Inorg. Chem. **1991**, *30*, 800-802

Contribution from the Department of Chemistry,
West Chester University, West Chester, Pennsylvania 19383

Desorption Kinetics of 1:3 Erbium Cobalt Intermetallic Hydride

R. M. Donohue and A. J. Goudy*

Received July 12, 1990

A comparison was made of the desorption rates of hydrogen from the β and γ phases of $ErCo_3$ hydride. This represents the first time that such a comparison has been made of two phase transitions within the same intermetallic hydride. The sample was maintained at approximately isothermal conditions by blending it with a relatively large amount of aluminum powder, which served as a heat buffer. Experiments were also designed so that the ratio of the equilibrium plateau pressure to the opposing hydrogen gas pressure was the same in all cases. This was done to ensure that all experiments were carried out under constant thermodynamic driving forces. It was found that, under the conditions used, the rate of hydrogen evolution from the γ phase was approximately 7 times faster than that from the β phase. This indicates that hydrogen atoms in the β phase occupy more stable lattice sites than those in the γ phase. The facts that the enthalpy of formation for the β hydride is greater than that for the γ phase and that the activation energy for hydrogen desorption from the β phase is also greater than that from the γ phase further support this conclusion.

Introduction

A number of intermetallic compounds have been found to absorb and desorb relatively large amounts of hydrogen rapidly and reversibly at moderate temperatures and pressures.[1] Thus they are of practical importance as a means for storing hydrogen. Some of the alloys that have been most widely studied include $LaNi_5$,[2] $CaNi_5$,[3] FeTi,[4] Mg_2Ni,[5] RFe_3[6] (R = a rare-earth element), RCo_3,[7] and RCo_5,[8] as well as many others. The thermodynamics and structural features of these materials are fairly well understood; however, there is no general agreement about their kinetics. Aside from those on $LaNi_5$,[9-13] very few kinetic studies have been reported. This is because it is difficult to achieve reproducible results due to a number of experimental parameters that are difficult to control. For example, during successive hydriding and dehydriding cycles, the surface area and particle size continually change due to cracking. Also, isothermal conditions are difficult to maintain due to the large amount of heat associated with the sorption process. In 1983, Goudy et al.[11] eliminated this particular problem by demonstrating that if a small amount of $LaNi_5$ was blended with a relatively large amount of aluminum powder (heat buffer), nearly isothermal conditions could be achieved. The study showed that when less than 95 wt % aluminum was present, the rate of heat transfer to the sample controlled the kinetics. But when 95% or more heat buffer was present, heat transfer was no longer rate-controlling. In 1989, Koh et al.[12] proposed solutions to some of the remaining problems. They demonstrated that the rate at which hydrogen is adsorbed or desorbed from $LaNi_5$–H depends on the number of absorption–desorption cycles that a sample has been subjected to. They reported the reaction rates of this material to increase dramatically over the first 30 cycles. However, after this point there was only a minimal increase in the reaction rate. Thus it is possible to achieve reproducible measurements on samples that have been adequately cycled prior to beginning measurements. It was also established that when the kinetics of two or more hydrides are compared, in the two-phase region, the ratio of the equilibrium plateau pressure to the opposing hydrogen gas pressure in each material must be equivalent. If this is not done, kinetic differences will arise merely because of differences in the influence of pressure. By using these methods, Clay et al.[13] were able to compare the kinetics of $LaNi_5$–H with those of other materials made by replacing part of the La in $LaNi_5$ with other rare-earth elements. They found that when the stability of the hydrides decreased, the hydriding/dehydriding rates of the $\alpha \leftrightarrow \beta$ phase transition increased.

