



An approach to quantifying the chemical conditions necessary to form a magnetite layer on steels in lead and lead–bismuth eutectic



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HIGHLIGHTS

- Conditions for corrosion protection of steels in lead-based coolants were quantified.
- Maximum allowable temperatures spans of such loops are defined.
- The concept of a “protective triangle” for corrosion protection is introduced.

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ABSTRACT

In this study, the parameter space where a magnetite (Fe_3O_4) film forms on the surfaces of steels exposed to non-isothermal oxygen-controlled Pb and LBE coolant loops while avoiding PbO contamination has been quantified by a consistent set of 6 equations. These equations provide both the allowable temperature range of operation as well as the range of oxygen concentrations that must be maintained within the loop. The equations allow for a set of margins on the oxygen and iron concentrations in the system. Given a value for the maximum temperature within the loop, the minimum allowable temperature can be calculated and vice versa. The “protective triangle” concept was introduced to visualize the principles of the conditions promoting corrosion protection, and how these are affected by changing temperatures, concentrations and applied margins.

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1. Introduction

Research and development of lead and lead–bismuth eutectic (LBE, 45 wt.% Pb, 55 wt.% Bi) cooled nuclear technology is currently pursued worldwide under the framework of generation-IV nuclear programs and spallation neutron source development [1,2] (GIF LFR Provisional System Steering Committee). Active efforts backed by both public and private funding are pursued in the US [3–5], EU framework programs [6–9], Russia [10,11], Sweden [12,13], Italy [14], South Korea [15–17], Japan [18–21], India [22] and elsewhere.

As a nuclear reactor coolant, lead and LBE offer significant advantages over other available alternatives. They have no explosive chemical reactions with air, water and steam, very high boiling points (>1600 °C) and excellent natural circulation cooling capability compared to alternatives such as sodium-based coolants. Lead-based coolants are especially attractive for use in accelerator-driven systems (ADS) as they can be used as a combined spallation neutron source and coolant. The major technological

hurdles for the widespread adoption of lead-cooled fast reactor (LFR) technology are the problems of high temperature corrosion of structural materials, liquid metal embrittlement (LME) [23–27] and liquid metal enhanced creep (LMC) [28].

All of the major elements present in candidate steels for nuclear applications (iron, chromium, and nickel) have significant solubility in Pb and LBE [29]. In non-isothermal systems, the dissolution of elements in the hot part of the loop is continuous, as corrosion products precipitate out of the system at cold areas due to their reduced solubility at lower temperatures. This process leads to a reduction of wall thickness on the hot area steel, which can result in the subsequent mechanical failure of the components, as well as a clogging of the flow path inside the pipe in the cold section because of deposition. Therefore in order to safely operate coolant loops for extended time periods using lead or LBE, the rates of dissolution and deposition need to be minimized. The Russian nuclear submarine research program found a solution to this problem in using oxygen concentration control in the coolant to promote self-healing oxide layer formation on the steel surfaces [30]. Many excellent and comprehensive articles explaining the fundamentals and details of this process and how it is controlled have been

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published by CEA [31–33], LANL [34–38], FZK [39,40] and other groups and researchers previously. Much of the current state of knowledge is summarized in the 2007 OEC/NEA handbook [29].

An oxide layer on a steel surface provides a diffusion barrier that effectively limits the rate that steel components (Fe, Cr, Ni etc.) are being leached into the coolant. When an oxide film has formed, the only effective means of transferring structural materials into the liquid is through the reduction of the oxide film at the liquid/oxide interface. The reduction of the oxide film will reach a local equilibrium when the dissolved steel element concentrations near the interface equals an equilibrium value. This equilibrium concentration depends on the oxygen concentration in the liquid. If the oxygen level is maintained above a certain level, the dissolved steel element concentrations can be several orders of magnitude lower than the solubility limit at the given temperature. Because of this, it is possible to reduce the corrosion rate of the structural material to an acceptable level. At the same time, the oxygen concentration must remain below the solubility limit to avoid excessive formation of oxides with elements of the liquid (Pb and Bi).

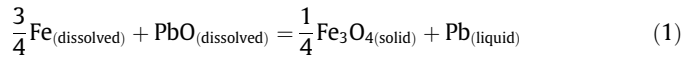
Steels with sufficient amounts of strong oxide formers (e.g. aluminum or silicon) will easily form very thin, dense and strong oxide layers, which are excellent diffusion barriers. It has been shown that the Russian martensitic alloy EP823 (containing 1.5 wt.% Si) behaves better than similar materials without Si and materials containing 5.5 wt.% Al do not show any significant signs of corrosion attack [41]. Surface alloying using the Gepulste Elektronenstrahl Anlage (GESA) process, with protection based on a thin layer of FeCrAlY welded to the surface by an intense electron beam, has been shown to provide excellent corrosion resistance to all steels subjected to the treatment [42]. Advanced steels of this type are often proposed as cladding materials (where temperatures are the highest), but they are rarely used for all coolant-facing surfaces in a complete coolant system.

