frac{P_{O_2,ind}a_{Me}^{4/m}}{P_{O_2,ref}}, \tag{7}$$

where $P_{O_2,ref}$ is the oxygen partial pressure in the reference electrode, $P_{O_2,ind}$ is the oxygen partial pressure in the working electrode, and a_{Me} is the activity of the metallic impurity dissolved in LBE.

Under these conditions, the oxygen partial pressure in molten Me/LBE system can be buffered using metallic impurities to values smaller than PbO formation in LBE or pure lead.

3. Results and discussion

The following metals were used as metallic impurities to study the oxygen activity in molten LBE:

In
Sn

Oxygen activity in the molten alloy (Me/LBE) was measured using potentiometric oxygen sensors described in our previous papers [6–8]. All the experiments were performed with a shift of the covering gas from a reductive environment (Ar + 10% H_2) to air (20% O_2). These covering gas conditions were used to enable the measurement of the electrochemical potential of the sensor in a low oxygen environment and under oxygen saturation conditions of the molten alloy (Me/LBE). All the experiments were done in an autoclave under stagnant conditions at 500 °C.

3.1. In

The free energy of In_2O_3 formation at 500 °C is −451 716 KJ/mol O_2 [9] and the corresponding oxygen partial pressure to this reaction is 2.68×10^{-31} bar (for $a_{In} = 1$, see Eq. (6)). In this situation, the oxygen partial pressure of the reference and the working electrode will be the same. As a result, the electrochemical potential measured by the sensor, under oxygen saturation conditions, should be equal to 0 V.

Fig. 1 shows the results obtained in the system In/LBE for an In concentration range of $0.8\times10^{-4} < X_{In} < 4\times10^{-4}$, expressed as molar fraction. It can be seen that, initially, using a reductive environment (40 ml/min Ar + 10% H_2) the potential remained in the region of low oxygen partial pressures for all In molar fractions. When the covering gas was changed to air, the potential evolved to more negative values, indicating the oxygen presence in the molten alloy (In/LBE). It is important to note that for In molar fractions smaller than 3.97×10^{-4}, the electrochemical potentials measured by the sensor do not correspond to the theoretical value of In_2O_3 formation (0 mV). In this concentration region ($0.8\times10^{-4} < X_{In} < 4\times10^{-4}$) the electrochemical potentials measured under oxygen saturation conditions, indicate higher oxygen partial pressures than the theoretical value for In_2O_3 formation (2.68×10^{-31} bar).

The electrochemical potential, under oxygen saturation conditions for the system In/LBE, versus the logarithm of the In molar fraction in LBE is shown in Fig. 2. In this Figure, two different regions can be seen:

- There is a region for In molar fractions smaller than 4×10^{-4} where the electrochemical potential are lower than the theoretical value of In_2O_3 formation (0 mV). The values obtained are from −270 mV to −410 mV, and they are close to PbO formation. Furthermore, the

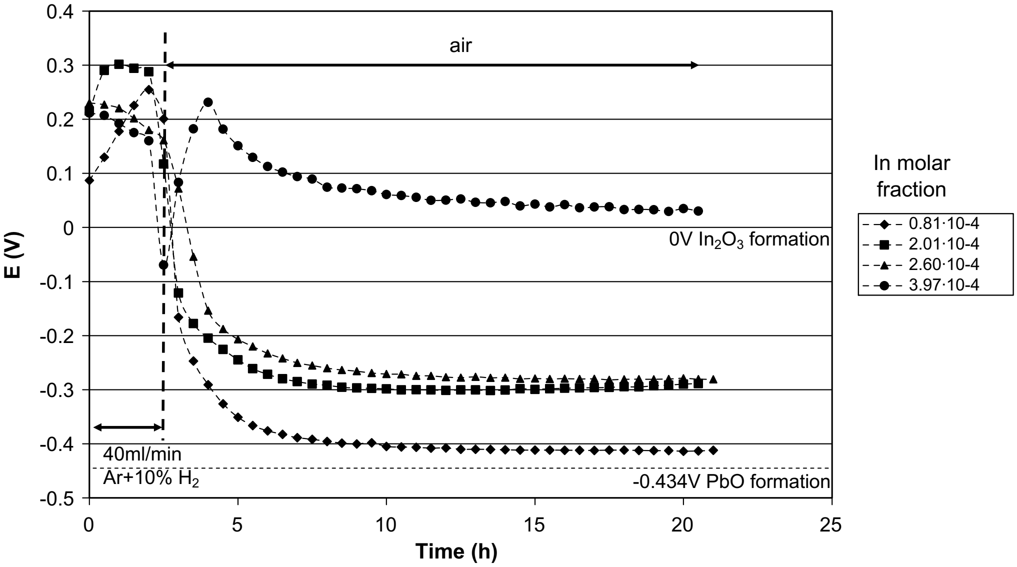

Fig. 1. Electrochemical potential of the sensor at $T = 500$ °C in In molar fractions range dissolved in LBE of $0.8 \times 10^{-4} < X_{In} < 4 \times 10^{-4}$. Ar + 10% H_2 and air were used as covering gases.