By using these methods, it should also be possible to do comparative kinetic studies on some of the other hydrogen-absorbing materials. One of the most interesting alloy systems is RCo_3. When absorbing hydrogen, these alloys undergo an α–β and a β–γ phase transition.[7] This is different from the case of $LaNi_5$–H and many other systems, which display only an α–β transition. Some of the alloys in the RCo_3 system were studied kinetically by Goudy et al.;[14] however this was done before it was known that heat-transfer effects could be minimized by use of a heat buffer. Also, no attempt was made in that study to actually compare the kinetics of the α–β and β–γ phase transitions within the same material. A study of this nature is potentially significant, for if differences are seen, this would be indirect evidence that hydrogen in the β phase occupies lattice sites different from those in the γ phase. Neutron diffraction studies have shown that, in transition-metal hydrides, the hydrogen can exist in tetrahedral or octahedral sites. For example, in the intermetallic hydride $NiZrH_3$ the unit cell contains hydrogen in both tetrahedral and octahedral sites.[15]

In this study, we have chosen $ErCo_3$ as a typical RCo_3 alloy. The rates of hydrogen evolution from the β and γ phases are determined by using the methods developed by Koh et al.

Experimental Section

The $ErCo_3$ used in this study was prepared from pure components by arc-melting under a purified argon atmosphere. The erbium was 99.9% pure, and the nickel was 99.99% pure. The sample was repeatedly melted to homogenize it and then annealed at 1000 °C for 1 week. X-ray diffraction was used to check whether the sample was single phase.

The experimental apparatus used to prepare the hydrides and perform kinetics measurements is shown schematically in Figure 1. It consisted of a stainless steel manifold with ports for adding hydrogen, venting, and evacuating. Aschroft gauges were used for measuring pressures up to 1400 psig. An oil bath was used to keep the sample at constant temperature to within ±0.1 °C. A mass flowmeter with a range of 0–1 standard liter of H_2 min^{-1} was used to measure hydrogen flows from the sample reactor. The accuracy of each flowmeter was ±1% full scale, and the response time to a change in flow was 500 ms. The flow rate data were collected by using an IBM PC equipped with an Adalab interface board (Interactive Microware). Kinetic data were collected at a rate of one data point/s, and the amount of reacted hydrogen was obtained by integrating the area under flow versus time curves. An iron constantan

---

* Address all correspondence to this author.

(1) Wallace, W. E.; Craig, R. S.; Rao, U. V. S. *Adv. Chem. Ser.* **1980**, *186*, 207.
(2) Van Vucht, J. H. N.; Kuijpers, F. A.; Bruning, H. C. A. M. *Philips Res. Rep.* **1970**, *25*, 133.
(3) Sandrock, G. D. *Proc. Intersoc. Energy Convers. Eng. Conf., 12th* **1977**, 1, 951.
(4) Reilly, J. J.; Wiswall, R. H. *Inorg. Chem.* **1974**, *13*, 218.
(5) Reilly, J. J.; Wiswall, R. H. *Inorg. Chem.* **1968**, *7*, 2254.
(6) Goudy, A. Ph.D. Thesis, University of Pittsburgh, Dec 1976.
(7) Bechman, C. A.; Goudy, A.; Takeshita, T.; Wallace, W. E.; Craig, R. S. *Inorg. Chem.* **1976**, *15*, 2184.
(8) Kuijpers, F. A. Ph.D. Thesis, Technische Hogeschool, Delft, The Netherlands, 1973.
(9) Boser, O. *J. Less-Common Met.* **1976**, *46*, 91.
(10) Park, C. N.; Lee, J. Y. *J. Less-Common Met.* **1982**, *83*, 39.
(11) Goudy, A. J.; Stokes, D. G.; Gazzillo, J. A. *J. Less-Common Met.* **1983**, *91*, 149.
(12) Koh, J. T.; Goudy, A. J.; Huang, P.; Zhou, G. *J. Less-Common Met.* **1989**, *153*, 89.
(13) Clay, K. R.; Goudy, A. J.; Schweibenz, R. G.; Zarynow, A. *J. Less-Common Met.* **1990**, *166*, 153.
(14) Goudy, A.; Wallace, W. E.; Craig, R. S.; Takeshita, T. *Adv. Chem. Ser.* **1978**, *167*, 312.
(15) Peterson, S. W.; Sadana, V. N.; Korst, W. L. *J. Phys.* **1964**, *25*, 451.

