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Preliminary studies on PbO reduction in liquid Pb–Bi eutectic by flowing hydrogen

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Abstract

In the framework of the Italian research program TRASCO for ADS, the device ORE has been designed and operated at the ENEA C.R. Brasimone in order to study the kinetics of lead oxide reduction by flowing hydrogen, diluted at 3% by volume in argon. From the measurement of water generated by the reaction between hydrogen and lead oxide, the rate of PbO reduction was determined and a first estimation of the activation energy was found. The experimental results so far achieved in terms of reaction rate, activation energy and kinetic constant, as well as the experimental set-up and the methodology, are here summarised and discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Control of the oxygen content in molten lead–bismuth eutectic alloy is a key issue in operating a nuclear reactor of ADS family. As a matter of fact, compatibility studies performed in the past [1–4] showed that the oxygen activity in the lead–bismuth alloy strongly affects the corrosion behaviour of the structural materials. At very low oxygen content, when the oxygen activity is lower than that of the oxide formation, the corrosion dissolution regime takes place [1,2]. In this case, the technology of corrosion control by the formation of oxide protective layer cannot be adopted and suitable materials, with element characterised by a very low dissolution rate in the liquid metal, have to be used. On the contrary, when the oxygen activity reaches the value for the formation of oxide of elements in the structural materials, oxide layers start to grow up [3,4]. Also in this case, the materials to be used have to be carefully selected, because they have to contain elements whose oxides are stable against erosion. In both cases, if the material selection is not coupled with an effective oxygen control system, an unacceptable corrosion rate can occur, leading to heavy consequences.

Moreover, also the thermal hydraulics of the liquid metal can be significantly influenced by the oxygen content. As a matter of fact, when the oxygen concentration at a given temperature reaches the solubility limit at that temperature, the formation of lead oxide starts. In this case, two are the main consequences: formation of slags on the liquid metal free surface and phenomena of partial or total plugging. In case of plugging, problems in terms of reduced liquid metal flow rate and degradation of thermal exchange properties with a coolant can arise.

A technique to lower the oxygen content in liquid lead or lead–bismuth is to add hydrogen which reacts with PbO, generating water [5]. This method seems to be particularly suitable during the start-up of a plant, in order to eliminate slags and crusts normally present just after the melting of the ingots and to repair consequences after off normal events in which a significant amount of oxygen polluted the liquid metal. The characteristics of this reaction in terms of equilibrium constants and kinetics must be evaluated in order to operate correctly the conditioning of the liquid metal. In this ambit, the aim of the experimental activity here presented is to evaluate the kinetics of PbO reduction with hydrogen addition at different temperatures. The PbO

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reduction with flowing hydrogen has been studied by adding solid PbO to liquid Pb–Bi in order to get oxygen content in the liquid metal above the limit of solubility. The experiments have been carried out on the device ‘ORE’, designed and installed at the ENEA site of Brasimone. PbO reduction rate was evaluated at different temperatures and reaction rate constants were determined. On the other hand the results herein obtained refer to a solid–gas system and cannot be extended to the oxygen extraction from a Pb system with oxygen in solution and under the limit of solubility.

2. Experimental

In its basic configuration (Fig. 1), ORE consists of a cylindrical crucible in AISI 316 stainless steel containing a given amount of Pb–Bi eutectic alloy. The eutectic alloy has a Pb–55.5Bi at.% composition with a melting point as low as 125 °C. The crucible, externally heated by electric wires and thermally insulated, has an internal diameter and height respectively of 78 and 160 mm. It is supplied by Ar + H_2(3% vol.) gas mixture at a given flow rate, controlled and detected by MKS flow controller/meter. The Ar + H_2 gas stream is supplied to the liquid metal from the top of the crucible.

After reacting with the oxygen present in the liquid metal (in form of solubilised oxygen and/or lead oxide), the gas mixture, containing argon, un-reacted hydrogen and water (as reaction product) is analysed by a capacitance hygrometer type CERMET supplied by Michell Instruments. Its dew point range is -100 to $+20$ °C with an accuracy of ± 2 °C. The hydrogen content in the gas mixture downstream the crucible is detected by a thermal conductivity analyser supplied by Leeds and Northrup.

All piping and valves, made in AISI 316 L stainless steel, are electrically heated and thermally insulated. In order to reduce the water background in the system, before each test a degassing is carried out under vacuum (10^{-6} mbar) at 150 °C for 4 h.

Taking into account the stoichiometry of the reaction between PbO and H_2, as shown in Eq. (2), the lead oxide reduction rate is connected to the water molar fraction y_{H_2O} by the relationship

$$V\frac{d[PbO]}{dt} = -\Gamma y_{H_2O}, \qquad (1)$$

where Γ is the gas mass flow rate at the exit of the crucible, V is the volume of liquid metal in the crucible and y_{H_2O} is the water molar fraction as detected by the hygrometer. Integrating over the time both sides of the above equation it can be seen that the total variation of lead oxide in the liquid metal is proportional to the amount of water produced by the reaction.

