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Hydriding–dehydriding reactions of $LaNi_{4.7}Al_{0.3}$–H system under quasi-isothermal conditions

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Abstract

Using a highly heat-sensitive reactor, the average temperature deviations were kept within ±0.1 °C of a set temperature during hydriding and dehydriding reactions of metal hydrides. The reaction kinetics of the $LaNi_{4.7}Al_{0.3}$–H system were measured in this reactor by a stepwise method in the temperature range 313.2–443.2 K. Experimental data obtained under quasi-isothermal conditions are presented.

1. Introduction

Reproducibility of experimental hydriding and dehydriding rate data has not been obtained in the past because of the difficulty in eliminating thermal effects [1-3].

In the study of reaction kinetics, considerable efforts have been made to eliminate thermal effects by improving the heat transmission characteristics of the reactor system [4–6], by decreasing the quantity of the sample [7, 8] and by using thermal ballasts [9–12]. Of these methods, thermal ballasting seems to be the most promising and thermal effects have been significantly reduced. Goodell and Rudman [9] have used mixtures of $LaNi_5$ hydride with Ni powder and have succeeded in attaining semi-isothermal conditions ($\Delta T = 12$ °C) with 98 wt.% Ni powder. With a large weight fraction of thermal ballast, the temperature rise has been reduced to within 2 °C [13] in a mixed system of 0.8 g of Mg_2Ni with 36.5 g Ni (98 wt.%) in a copper tube reactor.

The ballasting method significantly reduces thermal effects but the high weight fraction of the ballasting material may cause other experimental difficulties. The ballasts can restrict gas flow, reduce measurement sensitivity, adsorb hydrogen, etc. The catalytic effect of transition elements, such as Ni, cannot be ignored. Schlapbach *et al.* [14] have reported that metallic Ni acts as a catalyst for the dissociation of hydrogen at the beginning of the hydriding process.

In addition, to perform kinetics measurements at higher temperatures, it has been customary to use a reactor in temperature-controlled oil, molten-salt or air baths. In such cases, these heat-exchanging media maintained at high temperatures cannot release the abrupt temperature changes in the metal hydride (MH) bed. However, the reactor developed in this work is suitable for high-temperature conditions.

A highly heat-sensitive reactor system has been designed to minimize thermal effects [15]. Heat transfer in the MH bed is greatly improved. Temperature changes in the MH bed are compensated by introducing high-pressure CO_2 gas into the reactor heat exchanger during the hydriding reaction and by introducing pre-heated N_2 gas during the dehydriding reaction. The flow rate of heat exchanging media is controlled by a PID controller. Temperature deviation from the set value is successfully kept constant within ±0.1 °C without introducing any extra experimental errors.

The aim of this work is to measure the hydriding–dehydriding reaction kinetics over a wide temperature range under quasi-isothermal conditions, and to evaluate the kinetic parameters based on the consistent kinetic data. The sample used in this work was $LaNi_{4.7}Al_{0.3}$.

2. Experimental details

Experiments were performed under isochoric and variable pressure conditions using a stepwise method in a highly heat-sensitive reactor.

Figure 1 shows the details of the configuration of the reactor where the dimensions are in millimetres. Detailed descriptions have been given in ref. 15. In the reactor, two round-shaped thin spaces of 0.76 ml with 0.5 mm clearance were used as the sample port

