Analysis of hydriding and dehydriding modeling characteristics in metal hydrides

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1. Introduction

The energy crisis is more aggravating in the present age than in past times, and many countries are developing next-generation energy sources. Among the next-generation energy sources, nuclear fusion energy is a concern for many countries, and common international research has been conducted. The sources of nuclear fusion reaction are deuterium (D) and tritium (T). Generally, D is fused into T, which generates helium atoms and neutrons. At this time, a tremendous amount of energy is generated [7].

$$D + T \rightarrow {}^{4}He + n \ (E = 17.6\ MeV) \qquad (1)$$

Hydrogen is a gas, and cannot be stored in large amounts. In addition, it can be explosive. Therefore, one of the storing methods for hydrogen is metal hydride. In this research, several kinds of metal hydrides [1-8], including U, Zr, ZrCo, ZrNi, and $LaNi_5$ have been simulated through modeling work of hydrogen absorption, desorption, and pressure effect in a bed using DU. For the hydriding and dehydriding process in a metal hydride bed, the driving force is the difference between the gas pressure in the bed and the equilibrium pressure between the metal hydride and hydrogen.

2. Methods and Results

1. Model assumptions.

For a simplified analysis, several hypotheses were stated for modeling.

- Hydrogen gas is an ideal gas.
- Physical properties of hydrogen follow the ideal gas law.
- The specific heat, thermal conductivity, and density of DU are constants.
- The pressure of the bed entrance is the same as the tank pressure, i.e., the pressure drop in a tube is negligible.
- Hydrogen gas flow is laminar.

2. The governing equation and generation terms.

The following equations are generally used to express the mass transfer phenomena [4]

- The mass balance for the gas phase.

$$\emptyset \frac{\partial \rho_g}{\partial t} + \nabla\left(\overrightarrow{V_g} \cdot \rho_g\right) = -\dot{m} \qquad (2)$$

- The mass balance for the solid phase.

$$(1-\emptyset)\rho_{s,o} \frac{\partial Y}{\partial t} = \left(\frac{M_{Me}}{M_H}\right)\dot{m} \qquad (3)$$

where the value of $\overrightarrow{V_g}$ is obtained from the following Kozeny-Carman equation [6].

$$V_g = -\frac{K}{\nu} \cdot \nabla P, \quad K = \frac{D_p^2 \cdot \emptyset}{180(1-\emptyset)^2} \qquad (4)$$

where D_p is the diameter of a particle, K is the permeability, ϕ is the porosity, and ν is the kinematic viscosity.

In equation (5), $\dot{m}$ can be expressed as the following equations [5].

- During absorption:

$$\dot{m} = C_{a,o}\exp\left(-\frac{E_a}{RT}\right)\ln\left(\frac{P_g}{P_e}\right)(\rho_{ss} - \rho_s) \qquad (5)$$

- During desorption:

$$\dot{m} = C_d\exp\left(-\frac{E_d}{RT}\right)\left(\frac{P_e - P_g}{P_e}\right)\rho_s \qquad (6)$$

where E_a and E_d are the activation energies of the hydriding and dehydriding, respectively, and C_a and C_d are the rate constants of hydriding and dehydriding. R is the universal gas constant, T is the absolute temperature, P_g is the present gas pressure, P_e is the equilibrium gas pressure, $\rho_{s,o}$ is the density of DU before hydriding or dehydriding, and ρ_s is the density of the metal hydride.

3. Temperature effect.

In the hydriding process by a metal hydride, the temperature effect is expressed by Arrhenius's law, as indicated in the following equation.

$$k = k_o\exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

where k_o is the rate constant regardless of the temperature and pressure, E_a is the activation energy of the hydriding reaction, R is a gas constant, and T is the absolute temperature.

The hydriding process by metal hydride is very sensible to temperature because the temperature affects the rate constant directly, and is indirectly related to the gas pressure. Generally, the hydriding rate is faster at high temperature than at room temperature. The activation energy (E_a) and R are constants, and thus the reaction rate depends on the temperature (Fig. 1).

4. Pressure effect.

With the reaction temperature, the gas pressure of the bed is also an important variable. The difference between the bed pressure and equilibrium pressure is a driving force of the hydriding process. In addition, it is difficult to analyze for exact modeling. Because metal

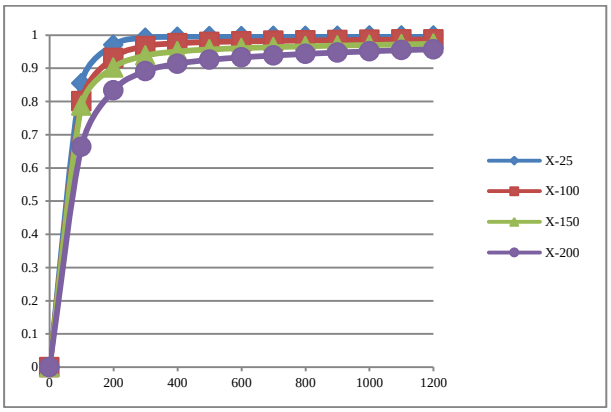

Fig. 1. Temperature effect of hydriding process by metal hydride

hydride is expanded through the hydriding process, and in our system the hydrogen is transferred from the tank to the bed through a pipe, for an exact computation, the pressures of the bed and tank, and that absorbed by the metal hydride, are wholly calculated. In addition, the pressure effect term varies according to the metal hydride [5].

If the rate-limiting step is hydrogen diffusion, the pressure effect is expressed through the following equation:

- Absorption : $K(P) = 1 - \left(\frac{P_e}{P}\right)^{1/2}$
- Desorption : $K(P) = 1 - \left(\frac{P}{P_e}\right)^{1/2}$

For adsorption as a rate-limiting-step, physisorption of the H_2 molecules relies linearly on the hydrogen pressure.

- Absorption: $K(P) = P - P_{eq}$
- Desorption: $K(P) = P_{eq} - P$

For phase transformation as a rate-limiting step, K(P) is related to the logarithm of the ratio between hydrogen pressure and equilibrium pressure.

- Absorption : $K(P) = \ln\left(\frac{P}{P_e}\right)$
- Desorption : $K(P) = \ln\left(\frac{P_e}{P}\right)$

Last, using a semi-empirical method through normalization, the pressure effect is expressed through the following equation:

- Absorption: $K(P) = \left(\frac{P-P_e}{P_e}\right)$
- Desorption: $K(P) = \left(\frac{P_e-P}{P_e}\right)$

Generally, in the case of absorption, the phase transformation pressure effect has the greatest fit, and the semi-empirical normalization has the highest fit of desorption in the DU modeling.

3. Conclusions

The temperature effect of the hydriding/dehydriding process by metal hydride is expressed as Arrhenius' law. In the hydriding process, the hydriding rate is the fastest at room temperature, and the temperature rises more and more, rate speed is slower step by step. k_o is a rate constant regardless of the temperature and pressure, and thus is a parameter of the activation energy.

The pressure effect is varies for different kinds of metal hydride species. It is reason to rate-limiting step is different for metal hydride. The rate-limiting step is divided greatly 3 stages: diffusion, physisorption, and phase transformation. In general, rate-limiting step of absorption is phase transformation, but in case of desorption, pressure effect is analyzed by semi-empirical normalization method. However, the pressure effect is expressed in various forms, and thus it must be decided prudently.

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