ELSEVIER

Journal of Nuclear Materials 296 (2001) 301–304

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Kinetics of gas phase oxygen control system (OCS) for stagnant and flowing Pb–Bi Systems

C.H. Lefhalm *, J.U. Knebel, K.J. Mack

Forschungszentrum Karlsruhe – Technik und Umwelt, Institut für Kern- und Energietechnik (IKET), Postfach 3640, 76021 Karlsruhe, Germany

Abstract

Pb and Pb–Bi are known to be very corrosive to structural materials at elevated temperatures. In recent studies, the necessity of measurement and control of the oxygen concentration in the liquid metal in order to safely operate a liquid Pb or Pb–Bi loop has been shown. The dynamic behaviour of the gas phase oxygen control system (OCS), which was developed at Forschungszentrum Karlsruhe (FZK), is investigated with respect to diffusion as the limiting process of oxygen exchange between the gas phase and the liquid metal. In this paper the development of a physical model for this diffusion process is described and compared to experimental results of a stagnant liquid Pb–Bi system. The experimental findings are in very good agreement with the theoretical equations describing the thermodynamic and kinetic behaviour of such a system. Recent investigations in a Pb–Bi loop at the Karlsruhe Lead Laboratory (KALLA) indicate that this gas phase OCS is a promising candidate system for an accelerator-driven subcritical system (ADS). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

At the Forschungszentrum Karlsruhe (FZK) a project was carried out in the framework of the Programme Nuclear Safety Research (PSF) investigating an accelerator-driven subcritical system (ADS) [1].

The ADS will use liquid lead (Pb) or eutectic lead–bismuth (Pb–Bi) as the spallation material and coolant for the target module [1]. However, liquid-metal corrosion is a serious problem for such systems. Because of the high solubility of some steel components, strong corrosion effects could be observed [2,3]. One way to protect the metal surface is using an oxide layer that has the ability to slow down the dissolution of the metal components to tolerable values, [3,4].

The oxygen control system (OCS) developed at FZK provides the possibility to control the oxygen content in the liquid metal. As stated in [3], an oxygen concentration between 10^{-6} and 10^{-7} at.% in lead is desired to prevent both liquid-metal corrosion and oxygen corrosion due to excessive oxidation of the steel surface.

One key question of such an OCS is its kinetics. The time needed to reach a desired oxygen concentration in a Pb–Bi system within a given volume is crucial for the usability of such systems at an industrial scale.

2. Oxygen Control System

With the OCS, the oxygen concentration is controlled via a gas atmosphere with a definite oxygen partial pressure p_{O_2} that determines the chemical potential of oxygen within the liquid-metal bath. To prevent PbO precipitation and to support Fe_3O_4 formation the following condition must be established [5]:

$$2\Delta G^0_{PbO} > RT \ln p_{O_2} > 0.5\Delta G^0_{Fe_3O_4}. \qquad (1)$$

The standard values ΔG^0 of the Gibbs energies are known for the oxides in question, so the oxygen partial pressure that retains the stable condition can be calculated. To set the desired oxygen partial pressure in the gas phase, a mixture of hydrogen and water vapour

---

[*] Corresponding author. Tel.: +49-7247 82 6329; fax: +49-7247 82 4837.

E-mail address: lefhalm@iket.fzk.de (C.H. Lefhalm).

PII: S0022-3115(01)00567-0

within the argon carrier gas is used. The H_2/H_2O ratio determines the oxygen potential as shown by the following relation [5]:

$$p_{O_2} = \frac{p_{H_2O}^2}{p_{H_2}^2} \exp\left(\frac{2\Delta G_{H_2O}^0}{RT}\right). \tag{2}$$

For the safe operation of a Pb–Bi or Pb loop at ADS relevant temperatures, the typical working conditions are between $p_{O_2} = 10^{-31}$ bar at 400°C and $p_{O_2} = 10^{-24}$ bar at 550°C, respectively. This results in a corresponding H_2/H_2O ratio of 0.4 [3]. In the case of stagnant Pb–Bi or Pb, at both temperatures corrosion-preventing iron oxide is formed but not PbO. In the case of a liquid Pb–Bi or Pb loop (flowing liquid metal), there is no equilibrium across the operational temperature region (300–450°C for Pb–Bi and 400–550°C for Pb) via the H_2/H_2O ratio but via the oxygen dissolved in the flowing liquid Pb–Bi or Pb [7].

