Journal of Nuclear Materials 296 (2001) 289–294

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Section 5. Liquid metal technology

Development of oxygen meters for the use in lead–bismuth

J. Konys [*], H. Muscher, Z. Voß, O. Wedemeyer

FZK, Forschungszentrum Karlsruhe GmbH, Institut fur Materialforschung III, Postfach 3640, 76021 Karlsruhe, Germany

Abstract

Liquid lead and the eutectic lead–bismuth alloy (PbBi) are considered both as a spallation target and coolant of an accelerator driven system (ADS) for the transmutation of long-lived actinides from nuclear waste into shorter living isotopes. It is known that both, pure lead and PbBi, exhibit a high corrosivity against austenitic and ferritic steels, because of the high solubility of nickel and iron in PbBi. One way of reducing the strong corrosion is the in situ formation of stable oxide scales on the steel surfaces. Thermodynamic calculations and experimental results have confirmed, that the control of oxygen in lead or PbBi within a defined activity range can lead to acceptable corrosion rates. To control the level of oxygen dissolved in lead or PbBi, a sensor for measuring the oxygen activity is required. Within the sodium fast breeder reactor development, an adequate technique was established for estimating oxygen in liquid sodium. This knowledge can be used for other metal/oxygen systems like oxygen in PbBi. For measuring the oxygen activity and calculating its concentration, the relevant thermodynamic and solubility data have to be considered. Two reference electrode systems: Pt/air and In/In_2O_3 (both based on yttria-stabilized zirconia as solid electrolyte) are investigated to evaluate their electromotive force (EMF)–temperature dependency in saturated and unsaturated oxygen solutions. Results with both types of oxygen meters in PbBi at different oxygen levels were compared with theoretical calculations. The experimental data indicate that the design, construction and integration of an oxygen control unit in a large scale PbBi-loop seems to be very feasible. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Lead and lead–bismuth alloys are considered as spallation target for a so-called accelerator driven system (ADS) in which long-lived actinides should be transmuted [1,2]. Pb and PbBi have a high neutron yield and are very transparent to neutrons of energies below 1 MeV. The molten metal could be used not only as a target but also as a coolant in this reactor system. But it is known from literature that lead and bismuth are much more corrosive than alkali metals [3–5]. Hence, an important issue of an ADS is the corrosion of the structural and window materials in the liquid PbBi target. This corrosion process must be understood, controlled and reduced for safety and economic reasons.

One way to reduce corrosion of metals in liquid Pb or PbBi would be the use of metals with very low solubility, e.g., tungsten or molybdenum. Another way is to form a stable oxide layer on the materials surface. Thermodynamic investigations of Al–Fe alloys showed the possibility that self-healing of the alumina scale can take place if the kinetics of the process are fast enough [6]. Gromov et al. [7] and Markov [8] stabilized the oxide layer by maintaining an oxygen concentration of 10^{-6} at.% in liquid Pb or PbBi with an oxygen control system.

An oxygen control system in a PbBi loop requires the continuous measurement of the oxygen potential in the liquid alloy. A very suitable technique is the use of solid electrolyte oxygen sensors. Based on the experience in other liquid metal (LM) systems like sodium, lithium or lead–lithium [9–11], an adaptation to the specific conditions of the eutectic lead–bismuth alloy is necessary. Furthermore the thermodynamic database has to be established to allow theoretical calculations regarding the temperature and oxygen concentration dependency of the electromotive force (EMF) of such kind of zirconia-based oxygen sensors.

---

[*] Corresponding author. Tel.: +49-7247 823 720; fax: +49-7247 823 956.

E-mail address: juergen.konys@imf.fzk.de (J. Konys).