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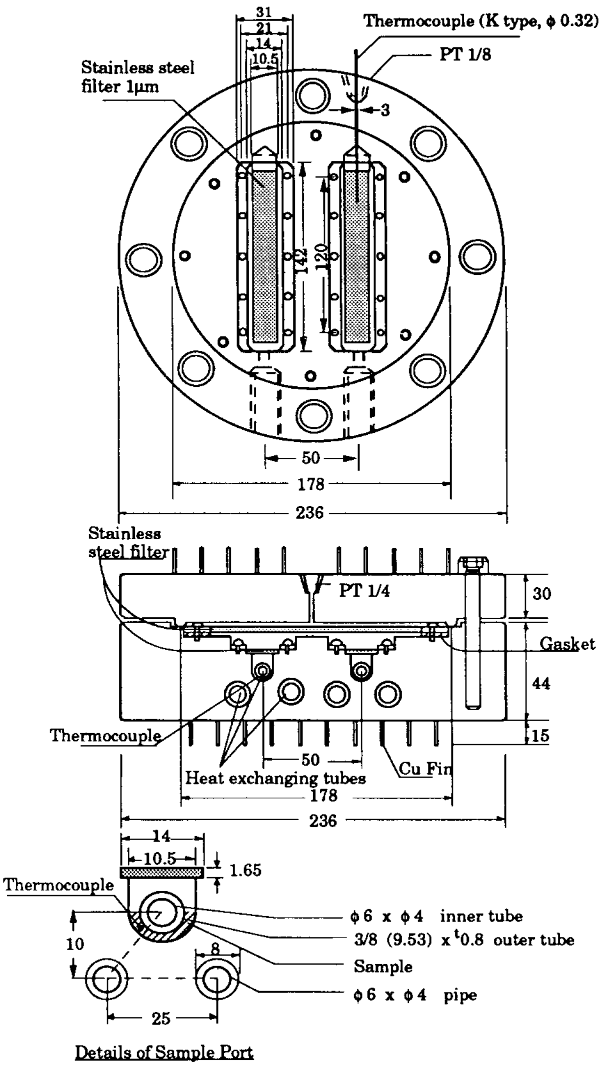

Fig. 1. Details of the highly heat-sensitive reactor (dimensions are in millimetres).

to hold the granular particles. To maintain uniform sample distribution, the particles were only placed in the lower part of the round-shaped space. The temperature of the reacting bed was continuously measured during the reaction by a sheathed CA thermocouple of 0.3 mm in diameter which was inserted directly into the sample layer. As the reactor was precisely designed, it was sufficient to insert one thermocouple into one of the MH beds.

The stepwise method employs step-by-step changes in the hydrogen concentration, H/M, by controlling the hydrogen pressure exerted on the experimental system. The experimental procedure for measuring the hydriding reaction kinetics by a stepwise method is illustrated in Fig. 2. The hydriding reaction proceeds linearly from P_0 to P_f in each run, where C_0 (C=H/M) refers to the hydrogen concentration at the point where the reaction was started and P_0 is the initial pressure. P and C are the hydrogen pressure and concentration at a given reaction time. P_f and C_f are the final equilibrium pressure and concentration respectively. The concentration C_f in turn becomes the next starting concentration. Each experimental run can be continued by changing the pressure in the gas reservoir to higher than the equilibrium pressure of the previous run. The reaction can be started or terminated at any desired level of hydrogen concentration in the α, $\alpha+\beta$ or β phase regions by adjusting the pressure level in the gas supply system.

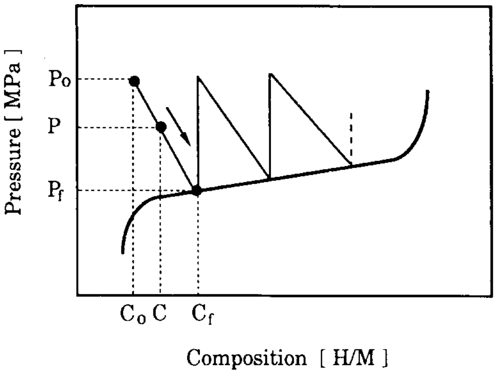

Fig. 2. Schematic diagram showing the stepwise method for measuring hydriding reaction kinetics.

The experimental procedure for the dehydriding reaction is the reverse of the hydriding reaction.

