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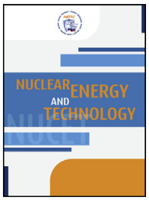

Ensuring the corrosion resistance of steels in heavy liquid metal coolants

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Abstract

The paper analyzes up-to-date, experimentally approved methods and means to provide conditions for the formation of anticorrosive oxide films on the surfaces of structural steels and keep them intact during operation of plants with heavy liquid metal coolants (HLMC). Since the basis of protective films is formed by oxide compounds of steel components, the content of the oxygen dissolved in the coolant is one of the parameters the film integrity depends on. Data from Russian and foreign studies on the solubility of oxygen in lead and lead-bismuth is analyzed. The paper also presents a review of the latest developed devices for the monitoring of oxygen content in molten lead and lead-bismuth that have proved themselves to perform well both under laboratory conditions and as part of experimental facilities and test circuits when justifying the designs and testing components of reactors with HLMC now under design in Russia (BREST-OD-300, SVBR-100). Major designs of mass exchangers (devices for dosing of oxygen into the coolant) developed by IPPE for the past 15 years have been analyzed.

Keywords: Oxygen detector; Corrosion protection; Oxygen concentration; Mass exchanger; Oxide film; Solubility; Lead; Lead-bismuth; Coolant; Coolant technology.

Introduction

Heavy liquid metals (lead and the eutectic alloy 44.5% Pb–55.5%Bi) are used as coolants for advanced nuclear power plants (NPP) (SVBR-100, BREST-OD-300, ELFR and other projects) and are considered for designs of accelerator driven systems (MYRRHA, CLEAR-I and others), as well as of innovative melting units (MAGMA project).

An important HLMC impurity is oxygen in a dissolved form. When dissolved oxygen is present in the lead (lead-bismuth) coolant, oxide films are formed on the surfaces of the circuit and equipment structural steels which protect the surfaces against the corrosive and erosive action of the coolant. Being oxides by nature, protective films have their in-service condition depending greatly on the oxygen behavior, that is, on the content of dissolved oxygen in the coolant.

The purpose of the study is to analyze modern means for the monitoring and control of the content of dissolved oxygen, allowing the corrosion resistance conditions in the HLMC environment to be ensured for steels.

Solubility of oxygen in molten lead and lead-bismith

Equilibrium is established between the solid body and the solution under conditions of a particular concentration called the concentration of saturation or solubility. Solubility is an essential physicochemical and process parameter an analysis or calculation of any dissolution process starts with, being indicative of the solvent capacity and its capability to take up the substance dissolved. Solubility is the factor that affects to a great extent the dissolution process rate.

For the time being, no curve for the oxygen solubility in liquid metals can be calculated theoretically due to the absence of a quantitative expression for the energy of mutual components exchange in the liquid metal. Therefore,

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Table 1
Coefficients of Eq. (1) obtained by different authors.

Lead				Lead-bismuth eutectics			
Authors, year	*t* [°C]	*A*	*B*	Authors, year	*t* [°C]	*A*	*B*
Rodigina, 1961 [1]	300–400	3.1	4900	Martynov,1998, [4]	400–700	1.2	3400
Alcock, 1964 [2]	510–700	3.42	5240	Ghetta, 2004, [5]	300–500	3.27	4852
Ganesan, 2006 [3]	540–740	3.21	5100	Müller, 2003, [5]	200–600	2.52	4803
Isecke, 1977 [5]	900–1100	3.38	5182	Courouau, 2004, [5]	350–500	3.34	4962
Martynov,1998 [4]	400–700	3.2	5000	Ganesan, 2006, [3]	540–740	2.42	4287

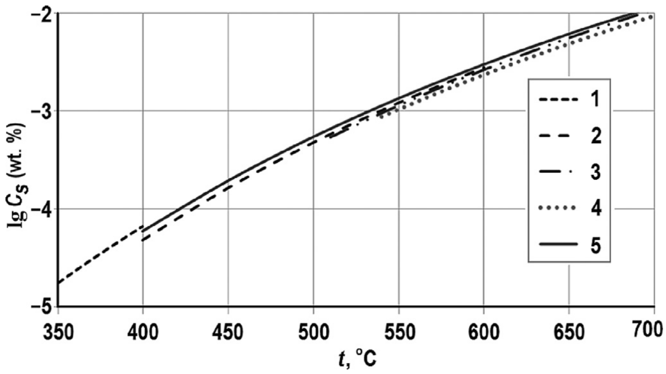

Fig. 1. Oxygen solubility in liquid lead obtained by different authors: 1 – [1]; 2 – [5, Isecke]; 3 – [2]; 4 – [3]; 5 – [4].

