Comparing hydrogen absorption kinetics of the samples of intermetallic compound and metal hydride compact on its basis

I A Romanov, V I Borzenko and A N Kazakov

Joint Institute for High Temperatures of the Russian Academy of Sciences, Bld 2 Izhorskaya Street, 13, Moscow, Russia

E-mail: romanoff_i_a@mail.ru

Abstract. This work is devoted to an experimental study and comparison of the kinetics of hydrogen absorption by an intermetallic compound \( \text{LaNi}_{4.4}\text{Al}_{0.3}\text{Fe}_{0.3} \) in form of pure intermetallic compound free backfill and a compact based on it obtained by cold pressing with a spiral matrix of nickel-foam. To calculate the kinetic parameters of the hydrogen absorption reaction, the initial rates method is used. The PCT absorption isotherms are measured at temperatures of 313, 333, and 353 K. The experimental data are described with quite high confidence by the chosen model, which assumes that the reaction rate controlling step is the dissociative absorption of hydrogen on the surface of the \( \alpha \)-phase. The rate of hydrogen absorption increases with increasing pressure drop and temperature. It is shown that the rate of hydrogen absorption by the sample of pure IMC is significantly less dependent on temperature compared to the compact sample. In addition, the reaction rate at temperatures of 313 and 333 K is higher for the free backfill sample, and at 353 K it is higher for the metal hydride compact. The values of the absorption constant and the activation energy of the hydrogen absorption reaction are determined for both samples.

1. Introduction

The use of hydrogen as an intermediate energy source is one of the most promising ways to create full-fledged sustainable energy systems based on renewable energy sources [1]. The problem of hydrogen storage is the key to the creation of such systems. Lightweight composite high-pressure cylinders (over 70 MPa) require compressor stations, and liquid storage is too expensive for small power systems. The best solution is solid state storage of hydrogen in the form of metals or intermetallic compound (IMC) hydrides. This technology scales to power systems of various capacities, has flexibility due to a large selection of different hydrogen absorbing materials, and allows using low-potential heat for hydrogen compression.

One of the main advantages of metal hydride storage technology is quick charge and discharge due to the high rate of interaction of intermetallic compounds with hydrogen. Many experimental and theoretical papers have been devoted to the study and modeling of the thermodynamics and kinetics of the reaction of metals and intermetallic compounds with hydrogen [2-5]. During this reaction, there is great release of heat, which is difficult to remove from the fine-dispersed backfills of metal hydrides due to their low thermal conductivity [6], especially in large-scale reactors containing tens or even hundreds of kilograms of hydrogen-absorbing materials. This problem may be solved by forming metal hydride compacts by pressing fine intermetallic powders in a heat-conducting matrix. Our
previous studies [7,8] show that the use of matrices made of metal foam materials (copper, nickel) and cold pressing for the formation of metal hydride compacts can significantly improve the thermal conductivity of samples and reduce the impact of the crisis phenomena of heat and mass transfer during the absorption and desorption of hydrogen.

This work is devoted to an experimental study and comparison of the kinetics of hydrogen absorption by an intermetallic compound LaNi$_{14.4}$Al$_{0.3}$Fe$_{0.3}$ in form of pure free backfill and a compact based on it obtained by cold pressing using a spiral matrix of nickel-foam. The experiments are carried out on a Sievert's-type test bench, and the data are analyzed by the method of initial rates in the two-phase coexistence region of the metal hydride.

2. Experiment details and data analysis

The intermetallic compound AB$_3$-type of LaNi$_{14.4}$Al$_{0.3}$Fe$_{0.3}$ composition with a low equilibrium pressure of hydrogen absorption and desorption at room temperature (less than 0.1 MPa) was chosen as the object of research. The low equilibrium pressure allows using more accurate sensors, which improves the quality of the calculations performed, as will be discussed below. Two samples are studied: one of which is a sample of pure intermetallic compound weighing 50 g, and the second sample is a metal-hydride compact prepared by cold pressing from 50 g of the initial intermetallic compound with a spiral matrix of nickel-foam weighing 3 g. The compact was made in a dry box in an inert atmosphere. A heat-conducting matrix was made from a strip of 10 mm wide and 1.6 mm thick nickel foam, which was folded into a spiral. The powder of the activated alloy was carefully distributed through the matrix using vibration. Pressing was carried out directly in the working vessel in a dry box using a steel rod [8]. Experimental studies in this work are carried out on a Sievert's-type test bench US-150 to investigate hydrogen interaction with samples of metals and intermetallic compounds weighing from 10 to 800 g at a temperature of 243 to 673 K and a pressure of up to 15 MPa. A detailed description of the components of the installation and its operation is published in [9]. It is worth noting that the setup has a cascade of pressure sensors to improve the accuracy of measurements: a low pressure sensor in the range from 0 to 0.1 MPa (the division price is 10 Pa), a medium pressure sensor in the range from 0.1 to 1 MPa (spacing of $10^3$ Pa) and a high pressure sensor in the range from 1 to 15 MPa (spacing of $10^4$ Pa). To calculate the kinetics of hydrogen absorption, data are obtained only with the help of low and medium pressure. The high-pressure sensor has too rough scale and its data cannot be adequately used for calculations with the used method.