2.1. Kinetics and diffusion

The physical process found to determine the timescale of the oxygen control process via OCS is the diffusion. The exchange of oxygen atoms through the interface between the gas phase and the liquid metal can be modelled with solutions of the diffusion equations, Fick's laws [6,7]:

$$j = -D\frac{\partial c}{\partial x} \quad \text{and} \quad \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{3}$$

In this case a solution can be obtained by the use of Laplace transformation. Therefore a rigid plane of stagnant liquid metal (height l) is assumed, with a given oxygen concentration on the surface due to a set H_2/H_2O ratio in the gas phase. The time-dependent solution for oxygen uptake or loss with a constant diffusion coefficient results in [6]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n-1)^2\pi^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right\}, \tag{4}$$

where M_t is the amount of oxygen exchanged between gas phase and liquid metal in the time t owing to the concentration difference.

However this model was too simple to describe the experimental findings. Further calculations with more complex boundary conditions (stagnant liquid-metal plane with variable oxygen concentration on the surface with respect to a concentration-dependent diffusion coefficient) were made. The final solution [6,7],

$$\frac{M_t}{2lc_1} = 1 - \sqrt{\frac{D}{\beta l^2}} \tan\sqrt{\frac{\beta l^2}{D}} e^{-\beta t} - \frac{8}{\pi}\sum_{n=0}^{\infty} \frac{\exp(-D(2n+1)^2\pi^2 t/4l^2)}{(2n+1)^2[1-(2n+1)^2(D\pi^2/4\beta l^2)]}, \tag{5}$$

fits the experimental results (see Fig. 3).

3. Oxygen control test stand

The oxygen control test stand Kinetics of Oxygen Control Systems (KOCOS), see Fig. 1, is installed at the Karlsruhe Lead Laboratory (KALLA) [1]. KOCOS allows the investigation of kinetics of the oxygen control process via the gas phase as described in theory above. A mixture of Ar and Ar/5% H_2 is used to adjust the hydrogen concentration in the gas phase. Water vapour is added by passing the gas through water at a given temperature in a thermostat. By changing the gas flow of Ar/5% H_2, the H_2/H_2O ratio and therefore the oxygen partial pressure in the gas phase can be controlled. The gas mixture is guided over a chilled-mirror moisture sensor and then over the surface of 680 g of stagnant liquid Pb–Bi at a constant temperature of 430°C. The liquid metal is held in a crucible of aluminium oxide to prevent contact with the steel wall of the oven. The oxygen partial pressure in the escaping gas mixture is measured by a solid electrolyte cell at 750°C with a Pt/Air reference system. A constant total gas flow rate (Ar + Ar/5% H_2) of 18 l/h is set.

For the experimental investigations, changes in the H_2/H_2O ratio from 0.053 (297 sccm Ar, 3 sccm Ar/5% H_2) to 1.725 (198 sccm Ar, 102 sccm Ar/5% H_2) were made in eight steps. The system was observed until thermodynamic equilibrium had been reached in each step. Due to limitations in the precision of the measurement equipment for the oxygen partial pressure in the gas phase, one has to take into account that the

