Journal of Alloys and Compounds, 191 (1993) 5–7
JALCOM 417

Effects of Al-substitution on hydriding reaction rates of $LaNi_{5-x}Al_x$

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(Received June 22, 1992)

Abstract

By means of a step-wise method with a double-walled reactor, the effects of Al-substitution on the reaction kinetics of $LaNi_{5-x}Al_x$ ($x=0$, 0.1, 0.2, 0.3) were determined. Al-substitution does not change the reaction orders but increases the apparent activation energy and decreases the rate constants in comparison with those of $LaNi_5$ hydride. The reaction order a with respect to hydrogen pressure and reaction order b with respect to hydrogen concentration were determined to be 2 and 1, respectively. The rate-controlling step of hydriding reaction is assumed to be the nucleation and growth of hydride in the $\alpha+\beta$ phase region.

1. Introduction

$LaNi_5$ is a typical AB_5 intermetallic compound for hydrogen storage because of its large hydrogen capacity and rapid hydriding–dehydriding rates. The partial substitution of Ni in $LaNi_5$ by third elements is commonly employed to improve the thermodynamic and kinetic properties [1]. Al-substituted alloys are of great interest from an engineering viewpoint because of their tailorability in P–T relations [2–5]. The thermodynamic properties of these alloys are expected to affect the reaction kinetics. In this work, hydriding reaction kinetics of $LaNi_{5-x}Al_x$ ($x=0$, 0.1, 0.2, 0.3) hydrides were determined to study the effects of Al-substitution.

2. Experimental details

The experiments were performed using a step-wise method under isochoric and variable pressure conditions. The apparatus used for the present kinetic study was described by Suda *et al.* [6]. The experiments were carried out using a double-walled reactor with a 0.5 mm annular space as the sample holder. The sample was fully activated by more than 40 hydriding–dehydriding cycles. Data were then taken at temperatures between 313.2 and 363.2 K. A sample mass of 5 g was used for each run. The Al-content was varied as $x=0$, 0.1, 0.2, 0.3 in $LaNi_{5-x}Al_x$ alloys. Data were recorded in an HP-3052 A data acquisition system at 0.2 s intervals for 2 minutes.

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3. Results and discussions

3.1. Results

The effects of Al-substitution on the hydriding P–C isotherm at 333.2 K are shown in Fig. 1. Al-substitution contributes to lower the plateau pressure with minor loss of hydrogen capacity and increases the plateau slope. These facts have also been reported earlier by several researchers [3–5].

A general rate equation for the hydriding reaction was derived in a past study [7],

$$dc/dt = k_h(P/P_e)^a[1-(P_f/P)^a(C/C_f)^b] \quad (1)$$

$$k_h = Ae^{-E_h/RT}$$

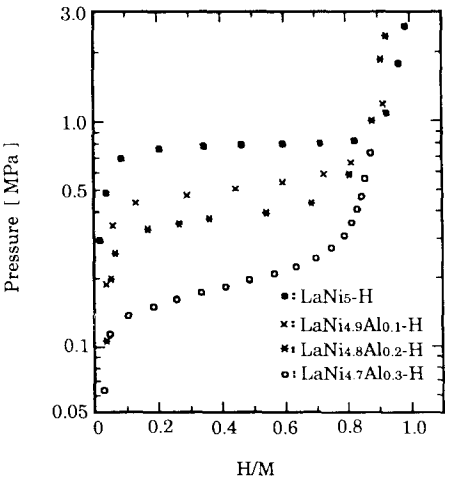

Fig. 1. The hydriding P–C isotherms for the $LaNi_{5-x}Al_x$ at 333.2 K.

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In eqn. (1), the constant, k_h is the rate constant, constants a and b are the reaction orders; P is the hydrogen pressure at a given time during the reaction; P_f is the final equilibrium pressure for a given experimental run; P_e is the plateau pressure; C and C_f are the hydrogen concentrations, H/M, at a given time and at the final equilibrium condition, respectively.

