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A New Method of Controlling Dissolved Oxygen in Liquid Lead-Bismuth Eutectic Systems by Electrochemical Oxygen Pumping

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ABSTRACT. *Liquid lead-bismuth eutectic (LBE) was used as coolant and spallation target in Accelerator Driven Sub-critical System(ADS). However, structural material corrosion caused by LBE is a serious problem which can lead to a system failure. Through controlling concentration of dissolved oxygen in LBE, the oxide scales can form on the surface of the material and protect the material from corrosion. At present, there are mainly two methods of oxygen control, which are gas phase oxygen control and solid phase control. Both of them have considerable disadvantages when applying to large scale nuclear systems. In this paper, the researcher fabricates an electrochemical oxygen pumping (EOP) which has been widely used in industry production in order to achieve highly accurate control of the dissolved oxygen concentration in LBE systems. In this paper, a set of electrochemical oxygen pumping is designed.*

KEYWORDS: *oxygen pumping, lead-bismuth eutectic, dissolved oxygen concentration, oxygen control system*

1. Introduction

Nuclear is becoming more and more important with the shortage of energy resources. Until now, nuclear reactor has been developed to the fourth generation. According to the The Generation IV International Forum’s latest report, the Lead-Cooled Fast Reactor (LFR) is expected to become the first commercial reactor in Generation IV advanced systems [1]. At the same time, Accelerator Driven Sub-critical System (ADS) is developed. Liquid lead-bismuth eutectic (LBE) was used as coolant and spallation target in ADS due to its good thermal-physical and chemical properties etc. [2]. However, LBE is very corrosive to structural materials, especially nickel, iron, and chromium. So it should take appropriate protective

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measures in order to prevent corrosion of the pipeline caused by LBE dissolve materials or intergranular embrittlement. Researchers have founded that oxygen concentrations in LBE influence the formation of oxide impurities and the solution of structural materials. The oxygen concentration is too high to form oxide impurities whereas to dissolve materials. Therefore, it's a research central issue in LBE fields to accurate control the oxygen concentration in a proper range.

According to earlier studies, there are mainly two methods of oxygen control, which are gas phase oxygen control ($Ar/H_2/O_2$, $Ar/H_2/H_2O$) and solid phase control (PbO) [3-5]. Both of them have disadvantages when applying to nuclear system. The former could release gaseous radioactive waste or explore. The latter need to replenish PbO particles timely which is inconvenient. Besides those, J. Lim have put forward a new method to control oxygen concentration in LBE by electrochemical oxygen pumping (EOP) which was tested in 500mL stagnant LBE. He had found that highly accurate control of the oxygen concentration by EOP was feasible [6].

In this paper, the researcher design a new electrochemical oxygen pumping which is more suitable for large scale flowing LBE. and it will be applied in the LBE container (ϕ360mm, 360mm in height) of the oxygen control system at Beijing key laboratory of passive safety technology for nuclear energy of North China Electric Power University (NCEPU) in Figure 1.

Figure. 1 The oxygen control system at NCEPU

2. Theory

To prevent structural material from corrosion and formation of oxide, it should give a proper range of dissolved oxygen. There is a main chemical equilibrium in LBE:

$$\frac{1}{4}Fe_3O_{4(s)} + Pb \Leftrightarrow \frac{3}{4}Fe_{(Pb)} + PbO_{(Pb)} \tag{1}$$

Investigation results show two factors considered about oxygen concentration [7]:

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1) The upper limit of dissolved oxygen is no oxide in LBE;

2) The lower limit of dissolved oxygen is forming an oxide film on the surface of the material.

2.1 The upper limit of dissolved oxygen

According to IPPE research, the solubility of main elements in LBE can describe as [8]:

$$\log C_{o,\max} = A_1 + \frac{B_1}{T/K} \tag{2}$$

The value of *A1* and B_1 for main elements are tabulated in Table 1.

Table 1 Experimental data of sensor measurement accuracy

Cs (wt %)	Ni	Fe	Cr	O
A_1	1.53	2.01	-0.02	1.2
B_1	-843	-4380	-2280	-3400

According to (2) and Table 1, relationship between solubility and temperature is:

$$\log C_{s,o}[wt\%] = 1.2 - \frac{3400}{T/K} \tag{3}$$

Where, $C_{s,o}$ is saturated oxygen concentration of LBE and T is temperature.

The variation trends of dissolved oxygen and solubility of metals are consistent in LBE. The concentration of oxygen increased as the temperature increases. When dissolved oxygen is saturated, there will form PbO in LBE. It means there is more easier to get PbO oxide at low temperature in the loop when dissolved oxygen concentration is same.