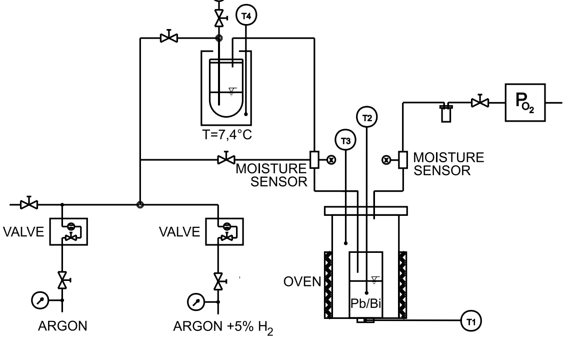

Fig. 1. Scheme of the oxygen control test stand KOCOS with stagnant liquid Pb–Bi.

concentration of oxygen in the liquid-metal bath is not homogeneous when the thermodynamic equilibrium on the interface reaches stability. The closer the concentration of oxygen in the liquid Pb–Bi is to the equilibrium concentration, the smaller the rate exchange of oxygen atoms between the gas and liquid-metal phase. Therefore one can only detect relatively high exchange rates and so the given results are related only to the exchange of oxygen at the interface between gas phase and the liquid Pb–Bi. However, this is the process that determines the kinetics of the gas phase OCS, especially for loop systems.

4. Results

Besides the issue that the oxygen control process is reversible in time, three important results have been found. First, the measured values for the H_2/H_2O ratio in equilibrium conditions are in very good agreement with the values calculated from the given gas flows and dew point (moisture). The error is less than 2%. So the control of partial pressure is warranted even at low gas flow rates, especially for hydrogen (Fig. 2).

Second, the physical model of the diffusion process with consideration of variable oxygen concentration on the surface of the liquid metal as described in the theory above fits the experimental findings. After a change of the H_2/H_2O ratio, the loss of oxygen was observed and compared to the calculations (Fig. 3). To the author's knowledge, this is the first theoretical approach to the description of the process of oxygen exchange between gas phase and liquid metal under oxygen control with respect to variable surface concentrations. With this model, predictions are possible about the time that is needed to reach a desired concentration in the surface layer of a liquid-metal bath using the OCS.

Third, the diffusion coefficient was found to be concentration dependent. From the experimental data, for stepwise changes in the H_2/H_2O ratio, the diffusion coefficient for oxygen loss was calculated. For each step of concentration difference another diffusion coefficient was found. One important consequence of this result is the different time behaviour of uptake and loss of oxygen. In the experiments a faster loss than uptake of oxygen was always observed. Furthermore the expected dependency of the diffusion on the ratio between surface and volume was observed (Fig 4). The oxygen uptake of a higher liquid-metal volume with the same surface area takes accordingly longer which results in higher diffusion coefficients in these calculations.

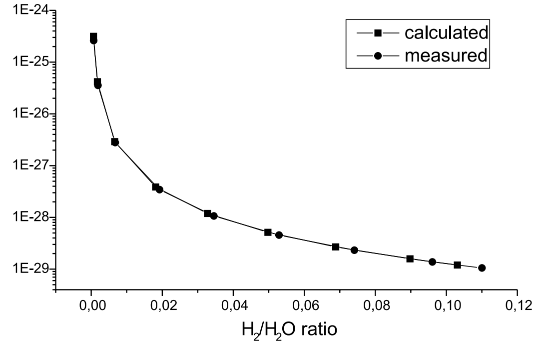

Fig. 2. Oxygen partial pressure over H_2/H_2O ratio. Measured and calculated at Pb–Bi temperature of 430°C.

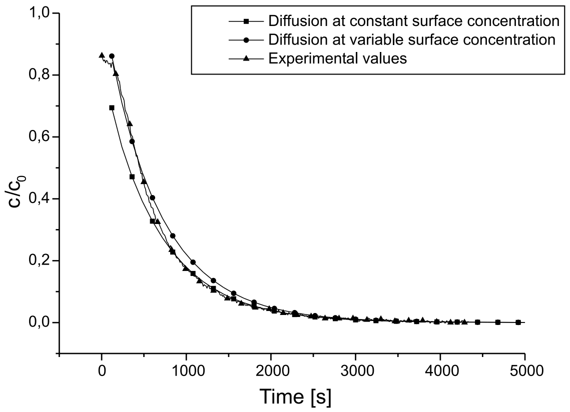

Fig. 3. Comparison between diffusion models and experimental data, concentration over time, c = concetration at a given time, c_0 = start concentration.

