Hydrogen Permeation Measurement Of Iron And Its Oxide Membranes By Using A Dew Point Hygrometer

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Introduction- Oxide scale, which forms inside the boiler tubes in fossil-fuel fired power plant, contains many voids. The hydrogen may dissolve into the oxide scale from water vapor and affects the scale growth, microstructure and void formation. For quantitatively discussing the effect of water vapor on the high temperature steam oxidation of the ferritic steel, it is important to measure the hydrogen permeability, diffusivity and solubility in the iron oxide scale. However, few attempts have been made to measure the hydrogen permeation in the oxide scales[1,2]. In this study, hydrogen permeability of iron and its oxide membranes will be measured at the temperature range from 823 K to 1073 K by using a chilled mirror dew point hygrometer.

Experimental- Iron membranes (15 x 15 mm^2 in size, thickness: 50 and 100 □m) were used for the hydrogen permeation measurements. Figure 1 shows a schematic illustration of the experimental apparatus. Ar-20%H_2 gas was flowed in hydrogen provided side of the membrane and Ar gas (dew point : less than 223 K) was flowed in hydrogen detected side. Flow rate of the gas at the each sides were 2.5×10^{-6} m^{3}s^{-1} and 5×10^{-7} m^{3}s^{-1}, respectively. Iron membrane and ceramics cylindrical tubes were sealed by Pyrex glass rings (□ : 15 mm, thickness : 3 mm). The iron membrane heated up with the rate of 5 K/min, and held at 1073 K, and then temperature was changed to measurement temperatures (823-1073 K). Permeating hydrogen was flowed into the hydrogen combustion furnace and was perfectly converted to water vapor by Ar-21%O_2 gas with Pt catalysis. Partial pressure of water vapor in the gas stream was measured continuously by chilled mirror dew point hygrometer to determine the hydrogen permeation rate. After the measurement of hydrogen permeation of the iron membrane, Ar gas, which was flowed in the hydrogen detected side, changed to Ar-21%O_2 gas in order to form the iron oxide scale on the one side of the iron membrane. Dew point was continuously measured during the oxidation of the iron membrane. After the hydrogen permeation measurements, oxide scale was identified by an X-ray diffraction and its thickness was measured by a scanning electron microscopy to determine parabolic rate constant.

Results and Discussion- Figure 2 shows the flux of hydrogen as a function of oxidation time at 1073 K. Before the oxidant gas (Ar-21%O_2) reached to the dew-point hygrometer, the flux of hydrogen was constant. Hydrogen permeation of the iron membrane at 1073 K was determined to 8.6×10^{-10} molm^{-1}s^{-1}Pa$^{-1/2}$. After the oxidant gas had reached to the dew point hygrometer, the flux of hydrogen was gradually decreased.

Once the oxide scale formed on the hydrogen detected side of the membrane, rate-determining step changes diffusion in the iron membrane to diffusion in the oxide scale. Permeation rate of hydrogen decreases with the growth of the oxide scale. In this study, permeation rate of hydrogen was calculated by using hydrogen permeability and parabolic rate constant of growing scale. The measurement data compared with the calculation to determine the hydrogen permeability in the oxide scale. Hydrogen permeability of the oxide scale was assumed to linear function of the hydrogen permeability of the iron membrane measured in this study ($K_{scale}=\square K_{Fe}$ [□<1]).

Figure 3 shows the temperature dependence of the hydrogen permeation of the iron and its oxide membranes. Hydrogen permeation of the iron membrane was in good agreement with the previous reports [e.g. 3,4]. Hydrogen permeability of the oxide scale which mainly consists of Fe$_3$O$_4$ was determined to 1.6×10^{-12} molm^{-1}s^{-1}Pa$^{-1/2}$ at 823 K and hydrogen permeability of the oxide scale which mainly consists of wustite was 4.3×10^{-11} molm^{-1}s^{-1}Pa$^{-1/2}$ at 1073 K. It is concluded that hydrogen permeation of the iron oxide scale is one to two order of magnitude smaller than that of the iron. Kurokawa et al.[5] measured the hydrogen permeability of Cr$_2$O$_3$ at 1073 K by using dew point hygrometer. Hydrogen permeation of Cr$_2$O$_3$ is more three orders of magnitudes smaller than that of the iron oxide.

References

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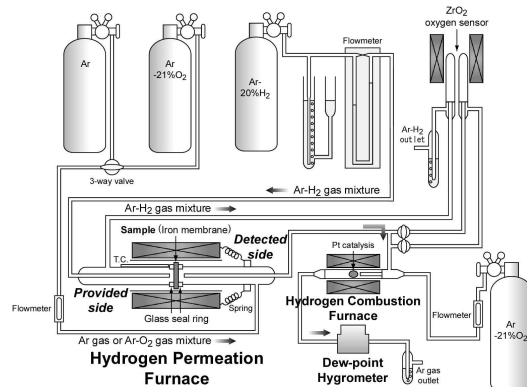
Figure 1 Schematic illustration of the experimental apparatus for the hydrogen permeation measurements.

(t = 0 ks) The oxidant gas reached to the hygrometer.
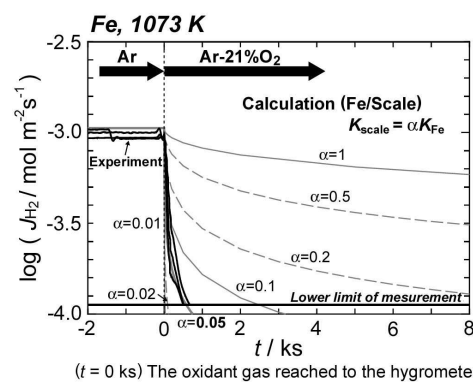
Figure 2
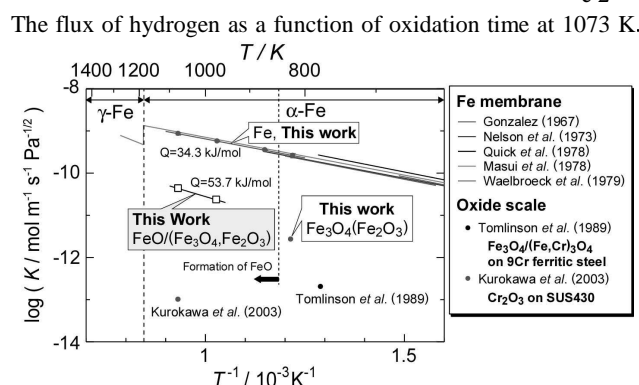The flux of hydrogen as a function of oxidation time at 1073 K.

Figure 3 Temperature dependence of the hydrogen permeation of the iron and its oxide membranes.