Experimental Study on Thermophysicochemical Properties of the LaNi$_5$–H$_2$ System[1]

A. Yoshida,[2] W. Luangdilok,[2] T. Ogura,[2] and Y. Naka[2]

Thermophysicochemical properties of the LaNi$_5$–H$_2$ system are investigated for the practical utilization of hydriding alloys. The equilibrium pressure–composition isotherms are measured in full consideration of the thermal history. It is made clear that they are susceptible to the maximum temperature in operation processes. The kinetic properties are measured under isobaric and isothermal conditions. The results indicate the difference in reaction mechanism between the absorption and the desorption processes.

KEY WORDS: chemical reaction rate; LaNi$_5$–H$_2$ system; metal hydride; pressure-composition isotherm; reaction mechanism; thermal history.

1. INTRODUCTION

Rechargeable hydriding alloys have attracted industrial interests as functional materials capable of storing hydrogen and/or thermal energy. There have been numerous studies on their basic properties. However, a scrutinized data base on the thermophysicochemical properties is needed for optimum design applications.

The thermophysicochemical properties studied in the present paper are the equilibrium hydrogen pressure-composition of metal hydride-temperature characteristics (P-C isotherms) and the chemical reaction rates. Among several promising candidate materials, LaNi$_5$ is chosen as a specimen for the measurements.

The P-C isotherms are considered to be well known. However, in the previous study [1], it was suggested that they were influenced by the cyclic

operating conditions. In the present paper, the P-C isotherms are measured in full consideration of the thermal history.

Various types of formulas of the overall reaction rates have been reported [2, 3]. In the present paper, the formulas for the intrinsic reaction rates without the heat and the mass flow effects are derived as a function of composition.

2. P-C ISOTHERMS

2.1. Experimental Apparatus and Procedure

The schematic diagram of the experimental apparatus for measuring the P-C isotherms is shown in Fig. 1. The temperature of the water bath (12) can be controlled within ±0.13 K. The pressure is measured with two pressure gauges (7) rated at 10 MPa with a full scale accuracy of ±0.25%.
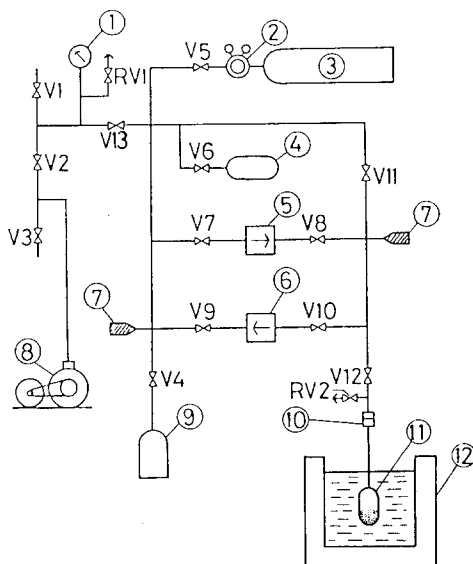

Fig. 1. Schematic diagram of the experimental apparatus. (1) Pressure gauge; (2) pressure regulator; (3) hydrogen gas tank; (4) gas reservoir; (5) pressure regulator; (6) back pressure regulator; (7) strain-gauge pressure transducer; (8) rotary vacuum pump; (9) gas reservoir; (10) 2-μm in-line filter; (11) hydrogen chamber; (12) thermostat water bath; (V1–V13) valves; (RV1, RV2) relief valves.

The gas reservoirs (4 and 9) and the chamber (11) are 1.00×10^{-3}, 1.50×10^{-4}, and $1.20 \times 10^{-4}\,\mathrm{m}^3$ in volume, respectively. Two gas reservoirs are properly used depending on the amount of absorption or desorption. The pressure regulators (5 and 6) are used to measure the kinetic properties as described later. The instruments, the valves, and the tubes for piping in the apparatus are made of stainless steel. The specimen charged in the chamber is 41.9 g in weight with a void fraction of 0.52 and a bulk density of $3.94 \times 10^3\,\mathrm{kg \cdot m}^{-3}$. It contains impurities such as aluminum (0.2 wt%). The purity of hydrogen is 99.999%.