In practical LBE loop, the value of saturated oxygen concentration is not always same because the LBE loop is non-isothermal. Therefore, the upper limit of dissolved oxygen is saturated oxygen concentration at the lowest temperature of LBE loop.

2.2 The lower limit of dissolved oxygen

Researches have found that the formation of oxide is decided by the Gibbs free energy. It is more easier to form oxide when the free energy is low. According to 'The Oxide Handbook', the free energy of formation data is tabulated in Table 2 [9]. The relationship between the temperature and the free energy can be expressed as:

$$\Delta G^0 = C_1 + D_1 T \tag{4}$$

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According to (4) and Table 2, the relationship is shown in Figure 2.

Some researches show that the main protective oxide on the structural material surface is Fe_3O_4. Therefore, the lower limit of dissolved oxygen is forming a Fe_3O_4 oxide film on the surface of the material. Now the dissolve oxygen concentration can be described as [3]:

$$\log C_{o,\min}[wt\%] = -\frac{3}{4}\log C_{Fe}[wt\%] + 1.2375 - \frac{9757}{T/K} \tag{5}$$

Table 2 Free energy data

ΔG⁰(J/mol)	Bi_2O_3	PbO	Fe_3O_4
C_1	-582070	-220670	-1108300
D_1	282.0	101.0	313.3

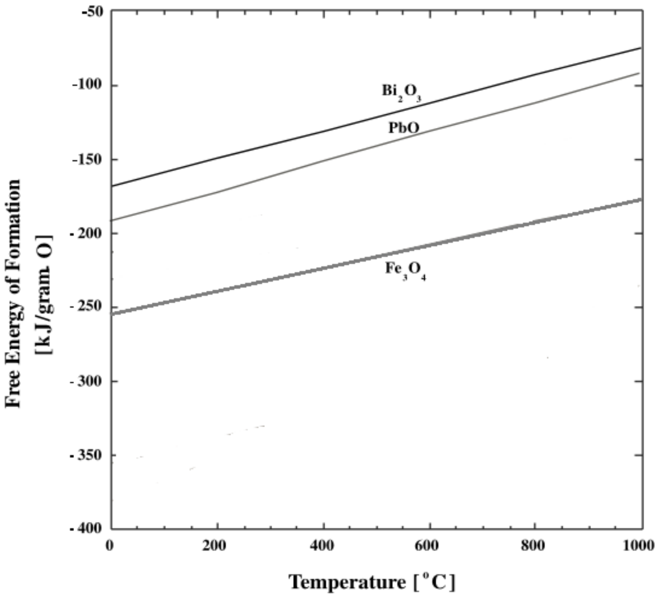

Figure. 1 The free energy of formation for various species in LBE

It can be seen that if Fe_3O_4 is formed at the high temperature of the LBE loop, there must have Fe_3O_4 film on the surface of the material everywhere. Therefore, the lower limit of dissolved oxygen is saturated oxygen concentration at the highest temperature of LBE loop.

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3. Work pinciple

Based on fundamental of electrochemistry, the EOP was made of a cathode and a solid electrolyte using yttria stabilized zirconia (YSZ). The whole oxygen control system includes the EOP, an oxygen sensor and a DC current source shown in Figure 3. The concentration of dissolved oxygen in LBE is controlled by giving an externally applied electrical potential to DC current source. The oxygen sensor measures the current oxygen concentration in the LBE. Then the system calculates the saturated oxygen concentration according to the data measured by the thermal couple. Use a PID controller with feedback from the oxygen sensor to adjust the current oxygen concentration to saturation. The solid electrolyte YSZ is totally passable for oxygen ions at high temperatures. By adjusting the direction and the size of externally applied electrical potential, the EOP control the addition of the oxygen ions into or the removal of the oxygen from the LBE shown in Figure 4. According to the reference, the oxygen flux J_o is proportional to the current I [6]:

$$J_O = t_e \frac{I}{4F} \tag{6}$$

Where, t_e is the ionic transport number of the solid electrolyte and F is the Faraday constant. In this oxygen control system, there has the Nernst potential V_N generated by the difference of chemical potential of oxygen. It should be lower than the applied electric potential V to avoid the decomposition of the solid electrolyte [10]. Therefore, the oxygen flux J_o is:

$$J_O = \mathrm{t_e} \frac{(V - V_N)}{4FR} \tag{7}$$

Where, R is total resistance.