Two kinds of experimental campaigns were carried out. In the first one, a significant amount of PbO (50 g) was added into the crucible, floating on 6.2 kg of Pb–Bi, and tests at 250–300–350–400 °C were performed in order to evaluate the activation energy of the reaction. In this case the amount of PbO present in the crucible can be considered as constant, taking into account the small amount of PbO reduced in each run, which was determined not larger than 0.3 g.

In the second type of experiments, small amounts of PbO were added into the crucible, also in this case floating on Pb–Bi, and tests were carried out at 400 and 450 °C in order to determine the reaction rate as a function of time and, as a consequence, as a function of PbO concentration.

3. Results and discussion

The results in terms of reaction rate as a function of temperature in the range of 250–400 °C and activation

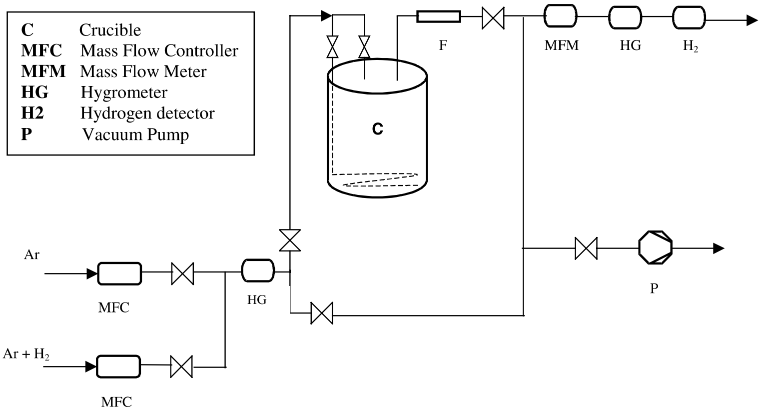

Fig. 1. Schematics of ORE device.

energy when 50 g of PbO are introduced into the crucible are shown in Fig. 2. In Table 1 the reaction rate is expressed in grams of reduced PbO per unit area and unit time. As one can clearly see, PbO reduction rate, at a fixed concentration, varies more than one order of magnitude passing from 250 to 400 °C. The exponential correlation of the reaction rate with an Arrhenius type equation is acceptable, giving the possibility to extract the activation energy of the reaction, estimated to be 67.7 kJ/mol$_{PbO}$.

The second experimental campaign was aimed at determining the kinetics of PbO reduction with hydrogen. This heterogeneous reaction can be described as

$$PbO(s) + H_2(g) \rightarrow H_2O(g) + Pb(s,l). \quad (2)$$

The kinetic equation is

$$r = k[PbO]^n[H_2]^m, \quad (3)$$

where r is the reaction rate, k the reaction rate constant, [PbO] and [H_2] the lead oxide and hydrogen concentrations respectively, n and m the order of the reaction rate with respect to the PbO and H_2 concentrations. Moreover, in the ORE experiments the H_2 concentration is exceeding that of PbO, so that a variation of the H_2 concentration is negligible and $[H_2]^m$ could be treated as a constant. In this way Eq. (3) is simplified as follows:

$$r = k_1[PbO]^n. \quad (4)$$

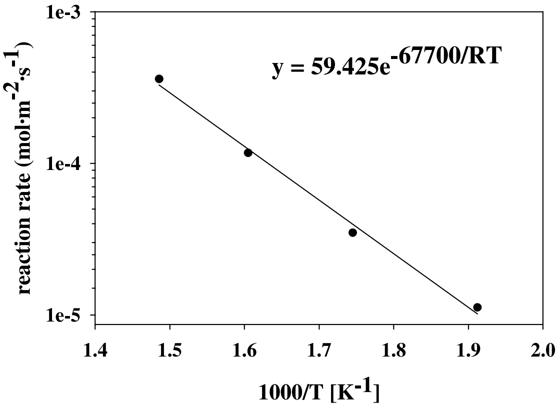

Fig. 2. PbO reduction rate as a function of temperature, 50 g of PbO in the crucible.

Table 1
Lead oxide reduction rate

Temperature (°C)	PbO reduction rate ($g\,m^{-2}\,h^{-1}$)	Activation energy
250	9	67.7 kJ/mol$_{PbO}$
300	28	
350	94	
400	288	

The experimental results were tentatively correlated with a first order model. In this case, the integration of Eq. (4) gives

$$-\ln[1 - N(H_2O)/N(PbO^0)] = k_1t, \quad (5)$$

where $N(H_2O)$ are the moles of water produced from the beginning of the experiment to time t and $N(PbO^0)$ is the initial quantity of PbO.