The entire test section is enclosed with valves V5 and V13 except for the sections between valve V7 and valve V8 and between valve V9 and valve V10. Valves V7–V10 are always closed during the measurements of the P-C isotherms. The test section is divided into two sections by valve V11. One, which includes the hydrogen chamber, is called the reaction section or B section. The other is called the hydrogen supply section or A section.

The activation process is necessary to take place before the measurements so that hydriding alloys absorb and desorb hydrogen gas steadily. The specimen is activated by several pressurizing–evacuating cycles.

After the water bath is set at the desired temperature, the specimen is degassed in the chamber under 50 Pa to determine the origin of the composition. The composition (H/M) is defined by the atom ratio of hydrogen to LaNi₅. A pair of P-C isotherms in absorption and desorption processes is gradually obtained by a volumetric technique. The measurements are started from the origin of the composition and are carried out under the constant temperature of the water bath. The procedure is as follows. (1) After finishing the measurement of a point on the P-C isotherm, valve V11 is closed. (2) The A section is pressurized from the gas tank in the absorption process. In the desorption process the pressure of the A section is reduced by using a vacuum pump. (3) The pressure is measured by the pressure gauge on the left side in Fig. 1. Another pressure gauge is used to monitor the pressure of the B section, which is equal to the previous equilibrium pressure. (4) Valve V11 is opened, and the specimen in the chamber begins to absorb or desorb hydrogen gas. A duration of 30 min to several hours is required to finish the reaction and to stabilize the pressure. (5) The equilibrium pressure is measured by the pressure gauge. (6) The amount of absorption or desorption is inferred from the pressures in both sections before and after adding or removing an appropriate amount of hydrogen and from the volumes of both sections measured earlier. Hydrogen is treated as an ideal gas. The section outside of the water bath is assumed to be at room temperature. Finally, the composition is deter-

mined, and then the point is marked on the P-C isotherm. A pair of P-C isotherms is obtained by repeating these procedures.

2.2. Experimental Results and Discussion

After the activation process is repeated 15 cycles in the range of 500 Pa to 1.3 MPa at 298 K, the P-C isotherms are measured in the following temperature order: (1) $313 \rightarrow$ (2) $333 \rightarrow$ (3) $343 \rightarrow$ (4) $343 \rightarrow$ (5) $333 \rightarrow$ (6) $313 \rightarrow$ (7) 343 → (8) 333 → (9) 313 → (10) 353 → (11) 333 → (12) 373 → (13) 333 K. Figure 2 shows the results of the ordinal numbers from 1 to 3. Figure 3 shows the results of the ordinal numbers from 3 to 9, and the temperatures are the same as those in Fig. 2.

In Fig. 3, P-C isotherms have two plateau regions on every desorption curve. However, in Fig. 2, the isotherms at 313 and 333 K show only one plateau, and two plateaus appear at 343 K. Moreover, an important finding here is that the capacity of the hydrogen storage is smaller in the P-C isotherms with two desorption plateaus. In Fig. 3, the maximum temperatures in absorption and desorption processes before each measurement are 343 K at every isotherm. In this case, the P-C isotherms are independent of the cycle number.
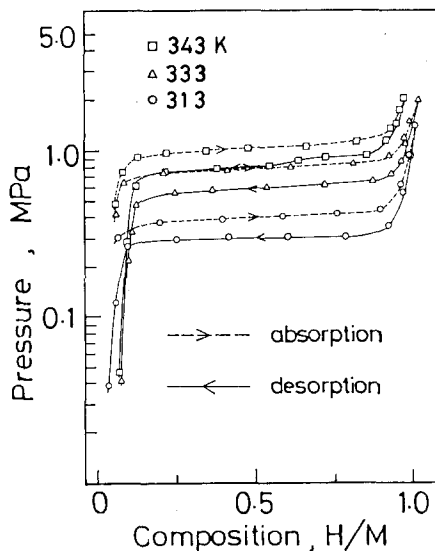