Conventional steels that are used for the rest of the structural components are primarily protected from corrosion by a thin iron–chromium spinel layer ($\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$). While it is understood that the Fe–Cr spinel is the main protective layer, this study conservatively focuses on the conditions required for the formation of the iron oxide *magnetite* (Fe_3O_4) while avoiding contamination by coolant oxides. Magnetite is the thermodynamically least stable oxide of relevance for standard fast reactors steels such as HT9, T91 or D9. For conditions where magnetite is formed, an underlying spinel layer has already formed, which means corrosion protection is assured. The first oxide that forms in the liquid of either pure lead or LBE is the lead oxide PbO.

The focus of this paper is to define a consistent set of equations that quantify the chemical conditions and temperature spans that allow for the formation of a magnetite layer while avoiding the excessive formation of PbO. Section 2 gives correlations for the theoretical minimum required oxide concentration. Section 3 introduces a new concept called a “protection triangle”, which visualizes the conditions under which effective corrosion protection can be achieved and how this varies with concentrations and temperatures. Section 4 explains how the theoretical maximum temperature span of any Pb or LBE coolant loop can be defined. Section 5 introduces and defines margins that are applied in the analysis, which are used in Section 6 to define a set of 6 equations that define allowable loop temperatures and oxygen concentrations for effective corrosion protection. These equations are applied to show optimal conditions for various types of coolant loops. Section 7 provides limited experimental and reference verification of parts of the developed methodology. Section 8 summarizes conclusions and the direction of future work.

2. Determining the lower limits of oxygen concentration

The reaction on the protective magnetite film on steels submersed in lead and or lead-alloys (assuming Fe_3O_4 is insoluble) is [34]:



In a clean melt of Pb or LBE there is a very low concentration of dissolved Fe, which means the liquid will begin to destroy the magnetite film. If the oxygen concentration is allowed to freely decrease while the film is being destroyed, the Fe concentration will continue to rise due to excessive dissolution–corrosion until it finally reaches its solubility limit at the liquid temperature near the surface. However, if active oxygen control is employed and the oxygen concentration is kept constant, the reaction halts when the Fe concentration near the surface reaches equilibrium. The dynamic equilibrium concentration of Fe is a function of oxygen concentration and can be kept at orders of magnitude lower than the Fe solubility in either lead or LBE. Once the equilibrium state has been established, the dissolution–corrosion rate is significantly reduced and the oxide acts as an effective diffusion barrier for Fe. With this diffusion barrier in place, the removal rate of Fe by the coolant at the surface is larger than the Fe diffusion rate, which means that no new oxide is formed at the outer surface. Inward diffusion of oxygen from the liquid through the oxide layer enables the regeneration of the oxide film at the substrate. Through this process, an oxide film immersed in an oxygen-concentration-controlled lead or lead-alloy liquid is self-healing. The activity product of magnetite formation in equilibrium conditions can be written as [31]:

$$\alpha_{\text{O}} \times \alpha_{\text{Fe}}^{3/4} = \exp \left[\ln(\alpha_{\text{Pb}}) + \frac{\Delta_f G^0}{RT} \right] \quad (2)$$

where α_{O} , α_{Fe} and α_{Pb} are the oxygen, iron and lead activities respectively. R is the universal gas constant ($= 8.314 \text{ J/mol K}$) and $\Delta_f G^0$ is the standard free enthalpy of the magnetite formation reaction. The oxygen and iron activity ratios α_{O} and α_{Fe} are defined as the ratio between concentration and solubility (assuming that Henry's law is valid [43]):

$$\begin{aligned} \alpha_{\text{O}} &= \frac{C_{\text{O}}}{C_{\text{O}}^s} \\ \alpha_{\text{Fe}} &= \frac{C_{\text{Fe}}}{C_{\text{Fe}}^s} \end{aligned} \quad (3)$$

Combining Eqs. (2) and (3) yields the following general expression for the minimum required oxygen concentration:

$$C_{\text{O}}(\text{min}) = \frac{\exp \left[\ln(\alpha_{\text{Pb}}) + \frac{\Delta_f G^0}{RT} \right] \times C_{\text{O}}^s}{\alpha_{\text{Fe}}^{3/4}} \quad (4)$$

The solubility of oxygen in pure lead and LBE is given by [44,45]:

$$\begin{aligned} C_{\text{O}}^s(\text{Pb})\text{wt.}\% &= 10^{(3.2 - \frac{5000}{T})} & 673 \leq T \leq 973 \text{ K} \\ C_{\text{O}}^s(\text{LBE})\text{wt.}\% &= 10^{(1.2 - \frac{3400}{T})} & 673 \leq T \leq 973 \text{ K} \end{aligned} \quad (5)$$

The correlations of Eq. (5), while reported to be valid in the temperature range 400–700 °C, are assumed in this study to be valid down to the melting temperature of both Pb and LBE. The standard free enthalpy of the reaction to form magnetite was computed by Courouau and Robin as [31]:

$$\Delta_f G^0 = -57190 - 21.1 \times T \left(\frac{\text{J}}{\text{mol}} \right) \quad (6)$$

The lead activity in lead and LBE are given as [31]:

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