Temperature changes in the MH bed were controlled by introducing CO_2 gas at 3.4 MPa into the hydriding chamber during hydriding and introducing pre-heated N_2 gas at 1.0 MPa during dehydriding. A pneumatically operated flow rate regulator (Fujikin SR 100) was set on the pipe line to control the flow rate of the heat-exchanging medium. The change in temperature detected by a thermocouple was transferred to the PID controller to actuate the regulator. The larger the deviation of the temperature of the reacting bed, the higher the flow rate of the heat-exchanging medium.

$LaNi_{4.7}Al_{0.3}$ (10.0 g) was placed in the sample space with 0.5 mm thickness between the outer surface of the centre tube and the inner surface of the reactor body. Experimental data were taken after repeating more than 60 hydriding–dehydriding cycles. The changes in pressure were measured using a data acquisition system (Hewlett–Packard 3052A) with an electric pressure transducer (model PLC) every 0.5 s for a period of 2.5 min. Temperature changes in the MH bed were measured by the same system with a 0.3 mm CA thermocouple.

3. Results and discussion

3.1. Temperature deviations

For the hydriding reaction, experiments were performed at several initial hydrogen pressures and hydrogen concentrations. Figure 3 illustrates the results obtained at 333.2 K. The temperature deviation from the set value was successfully kept within ±0.1 °C except for a few seconds at the very beginning of the reaction.

Typical dehydriding results obtained at 333.2 K are illustrated in Fig. 3. As with the hydriding reaction, the temperature deviation from the set value was successfully maintained within ±0.1 °C except for the initial few seconds.

From the above experiments, it can be seen that by using a stepwise method with a heat-sensitive reactor, the temperature of the MH bed can be maintained constant and very close to isothermal conditions for both hydriding and dehydriding reactions. Although the abrupt temperature changes were not completely eliminated at the initial part of the reaction, the experiments are believed to have been performed under conditions close to constant temperature, *i.e.* quasi-isothermal conditions. The temperature itself is controllable by this method, but this system is not isothermal because heat and work are transferred across the boundary of the reactor [16]. We define such an isothermal condition as "quasi-isothermal" from the thermodynamic point of view.

3.2. Reactions under quasi-isothermal conditions

In the hydriding and dehydriding processes, several steps can be considered as rate controlling. During the progress of a reaction, the rate-controlling step may be changed at the phase transition when the reaction proceeds from one phase region to another [17, 18]. For example, in the hydriding reaction, four possible rate-controlling steps can be considered: the gas film control process, the surface process, the hydrogen diffusion process and the phase transformation process. Rate equations corresponding to each rate-controlling step for both hydriding and dehydriding reactions have been derived [17–19]. Since the rate-controlling step for both hydriding and dehydriding reactions in the $\alpha+\beta$ phase region has been determined as the phase transformation process [17, 18], the rate equations corresponding to this process are used for data analysis.

Hydriding reaction

$$dc/dt = k_h(P/P_{eh})^a[1-(P_f/P)^a(C/C_f)^b] \tag{1}$$

$$k_h = A\ e^{-E_h/RT}$$

Dehydriding reaction

$$dc/dt = k_d(C^b/P_{ed}{}^a)[1-(C_f/C)^b(P/P_f)^a] \tag{2}$$

$$k_d = A'\ e^{-E_d/RT}$$

where the constants k_h and k_d are the rate constants, a and b are the reaction orders, P is the hydrogen pressure at a given time, P_f is the final equilibrium pressure, P_e is the plateau pressure and C and C_f are the hydrogen concentrations, H/M, at a given reaction time and at the final equilibrium condition.

Data obtained under quasi-isothermal conditions were characterized by the above rate equations. In the case of the hydriding reaction, the reaction orders a and b were determined to be 2 and 1 by fitting the hydriding rate equation to the experimental data. Data obtained at 333.2 K for the hydriding reaction are illustrated in Fig. 4, where the reaction rates were plotted as a function of $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$ at various initial pressures and concentrations. Excellent linearity was obtained, whereas it was hard to obtain a linear relation using a conventional reactor (see ref. 15). Experiments under other quasi-isothermal conditions are shown in Fig. 5. The rate constants were found to remain constant regardless of the change in concentration and pressure within the two-phase region.