0022-3115/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(01)00531-1

2. Oxygen measurement in lead and lead–bismuth

The amount of oxygen in lead which is necessary for the formation of a protective oxide scale on steel can be controlled. Details are presented elsewhere [7]. If we consider a LM loop, there will be no equilibration across the temperature field via gas phase but rather through the oxygen dissolved in lead or PbBi. In this case we have to consider the variation of the oxygen activity throughout the temperature field between 400°C and 550°C. The calculation of the oxygen activity a_O in equilibrium with an oxygen partial pressure p_{O_2} can be derived from the modified Lewis–Randall equation, assuming that the system obeys Henry's law (very dilute oxygen solutions in PbBi):

$$a_O = \gamma_O c_O = \frac{c_O}{c_O^s} = \left(\frac{p_{O_2}}{p_{O_2}^s}\right)^{1/2}. \tag{1}$$

The suffix '*s*' indicates the values of saturation at which the activity a_O of oxygen dissolved becomes unity. That is because at saturation, the standard ΔG^O value of the Gibbs energy of oxygen solubility in PbBi becomes equal to the standard ΔG^O value of the Gibbs energy of the oxide formation – solid PbO begins to precipitate as a new phase [12].

To control the oxygen level in PbBi, an oxygen sensor has to be incorporated into the system. Usually electrochemically based oxygen meters are taken to fulfill this requirement. Galvanic cells used for the EMF measurement of oxygen dissolved in liquid metals have been developed in our laboratory over the last 30 years for different applications (Na, K, Pb–17Li) [9,10]. Inherent problems associated with these meters were initially, in the early seventies, breakage of the ceramic electrolyte tube, non-theoretical response to oxygen activity and other design related failures. To our knowledge, only very few data mostly from Russian authors have been published up to now concerning long-term use of such EMF-meters in flowing lead and/ or PbBi [7,8]. Within this recently started work the activities are focused on the development of oxygen cells for the use in lead–bismuth. This includes the selection of appropriate reference systems, the estimation of deviations from theoretical behavior and testing of their long-term stability.

3. Theoretical background

The EMF of the following concentration cell,

$$p'_{O_2}//\text{solid electrolyte}//p''_{O_2}, \tag{2}$$

where p''_{O_2} and p'_{O_2} are the oxygen partial pressures of the reference electrode and of the corresponding LM/oxygen system, is given by the Nernst equation:

$$E = \frac{RT}{4F}\ln\frac{p''_{O_2}}{p'_{O_2}}. \tag{3}$$

For fixing the oxygen activity of the reference side, pure oxygen ($p = 1$ bar) or air ($p = 0.21$ bar) as gas electrodes or metal/metal oxide buffers such as $In/In_2O_3, Bi/Bi_2O_3,$ $Sn/SnO_2, Cu/Cu_2O$ and many others so-called coexistence electrodes of that type have been used worldwide. The oxygen partial pressures can be calculated using the according standard Gibbs energies of formation data [13]. The requested p'_{O_2} value can thus be estimated from the measured EMF value for a given set of temperatures.

4. Platinum/air reference electrode

Using data from Ullmann et al. [14], the following relationship between the resulting EMF and p'_{O_2} was calculated:

$$E\ (\text{mV}) = -0.03369T - 0.021526T\ln p'_{O_2} \tag{4}$$

With:

$$\Delta G^O_{PbO} = -436850 + 197.991T\ (\text{J/mol } O_2) \tag{5}$$

and assuming the activity value of lead in PbBi to be ca. 0.5, the EMF for an oxygen saturated solution of lead (if PbO is the first precipitating oxide) is as follows:

$$E\ (\text{mV}) = 1131.06 - 0.5762T\ (\text{K}). \tag{6}$$

For unsaturated solutions of oxygen, one has to take into account the solubility of oxygen in PbBi, which is simply correlated with its thermodynamic activity value. With the following temperature-dependent solubility data of Orlov et al. [15]:

$$\ln c_{O,PbBi} = 11.969 - 7827/T \tag{7}$$

and from the above equation one can calculate the dependency of the EMF on the oxygen concentration in PbBi as

$$E\ (\text{mV}) = 794.09 - 0.06085T - 0.0431T\ln c_{O,PbBi}, \tag{8}$$

where $c_{O,PbBi}$ is in wppm oxygen.