0020-1669/91/1330-0800$02.50/0

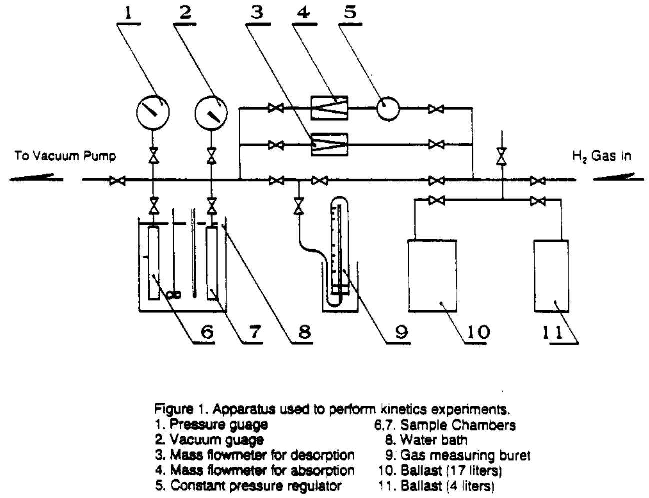

Figure 1. Apparatus used to perform kinetics experiments.

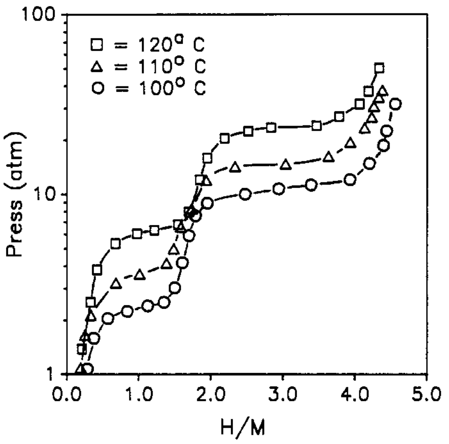

Figure 2. Pressure-composition isotherms for the ErCo$_3$-H system. Composition (H/M) is expressed as moles of H per mole of ErCo$_3$.

thermocouple (time constant = 0.55 s) that was enclosed in a metal sheath and lowered to 2 cm above the bottom of the sample reactor was used to monitor the temperature of the sample.

Prior to conducting kinetics measurements, it was necessary to determine pressure-composition isotherms for desorption at least two temperatures. To accomplish this, approximately 5 g of sample was placed into the sample holder and activated by allowing it to sequentially absorb and desorb hydrogen until the amount of hydrogen absorbed became constant. The desorption isotherm was determined by allowing a known quantity of hydrogen to flow from a fully charged sample out through water into an inverted buret to atmospheric pressure. After a sufficient period of time for equilibrium, the pressure was recorded and the process repeated until the sample was depleted of hydrogen. Time to reach equilibrium varied from 0.5 to 2 h. The dead spaces in the hydriding apparatus had been calibrated, and appropriate allowance was made for hydrogen remaining in the dead space. Desorption isotherms obtained at 100, 110, and 120 °C are presented in Figure 2. The plateau pressure corresponds to the horizontal portions of each isotherm. The lower plateau of each isotherm represents an α-β phase transition whereas the upper one corresponds to a β-γ transition.

Desorption kinetics measurements were performed in the two-phase regions. This was done by blending 1 g of sample with 19 g of aluminum powder and placing the mixture in a stainless steel reactor which was 1.8 cm in diameter and 10 cm long. The sample was subjected to at least 50 absorption-desorption cycles to ensure that the surface was clean and active. Then the hydrogen pressure in the reactor was adjusted to a value just slightly higher than that of the midplateau pressure (P_m), to ensure that only β-phase or γ-phase hydride was initially present, and sealing off the reactor. The pressure in the remaining system was then adjusted to a value such that the ratio of the midplateau pressure to the opposing pressure was 2. This ratio in the remainder of the text has been referred to as the N value. The gas from the reactor was allowed to flow from the reactor through the flowmeter and into a ballast of sufficient size to prevent any significant change in the overall pressure of the system.