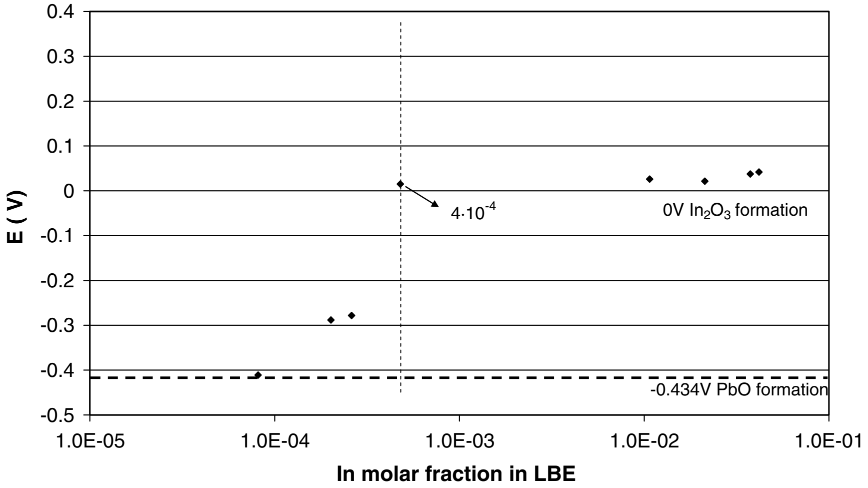

Fig. 2. Electrochemical potential under oxygen saturation conditions of the working electrode (In/LBE) versus In molar fraction ($T = 500$ °C).

potentials obtained in this concentration region indicate higher oxygen partials pressures than the value for In_2O_3 formation. This implies, that for In molar fractions smaller than 3.97×10^{-4} the oxygen sensor is not able to detect In_2O_3 formation in molten LBE. It may be because In at very low concentration ranges is rapidly oxidized and the sensor cannot detect the formation of In_2O_3.

- For molar fractions higher than 4×10^{-4}, the electrochemical potentials obtained under oxygen saturation conditions of the working electrode (In/LBE), were in good agreement with the theoretical value of In_2O_3 formation at 500 °C (0 mV).

3.2. Sn

The free energy of SnO formation at 500 °C is −417850 KJ/mol O_2 [9]. Then, the corresponding oxygen partial pressure to this equilibrium reaction is 3.19×10^{-29} bar (for $a_{Sn} = 1$, see Eq. (6)). In this situation, the electrochemical potential measured by the sensor, under oxygen saturation conditions of the system Sn/LBE using a metal impurity activity equal to unity, should be equal to −79 mV (see Eq. (7)).

Fig. 3 shows the results obtained in the system Sn/LBE for a Sn concentration range of $2 \times 10^{-5} < X_{Sn} < 1.8 \times 10^{-4}$. Initially, when the molten alloy was exposed to a reductive environment, the potentials in all Sn concentrations remained in the low oxygen concentration region. When the covering gas was changed to air, the potential evolved to more negative values, indicating the oxygen presence in the molten alloy (Sn/LBE). In this Sn concentration range the electrochemical potentials measured, under oxygen saturation conditions of the working electrode, do not correspond to the theoretical value of SnO