5. In/In_2O_3 reference electrode

According to the stoichiometry of the indium sesquioxide formation one obtains

$$RT\ln p''O_2 = \frac{2}{3}\Delta G^O In_2O_3\ (\text{J/mol } In_2O_3) \tag{9}$$

with

$$\Delta G^O In_2O_3 = -618365 + 216.3T\ (\text{J/mol } O_2) \tag{10}$$

[16] and assuming the activity value of lead in PbBi to be ca. 0.5, the EMF for oxygen saturated PbBi can be calculated as

$$E\ (\mathrm{mV}) = 470.3 - 1.7567 \times 10^{-2} T\ (\mathrm{K}). \qquad (11)$$

In case of unsaturated solutions of oxygen in PbBi, the EMF of the cell can be estimated using the temperature-dependent solubilities from Orlov [15] as

$$E\ (\mathrm{mV}) = 133.09 + 0.46823T - 4.308 \times 10^{-2} T \times \ln c_{\mathrm{O,PbBi}}, \qquad (12)$$

where $c_{\mathrm{O,PbBi}}$ is in wppm oxygen, too.

6. Design of oxygen meter

The schematic design of the oxygen meter can be seen in Fig. 1. The meter was connected to the test capsules with a leak tight flange. Regardless of the type of reference electrode, only O^{2-} ions are moving through the ceramic solid electrolyte lattice towards the PbBi-side where the oxygen ions are subsequently discharged. The cationic flux and the electronic flux through the ceramics is negligible. The EMF was measured by means of a Keithley high impedance voltmeter, the acquired data were stored on a PC. All oxygen meters were built and prepared for testing in an inert argon glove box.

7. Results and discussion

A large number of different oxygen meters with both types of reference electrodes were tested in liquid PbBi with varying amounts of dissolved oxygen. The oxygen saturated solutions were prepared by bubbling of dry air through the liquid PbBi eutectic as a dispersed bubble flow. For the purpose of producing nearly oxygen-free lead–bismuth of 'very pure' quality Ar + 5% H_2 gas was bubbled through the melt for 24 h.

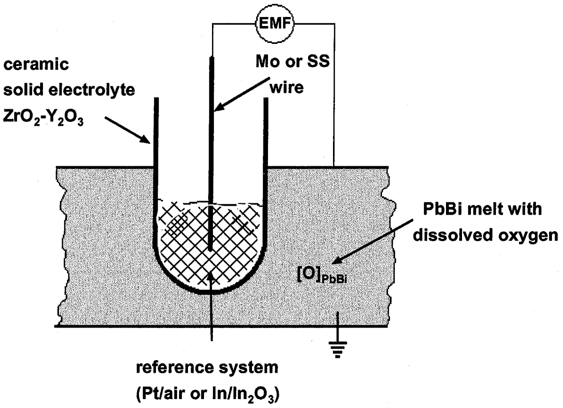

Fig. 1. Schematic view of the electrochemical oxygen meter.

The results of the EMF-measurements are compared with the expected dependencies of the EMF on temperature and concentration of oxygen dissolved in PbBi, according to theoretical calculations (Figs. 2 and 3). In both figures the dashed lines represent the theoretical temperature dependency of the EMF for unsaturated solutions of oxygen in the liquid PbBi eutectic corresponding to the indicated oxygen concentrations, given in wppm, whereas the full lines give the EMF–temperature dependency for oxygen saturated PbBi. For the plots of theoretical dependencies of EMF(T/K), an assumption was made that the activity of lead in the PbBi eutectic can be described by a numerical value close to 0.5. It seems to be a sufficient approximation, because the PbBi eutectic is nearly equal in concentration of both metals. Apart from this Pb and Bi elements with high

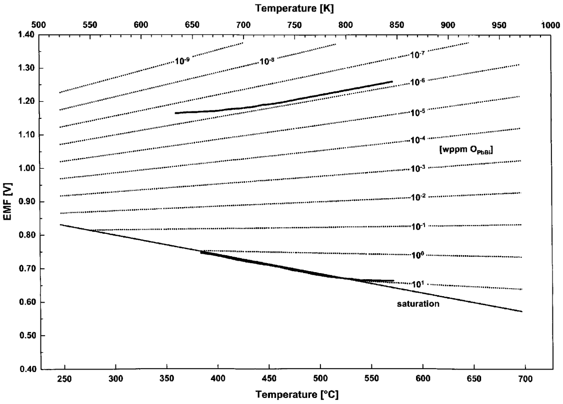

Fig. 2. Comparison of calculated and measured EMFs for a cell with Pt/air reference system.

