Self-Annealing in ZrCo Degradation during Hydriding & De-hydriding Reaction

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1. Introduction

Regeneration of the disproportionated ZrCo due to the formation of thermally stable components, ZrH_2 and $ZrCo_2$, from the ZrCo hydride at a certain high temperature range is the key factor to sustain a long life performance in cycling of hydriding and de-hydriding of the metallic hydrogen storage system, especially for ZrCo material [1,2]. In thermal annealing a deactivated ZrCo hydride material is known to reproduce its performance, however, the rate of regeneration is not explained in detail as well as the importance for real application [2,3]. In this paper a sequential elementary reactions for hydriding and dehydriding of the ZrCo system was assumed to estimate the deactivation rate, thereafter, a self-annealing rate in the regeneration step was introduced to correlate the overall reaction scheme.

2. Metal Hydride Reaction Model and Results

Disproportionation in the ZrCo hydride under high temperature system is shown in Fig. 1, in which two literature data are combined [4,5]. A certain amount of increase of the residual hydrogen in ZrCo metal is accompanied by reduction of hydrogen storage capacity at high temperature range [2].
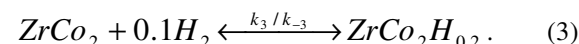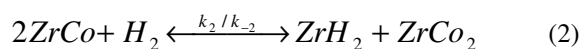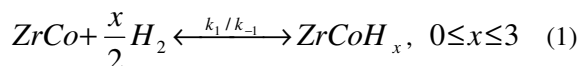
2.1 Self-Annealing Reaction

In Fig. 1 the small symbols from Hara et al.'s [4] show rather a moderate deactivation than the larger symbols from Besserer's [5], since the reaction mode is different in two cases. However, the temperature effect is obviously shown in both of data that, at first, the deactivation rate is increasing faster in higher reaction temperature (Besserer and Hara); at second, the inverse rate occurs in more than 600°C (Hara). This inverse rate of deactivation is assumed to cause by the self-annealing effect. Therefore, the reaction of the ZrCo hydride system is considered to have complexity by some of sequential reactions.

2.2 Model Equations

2.2.1 Elementary Reaction Equation

The elementary reaction representing the hydriding & dehydriding of ZrCo with hydrogen in a certain temperature and pressure system is shown by the following chemical sequence [1,2,4]:

$$ZrCo + \frac{x}{2}H_2 \xleftrightarrow{k_1/k_{-1}} ZrCoH_x, \quad 0 \le x \le 3 \quad (1)$$

$$2ZrCo + H_2 \xleftrightarrow{k_2/k_{-2}} ZrH_2 + ZrCo_2 \quad (2)$$

$$ZrCo_2 + 0.1H_2 \xleftrightarrow{k_3/k_{-3}} ZrCo_2H_{0.2}. \quad (3)$$

Where

$ZrCo$ = zirconium cobalt, intermetallic compound

H_x = hydride (in x ratio)

ZrH_2 = zirconium hydride (deactivated form)

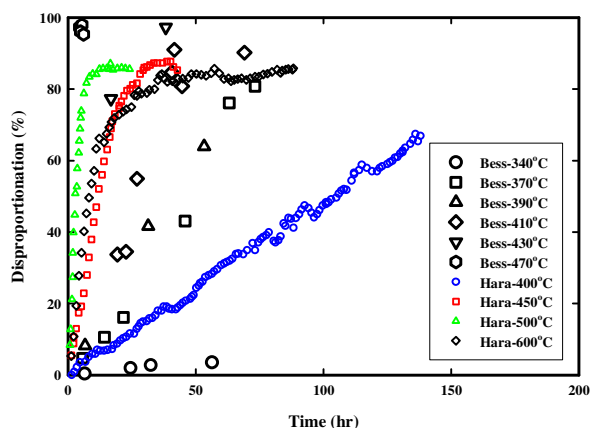k = coefficient of reaction kinetics.

Fig. 1. Disproportionation of ZrCo hydride (%) vs. time at different temperature conditions [4,5].

Reaction step (2) is a major consideration for the regeneration in the above sequence reactions. Reaction step (1) is a normal operating reaction scheme and reaction step (3) is a final capability of the hydride system to breathe hydrogen gas in and out of the metal hydride system—hydriding and dehydriding in the worst case. Combining of reaction step (2) and (3), the rate controlling step for the disproportionation is expected to describe the ZrCo hydriding system. The reverse step of reaction step (2) might be considered as a regeneration scheme. Fig. 1 shows that the ratio of the reaction kinetics coefficient in Reaction step (2) has the following criteria:

$$k_2/k_{-2} >> 1, \text{ at } T < 350^o C$$

$$k_2/k_{-2} << 1, \text{ at } T > 500^o C.$$

2.2.2 Calculation Approaches for Self-Annealing

In considering of the self-annealing rate the overall proposed reaction mechanism can be applied at first with only one empirical value (% of disproportionation). This approach is useful in the calculation, even though several complex parameters in the overall sequence reactions must be determined.

