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Hydrogen storage properties of (La–Ce–Ca)Ni_5 alloys and application for hydrogen compression

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Abstract

In this paper, the hydrogen storage properties of (La–Ce–Ca)Ni_5 alloys were studied and an empirical equation was deduced for predicting the dependence of hydrogen dissociation pressure on the composition of the alloys. The theoretically predicted curves are in good agreement with the experimental results. Based on the theoretical analysis and experimental results, $La_{0.4}Ce_{0.4}Ca_{0.2}Ni_5$ was selected as the hydrogen storage alloy for a metal hydrogen hydride compressor (MHHC). It absorbs hydrogen at 298 K and 1.9 MPa and desorbs hydrogen at 371 K and 12.0 MPa. Moreover, using industrial hydrogen with 98% purity. The MHHC produces ultrapure product hydrogen with 99.9999% purity. Namely, the compressor integrates the compression function with purification function.

Keywords: Hydrogen storage alloy; Hydrogen compression; Hydride; Rare earth

1. Introduction

It is well known that metal hydrides have a wide range of applications such as gaseous applications, electrochemical applications and thermal applications. Among gaseous applications, metal hydride hydrogen compressor (MHHC) has attracted much attention in the past years [1–4]. However, the hydrogen storage alloys used in most cases of the MHHC have not been optimized, and $LaNi_5$ or $La(NiAl)_5$ hydrogen storage alloy is generally selected. Therefore, it is difficult for the MHHC using the above hydrogen storage alloys to increase the hydrogen pressure to above 10 MPa in a single stage operation using hot water at 373 K.

In order to increase the pressure level at the operation temperature, Ce-rich mischmetal is usually used instead of La. But the mischmetals produced by different companies vary greatly in composition which remarkably influences the hydrogen absorption/desorption pressure of the hydrogen storage alloys. In addition, partial substitution of Mm with Ca in $MmNi_5$ based alloys is useful for improving the hydrogen compression properties [4]. However, for Ca-containing AB_5 type alloys, the results of many investigations showed an interesting phenomenon, i.e., the dissociation pressure of the hydrides of $R_{1-x}Ca_xNi_5$ (R=La or Ml, Ml stands for La-rich mischmetal) compounds increases first to a maximum value and then decreases with increasing Ca content x [5–7]. This phenomenon conflicts with the empirical crystallographic rule proposed by Lundin et al. [8] and Busch et al. [9].

In this paper, we deduced an equation for correlating the hydride dissociation pressure with the composition of (La–Ce–Ca)Ni_5 alloys, and experiments were carried out to confirm it. Finally, based on the theoretical and experimental results, an alloy was selected as the hydrogen storage alloy for a hydrogen compressor prototype, and its compression characteristics were studied.

2. Experimental details

The purity of the metallic elements for sample preparation is as follows: La, Ce and Ni are all 99.9% pure and Ca is 98% pure. The hydrogen used for the hydrogenation/dehydrogenation properties measurements is 99.999% pure. Samples were prepared in an r.f. induction furnace in an argon atmosphere. The cell volumes of unhydrided alloys were determined by X-ray diffraction analysis using a Rikagu D/Max PC2500 diffractometer with Cu Ka irradiation.

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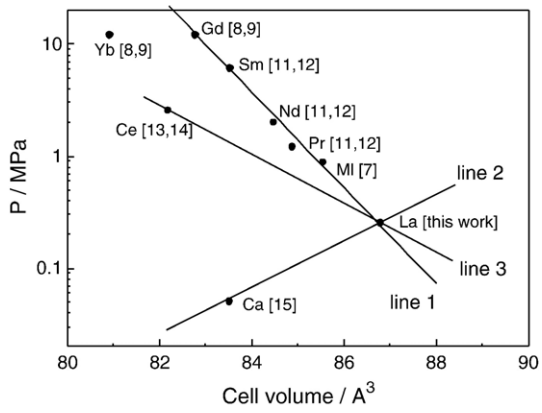

Fig. 1. Dependence of hydrogen dissociation pressure on cell volume.