For accurate calculations of the kinetics of the hydrogen absorption reaction, it is extremely important to observe the isothermal conditions of the system. However, the interaction of intermetallic compounds with hydrogen is characterized by a high thermal effect, and the low thermal conductivity of the backfill prevents from rapid removal of this heat. In large samples with a significant layer thickness, such as those studied in this paper, it is impossible to observe the isothermal condition during the entire experiment. Therefore, measuring the sample temperature is crucial. The design of the working vessel of the US-150 test bench involves measuring the temperature with a thermocouple, located 3 mm from the bottom of the working vessel in the cover directly in the thickness of the sample. In addition, individual sensors (thermocouples or platinum resistance thermometers) measure the temperatures of the buffer and vacuum vessels, as well as the pipelines connecting them. The spacing of all the temperature sensors is 0.1 K. The working vessel with the samples was placed in the bath of the liquid thermostat. The experiments were carried out at temperatures of 313, 333, and 353 K, and the isothermal condition was assumingly satisfied when the sample temperature was within 0.2 K. When hydrogen was absorbed by the samples of the intermetallic compound and compact, the above condition was observed in the time interval from 1.5 to 4 seconds (depending on the initial temperature and the value of the pressure drop) from the moment of the reaction, which provided a sufficient number of experimental points for calculations. The data for the analysis were obtained during the measurement of hydrogen absorption isotherms (PCT- isotherms), which was carried out by introducing portions of hydrogen from a buffer or/and vacuum vessel into a working one with a different pressure drop through connecting pipelines. After the system reached a state of quasi-
equilibrium (temperature and pressure assumed to be constant), the next iteration was performed. For each temperature, several PCT isotherms with different pressure drop values were measured.

The experimental points used for kinetic calculations were located within the concentration limits corresponding to the two-phase region on the PCT isotherms (the plateau region).

The calculation of the amount of hydrogen gas was carried out using a modified Van der Waals equation proposed by Hemmes et al. \[10]\]. To calculate the kinetic parameters of the hydrogen absorption reaction, the initial rates method proposed by Nahm et al. \[11]\] was used. The kinetic model that underlies this method contains the following important assumptions: intermetallic particles have a spherical shape and the same radius, the particle density does not change during absorption. It is assumed that the rate controlling step is the dissociative chemisorption of hydrogen on the surface of a solid solution of hydrogen in an intermetallic compound (α-phase), which can be described by the following equation:

\[
H_2 + 2S \frac{k_a}{k_d} \times 2H - S
\]  

(1)

The process of dissociative chemisorption is described using the Langmuir isotherm. Given that the hydrogen molecule dissociates into two atoms, which are then absorbed, the reaction rate can be expressed as follows \[11]\):

\[
\frac{dx}{dt} = \frac{4r_0 k_a}{n_f (1 + \sqrt{k_d P_{eq}})} \times (P_0 - P_{eq})
\]  

(2)

Where \(X\) is the degree of transformation, \(r_0\) is the radius of the particles, \(k_a\) is the absorption constant, \(K_a\) is the equilibrium constant, \(n_f\) is the maximum amount of adsorbed hydrogen in the plateau region, \(P_0\) and \(P_{eq}\) are the initial and equilibrium pressure, respectively. At constant temperature and pressure, the right-hand side of equation (2) is a constant, so integration from \(X=0\) and \(t=0\) to \(X\) and \(t\) gives:

\[
X = K_{ad} t
\]  

(3)

where \(K_{ad}\) is the constant. If we assume that the reaction obeys the Arrhenius law (see equation 4), then \(K_{ad}\) consists of two terms, one of which depends on the pressure drop, and the other depends on the temperature. The values of these terms can be calculated from experimental data.

\[
\frac{dx}{dt} = k_a (P_0 - P_{eq}) \cdot e^{-\frac{k_A}{RT}}
\]  

(4)

3. Results and discussion

The isotherms of hydrogen absorption by samples of intermetallic compound LaNi\(_{4.4}\)Al\(_{0.3}\)Fe\(_{0.3}\) (IMC) and a compact based on it (Compact) are shown in Figure 1, were \(P\) is equilibrium pressure of hydrogen and H/IMC is amount of hydrogen atoms per formula unit.