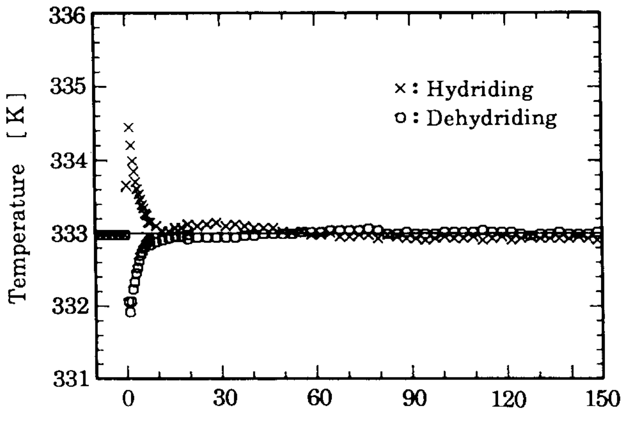

Fig. 3. Temperature deviations during hydriding and dehydriding reactions at 333.2 K.

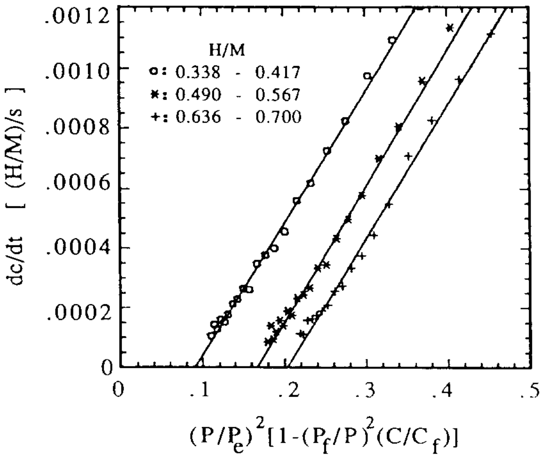

Fig. 4. Hydriding reaction rates *vs.* $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$ as a function of hydrogen concentration in the highly heat-sensitive reactor.

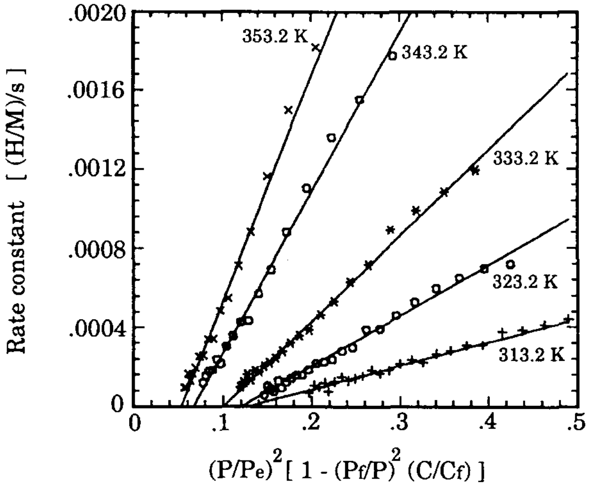

Fig. 5. Hydriding reaction rates vs. $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$ at different temperatures in the highly heat-sensitive reactor.

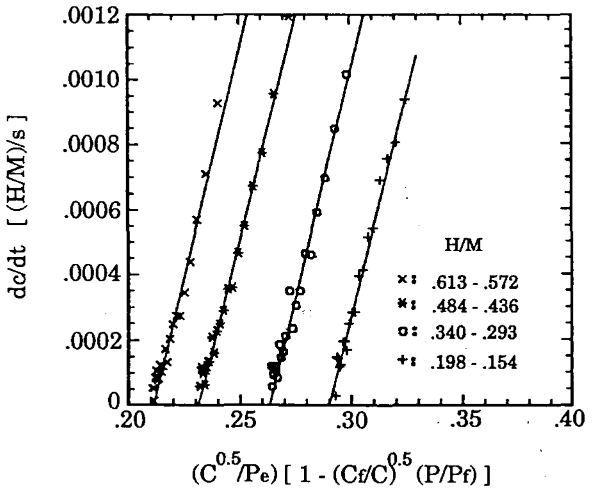

Fig. 6. Dehydriding reaction rates vs. $(C^{0.5}/P_e)[1-(C_f/C)^{0.5}(P/P_f)]$ as a function of hydrogen concentration at 333.2 K in the highly heat-sensitive reactor.