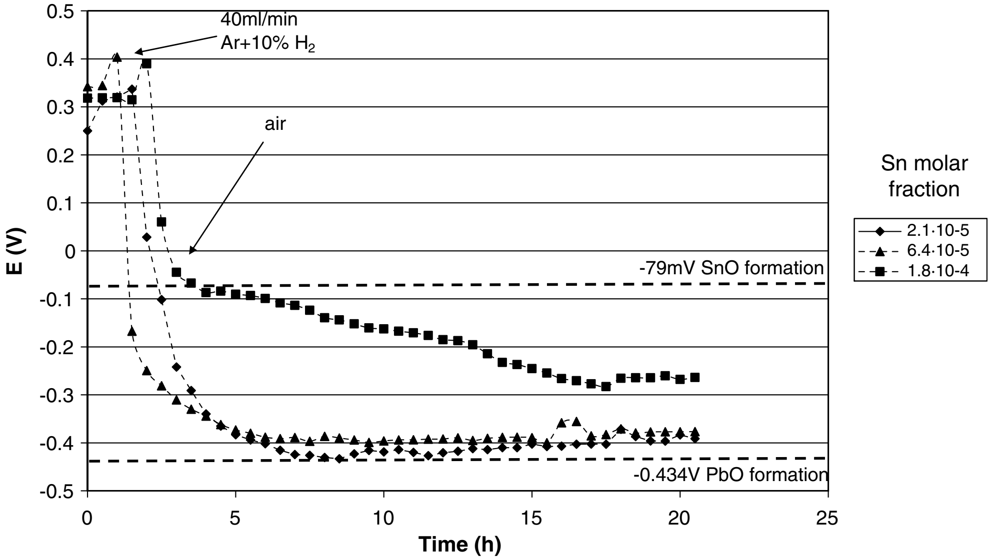

Fig. 3. Electrochemical potential of the sensor at $T = 500$ °C in Sn molar fractions range dissolved in LBE of $2.1 \times 10^{-5} < X_{\mathrm{Sn}} < 1.8 \times 10^{-4}$. Ar + 10% H_2 and air were used as covering gases.

formation (−79 mV). The values obtained are from −260 mV to −410 mV, values which are close to the PbO formation, as it happened in the lower In concentrations. In all cases, the potentials obtained indicated higher oxygen partial pressures than the required pressure to form SnO.

In a Sn concentration range of $5.56 \times 10^{-4} < X_{\mathrm{Sn}} < 1.51 \times 10^{-3}$ a different behaviour was observed compared with Sn lower concentrations (Fig. 4). When the covering gas was changed to air, the electrochemical potential evolved to more negative values and remained constant in an oxygen partial pressure region smaller than the value of SnO formation ($\Delta E_{\mathrm{SnO\ formation}} = -79$ mV). After this initial stage, the potential dropped again to more negative values and remained constant in a region of oxygen partial pressure higher than the value of SnO formation. It is important to note the time required for sensors in the system Sn/LBE, under oxygen saturation conditions of the working electrode, to drop its potential after the initial stage is a function of the Sn concentration: It increases with the Sn concentration in LBE.

Finally, in the highest Sn concentration range tested ($X_{\mathrm{Sn}} > 3.3 \times 10^{-3}$) (see Fig. 5) the potentials obtained, under oxygen saturation conditions of the molten Sn/LBE alloy, were close to the initial value, approximately +20 mV. The fact that the potentials remained constant

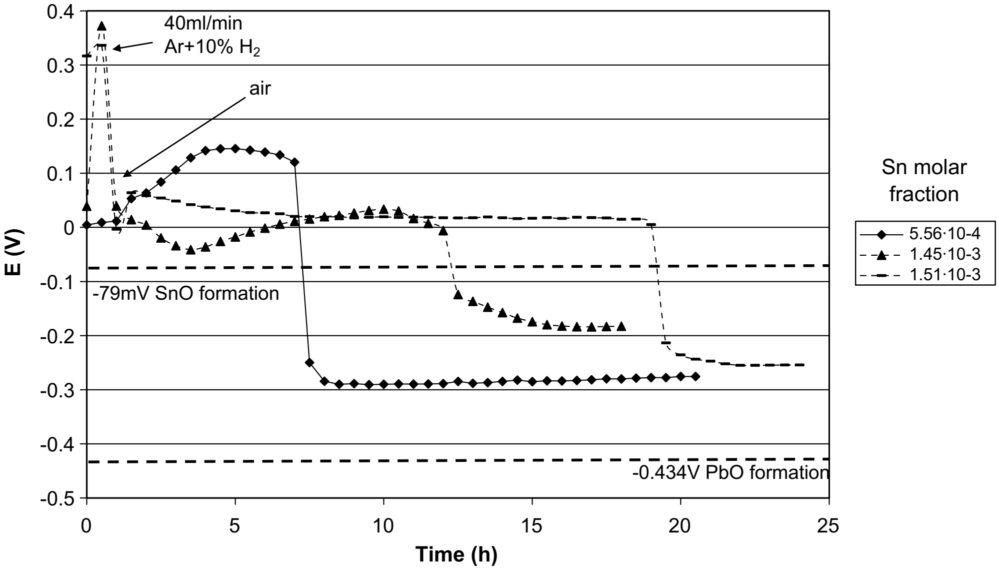

Fig. 4. Electrochemical potential of the sensor at $T = 500$ °C in Sn molar fractions range dissolved in LBE of $5.56 \times 10^{-4} < X_{\mathrm{Sn}} < 1.51 \times 10^{-3}$. Ar + 10% H_2 and air were used as covering gases.

