§8. Study on Online-measurement of Hydrogen (Isotope) Transport in Molten Flinak by Solid Electrolyte Sensor

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Molten salt LiF-BeF_2 (Flibe) is a candidate of tritium breeding materials for fusion blankets. Molten salt LiF-NaF-KF (Flinak) has potential to be used as a liquid breeder and simulant fluid because of the similar thermofluid and chemical characteristics to Flibe. Control of tritium is one of the key issues for the molten-salt blankets. For this purpose, on-line monitoring of hydrogen (isotope) transport is the essential technology.

The application of hydrogen sensor made of proton conductive solid electrolyte ceramics to the measurement hydrogen (isotopes) in liquid blanket has been studied by the authors. The Palladium (Pd) membrane electrodes of the sensor that worked as protection layer for the ceramics in corrosive condition were developed by the authors. The purpose of this study is to investigate the hydrogen transport characteristics in Flinak using the hydrogen sensor made of proton conducting solid electrolyte. The hydrogen sensor used cap-shaped $CaZr_{0.9}In_{0.1}O_{3-a}$ as solid electrolyte ceramics. The outer and inner electrodes were used Pd membrane. The solid electrolyte ceramics was fixed Al_2O_3 tube by low melting glass seal. Pt wire was wound around the electrode of the measurement side. The grassy carbon was used as the armor for the protection of sensor tip from Flinak. The tip of the armor had a hole of 2mm diameter. The armor was fixed to Al_2O_3 tube with low melting glass. The structure of sensor is shown in Fig. 1(a).

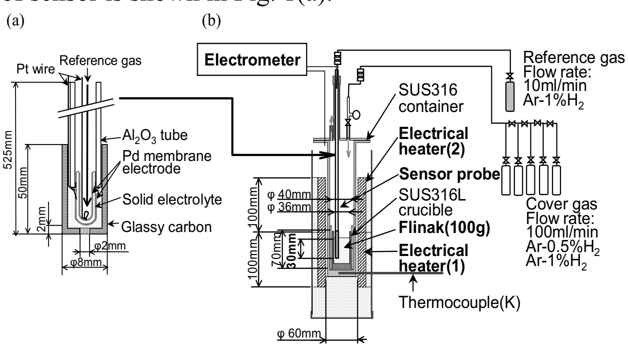

Fig. 1 (a) the structure of sensor, (b) experimental apparatus for sensor test in Flinak

The experiment apparatus for the Flinak is shown in Fig. 1(b). The crucible was filled with 100g of Flinak. The electrical heaters (1) and (2) were used to control the temperature of Flinak near the bottom and free surface, respectively. The container of the apparatus was filled with high purity Ar.

The sensor was immersed in Flinak to the depth of 30mm from the free surface. After the sensor immersion, the gases of Ar-1%H_2 or Ar-0.5%H_2 were filled in the container. The electromotive force (EMF) of the sensor was measured at the temperature between 514°C-667°C. In this system, there were two interface of gas-liquid equilibrium for the hydrogen transport. The one interface was the free surface of Flinak, which was used for the hydrogen control of the Flinak. The other interface was at the sensor tip, which was used for the measurement of hydrogen partial pressure.

The results of test in Flinak at isothermal condition made by heaters (1) and (2) are shown in Fig. 2 with the mark of open squares and open circles.

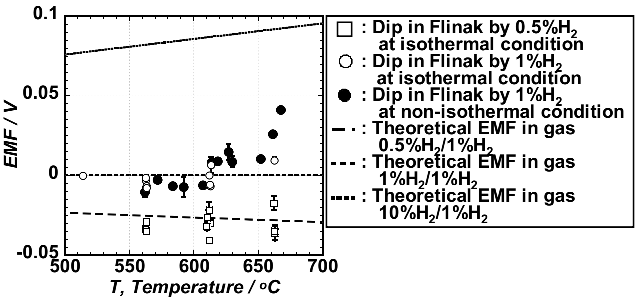

Fig. 2 EMF of hydrogen sensor in Flinak at isothermal and non-isothermal conditions

The sensor showed stable output in the Flinak at the temperature. The EMF signals agreed with the theoretical value given by Nernst's equation though there was error within 10mV from the theoretical value.

$$\mathbf{E}_{\mathbf{theory}} = \frac{\mathbf{RT}}{\mathbf{2F}} \ln\left(\frac{\mathbf{P}_{\mathbf{H_2},\mathbf{measurement}}}{\mathbf{P}_{\mathbf{H_2},\mathbf{reference}}}\right) \qquad (1)$$

here, R is gas constant, T is temperature K, F is Faraday constant, PH_2 is hydrogen partial pressure of measure side and reference side.

The results of test in Flinak at non-isothermal condition made only by heater (1) are shown in Fig. 2 with the mark of close circles. The sensor showed the temperature dependence of EMF output. The difference between theoretical and experimental EMF was indicated. The large difference in EMF between experiment and theory is considered focusing on the temperature dependence of hydrogen solubility. Fukada et al. reported that the dissolution of hydrogen as molecule, and the equilibrium state was expressed as Henry's law[1].

The EMF of experiment was written as

$$E_{experiment} = \frac{RT}{2F} \ln\left(\frac{K_{surface}}{K_{sensor}} \frac{P_{H_2,surface}}{P_{H_2,reference}}\right) \qquad (2)$$

here, K is Henry's constant at gas-liquid boundary. Henry's constant has a temperature dependence. The EMF of experiment depends on Henry's constant when there is thermal difference between the free surface and the sensor tip. Hydrogen solubility in the Flinak was lower at higher temperature.

Major conclusions are follows,

(1) The hydrogen sensor showed stable output on Flinak when the hydrogen concentration was controlled by the gas-liquid equilibrium for hydrogen transport at isothermal condition.

(2) The hydrogen sensor showed EMF largely different from theoretically estimated EMF when there was temperature difference between the free surface and immersed sensor part in Flinak. Hydrogen solubility in the Flinak was lower at higher temperature.

1) Fukada, S. et al. : J. Nucl. Mater. **358**, 235 (2006)