Thermodynamic features of corrosion processes in liquid lead coolant in the presence of dissolved oxygen

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Abstract. In this work, the thermodynamic formalism of the law of acting masses is used to analyze the chemical equilibrium in a lead-based liquid metal solution in the case when iron and oxygen are present in the melt as impurities. The calculations were carried out using iron as an example, since it is this chemical element that is the main component of steels, which are currently regarded as the most promising container material for lead liquid-metal systems. The technology for controlling oxygen activity comes down to the fact that while maintaining the required oxygen concentration, lead becomes less chemically aggressive towards iron. By ensuring the constant required amount of oxygen in the liquid lead coolant, it is possible to maintain the basis of protective films on the surface of steel, which include iron and chromium oxides.

1 Introduction

Concentrated solar power (CSP) with thermal energy storage (TES) is currently the most cost effective technology, which will play a crucial role in the future thanks to its rising economic competitiveness with fossil fuels [1]. Central receiver systems (CRS) as the most promising direction of development of solar thermal power are characterized by higher operating temperatures and larger heat flux densities. An important step in creating an economical CRS is the selection of an efficient heat transfer fluid. The use of liquid metals will expand the operating temperature range in which the central control systems will operate.

When compared with the alkali metals liquid lead as a coolant has the advantage of being safe because its reaction with air and water results in a slow oxidation only. In addition, Pb is characterized by a lower vapor pressure above the melt. However, lead corrosion towards structural materials is a critical barrier to the use of this coolant for technical applications. Unlike, for example, the Na-Nb-O system [2], in which dissolved oxygen intensifies the corrosion of niobium in liquid sodium, in the Pb-Fe-O system the effect of oxygen impurity in liquid lead on the corrosion rate of iron-based materials, manifests itself in a more complex way [3].

This paper examines the thermodynamic basis of corrosion of steel components in oxygen-containing liquid lead (using iron as an example) and provides data that is necessary

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to formulate requirements for the content of oxygen dissolved in lead to ensure favorable operating conditions for the liquid metal system.

2 Basic considerations

Depending on the oxygen content in the lead melt, either oxidation (at a high oxygen concentration) or dissolution (at a low oxygen concentration) of structural materials, in particular iron, as a component of steel, can occur [3]. Lead oxides are less stable than the oxides of elements that are part of structural materials. When the lead melt is intensively saturated with oxygen, solid oxide PbO is formed. The consequence of this process is the deposition of PbO on the surfaces of structural materials, which can cause slagging of the liquid metal circuit. The technology for controlling the thermodynamic activity of oxygen comes down to the fact that while maintaining the required oxygen concentration, lead becomes less chemically aggressive towards steel components (Fe, Ni, Cr, etc.). By ensuring the constant required amount of oxygen in the alloy, it is possible to maintain the basis of protective films, which include iron and chromium oxides [4].

The oxide film formed on the surface of the materials prevents their dissolution, since the rate of diffusion of steel components in the oxide is very low. The mass transfer effect is observed only in places where impurities diffuse, reaching the surface of the oxide film through the thinnest or porous areas. Where the film thickness decreases or porosity increases, a local increase in iron concentration occurs near the surface, which leads to the establishment of its equilibrium concentration in this area. It turned out that the concentration of Fe depends on the oxygen content in lead. In liquid metal circuits, with some constant oxygen content, the iron concentration will differ from the level of iron solubility in pure Pb melt. As a result, it is possible to reduce corrosion and ensure long-term operation of the liquid metal circuit.

Near the surface of the material, the concentration of steel components is a function of temperature as well as the oxygen concentration in liquid Pb. The mass transfer process occurs most intensively in non-isothermal circuits, since at a constant temperature, oxygen is eventually distributed evenly and the corrosion process occurs less intensely. When the temperature is uneven, the chemical elements that make up the steels come out of the pipeline walls in places with the highest temperatures and are deposited in cold places, which can lead to a narrowing of the flow area of the pipelines.

It has been established that the formation of an oxide film leads to the suppression of the diffusion of steel cations into the liquid metal and vice versa. The thermodynamic activity of oxygen in molten lead can be used as a parameter controlling the corrosion rate. If the thermodynamic activity of oxygen is too high, then the process of PbO precipitation takes place. If the values of the thermodynamic activity of oxygen take values below a certain threshold value for a given temperature, then the formation of an oxide layer with protective properties will not occur on the steel surface [5]. For steel coated with an oxide film, the term steel passivation was introduced.

Below is a method for calculating the temperature dependence of the oxygen concentration required for the formation of iron oxide and lead oxide.

Let's write down the reaction of the formation of iron oxide in lead

\[ 3\text{Fe}_{} + 4\text{O}_{} = \text{Fe}_3\text{O}_4 \]. (1)

At equilibrium, the change in Gibbs energy of this reaction is zero, then

\[ \Delta_f G^* (\text{Fe}_3\text{O}_4) = RT \ln \left( \frac{a_3^\text{Fe} a_4^4}{a_0} \right) \], (2)
or

\[
\Delta_f G^\circ(Fe_3O_4) = 3RT \ln(a_{Fe}) + 4RT \ln(\gamma_O x_O),
\]

(3)

where \(a_{Fe}\) and \(a_O\) is the thermodynamic activity of iron and oxygen in liquid Pb, respectively; \(\Delta_f G^\circ(Fe_3O_4)\) is the Gibbs energy of formation \(Fe_3O_4\) at temperature \(T\); \(\gamma_O\) is the coefficient of thermodynamic activity of oxygen in liquid Pb; \(x_O\) is the oxygen concentration in liquid Pb; \(R\) is the universal gas constant and \(T\) is the absolute temperature.