Fig. 2. P-C isotherms for LaNi$_5$ in the temperature order, 313, 333, and 343 K after the activation at 298 K.
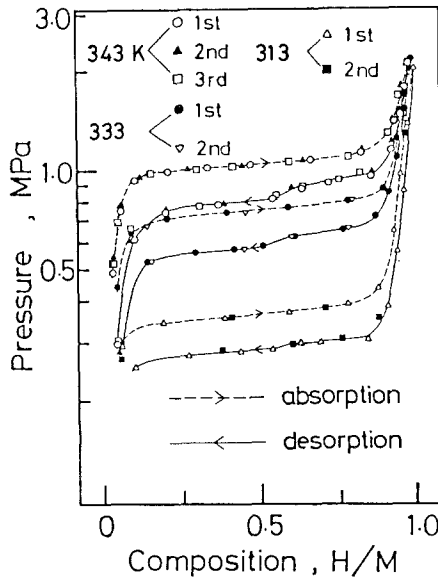
Fig. 3. P-C isotherms for LaNi$_5$ after the measurements shown in Fig. 2.

Figure 4 shows the P-C isotherms at 333 K. Four cases correspond to the ordinal numbers of 2, 5, 11, and 13 and represent the maximum past operating temperatures 313, 343, 353, and 373 K, respectively. These results indicate that once the operating temperature exceeds 343 K, the plateaus decrease in pressure and split into two segments, and the hydrogen storage capacity declines in comparison with the initial state given by the open triangles. These changes become more remarkable at the higher maximum temperature in operation processes. The P-C isotherms are sensitive to the thermal history. The degradation such as the decrease in the hydrogen storage capacity progresses gradually as a result of many cyclic operations at every temperature. Despite the common understanding of the degradation, the results indicate that it makes rapid progress irreversibly by a small number of cycles.

The hypothesis that the changes of the hydrogen storage capacity and the plateau pressure are due to phase separation is acceptable. The separation is caused by the following irreversible reaction [1].

$$LaNi_5 + H_2 \rightarrow LaH_2 + 5Ni \tag{1}$$

The reaction would lead to the stable nonhydriding products such as nickel. As shown in Fig. 4, the kinetics depends strongly on the tem-
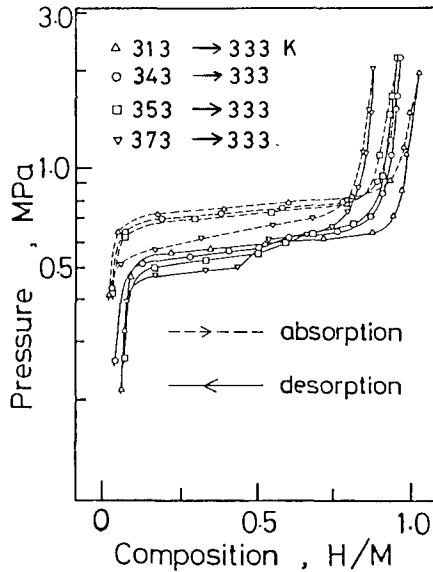
Fig. 4. Effect of the thermal history upon the
P-C isotherms for LaNi$_5$ at 333 K.

perature. The occurrence of the two desorption plateaus suggests two hydride phases such as the TiFe–H$_2$ system. Ono et al. [4] have reported the existence of a new hydride phase of LaNi$_5$H$_3$ besides the solid-solution phase and the hydride phase of LaNi$_5$H$_6$. In order to clarify the behavior of the P-C isotherms, this problem needs further careful investigation in view of the structure of crystals such as the lattice strain and defect.