By means of the rate equation, the kinetic data obtained at 333.2 K for four hydride systems are illustrated in Fig. 2, where reaction rates are plotted as a function of $(P/P_e)^a[1-(P_f/P)^a(C/C_f)^b]$ in the concentration range of 0.3–0.5 H/M. Although the plateau pressure P_e of each hydride in the $LaNi_{5-x}Al_x$ hydrides is quite different, all plots exhibit excellent linear relations. Corresponding plots for other hydrogen concentrations and isothermal conditions also give excellent linearity. The reaction orders a and b were determined to be 2 and 1 for each hydride system by fitting the rate equation to experimental data. From the slopes of these straight lines, the rate constants were determined and the values obtained at 333.2 K are listed in Table 1.

The apparent activation energies of $LaNi_{5-x}Al_x$ hydrides were determined from the Arrhenius equation. Figure 3 shows these Arrhenius plots for the four individual hydride systems. The reaction order and activation energy values obtained from these plots are listed in Table 2.

3.2. Discussions

From the above observations, it can be seen that excellent linear relationships of dc/dt against $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$ were obtained and these results indicate that the kinetic data obey our rate equation for $LaNi_{5-x}Al_x$ hydrides. The hydriding reaction of $LaNi_{5-x}Al_x$ hydrides is of the second order with respect to hydrogen pressure and of the first order with respect to hydrogen concentration. The rate constants within the $\alpha+\beta$ phase region were observed to be constant regardless of pressure and concentration for the $LaNi_{5-x}Al_x$ hydrides measured here. Regarding the effects of Al-substitution, the rate constant is decreased whereas the apparent activation energy is increased in comparison with those of $LaNi_5$ hydride. For the Al-containing hydrides, the rate constants are very close and the apparent activation energy increases slightly with increasing Al-content.

The independence of rate constants on pressure and concentration in the $\alpha+\beta$ phase region indicates that a single rate-controlling step exists in this phase region.