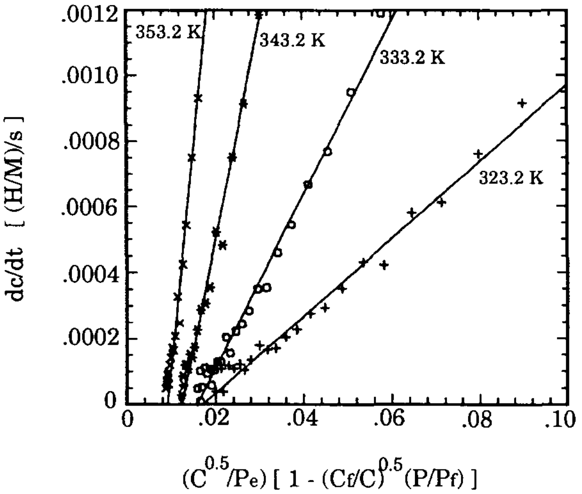

Fig. 7. Dehydriding reaction rates vs. $(C^{0.5}/P_e)[1-(C_f/C)^{0.5}(P/P_f)]$ at different temperatures in the highly heat-sensitive reactor.

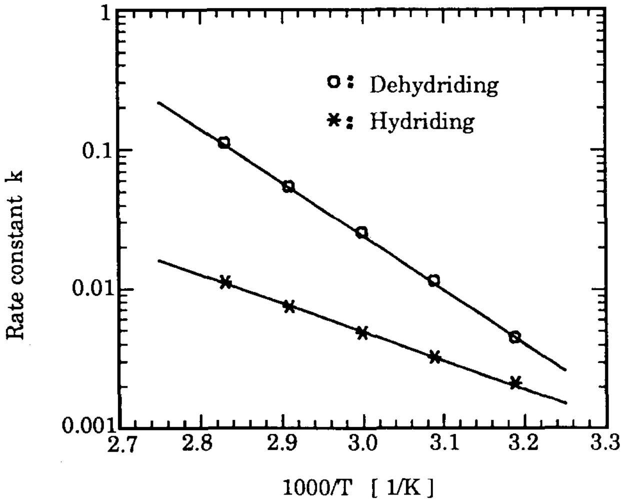

Fig. 8. Arrhenius plots of hydriding and dehydriding reactions in the $\alpha+\beta$ phase region under quasi-isothermal conditions.

In the dehydriding reaction, the results obtained at 333.2 K in the $\alpha+\beta$ phase region are illustrated in Fig. 6. By fitting eqn. (2) to the experimental data, the reaction orders a and b were evaluated to be 1.0 and 0.5 respectively. Excellent linear relationships were obtained in the plots of dc/dt against $(C^{0.5}P_e)[1-(P/P_f)(C_f/C)^{0.5}]$. Figure 7 is an illustration of the linearity in the temperature range 313.2–353.2 K where the reaction was initiated at 0.5 H/M and terminated at 0.4 H/M.

The rate constants obtained for both hydriding and dehydriding reactions are independent of pressure and concentration in the $\alpha+\beta$ phase region. This observation may indicate that a single rate-controlling step exists in this phase region. There are three different phase regions in general in a metal hydride. The kinetic characteristics may be different for each phase region. The rate constants and reaction orders should be constant regardless of the pressure and concentration under isothermal conditions if there is no change in mechanism [17, 18]. In this study, experiments were performed only in the $\alpha+\beta$ phase region and therefore the rate constants obtained at different levels of pressure and concentration remained constant.