In order to find the coefficient of thermodynamic activity of oxygen in molten lead, it is necessary to consider the following reaction:

\[
Pb(l) + O(l) = PbO(s).
\]

(4)

Equating \(\Delta_r G^\circ\) of this reaction to zero, we can write

\[
\ln(\gamma_Pb) = \frac{\Delta_f G^\circ(PbO)}{RT},
\]

(5)

\[
\ln(\gamma_Pb) = \frac{\Delta_f G^\circ(PbO)}{RT} + \ln(x_{O(sat)}),
\]

(5a)

Eq. (5a) takes into account that the thermodynamic activity of pure lead is equal to unity. For a binary Pb-O melt, when dissolved oxygen is in equilibrium with the solid oxide, we can write

\[
RT \ln(\gamma_O x_{O(sat)}) = RT \ln(\gamma_O) + RT \ln(x_{O(sat)}) = \Delta_f G^\circ(PbO),
\]

where \(x_{O(sat)}\) is the solubility of oxygen in liquid lead.

Hence it follows

\[
ln(\gamma_O) = \frac{\Delta_f G^\circ(PbO)}{RT} - ln(x_{O(sat)}).
\]

(6)

Let us define the thermodynamic activity of iron in the Pb-Fe-O melt as

\[
a_{Fe} = \frac{x_{Fe}}{x_{Fe(sat)}},
\]

(7)

where \(x_{Fe(sat)}\) is the solubility of iron in liquid lead at a given temperature in the binary system Pb-Fe, \(x_{Fe}\) is the concentration of iron in liquid lead \((x_{Fe} \leq x_{Fe(sat)})\).

Substituting Eqs. (6) and (7) into Eq. (3), we obtain
\[ \Delta_f G^\circ (\text{Fe}_3\text{O}_4) = 3RT \ln(x_{\text{Fe}}) - 3RT \ln(x_{\text{Fe(sat)}}) + 4RT \ln(x_{\text{O}}) + 4 \Delta_f G^\circ (\text{PbO}) - 4RT \ln(x_{\text{O(sat)}}), \]

(8)

where \( x_{\text{O}} \) is the concentration of oxygen in lead.

Let's rewrite Eq. (8) in the following form

\[
RT \ln(x_{\text{Fe}}^3) + RT \ln(x_{\text{O}}^4) = \Delta_f G^\circ (\text{Fe}_3\text{O}_4) + 3RT \ln(x_{\text{Fe(sat)}}) - 4 \Delta_f G^\circ (\text{PbO}) + 4RT \ln(x_{\text{O(sat)}}).
\]

(9)

Hence, we have

\[
x_{\text{Fe}}^3 \cdot x_{\text{O}}^4 = x_{\text{Fe(sat)}}^3 \cdot x_{\text{O(sat)}}^4 \cdot \exp \left( \frac{\Delta_f G^\circ (\text{Fe}_3\text{O}_4) - 4 \Delta_f G^\circ (\text{PbO})}{RT} \right).
\]

(10)

The initial data for the calculation are given in Tables 1 and 2.

**Table 1.** Gibbs energy change during oxide formation reactions from components in standard states.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta_f G = \Delta_f H - \Delta_f S \cdot T )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta_f H, \text{[J/mol]} )</td>
</tr>
<tr>
<td>( \text{Pb} + \frac{1}{2} \text{O}_2 = \text{PbO} )</td>
<td>202523</td>
</tr>
<tr>
<td>( 3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4 )</td>
<td>1118300</td>
</tr>
</tbody>
</table>

**Table 2.** Parameters of temperature dependence of iron solubility

\( \ln x_{\text{Fe}} \) [mol fractions] = \( A + B / T + C / T^2 \) and oxygen solubility \( \ln x_{\text{O}} \) [mol fractions] = \( A + B / T \) in liquid Pb.

<table>
<thead>
<tr>
<th>Element</th>
<th>( A )</th>
<th>( B, \text{K} )</th>
<th>( C, \text{K}^2 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>8.992</td>
<td>-27.004\cdot10^3</td>
<td>-8.365\cdot10^6</td>
<td>[7]</td>
</tr>
<tr>
<td>O</td>
<td>1.732</td>
<td>-8.066\cdot10^3</td>
<td>-</td>
<td>[8]</td>
</tr>
</tbody>
</table>

After substituting the values of thermodynamic parameters into formula (10), we arrive at the following expression

\[
x_{\text{Fe}}^3 \cdot x_{\text{O}}^4 = \exp \left( 16,25 - \frac{117542}{T} \right).
\]

(11)

Eq. (11) relates the maximum Fe concentration in liquid Pb with the oxygen concentration, provided that we are in the stability region of \( \text{Fe}_3\text{O}_4 \) in terms of the oxygen content in lead. Thus, the concentrations of iron and oxygen in molten lead are related by a value that is constant for a given temperature. An increase in oxygen content leads to a
decrease in iron concentration. This is the basis for the principle of protecting steel from corrosion in a lead coolant.