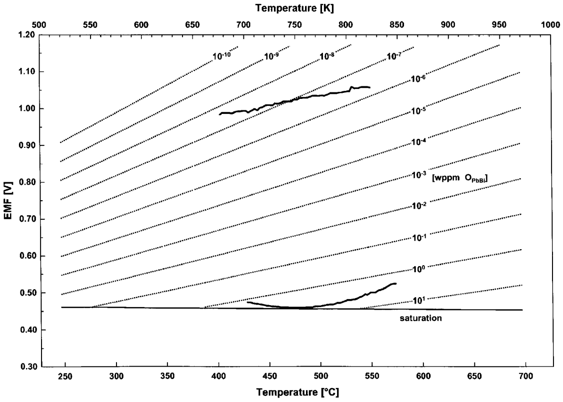

Fig. 3. Comparison of calculated and measured EMFs for a cell with In/In_2O_3 reference system.

atomic numbers $Z = 82$ and $Z = 83$, are both somewhat 'similar' in their physical/ chemical properties.

For the Pt/air system (Fig. 2) coming from the unsaturated state (high temperature range), the point of coincidence of the cooling curve with the theoretical expected EMF(T) line for the oxygen-saturated state is reached at about 530°C. At lower temperatures both lines are in excellent agreement for the whole temperature range of about 150° down to ca. 370°C. Regarding EMF measurements in strong unsaturated oxygen solutions, the slope and magnitude of the EMF(T) cooling curve coming from 570°C down to 370°C are identical with the expected values for a solution with dissolved oxygen content slightly below 10^{-6} wppm. A very flat ascending deviation to higher EMF values was observed here only at temperatures below 400°C.

In Fig. 2 the EMF lies at about 0.7 V for the loop-relevant temperatures between 500°C and 550°C. In oxygen saturated PbBi nearly theoretical behavior of the EMF(T) dependency with the same negative slope down to 400°C and a small constant shift in the EMF level is observed. Another test in nearly oxygen-free PbBi solution revealed also the expected EMF(T) dependency – in this case a positive slope of the straight line was detected – as predicted from the theory. However, such low real values for the oxygen concentration could not be evaluated analytically up to now. Special analytical methods and equipment have to be developed. In comparison to Pt/air with its very good EMF-response, the dependency on temperature of the EMF readings obtained with meters based on In/In_2O_3 reference system, exhibit a much more complicated form (Fig. 3). The measurements showed no simply coincidence with the theoretical straight lines: The slope – measure of the cell's entropy – changes in magnitude and sign. This could also be due to kinetic reasons: the cooling rate could be too fast to reach equilibrium. Coming from the unsaturated state (high temperatures) the tangential point of the cooling curve with the theoretical expected EMF(T) line for the oxygen-saturated state is reached by ca. 480°C. An agreement of both lines was only found in a narrow temperature band of about 20° down to 460°C, where the measured EMF value became slightly higher for the second time. Measurements in a strong unsaturated oxygen solution exhibited the slope of the EMF(T) cooling curve (straight line) to be lower as expected from the theory. The reason for the slope deviation is perhaps of kinetic nature (coexistence electrode, transport phenomena between liquid indium and the solid indium sesquioxide). The general conclusion is, that both for the oxygen saturated and unsaturated probes, the In/In_2O_3 cell give the best performance at temperatures of about 460–480°C. The non-linearity at other temperatures could be a limiting factor for the general use of that electrode in PbBi, but because these non-linearities are deterministic (reliable data obtained), the observed performance of In/In_2O_3 on temperature seems not to be a serious disadvantage. Cells which exhibit even partial irreversible behavior cannot be linearly calibrated. The reason could also be kinetically related, because of a strong correlation of the EMF-output with the cooling rates. At temperatures lower/higher then 460–480°C the EMF was found to decrease/increase with temperature, respectively, possibly as a result of polarization changes on the 3-phase coexistence electrodes. It is well known, that in case of slower oxygen diffusion (low temperature range) the measured oxygen activity may be different from the oxygen activity in the bulk causing additional EMF value – increments due to kinetic reasons.