$N(PbO^0)$ in these tests were 6.3 and 4.3 g at 400 and 450 °C respectively. The experimental results obtained were fitted with a linear kinetic model, following Eq. (5), and are shown in Figs. 3 and 4. The quality of fitting is good and, as a consequence, these results seem to show that the reaction kinetics are of the first order with respect to PbO reactant.

The values of kinetic constants, as determined at 400 and 450 °C, are shown in Table 2. It must be pointed out that these values refer only to a hydrogen partial pressure of 30 mbar. With the value of kinetic constant found at 400 °C, the reduction rate corresponding to a PbO amount of 50 g is 271 $g\,m^{-2}\,h^{-1}$, close to the value

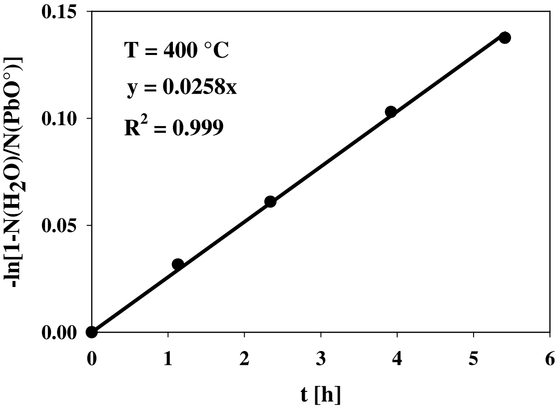

Fig. 3. PbO–H_2 reaction kinetics at 400 °C.

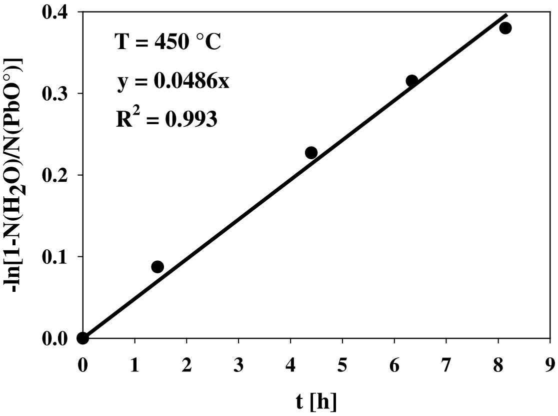

Fig. 4. PbO–H_2 reaction kinetics at 450 °C.

Table 2
Kinetic constant for PbO reduction with H_2

Temperature (°C)	Kinetic constant (h^{-1})
400	2.60×10^{-2}
450	4.86×10^{-2}

experimentally achieved in the previous test at that temperature. Moreover, the ratio of the two extraction rates obtained at 400 °C and with initial amounts of 6.3 g of PbO and 50 g of PbO respectively is close to the ratio between the two initial amounts of PbO. As a consequence, it can be reasonably supposed that an increase of the PbO amount did not correspond to an increase of reactive surface area and this last one was thus considered as the free surface directly exposed to the gas phase in the upper part of the crucible. In order to simplify the calculations, the PbO reactive surface area was approximated to the geometrical cross-section of the crucible. With regard to the results obtained it should be pointed out that the performed approximation on the reactive surface area did not affect the evaluation of the activation energy of the reaction.

The quite large activation energy determined during the first experimental campaign has a significant impact from an engineering point of view. As a matter of fact, the large increase in the PbO reduction rate with temperature suggests that, at least when diluted hydrogen is used, the operation of PbO reduction on a plant scale should be carried out at a temperature not lower than 400 °C, in order to operate with a significant reduction rate.

4. Conclusion

The compatibility study of structural materials with liquid lead–bismuth alloy showed that the oxygen activity has a strong effect on the corrosion rate of the metal and could affect the thermal hydraulics of the system. In order to reduce the total oxygen content in the liquid metal the reduction with H_2 was suggested. In ORE device the reaction of lead oxide reduction was studied in terms of activation energy and reaction order. It was shown that, maintaining constant the hydrogen concentration, the reaction rate is of the first order with respect to the PbO concentration. The activation energy of the reaction was evaluated to be 67.7 $\mathrm{kJ/mol_{PbO}}$. As a consequence of this value, it is suggested that the PbO reduction by hydrogen should be performed on plant scale at temperature not lower than 400 °C in order to operate with a significant reaction rate.

The results here reported are preliminary and further activities are foreseen to determine the order of reaction with respect to hydrogen and to confirm the activation energy in a wider temperature range.

In this work the potentiality of the hydrogen addition technique to reduce the lead oxide was demonstrated. The next step will be the evaluation of the suitability of this technique when applied to liquid lead–bismuth containing oxygen solubilised below its saturation limit.

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