From studies of the hydriding [17] and dehydriding [18] reactions of $LaNi_{4.7}Al_{0.3}$–H, the rate-controlling step for the hydriding reaction in the $\alpha+\beta$ phase region is considered to be the nucleation and growth of the β hydride phase; in the dehydriding reaction, the rate-controlling step is the decomposition of hydride in the $\alpha+\beta$ phase region.

Figure 8 shows the Arrhenius plots of the rate constants against $1/T$ for both hydriding and dehydriding reactions. The activation energies of the hydriding and dehydriding reactions in the $\alpha+\beta$ phase region were determined to be 39.2 and 83.5 kJ (mol H_2)$^{-1}$ respectively.

Comparison with the results obtained in other studies (activation energies for the hydriding and dehydriding reactions were estimated to be 36.8 kJ (mol H_2)$^{-1}$ [17] and 54.1 kJ (mol H_2)$^{-1}$ [18]) reveals that our value for the dehydriding reaction is different, but the value for the hydriding reaction is in good agreement. The dehydriding rate equation used in ref. 18 was thought to be inappropriate because the effect of the plateau pressure was not considered. In later studies, the rate equation was improved. In this paper, the improved dehydriding equation was used and thus a different activation energy was obtained.

3.3. Reactions at higher temperatures

The temperature deviation at higher temperatures is shown in Fig. 9. The general deviations from the set value were again kept within ±0.1 °C. The maximum deviation was less than 1 °C for a few seconds at the very beginning of the reaction. This indicates that, even at higher temperatures, the temperature can be maintained constant close to isothermal conditions in this highly heat-sensitive reactor.

Experimental data obtained under these conditions were found to be reproducible. The reaction orders a and b were determined to be 2 and 1 in the $\alpha+\beta$ phase region by fitting eqn. (1) to the experimental data. Excellent linear relationships were obtained by plotting the reaction rates as a function of $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$.

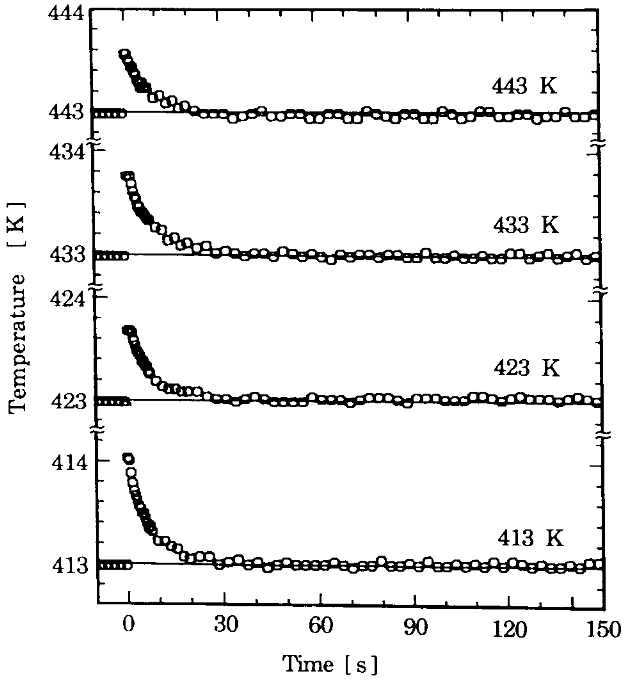

Fig. 9. Temperature deviations of the MH bed during the hydriding reaction at different temperatures (in the high-temperature range).

4. Conclusions

Using a highly heat-sensitive reactor, the temperature deviation from a set value was maintained within ±0.1 °C except for a few seconds during the initial part of the reaction. This is the first successful approach for obtaining kinetic data under "quasi-isothermal" conditions with reasonable reproducibility. Data obtained under these conditions show that the reaction order, rate constant and apparent activation energy are constant within the $\alpha+\beta$ region.

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