This procedure can be illustrated by the following example. Figure 2 shows that at 100 °C the upper plateau (β-γ) pressure is 10.7 atm and the lower plateau (α-β) pressure is 2.3 atm. To perform desorption kinetics on the upper plateau at 100 °C, the pressure in the reactor is adjusted to 12 atm to ensure that only γ-phase hydride is initially present. The reactor is sealed off, and the pressure in the remaining system is adjusted to 5.35 atm (i.e. $^1/_2P_m$). The gas from the reactor is then allowed to flow from the reactor through the flowmeter and into the ballast. To perform desorption measurements on the lower plateau, the pressure in the ballast is adjusted to 3.0 atm to ensure that only β-phase hydride is initially present. The reactor is sealed off, and the pressure in the remaining system is adjusted to 1.15 atm. In both determinations the ratio of the plateau pressure to the opposing pressure (the N value) is approximately 2. Actually, the N value is not exactly 2 because the temperature, as measured by the thermocouple, decreased by about 2 °C during each run. If this is taken into account, the actual N values for both phase transitions are approximately 1.8. This is not a problem in this study because the most important aspect is that the N values be the same for both transitions. In addition, since all measurements are performed on the same sample and in the same reactor, any effects due to reactor geometry, thermal gradients, etc. will not affect the comparisons being made in this study.

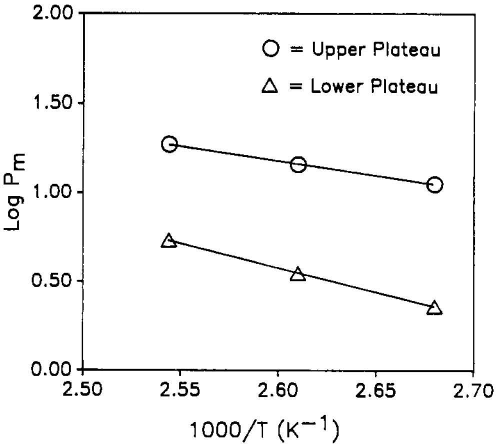

Figure 3. Plots of the log of the midplateau pressure (atm) vs 1/T for the ErCo$_3$-H_2 system.

Results and Discussion

The pressure-composition isotherms shown in Figure 2 indicate that, in addition to the solid-solution α phase, there exist two distinct hydride phases, β and γ, with limiting compositions of approximately 2 and 5 mol of H/mol of ErCo$_3$, respectively. This is in good agreement with an isotherm reported by Takeshita et al.[16] If the plateau pressure is determined at two or more temperatures, a linear relation corresponding to the expression

$$\log [P \text{ (atm)}] = -2549/T + 7.20 \pm 0.02 \qquad (1)$$

is obtained for the α-β phase transition. The expression

$$\log [P \text{ (atm)}] = -1861/T + 6.02 \pm 0.02 \qquad (2)$$

is obtained for the β-γ transition. Plots of log P vs 1/T are presented in Figure 3.

From eqs 1 and 2, the heat of formation of the β phase is obtained as 49 kJ/mol of H_2 and of the γ phase as 36 kJ/mol of H_2. The result obtained for the β-γ transition is in good agreement with that obtained by Bechman et al.,[7] who reported a value of 38 kJ/mol of H_2. They did not however report the heat of formation for the α-β transition.

Desorption kinetics measurements were performed at temperatures of 90, 100, 110, and 120 °C and at N values of 2. At these temperatures the plateau pressures were both above 1 atm. In Figure 4, plots of percent desorbed versus time are presented for the α-β and β-γ transitions at 100 °C and N = 2. Since both determinations were done at equivalent N values, the thermodynamic driving forces are the same. For the sake of clarity, the data points, which were collected at 1-s intervals, have been omitted and only the interconnecting lines have been shown. These plots show 90% of the hydrogen to be desorbed from the upper

---

(16) Takeshita, T.; Wallace, W. E.; Craig, R. S. *Inorg. Chem.* **1974**, *13*, 2282.

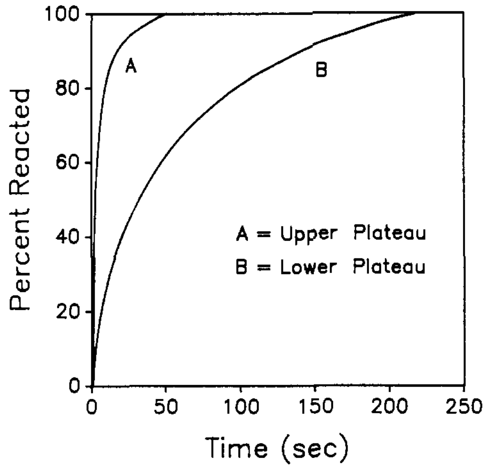

Figure 4. Plots of percent $ErCo_3$ reacted vs time at 100 °C and $N = 2$.