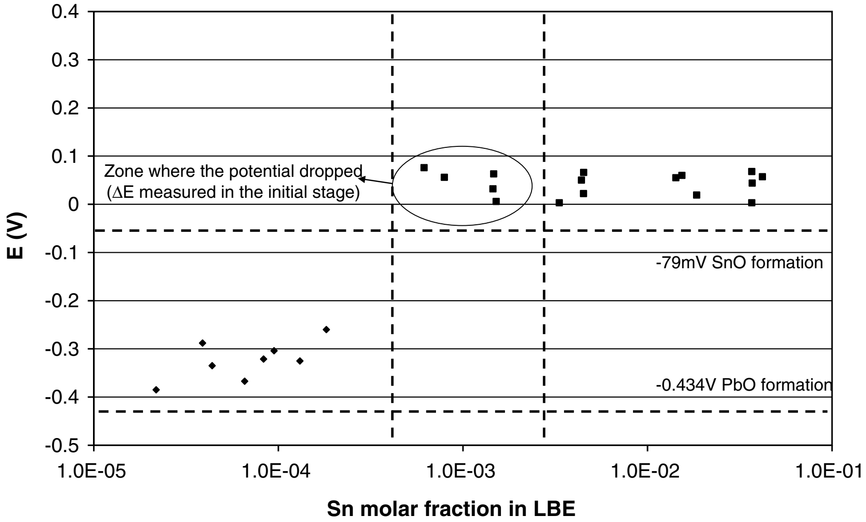

Fig. 5. Electrochemical potential under oxygen saturation conditions of the working electrode (Sn/LBE) versus Sn molar fraction ($T = 500$ °C).

may indicate a metal impurity activity equal to unity despite of the discrepancy with the theoretical value calculated for SnO formation ($\Delta E_{\text{measured}} = +20$ mV, $\Delta E_{\text{SnO formation}} = -79$ mV). It is important to note that this value (+20 mV) indicates smaller oxygen partial pressures than the value for SnO formation (3.19×10^{-29} bar).

The electrochemical potential, under oxygen saturation conditions for the system Sn/LBE, versus the logarithm of the Sn molar fraction in LBE is shown in Fig. 5. In this Figure, three different zones can be observed:

- An initial zone with a Sn concentration range of $2 \times 10^{-5} < X_{\text{Sn}} < 1.8 \times 10^{-4}$. In this region, the electrochemical potentials obtained, under oxygen saturation conditions, indicated higher oxygen partial pressure than the value for SnO formation (−79 mV, 3.19×10^{-29} bar). As a result, in this concentration range, the oxygen sensors cannot detect the formation of SnO in the system Sn/LBE. As it happened with In, it can be because working in a very low concentration range, metallic Sn may be rapidly oxidized and the sensor cannot detect it.
- An intermediate region ($5.56 \times 10^{-4} < X_{\text{Sn}} < 1.51 \times 10^{-3}$) where after an initial stage the potential drop to more negative values. This phenomenon may be explained by the diminution of the Sn concentration in the system Sn/LBE when forming SnO. For very low Sn concentrations, the system evolved to form PbO.
- A final zone, for concentrations higher than 3.33×10^{-3}, where the potential kept constant around +20 mV and independent from the concentration. That, indicates a metal impurity activity equal to unity despite of the discrepancy with the theoretical value calculated for SnO formation ($\Delta E_{\text{measured}} = +20$ mV, $\Delta E_{\text{SnO formation}} = -79$ mV). It is important to note that this value (+20 mV) indicates smaller oxygen partial pressures than the value for SnO formation (2.68×10^{-31} bar). A similar deviation was reported using Sn/SnO as a reference system in a potentiometric oxygen sensor for molten LBE [10]. It was described that the sensor initially measured over-potential values, under oxygen saturation conditions in molten LBE, and slowly evolved to theoretical value. It was hypothesized that the system Sn/SnO required a long time to stabilize the oxygen partial pressure to its equilibrium value. The time required for the potential to drop to more negative values in all cases is smaller than 20 h. Then, it may seem that the same type of instability was observed using Sn in the system Sn/LBE.

4. Conclusions

Using In as a metallic impurity in molten LBE, the oxygen partial pressure of the system Me/LBE is buffered to the value of In_2O_3 formation for molar fractions higher than 4×10^{-4}. For molar fractions smaller than this value, the oxygen sensor is not able to detect In_2O_3 formation in molten LBE.

If Sn is used as metallic impurity in molten LBE, the Sn molar fraction in LBE to buffer the oxygen content in the system forming SnO should be higher than 3.3×10^{-3}. For Sn molar fractions smaller than 1.8×10^{-4} the oxygen sensor is not able to detect SnO formation in molten LBE. In an intermediate Sn concentration range ($5.56 \times 10^{-4} < X_{\text{Sn}} < 1.51 \times 10^{-3}$), the system initially is buffered forming SnO but when metallic Sn is totally oxidized the system evolved to form PbO.

In and Sn, as a metallic impurities in molten LBE, can buffer the oxygen partial pressure of the system Me/LBE. These partial pressures are intermediate between those obtained with reducing gases and the corresponding value to the formation of PbO.

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