Measurements of Henry's Law Constant for Hydrogen in Simulated PWR Primary Water

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1. Introduction

In pressurized water reactors (PWRs), the primary water contains dissolved hydrogen to maintain the reducing conditions [1]. This is necessary because oxidizing environment can cause general corrosion of primary structural materials. The dissolved hydrogen concentration in PWRs has been controlled in a range of 25~50 cc (STP)/kg-H_2O, though less than 15 cc (STP)/kg-H_2O is necessary to prevent an oxidizing condition. However, recent reports indicate that increasing the hydrogen concentration in primary water reduces primary water stress corrosion cracking (PWSCC) of alloy 600 components and thus operation above 50 cc (STP)/Kg-H_2O is considered to minimize PWSCC [1,2]. During operation, the hydrogen concentrations are controlled by varying a volume control tank (VCT) hydrogen overpressure. However, as the primary water flows from the VCT into the RCS, the temperature, system pressure, and solution chemistry in the RCS can affect the hydrogen concentration. Therefore, the accurate measurement and monitoring of hydrogen partial pressure which governs corrosion potential of alloy 600 in high temperature primary water are needed to ensure the merit of PWSCC reduction by increasing the hydrogen concentration.

In the present work, the in situ hydrogen partial pressures were measured by using Pd-Ag cell in the simulated high temperature primary water condition (2 ppm Li and 1200 ppm B) and effects of the temperature and pressure on the hydrogen partial pressure were determined.

2. Methods

Tests were conducted in demineralized high-purity water (18 ㏁·㎝) containing 2 ppm Li and 1200 ppm B. A feed tank solution was deaerated with high-purity (99.999%) hydrogen gas to obtain a low level of dissolved oxygen (> 5 ppb). The concentration of the hydrogen gas in the solution was controlled at the feed tank by varying the hydrogen overpressure and by calculations using Henry's law [3]. For this test, 35 cc (STP)/kg-H_2O of dissolved hydrogen was applied.

In situ measurements of the hydrogen partial pressure were performed using a hydrogen sensor installed in the simulated primary water test loop, as shown in Fig. 1. The sensor, equipped in an autoclave, consists of a Pd-25% Ag tube with a 3.2 mm external diameter and a thickness of 0.43 mm. The inside of the tube is reinforced with a spring type of Inconel wire to prevent the collapse of the tube from 210 bar of external pressure in the autoclave. One end of the tube is sealed with an Inconel plug and the other end is brazed with gold to a 316 SS tube connected to an external low-pressure gauge and a vacuum pump.

Measurements of the partial pressure of the hydrogen were performed at different internal autoclave pressures (2000, 2200, 2600, and 2900 psig) and temperatures (290, 300, 310, 320, and 330℃). The hydrogen partial pressures were measured after 48 h at each testing temperature, as the internal hydrogen pressure of the sensor reached at equilibrium with the external pressure in water after 4~12 h at each tested temperature [2].

Fig. 1. Photograph of the simulated primary water test loop.

3. Results and Discussion

Fig. 2 shows the results of measured hydrogen partial pressures in the 2 ppm Li and 1200 ppm B solutions as a function of the temperature and pressure. As the temperature increases, the values of the hydrogen partial pressure decrease due to the high solubility of hydrogen. The concentrations of hydrogen in the solutions decreased with an increase in the internal autoclave pressure. This indicates that the hydrogen solubility is affected more by the internal autoclave pressure at a high temperature.

Henry's coefficients for the dissolved hydrogen in the Li and B solutions were calculated from the measured values of the hydrogen partial pressure. Fig. 3 presents the constants according to Henry's Law. With an increase in the temperature, these constants decrease, indicating an increase in the hydrogen solubility in the solution. As the system pressure increases, the Henry's

coefficients increase. These trends are similar to those reported by several researchers in the temperature range of 290~330℃ [2-5]. Giraudeau et al. reported that the solution chemistry affects the Henry's Law constants [6]. However, Lee et al. reported that the measured data of the hydrogen partial pressure was not strongly dependent on the solution chemistries [2]. The temperature, system pressure, and solution chemistry must be considered to predict the equilibrium hydrogen partial pressure during the operation of a reactor coolant system.
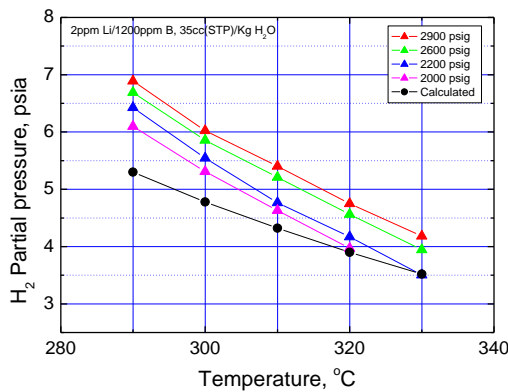

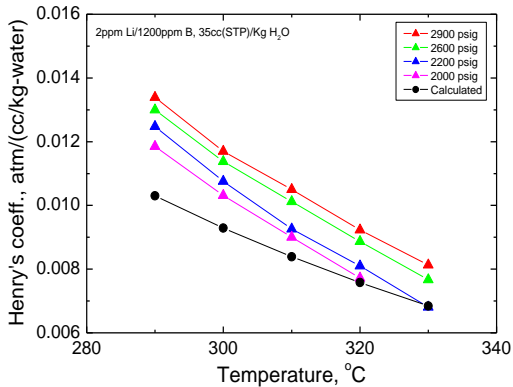Fig. 2. Equilibrium hydrogen partial pressures in solutions containing 2 ppm Li and 1200 ppm B.

Fig. 3. Henry's Law constant as a function of the temperature and pressure.

4. Conclusions

The values of the hydrogen partial pressure were measured using a Pd-Ag cell in the 2ppm Li and 1200ppm B solutions within the temperature and pressure ranges of 290~330℃ and 2000~2900 psig, respectively. The solubility of hydrogen in the solutions was largely affected by solution pressure. Also, the solubility of hydrogen decreased with an increase in the temperature.

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