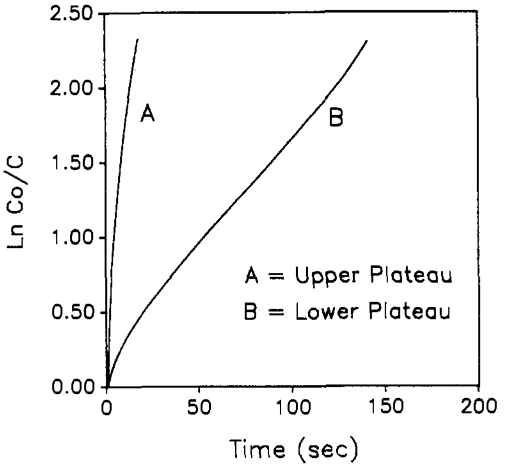

Figure 5. First-order plot for hydrogen desorption at 100 °C and $N = 2$. C_0 is the concentration of hydrogen initially in the sample, and C is the concentration at any given time.

plateau in approximately 20 s whereas 140 s is required for the same fraction of hydrogen to desorb from the lower plateau under identical conditions. This represents a significant difference. Apparently, hydrogen atoms in the β phase are in more stable sites than those in the γ phase. The exact nature of these sites, however, can be determined only by techniques such as neutron diffraction.

It was also possible to determine the reaction order and rate constant by fitting the experimental data to a rate equation, the general form of which is

$$-\mathrm{d}C/\mathrm{d}t = kC^n \qquad (3)$$

where C is the concentration of hydrogen in the metal hydride, k is the rate constant, t is the time, and n is the order of the reaction. If first-order kinetics are assumed, the equation in integrated form is

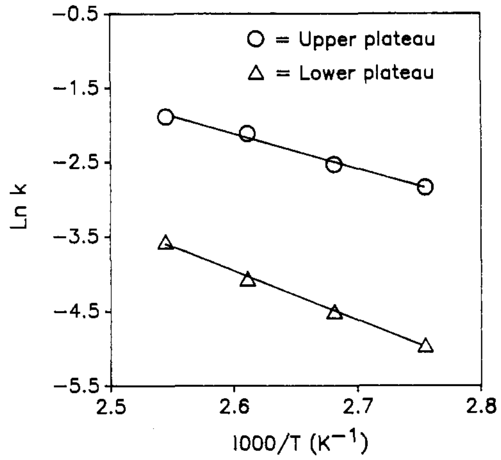

Figure 6. Arrhenius plot for $ErCo_3$ desorption kinetics at $N = 2$.

$$\ln (C_0/C) = kt \qquad (4)$$

in which C_0 is the hydrogen concentration in the metal hydride when $t = 0$.

Plots of ln (C_0/C) vs time for the upper and lower plateaus at 100 °C and $N = 2$ are given in Figure 5. The plots were found to be fairly linear. There is however some curvature, especially near the ends. This may be due to the fact that measurements were begun above the plateau in a single-phase region. Then, as the experiment progressed, hydrogen desorbed from the two-phase plateau region and eventually from another single-phase region. If the slope of each plot is determined over the portion that is most nearly linear, first-order rate constants can be approximated. For the upper and lower plateaus the rate constants, under these conditions, are 0.079 and 0.011 s^{-1}, respectively.

When rate constants were determined at the other temperatures and at $N = 2$, it was possible to construct the Arrhenius plots shown in Figure 6. From these plots, it was possible to determine the linear relations

$$\ln k = -6548/T + 13.1 \pm 0.04 \qquad (5)$$

for the α–β phase transition and

$$\ln k = -4695/T + 10.1 \pm 0.05 \qquad (6)$$

for the β–γ transition. The activation energies for the α–β and β–γ transitions are 54 and 39 kJ/mol of H_2, respectively. The larger value for the α–β transition is consistent with the idea that hydrogens in the β phase are in more stable sites than those in the γ-phase. Confirmation of the nature of these sites must await neutron diffraction studies.

Acknowledgment. This work was supported by grants from the National Science Foundation and the West Chester University Faculty Development Committee.