It is important to say that the mentioned diffusion coefficients are used to describe the process of oxygen exchange (loss and uptake) at the boundary layer between the gas phase and the liquid metal which is a kind of diffusion process [7,8]. They are not concerned with the diffusion motion of oxygen within the liquid-metal bulk.

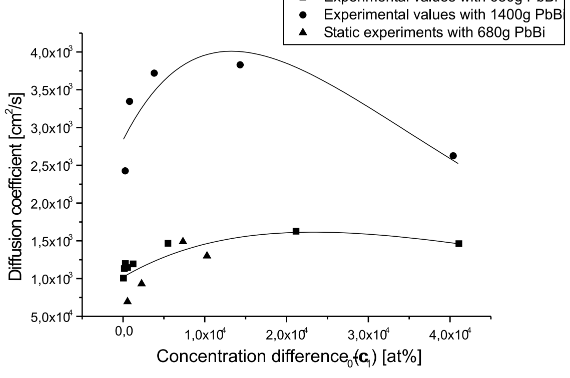

Fig. 4. Dependency of diffusion coefficient on concentration difference for different Pb–Bi masses at 430°C, with c_0 = start concentration, c_1 = target concentration determined by H_2/H_2O ratio.

At the moment, the experimental results described for a stagnant system are to be tested in a Pb–Bi loop at the KALLA Laboratory. One objective is to take the forced convection into account and enhance the physical model of oxygen exchange for flowing liquid-metal systems. In addition, solid electrolyte oxygen sensors will be installed to measure the oxygen concentration directly in the liquid metal to obtain data about the oxygen distribution in the liquid metal and to correlate them with the known behaviour of the gas phase OCS.

5. Summary

Liquid-metal loops with Pb or Pb–Bi as spallation material and as coolant that are of interest for ADS are only feasible if the problem of steel corrosion at relevant temperatures can be solved.

It is known that an oxide scale at the surface of steel can act as a protective barrier against the dissolution of steel components in the liquid metal. The conditions are described under which a protective oxide scale is formed on the steel surface. These conditions are maintained by an oxygen concentration in liquid Pb–Bi that is in equilibrium with a gas phase which contains hydrogen and water vapour with a defined H_2/H_2O ratio.

The exchange of oxygen between gas phase and liquid metal is limited by the process of diffusion. With a physical model the kinetics of such a gas phase OCS can be described. Experimental findings at the oxygen control test stand KOCOS are in excellent agreement with the results of the developed diffusion model. Dependencies on the variable oxygen concentration in the gas phase and the total concentration differences are determined.

Recent investigations with solid electrolyte oxygen probes shall prove the feasibility of the OCS for liquid-metal loop systems and will give insight into the oxygen distribution in the flowing Pb–Bi.

References

[1] J.U. Knebel, G. Heusener, Internationale Zeitschrift für Kernenergie, Heft 6, June 2000, p. 350.

[2] T.B. Massalski (Ed.), Binary Phase Diagrams, 2nd Ed., ASM International, Ohio, 1990.

[3] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.

[4] V. Markov, Seminar on lead cooled fast reactors, Cadarache, September 22–23, 1997, personal communication.

[5] G.S. Upadhyaya, R.K. Dube, Problems in Metallurgical Thermodynamics and Kinetics, 1st Ed., Pergamon, New York, 1977.

[6] J. Crank, The Mathematics of Diffusion, 2nd Ed., Clarendon, Oxford, 1975.

[7] W. Jost, Diffusion in Solids, Liquids, Gases, 6th Ed., Academic, New York, 1970.

[8] G.K. Bandyopadhyay, H.S. Ray, Metall. Trans. 2 (1971) 3055.