3. KINETIC PROPERTIES

3.1. Experimental Apparatus and Procedure

The reaction cell shown in Fig. 5 is connected to the experimental apparatus instead of the chamber (11) shown in Fig. 1. The specimen is sealed in the narrow space, about 1.8 mm in width, between the tee-fitting (1) and the stainless tube (2) in Fig. 5. The cell is immersed in the water bath. The water at constant temperature is forced, by a pump, to pass through the tubes (2 and 3) for the removal of the reaction heat from both sides of the specimen layer. The temperature change in the specimen can be controlled within ±0.7 K. The temperature is measured with a thermocouple.
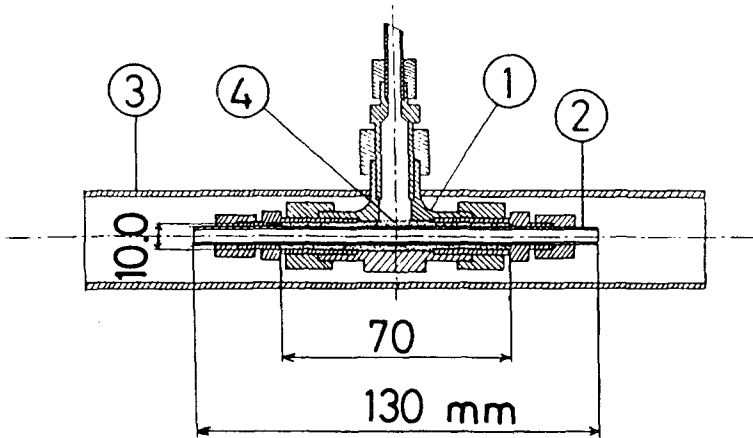
Fig. 5. Reaction cell for the kinetic measurements. (1) Tee-fitting; (2) stainless
tube, 6.35-mm o.d.; (3) plastic tube, 28.0-mm i.d.; (4) specimen.

The entire test section is divided into two sections called the A and B sections by two regulators (5 and 6) and valve V11 shown in Fig. 1 in the same manner as the measurements of the P-C isotherms. Valve V11 is closed except for the determination of the intial state of the specimen. The regulators (5 and 6) control the outlet and the inlet pressures, respectively. For more than 99% of the regulated pressures, the actuation times of the regulators are less than 1 s.

First, the water bath is adjusted to a desired temperature. Next the reaction cell is evacuated or pressurized through valve V11 in order to determine the intial composition of the specimen. After the regulator (5 or 6) is adjusted to the desired pressure, the hydrogen gas flows through the regulator. The pressure in the reaction cell (B section) is kept constant by pressure regulator (5) for the absorption process or (6) for the desorption process. The pressure in the A section is measured by the pressure gauge as a function of time. The amount of absorption or desorption per unit time is inferred from the pressure change and from the volume of the A section. According to this, the experimental result can be transferred to the figure of composition vs time. Finally, the intrinsic chemical reaction rate under constant pressure and temperature is obtained through the analysis of the figure.

The activation is fully carried out for more than 20 cycles in the range of 500 Pa to 2.0 MPa at 313 K without the effects of the thermal history. After the activation, the results are independent of the cycle number. The weight of the specimen is 2.0 g.

3.2. Experimental Results and Discussion

The reaction rate dC/dt is expressed empirically by the following equation:

$$dC/dt = Kg(C) \tag{2}$$

where K is the reaction rate constant and is a function of the hydrogen pressure P and the temperature. The temperature dependence is usually given by an Arrhenius form. In the previous studies [2, 3], the reaction rate is considered to be proportional to $(P - P_e)$ or $\ln(P/P_e)$, where P_e is the plateau pressure. However, a function of the composition $g(C)$ is not formulated, because of the difficulties in satisfying the isobaric and the isothermal conditions.

In the absorption process, the solid-solution phase (α phase) is formed at the first stage. As the reaction proceeds further, the hydride phase (β phase) is liberated from the α phase. The transformation of the β phase from the α phase is considered to be the dominant kinetic process. The rate equation for nucleation and growth is known as Johnson-Mehl's equation [5] and is given by

$$C = 1 - \exp\{-(Kt)^n\} \tag{3}$$

where n is a restricted constant dependent on the mode of transformation. If Eq. (3) is differentiated with respect to time t, the following equation is obtained:

