



# Electrochemical impedance spectroscopy on in-situ analysis of oxide layer formation in liquid metal



M. Kondo<sup>a,\*</sup>, N. Suzuki<sup>a</sup>, Y. Nakajima<sup>a</sup>, T. Tanaka<sup>b</sup>, T. Muroga<sup>b</sup>

<sup>a</sup> Department of Nuclear Engineering, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka-shi, Kanagawa 259-1292, Japan

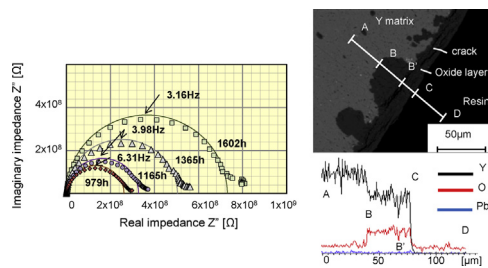
<sup>b</sup> National Institute for Fusion Science, Toki, Gifu 502-5292, Japan

## HIGHLIGHTS

- The electrical properties and the thickness of lead oxide layer formed in liquid Pb were obtained by electrochemical impedance spectroscopy (EIS).
- The Fe oxide, Cr oxide and Fe–Cr oxide formed on the electrodes in liquid Pb were not detected by EIS due to their small electrical resistance.
- The formation and the growth of Y oxide formed in liquid Pb was detected by EIS.

## GRAPHICAL ABSTRACT

Some test materials (i.e. Fe, Cr, Y and JLF-1 steel) were immersed to liquid metal lead (Pb) mainly at 773 K as the working electrode of electrochemical impedance spectroscopy (EIS). Some oxide layers formed on the electrodes in liquid Pb were analyzed by EIS. The impedance response was summarized as semicircular Nyquist plot, and the electrical properties and the thickness of the oxide layers were evaluated in non-destructive manner. Large impedance due to the formation of Y oxide formed in liquid Pb was detected by EIS, though impedance of Fe oxide and Cr oxide could not be detected due to their small electro resistance. The time constant of the oxide layers was evaluated from the impedance information, and this value identified the types of oxides. The change of the time constant with the immersion time indicated the change of the electrical properties determined by the chemical composition and the crystal structure. The thickness of the oxide layer estimated by EIS agreed well with that evaluated by metallurgical analysis. The growth of Y oxide layer in the liquid Pb was successfully detected by EIS in non-destructive manner.



## ARTICLE INFO

### Article history:

Received 14 September 2013  
 Received in revised form 11 April 2014  
 Accepted 16 April 2014  
 Available online 15 May 2014

### Keywords:

Liquid blanket  
 Corrosion  
 Lead lithium alloy  
 Electrochemical impedance spectroscopy  
 Functional layer

## ABSTRACT

Some test materials (i.e. Fe, Cr, Y and JLF-1 steel) were immersed to liquid metal lead (Pb) mainly at 773 K as the working electrode of electrochemical impedance spectroscopy (EIS). Some oxide layers formed on the electrodes in liquid Pb were analyzed by EIS. The impedance response was summarized as Nyquist plot, and the electrical properties and the thickness of the oxide layers were evaluated in non-destructive manner. Large impedance due to the formation of Pb oxide and Y oxide in liquid Pb was successfully detected by EIS, though impedance of Fe oxide and Cr oxide could not be detected due to their small electro resistance. The time constant of the oxide layers was evaluated from the impedance information, and this value identified the types of oxides. The change of the time constant with the immersion time indicated the change of the electrical properties determined by the chemical composition and the crystal structure. The thickness of the oxide layer estimated by EIS agreed well with that evaluated by metallurgical analysis.

© 2014 Elsevier B.V. All rights reserved.

\* Corresponding author. Tel.: +81 463 58 1211.

E-mail address: [kondo.masatoshi@tokai-u.jp](mailto:kondo.masatoshi@tokai-u.jp) (M. Kondo).

## 1. Introduction

Liquid breeders such as lithium (Li) and lead lithium alloy (Pb–17Li) have the potential for high performance blankets. Liquid metals such as lead (Pb), tin (Sn) and gallium (Ga) are considered as a coolant of liquid diverter.

The application of functional layers such as  $Y_2O_3$  and  $Er_2O_3$  for the loop piping is necessary to suppress the tritium leaks and the pressure drop of MHD flow in the blanket system [1]. The fabrication of these functional layers was based on two methods. One is the fabrication of the ceramic coating on the tube wall by means of MOD [2] or MOCVD [3] method before the exposure. The other is the in situ formation due to the oxidation of some metals plated or added to the steel. The plating of erbium metal to RAFM steel was carried out [4] for formation of  $Er_2O_3$  layer by the oxidation in liquid breeders [5]. The metal such as aluminum (Al) added as the steel composition contributed to the formation of Al rich compact oxide layer in liquid metal [6]. These layers have a function of self-healing in the liquid metals, and enable a longer-term use in fusion blanket system. The corrosion reactions caused on the surface of these ceramic coatings and the oxides in the liquid metals were reported in the previous studies [7–10]. Then, just the corrosion analysis of the specimen surface after the exposure to the liquid metals does not make clear the corrosion process in detail. The electrical property of the oxide layers formed on some materials in the liquid Pb–Bi was analyzed by an electrochemical impedance spectroscopy (EIS) [11,12]. The EIS method must be feasible technique to follow the formation of the functional oxide layer and the degradation of ceramic coating in liquid metals. The EIS is a non-destructive way to figure out the change of the electrical properties and the thickness of the functional layer in liquid metals. However, the information on the performance of the EIS in the liquid metals is limited.