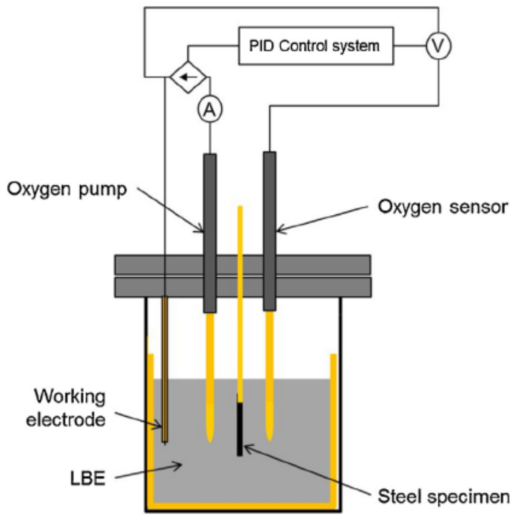

Figure. 2 The oxygen control system [6]

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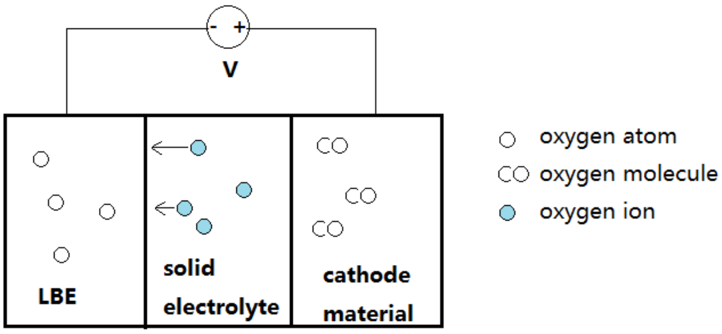

Figure. 3 Working principle of the EOP

4. Design

The researcher design an EOP which is suitable for LBE container at NCEPU. The left picture of Figure 5 shows the 3D model of the EOP. The EOP concludes joint, mental shell, steel cage, and spring and YSZ tube. All parts are made of 316L stainless steel, except YSZ tube. The connection mode of the EOP is shown in the right picture of Figure 6 where omits the spring.

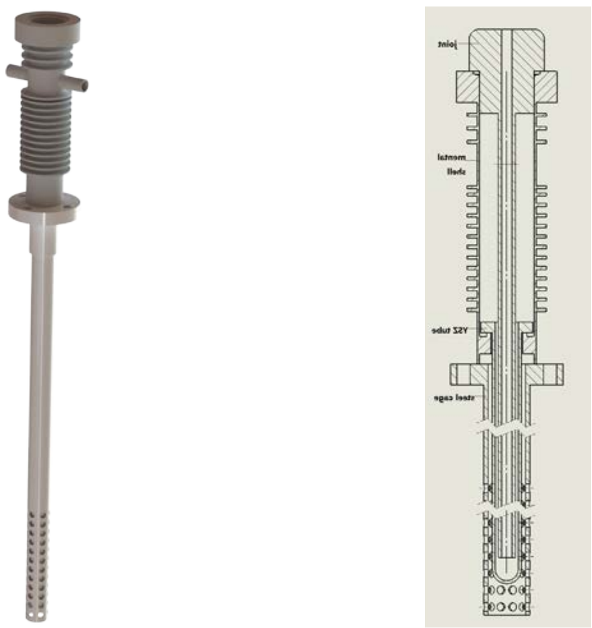

Figure. 4 The 3D model and the connection mode of the EOP

It do not require high air-tightness for the upper half part of the EOP. Therefore, weld the metal shell and the steel cage. The joint and the mental shell are connected by the internal thread. There is a boss in the mental shell which is sealed with YSZ tube by a O sealing ring. The spring give a axial pressure to the YSZ tube to prevent the outer oxygen from leaking into the LBE. Also, it is convenient to replace the YSZ tube when it rupture. The steel cage decreases the vibration of the YSZ tube at a high speed and prevent YSZ fragments from blocking the coolant loop when YSZ tube rupture. The hole on the steel cage make the LBE and the YSZ tube outer wall surface sufficient contact. An SS304 wire is connected to the cathode. The outer air or oxygen get into the YSZ tube and then flow through the annual space. That make it have full contact with three-phase boundary of air/oxygen, electrolyte and cathode material. The cathode material usually uses LSM (strontium doped lanthanum mangaite)-GDC (gadolinium doped ceria) or Pt. Studies have found that cathode used LSM-GDC had high accuracy and could be used in lower temperature [11].

In this design, the outer diameter and the inner diameter of the YSZ tube is 14 mm and 11 mm, respectively. The active area is 10.7 cm2.

5. Conclusion

Compared with gas phase oxygen control and solid phase control, the EOP is a simple and clean way to control the oxygen concentration. In this paper, the researcher aim to design a EOP suitable for large scale flowing LBE. It will use LSM-GDC/Air and Pt/Air as cathode material. In latter experiment, we still need to debug the experiment device to achieve high control accuracy.

Acknowledgements

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