$$dC/dt = Kn(1 - C)\{-\ln(1 - C)\}^{(n-1)/n} \tag{4}$$

Figure 6 shows the relation between the reaction rate dC/dt and the composition C ($=$H/M) in the absorption process. The rates have maxima
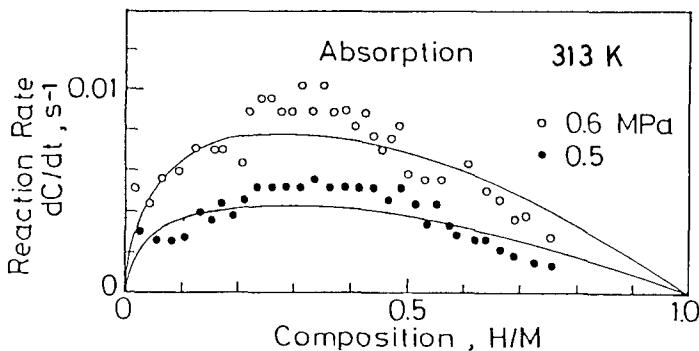

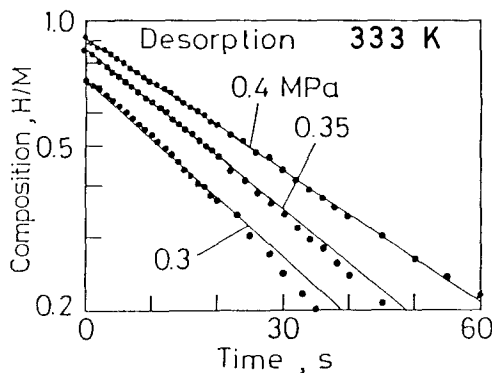Fig. 6. Effect of the composition upon the reaction rate in absorption for LaNi$_5$.

Fig. 7. Composition vs time in desorption for LaNi$_5$.

at about H/M = 0.3. The tendency is commonly observed for several conditions of temperature and pressure. Therefore, the most suitable value of n is determined to be 3/2 for the data points. The maximum rate appears at about H/M = 0.28. The rate-limiting process is the diffusion of the β phase. According to Rudman [6], the number of nuclei is constant, and the growth is three-dimensional. In this case, the reaction rate is expressed by

$$dC/dt = (3/2)\, K(1 - C)\{ -\ln(1 - C)\}^{1/3} \tag{5}$$

The reaction rate constants K are obtained so as to fit the data points. Then the calculated results are drawn as the solid lines in Fig. 6.

Figure 7 shows the composition C ($=$H/M) as a function of time t in the desorption process. The reaction rate is easily expressed by

$$dC/dt = -KC \tag{6}$$

In consideration of the reverse reaction against the absorption process, Eq. (6) is obtained by substituting 1 for n in Eq. (4). According to Belkbir et al. [7], the reaction model shows the appearance of nuclei with a constant probability in time and space, with no further growth. The solid lines shown in Fig. 7 represent the calculated results in the same way as in Fig. 6.

5. CONCLUSIONS

Thermophysicochemical properties of the LaNi$_5$–H$_2$ system have been experimentally examined. The results are summarized as follows.

(1)   The P-C isotherms are greatly affected by the maximum operating temperature, if it exceeds 343 K.

(2)   The intrinsic chemical reaction rates can be expressed as a function of the composition according to the reaction mechanism in the absorption and desorption processes.

ACKNOWLEDGMENTS

REFERENCES

1. P. D. Goodell, *J. Less-Common Metals* **99**:1 (1984).
2. S. Tanaka, J. D. Clewley, and T. B. Flanagan, *J. Less-Common Metals* **56**:137 (1977).
3. M. Miyamoto, K. Yamaji, and Y. Nakata, *J. Less-Common Metals* **89**:111 (1983).
4. S. Ono, K. Nomura, E. Akiba, and H. Uruno, *J. Less-Common Metals* **113**:113 (1985).
5. W. A. Johnson and R. F. Mehl, *Trans. AIME* **135**:416 (1939).
6. P. S. Rudman, *J. Less-Common Metals* **89**:93 (1983).
7. L. Belkbir, E. Joly, N. Gerard, J. C. Achard, and A. Percheron-Guegan, *J. Less-Common Metals* **73**:69 (1980).