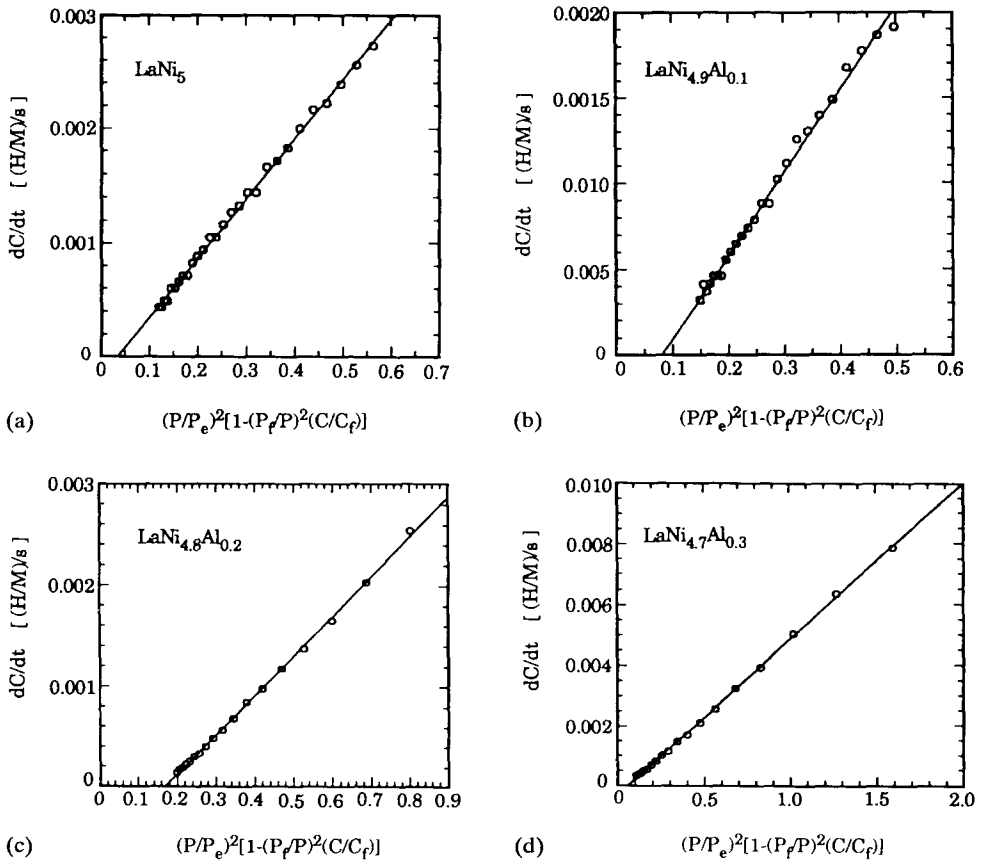

Fig. 2. Hydriding reaction rates vs $(P/P_e)^2[1-(P_f/P)^2(C/C_f)]$ for the $LaNi_{5-x}Al_x$ in the $\alpha+\beta$ phase region at 333.2 K: (a) $LaNi_5$–H system, (b) $LaNi_{4.9}Al_{0.1}$–H system, (c) $LaNi_{4.8}Al_{0.2}$–H system, and (d) $LaNi_{4.7}Al_{0.3}$–H system.

TABLE 1. Hydriding reaction rate constants for $LaNi_{5-x}Al_x$ in the $\alpha+\beta$ phase region at 333.2 K (values $\times 10^{-3}$ (H/M s^{-1}))

Hydrogen concentration (H/M)	0.1–0.3	0.3–0.5	0.5–0.7	0.7–0.85
$LaNi_5$	5.21	7.47	6.67	6.65
$LaNi_{4.9}Al_{0.1}$	3.63	4.59	4.72	5.58
$LaNi_{4.8}Al_{0.2}$	4.28	5.14	4.68	4.15
$LaNi_{4.7}Al_{0.3}$	5.16	5.06	4.91	5.54

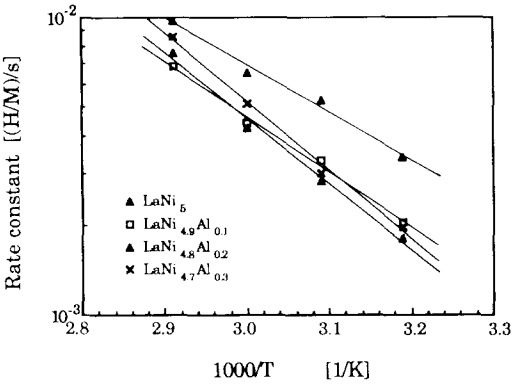

Fig. 3. Arrhenius plots for the hydriding reactions of $LaNi_{5-x}Al_x$.

TABLE 2. Reaction orders and apparent activation energies of the $LaNi_{5-x}Al_x$

	Reaction order		Activation energy (kJ/mol H_2)
	a	b	
$LaNi_5$	2	1	31.34
$LaNi_{4.9}Al_{0.1}$	2	1	35.24
$LaNi_{4.8}Al_{0.2}$	2	1	36.76
$LaNi_{4.7}Al_{0.3}$	2	1	36.80

As kinetic characteristics are different between each phase region [7], rate constants and reaction orders might be different, however, they are constant regardless of pressure and concentration within a given phase region if there is no change in mechanism. 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.

Regarding the rate-controlling step for the hydriding reaction of $LaNi_{5-x}Al_x$ hydrides, the same conclusion was obtained as that of the $LaNi_{4.7}Al_{0.3}$ hydride [7], namely, the nucleation and growth of hydride in the $\alpha+\beta$ phase region is the rate-controlling step. This is because every Al-containing hydride examined in this work gives the same reaction orders, close rate constants and apparent activation energies.

4. Conclusions

Al-substitution does not change the reaction orders but increases the apparent activation energy and decreases the rate constants in comparison with those of $LaNi_5$ hydride. The rate-controlling step of hydriding reaction is not changed by Al-substitution. The reaction order a with respect to hydrogen pressure and reaction order b with respect to hydrogen concentration were determined to be 2 and 1, and the rate-controlling step of hydriding reaction is the nucleation and growth process in the $\alpha+\beta$ phase region for the $LaNi_{5-x}Al_x$ hydrides.

Acknowledgments

The authors wish to thank undergraduate students, K. Yamasaki, T. Hasegawa, T. Kai and H. Kasada for their experimental assistance.

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