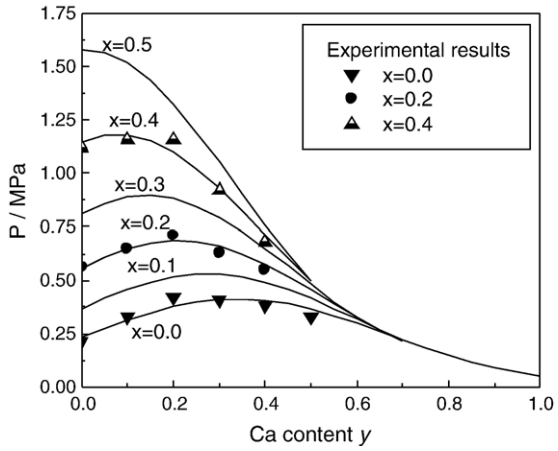

Fig. 2. Hydrogen desorption pressure as a function of composition.

Samples were mechanically crushed into fine powder in air, and then introduced into a stainless steel reactor and placed in the hydrogenation setup. Prior to p–c–T measurements, several hydriding/dehydriding cycles were carried out to ensure the samples were fully activated. The details of p–c–T measurements were described elsewhere [10].

3. Results and discussion

3.1. Correlation between hydride dissociation pressure and composition of (La–Ce–Ca)Ni5 alloys

Busch et al. [9] proposed an empirical crystallographic rule, in which they believed that the desorption pressure of RNi_5 (R is rare earth metal) varies exponentially with the cell volume of the unhydrided compound as shown in Fig. 1, namely,

$$p = ce^{k_1 V} \tag{1}$$

or

$$\ln p = kV + b \tag{2}$$

Where P and V were dissociation pressure and cell volume, respectively; k and b were constants with $k<0$.

It can be seen from Fig. 1 that the data points of Gd [8,9], Sm, Pr, Nd [11,12], Ml (La-rich mischmetal) and La (hereafter we denote them as R elements) fell closely on line 1, while those of Yb [8,9], Ce [13,14] and Ca [15] (hereafter we denote them as A elements) were far below line 1 and showed a significantly lower dissociation pressure for the same cell volume. We believe that the valence difference between the R elements and A elements is one of the main reasons leading to the deviation from line 1 for A elements, because these R elements more closely associated with line 1 are all trivalent, while Yb and Ca in $YbNi_5$ and $CaNi_5$ are divalent atoms, and Ce in $CeNi_5$ is reported to be quadripositive [14].

We regard the effect that the dissociation pressure decreased with increasing cell volume for the hydrides of trivalent R elements as the geometrical factor. In this case, the dissociation pressure varies with cell volume according to line 1, i.e.:

$$\ln p = k_1 V + b_1 \tag{3}$$

where k_1 and b_1 are constants with $k_1<0$.

And we regard the deviation from line 1 caused by the different valence of A elements as the electric factor. In this case, the dissociation pressure varies with, for example, line 2 or line 3, which is a line drawn from pressure/cell volume data of RNi_5 to that of ANi_5 (A=Ca, Ce and Yb) as shown in Fig. 1.

$$\text{In case of A} = \text{Ce}, \qquad \ln p = k_2 V + b_2 \tag{4}$$

$$\text{In case of A} = \text{Ca}, \qquad \ln p = k_3 V + b_3 \tag{5}$$

where k_i and b_i (i=2, 3) are constants.

For RNi_5 compounds, the geometrical factor governs the stability of their hydrides. For ANi_5 compounds, the electric factor controls their hydride stability. We believe that the stability of $R_{1-x}A_xNi_5$ compounds may be influenced by the joint effect of the geometrical factor and the electric factor.

For the $La_{1-x-y}Ce_xCa_yNi_5$ compounds, the dissociation pressure can be expressed as,

$$\ln p = (k_1 V + b_1)(1-x-y) + (k_2 V + b_2)x + (k_3 V + b_3)y \tag{6}$$

where $x+y<1$.

In the above Eq. (6), the first term stands for the geometrical effect due to La, the second and third terms stand for the electric factors due to Ce and Ca, respectively.

Table 1
Constants k_i and b_i obtained from Fig. 1

k_1	b_1	k_2	b_2	k_3	b_3	k_4	k_5	b
−0.9840	83.9700	−0.6435	54.4687	0.4907	−43.9775	−4.5920	−3.2800	86.8100