The results of calculation of temperature dependence of iron concentration in lead melt on oxygen content are presented in Table 3.

The dissolved oxygen concentration is limited from above by PbO precipitation, which occurs when the oxygen saturation concentration is reached. The lower limit of the concentration range of oxygen concentrations in liquid lead at each temperature is determined by the minimum values of this parameter at which the Fe₃O₄ compound can still exist in equilibrium with the Pb alloy.

From the analysis of the thermodynamic model discussed above, it follows that at a low oxygen concentration, iron dissolves, and with a further increase in the amount of oxygen in the melt, steel oxidizes with the formation of a protective oxide film. The composition of the protective film includes Fe₃O₄ and the presence of dissolved oxygen in the melt leads to a decrease in the concentration of dissolved iron in liquid lead. A further increase in oxygen content leads to the formation of lead oxide PbO and its deposition on the surfaces of materials.

The above thermodynamic analysis can be considered as a thermodynamic justification for a possible method of protecting structural materials from the aggressive effects of lead-bismuth eutectic. It is important to emphasize that the first to propose the considered method of protection were Russian scientists who worked on this problem at the Institute for Physics and Power Engineering A.I. Leypunsky in Obninsk [9].

According to the authors of [10], the disadvantage of this method of protection in a lead-bismuth coolant is the weak effectiveness of corrosion inhibition. Despite a certain slowdown in mass transfer, which is achieved when creating an oxide film on the surface of steel when heated in air, corrosion of materials under the influence of liquid lead develops in places where the continuity of the oxide film is disrupted and spreads in the absence of conditions for self-healing of defects deep into the metal.

Table 3. Calculated values of the maximum concentration of iron $x_{Fe}$ in liquid Pb in the presence of dissolved oxygen at various concentrations $x_{O}$.

<table>
<thead>
<tr>
<th>$t°$=400°C</th>
<th>$x_O$ (mol fraction)</th>
<th>$x_{Fe}$ (mol fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-7}$</td>
<td>$5.10^{-7}$</td>
</tr>
<tr>
<td>$x_O$</td>
<td>$2.60.10^{-14}$</td>
<td>$3.05.10^{-15}$</td>
</tr>
<tr>
<td>$x_{Fe}$</td>
<td>$1.21.10^{-15}$</td>
<td>$5.64.10^{-17}$</td>
</tr>
<tr>
<td>$t°$=600°C</td>
<td>$x_O$ (mol fraction)</td>
<td>$x_{Fe}$ (mol fraction)</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>$5.10^{-8}$</td>
<td>$1.10^{-6}$</td>
</tr>
<tr>
<td>$3.42.10^{7}$</td>
<td>$4.01.10^{7}$</td>
<td>$7.42.10^{11}$</td>
</tr>
<tr>
<td>$t°$=700°C</td>
<td>$x_O$ (mol fraction)</td>
<td>$x_{Fe}$ (mol fraction)</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>$5.10^{-5}$</td>
<td>$1.10^{-5}$</td>
</tr>
<tr>
<td>$1.60.10^{-6}$</td>
<td>$1.87.10^{-7}$</td>
<td>$3.46.10^{-9}$</td>
</tr>
<tr>
<td>$t°$=800°C</td>
<td>$x_O$ (mol fraction)</td>
<td>$x_{Fe}$ (mol fraction)</td>
</tr>
<tr>
<td>$6.10^{-7}$</td>
<td>$5.10^{-6}$</td>
<td>$1.10^{-4}$</td>
</tr>
<tr>
<td>$6.24.10^{-6}$</td>
<td>$3.16.10^{-6}$</td>
<td>$8.03.10^{-10}$</td>
</tr>
</tbody>
</table>

Films may further lift, chip, and peel during use due to differential thermal expansion and other factors. Experiments revealed severe corrosion when the films were destroyed [11]. One of the areas of research aimed at developing corrosion-resistant materials is to study the corrosion behavior of steels with a high silicon content in a lead-bismuth coolant [12].
3 Concluding remarks

Using available thermodynamic and solubility data obtained from several different sources, refined equations are formulated that allow the implementation of a method for active oxygen control in lead systems to prevent corrosion and contamination.

The thermodynamic model considered in the present work can be refined in the future if we take into account the fact that the values of the oxygen and iron thermodynamic activity coefficients in the ternary system Pb-Fe-O differ from the corresponding values for the binary systems Pb-O and Pb-Fe.

In the case where it is necessary to expand the operating temperature range in which the central receiver systems will operate up to 1000 °C and above, it seems that oxide-ceramic materials should be considered as an acceptable container material compatible with liquid lead instead of metallic materials.

References

10. J. Yang, J. Liang, G. Wang, Corrosion Science. 222, 111407 (2023)