Fig. 4 describes the response of a oxygen meter with Pt/air reference system during bubbling of reducing and oxidizing gases through the PbBi melt. First $Ar + 5\%\ H_2$, then air ($p = 0.21$ bar) with subsequent $Ar + 5\%\ H_2$ bubbling was performed. The rate of meter response to oxygen activity changes in the PbBi has been found to be very rapid. Transient response to step changes of the oxygen activity in PbBi exhibit no unusual behavior. The excellent time response of the EMF values after replacing of the $Ar + 5\%\ H_2$ with air bubbling (no time delay) is obvious. By changes in the opposite direction there is some phase shift detected. The intrinsic temperature fluctuations at the beginning of the curve (Fig. 4, lower part) are due to the reaction enthalpies of oxide scales degradation (oxygen removed by $Ar + 5\%\ H_2$) and growth of oxides (air bubbling), respectively, whereas at the end of the curve only the noise level of the control unit was measured.

A very similar behavior was seen for the In/In_2O_3 cell at 552°C (Fig. 5). Shortly after starting of $Ar + 5\%\ H_2$ bubbling from a intermediate oxygen level, a strong increase of the EMF, corresponding to a decrease in oxygen activity in the PbBi, was measured.

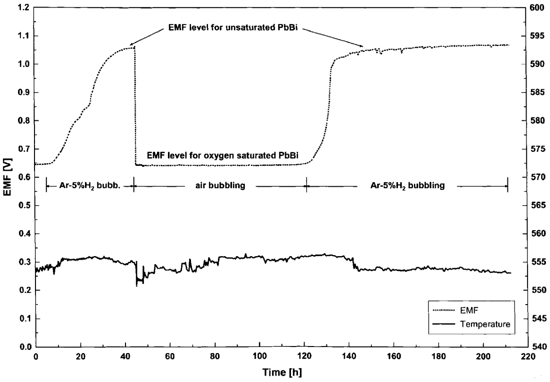

Fig. 4. Changes of EMF for a cell with Pt/air reference system due to bubbling of reducing and oxidizing gases through the PbBi.

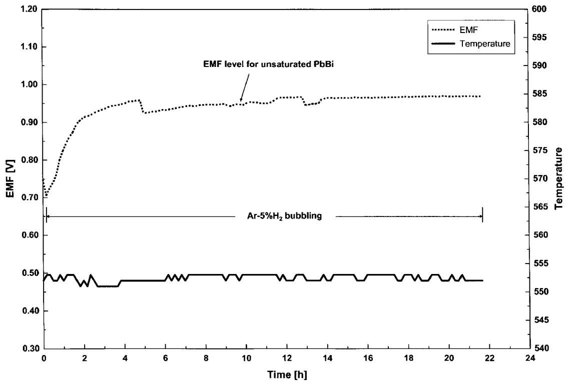

Fig. 5. Change of EMF for a cell with In/In_2O_3 reference system due to bubbling of a reducing gas through the PbBi.

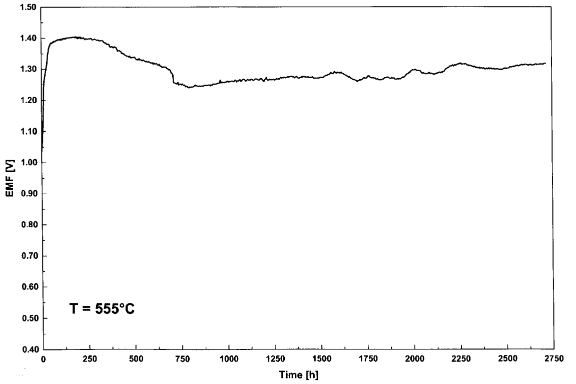

Fig. 6. Mid-term behavior of EMF at 555°C for a cell with Pt/air reference system.

After about 5 h, an EMF level of ca. 0.95 V was reached, which stayed nearly constant for the rest of the bubbling period.

Fig. 6 shows the mid-term-stability of the EMF of a cell with Pt/air reference electrode at 555°C over ca. 4 months of continuous collecting of data during the immersion of the oxygen meter in the PbBi melt. Regardless of the high level of the EMF during and after the equilibration, the long-time-stability within a small range of 75 mV over months without any intermittencies buried in noise seems to be very good. The ascending of the EMF at the beginning of the experiment was due to the chemical reaction of the dissolved oxygen with the steel of the container wall.