In a strict observation of the above reversible consecutive reaction the disproportionation reaction is simply assumed to follow the irreversible reaction steps:

$$A \xrightarrow{\nu_1} B \quad \text{and} \quad A \xrightarrow{\nu_2} C. \tag{4}$$
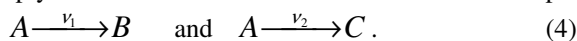
Where
A, B, C = ZrCo, ZrH$_2$ and ZrCo$_2$H$_x$, respectively.

Integration form of the disproportionation rate equation, dB/dt, becomes

$$\frac{C_B + C_C}{C_{A_0}} \times (100) = \alpha_1 (1 - e^{-\nu_1 t}) + \alpha_2 (1 - e^{-\nu_2 t}). \tag{5}$$

Where $(C_B + C_C)/C_{A_0}) \times (100)$ is the percentage of disproportionation (%) in Fig. 1, α_1 and α_2 are weight factors related to the simultaneous reaction in Eq. (4). The rate determining step in Eq. (4) is assumed to be a representing equation for the overall reaction:

$$\frac{C_B + C_C}{C_{A_0}} \times (100) = \beta_1 - \beta_2 e^{-\nu_1 t}. \tag{6}$$

Where β_1 and β_2 are constants in Eq. (6). ν_1 is simply noted by the Arrhenius equation ($= \nu_0 e^{-E/RT}$). In the combined form of disproportionation equation, however, the activation energy term in the exponential, $(-E/RT)$, is not simply described by the straight line.

Another way to simulate the complex form of the metallic hydriding and dehydriding reaction is to be considered as a combination of first-order reactions [6].

2.3 Calculation Results in Simplified Model

Solving of simplified Eq. (6) that implies both of deactivation and regeneration during heat treating in the ZrCo hydride system including self-annealing is shown in Fig. 2, and temperature dependency of ν_1 is shown in Fig. 3 by means of the reciprocal term of temperature versus logarithm of ν_1. Three parameters in Eq. (6) were estimated to correlate the Hara's data. The function of $\nu_1(T)$ in Fig. 3 is assumed to have a hyperbolic shape.

3. Conclusions

In regeneration of the disproportionated ZrCo hydride self annealing was introduced by means of a simplified irreversible model, having three parameters, to shorten the whole complex deactivation model of the ZrCo in

hydriding and dehydriding cycles. Temperature dependency of the rate constant, however, has a hyperbolic shape in this model.
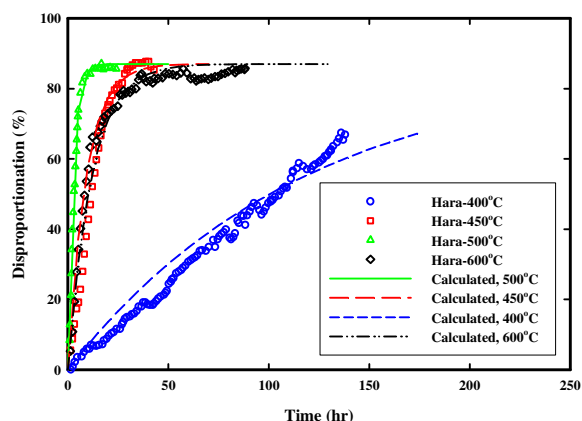

Fig. 2. Calculation result with the simple model of Eq. (6) for the disproportionation of ZrCo hydride vs. time at different temperature conditions (Comparison with Hara's data).
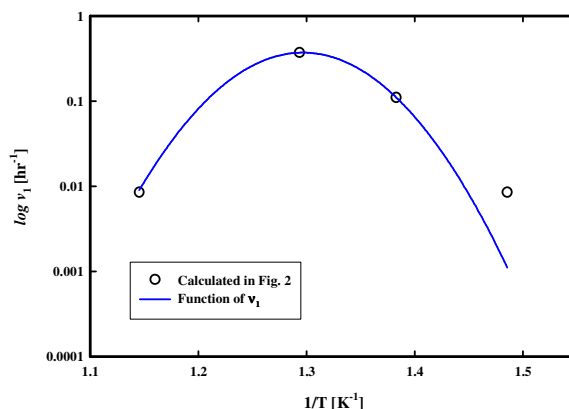

Fig. 3. Combined form of disproportionation and regeneration in the plot of $\log \nu_1$ vs. $1/T$ using Eq. (6) for the ZrCo hydride reaction system (in Fig. 2).

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