The measurement of the PCT isotherms is necessary to determine the value of the equilibrium pressure. In addition, the inflection points of the isotherms are necessary to determine the maximum amount of adsorbed hydrogen on the plateau \(n_f\), and therefore to determine the degree of transformation \(X\). It is worth noting that the isotherms of pure intermetallic and compact differ slightly and have a noticeable slope in the plateau region.

Figure 2 shows the dependence of pressure and temperature on time during the hydrogen absorption process at a temperature of 333 K and a pressure drop of 0.11 MPa. The figure shows that the temperature of the compact rises slightly higher during absorption. On the other hand, this peak is sharper compared to pure intermetallic, that is, the sample of the compact cools faster. Complete relaxation of temperature and pressure takes about 3-4 thousand seconds (from 50 to 70 minutes).
Figure 1. Isotherms of hydrogen absorption by pure intermetallic compound and metal hydride compact at temperatures 313, 333 and 353K.

Figure 2. Temperature and pressure evaluations during hydrogen absorption.

Figure 3 shows the initial section of the kinetic curves with a length of 10 seconds. It may be used to determine the value of the initial part of absorption, where the conditions can be considered isothermal (temperature fluctuation below 0.2 K). This area in Figure 3 is separated by a vertical control line. For each point in the plateau region of all the PCT isotherms, the value of this area is determined separately by analysing the corresponding temperature curves.

The amount of absorbed hydrogen was calculated from the time-pressure data, and since in some cases the pressure drop was quite large, the molar volume of hydrogen was calculated separately for each point. As a result, data were obtained on the dependence of the degree of transformation on time at various pressure drops and temperatures.
Figure 3. Initial section of the hydrogen absorption kinetic curves.

Figure 4. Dependence of the degree of transformation on time for the IMC (left) and the compact (right) at different temperatures.

Figure 4 shows the dependence of the degree of transformation on time at a pressure drop of 0.115 MPa and temperatures of 313, 333, and 353 K for the samples of pure IMC (a) and compact (b). As can be seen from the figure, the experimental data are well approximated using a linear dependence, that is, the degree of transformation depends linearly on time, and the reaction rate is constant at constant pressure drop and temperature. This conclusion is in good agreement with the assumptions about the reaction mechanism made in the previous section. In addition, Figure 4 clearly demonstrates that the reaction rate increases with increasing temperature.

It can also be seen that the reaction rate of hydrogen absorption by the pure IMC sample is significantly less dependent on temperature compared to the compact sample: thus, at a temperature of 313 and 333 K, the absorption rate is higher for the pure intermetallic compound, and at a temperature of 353 K, the reaction rate is higher for the compact. Similar graphs are constructed for all other points of the PCT isotherms in the plateau region with different pressure drops, which serves to determine the dependence of the reaction rate on the value of the pressure drop. The results of these calculations at temperatures of 313, 333, and 353 K are shown in Figure 5 for the sample of pure IMC (a) and compact (b).
Figure 5. The dependence of the reaction rate on the pressure drop for the pure IMC (left) and the compact (right) at different temperatures.

As can be seen from the figure, the reaction rate depends linearly on the magnitude of the pressure drop at a constant temperature. These graphs allow determining the value of the average reaction rate at temperatures of 313, 333 and 353 K. If we assume that the reaction rate depends on pressure and temperature in accordance with equation (4), then by constructing the dependence of the logarithm of the rate constant on the inverse temperature (Figure 6), we get a straight line, the equation for which will serve to determine the value of the absorption constant and the activation energy.

Figure 6. The Arrhenius plot of hydrogen absorption of the pure IMC ($R^2=0.999$) and compact ($R^2=0.964$).

