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Henry's Law Constant for Hydrogen in Li/H_3BO_3 solution using a Pd-Ag Sensor

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1. Introduction

In pressurized water reactors (PWRs), hydrogen is added to the reactor coolant system (RCS) in order to reduce the oxidation of water by radiolysis and to maintain reducing conditions [1]. The dissolved hydrogen concentration in PWRs has been controlled within the range of 25~50cc (STP)/kg-H_2O [1]. It is well known that the dissolved hydrogen leads to primary water stress corrosion cracking (PWSCC), general corrosion of the primary structural materials, higher radiation fields, and deposit build up on the fuel rods in PWRs [2]. Therefore, the optimization of the hydrogen concentration in the RCS is regarded as one of several effective approaches to manage the material integrity and reduction of the radiation sources in the primary circuit [3]. During PWR operation, the hydrogen concentrations are controlled by varying hydrogen over pressures of a volume control tank (VCT). 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. In order to predict the content of the hydrogen partial pressure which affects the structural materials, it is needed to measure and monitor the hydrogen partial pressure accurately.

In this paper, we fabricated a Pd-25wt.%Ag alloy hydrogen sensor to measure hydrogen partial pressures directly at high temperatures and high pressures. From the measured data, we determined the Henry's constants for various fields' applications.

2. Methods

The schematic diagram of a hydrogen gas sensor is shown in Fig. 1. The fabrication of the hydrogen sensor has been described previously [3]. The permeating hydrogen from the solution through the Pd-Ag tube wall was measured by an external low-pressure gauge and a vacuum pump.

A test loop was designed and fabricated [3]. The hydrogen sensor was mounted in the autoclave with temperature control to ± 0.5℃ precision. Test solution of 100 ℓ was prepared by additions of nuclear-grade 2 ppm of Li (added as LiOH) and 1200 ppm of B (added as H_3BO_3) into purified water. For these tests, 35 cc (STP)/kg-H_2O of hydrogen gas was applied to the feed tank and the measured oxygen concentration was less than 1 ppb during tests. In situ measurements of the hydrogen partial pressure were conducted using the hydrogen sensor at different system pressures (2000, 2200, 2600, and 2900 psia) and temperatures (290, 300, 310, 320, and 330℃). The measured data were used to determine Henry's constants at temperatures and at pressures [4].

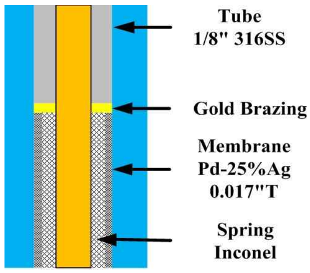

Fig. 1. Schematic diagram of the Pd-Ag hydrogen sensor.

3. Results and discussion

The hydrogen partial pressures were measured 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. The hydrogen partial pressure in the solutions increased with an increase in the internal autoclave pressure. This indicates that the hydrogen solubility was affected by the pressure as well as temperature.

Fig. 2 shows the Henry's constants determined in the literature and in this paper. As the temperature increased, as shown in Fig. 2, the values of the Henry's constants decreased. This is because the concentration of hydrogen in the solution decreased with an increase in the internal autoclave temperature. As the system pressure increased, the Henry's constants increased indicating an increase in the hydrogen solubility in the solution. These trends were similar to those reported by several researchers in the literature [3]. From the data in Fig. 2, experimentally determined the Henry's constants at high temperatures and at high pressures were quite deviate from the values calculated from the Himmelblau's theoretical equations [4]. Himmelblau has studied only the effect of temperature on hydrogen solubility. However, the effect of pressure on the hydrogen solubility cannot be disregarded when the solubility of the hydrogen is measured at high pressures, as shown in Fig. 2. In this paper, the measured Henry's constants were in close agreement with those of Lee et al.'s at high pressure, 2900 psia, and at temperature ranges of 290℃ to 310℃. The deviation at high temperatures may be due to the uncertainty of experimental measurements. However, the deviation at pressures of 2600, 2200, 2000 psia presents that the hydrogen partial pressure in the solution depends on the system pressure. From the experimental data, both of the temperature and pressure must be considered to predict the Henry's constants.

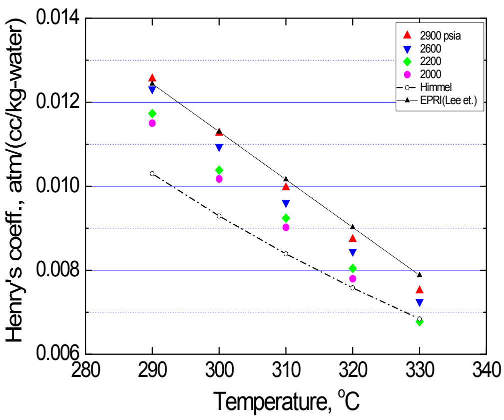

Fig. 2. Henry's Law constant as a function of the temperature and pressure.

3. Conclusions

The hydrogen partial pressures were measured using a Pd-Ag hydrogen sensor in the 2 ppm Li and 1200 ppm B solution within the temperature and pressure ranges of 290~330℃ and 2000~2900 psia, respectively. The Henry's constants were determined from the measured data. The Henry's constants increased with a decreasing temperature and with an increasing temperature. The pressure as well as temperature affected the hydrogen partial pressure in the solution.

Acknowledgements

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