8. Conclusions

Electrochemical oxygen meters with Pt/air and In/In_2O_3 reference systems can be used as in situ devices for measuring the chemical activity of dissolved oxygen in liquid PbBi. The data obtained confirm the feasibility of using oxygen meters for the purposes of oxygen control in PbBi.

The Pt/air system is a suitable reference electrode capable of maintaining stable EMF values over a long-time of immersion in PbBi. Pt/air offers both a fast response-kinetics and a very good mid-term stability. Successful performance has been demonstrated in a lot of experiments. Calibration slopes EMF versus temperature for Pt/air were fitting to theoretical calculations very well.

Similar results have been obtained for oxygen meters with In/In_2O_3 reference systems. The operational experiences are less good, compared to Pt/air results, regarding to the theoretical estimations. The deviations in the slopes of the EMF–temperature curves, especially in unsaturated PbBi, might be due to a more pronounced sensibility to the time to reach thermodynamic equilibrium during cooling.

The current results from mid-term stability tests indicate for cells with Pt/air reference systems a very satisfactory behavior. Up to nearly 3000 h, no degradation of the oxygen sensor was detected. Comparable results for In/In_2O_3 Cells are not existing at the moment.

Sensors with both types of reference electrodes revealed an excellent response to changes in the oxygen activity of the PbBi. The response time for significant reactions of the EMF was in the range of minutes. The reproducibility of this behavior was very good for cells with Pt/air reference system, when cycling between reducing and oxidizing gases.

The results from the EMF–temperature dependency tests have shown, that the minimum operational temperature of the oxygen sensor is ca. 400°C for Pt/air. This is much lower than the measured ca. 480°C for In/In_2O_3. The reason for such differences could be due to higher internal resistances of the In/In_2O_3 electrode.

Acknowledgements

This work has been performed in the framework of the Nuclear Safety Project of the Forschungszentrum Karlsruhe and is supported by the HGF Hermann von Helmholtz Gesellschaft Deutscher Forschungszentren as the Strategy Fund Project 99/16. The support of the HGF for this work is gratefully acknowledged.

References

[1] G. Heusener, M. Salvatores, Use of heavy liquid metals, a perspective for critical/subcritical fast neutron concepts, in: Proceedings of the Heavy Liquid Metals Conference'98, Obninsk, Russia.

[2] C. Rubbia, J.A. Rubio, S. Buono, F.S. Carminati, Conceptual design of a fast neutron operated high power energy amplifier, CERN/AT/95-44(ET).

[3] W.E. Berry, in: Corrosion in Nuclear Applications, Wiley, New York, 1971, p. 308.

[4] G.M. Tolson, A. Taboada, A study of lead and lead-salt corrosion in thermal-convection loops, ORNL-Report TM-1437, 1966.

[5] R.C. Asher, D. Davies, S.A. Beetham, Corros. Sci. 17 (1977) 545.

[6] H. Kleykamp, H. Glasbrenner, Z. Metallkd. 88 (1997) 230.

[7] B.F. Gromov, Yu.I. Orlov, P.N. Martynov, K.D. Ivanov, V.A. Gulevski, in: H.U. Borgstedt, G. Frees (Eds.), Liquid Metal Systems, Plenum, New York, 1995, p. 339.

[8] V. Markov, Corrosion of structural materials in Pb–Bi and Pb, Seminar on the Concept of Lead-Cooled fast Reactor, Cadarache, September 22–23, 1997.

[9] N.P. Bhat, H.U. Borgstedt, in: Proceedings of the National Symposium on Electrochemistry in Nuclear Technology, Kalpakkam, India, 1994.

[10] H.U. Borgstedt, Fachtagung Gase in Metallen, DGM, Oberursel, 1984, p. 117.

[11] M.G. Barker, J.A. Lees, T. Sample, in: Proceedings of the Fouth International Conference on Liquid Metal Engineering and Technology, 1988, Avignon, France, vol. 1, p. 206.

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

[13] JANAF Thermochemical Tables.

[14] H. Ullmann, K. Teske, T. Reetz, Kernenergie 16 (1973) 291.

[15] Y.I. Orlov, personal communication at FZK Karlsruhe, Germany, July 8, 1998.

[16] I. Barin, in: Thermochemical Data of Pure Substances, VCH, Weinheim, 1989.