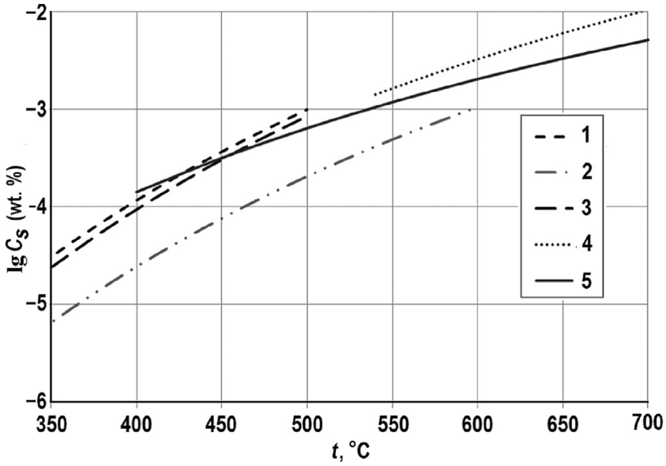

Fig. 2. Oxygen solubility in liquid lead-bismuth obtained by different authors: 1 – [5, Ghetta]; 2 – [5, Müller]; 3 – [5, Courouau]; 4 – [3]; 5 – [4.].

semiempirical theories are used to calculate the solubility of impurities in liquid metals based on experimental data.

In a general case, the temperature dependence of the oxygen solubility (C_S) in the considered molten metals may be described by the equation

$$\lg C_S(\mathrm{wt}\,\%) = A - B/(t[^\circ\mathrm{C}] + 273.15). \qquad (1)$$

Data in [1–5] on the oxygen solubility for liquid lead is presented in Fig. 1 and that for lead-bismuth is presented in Fig. 2 as temperature dependences of the saturation concentration logarithm. Table 1 presents coefficients A and B of Eq. (1) obtained by different authors.

There is rather a good convergence of data for the oxygen solubility in lead though a certain divergence is observed for that in lead-bismuth. The difference in the data is likely to be caused by a difference in the purity of initial molten metals, the accuracy of measurement and so on.

Monitoring of the oxygen content in heavy liquid metal coolants

This is a common practice to monitor the thermodynamic activity (TDA) of oxygen in a lead-bismuth (lead) coolant as a quantitative parameter the HLMC oxidation potential depends on. The TDA association with the oxygen concentration is roughly represented by relation [6]

$$a_{[\mathrm{O}]} = C/C_S, \qquad (2)$$

where C is the concentration of dissolved oxygen in the HLMC; and C_S is the oxygen solubility in the HLMC.

To monitor the oxygen dissolved in the coolant, oxygen TDA detectors (OAD) are being developed at IPPE based on solid oxide electrolyte. The detectors feature high speed of response, high sensitivity, a capability for long-term operation under conditions of elevated temperatures and thermal shocks, reliability and stability of conducting and mechanical properties in a broad range of temperatures and oxygen partial pressures [7].

Essentially, the oxygen measurement method consists in the formation of a galvanic concentration element, including a comparison electrode, solid oxide electrolyte and a test electrode. The electrochemical element acts as the concentration element for the oxygen on the electrodes. The cumulative potential forming process is the transport of oxygen from the electrode, where its chemical potential is higher, to the electrode, where its chemical potential is lower.

By measuring the temperature and the electromotive force (EMF) of the element with a known chemical potential of the comparison electrode in a standard state, one may determine the thermodynamic activity of oxygen in the test electrode.

The relation between the EMF developed by the galvanic element (in the detector), the coolant temperature and the measured value of the oxygen TDA is found by a Nernst equation

$$E_0 = \frac{RT}{nF}\ln\frac{a_B}{a_A} \qquad (3)$$

where a_A is the TDA of oxygen in the comparison electrode and a_B is the TDA of oxygen in the test electrode.