As can be seen from the figure, the results of processing the experimental data are approximated by a linear dependence with high confidence ($R^2=0.999$ and 0.964 for the pure IMC and compact, respectively). Thus, we can write down the reaction rate equations for the pure IMC:

$$\frac{dx}{dt} = 2.74 \times (P_0 - P_{eq}) \cdot e^{\frac{-5600}{RT}}$$

(5)
and for the compact based on it:

$$\frac{dx}{dt} = 17.46 \times (P_0 - P_q) \cdot e^{-\frac{10900}{RT}} \tag{6}$$

The calculations show that the value of the observed absorption constants and activation energy for the sample of a metal hydride compact is significantly higher than for the sample of a pure IMC. In addition, the description using the proposed model shows noticeably lower values of quadratic confidence in comparison with the sample of pure intermetallic. Most likely, this is caused by the increased density of the compact compared to the free backfill, which complicates hydrogen diffusion through the sample and increases the contribution of diffusion to the overall reaction rate. It is also worth noting that, although the reaction rate of hydrogen absorption at the initial sites at a temperature of 313 and 333 K in a sample of a metal hydride compact is lower than in a free backfill, the overall relaxation rate of temperature and pressure in the compact is higher (the time is, correspondingly, lower) in the entire range of measurements performed. This confirms the greatest significance of heat transfer for systems based on metal hydride materials.

Conclusions

This work is devoted to the study of hydrogen absorption by samples of the intermetallic compound of the composition LaNi$_4$Al$_{0.3}$Fe$_{0.3}$ in the form of the free backfill weighing 50 g and the compact with a matrix of nickel-foam in terms of the reaction kinetics. The PCT absorption isotherms have been measured at temperatures of 313, 333, and 353 K. The isotherms have a noticeable slope and almost coincide in both samples.

The initial rates method is used to determine the dependence of the hydrogen absorption reaction rate on the pressure and temperature drop in the plateau region. The experimental data are described with a sufficiently high confidence by the chosen model, assuming that the reaction rate controlling step is the dissociative absorption of hydrogen on the surface of the $\alpha$-phase. The rate of hydrogen absorption increases with increasing pressure drop and temperature.

It is shown that the rate of hydrogen absorption by the sample of pure IMC is significantly less dependent on temperature compared to the compact sample. In addition, the reaction rate at temperatures of 313 and 333 K is higher for the free backfill sample, and at 353 K it is higher for the metal hydride compact. The values of the absorption constant and the activation energy of the hydrogen absorption reaction have been determined for both samples. As it has been found the value of the absorption constant for the sample of free intermetallic compound backfill is 2.74 and the activation energy of the reaction is equal to 5.6 kJ/mole. For the metal hydride compact they are 17.46 and 10.9 kJ/mole, respectively.

The differences in the behaviour of the samples are probably due to the higher density of the compact and the greater contribution of diffusion through the sample to the overall reaction rate. Despite the lower rate of the hydrogen absorption reaction at temperatures of 313 and 333 K, the complete relaxation of temperature and pressure occurs faster in the sample of the metal hydride compact due to the greater thermal conductivity.

Acknowledgments

This work was supported by a RSCF grant No.17-19-01738.

References

[1] Malyschenko S, Borzenko V, Dunikov D and Nazarova O 2012 Thermal Engineering 59(6) 468–78
[2] Lototskyy M 2016 Int J Hydrogen Energy 41 2739–61
[3] Yang F, Zhang Y, FCiucci F, Wu Z, Wang S, Wang Y and Zhang Z 2018 J. Alloys Comp. 741 610–21
[4] Ledovskikh A, Danilov D and Notten P 2007 Physical Review B 76 064106
[5] Rodriguez P, Gallandat N and Zuttel A 2019 Int J Hydrogen Energy 44 13583–91
[6] V Borzenko, D. Dunikov and S Malyshenko 2011 *High Temperature* **49**(2) 249–56
[7] Romanov I, Borzenko V and Kazakov A 2020 *Nanotechnologies in Russia* **15**(3–6) 314–8
[8] Romanov I, Borzenko V and Kazakov A 2019 *J. of Physics: C S* **1359**(1) 012103
[9] Malyshenko S and Romanov I 2014 *High Temperature* **52**(3) 403–10
[10] Hemmes H, Driessen A and Griessen R 1986 *J. Phys. C: Solid State Phys.* **19** 3571
[11] Nahm S, Kim W, Hong S and Lee W 1992 *Int J Hydrogen Energy* **17** 333–8