In the present study, a series of EIS experiments was performed in the liquid metal system. Liquid lead (Pb) saturated with oxygen was used to form various oxides in the melt. The electrical properties of the oxide layers formed in the liquid metal were evaluated by EIS. The purpose is to investigate the potential of the EIS method in the liquid metal system.

## 2. Experimental condition

Fig. 1 shows the experimental apparatus. 300 g of liquid Pb was placed in the crucible made of  $Al_2O_3$ . The temperature condition was controlled by the thermocouple placed at the bottom part of the test container and the heater wound around the container. The cover gas in the container was air. Table 1 presents the experimental conditions. The test materials are Fe, Cr, Y and JLF-1 steel. The purity of the Fe, Cr and Y specimens is 99.9%. Reduced activation ferritic martensitic (RAFM) steels are the candidate structural material. The chemical composition of the RAFM steel JLF-1 (JOYO-HEAT) is 9Cr–1.94W–0.09C–0.49Mn–0.2V–Fe balance [13]. The specimens were cleaned with acetone before the exposure. These surfaces were not mechanically polished, and some initial oxides must be on their surface. The specimens were oxidized under air atmosphere during the heating process before the immersion to the liquid Pb. The oxide scales of  $(Fe, Cr)_2O_3$  could be presented on the RAFM steel before the immersion [14]. The thickness of the oxide scales initially formed on the Fe and Cr specimen in air condition could be several nanometers [15]. The variation of the test temperature in Table 1 was due to the evaluation of the temperature dependence on the impedance response of some oxide layers formed in liquid Pb.

The oxygen potential in liquid Pb was not measured by solid electrolyte sensors [16]. The presence of oxide particles on a free

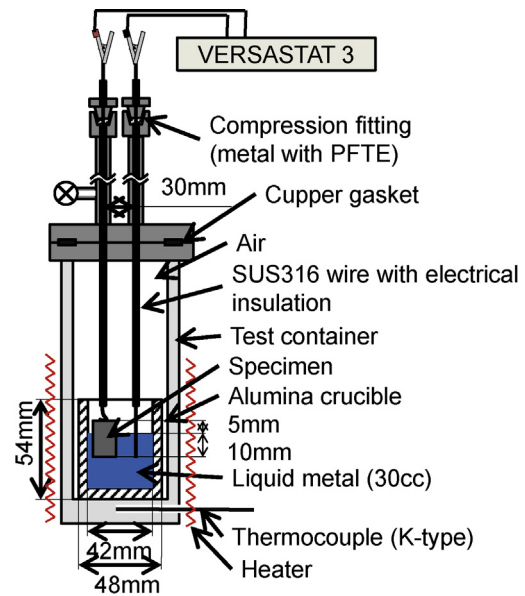


Fig. 1. Experimental apparatus.

surface of liquid Pb before and after the exposure was checked by visual inspection. The cover gas was air, and oxygen was sufficiently fed to liquid Pb from the cover gas. Then, these facts indicated the oxygen saturation in liquid Pb was kept during the experiment. Then, the equilibrium oxygen potential in liquid Pb is expressed as



The oxygen concentration saturated in liquid Pb was estimated as  $3 \times 10^{-5}$  wt% at 648 K [17]. The oxygen potential in the present work is equal to the equilibrium potential of PbO formation. Fig. 2 shows Gibbs free energy for formation of the relating oxides. The oxides placed in the region surrounded by solid line in Fig. 2 are chemically stable. These oxide layers are formed and growing on their substrate. The specimens of Fe, Cr and RAFM steel can be easily oxidized. On the contrary, the oxygen potential in liquid breeders Li and Pb–17Li was quite low. Then, limited types of oxides can be stable in the liquid breeders. The aluminum oxide ( $Al_2O_3$ ) is

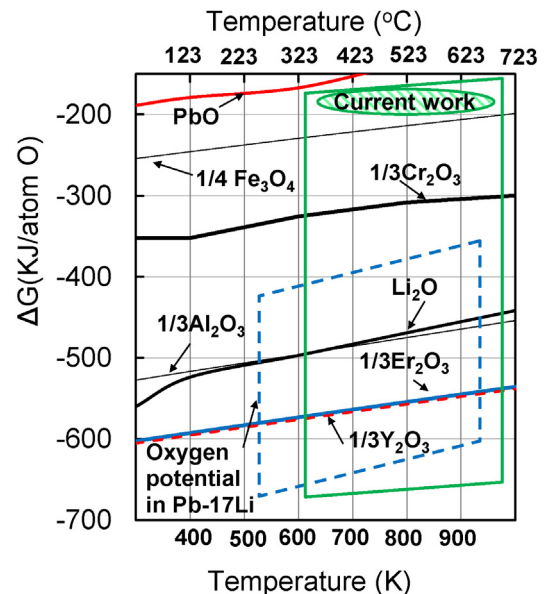


Fig. 2. Gibbs free energy for formation of relating oxides and oxygen potential in liquid metal.

Download English Version:

<https://daneshyari.com/en/article/271205>

Download Persian Version:

<https://daneshyari.com/article/271205>

[Daneshyari.com](https://daneshyari.com)